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J. W. POWELL, DIRECTOR

REPORT OF WORK DONE

IN THE

DIVISION OF CHEMISTRY AND PHYSICS

MAINLY DURING THE

FISCAL YEAR 1889-'90

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PREFACE.

This bulletin, like the bulletins issued in previous years and numbered 9, 27, 42, 55, 60, and 64, contains a partial record of work completed in the chemical and physical laboratories of the Survey during one fiscal year. It represents, however, only a portion of the whole work done, for various investigations, begun during the year 1889–'90, are still unfinished; many analyses are reserved for publication in other reports; and certain of the larger researches, notably the physical studies of Dr. Barus, will appear in independent form as separate bulletins. In the annual reports of the Director of the Survey a tolerably complete summary of the work done in the Division of Chemistry and Physics is always given, and such summaries, taken in connection with these bulletins, convey a fair idea of the amount of ground actually covered.

WORK DONE IN THE DIVISION OF CHEMISTRY AND PHYSICS IN 1889-'90.

EXPERIMENTS UPON THE CONSTITUTION OF THE NATURAL SILICATES.

By F. W. Clarke and E. A. Schneider.

During the last six years the constitution of the natural silicates has received a good deal of attention in the laboratory of the U. S. Geological Survey. A number of papers have been published by one of us, partly theoretical and partly analytical, but the evidence so far considered has been drawn only from careful analyses of various minerals, and a study of their obvious relations, their associations, and their alteration products. Within certain limits the results obtained have been satisfactory and suggestive, but in several cases it was found that ordinary analysis failed to discriminate between possible alternative formulæ, and it was plain that the uncertainties could be cleared up only by new lines of experimental investigation. With such investigations the present paper has to do. Sixteen minerals, including varieties, all of the magnesian class, have been examined, and it has been found quite possible to separate some of them into distinct fractions of definite character in such a way as to shed much light upon their inner chemical structure. In general the methods which have been employed by us are not new, except in their application to the silicate problem, but in their analogies to the processes used for the elucidation of organic compounds we believe that they will be found interesting.

In brief our mode of procedure has been as follows: First, each mineral, selected and purified with great care, has been completely analyzed, and in each case enough material was ground to a uniform sample to suffice for all subsequent experiments. Secondly, each mineral has been subjected to the action of *dry* hydrochloric acid gas under quantitative conditions. For this purpose a quantity of material was weighed out in a platinum boat, which was then placed in a glass tube and heated in a stream of the dry gas until, after repeated weighings, constant weight was attained. The sample was then treated with water and a drop or two of nitric acid, and the soluble constituents of the mass were determined by the usual methods of analysis. In every instance a sample was thus treated at a temperature between 383° and 412° C., but in some cases other temperatures were studied also. For heating the tubes an ordinary combustion furnace was used, and the temperature was kept within the indicated range by placing on one side of the platinum boat a sealed capillary tube containing lead iodide, melting point 383°, and on the other side a tube containing zinc, which fuses at 412°. The flames of the furnace were then so adjusted that the iodide fused, while the zinc did not. For a higher range of temperatures, which was employed in some cases, the indicators similarly used were lead chloride, m. p. 498°, and silver iodide, m. p. 527°. These melting points are given according to Carnelley. As a rule, in each series of experiments the sample under treatment was weighed every two hours, and before reheating was stirred with a fine platinum wire in order to expose a fresh surface to the action of the acid. By this mode of treatment different minerals are very differently affected, there being almost no action in some cases, and very notable action in others. With this action of gaseous acid, the action of aqueous hydrochloric acid upon each mineral was carefully compared, and some points of great importance were thus brought out. As a rule one gramme of mineral was treated with 75cm^3 of fuming hydrochloric acid on the water bath, and the mixture was evaporated to dryness. When decomposition was not complete, the mineral was further treated with hydrochloric acid of sp. gr. 1·12 for three days or even longer, and the amount of action was ascertained and recorded. In several instances this treatment with aqueous acid was repeated after strong ignition of a mineral, and it was sometimes found that a species previously soluble could be thus split up into a soluble and an insoluble part. In a number of cases ignition of a mineral caused the liberation of silica, which could afterward be dissolved out with soda solution and quantitatively determined. For this purpose a solution of sodium carbonate, 250 grammes to the litre, was employed. Finally, in almost every case the nature of the water in a mineral was investigated, by a study of the temperatures at which its several fractions were expelled. For low temperatures, an ordinary air bath was used; for higher temperatures the minerals were heated in a stream of dry air, between indicators of known melting points, just as in the treatment with gaseous hydrochloric acid.

So much for the methods of research, which will be more clearly understood from a study of the details to be given presently. On the theoretical side we have adhered to the working hypothesis that the more complex silicates are substitution derivatives of normal salts, as has been suggested by one of us in several earlier publications. From this point of view the normal orthosilicate of magnesium is the fittest starting point for discussion, and this salt is approximately represented by olivine. The purer forsterite was not available.

OLIVINE.

For this species the only material at hand was a supply of the chrysolite pebbles from near Fort Wingate, New Mexico. The mineral from this locality, we believe, has not been previously analyzed; and as it is rich enough in color and is sufficiently clear it is often cut as a gem. It has the characteristic color of the peridot, and is apparently quite free from inclusions. The analysis gave the following results:

SiO_2	41·98
Fe_2O_3	·51
FeO	5·71
NiO	·42
MnO	·10
MgO	51·11
H_2O	·28
	100·11

Only 0·05 per cent. of the water was lost at 105°.

1·1027 grammes of the mineral were heated in gaseous hydrochloric acid for twenty-two hours, and gained in weight 0·0157 grm. On leaching with water and a drop of nitric acid the following percentages of material went into solution:

MgO	1·47
Fe_2O_3	·43

Hence olivine, at the temperature of 383°–412°, is hardly attacked by dry hydrochloric acid; and the slight action here recorded may possibly be due to incomplete drying of the gas. The aqueous acid, on the other hand, decomposes olivine with great ease. On this mineral no other experiments were necessary for our purposes.

TALC.

The mineral studied was a typical, apple-green, foliated talc from Hunter's Mill, Fairfax County, Virginia. Analysis as follows:

SiO_2	62·27
Al_2O_3	·15
Fe_2O_3	·95
MgO	30·95
FeO	·85
MnO	trace
H_2O	4·91
	100·08

In detail, the water determination was as follows:

Loss at 105°	·07
Loss at 250°–300°	·06
Loss at red heat	4·43
Loss at white heat	·35

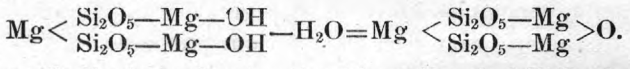
Hence the water is practically all constitutional.

Heated in dry HCl gas to 383°–412° for fifteen hours, the talc underwent inappreciable change of weight. Upon leaching, only 0·23 per cent of magnesia went into solution. By rapid evaporation with 75 cc. of fuming aqueous HCl, 1·05 per cent of MgO and 0·16 of $(FeAl)_2O_3$ were dissolved. Upon eight days' digestion on the water bath with acid of 1·12 sp. gr., 1·94 MgO and 0·23 of sesquioxides were removed. By digesting in like manner for thirty-two days, 3·94 MgO and 0·41 of sesquioxides were taken out. Talc, therefore, is, as should have been expected, remarkably stable in presence of hydrochloric acid, both aqueous and dry. This fact has a very important bearing upon the constitutional formula of the mineral.

In empirical composition the talc analyzed agrees quite sharply with the accepted formula $Mg_3H_2Si_4O_{12}$. This is commonly interpreted as an acid metasilicate, $Mg_3H_2(SiO_3)_4$; but Groth has lately proposed to consider talc as a basic salt of pyrosilicic acid, $H_2Si_2O_5$. On this supposition its rational formula becomes $Mg(Si_2O_5)_2(MgOH)_2$. Between these two formulæ, experiment is able to decide.

Against Groth's formula the stability of talc towards acids tells very strongly. The univalent group — Mg — OH ought to be soluble in hydrochloric acid; and evidence, to be presented later, goes to show that that particular group is easily removable by the dry, gaseous HCl. In fact, our experiments make it highly probable that all the magnesia taken from a silicate by perfectly dry HCl was originally present in the hydroxylated form. As regards the constitution of talc, however, other evidence is even stronger.

If Groth's formula is correct, then, upon ignition, talc should behave according to the equation



$$\mathrm{Mg}<\begin{matrix}\mathrm{Si_2O_5{-}Mg{-}OH}\\ \mathrm{Si_2O_5{-}Mg{-}OH}\end{matrix}-\mathrm{H_2O}=\mathrm{Mg}<\begin{matrix}\mathrm{Si_2O_5{-}Mg}\\ \mathrm{Si_2O_5{-}Mg}\end{matrix}>\mathrm{O}.$$

In other words the loss of water should produce but little change, and no silica should be liberated. If, on the other hand, the acid metasilicate formula is true, talc should split up into $3MgSiO_3+SiO_2+H_2O$; that is, one-fourth of the silica should be set free; which, in the present instance, would amount to 15·57 per cent. This actually happens; and a weighed quantity of talc, ignited very intensely for half an hour over a blast-lamp, gave up 15·36 per cent of SiO_2 upon subsequent boiling with a solution of sodium carbonate. Upon longer ignition, as might be expected, a part of this silica reverts to the insoluble form, and somewhat lower results are obtained. Upon the unignited talc, boiling with soda solution for 24 hours produced little or no effect; soda was not taken up, nor was silica removed.

In brief, both lines of evidence, the liberation of silica and the stability toward acids, confirm the ordinary formula for talc and controvert the views of Groth; and no other formula, out of several which are possible, satisfies both of the experimentally established conditions. The mineral, therefore, must be regarded as an acid metasilicate; although its ultimate structural formula can be written only when we have a better knowledge of metasilicic acid. It is a noteworthy fact, that no normal metasilicic ether is yet certainly known; for Ebelmen's results have not been confirmed by later observers. Troost and Hautefeuille, however, prepared an ether having the composition $(C_2H_5)_8Si_4O_{12}$. Possibly enstatite may be the normal magnesium salt corresponding to this ether; in which case talc would be a substitution derivative having H_2 in place of one atom of Mg.

SERPENTINE.

On account of the importance of this species, its variability in external characteristics, and its manifold relations to other minerals, several distinct samples were investigated.

A. Dull green serpentine from Montville, New Jersey, derived from pyroxene by alteration.

B. Dark green serpentine from the well known locality at Newburyport, Massachusetts.

C. Silky, fibrous chrysotile from Montville.

D. Grayish green picrolite from Buck Creek, North Carolina.

E. A grayish green mineral from Corundum Hill, North Carolina, which was supposed at first to be deweylite. It is an ordinary, massive serpentine.

Analyses as follows, with the itemized water determinations subjoined:

	A	B	C	D	E
SiO_2	42·05	41·47	42·42	42·94	41·90
H_2O	14·66	15·06	15·64	13·21	16·16
MgO	42·57	41·70	41·01	36·53	40·16
FeO	·10	·09	undet.	1·88	undet.
CaO	·05	none.	trace.	....	....
NiO	....	....	·23	·61	·10
Fe_2O_3	·30	1·73	·62	3·33	·91
Al_2O_3	....		·63	1·72	·71
	99·73	100·05	100·55	100·22	99·94
H_2O at 105°	·96	1·20	2·04	1·53	2.26
H_2O at 250°	·55	·55	·71	.44	1·01
H_2O at 383°–412°	·27	......	·27	·62	·98
H_2O at 498°–527°	·23	......	·56	....	·42
H_2O at red heat	12·37	13·01	11·81	10·58	11.32
H_2O at white heat	·28	·30	·25	·04	.17

From these data it is clear that practically all the water in serpentine is constitutional, and that none of it can be fairly regarded as crystalline. The small, variable amount lost below 250° is mainly hygroscopic and inclosed water, since the analyses refer to air-dried material. It is hardly necessary to state that in each fractional determination the material was heated to constant weight.

Upon heating in dry, gaseous hydrochloric acid all of these serpentines were stongly attacked; differing essentially in this particular from olivine and talc. The bases thus taken out as chlorides at 383°–412° were as follows:

	A	B	C	D	E
No. hours heated	54	68	54	78	41
MgO extracted	10·14	16·73	9·98	11·38	15·25
R_2O_3 extracted	....	·43	....	·66	·51

In the last determination the soluble magnesia was accidentally lost; and the value given was estimated by difference. A duplicate determination on the Newburyport mineral, at the same temperature, with 39 hours' heating gave only 14·43 per cent of magnesia removed as chloride. The different times required for obtaining constant weight and so fixing the limit of the reaction vary considerably.

Similar experiments upon serpentines A and B at the temperature 498°–527° gave similar results.

	A	B
Hours heated	18	18
MgO removed	10·83	14·28
R_2O_3 removed	·10	·16

In duplicate determinations at the same temperature, A yielded 14·17 and B gave 17·36 per cent of magnesia converted into chloride.

Now these data, although not satisfactorily concordant, have nevertheless some significance. They show first that the action of the gas is much the same at both of the temperature intervals, except that the limit of change is reached more quickly in the hotter series. They show, also, that the magnesia of serpentine is probably combined in two ways; one part being affected, the other unattacked by the acid. That part which is converted into chloride, and so rendered soluble, we may regard provisionally as represented by the group —Mg—OH; even though our estimate of its amount may not be so sharply accurate as might be desirable. No other hypothesis as to the nature of the dissolved magnesia seems to be practicable, or to account in any way for the results of the experiments. Roughly speaking, a maximum amount of *about* one-third of the magnesia in serpentine is extracted by dry HCl under the conditions of our experiments, the other two-thirds being more stable.

By aqueous hydrochloric acid all of the five serpentines were easily and completely decomposed. In three instances this fact was determined quantitatively; by evaporating the acid to dryness with the mineral, extracting with weak acid, and weighing the residue. In each case this residue agreed in percentage with the silica found by actual analysis. The data are as follows:

	A	C	D
Insoluble in HCl	42·32	42·21	42·55
Silica found................	42.05	42·42	42·94

By very weak hydrochloric acid, however, these three serpentines are but partially decomposed; the picrolite being the most stable of the series. A microscopic examination of the picrolite by Mr. Waldemar Lindgren showed no inclusions which could account for this difference in behavior, and it is probably due to merely mechanical conditions.

Upon boiling directly with sodium carbonate solution, none of the serpentines were attacked. By sharp ignition, however, a little silica was sometimes liberated; which, as in the case of the talc, could be dissolved out and estimated. The quantities of silica thus set free were as follows:

	A	B	C	D	E
Per cent	6·23 6·34	2·00 2·63	2.98	none	6·05 4·93

These results can not easily be interpreted. At most, only about one-seventh of the total silica is thus taken out; and this may represent either impurities in the minerals or secondary reactions of an undetermined kind.

When serpentine is heated to the point of fusion it is split up, as Daubrée has shown[1], into a mixture of olivine and enstatite.

$$H_4Mg_3Si_2O_9=2H_2O+Mg_2SiO_4+MgSiO_3.$$

Upon ordinary ignition, however, this breaking up of the molecule does not always take place; and when it does occur, it is as a rule only partial. In three experiments the serpentines A, C, and D, were strongly ignited over a blast lamp for an hour each, and then treated with strong hydrochloric acid. By this treatment, olivine, if formed, should be decomposed; while enstatite would remain unattacked in the residue. After evaporation to dryness and extraction with weak acid, the insoluble material was boiled with sodium carbonate solution to remove free silica, washed, dried, and weighed. The residues were as follows:

	A	C	D
Per cent........	4·32	20·80	39·96

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[1] Compt. Rend., vol. lxii, 1866, 661.

The residue from the massive Montville serpentine contained 43·28, and that from the chrysotile 41·34 per cent of magnesia, thus agreeing nearly with enstatite in composition. The picrolite residue was composed of—

MgO	36·31
SiO_2	54·88
R_2O_3	9·26
	100·45

showing it to be an impure enstatite, the impurities being analogous to those of the original mineral. In the last case the splitting up seems to have been practically complete; in the chrysotile it went fully half way, while in the ordinary serpentine it barely began. The conclusion is obvious. When serpentine is simply dehydrated, the molecule $Mg_3Si_2O_7$, decomposable by acids, remains; and this on further heating splits up in accordance with Daubrée's observations. The salt $Mg_3Si_2O_7$ corresponds to certain well known silicic ethers, and is probably a definite compound.

Now, bearing upon the constitution of serpentine, we have several lines of evidence. First, its empirical formula, $H_4Mg_3Si_2O_9$, is well-known and in this all the water is constitutional. Second, upon dehydration it yields the salt $Mg_3Si_2O_7$. Third, a part of the magnesia is less stably combined than the remainder of the base, and is presumably present as —Mg—OH. If one atom of magnesium, or one-third of the total, is thus combined, the excess of one atom of oxygen over the normal orthosilicate ratio in the formula is accounted for, and the conditions imposed by our experimental results are satisfied.

Taking all these considerations into view it seems highly probable that the constitutional formula of serpentine may be written $Mg_2(SiO_4)_2H_3(MgOH)$. In ultimate structural form this may be interpreted in several ways, any one of which will admit of a linking together of the two orthosilicic groups, after dehydration, with elimination of one oxygen atom, to form the acid group Si_2O_7. Between the several possible structures, however, we are not yet prepared to decide, and further investigation covering other hydro-magnesia silicates is necessary. Bearing in mind the very common derivation of serpentine from olivine, and the obvious relations of both species to chondrodite, the following formulæ are highly suggestive; the first one representing olivine with double its simplest expression:

$Mg_4Si_2O_8$	Olivine.
$Mg_3Si_2O_8(MgF)_2$	Chondrodite.
$Mg_2Si_2O_8H_3(MgOH)$	Serpentine.

In the chondrodite formula of course, the group -Mg-O-Mg- to a certain extent replaces the two univalent MgF groups. Although these formulæ are not absolutely proven, they are at least highly probable; and they conform perfectly to the general working hypothesis that the more complex silicates are substitution derivatives of normal salts.

One other formula for serpentine, $MgSi_2O_7(MgOH)_2H_2$, is reconcilable in part with our data. But such a compound ought to be acted upon more strongly by gaseous hydrochloric acid, and two-thirds of the magnesia should be removable. This limit was not even remotely approached in our experiments, although in two cases the one-third limit was definitely exceeded. It is a legitimate question, however, whether there may not be two isomeric serpentine molecules, corresponding to these two formulæ: and this question ought to be kept in view in future investigations.

THE CHLORITE GROUP.

In this interesting but very obscure group of minerals, three species were examined. First, the dark green, broadly foliated, mica-like ripidolite from Westchester, Pennsylvania. This mineral has been repeatedly analyzed, and our results confirm the older data. Second, a dark green, scaly-granular prochlorite, found in excavating the water-works tunnel in Washington, District of Columbia. Third, leuchtenbergite from the Schischimsk mine near Slatoust, Siberia. The last mineral was kindly sent us by Mr. A. Lösch, of St. Petersburg; but it unfortunately contained inclusions which render our work upon it of little value. The prochlorite was examined microscopically by Mr. Lindgren of the U. S. Geological Survey, who found it to be quite homogeneous. Analyses as follows:

	Ripidolite.	Prochlorite.	Leuchtenbergite.
SiO_2	29·87	25·40	32·27
Al_2O_3	14·48	22·80	16·05
Cr_2O_3	1·56		
Fe_2O_3	5·52	2·86	4·26
FeO	1·93	17·77	·28
NiO	·17		
MnO		·25	
MgO	33·06	19·09	29·75
CaO			6·21
H_2O	13·60	12·21	11·47
F		trace	
	100·19	100·38	100·29
H_2O at 105°		·80	·38
" 250°–300°	·95	.15	·21
" 383°–412°	·49	·62	
" 498°–527°		·09	
" red-heat	11·74	10·55	10·69
" white-heat	·42		·19

Here again we have to deal with water which is plainly constitutional. Hence the suggestion put forward by one of us that the chlorites are essentially micas plus water of crystallization, must be abandoned.[1]

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[1] Clarke, Am. Jour. Sci., Nov., 1889.

Upon treatment with dry hydrochloric acid gas at 383°–412°, the three minerals differ considerably. The times of heating and the bases converted into chlorides were as follows:

	Ripidolite.	Prochlorite.	Leuchtenbergite.
Hours heated	19	31	34
MgO removed	13·46	1·54	6·29
R_2O_3 removed	4·24	2·17	·42
SiO_2 removed	·92	....	....

In a second experiment with the ripidolite 58 hours of heating were required before constant weight was attained, and 13·36 per cent of magnesia plus 1·20 of sesquioxides were rendered soluble. In a third experiment the heating lasted 30 hours, and the percentages of MgO and R_2O_3 removed were 11·10 and 3·31 respectively. Even at the ordinary temperature of the laboratory ripidolite was decidedly attacked by the gaseous acid, 4·66 MgO and 3·43 R_2O_3 becoming soluble. In this case the experiment lasted 100 hours. In the case of the prochlorite the result obtained is of very doubtful significance. In a mineral containing so large a proportion of ferrous iron, secondary reactions due to oxidation are possible, and it is not practicable to determine exactly what changes have taken place. The group —Fe—OH might behave like MgOH, and yet subsequent alteration might prevent any estimate of the extent of the reaction.

By digestion with strong, aqueous hydrochloric acid, both ripidolite and prochlorite were completely decomposed. Leuchtenbergite, on the other hand, left an insoluble residue, resembling garnet, which was originally present as an inclusion in the mineral. All of these minerals decompose with aqueous acid more slowly than the serpentines.

By sharp ignition, ripidolite and prochlorite give up in the free state small quantities of silica, which are determinable by extraction with soda solution. The percentages were as follows:

	Ripidolite.	Prochlorite.
SiO_2 liberated	2·98	2·45

These quantities represent only one-tenth of the total silica in the minerals, and have no evident significance in a discussion of the chemical structure.

Although ripidolite is readily decomposable by aqueous hydrochloric acid, it appears to be split up by prolonged ignition into a soluble and an insoluble part. A weighed quantity of the mineral was heated for 9 hours over the blast-lamp, and then digested for 3 days with hydrochloric acid of sp. gr. 1·12. The residue amounted to 48·47 per cent of insoluble matter, from which boiling with sodium carbonate solution extracted 28·73 of silica belonging to the decomposed silicates. The final undissolved residue, 19·74 per cent, was analyzed, and, treated as an independent substance, gave as follows:

SiO_2	6·32
Sesquioxides	67·81
MgO	25·67
	99·80

If the small quantity of silica here found, only 1·25 per cent of the original material, be neglected as non-essential, the remainder, 18·49 per cent of the ripidolite, has exactly the composition of spinel. Like spinel it is quite insoluble, and in all reasonable probability it may be regarded as that compound. The formation of such a magnesian aluminate, $MgAl_2O_4$, is peculiarly suggestive when we come to consider the structure of the chlorites.

Similar experiments with the prochlorite gave similar but not identical results. After long ignition, 6 hours, and 3 days' digestion with hydrochloric acid, 35·61 per cent of residue remained, of which 18·16 per cent was insoluble in carbonate of soda. This last residue, however, was rich in silica, and therefore could not be spinel. The reaction deserves further study, but the oxidizability of the iron in prochlorite introduces elements of uncertainty which would render it very difficult to interpret the results.

In the case of the leuchtenbergite, little else was done. By means of Thoulet's solution 5·62 per cent of a yellowish garnet were separated from the mineral, which accounts for part, but not all, of the lime found in the analysis. On this species our results are of little value, except as regards the character of the water which it contains, and its comparative behavior towards gaseous HCl.

Now, in order to discuss the formulæ of the three chlorites, we may reject as adventitious the small quantities of water given up at or below 300°. This leaves, as essential water in ripidolite, prochlorite, and leuchtenbergite, 12·65, 11·26, and 10·88 per cent, respectively. Using these figures for water the analyses give the following molecular ratios:

	Ripidolite.	Prochlorite.	Leuchtenbergite.
SiO_2	·498	·423	·538
R_2O_3	·186	·241	·185
RO	·855	·727	·858
H_2O	·703	·626	·604

Hence we have the following empirical formulæ:

Ripidolite	$19R_2O_3$, 86RO, $70H_2O$, $50SiO_2$
Prochlorite	$24R_2O_3$, 73RO, $63H_2O$, $43SiO_2$
Leuchtenbergite	$19R_2O_3$, 86RO, $60H_2O$, $54SiO_2$

And these, reduced to an orthosilicate basis, become—

Ripidolite	$R'''_{38}R''_{86}H_{140}(SiO_4)_{50}O_{113}$
Prochlorite	$R'''_{48}R''_{73}H_{126}(SiO_4)_{42}O_{128}$
Leuchtenbergite	$R'''_{38}R''_{86}H_{120}(SiO_4)_{54}O_{95}$

This excess of oxygen over the orthosilicate ratio can only be interpreted as basic hydroxyl; whence we get—

Ripidolite	$R'''_{38}R''_{86}H_{27}(SiO_4)_{50}(OH)_{113}$
Prochlorite	$R'''_{48}R''_{73}\quad(SiO_4)_{42}(OH)_{127}$
Leuchtenbergite	$R'''_{38}R''_{86}H_{25}(SiO_4)_{54}(OH)_{95}$

The last of these formulæ is vitiated by the fact that the mineral analyzed was impure, a fact which appears in the low figure for the hydroxyl, which garnet does not contain. Otherwise it is clear that in general leuchtenbergite and ripidolite agree quite nearly with each other. The question now to be answered is, how shall the hydroxyl be apportioned between the bases?

Taking ripidolite as the mineral of the three which has been most completely examined, we may recall that two concordant experiments with gaseous hydrochloric acid gave 13·36 and 13·46 per cent. of removable magnesia, presumably representing the group MgOH. In mean, these percentages correspond to 34 atoms of magnesia. Regarding this as an index of the MgOH present, we may combine the remainder of the hydroxyl with the sesquioxides to form the univalent group AlH_2O_2, and the ripidolite formula now becomes $(AlH_2O_2)_{38}(MgOH)_{34}R''_{52}H_{27}(SiO_4)_{50}$, with three oxygen atoms unaccounted for and neglectable. Generalizing this expression we have

$$R''_{52}R'_{99}(SiO_4)_{50}$$

or almost exactly, $R''_2(SiO_4)_2R'_4$.

This is an olivine formula, with half of the R'' replaced by R'_2, and is strictly comparable with the formula of serpentine. It will be remembered that von Wartha[1] some time ago advanced the opinion that the chlorites and serpentines form one continuous series of minerals, and his view is by this discussion curiously supported. Furthermore, the probable juxtaposition of the groups AlH_2O_2 and MgOH in ripidolite accounts in great measure for the apparent formation of spinel when the mineral is decomposed by heat.

The ratios found by analysis between H, MgOH, and AlO_2H_2 indicate that ripidolite is probably a mixture of two isomorphous molecules, and the observed data are best satisfied by assuming the compounds $Mg_2(SiO_4)_2(MgOH)_3H$ and $Mg_2(SiO_4)_2(AlO_2H_2)_3H$ in equal proportions. For a mixture of these molecules in the ratio of 1 : 1, the composition is easily calculated, and the results agree well with the analysis. If, in the latter, we recalculate the ferric and chromic oxides to their equivalent in alumina and compute the ferrous oxide as magnesia, reducing

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[1] Groth's Zeitschrift, 1887, vol. 13, p. 71.

the summation afterwards to 100 per cent, we get the following direct comparison between analysis and theory:

	Found.	Theory.
SiO_2	31·18	31·09
Al_2O_3	19·87	19·82
MgO	35·74	36·27
H_2O	13·21	12·82
	100·00	100·00

A closer concordance could hardly be expected.

For prochlorite, notwithstanding the uncertainty as to the behavior of the ferrous iron, similar ratios appear. The expression $R'''_{48}R''_{73}(SiO_4)_{42}(OH)_{127}$ reduces to $(AlH_2O_2)_{48}(R''OH)_{31}R''_{42}(SiO_4)_{42}$, in which $R''OH$ is mainly $Fe''OH$ and R'' is almost entirely Mg. This, generalized, becomes $R''_{42}(SiO_4)_{42}R'_{79}$, which is quite nearly the olivine-serpentine type of formula. A mixture of such molecules, in which R' is satisfied by MgOH, FeOH and AlH_2O_2 in the ratio of 1 : 3 : 6, would have the subjoined composition, which is comparable directly with the results of analysis.

	Found.	Calculated.
SiO_2	25·40	24·88
Al_2O_3	22·80	25·37
Fe_2O_3	2·86	
FeO	17·77	17·91
MgO	19·09	19 90
H_2O, essential	11·26	11·94
	99·18	100·00

If the first column were recalculated to 100 per cent, with the ferric iron reduced to its equivalent in aluminum, the agreement would be even closer. In brief, prochlorite seems to have a constitution strictly analogous to that of ripidolite, although, on account of its high proportion of ferrous iron, it behaves differently towards gaseous hydrochloric acid. The leuchtenbergite evidently has a similar structure, but the impurities in the sample analyzed preclude us from discussing this species more in detail. Just as the micas are derived by substitution from normal aluminum salts, so the chlorites are derived from normal magnesium silicates; and in a very curious way the two series seem to approach each other. Thus a compound having the chloritic formula $Mg_2\ (SiO_4)_2\ (AlO_2H_2)\ H_2$, if halved, may be written as if it were a derivative of aluminum orthosilicate analogous to some of the more basic hydro-micas; and the close physical similarity between the two groups is thus remarkably emphasized.

THE MICAS.

In this group only three examples were studied, all of the magnesian or ferro-magnesian class. A. Phlogopite from Burgess, Ontario; the ordinary, slightly brownish, broadly foliated mica, somewhat resembling muscovite. B. Phlogopite from Edwards, St. Lawrence County, New York; the peculiar, non-fluoriferous variety, superficially resembling brucite, described by Penfield and Sperry, whose analysis is thoroughly confirmed by ours. C. A nearly black, broadly foliated iron mica from Port Henry, New York; commonly regarded as a lepidomelane. Analyses as follows:

	Burgess.	Edwards.	Port Henry.
SiO_2	39·66	45·05	34·52
TiO_2	·56		2·70
Al_2O_3	17·00	11·25	13·22
Fe_2O_3	·27		7·80
FeO	·20	·14	22·27
MnO			·41
(CoNi)O			·30
CaO	none.		
BaO	·62		
MgO	26·49	29·38	5·82
Li_2O		·07	·04
Na_2O	·60	·45	·16
K_2O	9·97	8·52	8·59
H_2O	2·99	5·37	4·39
F	2·24		·34
P_2O_5	trace.		trace.
	100·60	100·23	100·54
Less O	·94		·14
	99·66		100·40

The fractional water determinations gave—

	Burgess.	Edwards.	Port Henry.
H_2O at 105°	·66		·57
" 250°–300°	·35	·73	·45
" red heat	1·98	·73	3·37
" white heat		3·91	

In all the analyses of this investigation, when much iron was found, the total water was determined directly; so that the figures for the higher temperatures do not represent mere loss on ignition. In these micas the percentages of constitutional water, to be used in the discussion of formulæ, are 1·98, 4·64, and 3·37 respectively.

In the Burgess phlogopite numerous inclusions were observed, consisting of slender prisms, and at our request these were examined microscopically by Mr. Waldemar Lindgren. The mica, according to his examination, is made up of "thin foliæ, under the microscope colorless, dark between crossed nicols; interference figure apparently a cross, not separating into hyperbolas; seemingly uniaxial, but with better instruments it would probably be found to be biaxial with a very small axial angle. Shows excellent asterism, caused by interpositions arranged in three directions cutting each other at an angle of 60°. The inclusions are prisms of a strongly refracting and bi-refracting mineral, so thin as to show brilliant Newton's colors. In spite of the very small thickness, the interference colors are near the white of the first order. Extinction takes place strictly parallel to the prismatic surface. Terminal faces rounded, or unequally developed. Besides prisms there are square or rhomboidal foliæ, probably of the same substance. The inclusions were first observed by G. Rose,[1] who regarded them as kyanite. Rosenbusch describes them again, and determines them as tourmaline.[2] The prisms certainly correspond well in their optical characteristics to this mineral. Kyanite and apatite are excluded from among the possibilities. Probably, in spite of its apparent abundance, the mineral is but a very small fraction of the mica substance." At Mr. Lindgren's suggestion the mica was carefully tested for boron, but none was found. Hence tourmaline, if present, must be in exceedingly small quantities.

On account of the high proportion of titanium in the Port Henry iron mica, this too was examined by Mr. Lindgren, who reports as follows: "It is a dark brown, unusually deep colored, apparently uniaxial biotite, without inclusions, and especially, as far as examined, free from any titanium mineral." Hence the titanium is to be regarded as a constituent of the mica itself.

The action of gaseous hydrochloric acid upon these micas, at 383°–412°, was almost insignificant. The data are subjoined.

	Burgess.	Edwards.	Port Henry.
Hours heated	12	20	33
MgO removed	·40	1·00	trace.
R_2O_3 removed	none.	·21	·44
SiO_2 removed	....	·13	....

In the case of the Port Henry mica some iron was volatilized as chloride. This was estimated; and it was found that the total iron taken out, reckoned as FeO, amounted to only 1·62 per cent. An experiment on the Edwards phlogopite at 498°–527°, lasting 18 hours, gave 1·41 per cent of removable magnesia. This quantity has a possible bearing upon the formula of the mineral.

By aqueous hydrochloric acid all three of the micas were completely decomposed. Hence the Burgess phlogopite could have contained little

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[1] Neues Jahrbuch, 1863, p. 91.

[2] Physiog. der Mineralien, p. 486.

tourmaline, for that mineral is not soluble in the acid. Moreover, the solubility of the micas prevents us from assuming in either of them an admixture of a muscovite molecule, for muscovite also is insoluble. A careful comparison of the two phlogopites showed that the fluoriferous variety was much more stable towards acids than the rarer non-fluoriferous mineral; a fact which also appears in the action of the gaseous acid upon them. When the two varieties are treated side by side with hydrochloric acid, the Edwards phlogopite decomposes much more rapidly than the Burgess mica.

After very prolonged ignition the Edwards phlogopite and the Port Henry iron mica were still completely decomposable by aqueous hydrochloric acid. There was, therefore, no splitting up of their molecules which could be determined by this method. The Burgess phlogopite, on the other hand, showed a small amount of change. After eight hours of ignition over the blast, treatment with strong hydrochloric acid for three days, and subsequent leaching with soda solution to remove free silica, 2·45 per cent of insoluble residue remained. This, analyzed, gave

SiO_2	30·94
R_2O_3	48·06
MgO	19·01
Alkalies	undet.
	98·01

This agrees quite nearly with the formula $MgAl_2SiO_6$, which is the composition of a possible member of the clintonite group.[1]

Now from the analyses of the micas we get the subjoined molecular ratios; in which titanic oxide is thrown in with the silica, the alkalies are united as potash, and only the essential water, stable above 300°, is retained.

	Burgess.	Edwards.	Port Henry.
SiO_2	·668	·751	·609
R_2O_3	·169	·110	·177
RO	·669	·736	·464
K_2O	·116	·098	·094
H_2O	·110	·258	·187
F	·118	....	·018

Hence we have the following empirical formulæ:

Burgess...... $17R_2O_3 . 67RO . 12K_2O . 11H_2O . 67SiO_2 . 12F$.
Edwards..... $11R_2O_3 . 74RO . 10K_2O . 26H_2O . 75SiO_2$.
Port Henry .. $18R_2O_3 . 46RO . 9K_2O . 19H_2O . 61SiO_2 . 2F$.

Deducting oxygen equivalent to the fluorine we have

Burgess................ $R'''_{34}R''_{67}K_{24}H_{22}Si_{67}O_{269}F_{12}$.
Edwards............... $R'''_{22}R''_{74}K_{20}H_{52}Si_{75}O_{293}$.
Port Henry .... $R'''_{36}R''_{46}K_{18}H_{38}Si_{61}O_{249}F_2$.

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[1] The minerals prismatine and kornerupine have also this composition.

In all of these micas the silicon and oxygen are present in almost the exact orthosilicate ratio; but in order to discuss the expressions further it is necessary to recall the theory of the mica group which has already been cited. Upon that theory, all these salts should be substitution derivatives of normal aluminum orthosilicate, from which the more definite micas develop as follows:

Normal orthosilicate	$Al_4(SiO_4)_3$.
Muscovite	$Al_3(SiO_4)_3KH_2$.
Normal biotite	$Al_2(SiO_4)_3Mg_2R'_2$.
Normal phlogopite	$Al\ (SiO_4)_3Mg_3R'_3$.

Applying these formulæ to the expression given above for the Burgess phlogopite, and regarding the fluorine as present in a group —Mg—F, we have for the composition of that mineral:

$$Al(SiO_4)_3Mg_3KH_2 + Al_2(SiO_4)_3Mg_2K(MgF),$$

the two molecules being mixed in the ratio 1:1. Recalculating the original analysis to 100 per cent, uniting TiO_2 with SiO_2, Fe_2O_3 with Al_2O_3, FeO and BaO with MgO, and Na_2O with K_2O, we have this comparison:

	Found.	Calculated.
SiO_2	41·04	41·09
Al_2O_3	17·59	17·46
MgO	27·39	27·39
K_2O	10·62	10·73
H_2O	2·03	2·07
F	2·29	2·17
	100·96	100·91
Less oxygen	·96	·91
	100·00	100·00

The results for the non-fluoriferous phlogopite from Edwards are less satisfactory. Its formula, condensed a little from that given above, is

$$R'''_{22}R''_{74}R'_{72}Si_{75}O_{293},$$

in which the ratio between R''' and Si is 1:3·5 nearly. But in this mica three atoms of magnesia are removable by gaseous HCl, corresponding to 3MgOH. If we assume that this represents a small admixture of a foliated serpentine, and deduct proportionally, there remains

$$Al_{22}Mg_{65}H_{40}K_{20}Si_{69}O_{266},$$

which is very nearly $Al(SiO_4)_3Mg_3KH_2$, or normal phlogopite. At first, as the mineral occurs in a talc mine, we suspected that its anomalies might be due to intermingled talc; but its complete decomposability by hydrochloric acid showed that supposition to be incorrect. If the mica theory is correct, this mineral must contain a small amount of impurity; and a serpentinous or chloritic molecule is the most probable admixture.

In the Port Henry mica the ratios are perfectly simple. The formula,

$R'''_{36}R''_{46}K_{18}H_{38}(SiO_4)_{61}O_5F_2$, if we neglect the small amounts of fluorine and excessive oxygen, reduces easily to a mixture of the three typical molecules:

$$Al_2(SiO_4)_3Fe''_2KH,$$
$$Fe'''_2(SiO_4)_3Fe''_2KH,$$
$$Al\ (SiO_4)_3Mg_3KH_2,$$

in the ratio 2:1:1. This compares well with the analysis, reduced as usual, thus:

	Found.	Calculated.
SiO	37·02	37·41
Al_2O_3	13·39	13·34
Fe_2O_3	7·90	8·34
FeO	22·56	22·51
MgO..........	6·30	6·26
K_2O	9·08	9·79
H_2O	3·75	2·35
	100·00	100·00

Here the theoretical water is too low and the potash too high; both outside the allowable range of error. Their reciprocal replacements explain the slight discordance only in part; and the nature of the mineral suggests a small excess of water due to incipient alteration. Altogether the agreement between analysis and theory is remarkably close.

THE VERMICULITES.

Of this interesting group two examples were studied; the well known typical jefferisite from Westchester, Pennsylvania, and the kerrite from near Franklin, Macon County, North Carolina. The latter, presented to us by Prof. F. A. Genth, was part of his original sample, and the analysis agrees well with Chatard's. Analyses as follows, on *air-dried* material.

	Jefferisite.	Kerrite.
SiO_2	34·20	38·13
Al_2O_3	16·58	11·22
Fe_2O_3	7·41	2·28
FeO	1·13	·18
NiO......................	....	·48
CoO	....	trace
MgO......................	20·41	27·39
H_2O (ignition)	21·14	20·47
	100·87	100·15
H_2O over H_2SO_4............	10·56	9·62
H_2O at 105°	....	·24
H_2O at 250°–300°	4·20	4·10
H_2O at red heat...........	6·18	6·27
H_2O at white heat	·20	·24

Here the water falls into three sharply defined parts: one, lost by drying over sulphuric acid, very loosely held; a second, water of crystallization, lost below 300°; and the third, constitutional water.

By dry hydrochloric acid gas the minerals were little affected. The data are as follows for 383°–412°:

	Jefferisite.	Kerrite.
Hours heated	32	32
MgO removed	3·98	3·15
R_2O_3 removed	1·38	·09

By aqueous hydrochloric acid both of the vermiculites were easily and completely decomposed. By ignition, however, with fusion in the case of the kerrite, they were split up into soluble and insoluble portions. In the kerrite, after fusion, only 10·64 per cent of magnesia and 3·75 of sesquioxides were removable by aqueous hydrochloric acid, but nothing more could be determined for want of material. The jefferisite, after strong ignition and subsequent digestion with the acid for 3 days, gave 51·08 per cent of insoluble residue. From this, soda solution extracted 21·54 of silica, leaving 29·54 per cent of an undecomposed silicate. This, analyzed independently, contained

SiO_2	45·08
Al_2O_3	22·82
Fe_2O_3	10·01
MgO	21·48
	99·39

Hence the ratios $SiO_2 : R_2O_3 : MgO = 75 : 29 : 54$; which correspond nearly to a mixture of Al_2SiO_5 with $Mg_2Si_2O_6$. As to the real nature of this residue, we can only offer the foregoing suggestion as a plausibility. Positive knowledge is lacking. The vermiculites, however, are alteration derivatives of the micas; and by their metamorphosis kyanite, fibrolite, or andalusite might, perhaps, be generated in nature. Geologically, the suggestion is worthy of consideration.

Now, from the two analyses we get the subjoined molecular ratios:

	Jefferisite.	Kerrite.
SiO_2	·570	·635
R_2O_3	·209	·124
RO	·526	·694
H_2O, over H_2SO_4	·587	·524
H_2O, 250°–300°	·233	·226
H_2O, constitutional	·355	·363

Hence the empirical formulæ

Jefferisite	$R'''_{42}R''_{53}H_{70}Si_{57}O_{265}+82H_2O$
Kerrite	$R'''_{24}R''_{69}H_{72}Si_{63}O_{267}+75H_2O$

For the jefferisite gaseous hydrochloric acid removed 10 atoms of magnesia, and from the kerrite 8 atoms. Taking this, hypothetically, as MgOH, we have

Jefferisite .... $R'''_{42}R''_{43}(MgOH)_{10}H_{60}(SiO_4)_{57}O_{27}+82H_2O$
Kerrite .... $R'''_{24}R''_{61}(MgOH)_8H_{64}(SiO_4)_{63}O_7+75H_2O$

The small excess of oxygen in these expressions needs to be accounted for. To regard it as forming the group AlO, however, is impracticable; for then the residual aluminum atoms would be less than one-third the silicic groups, which is inadmissible under the mica theory. The simplest interpretation is as follows: In the clintonite group the general formula

seems to apply. If we treat the excess of oxygen in the two vermiculites as pertaining to molecules of this order, the composition of both minerals reduces to very simple terms; one term being a normal hydromica. In the jefferisite we have approximately $AlO_2MgSiO_4R'_3.3H_2O + Al_2(SiO_4)_3Mg_2H_2.3H_2O$; or a mixture in equal ratios of a hydro-clintonite and a hydro-biotite, the alkalies being replaced by hydrogen, and R′ being in part, about one-third, MgOH. The greatest uncertainty is in the loosely combined water, which is probably analogous to the water in laumontite. Two-thirds of the $3H_2O$ is of this type; the remaining one molecule being given off below 300°. Dried at 100° the salts become monohydrated. Reducing the bases of the analysis to terms of alumina and magnesia we get the following comparison with the formula:

	Found.	Calculated.
SiO_2	34·97	34·00
Al_2O_3	21·91	21·67
MgO	21·51	22·67
H_2O constitutional	6·52	6·37
H_2O, 250°-300°	4·30	5·10
H_2O, over H_2SO_4	10·79	10·19
	100·00	100·00

The concordance here is less perfect than in the previous cases, but for obvious reasons. First, the uncertainty in the water has already been mentioned. Secondly, the actual ratio between the clintonite and biotite molecules, as deduced from the empirical formula, is not 1 : 1 but 13 : 15. Finally, the observed MgOH is a little less than one-third R'_3. Still, considering the character of the mineral, the agreement between analysis and theory is as close as could be expected.

For kerrite, uniting the univalent factors, the formula becomes

$$R'''_{24}R''_{61}R'_{72}(SiO_4)_{63}O_7 . 75H_2O.$$

This, very nearly, is equivalent to

$$AlO_2MgSiO_4R'_3 . 3H_2O+Al(SiO_4)_3Mg_3H_3 . 3H_2O,$$

commingled in the ratio of 1:5, with two-thirds of R'_3 being MgOH. The second term in this mixture is a hydrous phlogopite; and here again we have trihydration, with two molecules of water loosely held and the third more firmly combined. In this case we may compare the analysis, reduced to alumino-magnesian form and 100 per cent, both with the formula given above and with that of the hydrous phlogopite taken separately.

	Found.	Calculated.	
		As given.	As a phlogopite.
SiO_2	38·51	38·33	41·66
Al_2O_3	12·79	12·38	11·84
MgO	28·02	29·12	27·77
H_2O, constitutional	6·61	6·55	6·25
H_2O, at 250°-300°	4·35	4·37	4·16
H_2O, over H_2SO_4	9·72	8·75	8·32
	100·00	100·00	100·00

This comparison, which is in the main satisfactory, makes it perfectly clear that kerrite is essentially a trihydrated phlogopite, with the alkalies replaced by hydrogen. The analogies between kerrite and jefferisite are perfectly clear, and both minerals become monohydrated by exposure over sulphuric acid. It is our intention to examine several other vermiculites in the near future, and we believe that all of them will be easy to interpret with the aid of the evidence already gained.

FINAL CONSIDERATIONS.

In the foregoing pages we have shown conclusively that gaseous and aqueous hydrochloric acid differ widely in their action upon magnesian silicates. We have also endeavored to show that in this group of minerals, the gaseous acid attacks only that part of the magnesium which is present as the univalent group —Mg—OH; and although the proof is far from complete, the evidence in favor of our view appears to be cumulative. In the first place olivine, which can not contain hydroxyl, is almost unattacked by the gas in the range of temperatures studied. Secondly, serpentine, which must contain MgOH, is attacked proportionally to the excess of oxygen over the orthosilicate ratio. The results, to be sure, are only approximations to quantitative accuracy, but they are uniform enough to warrant our conclusion. Finally, ripidolite behaves like serpentine, and gives an analogous formula; while the micas, which presumably contain little or no hydroxylated magnesia, are but slightly affected. All the evidence, so far, converges to the one conclusion; which has at least the status of a legitimate working hypothesis. All the hydrous silicates so far examined are not alike in their behavior towards the reagent, but only those are attacked by it in which there are strong reasons for assuming the presence of the basic MgOH.

In the course of the investigation certain collateral questions have arisen which have been the subject of experiment. For instance, in the action of gaseous hydrochloric acid upon silicates may not insoluble oxychlorides be formed, which would escape notice in the analysis of the soluble portion? To answer this question the residues were in several cases examined, and found to be practically free from chlorine. Traces only of chlorine were retained, insufficient to modify our ratios. Furthermore, precipitated and ignited magnesium oxide, heated at 498°–527° in gaseous hydrochloric acid, was almost quantitatively converted into chloride, showing the stability of the latter in a stream of the dry gas; 94·13 per cent of the required chlorine was taken up by the oxide, so that the possible formation of oxychlorides in our experiments may be fairly left out of account.

Similar experiments with brucite, however, gave apparently anomalous results. The mineral examined was typical material from Texas, Lancaster County, Pennsylvania, which was first analyzed and subjected to dehydration estimations. The data are as follows:

MgO	67·97
FeO	undet.
MnO	0·97
Fe_2O_3	0·39
H_2O	30·81
	100·14

Water lost at 105°	0·18
" " 250°	0·46
" " 383°–412°, 2 hours	7·57
" " " 3 " more	19·37
" " " 2 " "	0·06
" " 498°–527°, 1 "	0·23
" " " 1 " more	none
" " full ignition	2·94

The greater part of the water, therefore, nine-tenths of it, is lost at about 400° C., but is given off somewhat slowly.

Heated for 28 hours to 383°–412° in dry hydrochloric acid gas, constant weight was not attained; but at this point the experiment was stopped, and only 10·33 per cent of the magnesia had been converted into chloride, or a little less than one-seventh of the total amount. Several other experiments, at temperatures ranging from 200° to 500° gave similar results, all low, and in no case was more than one-fifth of the required chlorine absorbed. At the higher temperature, 498° to 527°, the reaction went farthest, and the absorption of chlorine was still going on at a very slow rate. In this case, the brucite must have become almost dehydrated; but the oxide so formed was different in its behavior from the precipitated oxide previously examined. The difference may have been due to physical causes, such as a different degree of compactness in the material; but it is doubtful whether that supposition would fully account for the anomaly. Probably magnesium hydroxide, like other hydroxides investigated by Carnelley and Walker,[1] undergoes progressive dehydration through a series of stages; each step being attended by a polymerization of the residue. An oxide so formed might conceivably be more stable than the oxide with which we previously worked; at all events, the two are not necessarily identical. As regards the bearing of these data upon our silicate work, we can hardly offer satisfactory conclusions. Still, magnesium saturated by hydroxyl is quite differently combined from magnesium which is but half saturated with that radicle, and in the mixed union in a silicate, the polymerization attending dehydration above referred to could hardly occur. We are inclined to believe, on the whole, that MgOH in a silicate has a lower order of stability towards gaseous HCl than the compound $Mg(OH)_2$; but this point remains to be proved. We hope to continue this investigation among other silicates; and we feel confident that the data so far obtained have value quite independently of our conclusions.

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[1] Jour. Chem. Soc., 1888, vol. 53, p. 59.

THE RELATIVE ABUNDANCE OF THE CHEMICAL ELEMENTS.

BY F. W. CLARKE.

In the crust of the earth, with its liquid and gaseous envelopes, about seventy chemical elements are at present recognized. Others, as yet unknown, are indicated by gaps in the periodic system and will probably be discovered in the future. Some of the elements are quite plentiful, some are exceedingly rare, and in any thorough discussion of their nature and relations this comparative abundance or scarcity should be taken into account. Even though the full meaning of the facts may not be discoverable for many years to come, it is worth while to put them into something like systematic order.

In its larger aspects the general problem is at present unsolvable, for the reason that we know nothing of the earth's interior. Its surface only is within our certain reach, and from the composition of that we must draw nearly all our conclusions. For that which lies below the crust we must be content with inferences based upon the scantiest of data. Of the crust itself the average composition is easily computable, and the calculation gives results which are in some respects surprising.

In order to have a definite mass of matter under consideration, we may assume for the earth's *known* crust a thickness of ten miles below sea-level. The volume of that crust, including the mean elevation of the continents above the sea, is 1,935,000,000 cubic miles. Of this amount 302,000,000 cubic miles are ocean and 1,633,000,000 are solid matter. The mass of the atmosphere is equivalent to that of 1,268,000 cubic miles of water, the unit of density. For these data, which cover all the terrestrial matter accessible to us, I am indebted to Mr. R. S. Woodward, of the U. S. Geological Survey, and from them the relative masses of solid crust, ocean, and atmosphere can be determined within narrow limits of uncertainty. To sea water we may assign a density of 1·03, which is a trifle too high, and to the solid rocks, a specific gravity not lower in average than 2·5, nor much higher than 2·7. With these values we can get the following expression for the percentage composition of the known matter of the globe:

Per cent.	Density of crust 2·5.	Density of crust 2·7.
Atmosphere	·03	·03
Ocean	7·08	6·58
Solid crust	92·89	93·39
	100·00	100·00

In short, we may regard the earth's crust, to a depth of ten miles, as composed essentially of 93 per cent. solid and 7 per cent. liquid matter, treating the atmosphere as a small correction to be applied later. More elaborate estimations are unnecessary. Since the known nitrogen of the earth is mainly in the atmosphere, its relative scarcity as an element is at once curiously manifest. It cannot possibly exceed 0·025 of 1 per cent. of the total.

For the composition of the ocean, the data given by Dittmar in the Reports of the Challenger Expedition are perhaps the best available. The maximum salinity he puts at 37·37 grammes of salts in the kilogramme of water, and by taking this figure instead of a lower value we can make an allowance for saline masses inclosed in the solid crust, which would not otherwise appear in the final averages. Combining this datum with Dittmar's statement of the average composition of the ocean salts, we get the second of the subjoined columns. The traces of other elements, not named here, which have been found by various observers in sea water, are too small to be considered.

Composition of salts.		Composition of ocean.	
$NaCl$	77·76	O	85·79
$MgCl_2$	10·88	H	10·67
$MgSO_4$	4·74	Cl	2·07
$CaSO_4$	3·60	Na	1·14
K_2SO_4	2·46	Mg	·14
$MgBr_2$	·22	Ca	·05
$CaCO_3$	·34	K	·04
	100·00	S	·09
		Br	·008
		C	·002
			100.000

Dissolved gases need not be taken into account, and no other constituent of the ocean can reach 0·001 of 1 per cent.

In the case of the solid crust of the earth the problem of ascertaining its mean composition is far less simple; for the crust is not a homogeneous body, but is made up, so to speak, of shreds and patches—of old crystalline rocks, of volcanic outflows, and of all manner of deposits of sedimentary origin. It is veined and seamed with diverse minerals, it incloses pockets of various materials, and upon its surface are quantities of organic matter and great bodies of fresh water. At first sight it would seem to be impossible to determine the average composition of such a mass, and yet, upon consideration, the question is not seriously complicated. In a crust ten miles thick a section having the superficial area of the United States represents only about 1·5 per cent of the total; so that all veins, pockets, patches, organic substances, etc., become insignificant in comparison with the whole mass, and even the lakes and rivers are neglectable quantities. On any attempt to compute their percentages they vanish into the dim recesses of the remoter decimals. Discarding these trivial constituents the question becomes one of the mean composition of the dominant rock material, and in that form it is comparatively simple.

In the first place, we may assume that the volcanic and crystalline rocks represent pretty closely the general composition of the whole crust; for from them the sedimentary rocks have been formed, and the latter differ from the parent formations only in the carbon which they have taken up from the air and in the loss of saline constituents which have been leached out to the ocean. For this gain and loss, respectively, approximate corrections are possible.

In the second place, we must regard the original rock matter, volcanic and crystalline, as being in a large sense fairly homogeneous. However greatly these formations may vary locally, they should average pretty much alike all over the world when sufficiently large areas are considered. This assumption can be tested in the light of evidence, as follows: We may average together great numbers of analyses, grouped in various ways, and so determine whether the results are sensibly constant. This has been done in the subjoined table, minor and occasional constituents being temporarily omitted, to be separately considered later.

Table of analyses of rocks.

A. The mean of 82 analyses of volcanic rocks from the Western Territories of the United States, published in Clarence King's Survey of the Fortieth Parallel.

B. 64 analyses of rocks from the Yellowstone Park, taken from the laboratory records of the U. S. Geological Survey.

C. 54 analyses of volcanic rocks collected in northern California; also from the Survey records.

D. 39 analyses of eruptive rocks from various localities in the Western United States, taken from the Survey records.

E. 80 crystalline and archean rocks from all parts of the United States. Of these analyses 50 were taken from the Survey records, 23 from the 40th Parallel Report, and 7 from the report of the New Hampshire Survey, vol. 3.

F. 75 analyses of European volcanic and crystalline rocks, taken at random from five recent volumes of the Neues Jahrbuch.

G. 486 miscellaneous plutonic rocks, analyzed between 1879 and 1883, and collected by Roth in his "Beiträge zur Petrographie der plutonischen Gesteine."

H. The mean of the foregoing 880 analyses.

	A.	B.	C.	D.	E.	F.	G.	H.
SiO_2	61·89	61·89	60·49	60·66	60·50	59·80	56·75	58·59
Al_2O_3	15·71	15·73	16·08	15·46	14·30	14·65	14·90	15·04
Fe_2O_3	1·81	3·18	2·47	2·74	3·35	4.99	4·58	3·94
FeO	3·65	2·40	2·86	2·27	4·31	2·92	3·71	3·48
CaO	4·51	4·58	6·15	4·71	3·52	5·19	5·79	5·29
MgO	2·40	3·08	4·31	3·35	5·00	3·45	5·22	4·49
K_2O	3·54	2·70	1·80	3·97	2·52	3·06	2·90	2·90
Na_2O	3·28	3·70	3·31	3·54	2·49	2·98	3·24	3·20
H_2O	1·69	1·59	1·12	·97	2·53	2·09	2·12	1·96
	98·48	98·85	98·59	97·67	98·52	99·13	99·21	98·89

That these means are remarkably concordant, especially as regards the columns A to F, is at once evident; but a reduction to elementary form renders the agreement even more striking.

Table of analyses of rocks—Elementary substances.

	A.	B.	C.	D.	E.	F.	G.	H.
Si	28·88	28·88	28·23	28·31	28·23	27·91	26·50	27·34
Al	8·31	8·32	8·51	8·18	7·57	7·75	7·89	7·96
Fe	4·11	4·09	3·96	3·68	5·71	5·77	6·09	5·47
Ca	3·22	3·27	4·39	3·37	2·51	3·71	4·13	3·78
Mg	1·44	1·85	2·58	2·01	3·00	2·07	3·13	2·69
K	2.94	2·24	1·49	3·29	2·09	2·54	2·41	2·41
Na	2·43	2·74	2·46	2·63	1·85	2·21	2·56	2·37
H	·19	·18	·12	·11	·28	·23	·24	·22
O	46·96	47·28	46·85	46·09	47·28	46·94	46·26	46·65
	98·48	98·85	98·59	97·67	98·52	99·13	99·21	98·89

The thesis that the crust of the earth is fairly homogeneous in composition is thus sustained by positive evidence. The variations in the foregoing table are as small as could reasonably be expected.

So far, however, only nine of the rock-forming elements are accounted for. The proportions of the others are less easily computable, although in some cases fair estimates can be made. In certain directions very many of the analyses considered, especially in the columns A and G, were incomplete, constituents like titanium, manganese, phosphorus, etc., having been ignored as not essential to the purpose of the analyst. These substances appear in part, therefore, as impurities in the silica and alumina, rendering the latter a trifle too high.

For several of the less frequently determined elements the laboratory records of the U. S. Geological Survey furnish data. In 211 analyses of volcanic and crystalline rocks there recorded, titanium, manganese, and phosphorus were determined in a great majority of cases, and other elements appear frequently enough to prove something as to their relative abundance. Taking these 211 analyses all together, they show the following mean percentages for the constituents in question:

TiO_2	0·55
P_2O_5	·22
MnO	·10
CO_2	·37
S	·034
Cr_2O_3	·021
BaO	·033
SrO	·009
Cl	·012
Li_2O	·011

All of these figures, obviously, are *under*-estimates, for the determinations were not made in all cases. Furthermore, the rocks analyzed were varied enough in origin, locality, and character, to avoid any cumulative error due to the peculiarities of any one formation or area. The value for titanic oxide includes whatever zirconia may have been present in the various rock samples, but although the latter base is widely diffused, its proportion can not be very high. Titanium, therefore, must be regarded as more abundant than phosphorus, manganese, or sulphur—a result hardly to have been expected. This conclusion, however, is borne out by evidence from other sources. Titanium is rarely absent from the older rocks; it is almost universally present in soils and clays, and it is often concentrated in great quantities in beds of iron ore. Having no very striking characteristics and but little commercial importance, it is easily overlooked, and so it has a popular reputation for scarcity which it does not deserve. Among all the elements it probably ranks tenth or eleventh in point of absolute abundance and is rare only as regards obvious concentrations. In the solar spectrum it is one of the most conspicuous of substances.

For phosphoric acid and manganese the data given are probably not far out of the way, but in the case of carbon the estimation is more troublesome. The percentage of CO_2 in volcanic and crystalline rocks, 0·37, is doubtless untrustworthy, for the reason that surface rocks are mainly represented, in many of which alteration may have begun. The figure, however, may be used as an offset for the undeterminable carbon existing in coal, shales, petroleum, etc. As regards the limestones, rough estimates of their quantity must suffice, and we may provisionally accept that of T. Mellard Reade as given in his essay on "Chemical Denudation in Relation to Geological Time." According to Reade, the existing bodies of limestone are equivalent to a layer of the rock 528 feet thick and completely enveloping the globe. This is approximately 1 per cent of the crust under consideration, and represents 0·44 per cent of CO_2. To this we may add the 0·37 per cent given above, making 0·81 per cent in all—an estimate which can hardly be too low.

In the case of sulphur, the figure given, 0·034 per cent, is surely much too low; for sulphur is abundant both in sulphates and in sulphides, and iron pyrites especially is widely diffused. The absolute proportion of this element seems to be hardly determinable. It should be at least 0·05 and probably not over 0·10 per cent. For chlorine, chromium, barium, and strontium the figures are minima, but can not be very largely increased. The value for lithia is probably not far out of the way, for that oxide is almost universally present in minute traces in the older crystalline rocks, although it is rarely estimated in ordinary analyses.

Now, taking the mean of 880 analyses as cited in column H of the table, we may insert in it the additional values so far determined, but with certain qualifications. In about half of the analyses TiO_2, P_2O_5, and Cr_2O_3 were not estimated, but their amounts appear in the figures for silica and alumina. The silica, then, may be reduced by about one-fourth the percentage of the titanic oxide, and the alumina by the other fourth, plus half the values assigned to P_2O_5 and Cr_2O_3. Making these corrections, reducing to elementary form, and recalculating to 100 per cent, we get a rough approximation to the mean composition of the solid crust of the earth. To this approximation the other unestimated elements may be regarded as future corrections of very small amount. Combining this result with the mean composition of the ocean, and including 0·02 per cent for the nitrogen of the air, we get the final column to illustrate the abundance of the elements so far as at present known. Quantities less than 0·01 per cent are left out of consideration.

	Solid crust, 93 per cent.	Ocean, 7 per cent.	Mean, including air.
Oxygen	47·29	85·79	49·98
Silicon	27·21		25·30
Aluminum	7·81		7·26
Iron	5·46		5·08
Calcium	3·77	·05	3·51
Magnesium	2·68	·14	2·50
Sodium	2·36	1·14	2·28
Potassium	2·40	·04	2·23
Hydrogen	·21	10·67	·94
Titanium	·33		·30
Carbon	·22	·002	·21
Chlorine	·01	2·07	·15
Bromine		·008	
Phosphorus	·10		·09
Manganese	·08		·07
Sulphur	·03+	·09	·04+
Barium	·03		·03
Nitrogen			·02
Chromium	·01		·01
	100·00	100·000	100·00

Nineteen of the elements are here provided for with very varying degrees of probability, although their order in the last column is presumably correct. The uncertainty may reach 1 per cent in the cases of silicon and iron, one-half as much with aluminum and oxygen, and is proportionally less for the other elements specified. The remaining elements, more than fifty in number, can hardly aggregate over 1 per cent altogether, and not one of them could pass 0·05 per cent in relative quantity. Some of them may be briefly considered in detail, as follows:

Fluorine.—Abundant in fluor-spar and apatite and present in many rocks as a constituent of topaz or mica. If the phosphorus in the foregoing estimate, 0·09 per cent, represents mainly apatite, the proportional amount of fluorine would be 0·02 to 0·03, the minimum assignable value.

Glucinum.—Widely distributed as beryl and easily overlooked in small traces. If determined, it would appear as a correction to the alumina.

Boron.—Comparatively abundant in tourmaline and datolite and conspicuous in certain volcanic waters; difficult to estimate.

The Cerium group.—According to Cross and Iddings, allanite is a widespread constituent of rocks. The same is true of monazite, as shown by Derby. These elements, together with thorium, zirconium, and the yttrium groups, would appear as corrections to alumina.

Nickel.—Frequent in rocks composed of or derived from olivine. Less than 0·01 per cent.

The metallic acids—stannic, molybdic, tungstic, columbic, and tantalic.—These, if determined, would form corrections to silica. The same is true to some extent of barium when present in rocks as sulphate.

The heavy metals.—Widely distributed in rocks, according to Sanberger's researches, but in very small quantities.

In the larger items, say from oxygen down to the alkaline metals, the estimates here given do not differ very widely from others which have been long current in chemical and geological literature. They rest, however, upon fuller evidence, and the discussion is, perhaps, more complete. In the smaller items the new results display the greatest novelty, and future modifications are most likely. The comparative rarity of carbon and sulphur is, to say the least, surprising.

On the theoretical side the results attained are not easy to interpret. That nine of the chemical elements should constitute, at the lowest estimate, 98 per cent of all known terrestrial matter is somewhat startling and difficult to comprehend. Are the other elements concentrated in the interior of our planet? On this point there is a little positive evidence.

The mean density of the earth, 5·5 to 5·6, is more than double that of the rocky crust, and the difference may be accounted for as a result of pressure, or by supposing that as the globe cooled the heavier elements accumulated toward the center. Both suppositions may be true in part, but less weight is to be placed upon the second, for the following reason: A mixture of the elements in equal proportions, in the free state and as they behave at the earth's surface, would have a specific gravity of about 7·3. In combination the density would be greater because of condensation, and below the surface it would also be increased by pressure. Hence it seems clear, since the density of the earth is only 5·5, that in the planet as a whole the lighter elements must very considerably exceed in quantity the heavier ones. Twenty-nine of the known elements have densities below 5·5, and forty exceed that figure, iron being the only one of the heavier group which is at all abundant. The greater part of the earth's mass is almost certainly to be found among the twenty-nine lighter elements. The others may be more plentiful at the center of the globe than upon its surface, but few beside iron can be dominant constituents. This evidence seems to be clear, even though it is not proof positive. Whether the composition of meteorites can be made to shed any light upon this question is very doubtful, although some interesting analogies might be discovered. The resemblance between meteoric stones and volcanic rocks is noteworthy, and the richness of meteorites in metallic iron and nickel is suggestive. The earth, below its crust, may be like a huge meteorite in composition, with the stony part predominating.

An attempt was made in the course of this investigation to represent the relative abundance of the elements by a curve, taking their atomic weights for one set of ordinates. It was hoped that some sort of periodicity might be evident, but no such regularity appeared. No definite connection with the periodic law seemed to be traceable. And yet certain other regularities are worth noticing. All of the abundant elements are low in the scale of atomic weights, reaching a maximum at 56 in iron. Above 56 the elements are comparatively rare, and only two of them, barium and strontium, appear in my estimates. Below oxygen, hydrogen alone approaches 1 per cent, while between oxygen and iron only scandium and vanadium are of neglectable rarity. Furthermore, in several elementary groups abundance diminishes with increase of atomic weight. This is plainly seen in the series potassium, rubidium, and cæsium; in sulphur, selenium, and tellurium; in chlorine, bromine, and iodine; in arsenic, antimony, bismuth, etc. The regularity is not certainly invariable, but it occurs often enough to be suggestive. Again, in the distribution of the elements with regard to each other there are indications of something like system. Closely allied elements commonly occur together, so that the presence of one implies the presence of the others; for example, cobalt and nickel are almost always associated; vanadium is rarely found unaccompanied by at least some phosphorus; nearly all native gold contains silver; no member of the platinum group ever occurs singly, and so on. Still another kind of order seems to appear among the compounds formed in the earth's crust, and elements of high atomic weight appear to seek each other. Thus in the series oxygen, sulphur, selenium, tellurium, the commonest oxides range from iron downward; the commonest sulphides range from iron upward, while the selenides and tellurides are preferably formed by the heavier elements silver, gold, lead, and bismuth. So also the phosphates are most abundant below iron, where arsenates are of extreme rarity; while above iron the arsenates occur more frequently. These relations can not be meaningless, but what they mean is not yet clear.

Perhaps a part of the difficulty in tracing periodic relations in the comparative abundance of the elements arises from the fact that our field of view is limited to the earth and does not include the whole solar system. Indeed, several writers, reasoning on the broader basis of the nebular hypothesis and noting the low densities of the outer planets, have argued that the latter may contain the lighter elements mainly, while the heavier substances are concentrated at the original nucleus, the sun. Along this line, however, close reasoning is impossible, partly because evidence is lacking and partly because the conditions of temperature and pressure differ so widely between the sun and the other heavenly bodies. As thus attacked, the problem becomes one of enormous complexity, and even the solar spectrum gives us no conclusive evidence. That oxygen and silicon are not conspicuous in the sun's atmosphere we may admit, but that nonvolatile silica is absent from the solar body is by no means certain. We may assume that compounds can exist nowhere in the sun, but the assumption is unprovable. As to the composition of the outer planets we know practically nothing. How far they may differ from each other, from the earth, and from the sun is as yet a matter of pure conjecture.

If, despite Mendelejeff's recent demurrer, we assume that the elements have been evolved from one primordial form of matter, their relative abundance becomes suggestive. Starting from the original "protyle," as Crookes has called it, the process of evolution seems to have gone on slowly until oxygen was reached. Below oxygen we have the elements hydrogen, lithium, glucinum, boron, carbon, and nitrogen, between which no remarkably strong affinities occur. With the appearance of oxygen strong affinities come into play, the process of evolution exhibits its greatest energy, and the elements forming stable oxides are the most rapidly developed and in the largest amounts. On this supposition, vague as it is, the scarcity of the elements above iron becomes somewhat intelligible; but the theory does not account for everything and is to be regarded as merely tentative. It is legitimate only so long as its purely speculative character is kept clearly in view. If, however, the evolution of the elements is admitted, it is clear that the later stages of the process must have been seriously conditioned by the chemical affinities developed at first.

ON THE OCCURRENCE OF NITROGEN IN URANINITE AND ON THE COMPOSITION OF URANINITE IN GENERAL.[1]

BY W. F. HILLEBRAND.

GENERAL INTRODUCTORY REMARKS.

When the work which is described in the following pages was commenced in 1888 it was simply as an analysis of a fragment of a large crystal of uraninite from Glastonbury, Connecticut, without thought of further extension. Thoria had been found in it and quantitative analysis was made in order to learn if possible whether this belonged to the uraninite or was due to an accidental admixture of thorium silicate as found by Penfield[2] to be the case, at least in part, for the thoria in monazite from Portland, Connecticut, and Amelia County, Virginia. It was hereby established that the 10 per cent of thoriafound was a constituent of the uraninite, and the unexpected discovery was made that no formula in the slightest degree corresponding to that found by Comstock[3] for the Branchville, Connecticut, uraninite and by Blomstrand[4] for the Norwegian and Bohemian varieties could be assigned to this from Glastonbury. The hitherto unanalyzed uraninite formerly found at Black Hawk, Colorado, was then examined and was likewise not referable to the orthouranate formula of Blomstrand. No thoria was found in it, but instead about 7 per cent of zirconia. In both cases about 60 per cent of UO_2 had been found, whereas the highest percentage given by any other analyst was in the neighborhood of 54 per cent for the Branchville variety. My own experiments had shown such extraordinary variations in the percentages of UO_2 found by the ordinary method of decomposing with sulphuric acid in sealed tubes filled with carbonic acid and titrating with potassium permanganate that a reexamination of the Branchville mineral seemed desirable.

Profs. Brush and Dana, of New Haven, very kindly placed at my disposal the remainder of their material from that locality, it being the same lot from which Comstock had selected his sample for analysis. While different samples showed different amounts of UO_2, the results were from 10 to 18 per cent higher than Comstock's, and moreover, about 7 per cent of thoria was found which had been entirely overlooked

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[1] An abstract of this paper was published in the Am. Jour. Sci., 1890, vol. 40, p. 384.

[2] Am. Jour. Sci., [3], 1882, vol. 24. p. 250.

[3] Am. Jour. Sci. [3[, 1880, vol. 19, p. 220.

[4] Geol. För. Förh., 1884, vol. 7, p. 59; and Jour. prakt. Chem., 1884, vol. 29, p. 191.

by him. This latter, as in the Glastonbury mineral, was not referable to any thorium silicate, nor to a phosphate, but belonged to the uraninite. Comstock's formula, $3RO_2+2RO_3$, for the Branchville uraninite was of course hereby invalidated. Of North American occurrences of this mineral it only remained to examine that from North Carolina. From the Black Hills, Dakota, where it has been reported to occur, I have been unable to procure specimens, and the same can be said of the at that time unknown Llano County, Texas, locality, whence a closely allied mineral, nivenite, has recently been described by Hidden and Mackintosh.[1] Owing to its evident alteration it was not expected that light would be thrown on the question of original composition by an examination of the North Carolina material, but the presence or absence of thoria could be ascertained, as it was affirmatively by finding that and other earths.

In view of what had thus been learned regarding the uraninites of this country it seemed advisable to reexamine the European varieties. Specimens from Przibram, Joachimsthal, and Johanngeorgenstadt contained no rare earths whatever, but they were so contaminated with carbonates and sulphides and some combination of vanadium that it seemed for the present useless to attempt an estimation of UO_2 in them. Through Prof. F. W. Clarke, of the U. S. Geological Survey, there were obtained from Prof. A. E. Nordenskiöld specimens marked cleveite from four localities near Moss, Norway, and to Prof. W. C. Brögger are due my thanks for specimens of Blomstrand's original bröggerite, and of the supposed thorium-free uraninite analyzed by Lorenzen[2] and quoted by Blomstrand[3] as a striking proof of the correctness of his view that all varieties of uraninite may be referred to the orthouranate type. These six samples contained, without exception, thoria and other earths, in no case less than 8 per cent, and the four from Prof. Nordenskiöld, with one exception, proved not to be cleveite. Notwithstanding certain variations in composition they were evidently one and the same mineral, just as were those from Branchville and Glastonbury; and the Norwegian and Connecticut varieties, though differing greatly in their relative proportions of UO_2 and UO_3 and in their resistance to the solvent action of acids, were manifestly specifically identical.

These analyses had been practically completed and a portion of the results very briefly communicated to the public from time to time,[4] when in consequence of a certain observation and its results an entirely new direction was given to the work and its scope wonderfully broadened. This was the discovery of a hitherto unsuspected element in uraninite, existing in a form of combination not before observed in the mineral world. As already published[5] all tests unite in showing

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[1] Am. Jour. Sci., 1889, [3] vol. 38, p. 482.

[2] Geol. För. Förh.; vol. 6, p. 744.

[3] Journ. prakt. Chem., 1884, vol. 29, p. 223 ff.

[4] Am. Jour. Sci. 1888, [3], vol. 36, p. 295; Bull. U. S. Geol. Survey No. 60, 1887-1888, p. 131.

[5] Am. Jour. Sci., 1889 [3], vol. 38, p. 329, whereby a typographical error UO_2 is made to read NO_2.

that this element is nitrogen, which is given off in a gaseous form on heating the mineral with a non-oxidizing acid, or, as ascertained later, by fusing it with an alkaline carbonate.

It is very unfortunate that this discovery of an escape of gas when treated with an acid, or rather the recognition of its important bearing, for the observation was made at an early date, did not occur sooner; for then more satisfactory results could have been obtained with the in more than one respect most valuable material from Branchville, and nearly all the analyses would have been carried out with the most painstaking care, in order to secure the utmost possible accuracy in summation, the importance of which will appear in the sequel. Inasmuch as the analyses were made solely with a view to ascertain the percentages of rare earths and the relative proportions of UO_2 and UO_3, where a variation of half a per cent or even more from the true summation was of very little consequence, that extreme care in the preparation and use of reagents and in analytical manipulation which subsequently acquired knowledge showed to be so necessary was not exercised. Partly in consequence of this and partly because of the length of time required for these investigations caused by a want of abundant material, which necessitated oftentimes awaiting the result of one experiment or analysis before venturing upon another, it has been impossible to bring this investigation as far forward as was expected. So much time has elapsed since it was begun, and results of so much importance have been achieved, that it seems advisable to make them public now in detailed form, incomplete as they are in some respects and difficult of interpretation in certain directions.

Before proceeding to discuss the analyses themselves it is necessary to give in some detail the methods of analysis pursued, in order that the degree of credence to be accorded the results may be fairly weighed, and to present the evidence upon which the gas obtained from uraninite has been pronounced nitrogen.

PREPARATION OF SAMPLES FOR ANALYSIS.

As a prelude to the description of analytical processes employed, the manner of freeing the sample as far as possible from adhering gangue may be briefly described. The specimens consisted, except in the case of the amorphous Colorado, Bohemian, and Saxon varieties, of crystals and crystal fragments more or less coated and invaded by a feldspar or mica, or both, sometimes by columbite or a little quartz, and the surfaces opened up by fractures were often more or less coated with a reddish infiltration product which was little, if at all, soluble in the weak nitric acid employed for dissolving the uraninite on commencing an analysis. The sample was reduced to two or three grades of fineness by crushing and passing through several small sieves superposed one upon the other, care being taken to form as little fine dust as possible. When all had passed the coarsest sieve, the different fractions were washed by decantation to free from dust, and then carefully panned in watch-glasses of suitable sizes. By this means all the mica and the greater part of the other lighter impurities were removed and a very fair degree of purification was reached. The columbite, if present, remained mostly with the uraninite, but caused little subsequent trouble. When no more gangue could be panned out without too great loss of material, the different portions were united, the specific gravity of the combined sample dried at 100° C. was taken, and it was then finely ground. The fine dust formed in the preliminary crushing was not used, unless for qualitative work, being generally too much contaminated with gangue. The panned material was always examined under the lens when dry, and aside from an occasional adhering reddish fragment appeared clean and free from foreign bodies.

METHODS OF ANALYSIS.

Ordinarily not less than two grammes was taken for the main analysis. Solution was effected in the least possible quantity of weak nitric acid at the temperature of the water bath so as to dissolve as little of the gangue as possible. When disengagement of gas bubbles had entirely ceased the uraninite was decomposed. Any black powder then remaining was treated as gangue, being columbite. The gaseous products of decomposition of the nitric acid are but faintly reddish. After filtering, the insoluble matter was ignited and weighed. A necessary refinement in cases where the amount of gangue is appreciable is to weigh it at 100°C. and then to ascertain how much, if any, water it contains. The filtrate was evaporated to dryness in platinum to obtain soluble silica, which after weighing was tested as to purity by hydrofluoric and sulphuric acids. From the filtrate lead was thrown down by hydrogen sulphide and weighed eventually as sulphate. Iron and manganese were then removed as sulphides while the earths and uranium were held in solution by ammonium carbonate and ammonia. This was effected in a flask of not over 250cm^3 capacity, in which the precipitate was allowed to settle over night. A precaution to be observed is to add ammonia as well as ammonium carbonate, otherwise the earths thrown down with uranium on neutralization of the originally acid solution will be only partially redissolved. In order to ascertain this it is best to remove the hydrogen sulphide from the filtrate from lead sulphide before proceeding to the precipitation of iron. On adding ammonia and ammonium carbonate it can then be readily seen when the earths are dissolved, which is not at all easy if the hydrogen sulphide has not been first expelled. Calcium could rarely be found with the iron. The sulphide precipitate and the filter were roasted and weighed as a check, and then iron was separated from manganese if necessary, and the amount of the former determined as Fe_2O_3, which was generally checked by resolution, reduction by hydrogen, and titration by potassium permanganate.

If any doubt had existed as to the completeness of separation from the earths, the iron and manganese were a second time precipitated as sulphides in the presence of ammonia and ammonium carbonate.

The filtrate, or filtrates as the case might be, were gently heated till all ammonium carbonate was driven off, the precipitate was dissolved in nitric acid, and separation of earths and uranium from any traces of magnesia and alkalies present effected by freshly prepared ammonium sulphide, allowing to digest for an hour in a covered platinum dish on the water bath. As others have experienced, it was found that no separation from calcium can be effected by this method. While this element was always present in small quantity, it could very rarely be detected in the filtrate. Nevertheless the above method was preferred to that of Alibegoff[1], in which uranium is separated from alkaline earths, magnesium, and alkalies by mercuric oxide, because of the necessity of converting the nitrates into chlorides for the success of the latter operation, whereby an additional reagent is employed and the manipulations are increased, both of which it was desired to reduce to a minimum.

From the precipitate of earths and uranous oxide mixed with sulphur, the oxides were extracted by nitric acid, the solution was evaporated to dryness, water was added, and then when boiling, oxalic acid and two or three drops of ammonium oxalate. The precipitated oxalates were washed in due time with weak oxalic acid solution, ignited, and preserved in the crucible till later. The filtrate, which still always contains some rare earth metals and calcium, was evaporated to dryness, ignited to destroy oxalates, redissolved in nitric acid and evaporated with sulphuric acid in quantity slightly more than sufficient to convert into sulphates. After removal of all nitric acid the residue was dissolved in a little water and two and a half to three times the bulk of alcohol was added. In the course of twelve hours or more the precipitate, containing all the calcium not originally thrown down by oxalic acid besides some sulphates of the rare earths, was collected on a filter, washed with alcohol, dried, dissolved in weak nitric acid, and the rare earths were separated from calcium by ammonia and weighed with the main portion.

The alcoholic filtrate was evaporated to dryness, ignited, dissolved in nitric acid, and the precipitate produced by boiling with ammonia was ignited repeatedly in air and in hydrogen until a constant weight was reached by reduction. The UO_2 thus obtained was apparently never entirely free from rare earths, amounting usually to a quarter or a third of a per cent of the mineral. They were in two analyses recovered by treating the perfectly dried nitrates with ether, filtering, washing with ether, dissolving the insoluble nitrates of the earths and some uranium in water acidulated with a drop of nitric acid, and then adding oxalic acid to the hot aqueous solution after evaporating to dryness. The

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[1] Ann. d. Chem., 1886, vol. 233, p. 133.

earths were weighed with the already tared main portion, and a proper deduction was made from the uranium oxide. It is best always to make a second precipitation by ether to insure extracting the last traces of earths from the uranium.

The earths as weighed contain the balance of the calcium and a small quantity of uranium. Solution was effected by prolonged digestion with sulphuric acid somewhat diluted, repeated after filtration if necessary. Thorium, cerium, lanthanum, and didymium were then separated from the yttrium earths by potassium sulphate in as nearly neutral a solution as could be obtained. Thorium and cerium were separated from lanthanum and didymium by long passage of chlorine gas through a solution of sodium hydrate holding the gelatinous hydrates of the earths in suspension. Finally thorium was separated from cerium by boiling with sodium hyposulphite. Small quantities of what might be zirconia were now and then found, but its identity could not be proved.[1] The turmeric paper test for this element has never proved of any value in my hands where small amounts of it were present. The earths of the yttrium group and the uranium were precipitated from the potassium sulphate solution by ammonia, redissolved in nitric acid, the solution was evaporated to dryness, and the earths were precipitated from aqueous solution by oxalic acid and weighed, after which they were examined for calcium, as was also the filtrate from them containing the uranium and that containing the potassium sulphate, in both of which calcium might be found. The combined calcium oxide was deducted from the original weight of the earths and added to the lime earlier separated by alcohol. The small amount of uranium recovered—usually 4 to 7 milligrammes as UO_2—was likewise deducted from the earths and added to the main portion.

In the last analysis of Glastonbury uraninite, which was made especially with a view to great accuracy in summation, and in analysis XVIII, a modification was introduced at one point which is perhaps worthy of retention in future work. Instead of evaporating the filtrate from iron sulphide to complete removal of ammonium carbonate, the gradually forming precipitate of carbonates was removed by filtration at a point where the earth carbonates are almost entirely thrown out and the uranium is still in solution. A little practice enables one to recognize this point readily. When the filtrate is treated as already described in the first method oxalic acid will generally fail to show any earths present with the uranium, but the precipitation by alcohol, and later by ether, must not be neglected. The carbonates are now dissolved in nitric acid, the solution is evaporated to dryness and the rare earths are separated by oxalic acid in perfect purity, except perhaps for a little lime, from the small amount of uranium they contain. The resulting filtrate will always contain a little of the earths, for it has been my experience that the precipitation by oxalic acid is never abso-

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[1] Except in the Colorado uraninite, which contains practically no other earths than zirconia.

lute. It is best to unite it with the main portion of uranium and separate lime and some of the earths at the proper stage by alcohol, and from the weighed UO_2 the remainder of the earths by ether. So far as my limited experience with this modification goes it has proved satisfactory and decidedly preferable to the procedure first given, the chief point gained being that a purification of the earths from uranium is unnecessary and the trustworthiness of the weight found for the combined earths is heightened.

It may be said as regards the purity of the different earths or groups of earths after separation that, whereas the original ignited mixture was somewhat dark, without sharply characterizable color tint, the thoria was pure white and gave the theoretical molecular weight; the ceric oxide dissolved with a strong yellow color in concentrated sulphuric acid, which was bleached instantly by sulphurous acid, and with lead peroxide and nitric acid it gave likewise a deep yellow color; the lanthanum and didymium were cinnamon-brown in color, soluble in weak nitric acid, and the gelatinous precipitate by ammonia from acetic acid solution gave sometimes a blue color with powdered iodine, due to lanthanum; the yttrium earths were pale straw-colored and dissolved very readily in weak acids. Although only a single separation of the yttrium group by potassium sulphate was made, it was probably nearly perfect, for any remainder should have been obtained subsequently with the lanthanum and didymium, and the quantity of these was so small as to preclude much contamination by earths of the yttrium group.

Concerning the estimation of magnesia and alkalies and traces of phosphoric acid nothing need be said.

Water was estimated by heating the mineral in a current of air and collecting the water in a calcium-chloride tube. In only one case—the last Glastonbury analysis—was the mineral fused in a boat with sodium carbonate in order to retain the substance or substances which imparted to the water expelled by simple ignition an acid reaction. The weight of water found was hereby slightly reduced, and perhaps a similar result would have followed the taking of a like precaution in other cases. The acid property of the water was perhaps due to fluorine, since a trace was found in the Glastonbury mineral, but by no means enough to account for even the slight difference observed between the gains of the absorption tube by the two modes of ignition.

The correct estimation of UO_2 is of the utmost importance, and it was in consequence of remarkable variations in results first obtained that much material which would have been of inestimable value at a later period was used up in endeavors to secure concordance. An obvious source of error at first was the formation, in the sealed tubes in which decomposition of the mineral with rather strong sulphuric acid was effected, of bright green crystals of a thorium-uranous sulphate which were almost insoluble in water, and hence necessitated such a length of time for titration as to seriously discredit the results. Dilution of the acid proved a remedy for this difficulty, and perfectly satisfactory solution[1] was obtained with one volume of concentrated sulphuric acid to six volumes of water. This proportion was employed in all subsequent work by this method, and decomposition of the uraninite was generally complete by leaving the tubes in an air bath over night at a temperature of 150–175° C. The end reaction with potassium permanganate was then always sharp and satisfactory, but the results were still discordant. The cause was eventually found to be in the manner in which the tubes were filled with carbon dioxide. This was done by introducing either solid sodium carbonate or a solution of the same and sealing as quickly as possible. It is, however, almost impossible to prevent access of air, often in considerable amount, through the drawn-out neck of the tube before the seal can be made. The following figures are the results of titration on one sample of Glastonbury uraninite. They are tolerably concordant compared with other series and yet are undoubtedly one and all too low. UO_2 found 55·00, 54·12, 56·98, 55·93, 56·15, 55·61. Every now and then a result would fall so far below all others of a series as to be positively startling.

When, however, the tubes were filled with carbonic acid from an external generator through a fine glass tube drawn out of the same kind of glass as that of which the decomposing tube consisted, and the fine tube was sealed into the other while the gas continued to pass, all air except the trace in the carbonic acid itself was excluded, and after decomposition the titration results showed a concordance and accuracy that could not be surpassed, as shown by the following series made on carefully purified U_3O_8, using freshly boiled distilled water:

UO_2 found 32·11, 31·90, 32·15, 32·12, 32·06, 32·17, 32·28.

Theory requires 32·07.

That it is immaterial whether the water is free from oxygen or has stood for some days exposed to the air is shown by the following series in which water several days old was used:

UO_2 found 32·11, 31·85, 32·37, 32·36, 32·13.

An excess over theory is to be expected, for it is difficult to prepare U_3O_8 with the theoretical percentage of UO_2.

In order to test the probable error of previous titrations the following

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[1] Although the green crystals were no longer formed, there still appeared, as when stronger acid was used, a curious crystallization, taking the form of excessively fine needles woven into a felt-like mass which covered the surface of the liquid from end to end of the tube, and when put in motion by a movement of the solution resembled an undulating white rope. This was readily soluble in water and did not affect the titration at all, but it was observed on a few occasions, when the heating of the tubes was continued for several days, that it gradually disappeared and in its place an abundant crop of unusually large and clear green crystals was formed. Of the latter ·5209 gramme gave on analysis: UO_2 49·53, ThO_2 3·61, SO_3 32·32, H_2O 13·59; total, 99·05; whence is derived the molecular ratio $UO_2(ThO_2):SO_3:H_2O$ as 1:2·06:3.84, and the formula $(UTh)O_4(SO_2)_2, 4H_2O$. Being formed from a much more dilute acid they may possibly differ from the crystals deposited from strong acid in the number of molecules of water. It is intended to make a more thorough examination of this salt at some future time.

determinations were made in which the tube was filled as carefully as possible with carbonic acid by using a solution of sodium carbonate:

UO_2 found 31·06, 31·07, 29·72, 29.33, 29·89, 30·69.

Theory requires 32·07.

Two out of the three experiments by Zimmerman,[1] in which UO_2 in U_3O_8 was estimated by permanganate after solution by hydrochloric acid in sealed tubes, using manganese sulphate to counteract the effect of the acid, gave 31·39 UO_2 instead of 32·07.

Finally a set of tests was made on a specimen of North Carolina uraninite in order to ascertain the degree of concordance to be reached on the mineral.

UO_2 found 38·14, 38·12, 38·12, 38·04, 38·07, 37·97, 37·87. Solution in the last two cases had been effected at 100° C., and was, perhaps, not quite perfect.

It is thus apparent that with due regard to the exclusion of all air from the tube, the method leaves nothing to be desired as regards accuracy. The acid employed was specially distilled and gave with brucine and diphenylamine no indication of nitric acid, the test being made as prescribed by Wagner[2], and it was absolutely without decolorizing power on permanganate. When wanted, a portion was diluted with about twelve volumes of water and boiled down to half the bulk, when it was rapidly cooled. In the mean time the mineral, in quantity from 0.3 to 0.5 gramme, having been introduced into the tube, about 2 $cm.^3$ of distilled water was added and brought to boiling for a few moments in order to expel air from the powder. When somewhat cooled, from 15 to 30 $cm.^3$ of the dilute sulphuric acid, according to the amount of mineral and the size of the tube, was added, and then the carbonic acid, which had been allowed to generate and escape from the apparatus for some time, was introduced and the seal was made as above described. No breakage of a tube in the oven ever occurred as a consequence of fusing the one tube into the other. The titrations were made in about half a litre of water, to which sulphuric acid had been added, as rapidly as possible, using a dilute solution of potassium permanganate, giving about 0·00036 gramme oxygen to the cubic centimetre that had been standardized by iron wire of known contents in iron and checked by pure oxalic acid, and taking account of the expansion or contraction of the titer liquid if its temperature varied more than a few degrees from that possessed by it at the time of standardization.

Zimmerman[3] decomposed U_3O_8 for the purpose of estimating UO_2 by concentrated sulphuric acid in a current of carbonic acid, but this method is not very applicable to uraninite, owing chiefly to its greater insolubility, particularly when rich in UO_2. Whereas, according to Zimmerman, quantities of U_3O_8 up to 1.2 grammes are decomposed thus

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[1] Ann. d. Chem., 1886, vol. 232, p. 287, lines 5 and 6.

[2] Zeit. f. Anal. Chem., 1881, p. 329 ff.

[3] Ann. d. Chem., 1886, vol. 232, p. 285.

in an hour, uraninite may be only moderately attacked after many hours boiling. The whitish green insoluble salt which soon separates out undoubtedly exerts a retarding effect in protecting the rest of the uraninite powder from the action of the acid. A couple of tests were made by this method which accorded fairly well with the others, but owing to the great uncertainty of securing complete decomposition they were not multiplied.

In the early part of the present investigation, when want of concordance in the results of UO_2 titrations was the rule, decomposition by hydrofluoric acid was sometimes employed as a method leading to the estimation of UO_2 gravimetrically, and the results go to show that this may be developed into a method of considerable accuracy, useful at any rate as a check upon the volumetric determination.

All uraninites, without exception, are decomposed completely by hydrofluoric acid, even in the cold, if time enough is given, the uranous uranium being thrown down with the earth metals and lead as an insoluble fluoride. The refractory Glastonbury variety was thus decomposed in about ten days. In order to accelerate action, the acid and very fine powder were placed in a wide and perfectly flat platinum dish provided with a loose fitting cover, which was set in a dentist's vulcanizer containing a solution of sodium carbonate to absorb acid vapors. Dish and vulcanizer having been filled with carbonic acid gas, the lid was adjusted, and a lamp placed beneath, so that decomposition should take place under high temperature and pressure, and in absence of air. The main difficulty in the subsequent manipulation, and probably the only element involving possible serious error, is the difficulty of washing the precipitate on the filter, owing to its strong tendency to run through as soon as washing begins. Experience seemed to show that this is best obviated by using water containing ammonium chloride and hydrofluoric acid, but the experiments made were too few in number to show whether the method can be developed into an exact quantitative one. An attempt will perhaps be made to perfect it. The following are some of the results obtained:

A specimen of Glastonbury uraninite, giving on a basis of 57·43 per cent UO_2 by titration 26·48 per cent of UO_3, gave gravimetrically 26·89 and 28·58 per cent UO_3.

Another specimen from Glastonbury, giving by titration 59·31 per cent UO_2, gave gravimetrically 60·05 per cent.

Colorado uraninite, giving 58·51 UO_2 by titration, gave 58·24 per cent gravimetrically.

A few trials with U_3O_8 gave results in part less satisfactory, namely, 34·89, 31·26, and 28·47 per cent UO_2 instead of 32·07.

Assuming the practical insolubility of UF_4 in hydrofluoric acid, the method should give a tolerably exact separation of UO_2 from FeO and UO_3, and thus in connection with the oxygen used in titration indicate the state of oxidation of iron, as well as uranium, in substances containing both where one does not predominate so enormously over the other as in uraninite. Even from Fe_2O_3 the separation should be exact, unless in the moment of breaking up of the molecule the ferric iron should exert an oxidizing effect on the uranous uranium before the latter is withdrawn from its influence by combination with fluorine. Hydrogen sulphide being without reducing effect on UO_3, the presence of sulphides would be immaterial so far as the separation of UO_2 from UO_3 and the oxides of iron is concerned, but of course the correct estimation of total oxygen by titration would be impossible if iron were present in its peroxidized state, or if even in its absence the hydrogen sulphide formed could not be expelled before titration.

It may be worth while before leaving the subject of estimation of uranium to add that, in accordance with Zimmerman's observations, I have met with no evidence of the existence of an oxide U_2O_5 as a result of strong heating in air, and the oxide U_3O_8, as he has so conclusively shown, is also by my own experience only to be obtained with its theoretical percentage of oxygen by igniting and cooling in oxygen.

DETECTION AND EXAMINATION OF NITROGEN.

At an early stage in the work it was noticed in a few instances where the sealed tubes in which UO_2 was to be estimated were left in an upright position for a short time, that an extremely slow disengagement of gas took place, which was especially noticeable if the tubes were gently tapped on the table occasionally, whereby the bubbles enmeshed by the powder were set free and rose through the liquid in the tube. This was supposed to be due to the presence of traces of carbonates in the mineral, and no particular attention was paid to it, although it seemed strange that they should not be entirely decomposed in a very few moments after contact with the acid. Later, when making the first estimation of UO_2 in Glastonbury uraninite above mentioned with hydrofluoric acid, solution in this case being made in the cold and with free access of air, it was observed that this slow escape of gas was continuous throughout the whole ten days required for decomposing the mineral. This seemed to exclude the possibility of its being carbonic acid, and it was determined to collect and examine it if possible. This was done in a manner to be hereafter described.

It may be here mentioned that U_3O_8 and UO_2 prepared from the residues obtained during this work, when examined under conditions precisely similar to those obtaining with uraninite, failed to give off the least trace of gas.

The gas was colorless, odorless, a nonsupporter of combustion, unchanged by mixture with air, neutral to moistened litmus papers, not absorbed by caustic alkalies, and insoluble in water, at least its coefficient of absorption was so small as to be inappreciable without elaborate experimentation.

In a Bunsen's absorption tube, containing gas from the original bröggerite, a potash ball caused no diminution in volume, neither did potassium pyrogallate, thus showing the absence of carbonic acid and of oxygen. Transferred from the absorption tube to a eudiometer the gas was then subjected to the tests prescribed by Bunsen.[1]

	Units.
Reduced initial volume	14·01
After exploding with oxyhydrogen	13·21
After a second similar treatment	13·20
After addition of hydrogen (32·79)	45·99
After explosion with oxyhydrogen	45·93
After addition of air in excess	181·82
After exploding	132·81
Contraction	49·01

two-thirds of which, or 32·67, is almost exactly the volume of the hydrogen introduced. Were it not for the relatively large contraction after the first explosion, 0·80 units, representing 5·71 per cent of the initial volume, the above tests would indicate almost incontestably that the gas could be nothing but nitrogen. Considering the small volume operated upon, and the great disadvantages under which the eudiometric experiments were made, the above is not a surprising error, and since in other experiments it did not recur, I have no hesitation in regarding it as without significance.

Gas liberated from bröggerite by hydrochloric acid had, after treatment in the absorption tube, in the eudiometer—

	Units.
A reduced initial volume of	27·73
After addition of hydrogen (25·77)	53·50
After exploding with oxyhydrogen	53·17
After addition of air	178·08
After exploding	138·20
Contraction	39.88

two-thirds of which, or 26·58, is sufficiently close to the volume of hydrogen added to show the purity of the gas.

Gas evolved from Branchville uraninite by sulphuric acid gave in the eudiometer

	Units.
An initial volume of	17·98
After exploding with oxyhydrogen	18·11
After addition of hydrogen (20·37)	38·48
After exploding with oxyhydrogen	37·36
After addition of air	106·32
After exploding	77·74
Contraction	28·58

two-thirds of which, or 19·05, is nearly that of the hydrogen introduced. The admission of a trace of air into the eudiometer with the gas or later with the hydrogen would account for the slight contraction

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[1] Gasometrische Methoden, 2d ed., pp. 73, 74.

after the second explosion and for the deficiency in the observed over the calculated final contraction. But such an assumption is hardly necessary, for the final readings on the eudiometer tube were very uncertain.

The evidence as to the nature of the gas while fairly conclusive was thus far purely negative. Proof of a more positive character was needed, and this was sought in various ways.

Long continued passage of the electric spark between the platinum wires of the eudiometer, in which was a mixture of the gas with pure oxygen, produced a marked contraction, and a few drops of water purposely introduced above the mercury before turning on the current gave, when taken out and tested with diphenylamine, and brucine, intense blue and red colors, respectively. Blue litmus paper was turned red by it. When the terminals of a Ruhmkorff coil were connected with a simple modification of Siemens's induction tube, devised for the employment of small quantities of gas, containing a mixture of the gas with 3 volumes of electrolytic hydrogen, a slow but constant contraction resulted, provided that the product of combination as fast as formed could be removed by water or an acid. A strip of moistened red litmus paper suspended in the apparatus turned deep blue, and water used as an absorbent gave a strong alkaline reaction with litmus, besides affording with Nessler's reagent the characteristic ammonia reaction in a marked manner. With dilute hydrochloric acid as an absorbent there was obtained 0·0190 gramme of ammonium-platinic chloride, which when heated with sodium hydrate gave off a strong ammoniacal odor, and a strip of red litmus paper held above the mixture was instantly turned deep blue. The nitrogen calculated from the above weight of $(NH_4)_2PtCl_6$ is 0·00121 gramme, or nearly 1 cubic centimetre at 0°C. and 760 millimetres. The roughly measured contraction of the mixed hydrogen and nitrogen gases was in accordance with this determination. It should be hardly necessary to say that all these chemical tests were duplicated simultaneously in blank.

In a Geissler tube under a pressure of 10 millimetres and less the gas afforded the fluted spectrum of pure nitrogen as brilliantly and as completely as was done by a purchased nitrogen tube. In order that no possibility of error might exist, the tube was then reopened and repeatedly filled with hydrogen and evacuated until only the hydrogen lines were visible. When now filled with the gas and again evacuated the nitrogen spectrum appeared as brilliantly as before with the three bright hydrogen lines added.

The success of these electrical experiments with Geissler and Siemens tubes is very largely due to Dr. William Hallock of the physical laboratory of the Geological Survey, for whose ever ready assistance and ingenuity in meeting difficulties I can not too strongly express my appreciation.

ESTIMATION OF NITROGEN.

The original apparatus for collecting the gas is depicted in the accompanying figure.

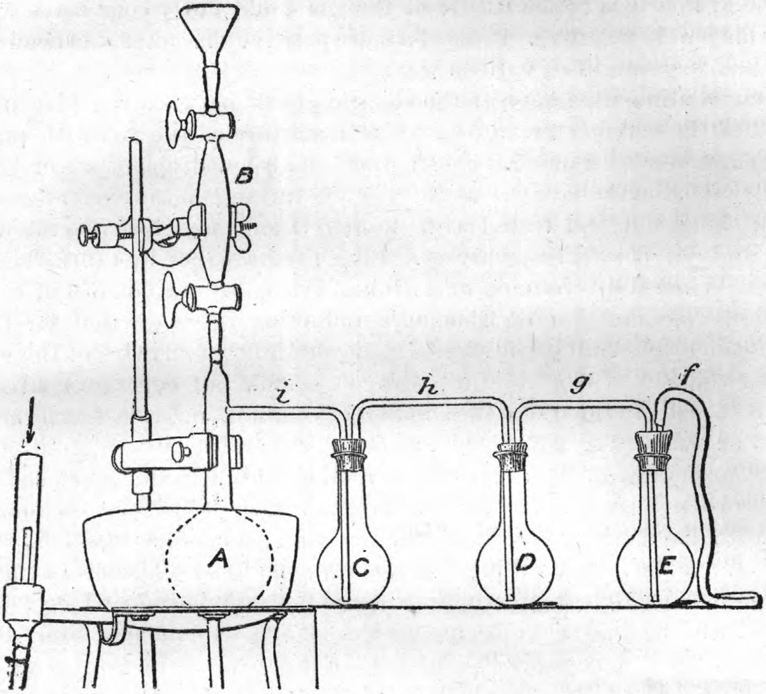

FIG. 1.—Apparatus for collecting nitrogen.

The decomposing vessel A is simply a fractional distillation flask of not more than 100 cm³ bulb capacity, drawn out at the top to allow of connection by means of rubber tubing with the receiver B, which should approach the cylindrical in form, be provided with two closely fitting, wide bore stopcocks, and have a capacity of 25 to 30 cm³. The very fine powder having been introduced into A and boiled with a few cubic centimetres of water to expel air, connection is made with B by tubing firmly wired, the receiver is suitably supported by a clamp so that A shall have the position given in the as yet empty water bath, and the flasks C, D, E are placed in position, fitted with corks and tubes as represented, but not yet closed by the corks. A rubber tube being now attached to B at the top, a thoroughly boiled sulphuric acid having the strength of that used for UO_2 estimations ($1H_2SO_4$: $6H_2O$ by volume) is poured into C, and continuously sucked into A and then into B until the latter is full above the upper stopcock, when this is instantly closed. C is then filled up with the same acid, and the water bath with water to relieve somewhat the strain on the rubber connection between A and B. E and D are now filled with freshly boiled distilled water, and the cork of E is pressed down. Then by blowing in at *f* the air in *g* is expelled and D can be corked without retaining the least bubble of air. By continuing the blowing *h* may be freed from air and C tightly corked. A may now be clamped in position for greater security, and a tin cover provided with a slit for the neck of A placed over the water bath. This is primarily to prevent the action of steam on the rubber connection between A and B, by which after several days it is softened and injured, and secondarily to economize heat. On top of B is attached a small short-stemmed funnel, which is kept filled with distilled water, in order to insure a water seal about the stopcock and certain exclusion of all air. Heat is now applied to the water bath, which is provided with a constant level arrangement and flow of water, so that it may be heated night and day without interruption. Soon an evolution of gas begins, the bubbles rise through A and the lower stopcock into B, and continue until the mineral is entirely decomposed. The fine powder which is carried up into B by the bubbles may be in great measure returned to A by tapping B, and if not, it is decomposed by the moderately warm acid in B, especially in case a readily soluble uraninite is being treated. The tube *i* should be very nearly horizontal, in order to prevent any of the powder reaching C as it falls from B. What little may collect along *i* itself will decompose in time and the gas from it reach B. The outlet tube of E not being closed, free movement and escape is afforded for water in E as acid in B is displaced by gas. C, D, and E likewise act as checks to the diffusion of air into B. One, or at most two, flasks would suffice where readily soluble uraninites are treated, and the duration of the experiment is at most twelve hours, but for refractory varieties a third is indispensable. The greatest difference exists between North American and Norwegian uraninites as to their solubility in sulphuric, hydrochloric, hydrofluoric, and even nitric, acids. Whereas the Colorado and both Connecticut uraninites are not entirely decomposed by nine days' continuous treatment at 100°C. with dilute sulphuric acid in the above-described apparatus, and even the much-altered North Carolina mineral requires five days for solution, all the Norwegian specimens examined are completely attacked in much less than twelve hours, and one (from Arendal) in three. Hydrochloric acid was used in one instance in place of sulphuric in the apparatus and with about the same effect.

When no gas is any longer given off the mineral is decomposed, as may be seen by removing the water from the bath and examining the residue in the bottom of the flask. It is either pure white sulphate of lead, or dark colored if columbite was mixed with the uraninite. Owing to the large volume of acid used there is no separation of insoluble uranium or thorium salts as in the UO_2 estimations.

When the operation is ended B is disconnected from A after closing the lower stopcock, and the gas can then be readily transferred to a graduated and rather narrow measuring tube, or it can be measured in the receiver itself, if this is graduated, by opening the lower stopcock under water and allowing the latter gradually to displace the acid in order that the vapor tension of pure water may prevail. All necessary thermometric and barometric readings having been made, the volume in cubic centimetres is reduced to 0°C. and 760 millimetres and multiplied by the weight of 1 cubic centimetre (·001256 gramme) of nitrogen, in order to obtain the weight whence the percentage is obtainable.

The error due to absorption of a portion of the gas by the acid liquid or by the water with which it is displaced in measuring is a vanishing quantity, because of the high temperature of the acid at the time of disconnecting and the low coefficient of absorption of both liquids for the gas. If transferred from the receiver to a measuring cylinder, the gas comes into contact with so much water that the element of absorption might have slight effect were time enough allowed; but the water levels within and without the measuring vessel having been brought into approximate accord, the temperature of the gas is reduced in a very few moments to that of the water by allowing a running stream of the latter to impinge on the top of the vessel and flow down on all sides, a thermometer being fastened thereto by a rubber band.

If necessary to use the solution for the titration of UO_2, disconnection of the apparatus and transfer of the gas can be so carried out that the result of titration is very nearly as exact as by the method already described.

The above described apparatus is well enough adapted for the estimation of nitrogen in readily decomposable uraninites, and admits of constant observation of its rate of evolution; but if the heating is continued beyond a few days, the glass of that portion of the decomposing flask under water becomes devitrified and more or less cracked. This does not necessarily prevent several days' further heating, but the danger of breakage is considerable. Moreover, but one experiment can be conducted at a time unless several sets of apparatus are available. Therefore recourse was had, in many cases, to decomposition in sealed tubes, exactly as described for UO_2 determinations, larger quantities up to 1 gramme of mineral being used, however, and the heating prolonged, if necessary, for two or three days to secure complete decomposition. After opening the tubes under water the gas was at once transferred by displacement of water to a test tube not too large to be closed by the thumb, a piece of potassium hydrate was rapidly inserted, the thumb placed over the mouth of the tube, and the latter agitated under water to dissolve the alkali and secure absorption of the carbonic acid. This was effected in a few moments, when pure water was allowed to displace the potash solution, and the gas was then transferred to the graduated tube and measured as before.

While the two methods of obtaining the nitrogen by decomposing with an acid gave pretty satisfactory results, it was desirable to estimate it by an entirely different process if possible. Fusion with alkaline hydrates produced no perceptible evolution of ammonia, and a quantitative combustion of bröggerite mixed with sugar by the soda-lime method and absorption of any ammonia by hydrochloric acid furnished an amount of $(NH_4)_2PtCl_6$ representing but 0·03 per cent. of nitrogen. Fusion with alkaline carbonates, however, liberated nitrogen gas and furnished a means of estimation that compared well with the acid method. The process was conducted as follows:

The substance mixed with sodium-potassium carbonate in a porcelain boat inclosed in a cylinder of platinum foil open at both ends was introduced into the rear end of a combustion tube already containing a considerable layer of copper oxide in the center, followed by eight inches of copper gauze plugs toward the front end. To the rear was attached a tube filled with manganese carbonate, and to the front a nitrometer containing potassium hydrate solution.

Repeated heating and cooling of the copper oxide and copper in a continuous current of carbonic acid having reduced the gas unabsorbable by the alkali solution to the smallest possible limit, heat was applied under the boat. The evolution of gas began long before incipient redness, and had to be soon checked by regulation of the temperature. Finally the heat was raised to fusion, and maintained there till the absorption of gas bubbles by the alkali was as complete as before beginning the experiment. The gas was then measured and reduced to 0°C. and 760 mm, with due regard to the vapor tension of the alkali solution, Kreussler's[1] table being used in this connection.

Of course the small quantity of nitrogen from which it is impossible to free the carbonic acid, even in a blank experiment, and which can not be allowed for with accuracy because it may vary slightly in each experiment, produced an uncertainty in the readings on the nitrometer, but one of very slight importance, since an admixture of even half a cubic centimetre of such nitrogen could affect the result by about 0·06 per cent. at the most when one gramme of mineral had been used. The platinum cylinder is a very necessary shield to prevent spattering of the contents of the boat onto the glass tube.

By this fusion in carbonic acid the lead contained in uraninite is apparently entirely reduced to the metallic state and collects in globules. This reduction is probably caused by the UO_2 of the mineral, notwithstanding the fact that litharge is not reduced when thoroughly mixed with U_3O_8 or UO_2 and fused with sodium-potassium carbonate under the conditions of the above experiment and for the same length of time. In the one case two molecules already existing must be torn asunder in order to admit of a rearrangement of their constituent atoms, while in the other these constituents are assumed to exist

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[1] Zeit. f. Anal. Chem., 1885, vol. 24, p. 445.

already united in a single molecule, and in the moment of its breaking up are most favorably situated for rearrangement.

Nitrogen obtained in this way from Glastonbury uraninite was submitted in the eudiometer to the same ordeal as that obtained by acid, with the following results:

	Units.
Reduced initial volume	84·69
After exploding with oxyhydrogen	84·95
After addition of hydrogen (29·02)	113·97
After addition of oxygen (25·12)	139·09
After exploding	94·40
Contraction	44·69

two-thirds of which, or 29·79, is nearly the volume of hydrogen added. The gas then is the same as that disengaged by acids.

ANALYSES OF URANINITE.

The analyses which follow were with two exceptions, V and XVIII, made before recognition of the nature or importance as regards quantity of the gas given off by acid, and as before said their object was chiefly to ascertain the relative percentages of UO_2, UO_3, and rare earths with a reasonable degree of accuracy.

The specific gravities of the Connecticut mineral were so much higher than any published that considerable care was exercised in their verification and in all subsequent determinations. The figures given represent the density of the mineral dried at 100° C., for the small amounts of hygroscopic moisture, varying as they did with different specimens, would exert a marked effect on the result if included.

A knowledge of the condition of the iron, which all analyses show accompanies uraninite in small quantity, is of prime importance for the correct volumetric estimation of UO_2. Comstock and Blomstrand have both assumed that it exists in the ferrous condition and from the oxygen transferred in titration have deducted a corresponding amount before calculating UO_2. While not in a position to deny the correctness of this assumption for a portion of the iron at least, I have, with one or two exceptions which will be noted in due order, preferred to consider all iron dissolved by dilute nitric acid as ferric oxide, and for the following reason: The matter insoluble in dilute nitric acid may consist of columbite, feldspar, quartz, mica, a very sparingly soluble phosphate, and the reddish infiltration matter filling the minute seams in the mineral, substances which it is practically impossible to remove entirely from any sample containing them. When the uraninite is dissolved this insoluble matter is decidedly red (unless columbite predominates largely) from ferric oxide, of which it is probable the infiltration matter is largely composed. In all such cases a large percentage of the insoluble matter is ferric oxide, and only in one case could any ferrous oxide be found in it aside from that belonging to columbite. It was further noticed that more iron was found in solution and correspondingly less in the insoluble when the heating had been prolonged beyond the usual time or when a stronger acid was employed. It seemed therefore certain that a portion of the iron in solution had been derived from ferric oxide of the gangue, and possibly all of it. It was impossible to tell how much, if any, might have existed in the ferrous condition, and therefore it seemed better to count the whole as ferric oxide. In any event the amount found is always so small as to affect the percentage of UO_2 but slightly, and never enough to cause trouble in comparing different analyses. That none of the iron belongs to uraninite itself appears from an experiment made upon Glastonbury material (No. V). When boiled for many hours with dilute hydrochloric acid till 25 per cent of the mineral had dissolved, not a trace of iron was left in the undissolved portion.

Proof is likewise lacking of the state of oxidation of cerium, but CeO_2 seems its more natural condition in the presence of other binoxides in overwhelming proportion. As with iron, however, its small amount renders this for purposes of calculation a matter of small importance.

It must be borne in mind that the combined earths are probably too low in all cases except Nos. V and XVIII, in which two precipitations of nitrates by ether were made to separate the last traces of earths from uranium. It is assumed that separation is then perfect, for by no known means could a further trace be extracted. That an appreciable amount of earths escaped separation in other analyses and went to increase the apparent percentage of UO_3 was at one time shown in working up some of the residues, amounting to ten or twelve grammes, for pure U_3O_8, when a considerable weight of earths was obtained, amounting to at least one-third of 1 per cent of the residues.

TABLE I.—*Uraninite from Glastonbury, Connecticut.*

	I.			II.	III.	IV.	V.		
	a.	*b.*	Mean.				*a.*	*b.*	Mean.
UO$_3$	....	....	22·08	23·35	22·22	‖26·48	23·13	22·94	23·03
UO$_2$	59·09	59·17	59·13	58·01	‡59·31	¶57·43	....	....	**59·93
ThO$_2$	9·09	9·50		9·78	10.31	9·79	10·01	11·13	
CeO$_2$						·25	·29		
ZrO$_2$?	......		9·57	......		......	·15		11·10
(LaDi)$_2$O$_3$	·55			·46		·13	·15		
(YEr)$_2$O$_3$						·20	·48		
PbO	3·14	....	3·14	3·24	3·07	3·26	3·08	3·08	3·08
CaO	·08	....	·08	....	undet.	·08	·17	·04	·11
MgO	....	....	....	....	undet.	....	....	....	....
Alk	....	....	....	....	undet.	trace	....	....	....
H$_2$O	·97	....	·97	undet.	undet.	·61	·43	·42	·43
N	undet.	undet.	undet.	undet.	undet.	undet.	....	....	††2·41
Fe$_2$O$_3$	*1·21	....	1·21	·33	§·67	·40	·28	·29	·29
MnO	....	....	....	....	....	trace	....	....	....
SiO$_2$	1·06	....	1·06	....	·25	·16	·15	·18	·16
P$_2$O$_5$	....	....	....	....	....	....	·02	....	·02
Fl	....	....	....	....	....	....	·04	....	·04
Insol	·85	....	·85	†1·74	·42	·70	·85	·92	·89
Cb$_2$O$_5$	·96	....	·96	....	....	....	....	....	....
Total	....	....	99·05	96·91	96 25	99 49	....	....	101·49
All U as UO$_2$	....	....	79·98	80·06	80·29	82·43	81·75	81·59	81·67
Sp. gr	....	....	9·139	9·051	....	9·587	....	....	9·622
Temp. °C	....	....	17½	21	....	21	....	....	19·4

* Estimated by weight; probably contaminated by earths or by alumina. Another fragment gave ·43 Fe$_2$O$_3$.

† Containing ·55 SiO$_2$, ·86 Fe$_2$O$_3$, ·33 Al$_2$O$_3$ etc.

‡ Mean of 59·07, 59·15, and 59·71. Separation by HFl gave 60·05.

§ Too high, since it was estimated by weight and found to contain some rare earths.

‖ Gravimetrically after separation by HFl there was found 28·58 and 26·89.

¶ Mean of 57·46 and 57·39. Probably too low, and UO$_3$ consequently too high, since they were among the earlier determinations made and no material was left for verification after the method was perfected.

** Mean of 59·88, 60·07, and 59·83.

†† Mean of 2·39 and 2·46 by decomposition with H$_2$SO$_4$ in sealed tubes, and 2·33 and 2·46 by fusion with NaKCO$_3$ in a current of CO$_2$. The first determinations were made in the apparatus depicted on page 56, and gave 2·14 and 2·21 per cent, but decomposition was incomplete and the percentage was calculated on the assumption that the undissolved residue had the same composition as the portion dissolved, a view hardly tenable in the light of subsequent experiments (p. 74). They are, therefore, not used in deriving the mean given in the analysis.

I. From a large crystal nearly an inch across which was collected by Prof. F. W. Clarke, the analysis of which led to all subsequent work. It was much contaminated with reddish feldspar, quartz, yellow muscovite, and, as examination of the insoluble showed, with columbite, besides a reddish infiltration product lining cracks and becoming apparent on broken surfaces. Most of these were removed, but enough remained to render the analysis in some respects unsatisfactory. The amount of soluble silica indicated thorite as a possible source of the thoria, which the other analyses show can not be the case. The presence of such an amount of columbic acid in a readily soluble form, for it was obtained by boiling the nitric acid solution of the mineral after filtration from the insoluble matter, points to some columbate other than columbite. Microscopical examination of a thin section of the crystal showed a few cracks filled with a reddish brown and yellow material, part of which was a readily decomposable silicate of some kind, as evidenced by the fuchsine test after treatment with hydrochloric acid and washing with water, but the total visible impurity was very little. A portion of the water undoubtedly belonged to the foreign matter.

II. Obtained from Prof. W. N. Rice, of Middletown, Connecticut.

III. Collected by myself as small crystals and fragments. Only a very small amount was available.

IV. Obtained from Mr. E. F. Sheldon, of Middletown, Connecticut.

V. From the same source as No. IV, but at a later date. A very large irregular crystal of this lot was crushed and purified as far as possible, and with this material a very careful analysis, duplicated in part, was made for the purpose of obtaining an accurate summation. This analysis post-dates all others published in this paper except No. XVIII. In addition several estimations of nitrogen were made by the different ways mentioned already, and numerous experiments which it was hoped might throw light upon the ultimate composition of the mineral.

All the above material came from Hales's quarry, in the town of Glastonbury, a few miles northeast of Middletown, Conn.

TABLE II.—*Uraninite from Branchville, Connecticut.*

	VI.	VII.	VIII.	Comstock's analysis.
UO_3	13·27	21·54	14·00	40·08
UO_2	72·25	*64·72	†70·99	54·51
ThO_2	7·20	6·93	6 52	....
ZrO_2?		·33		
PbO	4·35	4·34	4·35	4·27
MnO	·10	·07	?	....
CaO	·18	·22	·30	....
MgO	......	......	·15	....
Alk.				
H_2O	·68	·67	‡.68	·88
N	undet.	undet.	§2·63	....
Fe_2O_3	·11	·28	·27	FeO ·49
SiO_2	·03	·13	·20	....
Insol	·04	·14	‖1·40	....
Total	98·21	99·37	101·49	100·23
All U as UO_2	84·78	85·06	84·21	....
Sp. gr	9·733	9·560	9·348	....
Temp. °C	27·7	·30	15·7	....

* No material was left for a verification of this figure after perfection of the method of UO_2 estimation, but the low density compared with that of the others when corrected for insoluble matter of 2·7 sp. gr., and the fact that a UO_2 determination by Zimmerman's method (p. 51) in which, however, decomposition was not quite complete, gave 63·28 per cent, point to its correctness.

† Mean of 71.11 and 70.87.

‡ Assumed as in VI.

§ Only enough material for a single estimation was left, and being one of the earliest made it was carried out in the apparatus depicted on p. 56, wherein only 89·7 per cent of the powder had dissolved after about 210 hours, when the experiment was discontinued, because of danger of breakage to the flask. The figure here given is calculated on the basis of like composition for the dissolved and undissolved portions—an improbable assumption in the light of later experiments (p. 74)—and is probably too low.

‖ The gangue was mainly reddish feldspar, and contained ·31 (or 22 per cent) Fe_2O_3 besides, but only an indeterminable trace of FeO as ascertained on a separate portion. The increase in the percentages of CaO, alkalies, and SiO_2, with progressive increase of insoluble matter, indicates clearly a partial solution of the feldspar.

VI, VII, VIII. This material was all received from Profs. Brush and Dana, of New Haven, and was the residue of the material from which Comstock had taken his for analysis. No. VI was by far the purest of any material obtained from any locality, the crystals and fragments being brilliant and well defined and almost absolutely free from impurity. It is earnestly to be hoped that more of this excellent material may be found at Branchville for closer investigation, since it represents the extreme of perfection as regards crystallization and freedom from attached and infiltrated foreign matter, besides possessing the greatest density and the highest percentage in UO_2 and nitrogen of any known variety.

TABLE III.—*Uraninite from Colorado and North Carolina.*

	IX. Colorado.			X. North Carolina.	XI. North Carolina.
	a.	b.	Mean.		
UO_3	25·26	....	25·26	50·83	44·11
UO_2	58·47	58·56	58·51	39·31	46·56
TiO_2	trace.	trace.	trace.	....	....
ZrO_2	7·32	7·85	7·59	....	....
ThO_2	....	....	....	2·78	3·04
CeO_2	·22	·22	*·22	·26	
$(LaDi)_2O_3$	....	....	....	·50	
$(YEr)_2O_3$	....	....	....	·20	
PbO	·69	·71	·70	4·20	4·53
ZnO	·43	·44	·44	....	....
FeO	·32	....	†·32	trace.	....
MnO	·16	....	·16	....	....
CaO	·84	·85	·84	·85	·23
MgO	trace?	....	trace?	·30	·25
Alk	trace?	....	trace?		
H_2O	1·96	....	1·96	1·21	undet.
N	·15	....	‡·15	§·37	undet.
SiO_2	2·76	2·82	2·79	·08	·13
P_2O_5	·22	....	·22	?	....
As_2O_5	·43	....	·43	....	....
$CuFeS_2$	·12	....	·12	....	....
FeS_2	·24	....	·24	....	....
Insol.	....	....	....	·10	·06
Total	....	....	99·95	100·99	98·91
All U as UO_2	....	....	82·36	87·31	88·21
Sp. gr.	....	....	8·068	8·086	9·492
Temp., °C	....	....	20	15·8	20

*Lanthanum not tested for.

†Calculated from total iron after deducting that required by pyrite and chalcopyrite.

‡By fusion with $NaKCO_3$. H_2SO_4 failed to decompose entirely in nine days at 100°C.

§ Mean of ·38 by fusion with $NaKCO_3$ and ·35 by H_2SO_4.

IX. From a specimen in the National Museum from near Black Hawk, Colorado, where the mineral was originally identified by Mr. Richard Pearce about 1872. A very few tons represented the total product of the mine in uraninite, which was shipped to Great Britain for treatment.

This variety, differing in some respects so markedly in composition from all other known uraninites, is also distinguished from the other North American occurrences by its utter want of crystalline form. The specimen examined was largely contaminated with pyrite and chalcopyrite; in places it consisted of these alone, in others of pretty pure uraninite. But the purest of the latter was seamed with minute cracks filled with sulphides. A section as thin as possible showed under the microscope absolutely no other impurity. The material used for analysis was obtained after sifting to grades of fineness by first panning and then exposing the partly cleaned grains in a specially devised apparatus to an upward current of water, through which the heavy uraninite fell while the sulphides were held up. It was then further purified by most laborious hand picking under the lens. Even so it was impossible to free it altogether from sulphides, as the analysis shows, and this is especially unfortunate because of the uncertainty which is thereby thrown upon the UO_2 estimations. These, as above given, *include* the effect of any hydrogen sulphide and ferrous iron formed by the solvent action of sulphuric acid and of ferrous oxide possibly already existing. That they are not far from correct, however, is evidenced by a gravimetric estimation of UO_2 after separation by hydrofluoric acid, where sulphides and ferrous iron would be without effect, which gave 58·24 per cent UO_2. Another element of uncertainty in the volumetric determination is caused by want of knowledge of the condition in which arsenic is present. It has been assumed as As_2O_5, mainly for the reason that when even dilute nitric acid was used for dissolving, hydrogen sulphide precipitated the arsenic only after a considerable time. The condition of the zinc is likewise unknown. Its most natural form would be as sulphide, but as the sulphur was insufficient for the zinc alone, the negative element has all been credited to pyrite and chalcopyrite.

The analysis presented considerable difficulty. It was found that on solution in nitric acid a dirty white residue was left which contained silica, zirconia, and phosphoric acid, and that on boiling a further precipitate of zirconia containing phosphoric acid came out. None of the silica was present as quartz, for the residue in nitric acid was entirely free from grit; nor can it have been combined with zirconia as zircon for the same reason and because the latter is insoluble. But for the phosphoric acid it is probable that the residue would have held no zirconia, since a very little of the former seems able to carry down much of the latter, even in a very acid solution. The silica given in the analysis represents both that in the residue and that subsequently obtained by evaporation after boiling and filtering. The rest of the zirconia and the other earths were separated from uranium by potassium sulphate.

X, XI. From the Flat Rock mine, Mitchell County, North Carolina, through Mr. W. E. Hidden. Entirely unaltered uraninite seems never to have been found in North Carolina, and no analysis of it appears to have been made, though its alteration products have received attention. The crystal form of the original mineral is often preserved in the pseudomorphs, and it is decidedly more cubical than that of the Connecticut crystals, which are usually octahedral in habit. Even the least-altered material, though it may present a perfectly fresh aspect, is seamed in all directions by microscopic cracks filled with yellow alteration products. Such was the character of the piece used for analysis X, which was undertaken for the purpose of ascertaining whether or not the North Carolina mineral contained rare earths. In order to observe the effect of a weak solvent another lump was immersed for several days in very dilute cold hydrochloric acid, whereby it gradually fell into a fine powder, which was washed, dried, and analyzed with the results given under XI.

TABLE IV*a*.—*Uraninite from Norway.*

	XII.		XIII.		XIV.		XV.		XVI.		XVII.	XVIII.
	Anneröd.		Elvestad.		Elvestad.		Skraatorp.		Huggenäskilen.		Arendal.††	Arendal.
	a.	*b.*	*a.*	*b.*	*a.*	*b.*	*a.*	*b.*	*a.*	*b.*		
UO_3	30·56	30·70	25·34	25·49 25·26	22·02	22·06	31·93	32·08	35·52	35·57	41·71	26·80
UO_2	46·20	46·07	50·76	50·62 50·84	43·05	43·01	43·95	43·81	43·36	43·39	24·18	44·18
ZrO_2	·06	......	·08	......	8·43	......	......	......	......	......	......	....
ThO_2	6·00	......	8·48	......		......	8·98	......	6·59	8·13	3·66	4·15
CeO_2	·18	......	·21	......		......	·17	......	·20			none.
$(DiLa)_2O_3$	·27	......	·26	......		......	¶·36	......	·23			‡‡·67
$(YEr)_2O_3$	1·11	......	‡1·10	......		......	·97	......	1·03		9·76	9·05
PbO	9·04	......	10·06	......	8·58	8·58	9·50	9·42	9·46	9·45 9.41	10·54	10·95
CaO	·37	......	·77	......	·37	......	·36	......	·41	·41	1·06	·61
MgO	tr.	......	tr.	......	·13	......	tr.	......	·13	......	·10	·04
Alk											·23	·15
H_2O	·74	......	·73	......	·74	......	·77	......	·79	......	1·23	undet.
N	1·18	†1·15	1·28	§1·29	1·08	......	1·03	......	1·08	......	undet.	1·24
Fe_2O_3	.25	......	·21	......	·30	·31	·09	......	·32	·31	·03	·24
MnO	......	......	·06	......	......	......	......	......	......	......	......	......
SiO_2	·22	......	·38	·39	·28	·30	·53	......	·45	·51 ·50	·90	·50
P_2O_5	·02	......	·04	......	tr.	......	(?)	......	tr.	......	......	tr.
Insol	*4·42	......	·44	·46	‖15·50	15·41	**1·54	......	·41	·43	1·10	1·19
All U as UO_2	75·06	......	74·69	......	63·84	......	74·10	......	76·90	76·98	63·57	69·49

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*The gangue was mainly columbite and contained a total of ·61 FeO by trial on a separate portion. The columbite could be pretty well separated from the other and lighter gangue matter after solution of the uraninite in nitric acid, and it was found that of the total FeO ·30 belonged to the columbite and ·31 to the other gangue constituent. This latter was dissolved by the acid in UO_2 determinations, while the columbite was not; hence a correction has been made for ·31 FeO representing ·58 UO_2.

† The first result by fusion with $NaKCO_3$, the second by solution in HCl. Another result of 1·28 by H_2SO_4 was the first quantitative determination of nitrogen made and was probably too high through leakage of air into the receiver.

‡ Molecular weight, 277.

§ By fusion with $NaKCO_3$. The first result was obtained by H_2SO_4.

‖ Almost entirely columbite.

¶ Perhaps not fully freed from ThO_2.

** Mainly a phosphate.

†† A brief but brisk effervescence was produced by acids. The deficiency in the analysis, 5·50 per cent., was supposed to be satisfactorily accounted for as CO_2; a portion of it, however, is probably to be credited to nitrogen.

‡‡ The ignited oxides differed in appearance from the mixtures of La_2O_3 and Di_2O_3 obtained in all other analyses, being nearly colorless.

TABLE IV*b*.—*Means of analyses in Table IVa.*

	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.
	Anneröd.	Elvestad.	Elvestad.	Skraatorp.	Huggenäskilen.	Arendal.	Arendal.
UO_3	30·63	25·36	22·04	32·00	35·54	41·71	26·80
UO_2	46·13	50·74	43·03	43·88	43·38	24·18	44·18
ZrO_2?	·06	·08	8·43	....	....		....
ThO_2	6·00	8·48		8·98	6·63	3·66	4·15
CeO_2	·18	·21		·17	·20		none.
$(DiLa)_2O_3$	·27	·26		·36	·23		.67
$(YEr)_2O_3$	1·11	1·10		·97	1·03	9·76	9·05
PbO	9·04	10·06	8·58	9·46	9·44	10·54	10·95
CaO	·37	·77	·37	·36	·41	1·06	·61
MgO	tr.	tr.	·13	tr	·13	·10	·04
Alk						·23	·15
H_2O	·74	·73	·74	·77	·79	1·23	undet.
N	1·17	1·28	1·08	1·03	1·08	undet.	1·24
Fe_2O_3	·25	·21	·30	·09	·32	·03	·24
MnO	....	·06	....	....	....	....	....
SiO_2	·22	·38	·29	·53	·49	·90	·50
P_2O_5	·02	·04	tr.	(?)	tr.	....	tr.
Insol	4·42	·45	15·45	1·54	·42	1·10	1·19
Total	100·61	100·21	100·44	100·14	100·09	94·50	99·77
Sp. gr.	8·893	9·145	8·320	8·966	8·930	7·500	....
Temp., °C.	21·6	17	29·7	20	28·2	26·8	....

XII. The original bröggerite, from Gustavsgruben, Anneröd, near Moss, received from Prof. W. C. Brögger, who writes "es ist das originale Vorkommen des Bröggerit Blomstrands."

XIII. Likewise from Prof. Brögger, labeled Uraninit, Elvestad b. Moss. In addition Prof. Brögger writes, "so viel ich weiss, von derselben Stelle wie das Originalmaterial Lorenzens."

XIV–XVIII. From Prof. A. E. Nordenskiöld, through Prof. F. W. Clarke, of the U. S. Geological Survey. These specimens all bore, with one exception erroneously as the analyses show, the name cleveite, on labels of the Royal Museum of Stockholm; XIV was from Elvestad, XV from Skraatorp, XVI from Huggenäskilen, all being localities near Moss, and XVII and XVIII were from Arendal. The Arendal material was not in separate crystals and fragments like the others, but was inclosed in the original matrix of feldspathic rock. Of this there were three or four small pieces, from one of which some very inferior-looking material was extracted. It had every appearance of being much altered, which the evolution of carbonic acid by acids and the abnormally low percentage of UO_2 seemed so fully to demonstrate that no particular pains were taken beyond separating the earths from uranium and dividing them roughly into two groups. The material was in any case insufficient for a carbonic acid estimation. Later it became of interest to learn if this apparently greatly altered material contained nitrogen, and to this end further material was extracted from another of the pieces of rock. Its analysis unexpectedly gave the results under XVIII, the water alone being undetermined for want of material.

In the following table all the foregoing analyses of Norwegian material have been recalculated to the percentages found, excluding the insoluble matter, in order that their true relations may appear at a glance, whereby the sum of the rare earths combined is given instead of each earth or group of earths by itself. Only those constituents are tabulated which may be considered unquestionably in whole or in part as belonging to the uranium mineral. Silica, ferric or ferrous oxide as it may be, the small amounts of magnesia, alkalies, etc., may be thrown out as derived from admixed impurities. Lime from its close relationship to the other earths has been retained, though it is undoubtedly, in part at least, derived from foreign silicates.

TABLE V.—*Analyses of Norwegian uraninite recalculated.*

	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.
UO_3	32·04	25·48	26·04	32·50	35·69	42·11	27·12
UO_2	48·25	50·97	50·83	44·57	43·56	24·51	44·71
Earths	7·97	10·18	9·96	10·64	8·12	13·57	14·03
PbO	9·45	10·11	10·14	9·61	9·48	10·66	11·08
CaO	·39	·77	·45	·36	·41	1·07	·62
H_2O	·77	·73	* ·87	·78	·79	1·23	?
N	1·23	1·28	1·28	1·05	1·08	?	1·26

* A portion of this water was perhaps derived from the large amount of foreign matter contaminating the uraninite.

An examination of analyses XII to XVI as recalculated above hardly allows of any other conclusion than that the specimens from the above four different quarries about Moss belong to one and the same mineral species. While analysis XII differs in some respects from Blomstrand's analysis of bröggerite, which is here reproduced in its original form and as modified by substitution of Fe_2O_3 for FeO, it simply serves to show, assuming correct analyses, that the mineral may vary in composition in the same quarry, for as before mentioned this is the original material from which Blomstrand made the species.

Blomstrand's bröggerite.

UO_3	38·82	36·31
UO_2	41·25	43·62
ThO_2	5·64	5·64
Y_2O_3	2·42	2·42
Ce_2O_3	·38	·38
CaO	·30	·30
PbO	8·41	8·41
FeO	1·26	Fe_2O_3 1·40
H_2O	·83	·83
SiO_2	·81	·81
	100·12	100·12

The estimation of UO_2, in the analyses of table IV, is thoroughly to be depended on, aside from the slight deduction to be made for possible ferrous oxide, while in view of the want of evidence as to the manner of filling his tubes with carbonic acid there is no guarantee that Blomstrand's figure may not be too low. Leaving out of consideration for the moment the nitrogen, it is clear in any case that the formula evolved by him from his analysis can not be derived from No. XII.

In regard to analyses XIII and XIV, there can exist no doubt whatever as to the identity of the material derived from Profs. Brögger and Nordenskiöld independently. A comparison of them with Lorenzen's analysis, coupled with the fact that not one of the specimens from the neighborhood of Moss above analyzed contains less than 8 per cent. of earths, gives rise to the strongest possible suspicion that that analyst has overlooked thoria altogether, notwithstanding the fact that the present material is from Elvestad and Lorenzen's[1] was from Huggenäskilen.

Lorenzen's uraninite.

UO_3	38·23	37·73
UO_2	50·42	50·89
PbO	9·72	9·72
FeO	·25	Fe_2O_3 ·28
CaO	·21	·21
H_2O	·70	·70
SiO_2	·31	·31
	99·84	99·84

Prof. Brögger, as above quoted (p. 68), says, however, that the material sent by him is to the best of his knowledge from the same place as that analyzed by Lorenzen, and this appears probable from the fact that the specimens from Huggenäskilen sent by Prof. Nordenskiöld show a totally different ratio between UO_2 and UO_3 (anal. XVI). If it should prove that Lorenzen erred in overlooking thoria, another of Blomstrand's supports in favor of the orthouranate formula for all uraninites, including bröggerite and cleveite, is knocked away, the first being the earlier and, as shown, incorrect analysis of Branchville uraninite.

The oxygen ratios calculated for analyses XII to XVI, counting all earths as thoria, whereby the comparison is very little affected since the percentages of the other earths are almost alike in all analyses, are as given below, as also the ratios for Blomstrand's bröggerite calculated from the second column on page 69 instead of the first in order to compare properly with the others.

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[1] Nyt Mag. f. Naturv., vol. 28, p. 249.

	Mol. wt.	XII.		XIII and XIV.		XV.		XVI.		Blomstrand's bröggerite.	
UO_3	287	5·36	1	4·31	1	5·44	1	5·97	1	6·07	1
UO_2	271	5·70		6·01		5·26		5·14		5·15	
Earths	266	·96	1·37	1·21	1·85	1·28	1·33	·98	1·14	1·02	1·11
PbO	223	·68		·73		·69		·68		·60	

It is seen that none of the analyses conform even approximately to the ratio for Blomstrand's, except that of the mineral from Huggenäskilen. A recalculation of all on the basis of FeO for Fe_2O_3 and consequent changes in UO_2 and UO_3, and separation of the earths, would give the normal ratio 1:1 for Blomstrand's analysis, but the others would differ from it more widely than in the above exhibit.

The correctness of the orthouranate formula for bröggerite itself having been invalidated by the difference between his own analysis and anal. XII above, it is hardly worth while to discuss its applicability to the Bohemian and Saxon uraninites, of which no complete and reliable analyses seem to have been made, except perhaps the single one by Ebelmen in 1843 on Joachimsthal material, which on recalculation by Blomstrand was found to conform to his view. No more singular example can be furnished of incorrect conclusions founded on seemingly the best of evidence. No blame can attach to Blomstrand, but it can hardly be doubted that had he been able to analyze material from more than one quarry about Moss he would have seen the impossibility of reconciling the discrepancies in composition so as to admit of the application of one general formula.

It is apparent, notwithstanding the deficiency of earths and one or two other discrepancies, that analysis XVII was really made upon cleveite, as the label indicated. The density, too, corresponds almost exactly with that found by Nordenskiöld[1] and Lindström. In the latter's analysis, which is quoted below "water and a trace of CO_2" are given as loss on ignition, a result which under the circumstances must be considered unreliable.

The same objection applies to Hidden and Mackintosh's analysis of nivenite,[2] where it is stated plainly that the water represents loss on ignition. The analyses of cleveite and nivenite are here given together with XVII from table IV for convenient comparison. It may be mentioned that the 23·07 per cent of UO_2 in cleveite is the mean of two results differing by nearly 1½ per cent. Taking the higher as more nearly correct than the mean, almost exact agreement with the figures of analysis XVII for UO_2 and UO_3 is obtained.

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[1] Geol. För. Förh., 1878, vol. 4, p. 28; Zeit. f. Kryst. vol. 3, p. 201.

[2] Am. Jour. Sci., [3] 1889, vol. 38, p. 481.

	Nivenite.	Cleveite.	XVII.
UO_3	46·75	40·60	41·71
UO_2	19·89	23·07	24·18
ThO_2	7·57	4·60	3·66
Ce_2O_3 etc	....	2.25	
Y_2O_3 etc.	11·22	9 99	9·76
PbO	10·16	10·92	10·54
Fe_2O_3	·58	1·02	·03
CaO	....	·86	1·06
MgO	....	·14	*·33
SiO_2	....	....	·90
Ign	2·54	4·96	H_2O 1·23
Insol	1·22	2·34	1·10
CO_2 and N?	....	....	5·50
	99.93	100·75	100·00

* And alk.

The appearance of cleveite is at once suggestive of alteration, and, in view of the uncertainty attaching to the water determinations for both nivenite and cleveite, it is probable that they represent nearly the same stage of alteration of the same species. What this species is is pretty clearly indicated by analysis XVIII of table IV, where the earths are in about the same proportions and total amounts as in XVII, but the UO_3 and UO_2 stand in a very different ratio. The material for this, as before said, came from Arendal, and presumably from the precise locality of the cleveite of analysis XVII, since the pieces of feldspathic rock containing them were in one package without distinguishing labels, but it was unquestionably fresher. The extreme solubility of this material compared with the other Norwegian uraninites is shared by that of analysis XVII, by cleveite, and by nivenite, and is to be explained probably not so much by advanced decomposition as by the preponderance here of a more soluble yttrium-uranium compound. Whether or not this last Arendal material is the source whence cleveite and its American representative have been derived by alteration, as seems most probable, it is in any event a true uraninite of more basic character than any of the Norwegian thorium-uraninites, and consequently conforms still less than those to the orthouranate formula.

BOHEMIAN AND SAXON URANINITE.

Nitrogen was carefully sought for in uraninite from Przibram, Joachimsthal, and Johanngeorgenstadt, using the apparatus figured on page 56. The extremely small bulk of gas finally obtained from all of them, after cleansing with potassium hydrate, measured about .2cm^3 for Przibram and Joachimsthal, and much less for Johanngeorgenstadt, one gramme of mineral having been used. The above volume represents about ·02 per cent in weight of what can hardly be anything else than nitrogen.

None of the specimens contained zirconia, thoria, or other rare earths. Owing to the uncertainty of being able to determine with any close approach to truth the proportions of UO_2 and UO_3 in the presence of sulphides, and compounds of arsenic and vanadium of unknown degree of oxidation, no quantitative analyses have been carried out, but the attempt will yet be made to solve their composition.

DISCUSSION OF ANALYSES.

Hitherto the analyses have been considered in groups and without special reference to the nitrogen. It has been sought to show on grounds which would be valid even without its presence that the orthouranate formula is capable of no general application to uraninite, and that in the one or two cases where it does seem to apply this agreement is probably accidental. Taking into consideration the low atomic weight of nitrogen as compared with uranium, thorium, and lead, it is plain that it must play an important part in the constitution of the molecule, and that therefore its discovery alone, without other evidence furnished by the analyses, is sufficient to invalidate entirely the practically identical formulæ of Comstock and Blomstrand.

Throughout the whole list of analyses in which nitrogen has been estimated, the most striking feature is the apparent relation between the UO_2 and the nitrogen. This is especially marked in the second table of Norwegian uraninites (Table V), from which the rule might almost be formulated that, given either nitrogen or UO_2, the other can be found by simple calculation. The same ratio is not found in the Connecticut varieties, but if the imperfect determination of nitrogen in the Branchville mineral is to be depended on the rule still holds that the higher the UO_2 the higher likewise is the nitrogen. The Colorado and North Carolina minerals are exceptions, but it should be remembered that the former is amorphous, like the Bohemian, and possesses the further similarity of containing no thoria, though zirconia may take its place, and the North Carolina material is so much altered that its original condition is quite unknown.

In the absence of all positive knowledge whatever as to the rôle which nitrogen plays in the mineral, it would be idle to speculate at present upon the proper position of the latter in mineral classification. Much remains to be done before this question can be elucidated, but the general direction which the work must take can be fairly indicated.

But two explanations seem possible to account for the wide differences in the oxygen ratios for UO_3 and total bases, varying as they do from 1 : 4·37 for the Branchville material of analysis VI to 1 : 1 for Blomstrand's bröggerite, and even to a ratio indicating acidity for nivenite. Either all the others are alteration products of a mineral having the composition of the Branchville occurrence, or even of some unknown body entirely free from UO_3; or they are mixtures of two or more substances which need not necessarily be isomorphous, for Baumhauer's investigations have shown that even well developed crystals of smaltite and chloanthite are often mechanical mixtures. Fractional solution might throw light on this point, and the following are the results of experimentation:

I. In one of the nitrogen estimations in Glastonbury uraninite by the original method the operation had to be discontinued before solution was complete. The undissolved residue, amounting after extraction of lead sulphate to 0·1234 gramme, was found to contain 71·94 per cent UO_2, the original percentage having been 59·93.

II. 1 095 grammes were boiled for 12 hours with dilute hydrochloric acid in a flask connected with a reversed condenser. The residue was 0·9193 gramme, showing that but 16 per cent had been dissolved, and it contained 64·66 per cent UO_2. The nitrogen was lost.

III. 2·012 grammes when boiled with the same hydrochloric acid for 42 hours afforded a residue of 1·4975, showing solution of 25·5 per cent. Its composition was—

UO_3	16·63	All U as UO_2 82·52.
UO_2	66·82	
Earths	10·81	
PbO	3·02	
N	2·67	
H_2O	(?)	
Insol	·37	
	100·32	

Here it is seen that the UO_2 has increased, and likewise the nitrogen, both in about the same proportion, but it is not clear why the earths and lead oxide should not show a greater change.

These experiments require repetition and extension to other than the Glastonbury mineral, but so far as they go they indicate that uraninite as we know it is not a single chemical substance, and that, as was to be expected in such case, the portion containing most UO_2 is the least soluble. They are not decisive as between the hypothesis of original mixture and that of mixtures resulting from alteration. In this respect the following observations are of interest. In dilute hydrochloric acid a large piece of North Carolina uraninite falls wholly to finest powder in course of time, which would hardly happen were it one original substance in process of alteration, unless the change affected every smallest particle of the mineral simultaneously and to the same extent. Hydrofluoric acid speedily covers the faces of a bright crystal of Branchville uraninite with a network of fine cracks visible only under the glass, and soon powder can be rubbed off with the fingers.

Whatever may be the eventual conclusion, it will be found that the small amount of water afforded by all analyses must be carefully considered. Small as this amount is, in consequence of its low molecular weight as opposed to uranium, thorium, and lead, it must play an important part in the mineral as a homogeneous whole or in one of its parts if a mixture. In the latter case it will unquestionably be found to belong to the more soluble component.

It is significant that the two uraninites highest in UO_2 give the lowest water, and while it is true that the Branchville mineral appears to contain more than that from Glastonbury, this may be only apparent, for the former was simply ignited in a current of air, while the latter was fused with sodium carbonate, and it is known that the vapors from both possess an acid reaction, and in the latter case give an increased weight to the calcium chloride tube when no alkaline carbonate is used. It is important that in all future analyses stress shall be laid upon the utmost accuracy in the water determinations, and if insoluble matter is present, it must be ascertained if possible how much, if any, of the water is to be ascribed to this source.

Before leaving this portion of the subject it is necessary to call attention to one difficulty presented by the analyses for which no satisfactory explanation yet presents itself. In the majority of cases in which all constituents have been estimated, the summation is considerably in excess of 100, and in some cases, where only one or two are wanting, it is evident that they would, if determined, produce a like result. Although it did not seem possible that this almost constant excess could be due to impurities from reagents, or to want of sufficient care in washing or igniting precipitates, it was determined to make an analysis on Glastonbury material with the utmost possible care, using specially prepared reagents and only platinum vessels and reducing the number of weighings to be used as the basis for the summation to a minimum. This analysis, executed partially in duplicate, is No. V, of Table I, and the excess still appears. It seems as if some one of the weighings must have been uniformly too high, but how this can be is a mystery. Efforts will still be made to find a solution. It can not be sought in a replacement of oxygen by nitrogen in combination with uranium, like the replacement of oxygen by fluorine in many minerals, for since the nitrogen is freed as a gas by sulphuric acid, it is immaterial, so far as the summation is concerned, whether the proportions of UO_2 and UO_3 as found by titration are correct or not. A certain amount of oxygen has been used, and, assuming its correct determination, it does not alter the result whether this has been employed to oxidize a suboxide of uranium to UO_3, supposing nitrogen to have replaced a part of the oxygen in UO_2, or only in oxidizing UO_2 to UO_3. In the former case the actual percentage of UO_3 in the mineral would be increased, but the oxygen consumed would be the same.

In a former notice[1] it was mentioned that a relation appeared to subsist between the nitrogen and the UO_2, but this statement was based on two experiments which subsequent work showed to be illusory. There is certainly a relation, but not exactly such a one as was

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[1] Am. Jour. Sci., 1889, [3] vol. 38, p. 329.

then surmised. It was found, namely, on examining the portions used for water determinations (by ignition in dry air without sodium carbonate) for UO_2 and nitrogen, that the residual amounts of these were exactly in proportion to their original percentages, showing that the loss of nitrogen kept step with the oxidation of UO_2 to UO_3. It was later found that these results were accidental, for by sufficiently long heating the nitrogen was entirely eliminated, so far as the usual tests showed.

SPECIAL EXPERIMENTS RELATING TO THE NITROGEN IN URANINITE.

The last observation led naturally to a series of experiments as to the behavior of the nitrogen on heating in air, in carbonic acid, and in hydrogen, in the hope that thereby some clew might be obtained as to its probable condition in the mineral. They were all made on the material which had served for the final and most careful analysis of Glastonbury uraninite (No. V), not only because of the greater quantity at disposal, but also because of its high percentages in UO_2 and N. The results were in some respects perplexing to the last degree, and as yet no satisfactory explanation has been found. The mineral contained: UO_2 59·93, UO_3 23·03, N 2·41, H_2O 0·43, Fe_2O_3 0·29, total U as UO_2 81·67.

EFFECT OF HEATING IN AIR.

After ascertaining that no nitrogen could be obtained either by sulphuric acid or sodium-potassium carbonate when the mineral had previously been heated for a sufficient length of time in air, the following experiment was made to show if the final change in weight represented the difference between loss of water plus all nitrogen and gain of oxygen from oxidation of UO_2. The weight of ignited material, after determining water, in nearly all uraninites, had indicated that this could not be the case.

1·0028 gramme dried at 100° C.:

	gramme
When heated below redness gained	·0063
When heated at full redness for 6 hours gained	·0020
When heated at full redness for 6 hours gained	·0007
When heated at full redness for 6 hours gained	·0000
	·0090

Of the ignited product 1·0060 gramme equivalent to ·9970 gramme of unignited mineral, was decomposed in a sealed tube with dilute sulphuric acid. No nitrogen whatever was given off, and an amount of UO_2 was found representing 27·82 per cent of the unignited mineral. The UO_2 which had been oxidized to UO_3, therefore, was 59·93—27·82, or 32·11 per cent, which requires 1·90 per cent oxygen. The theoretical change in weight, assuming no nitrogen to have been expelled, would be the algebraic sum of the oxygen taken up, of the water driven off, and the small and uncertain additional loss which is shown by the gain of a calcium chloride tube when no sodium carbonate is used in the water determination, and which amounts to about ·0012 – ·0015 g. This would be 1·90—(.43+.13), or 1.34. Assuming all nitrogen to have been expelled there should appear a *loss* of 1·07, and such a result was to be expected in view of the failure to find nitrogen in the ignited matter. The actual result would indicate that only 0·44 per cent of nitrogen had been expelled by prolonged heating. If this is so no other explanation seems possible than that the nitrogen has entered into some other state of combination in which it is not set free by sulphuric acid or by fusion with an alkaline carbonate.

It is of the highest importance to ascertain definitely if the nitrogen is given off in whole or in part by heating in an oxidizing atmosphere, but there are difficulties connected with the carrying out of such an experiment which have hitherto prevented its being made. It is intended, however, to try the experiment of heating in oxygen and absorbing the latter by chromous chloride, after the manner recommended by Jannasch and Meyer[1] for nitrogen determinations in organic bodies.

EFFECT OF HEATING IN CARBONIC ACID GAS.

I. 1.0722 gramme (dry) heated in carbonic acid generated from manganese carbonate lost 0.49 per cent in weight and afforded but a doubtful trace of nitrogen.

II. 1.0111 gramme (dry) when treated in a similar manner for a longer time, lost 0.69 per cent in weight, and gave, approximately, 1.4cm^3 of gas or 0.17 per cent by weight of nitrogen. After several hours further heating the boat had lost no more in weight, and no additional gas seemed to be given off. Because of the impossibility of freeing the carbonic acid from all traces of atmospheric nitrogen—a copper roll having been used to retain its oxygen—it is impossible to say with any certainty whether small fractions of a cubic centimetre of gas were derived from the mineral or not.

EFFECT OF HEATING IN HYDROGEN.

The effect of heating in dry hydrogen was a reduction of practically all UO_3 to UO_2 and a slow expulsion of nitrogen; at least the usual methods showed less and less according to the duration of the heating. The following are the data obtained:

I. 1·1287 gramme (dry), after being heated for 3 hours in a combustion tube in a current of hydrogen purified by potassium hydrate and sulphuric acid, had suffered a loss of 0·0198 gramme. Of the ignited mineral 0·8022 gramme gave 1·62 per cent of nitrogen calculated to the original weight before reduction, and 0·3000 gramme required potassium permanganate equivalent to 81·18 per cent of UO_2 on the same basis. In view of the long heating required to reduce the percentage of nitrogen appreciably, it was not deemed practicable to collect any of it, because

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[1] Ann. d. Chem., 1886, vol. 233, p. 375.

of the difficulty of getting rid of such a large quantity of hydrogen and the impossibility of freeing the latter entirely from atmospheric nitrogen. When transferred to a eudiometer and exploded with air and electrolytic oxyhydrogen the gas was found to be absolutely free from hydrogen, which it was thought might have resulted from the action of reduced iron on the acid. An evolution of hydrogen was observed at first, and the tube was not filled with carbonic acid till this had entirely ceased. The fact that not quite the theoretical amount of UO_2 was found indicates that reduction was not complete. More than the theoretical amount should have been found, owing to the ferrous iron formed on solution in acid.

It was proved by passing the gases from the combustion tube through dilute hydrochloric acid and evaporating the latter with platinic chloride that no ammonia whatever was formed.

The loss in weight above given should represent the water in the mineral (0·0049), the oxygen of the UO_3 reduced to UO_2 (0·0148), all the oxygen of the iron existing as ferric oxide, possibly the oxygen of lead oxide, and lastly an amount of nitrogen represented by the difference between the original percentage (2·41) and 1·62, the residual percentage. The water and the oxygen of the UO_3, however, alone amount to 0·0197, or just the total loss.

II. 1·5700 gramme (dry) gave a loss of 0·0316 gramme after six hours heating in hydrogen. 1·1179 gramme of the reduced mineral gave 1·05 per cent of nitrogen, and 0·4177 gramme gave 81·46 per cent of UO_2, both calculated to unreduced mineral. The loss in weight should represent 0·0067 water, 0·0206 oxygen from UO_3, an uncertain amount from Fe_2O_3 and possibly from PbO, and the difference between 2·41 and 1·05 per cent nitrogen. But it does not exceed the sum of water and oxygen alone, and as in the first experiment no nitrogen seems to have been removed, although quantitative tests show that much has disappeared. Further tests at a higher temperature in a crucible, whereby some lead was reduced and partly volatilized, showed that all the nitrogen could be caused to disappear.

These results are as perplexing as those obtained by heating in air, and the explanation when found will doubtless lead to one for the other case. The apparent failure to expel nitrogen by hydrogen might be taken as additional evidence of its combination with uranous uranium, but it is as difficult to conceive why it should not still be set free by sulphuric acid after reduction of the UO_3, as after oxidation of a portion of the UO_2 to UO_3.

CONCLUSIONS.

Briefly summarized the conclusions are as follows:

First. Nitrogen exists in uraninite in quantities up to over 2.5 per cent, and seems generally to bear a relation to the amount of UO_2 present. This is the first discovery of nitrogen in the primitive crust of the earth, for the nitride of iron found by Silvestri[1] in lavas from Etna is of recent and secondary origin. It is rather strange that no works on mineralogy, so far as I am aware, make mention of his species.

Second. The condition in which the nitrogen exists is unknown, but it is entirely different from any hitherto observed in the mineral kingdom, being liberated as nitrogen gas by nonoxidizing acids and by fusion with an alkaline carbonate. Fusion with caustic alkalies does not give rise to the formation of ammonia, but probably liberates nitrogen.

Third. Analysis of uraninite from various localities has shown that, with in general the same constituents, the mineral varies widely in composition, and that its physical characteristics and its behavior toward certain solvents are often as distinct as the chemical differences.

Fourth. The formulæ of Comstock and Blomstrand are inapplicable to the zirconia, thoria, and yttria uraninites of North America and Norway, among which are to be reckoned bröggerite, cleveite, and nivenite, and probably to the varieties free from earths.

Fifth. Extended and most careful examination of uraninite specimens from all possible localities is necessary before any conclusion worthy of acceptance can be reached as to the character of the chemical combination, or combinations, represented by them. The work in this direction should likewise cover a study of the nitrides and oxynitrides of uranium and thorium, with synthetical experiments aiming at the artificial production of uraninite.

This latter work will probably be undertaken in this laboratory as opportunity may offer, together with some further experiments upon some of the material already examined. It is earnestly to be hoped that those possessing or in a position to procure uraninite specimens will take the trouble to examine them on the lines suggested in the foregoing pages, or if unable to do so, will kindly contribute material for examination here.

The interest in the matter is not confined merely to a solution of the composition of this one mineral; it is broader than that, and the question arises, may not nitrogen be a constituent of other species in a form hitherto unsuspected and unrecognizable by our ordinary chemical manipulations? And, if so, other problems are suggested which it is not now in order to discuss.

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[1] Gaz. chim. Ital., 1875, vol. 5, p. 303.

METACINNABARITE FROM NEW ALMADEN, CALIFORNIA.

BY W. H. MELVILLE.

An excellent specimen of metacinnabarite was recently found in the quicksilver mine at New Almaden, Santa Clara County, California, and a portion of it was given me for examination. Metacinnabarite was never before known to occur in these deposits, although in neighboring cinnabar localities the amorphous mineral has been met with. This specimen carries finely developed and brilliant crystals which are admirably adapted for measurement on the goniometer.

In the ore seam where cinnabar has been deposited, there appears an argillaceous mass which has resulted from sediments derived from the decomposition of the country rock by solfataric action. This mass is not homogeneous but consists of gray and green particles, the former evidently a mixture of clay and partly decomposed rock constituents with a small amount of carbonates, the latter a silicate the composition of which in shown in the following analysis:

Analysis of the green silicate.

SiO_2	67·59
Cr_2O_3	5·31
Al_2O_3 Fe_2O_3	12·24
NiO	4·57
CaO	0·73
MgO	7·84
Alkalies	very little
	98·28

In justice to these figures it should be said that only 0·1225 gramme of substance could be obtained in sufficient purity for study, and the little impurity which this sample contained could not be removed by Thoulet's solution; also alkalies could not be determined.

Throughout this sheet of soft argillaceous matter, or selvage, large quantities of metallic quicksilver easily seen by the naked eye are distributed, and bright red cinnabar often deeply coloring small areas of quartz has crystallized. Cinnabar is found mainly deposited on this selvage—on the specimen at hand about an inch thick—intimately mixed with quartz, thus forming a hard compact mass upon which have grown cinnabar crystals, and these in turn are coated with minute quartz crystals. To this quartz the acute apex of the metacinnabarite crystal is attached and consequently is always broken. The genesis of this metacinnabarite was certainly subsequent to the deposition of the cinnabar, and groups of flat rhombohedrons of white semitransparent calcite appear to have formed at the same time. Crystallized dolomite is common among the ores of New Almaden and to this a fibrous silicate, undoubtedly chrysotile, firmly adheres. Fine bluish opal and occasional spangles of pyrite complete the list of associated minerals.

One other brittle substance was discovered while picking out metacinnabarite for analysis. It forms almost perfect spheres of a brilliant black color, which volatilize at a high temperature in yellowish vapor with a strong bituminous odor. The substance is organic matter, and curiously mercury does not enter into its composition. These spheres can be detected under the microscope embedded in the faces of the crystals of metacinnabarite (Fig. 2), and some were obtained by sharply rapping the specimen.

The rather low specific gravity of metacinnabarite is thus accounted for in part. Again, the presence of minute particles of quartz was unavoidable, and therefore the given value was also influenced to a slight extent by this cause. The crystals used for the determination of the specific gravity contained far less impurity than is recorded in the analysis which follows. The specific gravity was in two cases 7·095 and 7·142, or mean=7·118, almost identical with that of guadalcazarite, 7·15.

Analysis of metacinnabarite.

				At ratio.	
S	13·68			0·855	
Hg	78·01	S corresponding=	12·48%	0·7801	
Fe	0·61		0·34	0·0218	0·0549
Co	trace				
Zn	0·90		0·44	0·0277	
Mn	0·15		0·09	0·0054	
$CaCO_3$	0·71				
Residue, quartz	4·57		13·35		
Volatile organic matter	0·63	S found	13·68		
	99·26				

For analysis 0·6237 gramme of substance was available, and both the qualitative and quantitative study proceeded contemporaneously. The small errors of analysis are distributed between the sulphur and organic matter, where the sulphur is as usual a trifle too high. An uncertainty naturally exists in the determination of the organic matter. Selenium was looked for, but its presence was not established.

The crystals belong to the rhombohedral system (Miller) and consist of two poles differently modified. The following forms were observed:

Analogue pole.

	Miller.	Bravais-Miller. ($h\ \bar{k}\ l\ m$)	Naumann.
Basal plane	$\kappa(111)$	$\kappa(0001)$	$c : \infty a : \infty a : \infty a$
Positive hemi-rhombohedron	$\kappa(100)$	$\kappa(1\bar{1}01)$	$c : a : a : \infty a$
Negative rhombohedron	$\kappa(33\bar{2})$	$\kappa(0\bar{5}54)$	$\frac{5}{4}c : \infty : 1 : 1$
Hemi-scalenohedron	$\kappa(21\bar{1})$	$\kappa(1\bar{3}22)$	$\frac{3}{2}c : 3 : 1 : \frac{3}{2}$

Antilogue pole.

	Miller.	Bravais-Miller.	Naumann.
Negative hemi-rhombohedron	$\kappa(33, \bar{17}, \bar{17},)$	$\kappa(50, \bar{50}, 0, \bar{1})$	$50c : 1 : 1 : \infty$
Hemi-scalenohedron	$\kappa(31, \bar{17}, \bar{15})$	$\kappa(48, \bar{46}, \bar{2}, \bar{1})$	$48c : 1 : \frac{24}{23} : 24$
Hemi-scalenohedron	$\kappa(26, \bar{15}, \bar{12})$	$\kappa(41, \bar{38}, \bar{3}, \bar{1})$	$41c : 1 : \frac{41}{38} : \frac{41}{3}$

Angle of axes (Miller) = 118° 11′ 20″.

Axial ratio $c : a = 0{\cdot}2372 : 1$ (Naumann).

Measurements.

		Measured.	Calculated.
$111 \wedge 100$	=	15° 19′	
$100 \wedge 010$		26 29	
$100 \wedge 21\bar{1}$		4 15	
$111 \wedge 33, \bar{17}, \bar{17}$		94 10	94° 10′ 36″
$111 \wedge 31, \bar{17}, \bar{15}$		94 31	94 33
$111 \wedge 26, \bar{15}, \bar{12}$		94 42	95 17
$33, \bar{17}, \bar{17} \wedge \bar{17}, 33, \bar{17}$		119 28	119 28
$33, \bar{17}, \bar{17} \wedge 31, \bar{17}, \bar{15}$		2 6	
$33, \bar{17}, \bar{17} \wedge 26, \bar{15}, 12$		3 55	

The poles of the scalenohedrons in the negative hemisphere almost belong in the zone circles passing through any two poles of the negative rhombohedron; therefore, as shown in the figures, the planes of the former do not exactly bevel the terminal edges of the latter. The faces of the former $\varkappa(26, \bar{15}, \bar{12})$ are tectonic and contain series of reëntering angles (Fig. 2) which indicate the building up of that portion of the crystal rather than twinning. Otherwise striations are absent, and owing to the brilliancy of the plane surfaces sharp reflections of the signals on the goniometer were obtained. Fig. 2 was drawn with the aid of cross-hair and graduated stage of the microscope and in such position that the face $(33, \bar{17}, \bar{17})$ is parallel to the plane of projection. The following plane angles were read: α=86° 20′, β=82° 45′, γ=39, δ=85° 30′, η=24°. The relations of these angles with the elements of the crystal have not been made out. With the exception of $\varkappa(33\bar{2})$ all the observed forms are represented in Fig. 1, and actually occur on one crystal with equal regularity. Fig. 2 is the combination of $\varkappa(111)$ with the planes of the antilogue pole tabulated above. The distances of the poles of all the rhombohedral faces from the pole of (111) were measured on the same crystals, and no doubt

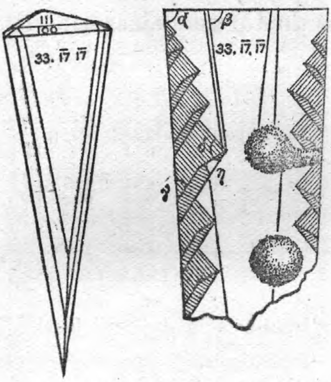

FIG. 2.—Metacinnabarite crystals.

can possibly exist as to the system of crystallization. Viewed as they are implanted on the rock, the crystals present much similarity to tetrahedrons, but examination shows that the face of the negative rhombohedron in combination with the basal plane forms an isosceles and not an equilateral triangle. Besides the measured angle $\beta=82°\ 45'$ the plane acute angle of $(33, \overline{17}, \overline{17})=14°\ 29'\ 40''$ was calculated from the fundamental angles. The crystals vary in length from 1·24mm to 2·3mm and in width from 0·59mm to 0·97mm; possess a high metallic luster, black color, black streak with slight reddish tinge; are brittle with hardness about 2; and give the reactions for zinc and sulphide of mercury.

This mineral I consider metacinnabarite, since the atomic ratios give a very improbable formula. Its specific gravity is much below that given to the species by Mr. G. E. Moore[1] 7·70 — 7·75 for the reasons stated above. On the other hand its somewhat close resemblance to guadalcazarite[2] in chemical and physical properties—for Castillo mentions rhombohedral crystals of this mineral—might point to its identity with this species. But it must be acknowledged to be metacinnabarite in composition with a small percentage of impurity of other sulphides such as would be naturally expected on precipitation and crystallization from solution. Again, the crystals of metacinnabarite, many of which I have examined from localities in California as far back as 1882, are very indefinite, and although they appear to be rough cubo-octahedrons, might really consist of the combination of basal plane and rhombohedron. Mr. S. L. Penfield[3] has described metacinnabarite crystals from California, and determines them to be hemihedral isometric forms. One measurement is there given, viz: $322_{\wedge}3\bar{2}\bar{2}=86°\ 54\frac{1}{3}'$ (mean of three) which approximates the angle $(\bar{1}\bar{1}\bar{1})_{\wedge}(33, \overline{17}, \overline{17})=85°\ 50'$, the supplement of which appears in the table above. It is possible that these two planes may form the combination I have indicated. No angle occurs on crystals in my possession near that of $211_{\wedge}112=33°\ 15'$ to $36°\ 54'$ which Mr. Penfield found. It is barely probable that metacinnabarite is dimorphous. If it should happen that brilliant crystals of metacinnabarite from the Knoxville quicksilver district should be found, I firmly believe that their habit could be reconciled with the symmetry of the crystals from New Almaden, the southern district.

It is through the kindness of Mr. Waldemar Lindgren, of the U. S. Geological Survey, and Mr. F. Von Leicht, the superintendent of the New Almaden quicksilver mines, that the material was available for this study.

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[1] Dana's Mineralogy, App. I, p. 10. [2] Ibid, App. II, p. 25. [3] Am. Jour. Sci., June, 1885, p. 452.

AN APPARATUS FOR THE DETERMINATION OF WATER IN MINERAL ANALYSIS.

BY THOMAS M. CHATARD.

In all cases where the water in minerals and rocks is easily expelled the apparatus described by me in the American Journal of Science, vol. XXXVII, June, 1889, p. 468, has been found very satisfactory. Many rocks and minerals, however, do not lose all of their water until exposed, for a considerable time, to a temperature at which glass softens. A more refractory tube is therefore necessary, and a platinum tube, such as is used for the determination of carbon in iron and steel, has been used to great advantage. The arrangement of the apparatus is shown in the cut.

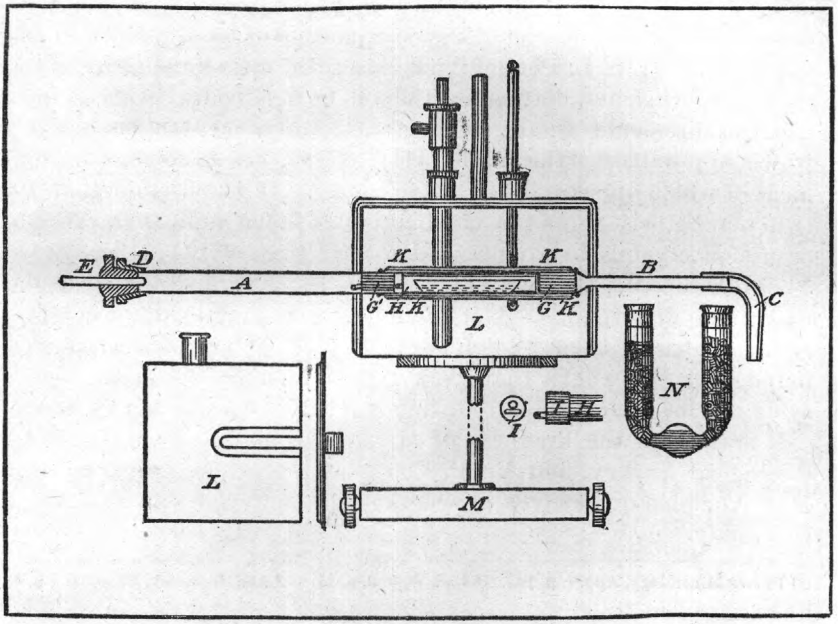

FIG. 3.—Apparatus for determination of water.

The tube A has an outside diameter of 16mm., the small tube B, 5mm. A need not be longer than 250—300mm., B, 80mm. C is a piece of lead glass tubing fused onto the end of B and bent and drawn out as shown.

D is a collar of phosphor bronze bored out with a slight taper and is fitted over the end of the platinum tube, the edge of which is flanged smoothly over the face of the collar. The phosphor-bronze plug E has a taper corresponding to that of the collar, which it fits very tightly and smoothly. The shoulders of both plug and collar are made hexagonal to insure a firm grasp when putting together or taking apart and should be stout enough to prevent any accidental deformation. The small tube F is closed at the inner end, a ring of small holes being bored through the side close to the face of the plug. By this arrangement all back circulation is prevented and the moisture which condenses in the cold part of the tube is easily and completely removed.

The platinum boat containing the substance to be examined is placed in a cylinder, H, made of platinum foil, which is closed at one end by a cap, I, in the center of which is a small hole to allow the passage of a current of air over the substance, while a small ring soldered to the cap enables one to put in or remove the cylinder with ease. The use of this cylinder prevents the loss of any of the substance by spattering, as when sodium carbonate is mixed with it, and also the frequently resulting adhesion of the boat to the tube.

The permeability of highly heated platinum to the gases of combustion, resulting in errors in the determination, is well known. To overcome this, and also to protect the valuable tube from injury, the part where the cylinder is placed, and which is ultimately exposed to the highest heat of a blast lamp, is wrapped with several layers of abestus paper soaked with a saturated solution of borax. The wrapping is secured with thread and thoroughly dried, more of the borax solution being put on if deemed necessary. When quite dry, the asbestus is covered with a sheet of platinum foil, KK, secured by wire. The whole is then highly heated and allowed to cool slowly. If properly made and put on, such a wrapping should last for months of steady use, can be easily replaced when necessary, and all risk of injury to the tube is avoided.

The air bath L, especially constructed for this tube, is a copper box open in front with a slit at each end, as shown in L′, suited to the size of the two portions of the tube. The front is closed by a plate of copper, on the inner side of which several layers of asbestus board are fastened. The edges of these are slightly beveled to insure a tight fit, and a hook at the top of the bath holds the plate in place. The bath is covered with asbestus board, and when in use the open portions of the slits are closed by asbestus plugs. The bath is furnished with thermostat, thermometer, and lamp, and the whole mounted on a stand, the base of which, M, is fitted with four small wheels so that it can be pushed into position or removed without disturbing the rest of the apparatus.

When using the apparatus the tube is fastened by a clamp near the end, the roll of platinum gauze G is shoved into place, the plug inserted, a slow stream of dry air passed through, and then heated throughout its length and allowed to cool. The boat containing the substance is now put into the cylinder, which is at once pushed into the tube far enough to touch the roll of gauze. The roll G′ follows, and the plug is reinserted, the current of air being kept up. The air bath, previously brought to its standard temperature, 105°, is now opened, run into position, the tube sliding smoothly into the slits, and then closed, regaining its temperature in a few minutes. When it is considered that the tube and contents are perfectly dry, the U tube N, described in the paper already quoted, is attached, and the air bath removed by opening it and rolling it back. The tightness of the apparatus is now tested, and, if satisfactory, the air current is regulated and the tube gradually heated, beginning at the roll G′ and using an ordinary burner. If much water condenses in the bent glass tube the heat must be very gradually increased, and this is best effected by keeping the part G′ quite hot, thus heating the air current and preventing as far as possible the always annoying back circulation. Finally the portion of the tube covered by the borax asbestus is exposed to the full heat of a blast lamp, to which a flat burner has been adapted.

When no moisture remains in the glass tube the blast lamp is removed and the apparatus allowed to cool. When cold the U tube is disconnected and weighed and the cylinder with its contents withdrawn. If the amount of material at disposal is small, this portion can be used for the determination of the silica and the bases, since any loss has been prevented by the cylinder, which can be washed clean with dilute hydrochloric acid and any insoluble matter filtered off and added to the rest of the substance in the boat, which can be fused with sodium carbonate in the usual manner.

The use of the cylinder and the abestus wrapping obviates the only serious objection to this method, namely, the high cost of the platinum tube, as in this way the tube is absolutely protected from all damage. By having duplicate boats, cylinders, and U tubes the determinations can be made quite rapidly, and a large number of determinations made in this way by myself and others have given very satisfactory results.

THE SEPARATION OF TITANIUM, CHROMIUM, ALUMINUM, IRON, BARIUM, AND PHOSPHORIC ACID IN ROCK ANALYSIS.

BY THOMAS M. CHATARD.

Having to examine some magnesian silicate rocks containing, in addition to iron and aluminum, small quantities of titanium, chromium, barium, and phosphoric acid, the methods for the decomposition of such rocks and the separation of their constituents were studied and compared so as to determine the most advisable manner of procedure. After repeated trials the following course, combining a number of well known methods, has been found to be the most satisfactory.

The silica and bases are determined by the ordinary sodium carbonate fusion method, in which the hydrates of titanium, iron, aluminum, and chromium, together with the phosphoric acid, are precipitated together and after weighing fused with sodium bisulphate, dissolved, the small amount of silica separated, and the solution, after reduction of the ferric oxide, titrated for total iron.

To separate these oxides and at the same time to determine the barium, two grammes of the finely pulverized mineral are put into a platinum crucible or dish, moistened with water, dilute sulphuric acid (1:1), and pure strong hydrofluoric acid added in considerable excess, the vessel put on a radiator to evaporate, and stirred from time to time. When the solution is so far evaporated that fumes of sulphuric acid begin to come off there should still be so much acid present as to form a solution or emulsion and not a paste, since the paste is liable to bake on the bottom of the vessel and form the difficultly soluble anhydrous sulphates produced by overheating, especially when magnesia is present in quantity. At this point it is well to add a few drops of nitric acid to oxidize the ferrous oxide and a little more hydrofluoric acid to insure the complete expulsion of the silica. The evaporation is then continued till the sulphuric acid fumes strongly and no odor of hydrofluoric acid can be detected when the solution is cooled below the point at which the sulphuric acid fumes.

Twenty-five cubic centimetres of dilute hydrochloric acid (1:5) is now added, stirring continually, and the material is then evaporated on the water bath till most of the HCl has been driven off. The material is then washed into a beaker and any residue adhering to the vessel can be removed by a few drops of hot strong HCl, rubbing with a bit of paper if necessary. If the solution is very turbid it can be digested on the water bath for some time, but ultimately it is diluted with hot water to 250—300 cubic centimetres, allowed to stand for several hours, and then filtered.

The residue contains the barium as sulphate and sometimes small amounts of chromite or other minerals of the same class. It is washed, ignited, and thoroughly fused with sodium carbonate in a small crucible, the fused mass being then digested with hot water and leached. The well washed residue is dissolved on the filter with dilute HCl, and this solution filtered through the same filter, which after washing is burned, the ash fused with a little sodium carbonate, the mass dissolved in dilute HCl, and added to the leachings, which are now acidified, and added to the main solution after reduction of the chromic acid. The HCl solution containing the barium is evaporated to a few drops to get rid of the excess of HCl, taken up with water, and precipitated with dilute H_2SO_4. The filtrate from the barium sulphate is added to the main solution.

This main solution, which should be perfectly clear and contain the iron and chromium as sesquioxides, is now made alkaline by NH_4HO and the precipitate redissolved by dilute HCl. A few drops of acetic acid are added, the liquid brought to a boil, NH_4HO added in very slight excess, the boiling continued for a few minutes, and the precipitate filtered and washed. As the sole reason for this precipitation is to get rid of the magnesia and the accumulation of other salts, the washing need not be thorough but the filtrate must be tested and precipitation proved complete.

The precipitate is dissolved in hot dilute HCl. The filter, after washing, is burned in a large platinum crucible into which the solution, concentrated to a small bulk, is put and evaporated on the water bath till it becomes pasty. Just enough water is now added to dissolve the salts and then dry sodium carbonate is added in small portions, with continual stirring till a comparatively dry mass results. This must be very carefully done, for if too much soda is added at a time and each addition is not thoroughly stirred into the mass the after fusion is apt to be "lumpy" and unsatisfactory.

When a good excess of carbonate has been thus added the mass is dried and gradually brought to clear fusion, which should be continued for about half an hour. If lumps form, which is, however, rarely the case if lime and magnesia are absent and the foregoing directions are followed, they can be broken up by shaking the crucible with a circular motion to detach them from its walls. When the fusion is complete the mass is spread around the walls of the crucible and slightly cooled. A small quantity of sodium nitrate is now added, the whole rapidly fused and carefully boiled for not more than five minutes, again spread over the crucible and rapidly cooled with a blast of air. The mass is boiled with water till completely disintegrated and then leached. Repeated tests have shown that the residue which contains the titanium is, when well washed, free from chromium and phosphoric acid.

The washed residue is dissolved in hot dilute HCl, the filter burned, the ash fused with $NaHSO_4$, dissolved in water and added to the solution. The titanium in this solution is separated by the excellent method of Dr. Gooch, following all the details as laid down by him in the Proc. Am. Acad., vol. 12, p. 435, et seq.[1] I have, however, found it convenient, after the destruction of the tartaric acid by potassium permanganate and the clearing of the solution by sulphurous acid, to add ammonia in slight excess, then at once acetic acid in excess, and boil with addition of sulphurous acid. The precipitate of titanium hydrate, mixed with some alumina, is filtered and washed with water containing sulphurous acid and a little acetic acid. It is thus freed from manganese and brought into a small compass, rendering the after work easier. Before the final precipitation of the titanium, the platinum, generally in the solution, should be removed by H_2S.

The filtrate containing the chromic and phosphoric acids is heated and ammonium nitrate cautiously added till no further precipitation of alumina occurs. The precipitation of the aluminum phosphate seems to be complete, but some alumina always remains in solution. The precipitate is allowed to settle, the supernatant liquid decanted, and the precipitate washed with solution of ammonium nitrate till the yellow tinge disappears; it is then dissolved in dilute HNO_3 and the phosphoric acid precipitated with molybdate solution.

The filtrate containing the chromic acid is acidified, boiled, neutralized with NH_4HO, and the chromic hydrate precipitated by freshly prepared ammonium sulphide. The precipitate, after some washing, is dissolved in hot dilute HNO_3, and after concentration, $KClO_3$ is added and the solution boiled, being finally evaporated nearly to dryness to expel the excess of acid. It is then diluted with cold water, and saturated solution of $NaHCO_3$ added in small excess separating the last traces of alumina. After standing about three hours the alumina is filtered off and washed with moderately dilute solution of $NaHCO_3$. The filtrate is acidified, and the chromic acid reduced, precipitated by ammonium sulphide, filtered, washed, redissolved to get rid of traces of alkali, reprecipitated, and finally weighed as Cr_2O_3.

This method, due to Baubigny, for the separation of chromium from aluminum is very good and convenient if the solution is free from iron and contains but little alumina. Careful tests have shown that if iron is present some of it always remains in solution, while if there is much alumina, it is almost impossible to wash out the chromate from the bulky precipitate with the cold solution of $NaHCO_3$, which must be used. It must also be noted in this connection that a solution of iron

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[1] Bull. 27, U. S. Geol. Surv., p. 16, et seq.

and chromium, prepared by the Baubigny method, was made ammoniacal, and it was proved that while all of the iron was precipitated, this precipitate, even after the most careful washing with hot water, contained chromium.

Although the number of details in this process may seem very great, experience has shown that none of them can be safely neglected for the purpose of shortening the work; if the whole process is carefully followed out, the results are very satisfactory, as shown by the following tests on a typical magnesian rock:

	Cr_2O_3.	TiO_2.	BaO.	P_2O_5.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
No. 1	0.270	0.46	0.040	0.375
No. 2	0.285	0.39	0.060	0.385
No. 3	0.317	0.46	0.055	....
No. 4	0.280	....	....	....
Average	0.288	0.44	0.052	0.380

The use of niter for the fusions is not absolutely necessary, though one is more sure of complete oxidation. In the analysis of chrome ores, the best results have been obtained by fusing the finely pulverized ore with sodium carbonate alone, but keeping it in clear fusion for an hour. The fused mass is treated like an ordinary silicate fusion, the silica, after weighing, being volatilized by HFl, and the residue, usually small, again fused with Na_2CO_3. This second fusion gives a clear solution in HCl.

SEVEN NEW METEORITES.

By L. G. Eakins.

STONY METEORITE FROM TEXAS.

The meteorite which forms the subject of this article was found in Travis County, Texas, and brought to notice by Prof. R. T. Hill, of the University of Texas, who presented the piece first obtained by him to the National Museum. This piece, of an irregular shape and weighing about 2½ kilograms, is supposed to be but a fragment of a much larger mass which Prof. Hill expects to obtain.

It has a superficial coating of a yellowish brown color where it has been subject to weathering, but on a fractured, unaltered surface it is dull black with a slight grayish tinge. It is hard, compact, and very tough; to the unaided eye the stony mass is very uniform in structure, and none of the composing silicates can be distinguished, but troilite can be plainly seen scattered throughout it, and on a ground and polished surface the metallic particles are also visible. Under the microscope, (for which information I am indebted to Mr. Whitman Cross,) the stony portion seems to consist chiefly of olivine and enstatite, with a small quantity of a colorless mineral which is probably a feldspar; as will be seen later, the analytical results also indicate the presence of a feldspar, while chromite also was found unmistakably.

The mass has a specific gravity of 3·543 at 30°, and its analysis as a whole is as follows:

SiO_2	44·75
Al_2O_3	2·72
Cr_2O_3	·52
Cu	tr.
FeO	16·04
Fe	1·83
NiO	·52
Ni	·22
Co	·01
MnO	tr.
CaO	2·23

MgO	27·93
K_2O	·13
Na_2O	1·13
P_2O_5	·41
S	1·83
H_2O	·84
	101·11
Less O for S	·92
	100·19

From some of the finely powdered material the metallic portion was extracted by the aid of an electromagnet, and as slight amounts of troilite and the silicates remained attached, this was then treated with a neutral solution of copper sulphate and the solution analyzed. This gave the metallic part as constituting 2·23 per cent of the mass, with the following composition, calculated to 100 per cent:

Fe	88·74
Ni	10·68
Co	·58
	100·00

The residue from which the metallic portion had been removed was then digested with dilute hydrochloric acid; this dissolved the troilite and olivine, and the soluble and insoluble portions were then separated and analyzed in the usual manner. The sulphur present was calculated as troilite, with the formula FeS, and has been deducted in stating the analysis of the soluble portion:

Soluble in HCl. (Troilite deducted.)				Insoluble in HCl.		
	Analysis.	Calculated to 100 per cent.	Molecular ratios.	Analysis.	Calculated to 100 per cent.	Molecular ratios.
SiO_2	15·67	38·13	·636	30·36	56·14	·936
Al_2O_3	1·06	2·58	·025	2·02	3·73	·036
Cr_2O_3	....	....	....	·54	1·00	·007
FeO	8·12	19·76	·274	4·95	9·15	·127
NiO	·49	1·19	·016	....	....	....
CaO	·42	1·02	·018	1·94	3·59	·064
MgO	15·34	37·32	·933	13·22	24·44	·611
K_2O	undet.	....	....	·10	·19	·002
Na_2O	undet.	....	....	·95	1·76	·028
	41·10	100·00	....	54·08	100·00	....

In the soluble portion the ratio of the RO group to the SiO_2 is as close to that of olivine as could be expected in work of this kind. The insoluble portion, after removing the Cr_2O_3 and a proportional amount of FeO to form chromite, gives these ratios:

$$\begin{array}{ccccc} RO & : & Al_2O_3 & : & SiO_2 \\ ·825 & : & ·036 & : & ·936, \end{array}$$

which seem to bear no definite relations to each other. It is noticeable, however, that the Al_2O_3 and alkalies present are nearly in the proportion required for a feldspar, and if one of the oligoclase type were present in proportion to this Al_2O_3, it would have these molecular values:

$$\begin{array}{ccccc} RO & : & Al_2O_3 & : & 4\frac{1}{2}\ SiO_2 \\ \cdot036 & : & \cdot036 & : & \cdot162; \end{array}$$

assuming this to be the case, and deducting this amount of feldspar, it would leave

$$\begin{array}{ccc} RO & : & SiO_2 \\ \cdot789 & : & \cdot774, \end{array}$$

which corresponds closely to enstatite.

By calculating the soluble and insoluble parts as having been determined on the original material minus the metallic portion and water, and taking all the sulphur as representing troilite (FeS), the general composition of the meteorite is shown to be

Metallic	2·23
Troilite	5·03
Soluble in acids	39·84
Insoluble in acids	52·42
	99·52

METEORIC IRON FROM NORTH CAROLINA.[1]

The iron here described was found in the latter part of 1880 on a farm near Ellenboro', Rutherford County, North Carolina, and its nature remained unknown until February, 1890, when it was brought for examination to Mr. Stuart W. Cramer, of the United States assay office at Charlotte, North Carolina, who ascertained that it was a meteorite and obtained half of the mass. This portion was sent by Mr. Cramer to the U. S. National Museum for description, and the iron was cut and divided between the Museum collection and that of the assay office.

The weight of the original mass, as near as can be determined, was about 2,200 grammes; in shape it was roughly two globular ends with a connecting bar the total length being about 150mm., with end of diameters of 75mm., and 50 mm. in the middle.

The iron is very tough and highly crystalline; the Widmanstätten figures show distinctly on a polished, unetched face, and after etching they are unusually strong. Small, irregularly distributed patches of troilite are visible, and schreibersite also seems to be present. On account of the small amount of material that could be obtained for analysis no attempt was made to determine carbon, and the sulphur found shows that very little troilite happened to be included in the material analyzed, which, of course, in such highly crystalline material could not represent the actual average composition without cutting up a large part of the mass.

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[1] Am Jour. Sci., May, 1890, vol. 39.

The analysis is as follows:

Fe	88·05
Ni	10·37
Co	·68
Cu	·04
P	·21
S	·08
Si	·02
	99·45

PALLASITE FROM KANSAS.

This is one of a group of meteorites found in Brenham township, Kiowa County, Kansas, and fully described by Mr. G. F. Kunz in Science, vol. 15, No. 384, and American Journal of Science, vol. 40, October, 1890.

First plowed up by the farmers some years ago, it was not until March, 1890, that their meteoric nature was discovered; there are now known to be about twenty in all, with an aggregate weight of 2,000 pounds, and ranging individually from 466 pounds to 1 ounce.

There are two distinct groups; one of the more common nickeliferous irons of highly crystalline structure, the other of the form known as pallasite, a meteoric iron containing olivine. It is one of the latter group that forms the subject of this article. In it the olivine scattered throughout the iron is roughly in two zones, an inner one of clear, brilliant material; and an outer one which is very dark, almost black in places, consisting, as was shown by the analysis and microscopical examination, of an intimate mixture of olivine and troilite.

In procuring material for the analysis of the olivine, transparent clear yellow crystals or fragments were carefully picked out, and for the dark zone care was taken to get as uniform material as possible. In addition to being in the dark olivine zone, troilite is scattered throughout the metallic iron, the iron on etching showing the Widmanstätten figures. The specific gravity of the iron free from olivine is 7·93 at 23·4° C., and of the pure olivine 3·376 at 23·2° C. The analyses are as follows

Iron.		Olivine.		Dark outer zone.	
Fe	88·49	SiO_2	40·70	SiO_2	34·14
Ni	10·35	Al_2O_3	tr.	FeO	23·20
Co	·57	Fe_2O_3	·18	NiO	tr.
Cu	·03	FeO	10·79	CoO	·03
P	·14	NiO	·02	MnO	·09
S	·08	MnO	·14	MgO	40·19
C	tr.	MgO	48·02	S	5·42
Si	tr.		99·85		103·07
	99·66			Less O for S	2·71
					100·36

METEORIC IRON FROM TEXAS.

This iron was received from Mr. E. E. Howell, who has published a description of it and the one following (from Puquios, Chili) in the American Journal of Science, vol. 40, September, 1890. It was found in Hamilton County, Texas, although first credited to Erath County, of that State.

Its original weight was about 81½ kilos, and its greatest dimensions 44 by 33 centimetres. A polished face of this iron plainly shows the crystalline structure, and on etching the Widmanstätten figures are of unusual beauty.

It has a specific gravity of 7·95 at 27° C. and furnished the following analysis:

Fe	86·54
Ni	12·77
Co	·63
Cu	·02
P	·16
S	·03
C	·11
	100·26

METEORIC IRON FROM CHILI.

This meteorite was found near Puquios, probably about 1885, and kept in Chili until 1889, when it came into the possession of Prof. H. A. Ward. Its weight was about 6½ kilos, and its greatest dimensions 25½ by 14 centimetres. The most noticeable feature of this iron is the faulting phenomenon, which is shown on the etched sections, and is fully described by Mr. Howell in the article referred to. Specific gravity, 7·93 at 25·2° C. Analysis:

Fe	88·67
Ni	9·83
Co	·71
Cu	·04
P	·17
S	·09
Si	tr. (?)
C	·04
	99·55

CHONDRODITE FROM IOWA.

An account of this meteorite is given in detail in the American Journal of Science, vol. 40, October, 1890, in an article by Mr. G. F. Kunz, who furnished the material on which this analysis was made. It fell on May 2, 1890, in Winnebago County, Iowa, the various fragments being scattered over a considerable area, while a part of the mass is believed to have passed over into Minnesota. The stone is somewhat porous, and on a fractured surface is spotted gray in color, showing visible particles of iron and of troilite.

The specific gravity of the mass is 3.804 at 28.5° C., and on analysis it yielded these results:

Approximate composition of the mass.		Analysis of the nickeliferous iron.	
Nickeliferous iron	19·40	Fe	92·65
Troilite	6·19	Ni	6·11
Silicates soluble in HCl	36·04	Co	·65
Silicates insoluble in HCl	38·37	P	tr.
			99.41

Analysis of the siliceous portion, with all magnetic extracted.

Soluble in HCl.				Insoluble in HCl.		
	(1)	(2)	Calculated to 100 per cent. (3)		(4)	Calculated to 100 per cent. (5)
SiO_2	17·82	17·82	39·74	SiO_2	26·49	55·51
FeO	*14·27	8·26	18·42	Al_2O_3	2·59	5·43
NiO	·17	·17	·38	Cr_2O_3	·12	·25
MnO	trace.	trace.		FeO	4·49	9·45
CaO	·31	·31	·69	NiO	trace.	
MgO	18·28	18·28	40·77	CaO	1·45	3·00
Alk	trace.	trace.		MgO	11·50	24·09
S	†2·67			K_2O	·07	·15
P	trace.	trace.		Na_2O	1·01	2·12
	53·52	44·84	100·00		47·72	100·00
O for S	1·34					
	52·18					

* Taking out 6.01 FeO equivalent to 4.67 Fe required by S to form FeS.

† Taking out S to form FeS.

The analyses numbered from 1 to 5 were made on the residue left after extracting all the magnetic material. No. 1 is the portion soluble in HCl; No. 2, that insoluble in HCl, the two added together giving the analysis of the non-magnetic portion as a whole. No. 2 is the same as No. 1 after deducting the S and a corresponding amount of FeO equivalent to the Fe necessary to form troilite with the S. No. 3 is No. 2 calculated to 100 per cent. No. 5 is No. 4 calculated to 100 per cent. The Cr_2O_3 probably represents chromite, and the alkalies and alumina with a little lime may come from a soda lime feldspar.

The method employed to determine as closely as possible the composition of the mass of this and similar meteorites is to extract everything possible with an electro-magnet; this removes all the nickeliferous iron and a little troilite, leaving the siliceous part and most of the troilite. The S present in the magnetic portion and that in the siliceous portion is calculated as FeS, and in stating the analysis of the nickeliferous iron the slight amount of attached troilite and silicates is first deducted. The silicates are split up by HCl as above, and from the different weights found the approximate composition is calculated.

LLANO DEL INCA METEORITE.

Fragments of this meteorite amounting to 27 pounds were obtained by Prof. Ward in 1889, they having been found the previous year 35 leagues southeast of Taltal, Atacama, Chili, on the Llano del Inca. Mr. E. E. Howell has described this meteorite in the proceedings of the Rochester Academy of Science, vol. 1. It consists of a mixture of iron and stone, superficially of a dark brown color, the fresh polished surface showing the iron scattered all through the stony mass.

Analyses.

Approximate composition of the mass.		Analysis of the nickeliferous iron.	
Nickeliferous iron	25·8	Fe	89·77
Troilite	10·6	Ni	9·17
Silicates soluble in HCl	30·9	Co	·61
Silicates insoluble in HCl	32·6		99·55

Analysis of the siliceous portion, with all magnetic extracted.

Soluble in HCl.				Insoluble in HCl.		
	(1)	(2)	Calculated to 100 per cent. (3)		(4)	Calculated to 100 per cent. (5)
SiO_2	11·53	11·53	28·08	SiO_2	23·15	53·11
Al_2O_3	5·23	5·23	12·74	Al_2O_3	1·01	2·32
FeO	*28·89	17·46	42·52	Cr_2O_3	·39	·90
NiO	1·19	1·19	2·90	FeO	8·20	18·82
MnO	·08	·08	·20	CaO	·76	1·75
CaO	3·83	3·83	9·33	MgO	10·07	23·10
MgO	·81	·81	1·98	P_2O_5	trace.	
P_2O_5	·93	·93	2·25		43·58	100·00
S	†5.08					
	57·57	41·06	100·00			
— O for S	2·54					
	55·03					

* Taking out 11.43 FeO equivalent to 8.89 Fe required by S to form FeS.

† Taking out S to form FeS.

ON A PETROLEUM FROM CUBA.

By H. N. Stokes.

At Santa Clara, Cuba, there is a spring known as the Sandalwood Spring, from which issues with the water a certain amount of petroleum, which, from its peculiar odor, is called "sandalina," or sandalwood oil, although it more closely resembles the odor of cedar. The oil is collected from the surface of the water, and used as illuminating oil and for other purposes without being refined. About two litres of this oil were sent to the laboratory of the U. S. Geological Survey by Mr. C. W. Cunningham, and its examination gave the results described below.

The oil, which is about as viscous as strong sulphuric acid, is somewhat turbid from suspended water, but when dried over calcium chloride it is perfectly transparent, amber colored, and shows the merest trace of bluish-green fluorescence. Its odor, as above mentioned, is agreeable, and in no way suggestive of even refined American petroleums, but rather of cedar wood. The specific gravity at $\frac{33}{33}^\circ$ is 0.901.

A single distillation, with simple distilling bulb, gave the following fractions in parts per hundred by weight:

Under 250° C	3.3	
250–260°	6.0	
260–270°	11.2	
270–280°	12.1	
280–290°	16.6	
290–300°	18.0	
300–310°	8.4	Over 300°, 32.8.
310–330°	13.1	
Residue	11.3	

The most noticeable feature of this table is the small amount boiling under 250° and over 300°. Engler and Levin[1] give a similar table for nine petroleums from different sources, none of which shows a similar composition. The first fraction passed over entirely between 230° and 250°, only a slight escape of gas being noticed below this point. The absence of volatile constituents is perhaps due in part to evaporation before collecting, but this does not explain the small amount of high boiling portions. The fractions under 290° were colorless, and those

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[1] Dingl. Polyt. Jour., 1886, vol. 261, p. 32. Post, Chem.-techn. Anal., 2te Aufl., vol. 1, p. 267.

from 250° to 270° possessed a peculiar camphor-like taste, but the characteristic odor was entirely lacking in the distillates. The residue boiling above 330° was dark, oily, and opaque, and when hot had a very irritating odor. The specific gravity of the fraction under 250° at $\frac{33}{33}$° was 0.855, and that of the residue boiling above 330° was 0.941.

The absence of *sulphur* compounds was to be inferred from the absence of disagreeable odor, which was confirmed by boiling a long time with metallic sodium and treating the product with sodium nitroprusside,[1] whereby not the slightest trace of a sulphur reaction could be obtained.

The carefully dried oil contains little but hydrocarbons, as shown by the elementary analysis:

	I.	II.
C	86.90	86.64
H.........	12.75	12.48

This leaves a margin of only 0.6 per cent for oxygen, nitrogen, and other substances. Shaking out with alkali, acidifying the latter, and extracting with ether gave the merest traces of residue, from which the absence of phenols and acids follows.

The fraction boiling under 250° gave—

C 86.76.

H 13.05.

The classes of hydrocarbons thus far recognized in petroleum are, as is well known:

1. *Paraffins*, C_nH_{2n+2}.
2. *Olefins*, C_nH_{2n}, and still more unsaturated fatty hydrocarbons.
3. *Aromatic hydrocarbons.*
4. *Naphthenes*, C_nH_{2n}, which, so far as their structure is understood, are perhydrides of aromatic hydrocarbons, or hexamethylene derivatives, with hydrocarbons containing more carbon,[2] but showing the same general properties, and probably related to the naphthenes C_nH_{2n}, as naphthalene, diphenyl, etc., to benzole; that is, containing several single or double hexamethylene rings.

With the small amount of oil at my disposal it was impossible to attempt to isolate any hydrocarbon in a pure state by fractioning, and I had to satisfy myself with general reactions indicating the presence or absence of the different groups. In fact, a high boiling petroleum like sandalina would contain so many closely allied bodies of nearly identical boiling points, that their separation would be at best an extremely tedious and difficult operation, especially as so little is known of the nature of petroleum hydrocarbons boiling over 250°.

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[1] Vohl, Dingl. Polyt. Journ., vol. 216, p. 47.

[2] Markownikoff, Liebig's Annalen, vol. 234, p. 115.

PARAFFINS.

The higher paraffins, constituting paraffin wax, are apparently entirely absent from sandalina, as not the slightest deposit was obtained by cooling in a freezing mixture, with or without addition of ether, either from the oil itself or from the residue boiling above 330°. In either case the only result was a slight increase of viscosity. No grounds could be found for assuming the presence of liquid paraffins; for, as shown below, the the oil seems to be entirely destroyed by continued action of fuming sulphuric acid, no residue being obtained which shows greater resistance towards this reagent than the oil itself.

UNSATURATED FATTY HYDROCARBONS.

These bodies, which are found in greater or less quantity in most petroleums, are almost entirely absent from sandalina, as shown by its inertness toward bromine, which is so readily absorbed by bodies of the ethylene, acetylene, and similar series. Careful bromine absorptions[1] were made with the following results. The figures indicate the weight of bromine absorbed by 100 grammes of oil:

Fraction under 250°	0.86
250°–270°	0 25
270°–290°	0.87
290°–310°	0.72
310°–330°	1.34
Residue above 330°	1.72
Sandalina, undistilled	0.80
Absorbtion of sandalina calculated from absorption of the fractions	0.83

For comparison, a sample of refined burning petroleum gave 2.69, and fine white paraffin 0.53. Remembering that under the conditions of the experiment bromine exercises a slight substituting action even on saturated hydrocarbons, and that the absorption found for sandalina corresponds to only 1.75 per cent of a hydrocarbon $C_{25}H_{50}$, and proportionally less of lower or more unsaturated bodies, it is safe to say that the unsaturated hydrocarbons do not exceed 1 per cent.

AROMATIC HYDROCARBONS.

A mixture of concentrated nitric and sulphuric acids attacks sandalina quite readily, forming notable quantities of nitro compounds, for the most part soluble in alkali. This is not an indication of the presence of aromatic bodies, as naphthenes are oxidized by nitric acid, with formation of small quantities of aromatic nitro-compounds.[2] Aromatic hydrocarbons are now usually sought for by first separating the constituents as perfectly as possible by fractional distillation, and then treat-

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[1] Allen, Commercial Organ, Anal., 2d ed., vol. 2, p. 331.

[2] Markownikoff, Liebig's Annalen, vol. 234, p. 91. Markownikoff and Spady, Ber. deutsch. chem. Gesell., Jahrg. xx, p. 1850.

ing each fraction separately with fuming sulphuric acid, which converts the aromatic hydrocarbons into sulphonic acids, which are separated by means of their salts, only those being sought whose hydrocarbons boil within the limits of the fraction.[1] Whether a sulphonic acid thus obtained is positive proof of the presence of the aromatic hydrocarbon rather than of the corresponding naphthene may be questioned,[2] but the absence of the acid may be regarded as proof of the absence of the aromatic body. This at least is true of the portions boiling below 250°; whether it applies to oils of such high boiling range as sandalina might be doubted.

In this case it was not possible to carry out a systematic fractioning, so I attempted to obtain only bodies having the general characteristics of aromatic sulphonic acids, or rather, of their salts. In two series of experiments, in which sandalina itself and the residue boiling above 300° were used, the oil was first shaken out with concentrated sulphuric acid, and then repeatedly with fresh portions of a mixture of equal parts concentrated sulphuric acid and crystallized pyrosulphuric acid, 10 per cent of the volume of the oil being used each time. The latter produced considerable rise of temperature, with evolution of sulphur dioxide. As soon as no further action was observed, the black tarry acid was drawn off and the process repeated. The action of the acid did not decrease in violence even after many such operations, and in one experiment nearly the whole of the oil went into solution without leaving a residue which acted differently from the sandalina itself. Crystalline pyrosulphuric acid acted with still greater violence, causing a rise of temperature of 20°. The acids were united, and after dilution, which gave dark amorphous masses slowly dissolving in water, were neutralized with caustic potash or barium carbonate, and the sulpho-salts sought for by appropriate means. Only in the case of the residue boiling above 300° were obtained 5 grammes of a barium salt of resinous appearance, dissolving to a sirup in water and totally destroyed by nitric acid with production of barium sulphate. It showed no resemblance to the aromatic sulphonates, and hence, so far as the method holds good in this case, aromatic hydrocarbons are absent. What substances are actually formed by the action of the acid was not determined, as their exceedingly disagreeable properties made such an examination undesirable.

NAPHTHENES.

Aromatic bodies were further sought for by oxidizing sandalina with chromic acid, hoping thus to obtain aromatic acids, which would at least indicate the presence of aromatic hydrocarbons. The result was in this case also negative, no such acids being obtained, even after total oxidation of the oil. Products of a totally different nature were, however, found, which threw some light on the nature of the bodies present.

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[1] Markownikoff, Liebig's Annalen, vol. 234, p. 92.

[2] Markownikoff and Spady, Ber. deutsch. chem. Gesell., Jahrg. xx, p. 1853.

Chromic and glacial acetic acid attack sandalina violently, forming products of peculiar odor, which were not further studied.

Sandalina is attacked only by strong chromic acid mixture; 150 grammes oil, boiled with 300 grammes potassium bichromate, and 450 grammes sulphuric acid, diluted with 2 volumes water, was scarcely affected; 150 grammes sandalina, 400 grammes bichromate, and 600 grammes strong sulphuric acid, diluted with 1½ volumes of water, were boiled in a flask admitting of the observation of the escaping gas, the collection of the distillate, and the replacement of the escaping water. From time to time the operation was interrupted, the oil shaken out with dilute alkali, and returned to the flask with fresh oxidizing mixture. After four oxidations the oil was practically all destroyed. The characteristic odor of sandalina was observable during the whole operation. The distillate, which was acid, smelled strongly of acetone, which after neutralizing was distilled off and recognized by the copious yield of iodoform with alkaline iodine solution. The distillate yielded 35 grammes of a potassium salt, which by appropriate fractioning was found to consist essentially of acetate, with traces of higher homologues. By far the greater portion of the acetic acid remained in the oxidizing mixture. By extracting the latter with ether, a small quantity of a sirupy acid was obtained, which deposited some crystals. Silver salts were prepared by fractional precipitation, but analysis of these gave no definite formula, and the quantity was too small to attempt to purify further.

The alkaline solutions obtained by extracting the oil during oxidation were united and acidified, whereby a mixture of oily acids separated.[1] It was purified by neutralizing, precipitating the lead salts, dissolving these in ether, and regenerating the acids. Thus treated, it formed a colorless oil of peculiar odor, which adhered very persistently to the person. It was obviously a mixture, and the comparatively small quantity did not admit of separation, but its properties indicated sufficiently to what class of acids its constituents belonged. It dissolved in alkali, but the solution was precipitated by excess of strong alkali, and also by dilution, in case no free alkali was present, whereby a solid acid salt and free alkali were formed. The potassium salt formed a mass of the consistency of soft soap, and foaming strongly with water.

The *barium* salt was a sirup, insoluble in water, difficultly in alcohol, but readily in ether.

The *silver* salt was white, amorphous, and always contained free acid, which could be removed by ether, with partial solution of the salt itself.

The *lead* salt was a pasty, amorphous mass, completely fusing under warm water, and very soluble in ether.

The *ethyl ester*, prepared from the silver salt, was an oily liquid of very pleasant fruity odor.

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[1] Extraction with alkali proved the entire absence of bodies of acid nature in the unoxidized oil.

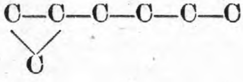
The acid (or rather mixture of acids) is not acted on in the slightest degree by bromine, a fact which distinguishes it sharply from the higher unsaturated fatty acids, such as oleic acid, which it resembles in the solubility of its easily fusible lead salts in ether. It is easily oxidized by chromic acid, forming apparently more volatile acids of the same nature, and acetic acid.

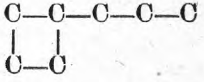
The above properties identify the acids in question with the *petroleum* or *naphthene* acids found by Hell and Medinger[1] in the alkaline waste from refining Wallachian petroleum. The following acids of this series have been isolated:

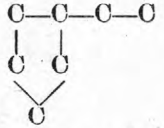
$C_7H_{12}O_2$[2],$C_8H_{14}O_2$[3],$C_9H_{16}O_2$[3].$C_{11}H_{20},O_2$[4],$C_{12}H_{22}O_2$[4],$C_{13}H_{24}O_2$[5],$C_{15}H_{28}O_2$[5].

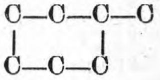
All these acids show the same general properties as those obtained from sandalina. Similar acids were obtained by Schaal[6], who, for technical purposes, oxidized petroleum with air in presence of alkali, the only statement regarding them being that they resemble the oleic acids.

The inertness toward bromine of the acids of the series $C_nH_{2n-2}O_2$, isomeric with the oleic series, is only explainable on the supposition that here, instead of the "double linkage" of carbon atoms, we have saturated or methylene rings. From this has been concluded that, as the naphthenes are hexamethylene derivatives, so also are the naphthene acids associated with them. This conclusion is not entirely justifiable. It has been definitely proved of but very few of the naphthenes that they are hexamethylene derivatives; it has been proved of none of the naphthene acids, and in no case has a proved hexamethylene hydrocarbon been oxidized to a definite acid or mixture of acids of the naphthene series. It is quite possible that some naphthenes as well as some naphthene acids may be tri-, tetra-, or penta-methylene derivatives. The carbon skeletons:









all give hydrocarbons C_7H_{14} and acids $C_7H_{12}O_2$ which would be inert toward bromine. We know a number of such bodies, and we know nothing to preclude their existence in petroleum. We may, however, include them all in the same general class, ***naphthenes***, and with this definition we are justified in inferring the presence of naphthenes in sand-

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[1] Ber. deutsch. chem. Gesell., Jahrg. VII, p. 1216; Jahrg. X, p. 451.

[2] Aschan, Ber. deutsch. chem. Gesell., 1890, Jahrg. XXIII, p. 867.

[3] Ibid, p. 875.

[4] Markownikoff and Ogloblin, J. d. russ. phys. chem. Gesell., 1883, (1) 237, 307; Ber. deutsch. chem. Gesell, Jahrg. XVI, pp. 1873, 1878.

[5] Krämer and Böttcher, Ber. deutsch. chem. Gesell., 1887, Jahrg. XX, p. 598.

[6] D. R. Pat. 32,705; Ber. deutsch. chem. Gesell., 1885, ref. 18, p. 680.

alina from the presence of naphthene acids among its oxidation products. The small quantity obtained is not surprising, remembering that the acids are attacked by chromic acid even more easily than the hydrocarbons, being burned up to acetic and carbonic acids and water. The amount obtained, about 5 per cent, was only that which had momentarily escaped oxidation by solution in the oil, at the four times when the operation was interrupted. By more frequent extractions with alkali, and perhaps other modifications, it might be possible to get a much larger yield, and sandalina would probably be found to consist mainly of naphthenes. Perhaps similar oxidation experiments, made with pure hydrocarbons isolated from petroleum, and with undoubted hexamethylene derivatives, whose constitution has been proved by synthesis or otherwise, would help to confirm the opinion, now resting on a very slender basis, that all naphthenes and naphthene acids contain saturated six-atom carbon rings.

The composition of sandalina, expressed in a formula, $C_nH_{1\cdot74n}$, indicates a larger amount of carbon than is required by C_nH_{2n}. This may well be caused by saturated ring hydrocarbons bearing the same relation to the naphthenes C_nH_{2n} as diphenyl, naphthalene, etc., have to benzene.

The results obtained may be thus summed up. Sandalina is characterized by its peculiar odor, suggesting cedar wood; by the almost total absence of bodies other than hydrocarbons and by the comparative absence of such of these as boil below 230° and above 330° C., these being 3·3 and 11·3 per cent, respectively.

Paraffin wax is absent, and other paraffins, if present, probably only in subordinate quantity.

Unsaturated fatty hydrocarbons do not amount to more than 1 per cent.

Naphthenes are present in large quantity, and probably make up the bulk of the oil. In this respect it is allied to the Russian petroleums.

Naphthene or petroleum acids are formed and may be separated in notable quantity even in a rapidly conducted oxidation with chromic acid. The final products of oxidation are carbonic acid, acetic acid, with traces of higher homologues, and water. Small quantities of acetone were also obtained.

JULY, 1890.

ON A SUPPOSED MINERAL RESIN FROM LIVINGSTON, MONTANA.[1]

By H. N. Stokes.

In the vicinity of Livingston, Montana, there is found, coming from the cracks of the limestone, in masses up to 12 or 15 pounds, an amber-colored substance of resinous appearance. It consists of irregular fragments, very brittle, and easily powdered. The surface, where not broken, appears as if fused. Many of the pieces have a stalactitic form, sometimes opaque, with concentric rings of lighter and darker substance, sometimes quite transparent, in which case a decided green fluorescence is observable. When cool it is odorless, but on heating it fuses and emits an odor suggesting fresh cherry-tree gum. On further heating, the odor suggests that of burning Indian hemp. The voluminous carbonaceous residue burns away easily, leaving a nearly colorless ash, consisting almost wholly of carbonates. An ash determination gave 10·3 per cent., consisting chiefly of calcium and magnesium carbonates, with some silica, phosphoric acid, ferric oxide, and potassium and sodium carbonates. It is insoluble in alcohol, ether, and other solvents, except water, which dissolves it easily and almost completely; and on adding an acid a resinous precipitate is formed, but much organic matter remains in solution. It obviously consists of salts of the above bases, with organic substances of acid nature, and in part, at least, of vegetable origin.

The organic substance obtained by decomposing it with an acid was partly soluble, partly insoluble in water, but almost entirely in alcohol and ether, and was not acted on by Fehling's solution or phenylhydrazine before or after heating. From this may be inferred the absence of gum and of true carbohydrates.

Eighty grammes of the substance were dissolved in hot water, the solution filtered, and barium acetate solution added until no further precipitate formed. This was washed, heated with dilute hydrochloric acid, and the insoluble residue, after washing with water, alcohol, and ether, dissolved in dilute caustic potash, and the highly diluted solution acidified with sulphuric acid. After some time crystalline plates separated, which were purified by redissolving in alkali and acidifying.

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[1] Sent for examination to the Smithsonian Institution by J. C. Vilas, of Livingston.

The yield was about 5 per cent. The substance thus prepared formed colorless, transparent, nearly rectangular plates, with serrated edges, or sometimes crossed prisms. On heating, it decomposed without fusing, giving off white vapors and leaving a porous coal. With sodium and iron solution it gave an intense reaction for nitrogen. The potassium salt was with difficulty soluble in concentrated alkaline solutions, and its solution was precipitated by carbonic acid. On evaporation with concentrated nitric acid it gave a reddish residue, becoming violet with ammonia; on adding caustic potash, this changed to purple. The last, the well known murexid reaction, as well as the other properties, indicated that the substance was no other than *uric acid.* This was confirmed by analysis.

The air-dried substance lost, partly over sulphuric acid, partly at 100°, 11·01 per cent water.

The dried substance gave:

	Found.	Required by $C_5H_4N_4O_3$
C	35·84	35·67
H	2·54	2·38
N	33·39	33·40

Pure uric acid, dissolved in alkali, diluted largely and acidified, gave crystals of exactly the same appearance as those of the substance in question.

It may be well to call attention to the fact that uric acid is always mentioned in the text books as free from crystal water. This is true only under certain conditions. When slowly separated from dilute solution it may contain it. The water found alone corresponds approximately to 1 mol. H_2O (calculated 9.68 per cent). In an apparently forgotten observation of Fritzsche[1], 2 mol. H_2O were found.

The filtrate from the barium urate precipitate was precipitated by an excess of lead acetate, and the filtrate from this again precipitated by basic lead acetate. The two precipitates thus obtained showed such similar properties that they may be considered together. They were decomposed under alcohol by hydrogen sulphide, and the alcohol boiled off, with gradual addition of water, which caused the deposition of a resinous substance which became very strongly electric when pulverized. Nitric acid oxidized it with formation of yellow nitro products. The aqueous solution from which this had separated left a vitreous mass on evaporation, which was largely soluble in water. By repeated extractions with hot water this was separated into a part easily soluble and one almost insoluble in water, but both soluble in alcohol and ether, and forming amorphous brownish masses. The substance soluble in water gave oxalic acid when oxidized by nitric acid. Analyses failed

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[1] Liebig's Annalen, vol. 32, p. 315.

to throw any light on the nature of these substances. The easily soluble substance contained :

C	56·88
H	6·39
N	2·88

It seems that these bodies, which make up the bulk of the substance in question, belong to the class of humus substances of which so little is understood and the properties of which rendered it useless to attempt anything further with these. The substances, fused with caustic potash, gave a solution which, after acidifying, was turned green by ferric chloride and red by subsequent addition of alkali, a reaction characteristic of protocatechuic acid, a usual product of the action of fusing potash on humus bodies.

The filtrate from the lead acetate precipitates, after throwing down the excess of lead with sulphuric acid, was many times shaken out with ether. The ether left, on evaporation, a transparent gummy mass, in which, after some time, well defined crystals appeared. On treatment with chloroform the amorphous substance dissolved, and the residual crystals were several times recrystallized from water with aid of animal charcoal. The substance, of which only a few decigrammes were obtained, formed fine white needles, and was strongly nitrogenous. Having found uric acid, this body at once suggested *hippuric acid.* That it was this is shown by comparison of the two :

Body in question.	*Hippuric acid.*
Needles, fusing at 187° ; soluble with difficulty in cold water ; soluble in alcohol ; insoluble in chloroform.	Needles, fusing at 187.5° ; soluble with difficulty in cold water ; soluble in alcohol ; insoluble in chloroform.
Decomposed by strong hydrochloric acid, giving benzoic acid ; recognized by its fusing point, 121°, and other properties, and an easily soluble sweet body.	Decomposed by strong hydrochloric acid into benzoic acid and glycocoll.

The remaining substance, less than 0.07 gramme, gave the following result on combustion :

	Found.	Required for $C_9H_9NO_3$.
C	61.73	60.33
H	5.88	5.03

The agreement is as close as could be expected with the small amount available for analysis.

The occurrence of two such characteristically animal products as uric and hippuric acids, together with substances of vegetable origin combined with lime and magnesia and forming stalactitic exudations from limestone, is easily explained. The mixed products of animal and vegetable life of acid nature soaking through the rock have combined with lime and magnesia, forming easily soluble salts which have been left on emerging by the evaporation of the water, forming this clear, amber-like substance, which shows no outward evidence of its connection with excremental materials.

JULY, 1890.

PRELIMINARY NOTE ON THE COEFFICIENTS OF THERMAL EXPANSION OF CERTAIN ROCKS.

By William Hallock.

The object of the present paper is to give only an outline of the aim and progress of the investigation which is being carried on in the physical laboratory of the U. S. Geological Survey for the purpose of collecting data as to the thermal expansion of all such rocks as may be interesting from a scientific or an economic point of view. Such an undertaking may never be called finished, and for this reason a report from time to time may be desirable.

It is hoped that the present investigation may be made more complete than previous ones by the addition of the complete chemical and microscopic petrographic analyses of each stone examined, such analyses being made by the corresponding branches of the Survey.

As regards the purely physical portion of the work the point of prime importance is the determination of the mean coefficient of expansion for ordinary ranges of temperature. Of minor, but sufficient, interest is the examination of any peculiarities, such as expansion differing in different directions coordinate to the bedding or cleavage planes of the rocks; behavior dry, saturated with water, and in their natural state, and perhaps other questions.

METHODS.

The imagined difficulty of obtaining bars of stone long enough and of sufficiently small cross section for convenient examination, combined with the existence in the National Museum of hundreds of cubes of various stones which seemed available for a determination of the coefficient of cubical expansion, and the apparent simplicity and compactness of the latter method, led to the attempt to obtain at least preliminary values of the mean coefficient by the displacement or pycnometer method.

With a view to using the 4-inch cubes collected by the Tenth Census and stored in the National Museum a cubical cast-iron box was constructed of a similar design to the cylindrical one soon to be described. Owing to the sharp corners and imperfect fit of the cover it was practically impossible to get this box air tight and perfectly filled with mercury. This fact, combined with the experience that the cubes would necessarily be more or less defaced and rendered unsuitable for exhibition, led to the abandoning of the cubical and the adoption of the cylindrical form, preparing our own samples from selected sources.

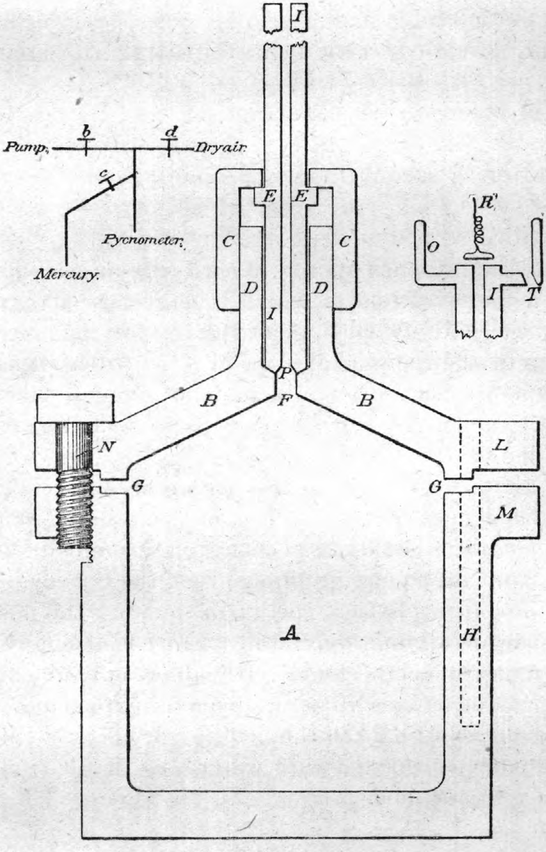

FIG. 4.—Pycnometer.

A vertical section of this design of pycnometer is given in Fig. 4. A[1] is a cylindrical box 3·2 inches in diameter and 3·2 inches high inside measurement. The walls are 0.5 inch thick and are constructed with a broad flange M and shoulder G at the top. The cover B having a corresponding flange L and shoulder G, is held to the box by six bolts, as shown at N. The opening in the tubulure D contracts by a conical seat P to the passage F. A cap C screws down over D, catching the flange E, and holding the tube I firmly into its conical seat at P. The lower end of I and its seat in B at P, are ground to a fit, as are also the cover and box on the shoulder G. A hole H runs down into the wall

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[1] This box was very nicely made by the American Tool and Machine Company, of Boston, Massachusetts.

of the pycnometer, and in it is placed the thermometer, surrounded by mercury. This whole vessel is in turn shut up in a second iron box, where it can be maintained at certain constant temperatures by surrounding it with vapors, as ether, methyl and ethyl alcohol, water, etc., with suitable appliances for establishing a continuous condensation of the vapor after use and returning it to the boiling reservoir. Of course, the thermometer and tube I extend through the lid of the vapor bath, and through the coating of asbestus felt with which it is surrounded.

The method of operating this apparatus is as follows: The cover B is screwed on, the joint at G being treated with a little powdered graphite. The tube I is connected to a sprengel pump by a system of tubes shown in the upper left corner of Fig. 4. The pycnometer is evacuated and filled with dry air several times; then while *a* remains closed it is once more pumped out and the valve *b* closed, whereupon by opening *c* the mercury rushes in and fills the space A completely, as well as the tube I. The whole apparatus is then put into the bath box and the cup O screwed onto the top of I. With a small platinum spoon, mercury is filled into I until it stands convex above the top; it is then "struck" off by pressing the plate R down on top of the tube, the overflow being always caught in the same little flask and weighed. This operation may be repeated as often as desired to obtain check readings at the same temperature, of course, refilling I each time out of the weighing flask. With practice and care such readings in extreme cases need not vary 5 milligrammes. The thermometer in the hole H gives the temperature of the materials. Such readings are made at various temperatures, and from the overflow of mercury, assuming the coefficient of mercury as known, it is possible to calculate the coefficient of iron, since the weight of the mercury gives us its volume. In order to determine the coefficient of any given rock, a sample is prepared, which should, as nearly as possible, fill the pycnometer; it is placed in the box, the cover bolted on, and the unoccupied space filled with mercury as before. The remaining operations are identical with those when the pycnometer contained only mercury. The volume of the mercury surrounding the stone, is deduced from its weight, and subtracted from the volume of the pycnometer, gives the volume of the stone. Then knowing the coefficient of the mercury and iron, and the volumes of the stone, iron, and mercury, and the apparent coefficient of the stone and mercury in the iron, a simple calculation gives the coefficient of expansion of the stone alone. The linear coefficient is practically one-third the cubical.

In order to test the speed with which the temperature penetrated such a block of stone, and the justice of assuming that a thermometer in H gave with sufficient accuracy the temperature of the stone, the following experiments were made: A block of marble[1] cut to fit the pycnometer was bored axially to receive a fire-clay tube, with two small bores carrying one joint of a thermo-element whose other joint was tied to the thermometer bulb in the mercury in H. The arrangement of the inner juncture will be understood from Fig. 5. A is the block of stone, B the clay tube, E the wires of the thermo-element, and C their juncture. B is cemented into A, and the space around C is filled with mercury, whose temperature must penetrate from the sides of A. This block was put into the pycnometer and surrounded with mercury, using a special cover in place of B, Fig. 4. Electrical determinations gave at any moment the difference in temperature between the two junctures, i. e., between the thermometer bulb and the center of the marble block. A series of observations was made, heating the vessel as rapidly as possible in a steam bath. From these data it appears that the difference in temperature, at a given instant, inside the marble and on the thermometer never exceeded 10° or 12° C., which of course occurred during the most rapid portion of the rise in temperature. It also appears that during the rapid rise the interior reached a given temperature between 4 and 5 minutes after the thermometer. Of course this period became longer as the difference of temperature became less. These results convinced me that after 30 to 60 minutes the thermometer gave the temperature of the whole stone within the limits of other errors.

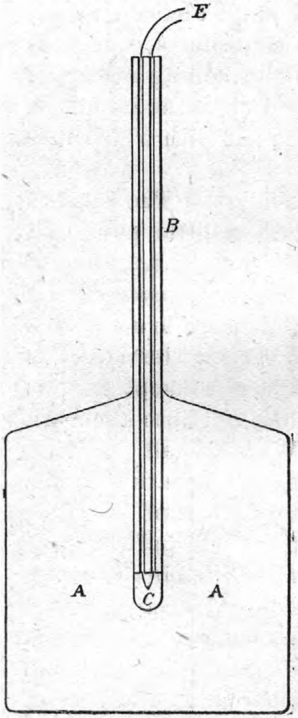

FIG. 5.—Apparatus for measuring penetration of temperature.

This method of obtaining the coefficient of cubical expansion was tried upon a Cockeysville (Maryland) marble, an obsidian from the Yellowstone National Park, and a Berea (Ohio) sandstone. The mercury penetrated the porous sandstone to such an extent that it was impossible to make any readings. In the case of the marble and obsidian fair values were obtained, but there seemed to be some uncertainty as to their behavior, and even with these stones it seemed almost impossible to completely eliminate air and moisture from the sample, either of which vitiated the results. There seemed also a source of error arising from the differences of "fit" of the mercury to the stone at high and low temperatures. In other words, the mercury when hot seemed to penetrate more perfectly into the angular cavities in the uneven surface of the stone. These objections might be overcome, and I hope at some time fully to investigate them; but they more than coun-

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[1] A Cockeysville marble, kindly furnished by Hugh Sisson & Sons, of Baltimore, Md.

terbalanced the expected simplicity and quickness of the method, and led to its temporary abandonment, a step urged, too, by the necessary limitations of the method to the determination of the coefficient of cubical (mean) expansion of especially compact and dry stones.

It was my desire from the first to measure directly the linear coefficient of at least the most interesting specimens, especially sets of three cut in directions coordinate to the bed plane. For this purpose a comparator was purchased of the Société Genévoise, of the usual form made by them, with some slight variations. Fig. 6 may serve as a diagramatic sketch of the comparator and attachments on a vertical section through one microscope. A heavy cast iron base A is furnished with a longitudinal projection on the back which is planed true and carries the sliding clamps B. Two upright posts D carry the counterpoise and arm E through which runs the microscope F. Parts of the bed plate A are cut transversely, forming a track for the car G; these tracks I extended by bolting on bars C so that the car could be removed at least one and a half feet from the bed A. Suitable guides and stops insured the return of the car to its proper place under the microscopes. This car G carried the bath KK surrounded by the box and asbestus felt H. The bar to be measured M rests on rollers L on a T bar I which is furnished with screws for the various necessary adjustments. N is a block of plate glass lying on the divisions and extending above the surface of the water, thus always allowing a reading without readjustment of the microscope and undisturbed by dirty water. Each of the microscopes is furnished with Ramsden micrometer ocular and 2-inch

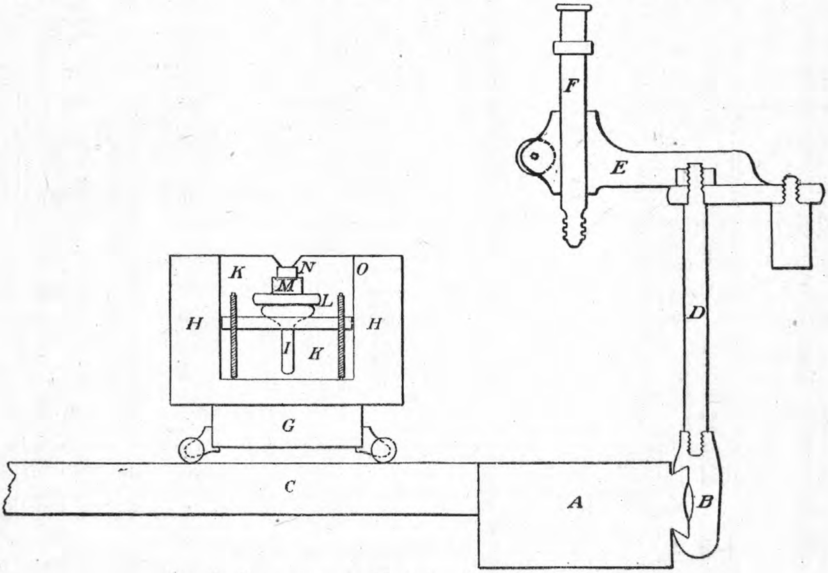

FIG. 6.—Comparator used in determining rock expansions.

objective. The car and bath are allowed to stand over the bed plate only long enough for a series of readings and then removed and a screen put up between them so the temperature of the bed remains independent of the temperature in the bath K.

The ocular micrometer screws are four threads to the millimeter, and the head is divided to fifty parts. The enlargement of the objectives is about three times, hence a whole division on the head $=\frac{1}{50}\times\frac{1}{4}\times\frac{1}{3}=\frac{1}{600}$mm on the bar, hence a theoretical accuracy of $\frac{1}{1000}$ is readily obtainable. Two thermometers bedded in mercury and covered with asbestus, one on the bed over A, the other against the back in the hollow opposite B, served to give the temperature of the comparator which always remained nearly constant at room temperature. Two other thermometers gave the temperature of the bath KK. These thermometers were divided to $\frac{1}{5}$° C., giving thus about $\frac{1}{20}$° to $\frac{1}{40}$° C. The extremes of temperature were about 20° and 100° C, thus the relative accuracy was about $\frac{1}{30}\times\frac{1}{80}$ or $\frac{1}{2400}$ or 0.04 per cent as regards temperature. A brass bar expands for 80° C. about 1.3mm; this measured with the micrometer accuracy of $\frac{1}{1000}$mm gives a relative accuracy of 0.08 per cent as regards length. Roughly, then, the theoretical limit of relative accuracy is not far from 0.1 per cent. Of course it would be less if the bar expanded less.

With this apparatus the coefficient of a standard brass bar was determined, as well as that of the iron bedplate, and of a standard meter belonging to the Physical Laboratory. It is intended to check many of the relative determinations by this absolute method, especially where any peculiar behavior occurs in a sample, or any one to which particular interest attaches.

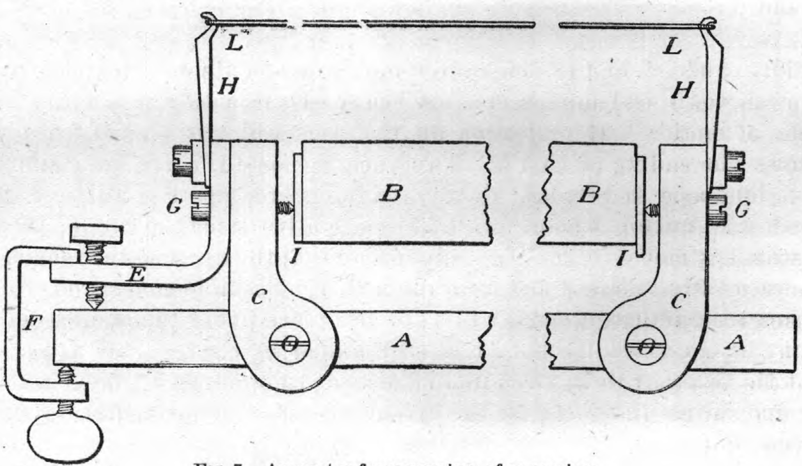

FIG. 7.—Apparatus for comparison of expansions.

In most cases a relative method will be employed and the rocks compared with the standard brass bar above mentioned. Fig. 7 is a plan of the apparatus for these relative determinations. A is the standard brass bar 110 centimetres long, and 1.4 centimetres square; B is the bar of stone 92 centimetres long and about 3 centimetres square; D is the stationary arm or lever held in place by the foot and adjusting screw E, and clamp F. The screw G, through D, ends in a blunt point, against which rests the glass plate I and the bar B. The method of fastening the levers D and C to the bar A is shown in Fig. 8. In the lever C the screw G is the counterpart of that in D. The extensions HH of C and D carry the wire L which is furnished with a spiral spring in the center, serving to hold the lever C snug against the glass and bar, and these in turn against the glass and screw in D. Thus, as the two bars expand or contract, the lever C, rotating around the center of the screw O, follows the relative changes of length. In Fig. 8 the parts are lettered as in Fig. 7. The screw O has a 60° point, N, as also the upright, T; these fit into center-punch marks on the bar A, so that when T is screwed down snug and clamped with the nut P, the lever is firmly held and yet free to rotate around the axis of T and O. The upper end of T carries a head R, which holds the mirror M. The clamp nut P allows the head to be fastened in any azimuth on T and the screws and spring Q allow slight adjustments of the mirror. The whole combination is hung in a water bath, one end of A being rigidly clamped, and its remaining parts rest on rollers. The stone bar is swung on spiral springs between the screws G, and has perfect freedom of motion. The upper part of T projects above the bath and allows the reading of the rotation of the mirror in the usual method with telescope and scale. The lever D carries a similar upright with head and mirror which furnishes the correction in case the whole system has moved. The long copper water bath is heated by a burner under its whole length and is protected on its sides with asbestos felt. When the bars are in place, the bath is covered with sheet lead and many layers of woolen blanket, nothing appearing above the blanket but the two mirrors and two thermometers. Appropriate inlet and outlet and gauge enable the apparatus to be run for many hours at any given temperature, nearly constant.

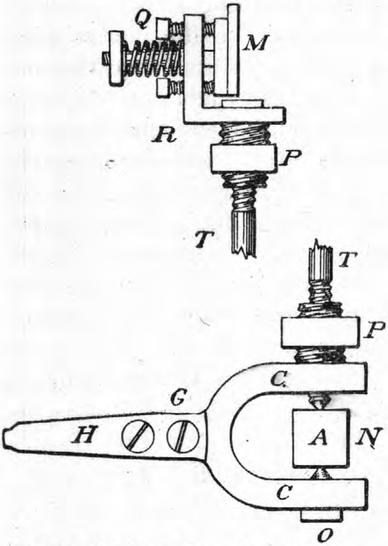

FIG. 8.—Portion of preceding apparatus.

MATERIALS.

In order to test the apparatus and determine its capabilities, as well as in view of their possible economic interest, several samples of commercial stones were investigated. They also possessed the advantage of being easily obtained in convenient shape. The local dealers, however, could not furnish samples three feet long and one inch thick, less than three or four inches wide. Consequently I rigged a saw in the laboratory shop and each such piece was cut into three available pieces, three feet long and a little over one square inch section.

In this way the following samples[1] were cut out and determined:

I. A slate from the Lake Shore quarry near Hydeville, Vermont. It is compact and fine, of a purplish color slightly mottled with green. Sample is cut parallel to the cleavage.

II. A marble from Rutland, Vermont, fine grained, apparently cut parallel to bedding plane and striated with seemingly thin strata of alternatingly light and dark material.

III. A marble from Knoxville, Tennessee, rather fine grained, pinkish marble of the "Tennessee" type.

IV. A marble, "Keowa," from the Happy Valley quarry, Georgia, medium grained, pinkish, mottled, and containing numerous masses rich in mica, *very* lacking in homogeneity.

V. A marble, "Creole," from the Happy valley Quarry, Georgia, coarse, even grained, largely mottled with blackish masses.

VI. A marble, "Cherokee," from the Happy Valley quarry, Georgia, very coarse, even-grained, nearly pure white.

As soon as possible oriented sections will be cut from these bars, and ground and microscopically examined.

The following analyses were made in the chemical laboratory of the Survey by Mr. L. G. Eakins.

The Roman numerals heading the vertical columns designate the corresponding sample above described.

	I.	II.	III.	IV.	V.	VI.
	Per cent.	*Pr. cent.*	*Pr. cent.*	*Pr. cent*	*Pr. cent.*	*Pr. cent.*
SiO_2	58·15	....	·17	2·23	....	....
TiO_2	·93	....	....	....	....	....
Al_2O_3	18·93	·39	·04	·91	·17	·15
Fe_2O_3	2·91	....	·23	·22	....	....
FeO	5·64	·14	....	....	·05	·06
MnO	·07	....	....	....	....	....
CaO	·60	50·79	55·47	52·16	53·91	53·69
MgO	2·70	trace	·30	2·09	·83	·83
K_2O	3.92	....	....	....	....	....
Na_2O	1·17	....	....	....	....	....
H_2O	4·56	1·01	·21	·45	·13	·17
P_2O_5	·12	....	....	....	....	....
SO_3	·16	....	....	....	....	....
CO_2	....	39·80	43·63	42·22	43·16	43·13
Insoluble	....	8·00	....	....	1·84	2·01
	99·86	100·13	100·05	100·28	100·09	100·04

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[1] All the samples were furnished by J. F. Manning, Washington, D. C.

Analyses of insoluble parts of II, V, and VI.

SiO_2	....	56·69	....	....	58·21	55·48
Al_2O_3	....	31 16	......	....	7·37	15·58
FeO	....	2·13	....	....	·31	trace
CaO	....	2·68	....	....	12·53	14·52
MgO	....	3·27	....	....	20·42	12·88
		Alkalies present undetermined.				
		95·93			98·84	98·46

The coefficients of linear thermal expansion of these samples is given below:

Standard brass bar	0·00001866
I	0088
II	00659
	*00661
III	00495
	00525
IV	00348
	00309
V	0110
VI	00740
	00786
	00855

From an examination of the above duplicate determinations it will be seen that, owing to the small coefficient of the stone compared with the brass, the absolute errors make a considerable relative error in the coefficients of some of the stones. In future better results are expected from the improved state of the apparatus, and also from absolute determinations by the comparator above described.

A peculiar phenomenon was developed in the later determinations on marbles, notably the Vermont and Knoxville samples. Being heated for the first time to 100° C. and allowed to cool, they did not contract to their original length, and the next two or three heatings resulted in continued but ever diminishing increments of length at ordinary temperatures; finally a permanent condition was reached, but not until the bar was 0·2 to 0·3mm longer at ordinary temperatures than originally. The length at 100° C. was practically constant from the first. These observations will be further tested and repeated in subsequent investigations.

A series of observations was made to determine the relative length of a bar in its natural condition, dry and saturated. The Vermont second sample was used. The bar had been lying twenty days in the laboratory when it was placed in the copper bath, which had been emptied and carefully dried. The length of the bar was accurately determined in this condition. Dishes containing concentrated sulphuric acid were next introduced, and the bath covered with glass and paraffine paper

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* The duplicate values are always from different bars of the same stone.

and sealed tight with paraffine. In this way the bar was gradually dried in a dry atmosphere. After several days the acid was removed and the bath filled with water. The accompanying curve shows the lengths reduced to the same temperature. From the curve it will be seen that the marble contracted on drying, and expanded on soaking full of water, the elongation amounting to about 0.0001.

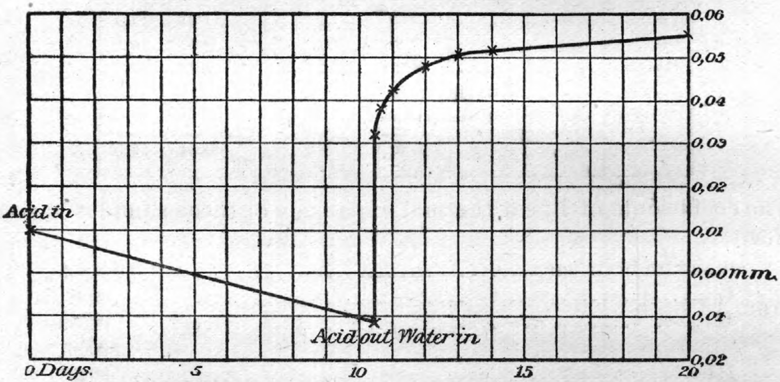

FIG. 9.—Diagram showing expansion of a bar of marble on wetting.

So many questions still need investigating and so many points must still be considered as not sufficiently established, that it seems best to leave all discussions and speculations until more abundant and better data are available.

MISCELLANEOUS ANALYSES.

ASTROPHYLLITE.

From El Paso County, Colorado.

[Analysis by L. G. Eakins.]

SiO_2	35·23
TiO_2	11·40
ZrO_2	1·21
Ta_2O_5	·34
Fe_2O_3	5·61
Al_2O_3	trace.
FeO	27·33
MnO	5·52
CaO	·22
MgO	·13
K_2O	5·42
Na_2O	3.63
H_2O	4·18
	100·22

BROWN HORNBLENDE.

From Pierrepont, New York. Specimen collected by G. H. Williams.

[Analysis by T. M. Chatard.]

H_2O at 110°	·05
H_2O at red heat	2·41
SiO_2	56·44
TiO_2	·11
P_2O_5	trace.
Al_2O_3	1·77
Fe_2O_3	·84
FeO	·73
MnO	·11
CaO	11·83
MgO	22·98
Na_2O	2·13
K_2O	·75
	100·15

KYANITE.

A pale green variety, intimately associated with the dumortierite from Clip, Arizona.

[Analyzed and collected by W. F. Hillebrand. Sp. gr., 3·656, 18°.5.]

SiO_2	36·30
TiO_2	
Al_2O_3	62·51
Fe_2O_3	·70
FeO	undet.
CuO	trace.
F	none.
B_2O_3	none.
Ign	·40
	39·91

Titanic acid is present in appreciable amounts, but was not separated from alumina. The mineral contained a few black, non-magnetic grains which may have carried the titanium.

LIEBENERITE ?.

A massive white mineral from the Brown tin mine, Rapid City, South Dakota.

[Analyzed by W. F. Hillebrand and E. L. Howard. Lime and magnesia not looked for.]

SiO_2	43·62
Al_2O_3	40·38
MnO	trace.
K_2O	10·20
Na_2O	1·12
H_2O	4·94
	100·35

KAOLIN.

A. From Garland County, Arkansas, 14 miles from Hot Springs.

B. From Greenville, Alabama. Contains fragments of quartz, feldspar, and mica.

C. From Georgia side of Savannah River, near Augusta.

[Analyses A (partial) by L. G. Eakins, B by T. M. Chatard, C by H. N. Stokes.]

	A.	B.	C.
H_2O	15·65	6·78	4·16
SiO_2	46·22	69·84	75·73
Al_2O_3	35·20	19·91	16·49
Fe_2O_3	....	·90	1·31
MnO	....	trace	....
CaO	....	·07	none
MgO	....	·28	·61
K_2O	....	2·14	undet.
Na_2O	....	·21	undet.
	97·07	100·13	98·30

PICRALLUMOGENE.

An aluminum sulphate, near picrallumogene in composition, from the vicinity of Las Vegas, New Mexico.

[Analysis by W. F. Hillebrand.]

Al_2O_3	9·71
MnO	·06
MgO	6·75
Na_2O	2·09
K_2O	·28
H_2O	43·75
SO_3	37·51
	100·15

BROCHANTITE.

From the United Verde mine, Jerome, Yavapai County, Arizona.

[Collected and analyzed by W. F. Hillebrand.]

CuO	69·45
PbO	·04
CaO	trace
Fe_2O_3	·28
P_2O_5	trace
H_2O	12·05
SO_3	16·75
CO_2	·71
Insoluble	·70
	99·98

KERATOPHYR FROM MARBLEHEAD NECK, MASSACHUSETTS.

[Received from J. E. Wolff, analyzed by T. M. Chatard. A, rock; B, separated feldspar.]

	A.	B.
H_2O at 110°	·91	·04
H_2O at redness	1·28	·37
SiO_2	70·23	65·66
TiO_2?	·03	undet.
P_2O_5	·06	undet.
Al_2O_3	15·00	20·05
Fe_2O_3	1·99	trace
FeO	undet.	trace
MnO	·24	·13
CaO	·33	·67
MgO	·38	·18
K_2O	4·99	6·98
Na_2O	4·98	6·56
	100·42	100·64

WEBSTERITE FROM NORTH CAROLINA AND MARYLAND.

Received from G. H. Williams. A, the rock from Webster, North Carolina, formerly supposed to be saxonite. B, from Hebbville, Maryland. C, bronzite from B. D, diopside from B.

[Analysis A, by E. A. Schneider; B, C, D, by T. M. Chatard.]

	A.	B.	C.	D.
SiO_2	55·14	52·55	54·53	51·80
TiO_2	trace	·14	undet.	·13
P_2O_5	·23	trace	trace	trace
Al_2O_3	·66	2·71	1·93	2·21
Fe_2O_3	3·48	1·27	1·70	1·29
Cr_2O_3	·25	·44	·30	·51
MnO	·03	·24	·28	trace
FeO	4·73	4·90	8·92	3·50
NiO	·11	....	....	....
MgO	26·66	20·39	29·51	17·76
CaO	8·39	16·52	2·25	20·99
K_2O	....	·27	....	undet.
Na_2O	·30		....	undet.
H_2O	·38	1·09	1·14	·65
	100·36	100·52	100·56	98·84

FELDSPARS FROM MINNESOTA GABBROS.

Received from C. R. Van Hise. A, from NW. $\frac{1}{4}$ of SE. $\frac{1}{4}$ of Sec. 23, T. 62 N., R. 10. B, center of Sec. 25, T. 64 N., R. 8. C, Duluth and Iron Range Railroad.

[Analyses by W. F. Hillebrand.]

	A.	B.	C.
SiO_2	52·50	52·61	53·45
TiO_2	trace	trace	trace
Al_2O_3	30·15	29·80	29·77
Fe_2O_3	·47	·57	·33
FeO	·15	·23	·15
MnO	....	trace	....
CaO	12·82	12·25	11·33
MgO	·10	·20	·11
K_2O	·53	·53	·68
Na_2O	3·72	3·80	4·33
Ignition	·25	·29	·23
	100·69	100·28	100·38

ERUPTIVE ROCK FROM MONTANA.

From Bear Creek, Madison County.

[Collected by A. C. Peale, analyzed by T. M. Chatard.]

H_2O at 110°	·84
H_2O at red heat	3·50
SiO_2	49·13
TiO_2	·42
P_2O_5	·38
Al_2O_3	9·05
Cr_2O_3	·39
Fe_2O_3	3·57
FeO	5·05
MnO	·15
NiO	trace
BaO	·05
CaO	5·68
SrO	none
MgO	17·21
K_2O	2·24
Na_2O	2·01
	99·67

ROCKS FROM CALIFORNIA.

Series collected in sandstone dikes of northern California, by J. S. Diller.

A. From sandstone vein on Salt Creek.
B. Middle Fork of Cottonwood.
C. Vein 1¼ miles below Ono Bridge.
D. 1½ miles up Byron Creek.
E. From Ono.

[Analyses by T. M. Chatard.]

	A.	B.	C.	D.	E.
H_2O at 110°	·78	1·13	·46	·64	·55
H_2O red heat	1·78	2·99	3·27	2·83	
CO_2	12·73	4.97	10·36	·72	....
SiO_2	48·13	55·85	48·10	67·62	68·10
TiO_2	·24	·76	·47	·48	·35
P_2O_5	·14	·18	·13	·08	·18
Al_2O_3	11·19	13·20	12·16	13·63	15·18
Fe_2O_3	1·25	2·56	1·02	1·25	1·34
FeO	1·47	4·77	2·14	3·27	1·70
MnO	·29	·24	·26	·15	·20
CaO	16·39	6·93	15·88	2·80	4·66
BaO	·04	undet.	undet.	·03	·06
MgO	2·22	1·90	1·65	2·34	2·06
K_2O	1·17	1·89	1·56	1·11	1·48
Na_2O	2·29	2·60	2·46	2·78	3·71
	100·11	99·97	99·92	99·73	99·57

Series from Mount Diablo.

A. Red shale.
B. Jasper.
C. Brown shale.
D. Bastite.
E. Gabbro.

[Analyses by W. H. Melville.]

	A.	B.	C.	D.	E.
H_2O at 105°	1·03	·21	8·74	·94	1·20
H_2O ignition	2·92	·72		12·43	1·83
SiO_2	69·98	93·54	45·64	36·57	47·49
P_2O_5	·05	....	·27	....	trace
CO_2	....	....	4·59	....	....
Cr_2O_3	....	....	·12	.33	....
Al_2O_3	11·69	2·26	15·42	·95	15·81
Fe_2O_3	6·23	·48	3·40	7·29	1·07
FeO	1·08	·79	3·73	·37	4·50
NiO	....	....	....	·31	·06
MnO	·49	·23	·33	·10	·41
CaO	·38	·09	8·11	·14	15·53
MgO	1·29	·66	4·62	40·27	10·39
Na_2O	3·72	·51	3·13	·31	1·16
K_2O	·73	·37	1·86	trace	trace
	99·59	99·86	99·96	100·01	99·45

SANDSTONE FROM ARIZONA.

A brown building stone from the Arizona Sandstone Company's quarries at Flagstaff.

[Analysis by T. M. Chatard.]

Insoluble in HCl	79·15
Soluble SiO_2	·04
Al_2O_3	1·30
Fe_2O_3	2·45
CaO	7·76
MgO	·23
CO_2	5·77
H_2O at 110°	·32
H_2O at red heat	2·94
	99·96

LIMESTONE FROM KANSAS.

A light-brownish, fossiliferous marble from Iola.

[Analysis by H. N. Stokes.]

$CaCO_3$	97·94
$MgCO_3$	1·07
Fe_2O_3	·29
Sand and clay	·86
H_2O	·04
	100·20

FIVE CHEROKEE LIMESTONES.

Collected by W. P. Jenney in the lead-zinc region of southwest Missouri and vicinity.

A and B. Quarries near Seneca, Newton County, Missouri.

C and D. From near Grand Falls, Newton County, Missouri.

E. Quarry on Short Creek, near Spring River, Cherokee County, Kansas.

[Analyses by L. G. Eakins, the carbonic acid being found by calculation from the bases.]

	A.	B.	C.	D.	E.
CaO	55·29	54·92	54 98	55·11	55·25
MgO	·23	·20	·31	·32	·35
Al_2O_3	·11	·13	·08	·13	·17
FeO	·05	·07	·05	trace	·20
MnO	trace	trace	·03	trace	·02
Insoluble	·66	1·21	1·01	1 01	·32
CO_2	43·69	43·31	43·54	43·65	43 79
	100·03	99·84	100·00	99·22	100·10

ORES OF IRON.

Series from Virginia, in or near Craig County.

A. McCortney opening, Mill Creek, between Little Mountain and Bailey's Mountain.

B. Red slate ore, top of Bailey's Mountain.

C. Robinson mine, 600 feet above valley, near Houston Station, Shenandoah Valley Railroad.

D. Grace Furnace mine.

[Analyses by L. G. Eakins.]

	A.	B.	C.	D.
Fe	45·01	33·31	49·52	54·45
Mn	1·17	·77	·36	·16
P	·39	·036	·34	·15
S	·21	·18	·14	.28
H_2O	11·54	8·83	10·33	11·19
Insoluble	18·01	37·96	13·39	7·18

Series from North and South Carolina.
A. From Troy, North Carolina.
B. Marietta, South Carolina.
C. Abbeville County, South Carolina.

[Analyses by L. G. Eakins.]

	A.	B.	C.
Fe	49·96	48·44	52·96
Mn	·92	....	none
P	·04	·07	·94
S	·04	·03	·05
H_2O	15·25	....	....
Insoluble	7·10	9·32	4·62

Series from Georgia and Alabama.
A and B. From Bartow County, Georgia.
C, D, and E. Round Mountain, Alabama.
  C. "Red Bank."
  D. "Ford Tunnel."
  E. "Furnace Tunnel."

[Analyses by L. G. Eakins.]

	A.	B.	C.	D.	E.
Fe	65·73	56·24	58·34	55·13	58·56
Mn	none	none	·10	·16	none
P	·03	·13	·209	·731	·212
S	....	·14	·043	·108	·079
H_2O	·19	12·90	....	....	....
Insoluble	4·63	3·28	9·73	11·28	9·59

Ore from Kentucky. Entry No. 3, Thacker Ridge, near Fitchburg, Estill County:

[Analysis by L. G. Eakins.]

SiO_2	9·41	
Al_2O_3	6·45	
Fe_2O_3	64·79 =	45·35 Fe.
MnO	1·98 =	1·53 Mn.
CaO	3·15	
MgO	·46	
H_2O	11·70	
P_2O_5	2·00 =	0·87 P.
SO_3	·16 =	·06 S.
As	none	
Ti	none	
	100·10	

From Kettle Island, branch of Straight Creek, six miles above Pineville, Bell County, Kentucky:

[Analysis by E. A. Schneider.]

Fe	46·46
Mn	·47
P	1·02
S	·62
Insoluble	4·37

Ores from Tennessee. Samples from Balsam Hollow, three miles west of Cumberland Gap, Claiborne County:

[Analyses by E. A. Schneider.]

	Top.	Middle.	Bottom.
Fe	53·00	35·50	34·60
Mn	·19	·55	·21
P	·24	·23	·40
S	none	·14	·13
Insoluble	21·26	41·53	10·64

Hematite nodule. From near Coyote, Mora County, New Mexico:

[Analysis by E. L. Howard.]

Fe	65·22
P	trace
S	·10
SiO_2	2·51

ORES OF MANGANESE.

From Virginia.

A. Round Head tract, near Marksville, Page County.

B. Trotter property, southeastern part of Augusta County.

[Analysis A by E. A. Schneider, B by L. G. Eakins.]

	A.	B.
Mn	51·46	14·38
Fe	2·94	6·87
Co	....	·10
P	·23	·760
S	....	·077
SiO_2	4·17	*62·53
H_2O	4·97	....

*Insoluble matter.

From Kentucky. Top of Cumberland Mountain, at Lewis Gap, three miles east of Cumberland Gap, Bell County:

[Analysis by E. A. Schneider.]

Mn	59·67
Fe	1·13
P	·24
S	none
Insoluble	1·63

From Tennessee.
A, 7 miles south of Johnson City.
B, small ridge near Johnson City.

[Analyses by L. G. Eakins.]

	A.	B.
Mn	48·51	37·12
Fe	·79	1.67
Cu	trace.	trace.
Co	1·08	1.26
P	·154	·130
S	·066	·088
Insoluble	5·50	20 40

From Bartow County, Georgia.

[Analyses by L. G. Eakins.]

Mn	44·81
Fe	9·51
Co	·35
P	·196
S	·080
Insoluble	1·85

TWO COALS FROM WEST VIRGINIA.

Near railroad from Grafton to Philippi, in Barbour County.

[Analyses by L. G. Eakins.]

	Top.	Bottom.
Fixed C	61·07	59·06
Volatile matter	32·23	33·96
Moisture	1·14	1·10
Ash	5·56	5·88
	100·00	100.00
Ash	White.	White.
Coke	Friable.	Friable.

WATER FROM WEBSTER GROVE, MISSOURI.

A spring 10 miles due west from the center of St. Louis.

[Analysis by W. F. Hillebrand and E. S. Howard. Stated in parts per million.]

SiO_2	26·4
$Al_2O_3 + Fe_2O_3$	2·6
CaO	135·6
MgO	21·2
Na_2O	20·2
K_2O	1·5
SO_3	15·4
Cl.	11·0
N_2O_5	15·3
Combined CO_2	104·5
	353·7
Less O=Cl	2·5
	351·2
Total CO_2	109·5
Albumenoid NH_3	·01
Free NH_3	·08

BRASS.

Used in standards of the United States Bureau of Weights and Measures.

[Analysis by W. F. Hillebrand. The estimations of Pb, Bi, and As are approximations only.]

Cu	76·50
Zn	21·99
Pb	·58
Bi	·26
As	·12
Fe	·18
Sn	trace ?
	99·63

INDEX.

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