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REPORT OF WORK DONE

IN THE

DIVISION OF CHEMISTRY AND PHYSICS

MAINLY DURING THE

FISCAL YEAR 1890-'91

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LETTER OF TRANSMITTAL.

SIR: In accordance with established usage, this bulletin, like its predecessors, bulletins 9, 27, 42, 55, 60, 64, and 78, contains a record of work done in the division of chemistry and physics during a fiscal year. It is, however, incomplete in certain respects; for unfinished investigations are not described, and the larger researches are reserved for independent publication. The physical studies of Dr. Barus, for example, and the work of Dr. Chatard upon the Florida phosphates, will appear in separate form; and many analyses of value which have been made in the chemical laboratory are to be published in the geological reports with which they properly belong. The bulletin, however, in spite of omissions, gives a fair idea of the range and variety of work done in the chemical laboratory.

F. W. CLARKE,
Chief Chemist.

Hon. J. W. POWELL,
Director.
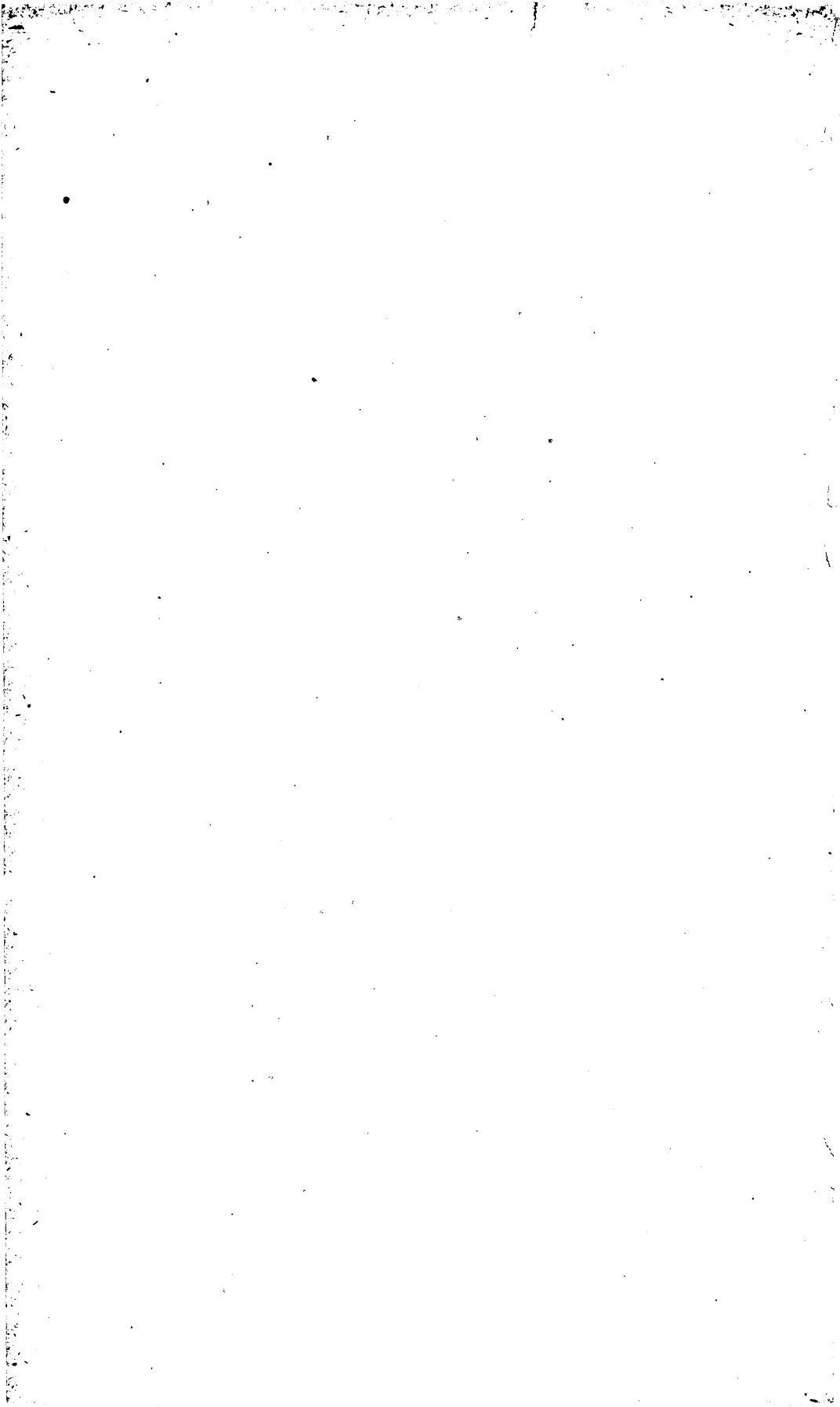
WORK DONE IN THE DIVISION OF CHEMISTRY AND PHYSICS IN 1890-'91.

ON THE CONSTITUTION OF CERTAIN MICAS, VERMICULITES, AND CHLORITES.

By F. W. CLARKE AND E. A. SCHNEIDER.

In a previous paper upon the constitution of the silicates,[1] we sought to establish some new lines of attack upon the problem, especially with reference to the mica and chlorite groups. The present communication is to be regarded as a continuation of the same research, and by essentially the same methods; although in some instances the experiments have been less elaborate, when elaborateness seemed to be unnecessary. Throughout the investigation the fundamental hypothesis that the minerals studied are substitution derivatives of normal salts has kept steadily in view; and, as we believe, it has been amply justified.

Of the so-called vermiculites, two only, jefferisite and kerrite, were considered in our former paper; and these were shown to be trihydrated micas, in which the original alkalies had been replaced by hydrogen. To these examples we now add several others; of which two varieties afford excellent checks upon the earlier work. The two minerals in question are an altered biotite from the zircon mine in Henderson county, N. C., and the protovermiculite from Magnet cove, Arkansas, described some years ago by König. The analyses, with itemized water determinations, are as follows:

	Henderson county.		Protovermiculite.	
	Analysis.	Molecular ratio.	Analysis.	Molecular ratio.
SiO_2	38·18	·636	34·03	5·67
TiO_2	1·68	·021	undet.	....
ZrO_2	none	....	....	....
Al_2O_3	14·02	·138	14·49	·142
Fe_2O_3	13·02	·081	7·71	·048
FeO	2·22	·031	0·14	·002
MnO	0·38	·005	0·09	·001

[1] Bulletin No. 78.

	Henderson county.		Protovermiculite.	
	Analysis.	Molecular ratio.	Analysis.	Molecular ratio.
MgO........................	14·62	·385	20·89	·522
CaO	0·17	·003	1·88	·034
BaO	0·06	....	....	....
K₂O	5·40	·057	....	....
Na₂O	0·48	·008	....	....
H₂O, 105°	3·20	·178	11·23	·624
H₂O, 250°-300°	2·52	·140	4·55	·253
H₂O, above 300°.............	4·80	·267	5·41	·301
	100·75		100·42	
H₂O over H₂SO₄	3·20		11·34	

The analysis of protovermiculite agrees with that of König as well as could be expected, but is carried out somewhat more in detail. In its appearance the mineral was dark brown, broadly foliated, much decomposed, and very brittle. Before the blowpipe it exfoliates and fuses easily. The Henderson county mica was also brown, brittle, and decomposed, exfoliating when heated and fusing at the edges. Both minerals were examined optically by Mr. Waldemar Lindgren. The protovermiculite he describes as "yellowish, containing in arborescent forms between the plates a great deal of a deep yellow or reddish substance, probably hydroxide of iron. Angle of optical axes larger than usual. Slight pleochroism; thicker plates remain light between crossed nicols." Of the Henderson county mica he says—"contains no titanium mineral. Contains a few grains of a colorless, strongly double-refracting mineral of uncertain nature, possibly zircon. Plates nearly dark between crossed nicols. Angle of optical axes small, but distinctly observed." In the material selected for analysis the impurities noted by Lindgren were, so far as possible, removed.

The composition of each mineral reduces quite easily, in accordance with the methods followed in our former work, to a mixture of simple isomorphous types. The only uncertainties appear to be in connection with the loosely combined water, which is driven off below 300°. In the Henderson county mica we have the molecules

$$
\text{Al}\!\!\begin{array}{c} \diagup\text{SiO}_4\equiv\text{MgK} \\ -\text{SiO}_4\equiv\text{MgH} \\ \diagdown\text{SiO}_4\equiv\text{Al} \end{array}
\quad
\text{Al}\!\!\begin{array}{c} \diagup\text{SiO}_4\equiv\text{H}_3 \\ -\text{SiO}_4\equiv\text{H}_3 \\ \diagdown\text{SiO}_4\equiv\text{H}_3 \end{array}
\quad
\text{Fe}\!\!\begin{array}{c} \diagup\text{SiO}_4\equiv\text{MgH} \\ -\text{SiO}_4\equiv\text{MgH} \\ \diagdown\text{SiO}_4\equiv\text{Fe} \end{array}
\quad
\text{Fe}\!\!\begin{array}{c} \diagup\text{O} \\ -\text{O} \\ \diagdown\text{SiO}_4\equiv\text{H}_3 \end{array}\!\!>\!\text{Mg}
$$
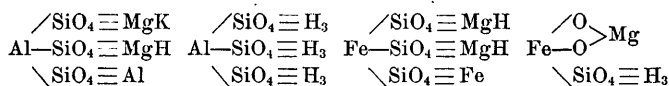
in the ratio $8:1:3\tfrac{1}{2}:3$. The loosely combined water is in the proper amount to monohydrate the four molecules; but its actual distribution is uncertain. In the subjoined table monohydration is provisionally assumed. In the protovermiculite we have the three molecules

$$
\text{Al}\!\!\begin{array}{c} \diagup\text{SiO}_4\equiv\text{H}_3 \\ -\text{SiO}_4\equiv\text{H}_3 \\ \diagdown\text{SiO}_4\equiv\text{H}_3 \end{array}
\quad
\text{Al}\!\!\begin{array}{c} \diagup\text{O} \\ -\text{O} \\ \diagdown\text{SiO}_4\equiv\text{H}_3 \end{array}\!\!>\!\text{Mg}
\quad
\text{Fe}\!\!\begin{array}{c} \diagup\text{O} \\ -\text{O} \\ \diagdown\text{SiO}_4\equiv\text{Al} \end{array}\!\!>\!\text{Mg}
$$
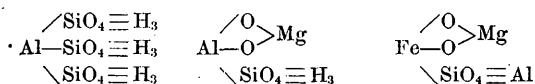
each plus three molecules of water, in the ratio 14 : 6 : 9. As in the case of jefferisite and kerrite, the three molecules of loosely combined water are unlike, two being given off over sulphuric acid and the third retained rather more tenaciously.

Reducing the original analysis to 100 per cent, uniting all similar oxides to similar type, reckoning FeO as MgO, Na$_2$O as K$_2$O, TiO$_2$ as SiO$_2$, etc., we get the following comparison between observation and theory:

	Henderson county.		Protovermiculite.	
	Found.	Calc.	Found.	Calc.
SiO$_2$	39·70	39·90	34·10	34·18
Al$_2$O$_3$	14·12	14·25	14·52	14·78
Fe$_2$O$_3$	13·11	13·15	7·72	7·20
MgO	16·32	17·08	22·41	22·79
K$_2$O	6·17	6·17	....	....
H$_2$O, essential	4·83	4·87	5·43	5·40
H$_2$O, hydration	5·75	4·58	15·82	15·65
	100·00	100·00	100·00	100·00

These results, taken in connection with our work on jefferisite and kerrite, and with the mica theory upon which all our formulæ are based, are exceedingly suggestive. Kerrite is essentially a trihydrated hydrophlogopite. Protovermiculite is the same substance, commingled with a trihydrated hydroclintonite, in the ratio 1 : 1 very nearly. Jefferisite is a similar mixture of hydrobiotite and hydroclintonite, also trihydrated, and in the ratio 1 : 1. The Henderson county mica is essentially a biotite, about half way transformed into a vermiculite, and is interesting as a transition product. The hydration of its several admixed molecules is naturally uncertain. At an early date we hope to imitate experimentally the process by which a mica becomes transformed into its corresponding vermiculite.

But although the above-named minerals appear to be very simple in their structure and relationships, a like simplicity does not characterize all of the vermiculites. In some members of the group there seem to be a small admixture of chloritic molecules, and it is even probable that many intermediate stages between mica and chlorite may exist. As bearing upon this question we have a series of vermiculitic minerals from Chester and Delaware counties, Pennsylvania, some of which have already been studied by Cooke, Gooch, Leeds, and others, while some have escaped examination hitherto. To begin with, we may consider the hallite, from Nottingham, Chester County, and the vermiculites from Lenni (not Lerni), Delaware County. The hallite, received through the kindness of Mr. W. W. Jefferis, was dark bluish green, and agreed perfectly with the published descriptions. The Lenni mineral, partly from the collection of the late Isaac Lea, and partly gath-

ered in the field by one of us, is represented by several varieties, which in a large series of specimens are seen to shade into each other. Three varieties were examined: one, silver white, resembling outwardly an ordinary mica; a second, bronzy brown, like jefferisite; and the third, dark green, similar to clinochlore. All four substances were examined microscopically by Mr. Lindgren, who reports as follows:

A. HALLITE.

Corresponds exactly to Cooke's description.[1] Contains spear-shaped rhombic or more rarely hexagonal inclusions of a dark brown mineral distributed along lines cutting each other at angles of 60° and 120°. Asterism apparently uniaxial, although the plates sometimes show slight double refraction between crossed nicols.

B. WHITE LENNI.

Silvery luster in large fragments. Thin foils colorless, thicker yellowish and yellowish brown. Substance pure; no inclusions, except small crystals of feldspar (?) once observed. Thin lamellæ very faintly double refracting, in streaks and patches. Interference figure a cross, not dissolved. Crossing lines on surface marked quite well.

C. BROWN LENNI.

Brownish yellow, similar to biotite. Hexagonal line system not very marked. Thin plates yellowish to deep yellowish brown. Substance pure, except containing in small foils and arborescent forms some $Fe_2 O_3$. Thicker plates do not extinguish in any position between crossed nicols. Angle of optical axes very small.

D. GREEN LENNI.

Thin lamellæ colorless, thicker light to deep green. No inclusions. Thin lamellæ faintly double refracting; in thicker plates the cross is dissolved into distinct hyperbolas. Does not get dark in any position between crossed nicols. Pleochroism notable in sections oblique to the cleavage plane. Fibers deep green when parallel to the principal plane of the microscope, light green when perpendicular to it. No line systems noted on the surface.

Upon analysis, the four minerals gave the subjoined results, with the water determinations itemized as usual:

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[1] Proc. Am. Acad. Arts. and Sciences, 1874, vol. 9, p. 35.

	A. Hallite.	B. Lenni 1.	C. Lenni 2.	D. Lenni 3.
SiO₂	35·54	36·72	35·09	34·90
TiO₂	undet.	0·18	0·58	0·10
Al₂O₃	9·74	10·06	12·05	10·60
Fe₂O₃	9·07	5·37	6·67	8·57
Cr₂O₃		0·26	0·46	0·23
FeO	0·28	0·12	0·11	0·22
MnO	0·25	0·31	0·27	0·17
NiO	0·16	0·20	0·20	0·19
MgO	30·05	29·40	27·62	28·21
BaO			trace	
H₂O, 105°	2·64	6·40	5·70	4·99
H₂O, 250°–300°	1·23	2·68	1·98	1.60
H₂O, red heat	10·91	8·69	9·22	9·88
	99·87	100·39	99·95	99·66
Loss over H₂SO₄	undet.	6·92	5·84	5·21

In these analyses we at once see that the combined water is mostly in excess of the crystalline water, and that the formulæ deduced must be correspondingly modified. The molecular ratios are as follows:

	A.	B.	C.	D.
SiO₂	·592	·614	·591	·583
R₂O₃	·152	·134	·163	·159
RO	·760	·744	·698	·712
H₂O, fixed	·606	·483	·512	·549
Aq.	·215	·504	·427	·366

In order to learn something as to the distribution of the hydroxyl indicated by these ratios, resort was had to the process of heating in dry, gaseous, hydrochloric acid, as described in our former paper. From this test, however, the brown Lenni vermiculite was omitted, as being intermediate in its character between the white and the green. Each experiment was made at the temperature 383°–412°.

	A.	B.	D.
Hours heated	16½	16	17
R₂O₃ removed	3·42	1·98	1·56
MgO removed	8·09	6·30	6·57
Molec. ratio MgOH	·202	·158	·164

Here it is assumed, on the grounds of our former work, that the magnesia rendered soluble by gaseous HCl is present as MgOH. Representing this by the symbol R′, the three vermiculites give the following empirical formulæ:

Hallite .... $R'''_{304}R''_{558}R'_{202}H_{1010}(SiO_4)_{592}O_{436}$,   215 aq.
White Lenni .... $R'''_{268}R''_{586}R'_{158}H_{808}(SiO_4)_{614}O_{259}$,   504 aq.
Green .... $R'''_{318}R''_{548}R'_{164}H_{934}(SiO_4)_{583}O_{408}$,   366 aq.

These reduce at once, subject to small uncertainties as to hygroscopic water, to mixtures of molecules of the hydroclintonite and hydro-phlogopite types, with small amounts of chloritic compounds $Mg(SiO_4)_2$ $(MgOH)_6$ and $Mg_2(SiO_4)_2H_4$. Upon this basis the three minerals become:

		Molecules.
Hallite.....................$Al(SiO_4)_3Mg_3H_3$	3 aq............	7
$AlO_2MgSiO_4H_3$	....	18
$Mg(SiO_4)_2(MgOH)_6$	....	3
$Mg_2(SiO_4)_2H_4$	....	2
White Lenni ....$Al(SiO_4)_3Mg_3H_3$	3 aq..........	6
$AlO_2MgSiO_4H_3$	....	5
$Mg(SiO_4)_2(MgOH)_6$	....	1
Green Lenni.................$Al(SiO_4)_3Mg_3H_3$	3 aq..........	4
$AlO_2MgSiO_4H_3$	....	8
$Mg(SiO_4)_2(MgOH)_6$	....	1

The actual ratios observed were slightly more complex, but the foregoing expressions accord well with the analyses. Here, as previously, we may reduce the analyses to typical form and 100 per cent, reckoning Fe_2O_3 as Al_2O_3, etc. The comparison is as follows:

Analyses reduced.

	A (Hallite).	B (White).	D (Green).
SiO_2	36·93	37·56	36·33
Al_2O_3	16·13	14·92	16·83
MgO	31·58	30·41	29·44
H_2O.....................................	11·34	8·86	10·26
Aq..	4·02	9·25	6·84
	100·00	100·00	100·00
MgO in MgOH..........................	8·09	6·30	6·57

Calculated.

	A.	B.	D.
SiO_2	36·47	38·11	36·61
Al_2O_3	15·82	14·25	16·97
MgO	31·75	30·49	29·95
H_2O	11·27	8·92	10·47
Aq	4·69	8·23	6·00
	100·00	100·00	100·00
MgO in MgOH	8·93	6·10	6·66

When we consider the nature of the vermiculites, as products of alteration, the agreement here shown is fully as close as could be expected. Many well crystallized minerals, fresh and unaltered, are less simply interpreted.
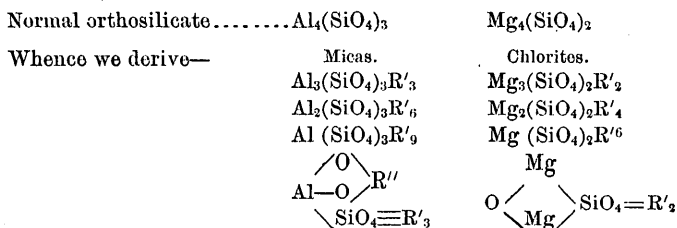
On the 19th of February, 1891, Prof. Tschermak read before the Vienna Academy a paper on the chlorite group,[1] in which he referred

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[1] Sitzungsb. Wien. Akad., 1891, vol. 100, p. 31.

certain vermiculites to that class of minerals. He also put forth some views concerning the constitution of the chlorites, which, however, we can not discuss in the present communication.

One fundamental molecule, regarded by Tschermak as a constituent of most chlorites, we may adopt for present purposes, under slightly different structural form from his. This is the "amesite substance," $SiAl_2Mg_2H_4O_9$, written by Tschermak $SiAl_2H_2O_7(MgOH)_2$. In default of experimental evidence this may be transformed into OMg_2SiO_4 $(AlH_2O_2)_2$, when it becomes part of a natural chloritic series parallel with the micas, thus:

Normal orthosilicate........$Al_4(SiO_4)_3$ $Mg_4(SiO_4)_2$

Whence we derive—

Micas.	Chlorites.
$Al_3(SiO_4)_3R'_3$	$Mg_3(SiO_4)_2R'_2$
$Al_2(SiO_4)_3R'_6$	$Mg_2(SiO_4)_2R'_4$
$Al (SiO_4)_3R'_9$	$Mg (SiO_4)_2R'_6$

$$Al{-}O{\overset{O}{\underset{SiO_4}{\diagdown}}}R'' \equiv R'_3 \qquad O{\overset{Mg}{\underset{Mg}{\diagup\diagdown}}}SiO_4 = R'_2$$

In other words, the "amesite substance" in our chlorite series is the basic equivalent of the clintonite molecule among the micas, and is applicable to the solution of certain obscure problems. Some of the vermiculites, as Tschermak suggests, are probably chlorites, and two examples have come under our notice in which this view is partly sustained. Both were originally received from Mr. Jefferis; one from the corundum mine at Newlin, Chester county, Pa., and the other from Middletown, Delaware county, in the same state. The Newlin mineral was dull green, and much resembled culsageeite both outwardly and optically. The Middletown vermiculite was bright golden yellow; strongly exfoliating before the blowpipe and fusible on the edges. It was found upon the farm of Mr. James Painter, whence Mr. Jefferis named it provisionally "painterite," a name which seems also to have been applied to a peculiar brownish, waxy, feldspathic matrix in which the broad golden laminæ were imbedded. A second sample of it was later collected by one of us. According to an optical examination by Mr. Lindgren, the matrix of the "painterite" is a mixture of plagioclase feldspar, probably labradorite, with serpentine. Concerning the three vermiculites he makes the following notes:

A. FROM NEWLIN.

Hexagonal surface marking quite distinct. Bluish green. In thin lamellæ colorless to pale bluish green. Substance pure. The greenish color is distributed somewhat unevenly through the mineral. Axial angle unusually large, being at least 25°.

B. "PAINTERITE" RECEIVED FROM JEFFERIS.

Yellowish brown. Strong hexagonal marking on the surface. Thin lamellæ colored yellowish by numerous interpositions of a very finely

distributed substance, probably hydroxide of iron. Even thin foils show slight double refraction between crossed nicols, and do not extinguish in any position. Angle of optical axes small but distinct.

C. "PAINTERITE" COLLECTED BY SCHNEIDER.

Surface marking quite distinct. Contains a great number of small foils of Fe_2O_3, and also some yellowish, finely divided substance. Not enough materially to affect the analysis. Otherwise like B. Analysis as follows: A, Newlin; B, painterite from Jefferis; C, painterite collected by Schneider; D, matrix of painterite.

	A.	B.	C.	D.
SiO_2	31·23	34·86	33·95	52·47
TiO_2		trace	trace	none
Al_2O_3	17·52	11·64	12·52	21·72
Cr_2O_3	0·14			
Fe_2O_3	4·70	3·78	4·40	1·23
FeO	1·20	0·20	0·20	0·17
MnO	0·20			
NiO	0·33	0·14	0·23	
MgO	31·36	31·32	30·56	9·26
CaO		0·07	none	3·25
K_2O				0.63
Na_2O				5·09
H_2O, 105°	1·08	1·64	1·56	1·14
H_2O, 250°–300°	0·40	1·03	0·59	
H_2O, ignition	12·15	15·75	16·46	4·74
	100·31	100·43	100·47	99·70

Upon treating the three vermiculites with gaseous hydrochloric acid at 383°–412°, the following results were obtained:

	A.	B.	C.
Hours heated	8	12½	19
R_2O_3 removed	1·09	·80	·78
MgO removed	5·86	8·26	9·56
Molecular ratio MgOH	·146	·207	·239

The molecular ratios are:

	A.	B.	C.
SiO_2	·520	·581	·566
R_2O_3	·202	·138	·150
RO	·808	·789	·770
H_2O	·675	·875	·914
Aq	·080	·148	·119

In these examples the water (Aq.) expelled below 300° is so small in amount that it may be left out of consideration. Part of it undoubtedly represents hydrated molecules, which, however, are relatively so few in number that they may be for present purposes disregarded.

From the remaining ratios, writing MgOH as R′, the subjoined empirical formulæ are directly derived:

Newlin ....$R'''_{404} R''_{662} R'_{146} H_{1204} (SiO_4)_{520} O_{903}$.

"Painterite" B ....$R'''_{276} R''_{582} R'_{207} H_{1543} (SiO_4)_{581} O_{709}$.

"Painterite" C ....$R'''_{300} R''_{531} R'_{239} H_{1589} (SiO_4)_{566} O_{763}$.

Reduced to structural form, these give less satisfactory results than the previously considered vermiculites. The Newlin mineral may be regarded as nearly a hydroclintonite, $AlO_2MgSiO_4H_3$, with an admixture of an amesite-like compound, $Mg_2OSiO_4(MgOH)_2$, in the ratio 4:1. In reality the mixture is more complicated and must contain other molecules. The "painterite" C is wholly chloritic, containing the amesite molecule $Mg_2OSiO_4(AlH_2O_2)_2$, with the molecules $Mg(SiO_4)_2(MgOH)_6$ and $Mg(SiO_4)_2H_6$, in the ratio 8:2:9. These compare with the actual analyses, reduced to typical form and 100 per cent, thus:

	Newlin.		"Painterite."	
·	Found.	Calc.	Found.	Calc.
SiO_2	32·42	31·57	35·03	35·59
Al_2O_3	21·39	21·47	16·22	16·13
MgO..........................	33·57	33·69	31·77	30·84
H_2O	12·62	13·27	16·98	17·44
	100·00	100·00	100·00	100·00
MgO in MgOH	6·09	8·42	8·56	9·49

The "painterite" B reduces less easily, but satisfies all the required conditions. It is like C, but contains other chloritic molecules in somewhat complex ratios. It must be remembered that all these minerals are *mixtures,* and the fact that they are reducible at all to simple expressions is a strong point in favor of the theory adopted for the chlorites and micas in general.

A very interesting example of the way in which the chloritic vermiculites approach the serpentines in composition and character has been furnished us by Mr. G. P. Merrill, of the U. S. National Museum. It was found by him at Old Wolf quarry, Chestnut hill, Easton, Pa., and is described by him as follows:

It occurs in the form of bright yellowish green inelastic scales of all sizes up to an inch in diameter, associated with a compact tremolite rock, which is here quarried and pulverized for use as a filler in paper manufacture. The character of the rock is greatly varied, but at the quarry opening the prevailing material is tremolite, more or less altered into serpentine, the vermiculite and other secondary products including calcite in both fibrous and granular forms.

The vermiculite, although occurring in plates of considerable thickness, readily separable into thin foliæ, never, so far as observed, shows good crystal outlines. Optically it is biaxial and negative, though the axial angle is small, basal plates in the thin section showing a black cross, which scarcely opens at all during the revolution of the stage. Cleavage plates a millimeter or more in thickness show plainly the biaxial character, though the figure is somewhat distorted. Dispersion, $\rho < v$.

The surface of the plates is at times plainly marked by sharp lines crossing at angles of 60° and 120°, and along which the mineral frequently separates readily. Before the blowpipe the mineral exfoliates and fuses readily on the edges to a thin glass.

According to Mr. Merrill this mineral is sometimes seen in cabinets labeled "talc;" and, indeed, in its appearance it resembles both talc and serpentine. Upon analysis the following results were obtained, the percentage of K_2O representing two identical determinations:

|	Analysis.	Molecular ratios.
SiO_2	43·71	·728
Al_2O_3	3·59	·035
Fe_2O_3	0·90	·006
MgO	38·58	·964
K_2O	2·22	·023
Na_2O	0·13	·002
H_2O, 105°	0·46	....
H_2O, 250°-300°	0·09	....
H_2O, ignition	10·70	·594
	100·38	

Treated with dry, gaseous HCl at 383°–412° for $16\frac{1}{2}$ hours, 4·36 per cent of magnesia became soluble, corresponding in molecular ratio to 109 mol. MgOH. Hence the mineral, although resembling serpentine in general composition, differs from the latter in its proportion of this molecular group.

Upon treatment with aqueous HCl, of specific gravity 1·12, a small portion remained undecomposed. Ten grammes of the mineral were therefore digested with the acid for three days on the water bath, and the residue was afterwards boiled out with a solution of sodium carbonate to remove liberated silica. The remaining residue, amounting to 3·10 per cent of the original material, was then analyzed separately and found to contain—

SiO_2	64·53
Al_2O_3, Fe_2O_3	2·03
MgO	33·04
	99·60

All the potash went into solution; whence it seems probable that no muscovite was present. The ratios of the insoluble residue agree very closely with those of talc, and we may therefore assume that mineral to be present as an impurity. Deducting from the molecular ratios

given above the quantity of talc indicated by experiment, we get for the empirical formula of the mineral the expression—

$$Al_{82}K_{50}Mg_{938}H_{1170}(SiO_4)_{695}O_{281},$$
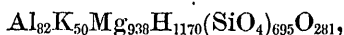
which becomes, if the excess of oxygen is regarded as hydroxyl, with $(MgOH)_{109}$ as observed,

$$Mg_{829}K_{50}H_{889}(MgOH)_{109}(AlH_2O_2)_{82}(OH)_9.$$
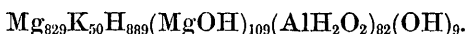
The small excess of hydroxyl is probably due to undistributed errors of analysis, and may be added to the MgOH, bringing the latter to 118 and reducing the Mg to 820. Then, generalizing, by uniting all the univalent groups and atoms, we get as an ultimate formula—

$$Mg_{820}(SiO_4)_{695}R'_{1139},$$
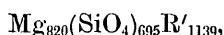
which equals, almost exactly,

$$125\ Mg_3(SiO_4)_2R'_2 + 223\ Mg_2(SiO_4)_2R'_4,$$
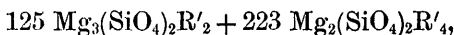
a result in accordance with our serpentine-chlorite theory. The distribution of the several components of R' is, however, not clear and remains to be ascertained. No other discussion of the analysis appears to give as satisfactory results as this, and we have tried several methods of reduction, representing various hypotheses.

One other mineral examined during this investigation remains to be noticed, a pale yellowish green mica collected by Mr. G. P. Merrill at a granite quarry in Auburn, Me., near where the Maine Central railroad crosses the Androscoggin river. It occurs in direct contact with ordinary, broadly foliated muscovite, sometimes forming marginal growths about the plates of the latter mineral, like lepidolite. Analysis gave:

SiO_2	46·54
Al_2O_3	34·96
Fe_2O_3	1·59
MgO	0·32
K_2O	10·38
Na_2O	0·41
F	none.
H_2O, 105°	0·71
H_2O, ignition	4·72
	99·63

This is the composition of muscovite, which the mica undoubtedly is. The case is interesting, however, as showing a secondary growth of muscovite on muscovite, with a marked difference in outward appearance between the two formations.

NEW ANALYSES OF URANINITE.

By W. F. Hillebrand.

Since the publication of a former paper on the occurrence of nitrogen in uraninite and on the composition of uraninite in general[1] no advance has been made toward clearing up the mystery surrounding the compo· sition of that mineral, although considerable work has been done in certain directions, some of which is of sufficient interest to be produced later in a separate publication. In addition, several analyses of urani- nite have been made, the material being in part from localities hitherto unrepresented by analytical data, and these form the subject of the present paper.

A first glance sufficed to show that the specimens were not fresh and that therefore analysis could throw no light on the ultimate composi- tion of the mineral, but valuable data to be obtained as to the presence or absence of nitrogen and of the rare earths furnished ample excuse for the work.

No. Ia is a reanalysis of nivenite from Llano county, Tex., the ma- terial for which was kindly given by Mr. W. E. Hidden. It agrees in the main with the original analysis of this variety by Hidden and Mack- intosh,[2] which is reproduced under Ib, and it confirms the presence of nitrogen, suspected but not proved by them. A small remnant of their original powdered sample gave me 0·52 per cent of nitrogen. In a the earths appear in slightly greater total amount than in b and they are more subdivided into groups and elements, which accounts fully for the difference between the atomic weights of the metals of the yttrium group of the two analyses. It was rendered certain by a second test that a group of earths whose sulphates are insoluble in potassium sulphate, other than those of Th, Zr, and Ce, is present.[3] A very satisfactory turmeric-paper reaction for zirconia was obtained in this analysis, as

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[1] Am. Jour. Sci., 3d ser., vol. 40, p. 384; Bull. U. S. Geol. Survey, No. 78, 1889-'90, p. 43.

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

[3] It may be here remarked that the subdivision of the earths into the groups indicated by $(La, Di)_2O_3$ and $(Y, Er)_2O_3$ in all my former analyses should not be taken too literally. By the former are meant those earths insoluble in potassium sulphate and by the latter those soluble in that reagent.

also in that next following, which would go to show that the hypothetical ZrO_2 of several of my earlier analyses was probably in fact zirconia. The cause of the considerable loss shown by the analysis is not known. It may be mentioned that nivenite is more soluble than any uraninite heretofore examined by me, not even excepting cleveite. One hour sufficed for complete decomposition in very dilute sulphuric acid ($1H_2 SO_4$ to $6H_2O$) at the temperature of boiling water.

	I.—Llano county, Tex.		II.—Marietta, S. C.	III.—Villeneuve P., Quebec, Canada.	IV.—Johanngeorgenstadt, Saxony.
	a. Hillebrand.	b. Hidden and Mackintosh.			
UO_2	44·17	46·75	} *83·95	41·06	59·30
UO_3	20·89	19·89	}	34·67	22·33
ThO_2	6·69	7·57	1·65	6·41	
ZrO_2	0·34	....	0·20	(?)	
CeO_2	0·34	....	0·19	0·40	none.
La group	2·36	....	2·05	1·11	
Y group	†9·46	‡11·22	§6·16	‖2·57	
CaO	0·32	....	0·41	0·39	1·00
PbO	10·08	10·16	3·58	11·27	6·39
H_2O	1·48	¶2·54	undet.	1·47	3·17
N	0·54	....	undet.	0·86	0·02
SiO_2	**0.46	....	} 0·20	0·19	0·50
Insoluble	††1·47	1.22	}	0·13	....
Fe_2O_3	0·14	0·58	trace.	0·10	0·21
Al_2O_3?	....	....		....	0·20
MgO.............	....	....	trace.	....	0·17
Na_2O	....	....	trace.	....	0·31
Bi_2O_3	....	....		0·09	0·75
CuO	....	....		....	0·17
MnO.............	....	....		....	0·09
P_2O_5	....	....		....	0·06
As_2O_5.............	....	....		....	2·34
V_2O_5.............	....	....			
W_2O_3.............	....	....			} 0·75
MoO_3	....	....			
SO_3	....	....			0·19
	98·74	99·93	98·39	100·72	97·95
Sp. gr..........	8·29	8·01	....	....	6·89

* As U_3O_8. † Atomic weight, 111·4. ‡ Atomic weight, 124·2. § Atomic weight, 113·6. The oxalates of this group were white, not pink like those in Ia, but the color of the ignited oxides was the same in both cases and very light. ‖ Atomic weight, 111·2, approximately. ¶ Ignition. ** From thorogummite. †† Mainly fergusonite.

No. II is from a new locality, Marietta, Greenville county, South Carolina, and the total amount found, a few small fragments, was kindly given by Mr. W. E. Hidden for examination. It was impossible to free the least altered portions from the yellow and orange alteration products with which they were intimately commingled; therefore the analysis represents the composition of a mixture. Unfortunately also the portion in which UO_2 and N were to be estimated was lost, but it was

seen that the mineral was very soluble and gave off considerable gas. From the preponderance of the yttrium group over the other rare earths the mineral is to be classed with nivenite and cleveite rather than with those varieties rich in thoria, a conclusion already foreshadowed by its ready solubility.

No. III is an analysis of uraninite from the Villeneuve mica mine, township of Villeneuve, Ottawa county, province of Quebec, Canada. To Mr. G. C. Hoffman, of the Canadian Geological Survey, who first recognized and reported this occurrence,[1] I am indebted for the material analyzed. It was evidently somewhat altered and was accompanied by oxidized alteration products. Hoffman gives the density of a piece as 9·055. Crystalline form was lacking, but it unquestionably belongs to the crystallized uraninites, being found, like most if not all of them, in coarse granite (pegmatite).

No. IV represents the composition of a specimen from Johanngeorgenstadt, in Saxony, received from Mr. A. Lösch, of St. Petersburg, through Mr. E. A. Schneider, of the U. S. Geological Survey. Notwithstanding the altered and crumbling character of the specimen it is proper to publish the analysis since the only one previously made that has come under my observation, by Pfaff in 1822, is very incomplete. By panning a very fair article as regards visible impurity was obtained. It is not known wherein the loss is to be sought. Like the great mass of the Bohemian mineral this showed no evidence of ever having been crystallized, and as in that also rare earths are absent, and also nitrogen, except for an uncertain trace.

From the analyses of uraninite thus far made it appears that the species may be broadly divided into two groups, the one of which is characterized by the presence of rare earths, the other by their absence. With the former group nitrogen appears to be invariably associated, while in the latter it is present, if at all, only in minute quantity. Besides these chemical differences there is one of another kind, for probably all varieties of the first group occur in more or less well defined crystals, while the members of the second group are generally, if not altogether, massive and free from crystalline form. These differences suggest naturally a dissimilarity of origin and environment. Examination shows that the manner of occurrence and the association of other minerals are different and in such a way as to render an unlike immediate origin probable. All of the rare earth uraninites, with exception of the zirconiferous variety from Black Hawk, Colorado, occur as an apparently original constituent of coarse granites (chiefly pegmatitic), while the others are evidently of secondary formation, as evidenced by their presence in metalliferous veins in more or less intimate association with numerous sulphides of silver, lead, cobalt, nickel, iron, zinc, copper, etc. The Colorado variety occupies an anomalous position as regards the two groups. I prefer to regard it provisionally as

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[1] Annual Report Can. Geol. Surv., 1886, vol. 2, Report T, p. 10.

a member of the second group, where its mode of occurrence and want of crystalline form as well as small percentage of nitrogen seem to place it, although its zirconia and traces of other earths would admit it to the first.

Attention is called to the above points merely to show that the chemical and physical differences of the two groups may be susceptible of more simple explanation than would appear from the face of the analyses.

ON THE ISOMORPHISM AND COMPOSITION OF THORIUM AND URANOUS SULPHATES.

BY W. F. HILLEBRAND AND W. H. MELVILLE.

I. CHEMICAL DISCUSSION, BY W. F. HILLEBRAND.

During the course of an extended investigation on uraninite it was often necessary to decompose the mineral in sealed tubes with sulphuric acid.[1] At first a deposit was generally observed on removing the tubes from the oven, the character of which depended on the concentration of the acid and the presence or absence of thoria in the mineral. In the absence of this earth it took the form of a greenish powder with a strong acid, and of bright green, brilliantly reflecting crystals when a weak acid was used, unless the ratio of liquid to mineral was sufficiently high in the latter case to prevent crystallization. As might naturally be supposed, these crystals were hydrated uranous sulphate. The best results as regards size of crystals were obtained with an acid containing one part of sulphuric acid to five or six of water, by volume. With about 100 parts by weight of such an acid to one of UO_2, it might pretty confidently be expected that no crystallization would take place.

In presence of thoria the green crystals still appeared, but they then contained thorium as well as uranium, and accompanying them was a beautiful white coherent spongy mass extending the length of the tube and consisting of a network of microscopic needles grouped in radiating bunches. This was likewise a double sulphate of uranium and thorium, resembling in every respect the deposit formed under similar conditions from a solution of thorium sulphate alone, except that when washed, dried, and compacted together there was a faint greenish tinge to it. Ordinarily the two forms of double salt appeared together, and it even seemed as if under favorable conditions, which have not yet been precisely determined, the crop of green crystals might be increased at the expense of the white deposit. At least on one occasion, when the heating was prolonged for several days, the latter gradually disappeared, while the former increased in size and number. The white deposit always preceded the green crystals, and, by regulation of the proportions of oxide and of acid and of duration of heating, it is possible in practice to obtain the former alone if desired.

In order to secure material for exact chemical and crystallographical determinations recourse was had to artificially prepared U_3O_8 and ThO_2,

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[1] Bull. U. S. Geological Survey, No. 78, p. 43, 1889-'90.

by using which, either alone or mixed, in varying proportions, different products were obtained. Neither uraninite nor UO_2 is well adapted for this purpose, because of contamination of the crystals by sulphate of lead in the one case and by undissolved UO_2 in the other. Even when using U_3O_8 care must be taken to avoid a like result by fine pulverization and avoidance of excess of oxide compared with acid. So little soluble are the green crystals that over 50 per cent of the UO_2 in uraninite or U_3O_8 can generally be obtained as sulphate. Hence it follows that when UO_2 is to be estimated volumetrically care must be taken to use sufficient dilute acid to render impossible the formation of these crystals. The white spongy deposit is not a hindrance to exact estimation of UO_2 by potassium permanganate, for it dissolves readily in cold water, though with extreme slowness when once it has been compressed.

The green crystals were separated from their mother liquor in a Gooch crucible, without asbestus felt, with the aid of suction; they were at once washed with hot dilute sulphuric acid, then with alcohol, and finally with ether. They were allowed to dry thoroughly in the air and were analyzed in that condition. It was found by experiment that alcohol was practically without solvent action on the sulphates and that none of the water of crystallization was removed by it. If both forms of deposition occurred at one time the spongy one was first removed with great ease by two or three rapid washings with cold water, the network of fine needles being partly dissolved and partly carried through the holes in the crucible by the powerful suction, after which alcohol and ether were used as before. The results of analyses were as follows:

	I.		.II.	
	Analysis.	Molecular ratio.	Analysis.	Molecular ratio.
UO_2	49·18	} 1·00	48·40	} 1·00
ThO_2	3·59		5·58	
SO_3	32·08	2·05	31·27	1·96
H_2O	14·18	4·04	14.84	4·13
	99·03		100·09	

A sample of uraninite decomposed by dilute sulphuric acid in a tube at about 170° C. furnished the product whose analysis is given under I. An earlier and very similar analysis of another preparation may be found on p. 50 of the bulletin already cited. The loss is mainly if not altogether undetermined PbO from included $PbSO_4$, which accounts in part for the excess of SO_3 found. For No. II U_3O_8 and ThO_2 were taken in such proportion that there should be about six times as much UO_2 as of ThO_2. Inasmuch as only 0·1622 gramme was available for SO_3 and H_2O determinations in this analysis the ratio is not bad. One

or two attempts to obtain a product with more ThO_2 and less UO_2, by starting with correspondingly different proportions of ThO_2 and U_3O_8, were unsuccessful, perhaps because of the tendency of the thorium sulphate to separate at once in the spongy state and thus to reduce the amount available for slow crystallization with the uranium. The specific gravity of No. II was kindly determined by Mr. L. G. Eakins in alcohol of ·7956 density. It was found to be 4·563 at 24·3° C., which reduced to water at the same temperature as standard becomes 3·63. The material examined contained 1·04 per cent of undissolved U_3O_8 which does not appear in the analysis, and allowing for this a density of 7·3 (Clarke's tables) that of the double sulphate having the given composition is 3·61 at 24·3° C.

The uranium sulphate, of which the analysis is here given, was obtained by decomposing U_3O_8 with dilute sulphuric acid in the manner already mentioned. Its density was not ascertained.

III.

	Analysis.	Molecular ratio.	
UO_2	53·99	1·00	
SO_3	31·94	2·00	
H_2O	14·13	3·94	
	100·06		

It appears, as was to be expected, that thorium is capable of replacing uranium in the sulphate of the latter, which holds in combination four molecules of water. That this is a true case of isomorphism is most fully shown by Mr. W. H. Melville in the crystallographical part of this paper, although the habit of the uranium sulphate differs from that of the double salt.

While, as above stated, failure resulted from attempts to lower the ratio between ThO_2 and UO_2 in the green double salt, it was found that the spongy mass, which almost always formed in the tubes when thoriferous uraninite was decomposed with dilute sulphuric acid, contained a very much higher proportion of ThO_2, and that by taking the dioxides in varying proportions double salts of correspondingly different composition could be readily obtained, as shown by the following analyses:

	I.		II.	
	Analysis.	Molecular ratio.	Analysis.	Molecular ratio.
UO_2	34·34	} 1·00	16·92	} 1·00
ThO_2	19·84		36·07	
SO_3	31·48	1·95	32·66	2·05
H_2O (diff.)	14·34	3·95	14·35	4·01
	100·00		100·00	

Both salts were obtained from a mixture of U_3O_8 and ThO_2. In case of No. II the proportion was such that the UO_2 of the U_3O_8 was to the ThO_2 as 2 to 1. It happened that the tube containing this preparation lay unopened for several weeks after removal from the oven, but during this time there had been no perceptible resolution of the precipitate, which on agitation made a thick emulsion with the acid. Both products were thrown on a Gooch crucible without asbestus felt, quickly washed twice or thrice with hot dilute sulphuric acid and then with alcohol and ether, whereupon they were allowed to dry thoroughly in the air.

There is no reason to doubt the isomorphism of this salt with that formed under similar conditions from thorium alone, but whether these are crystallographically referable to the green crystals before described or form a new case of dimorphism must remain undetermined until the crystallographic features of the former are known. In polarized light the needles of the double salt extinguish apparently parallel to their length.

Such contradictory statements appear in the literature of the subject regarding the composition of thorium sulphate separated from hot acid solutions, some authorities claiming four and a half molecules of water of crystallization and others only four, that it is very satisfactory to have evidence like that furnished by the above analyses to throw light upon the question. The tendency of late years has been to admit a mutual replaceability of ThO_2 and UO_2 in chemical compounds, though no direct proof seems to have been heretofore established,[1] and it was therefore reasonable to suppose that the composition of the thorium sulphate in question should correspond with that of the well known uranous sulphate with four molecules of water. In the light of the above analyses there is no room to doubt the complete isomorphism of the two sulphates, and that Demarcay[2] and Roozeboom[3] were right in accepting the formula $ThO_4(SO_2)_2, 4H_2O$, derivable from the more or less incomplete analyses of Berzelius, Berlin, and Chydenius, in preference to $ThO_4(SO_2)_2, 4\frac{1}{2}H_2O$, afforded by the more numerous ones of Delafontaine.[4]

In possible explanation of Delafontaine's high results for water Roozeboom (op. cit., p. 202) very justly remarks that because of its physical character the salt retains much mother liquor, and that if this be not

[1] Since this was written a paper by Rammelsberg, in the Sitzb. k. preuss. Akad. Wiss., vol XXXIV, 1886, which I had overlooked, has been brought to my attention. In it he shows that the uranous sulphate, formerly supposed to contain eight molecules of water of crystallization, contains in reality nine, and that this salt is isomorphous with the corresponding thorium sulphate.

[2] Comptes Rend., 1883, vol. 96, p. 1860.

[3] Zeit. phys. Chem., 1890, vol. 5, p. 198.

[4] Ann. Chem., vol. 131, p. 100. The statement by Kraut, near the foot of page 687 of Gmelin-Kraut's Inorganic Chemistry, vol. II, part I, is manifestly unwarranted. He considers the evidence in favor of the four-molecule H_2O salt as insufficient and thinks the analyses affording this formula were made upon mixtures which might have resulted through absorption of water by the three-molecule H_2O salt. It is strange that individuality should have been accorded to this latter salt by Chydenius and Cleve, which the former obtained by drying over sulphuric acid, after washing with hot water, the precipitate formed by boiling a weakly acid solution of the sulphates. Roozeboom is certainly correct in excluding this three-molecule H_2O salt from the list of thorium sulphates.

removed at a temperature above 45° C. the nine-molecule H_2O salt is formed from it on cooling, so that it is almost impossible not to find too much water. Notwithstanding numerous attempts to prepare the salt $ThO_4(SO_2)_2, 4H_2O$ from hot acid solutions as well as from warm neutral ones, I have never myself succeeded in reducing the water to four molecules, even though the mass of needles was rapidly washed with hot dilute sulphuric acid and then with alcohol and ether, after freeing from mother liquor by powerful suction on a Gooch crucible without asbestos felt, but my faith in the correctness of the formula with $4H_2O$ is not hereby shaken. A further possible cause of high results will appear from the following: The air-dried salt is said by Delafontaine to be thoroughly nonhygroscopic, and for a given temperature and hygrometric condition of the atmosphere it is true that no change in weight does occur; but if the salt is weighed from day to day, or even twice a day, a very marked gain or loss of weight is observed, depending in degree on the amount of change in the atmospheric conditions. In August and September, when hygrometric and thermometric readings were often high and marked and rapid changes were not infrequent, this gain or loss sometimes amounted within twenty-four hours to over half of 1 per cent of the total weight of the salt, and the extreme change during those months reached 1·22 per cent. It is therefore patent that the formula afforded by analysis may materially depend on whether the salt analyzed was weighed when the weather was hot and moist or cold and dry.

It may not be out of place here to call attention to a possible cause of the frequent discrepancies noticed in the statements of different writers in regard to the amounts of water given off by different substances when placed over sulphuric acid in a desiccator. No one would deny that sulphuric acid of maximum concentration is superior as a drying agent to the same acid somewhat, if only slightly, diluted; but it is probably not known to everyone how much may depend on the strength of the acid used. A case in point is the following: A thorium sulphate containing air-dried, 15·22 per cent H_2O, or 4·23 molecules, lost weight over concentrated sulphuric acid in a tightly closed desiccator as shown in column I, and as in column II over acid which had been in use in another desiccator for a considerable length of time and was subsequently found to have a density of 1·66. The cases are not rigidly comparable, perhaps, because of the different times devoted to the experiments, which were not carried on simultaneously, but they serve to illustrate the point.

I.—Acid of 1·84 sp. gr.		II.—Acid of 1·66 sp. gr.	
Time.	Per cent.	Time.	Per cent.
Days.		Days.	
1	3·80	1	2·87
3	2·78	1	0·40
5	1·37	3	0·06
9	0·22		
18	8·17	5	3·33

This may be considered an extreme case, but it shows plainly the importance of using fresh acid of full strength whenever experiments of this kind are to be made in order that results may be properly comparable.

Similarly it is improbable that a highly hydrated substance which loses much of its water at 100° C. would show as great a loss when dried in an ordinary air bath as in a current of dry air of that temperature.

Another point to be considered when it is desired to find the maximum amount of water that can be removed by any drying agent in a desiccator (which of course as a method is in general inferior to that in which a continuous current of dry air or other gas is passed over the substance) is that if many days are required for its removal—in other words if the substance is slow to part with its moisture—the later weighings should not be made from day to day but at ever-increasing intervals, otherwise a prematurely constant weight or even an increase may be observed. This is due to the fact that whenever the desiccator is opened, which must be twice for each weighing, it, at least in the upper part, becomes filled with moist air, and the substance itself may absorb some moisture before it can be returned to the desiccator; one or more days may then be required to restore the condition of equilibrium which obtained between the vapor tensions of water in the salt and in the air of the desiccator prior to opening the latter. Especially if the acid has become somewhat weakened is it possible for an increase to take place.

Originality is not claimed for the above observations on methods of drying, but it seems as if attention could not be too strongly or too frequently drawn to the points mentioned, which there is reason to fear are not always observed.

II. CRYSTALLOGRAPHIC DISCUSSION, BY W. H. MELVILLE.

The green crystals of sulphate of uranium and of the double sulphate of uranium and thorium described by Mr. Hillebrand are isomorphous and their crystallographic elements are almost identical. The angles between corresponding faces of the two salts differ by less than one degree, while their axial ratios are the same up to the second decimal

place.   Indeed the axes plotted for the drawing of the crystals of one
salt served for the drawing of those of the other.

The two sulphates crystallize in the prismatic (orthorhombic) system.
The habits of the two sets of crystals are quite unlike, and by simple
inspection no analogy would seem to exist between them, since those
of the double sulphate of uranium and thorium have all the appear-
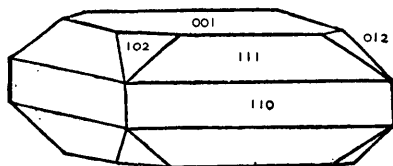ance of the pyramidal (tetragonal) combination of forms.

Fig. 1.—Crystalline form of uranium sulphate.

On the goniometer the simple sulphate of uranium presented the
most perfect faces, so that very accurate measurements were obtained.
On the other hand the similar angles of the double sulphate showed
great variations in the readings, often amounting to a difference of 40′
from the mean value.   The difficulty of preserving in artificial crystals
the same brilliancy of faces after drying which they possess in the
mother liquor accounts for the broad bands of these reflect signals.
However, after its system of crystallization was identified, the mean of
the most perfect and reliable measurements was taken.

The crystals of the double sulphate of uranium and thorium were
often twinned, the twinning plane being parallel to (100).[1]   Also indi-
viduals occurred on the faces (10$\bar{2}$) and (1$\underset{\cdot}{0}\bar{2}$) which were composed of
the face ($\bar{1}$10) in combination with minute planes of the forms (111) and
(012).
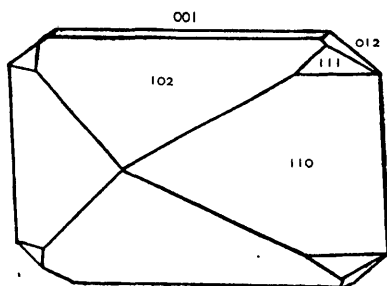
Fig. 2.—Crystalline form of uranium-thorium sulphate.

The forms observed on the crystals of both salts were the same, but
unequally developed, as the accompanying figures illustrate, in which

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[1] Since the original publication in the Am. Chem. Jour., vol. xiv, p. 1, of the results of the study of
the double sulphate it has been found that the twinning is of the nature of interpenetration, and that
the composition plane is parallel to (001) on those crystals in my possession.

the degree of development in the originals has been preserved. Forms: (001), (010) always a very narrow plane which does not appear in the drawings, (110), (111), (102), (012). Measurements:

(1) Uranium sulphate.	Measured.			Calculated.		
	o	′	″	o	′	″
001 ∧ 111	70	57	00	70	56	30
001 ∧ 102	52	13	00	52	10	07
001 ∧ 012	33	49	00	33	28	14
111 ∧ 1̄11	51	09	00	} fundamental		
111 ∧ 110	19	08	30			
110 ∧ 1̄10	54	23	00	54	21	00
102 ∧ 10̄2̄	75	34	00	75	39	46

Axial ratio: ă : b̆ : c̆ = 1 : 1·9478 : 2·5755

(2) Double sulphate of uranium and thorium.	Measured.		Calculated.		
	o	′	o	′	″
001 ∧ 102	51	57	51	57	37
001 ∧ 012	33	25	33	39	38
111 ∧ 1̄1̄1	51	46	} fundamental		
111 ∧ 110	19	08			
110 ∧ 1̄10	55	14	55	02	24
102 ∧ 10̄2̄	76	06	76	04	46

Axial ratio: ă : b̆ : c̆ = 1 : 1·9194 : 2·5563

Bull. 90——3

POWELLITE—CALCIUM MOLYBDATE: A NEW MINERAL SPECIES.

By W. H. Melville.

Attention has been recently called in mining journals to a locality in the western part of Idaho known as the "Seven Devils" where mining operations for some time past have been actively conducted. "The 'Seven Devils,' about 90 miles due north of Huntington and 15 miles east of Snake river, form a high, broken chain of mountains nearly 9,000 feet above the sea level. The mineral zone is about 1 mile wide by 4 miles in length."[1] The ore is worked for copper and silver, and is mainly the mineral bornite, a sulphide of copper and iron. "The formation on the west of the vein of ore is syenite and quartzite, while on the east wall is a soft white granite. A short distance to the east is a lime contact which extends south for some four miles, and forms a contact with granite. Along this contact some very good chimneys of ore have been discovered."

This bornite carries silver varying in quantity from 12 to 20 ounces to the ton. In one sample of very pure bornite Mr. R. L. Packard found by assay 14 ounces of silver to the ton. A sample from which I had separated for the most part the other mineral constituents gave me 15·65 ounces of silver to the ton. It was this latter fragment of bornite, weighing about 60 grammes, which Mr. Packard picked up from a dump before one of the tunnels in the mining claim called Peacock and which through this gentleman's kindness furnished the material for this paper. The specimen had evidently been exposed to weathering processes and had become friable to such an extent that between the fingers it could be crushed by slight pressure.

There were two associated minerals, one of which was identified by the following partial analysis as a lime alumina iron garnet. It was light brown, but not crystallized. It fused easily to a black glass.

	Per cent.
Loss on ignition	0·06
SiO_2	38·67
Al_2O_3	10·08
Fe_2O_3	16·00
FeO	0·91
CaO	33·35
MgO	0·77
CuO	trace
	99·84

[1] Quotations from Engineering and Mining Journal, Nov. 22, 1890.

Crystallized dark brown garnet is found in considerable abundance throughout this locality. The crystals exhibit the usual combination of rhombic dodecahedron and tetragonal trisoctahedron.

That which proved to be the most important constituent of the specimen, about 1·5 grammes, somewhat resembled scheelite at first sight, but a careful study of its characters excluded that mineral species from consideration. The strong reactions for molybdenum suggested a new species. The mineral was well cry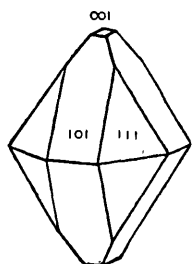stallized and easily detached in almost absolutely pure condition from its friable matrix. Angular measurements were obtained on a number of crystals, from which the crystallographic elements were calculated. The fundamental angle $(111)_\wedge(11\bar{1})$ was chosen because of its great accuracy, the signals on the goniometer being perfectly reflected from these planes. Other angles were read oftentimes between reflected signal and reflected light, and again between merely reflected light from the crystal faces.

Fig. 3.—Crystalline form of powellite.

The best crystals were about 0·04 (1ᵐᵐ) long, and others attained the maximum length of 0·10 inch. It was found that the crystals belonged to the pyramidal (tetragonal) system of crystallization, and were closely allied in habit and development to scheelite. In the following table of measurement this analogy is shown.

$a : c$	Powellite. 1 : 1·5445		Scheelite.* 1 : 1·5369
Between normals.	Observed.	Calculated.	
	° ′	° ′	° ′
$111 \wedge 11\bar{1}$	49 12	fundamental.	49 27
$111 \wedge 001$	65 24	65 24	65 16
$111 \wedge 1\bar{1}1$	79 56½	80 1	79 56
$101 \wedge 10\bar{1}$	65 55	65 51	66 6
$101 \wedge 111$	40 1½	40 1	39 58

* Dana's System of Mineralogy, 1883, p. 605.

From this comparison of angles and axial ratio it is evident that sharp and accurate observations must be obtained in order to distinguish by crystallographic means alone between these two species. Many crystals were examined and many trials were necessary before any difference in these angles from those of scheelite could be made out.

The following forms were observed:

$$(001) \ \infty\, a : \infty\, a : c$$
$$(111) \quad a : \quad a : c$$
$$(101) \quad a : \infty\, a : c$$
$$(110) \quad a : \quad a : \infty\, c$$

Small rudimentary planes appear on some crystals at the lower portion of the combination edges (111) (101), thus suggesting hemihedrism

as in scheelite. Indeed, the curved surface which often replaces these edges, giving the appearance of fused edges, adds greatly to the evidence in favor of this supposition.

No cleavage planes could be developed by mechanical means, yet occasionally fragments exhibited interrupted planes similar to cleavage surfaces. Hardness less than scheelite, about 3·5. Sp. gr. 4·526, mean of two determinations. Color yellow with a decided green tinge. Luster resinous. Crystals semitransparent. Brittle. The blowpipe characters are those ordinarily given under molybdates and tungstates, although the reactions of molybdenum in this case obscure those of tungsten associated with it. The mineral fuses at about 5 to a gray mass. Decomposed by nitric and hydrochloric acids.

With powellite was associated an olive-green substance which without doubt resulted from the decomposition of calcium molybdate, perhaps by water holding carbonic acid in solution, whereby molybdic ocher was formed.

The following analysis shows the unusual replacement of a part of the molybdic acid by tungstic acid. Rose's method of separating these acids was adopted, and abundant tests proved the purity of the respective products of separation. Molybdenum trisulphide was collected by reverse filtration and aliquot portions were taken for reduction. The molybdenum was weighed first as disulphide, and this weight was checked by reduction to metal in hydrogen gas by strong and long continued ignition. Mercurous tungstate was precipitated, then ignited, and tungstic acid was finally weighed.

Anaylsis of powellite.

	Per cent.	CaO required.
MoO₃.......................	58·58	22·79
WO₃........................	10·28	2·48
SiO₂.......................	3·25	25·28
CaO	25·55	
MgO........................	0·16	
Fe₂O₃......................	1·65	
Al₂O₃......................	trace	
CuO	trace	
S	undet.	
	99·47	

Calcium molybdate has never before been observed in nature, and although the mineral under discussion contains some calcium tungstate—according to analysis a little less than one molecule to eight molecules of calcium molybdate—yet the molybdate is now established as a species. It fills a gap heretofore existing in the series of isomorphous minerals of which scheelite is the type. If the natural molybdate and tungstate of lime have the same molecular volume as is most

probable, then the sp. gr. of pure $CaMoO_4$ should be $200 \div 46 \cdot 9 = 4 \cdot 267$ if the molecular volume, $288 \div 6 \cdot 14 = 46 \cdot 9$, is true for scheelite. By means of the equation for the determination of the sp. gr. of one constituent of a mixture containing two substances of which one is known, the sp. gr. of $CaMoO_4$ is $4 \cdot 3465$ assuming the sp. gr. of $CaWO_4$ to be $6 \cdot 14$ and that of the mixture $4 \cdot 526$ (sp. gr. of powellite). This close agreement in these two calculations of the sp. gr. of $CaMoO_4$ is an interesting and important confirmation of the chemical and physical data which are given above.

When this investigation was nearly completed my attention was called to a recent paper by H. Traube,[1] in which was discussed the influence of certain varying quantities of molybdic acid in scheelite upon the physical constants, namely, sp. gr. and axial ratio. The following scheme is interesting in that it illustrates those variations which different proportions of isomorphous mixtures of $CaWO_4$ and $CaMoO_4$ produce. No mathematical law seems to exist which will express these transitions.

	CaMoO₄.	Powellite.	Scheelite.			CaWO₄.
			Southwest Africa.	Zinnwald.		
				1	2	
%MoO₃	72	58·58	{ 8·09 7·63	8·23	1·92	0
Sp. gr.	4·267	4·526	5·96	5·88	6·06	6·14
a : c	1 : 1·5458	*1 : 1·5445		1 : 1·5349		1 : 1·5315

* Hiortdahl, Zeitsch. Kryst. u. Min., 1887, vol. 12, p. 413.

I take pleasure in naming this new mineral species in honor of Maj. J. W. Powell, Director of the United States Geological Survey.

[1] Neues Jahrbuch., 1890, Beil. Bd. 7, Heft 2.

MINERALOGICAL NOTES.

By W. H. Melville.

NATROLITE FROM MAGNET COVE, ARKANSAS.

The specimen of natrolite here described, from Magnet Cove, Arkansas, is associated with feldspar, while in the mass of the natrolite occur crystals of ægirite. From certain cavities crystals were selected which were adapted for measurements. The crystals were often acicular; others were stouter and terminated with brilliant planes. The general mass was compact and exhibited broad and perfect cleavage planes. The fusibility appeared somewhat higher than ordinarily given for natrolite, but thin splinters fused to a colorless bead. The sp. gr. 2·261 was determined.

The long terminated prisms proved to be trimetric and were built up of the forms (010), (100), (110), (111).

The following angles were read:

	°	′	°	′
$(110) \wedge (1\bar{1}0)$	88	51	[1]89	
$(010) \wedge (110)$	[2]44	16	45	30
$(111) \wedge (1\bar{1}1)$	36	56	36	40
$(111) \wedge (\bar{1}11)$	37	23¼	37	20
$(110) \wedge (111)$	63	18	63	20

The angle $(110) \wedge (1\bar{1}0) = 88° 51'$ was best obtained from cleavage planes which were found on the crystal, but the mean of all readings on the corresponding crystal planes gave 88° 44′.

Analysis.

	Per cent.		Per cent.
H_2O at 100° C	0·07	FeO	0·20
H_2O at 250° C	0·19	CaO	0·13
H_2O at 300°–350° C	3·42	MgO	0·09
H_2O over gas lamp	5·95	Na_2O	15·40
H_2O over blast	0·00	Total	99·83
SiO_2	47·56		
Al_2O_3	26·82		

[1] The second column of angles was taken from Dana's Mineralogy.

[2] Approximate.

TOURMALINE FROM NEVADA COUNTY, CALIFORNIA.

An uncommon form of tourmaline occurs in some localities of Nevada county, Cal. It is radiated and is composed of separable needles which show all the phenomena of hexagonal crystals under polarized light. The needles appear to cleave at right angles to their longer direction, or at all events the cross fracture has all the appearance of cleavage. A mass of these needles possess a dark brown color and silky luster, but singly they are transparent and almost colorless by transmitted light. The mineral fuses very easily to a light brown glass which is nonmagnetic. The specific gravity was found to be 3·065.

In the following analysis the boracic acid is determined by difference, although it was found, according to Marignac's method, to be much less than appears in the summary. The state of the iron was not determined. The analysis is therefore incomplete. Indeed all work upon the mineral ceased after identification.

Analysis.

	Per cent.		
Loss at 100° C	0·02		
Loss over lamp	3·04		
Loss over blast	0·47		
SiO₂	36·40		
Al₂O₃	33·64		
Fe₂O₂	3·13		
CaO	1·51		
MgO	10·01		
K₂O	0·12		
Na₂O	2·49		
F	0·74		
B₂O₃ by difference	8·74	direct.	6·52
	100·31		98·07
Less O	·31		·31
	100·00		97·76

The material analyzed was collected about two miles northwest of Colfax.

SPESSARTITE GARNET FROM LLANO COUNTY, TEXAS.

The following analysis of a yellow-colored mineral from Llano county, Texas, gave very closely the composition of spessartite garnet. It appears that the iron is in part replaced by calcium and magnesium, and hence it is very probable that the iron in this mineral exists in the protoxide state, although it could not be separately determined owing to the admixture of a little black oxide of manganese. The mineral was massive and was associated with quartz, a little magnetite, and black oxide of manganese. The silica was separated before analysis.

Analysis.

	Per cent.		Per cent.
Loss at 100° C	0·03	MnO	31·77
Loss on ignition	0·36	CaO	8·48
SiO$_2$	35·93	BaO	trace.
P$_2$O$_5$	none.	MgO...........................	0·69
TiO$_2$	trace.	Alkalis.....................	0·17
Al$_2$O$_3$	18·08		100·11
Fe$_2$O$_3$*	4·60		

*FeO corresponding = 4·39.

BISMUTHINITE FROM SINALOA, MEXICO.

A large deposit of bismuthinite occurs in the Rosario mining district, in the state of Sinaloa, Mexico, and it has been recently opened for the production of bismuth as well as for the recovery of silver and gold which the ore carries. An assay of carefully selected material was made, showing the contents of silver and gold to be 65·5 ounces and 0·25 ounce to the ton. This sulphide of bisumuth is associated with considerable chalcopyrite. and quartz and occurs in large brilliant blades with the broad cleavage so characteristic of bismuthinite. Its specific gravity is 6·624.

Analysis.

	Per cent.	S. required.
Bi	72·90	16·82
Pb................	6·03	0·93
Cu................	1·67	0·84
Fe	0·35	0·20
S	18·11	....
Quartz............	0·63	....
	99·69	18·79

The sulphur comes out too low in the analysis because it was determined in the filtrate from the carbonates precipitated by potassium carbonate, which does not wholly decompose bismuth sulphate.

NEW ANALYSES OF ASTROPHYLLITE AND TSCHEFFKINITE.

By L. G. Eakins.

I. ASTROPHYLLITE.

Near the noted cryolite locality at St. Peters dome, in the Pike Peak's region of Colorado, there was found some years ago an unusually fine lot of astrophyllite, and in such a pure condition that it was thought a new analysis would be not without interest, notwithstanding the fact that material from the same region had already been analyzed by König.[1]
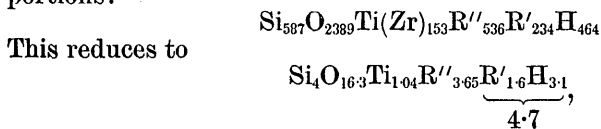
This astrophyllite occurs in large, brittle, micaceous blades, golden to brownish yellow in color, and perfectly free from admixed minerals, such as zircon, the only foreign matter being on the ends or sides of the blades which were in contact with the containing rock, so that pure material for analysis was readily obtained. In this analysis the zirconia was separated by a modification of the hydrogen peroxide method and weighed directly, being subsequently identified qualitatively. Fo comparison with this analysis, those made by König and by Bäckström[2] are added to the table below, König's being the one previously referred to, of material from the same region, and Bäckström's of the Eikaholmen mineral.

	Eakins.		König.		Bäckström.	
	Analysis.	Molecular ratio.	Analysis.	Molecular ratio.	Analysis.	Molecular ratio.
Ta_2O_5	0·34	·001	0·80	·002	....	....
SiO_2	35·23	·587	34·68	·578	33·02	·550
TiO_2	11·40	·143	13·58	·170	11·11	·139
ZrO_2	1·21	·010	2·20	·018	3·65	·030
Fe_2O_3	3·73	·024	6·56	·041	2·53	·016
Al_2O_3	trace.	....	0·70	·007	0·98	·009
FeO	29·02	·403	26·10	·362	21·76	·302
MnO	5·52	·078	3·48	·049	11·96	·169
CuO	0·22	·004	....	....	1·26	·023
MgO	0·13	·003	0·30	·008	0·92	·023
K_2O	5·42	·058	5·01	·053	5·78	·062
Na_2O	3·63	·059	2·54	·041	2·77	·045
H_2O	4·18	·232	3·54	·197	3·47	·193
			CuO ·42	·006	F 0·97	·051
	100·03		99·91		100·18	

[1] Proc. Am. Phil. Soc. Philad., 1877, vol. 16, p. 509.

[2] Given by Brögger in Groth's Zeitschrift, vol. 16. W. C. Brögger, Die Mineralien der Syenitpeg. matitgänge, etc.

From a discussion of these analyses of Bäckström and König, Brögger deduces the general formula $R''_4R'_4Ti(SiO_4)_4$ for astrophyllite. It will be seen that my analysis closely confirms this formula, agreeing with it better, in fact, than those from which it was derived. Calculating the small amount of ferric oxide present in with the R'' group, the molecular ratios of my analysis give the following elementary proportions:

$$Si_{587}O_{2389}Ti(Zr)_{153}R''_{536}R'_{234}H_{464}$$

This reduces to

$$Si_4O_{16\cdot3}Ti_{1\cdot04}R''_{3\cdot65}\underbrace{R'_{1\cdot6}H_{3\cdot1}}_{4\cdot7},$$

which is close to $R''_4R'_4Ti(SiO_4)_4$; the excess of the R' group is presumably due to the percentage of water being somewhat too large; this may result from incipient alteration of the mineral, which may also be the cause of the variation in color.

II. TSCHEFFKINITE.

A fragment of this rare mineral was last year sent to the National Museum by Mr. Horace M. Engle, of Roanoke, Virginia. And upon its identification he very kindly presented all at his disposal for the purpose of investigation; in addition to some small fragments there was one large mass, which before breaking weighed over $3\frac{1}{2}$ kilograms, most of it now being in the museum collection. - It was found in Bedford county, Virginia, a point considerably farther south than the locality of the material analyzed by Price.[1] The various pieces of this tscheffkinite when found were all more or less rounded nodules, with a superficial brownish yellow ocherous coating, evidently an alteration product, which at some later date may be made the subject of investigation to endeavor to determine the method of alteration. The beginning of this alteration was also seen in the numerous fissure planes developed in breaking up these nodules. Examination of a fresh surface showed a distinctly banded structure of lustrous black and dull black material, the bands varying from mere lines to over 5 millimeters in width. As well as could be these two differently appearing substances were separated and each analyzed by itself; such separation, however, was only approximate, as under a magnifying glass it was seen that each band contained veins of the other. Analysis I is that of the lustrous part and II that of the dull.

Duplicate determinations confirmed these specific gravities, the seemingly more altered one being the higher. The action of acids on the powdered materials shows a marked difference, the lustrous portion being completely decomposed in a few minutes by warm and moderately strong hydrochloric, sulphuric, or nitric acids, while an hour or more was necessary to decompose the dull portion under similar conditions.

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[1] R. C. Price, Am. Chem. Journal, Jan., 1888.

These analyses show that the two bands are practically identical in composition, the dull being somewhat more hydrated. The molecular ratios seem to lead to no definite or satisfactory formula, a result quite in accordance with the evidence furnished by the microscopical examination of sections. For this purpose chips were taken showing both bands, but as in the case of the chemical analysis, they were seen to be practically the same.

	I.		II.	
	Analysis.	Molecular ratio.	Analysis.	Molecular ratio.
Ta_2O_5	0·08	....	0·08	....
SiO_2	20·21	·337	21·49	.358
TiO_2	18·78	·235	18·99	·237
ZrO_2	trace (?)	....	trace (?)	....
ThO_2	0·85	·003	0·75	·003
$(Y, Er)_2O_3$	* 1·82	·006	† 1·64	·005
$(La, Di)_2O_3$	19·72	·059	17·16	·052
Ce_2O_3	20·05	·061	19·08	·058
Al_2O_3	3·60	·035	3·65	·036
Fe_2O_3	1·88	·012	2·89	.018
FeO	6·91	·096	5·92	·082
CaO	4·05	·072	5·24	·094
MgO	0·55	·014	0·48	·012
Na_2O	0·06	·001	0·04	·001
H_2O	0·94	·052	2·06	·114
	99·50		99·47	
Specific gravity	4·33 at 27°		4·38 at 22°.2	

* Molecular weight = 308.   † Molecular weight = 312.

I am indebted to Mr. Whitman Cross, of the U. S. Geological Survey, for the following notes on the thin sections:

The sections consist mainly of reddish and yellowish brown transparent amorphous substance, apparently the original material; this is traversed in all directions by cracks, from which there has proceeded a decomposition producing a reddish-brown opaque ocherous matter, which fills the cracks and replaces the original material so that in certain spots there is now merely a network of the two substances. In each section there are two parallel bands of secondary minerals, nothing corresponding to which was detected in the chips before the sections were made. These bands consist chiefly of two colorless minerals, the more abundant occurring in irregular grains closely resembling calcite in strength of refraction and double refraction; the other occurs in rounded grains and is probably sphene. In addition to the two colorless minerals in these bands, there also appear two brownish substances, one of which has distinct prisms, without terminal planes, shows strong pleochroism, and its absorption parallel to the vertical axis is so strong as to make it opaque, while at right angles to this axis it is yellow-brown. More abundant than this prismatic mineral is one occurring in apparent flakes of reddish-brown color; it is doubly refracting, but not strongly pleochroic, and can not be identified with any of the substances already mentioned. Adjacent to these bands, and replacing the amorphous material to varying distances, is still another substance, in general appearance similar to the prismatic mineral, but evidently different as it shows

no very marked absorption. This mineral is also strongly pleochroic, varying from yellow-brown to chestnut-brown. All of it in the sections seems to have a uniform crystallographic orientation, the cause of this uniformity not being apparent. Its relations to the amorphous substances are similar to those which I have observed in several instances between crystalline allanite and the amorphous variety.

The microscopical examination having shown this tscheffkinite to be such a mixture, it became desirable to examine others in the same way.

The only one available for this purpose was that analyzed by Price, a specimen of which is in the National Museum collection. This specimen has the same general appearance and banded structure as my own. Chips were taken from it for sections, which Mr. Cross examined and found to be in every respect similar to the other, about the only noticeable difference being in Price's material a somewhat greater development of the opaque ocherous decomposition product of the transparent amorphous substance than in mine, and a lesser development of the colorless minerals.

Taking into consideration the results of this work, and the manifest contradictions of most of the earlier analyses, it seems reasonable to conclude that, unless one of the earlier analyses can be shown to have been made on pure material, the so-called tscheffkinite is not a mineral in any strict construction of the word, but merely a mixture; the structure of the chemically complex body or bodies evidently its basis being a problem to be elucidated in the future when purer material may be found.

TWO NEW METEORITES.

By L. G. Eakins.

I. METEORIC IRON FROM PULASKI COUNTY, VIRGINIA.

The material for this analysis was furnished by Mr. G. F. Kunz, in whose possession the original mass, weighing about 30 pounds, now is. This iron calls for no special comment in itself. The specific gravity is 7·95 at 23°.

Analysis.

Fe	93·59
Ni	5·56
Co	0·53
Cu	trace.
P	0·27
S	0·01
Si	trace.
	99·96

II. STONE FROM WASHINGTON COUNTY, KANSAS.

The material for this work was also furnished by Mr. Kunz. A detailed account of its fall has been published by Mr. F. H. Snow, in Science, July 18, 1890. This stone fell on June 25, 1890, and was noted by several observers by the sound it made on falling, the actual fall also being seen by at least one; on striking the earth it buried itself out of sight in a hole about 4 feet deep.

The stone when taken up weighed 184 pounds, and was cracked in two.

In general appearance it is grayish black, with white particles scattered throughout, these being probably a pyroxene. Particles of troilite and of iron were also visible.

The specific gravity of the mass was 3·49 at 21·6°.

As is usual with this class of stones the metallic portion was extracted and analyzed by itself; the portion from which this was taken then being treated with dilute hydrochloric acid, this dissolving troilite and olivine.

The analyzes are as follows:

Metallic particles.

Fe .... 86·76
Ni .... 12·18
Co... ·83

_____

99·77

Material left after extracting metallic particles.

	Soluble in HCl.			Insoluble in HCl.	
	Analysis.	Less troilite.	Calculated to 100 per cent.	Analysis.	Calculated to 100 per cent.
SiO_2	19·15	19·15	38·50	24·29	53·80
Al_2O_3	....	....	....	1·95	4·32
Cr_2O_3	....	....	....	·64	1·41
FeO	16·15	11·71	23·54	5·41	11·98
NiO........	·34	·34	·69	....	....
CoO.........................	trace.	trace.	trace.	....	....
MnO.........................	·17	·17	·34	trace.	trace.
CaO	·06	·06	·12	1·84	4·08
MgO.........................	18·31	18·31	36·81	10·10	22·37
K_2O.........................	....	....	....	·12	·27
Na_2O.........................	....	....	....	·80	1·77
S	1·97	....	....	....	....
	56·15	49·74	100·00	45·15	100·00
Less O for S	·99				
	55·16				

It will be seen that in the analysis of the part soluble in hydrochloric acid all the sulphur found has been calculated as troilite. Taking this amount, the metallic particles found, and the relative proportions of the silicates, the approximate composition of the mass is found to be:

Nickel iron.. 7·7
Troilite .... 5·0
Silicates soluble in HCl.. 46·0
Silicates insoluble in HCl...................................... 41·5

_____

100·2

ON THE ACTION OF PHOSPHORUS OXYCHLORIDE ON THE ETHERS AND CHLORHYDRINES OF SILICIC ACID.

By H. N. Stokes.

That silica can combine with other acids, forming mixed anhydrides, has long been known, and several such bodies have been described. Friedel and Ladenburg[1] obtained the tetra-acetyl derivative $Si(O.CO.CH_3)_4$ by treating silicon tetrachloride with acetic acid or anhydride. Friedel and Crafts[2] obtained $Si(OC_2H_5)_3O.CO.CH_3$ from ethyl orthosilicate and acetic anhydride. Hautefeuille and Margottet[3] described a crystalline compound, $SiO_2.P_2O_5$, formed by fusing amorphous silica with metaphosphoric acid.

By the action of phosphorus oxychloride on silicic ethers and their chlorine derivatives, I have obtained bodies which consist of phosphoryl chlorides, in which the chlorine is partly replaced by a residue of silicic acid, and which are therefore chlorides of silicophosphoric acids.

Phosphorus oxychloride was caused to react upon *orthosilicic ethyltrichlorhydrine*, $SiCl_3.OC_2H_5$, hoping thereby to obtain the silicon oxychloride described by Friedel and Ladenburg[4] and by Troost and Hautefeuille:[5]

$$3SiCl_3.OC_2H_5 + POCl_3 = (SiCl_3O)_3PO + 3C_2H_5Cl,$$
and
$$2(SiCl_3O)_3PO = 3Si_2OCl_6 + P_2O_5.$$
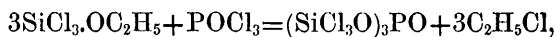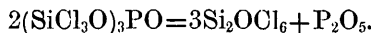
The experiment proved that this reaction does not take place.

If the trichlorhydrine be heated in a sealed tube with an excess of phosphorus oxychloride, no reaction is apparent below 175°, the contents remaining perfectly clear. If the temperature be kept at 180–200°, a white amorphous substance is soon formed, which is sufficiently porous to absorb all the liquid products. After two to three hours' heating the tube is opened, when ethyl chloride escapes in large quantities. On placing the tube in an air bath, heated at about 150°, and connecting it with a condenser, a large amount of liquid may be collected. The solid remaining in the tube may then be freed from excess of phosphorus oxychloride by passing a current of dry air over it by means of a capillary.

[1] Ann. Chem. (Liebig), vol. 146, p. 174.
[2] Ann. chim. phys. [4], vol. 9, p. 47.
[3] Compt. rend., vol. 96, p. 1052.
[4] Ann. Chem. (Liebig), vol. 147, p. 355.
[5] Ann. chim. phys. [5], vol. 7, p. 465.

The liquid, on fractioning, is readily separated into phosphorus oxychloride (boiling at 110°) and silicon tetrachloride (boiling at 57°–61°), though much of the latter is lost, being carried off by the ethyl chloride, which is abundantly held in solution. The product obtained after six distillations was analyzed.

	Calculated for SiCl$_4$.	Found.
Si............................	16·52	16·24

The view with regard to its nature was confirmed by converting it into ethyl orthosilicate (boiling at 165·5°). As the liquid passed over entirely below 112°, no silicon oxychloride was formed, and no substances other than those mentioned could be detected. Analyses of the solid substance gave—

	Calculated for SiP$_2$O$_6$Cl$_2$.	Found.	
		I.	II.
Si............................	10·92	10·17	10·06
P............................	24·15	25·16	25·11
Cl............................	27·59	27·33	....

The agreement is only approximate, as the substance could not be purified in any way; and on heating too long or at too high a temperature, when drying, phosphorus oxychloride is slowly given off. It is possibly a mixture of substances, in the formation of which the one supposed represents one stage. If heated above 200° phosphorus oxychloride is given off, and at red heat, phosphorus pentoxide; and the residue, left at a white heat, consists of amorphous silica imbedded in a vitreous substance, probably the compound SiO$_2$.P$_2$O$_5$ of Hautefeuille and Margottet. The loss on heating corresponds to the equation—

$$6SiP_2O_6Cl_2 = 3SiO_2 + 3(SiO_2.P_2O_5) + 4POCl_3 + P_2O_5.$$

	Calculated.	Found.
Loss.......................	49·01	51·86

The formation of the substance, which, for reasons given below, may be designated as *silico-pyrophosphoryl chloride*, is most simply expressed by the equation—

$$4SiCl_3(OC_2H_5) + 2POCl_3 = 3SiCl_4 + SiP_2O_6Cl_2 + 4C_2H_5Cl.$$
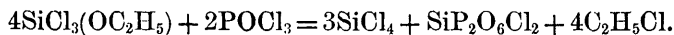
Silico-pyrophosphoryl chloride is a very bulky substance, resembling the lightest form of amorphous silica. It may be obtained perfectly colorless, but is usually more or less colored by organic matter, formed

by secondary reactions, when heated too high. It is extremely hygro-scopic, and gives off hydrochloric acid instantly when exposed to moist air. It is readily soluble in absolute alcohol, a proof that it contains no free silica. The alcoholic solution, which probably contains an ether of silico-phosphoric acid, may oe evaporated nearly to dryness or heated any length of time at 150° without decomposition. On heating at 225° it soon deposits transparent, gelatinous silica. The solution in alcohol is attended with considerable rise of temperature. The substance is insoluble in ether. If cold water be poured on the fine powder it read-ily dissolves, with the exception of a few flakes of silica; but if first moistened, or if in lumps, most of the silica remains undissolved. The best way to get a clear aqueous solution is to dissolve in a little alcohol and then to dilute with water. The reaction with water alone is some-what violent. The aqueous solution may be kept a long time—indeed, may be strongly concentrated on the water bath—but on evaporation *to dryness* a vitreous mass is left, from which water extracts phosphoric acid only.

All attempts to prepare salts of silico-phosphoric acid have failed. Ammonium carbonate precipitates gelatinous silica. If the cold aque-ous solution, prepared as described above, be acidified with nitric acid, excess of silver nitrate added, and filtered from silver chloride, a clear solution is obtained. If to this be added, drop by drop, dilute ammonia, a white precipitate is formed, which at a certain point changes to yel-low. The analysis of the white substance (dried at 100°) gave—

	Calculated for $Ag_4P_2O_7$.	Found.
Ag	71·17	·71·25

The yellow precipitate proved to be merely silver ortho-phosphate.[1] The filtrate from the silver salts gives an abundant precipitate of silicic acid when warmed with ammonia. The magnesia precipitate also shows the characteristic reaction of magnesium pyro-phosphate, dis-solving in acetic acid when precipitated in the cold, and being repre-cipitated from this solution on boiling.

The substance is therefore a derivative of pyro-phosphoric acid, and the formation of some ortho-phosphoric acid may be explained by the decomposition of the former, pyro-phosphoryl chloride dissolving in water with formation of ortho-phosphoric acid.[2]

Heated with phosphorus pentachloride at 100°, silico-pyrophosphoryl

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[1] The reaction described above affords a convenient method for separating, at least approximately, ortho- from pyro-phosphoric acid. A solution of the acids—or their soluble salts—is acidified in the cold with nitric acid and silver nitrate added in excess. On adding dilute ammonia, drop by drop, all the pyro-phosphoric acid is precipitated before any of the ortho-phosphoric acid comes down. At this point a single drop of ammonia gives a yellow tinge to the precipitate, which a drop of dilute nitric acid causes to disappear. If the liquid be now filtered, all the pyro-phosphoric acid will be in the pre-cipitate and all the ortho-phosphoric acid in the filtrate. The reaction is so sharp that it might pos-sibly be used to separate the acids quantitatively.

[2] Michaelis: Ber. d. deutsch. chem. Ges., vol, 4, p. 767,

chloride is readily and quantitatively converted into silicon tetrachloride and phosphorus oxychloride:

$$SiP_2O_6Cl_2 + 4PCl_5 = SiCl_4 + 6POCl_3.$$
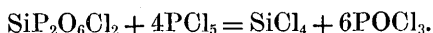
The tetrachloride was isolated, and expectations with regard to its nature were confirmed on converting it into the ether (b. p., 165·5°). No silicon oxychloride could be obtained. If heated with an insufficient amount of phosphorus pentachloride, the excess remains apparently unchanged.

The conversion of a derivative of silicic acid into silicon tetrachloride at so low a temperature has not been hitherto observed. R. Weber[1] obtained the tetrachloride and phosphorus oxychloride by passing the vapor of phosphorus pentachloride over silica at a red heat. As the pentachloride is completely dissociated at 300° into trichloride and chlorine, the reaction is due to the action of chlorine, combined with the reducing action of the trichloride—

$$SiO_2 + 2PCl_3 + 2Cl_2 = SiCl_4 + 2POCl_3—$$
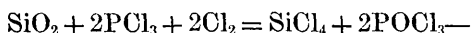
which is analogous to the old method of preparing the tetrachloride—

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$
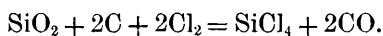
As I have convinced myself, phosphorus pentachloride does not act on amorphous silica (dried at 100°) even at 250°, further than to dehydrate it.

The action of a smaller quantity of phosphorus oxychloride on the trichlorhydrine is similar. Three-molecule trichlorhydrine and one-molecule oxychloride, heated at 180°, gave ethyl chloride, silicon tetrachloride, and a solid product completely soluble in alcohol and water, the composition of which differed, however, from that of the substance above described. (Found: Si, 15·25; P, 22·30; Cl, 14·13.)

The action of an excess of phosphorus oxychloride on the chlorhydrines $SiCl_2(OC_2H_5)_2$ and $SiCl(OC_2H_5)_3$ is essentially similar. At 180–200° a solid substance is formed, with much ethyl chloride and silicon tetrachloride. The amount of the tetrachloride is directly, and that of the solid inversely, proportional to the amount of chlorine in the chlorhydrine. In each case the tetrachloride was isolated in a state of approximate purity and converted into the ortho-ether, boiling at 165·5°. No other volatile substances could be detected. The solid body was completely soluble in alcohol and, in brief, showed all the properties above described as belonging to silico-pyrophosphoryl chloride. The analysis of the product from $SiCl_2(OC_2H_5)_2$ gave—

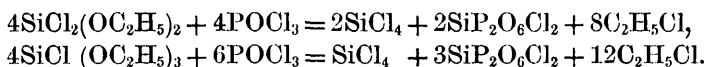|	Calculated for $SiP_2O_6Cl_2$.	Found.	
		I.	II.
Si	10·92	11·68	11·80
P	24·15	24·53	24·91

[1] Ann. der Phys., Pogg., vol. 112, p. 619.

The product from $SiCl(OC_2H_5)_3$ gave—

|	Calculated for $SiP_2O_6Cl_2$.	Found.
Si..................	10·92	10·15
P..............................	24·15	24·54
Cl	27·59	24·73

The results, as before, are only approximate; but, it must be remembered, the body loses phosphorus oxychloride slowly on heating, and only the crude product could be analyzed. The reactions in these cases are:

$$4SiCl_2(OC_2H_5)_2 + 4POCl_3 = 2SiCl_4 + 2SiP_2O_6Cl_2 + 8C_2H_5Cl,$$
$$4SiCl\ (OC_2H_5)_3 + 6POCl_3 = SiCl_4 \ + 3SiP_2O_6Cl_2 + 12C_2H_5Cl.$$

Orthosilicic ether, $Si(OC_2H_5)_4$, was heated with excess of phosphorus oxychloride for two hours at 180°–200°. The tubes contained a solid substance and ethyl chloride. On distilling off the excess of oxychloride and decomposing it with water only a trace of silica was left after evaporation, showing that practically nó volatile silicon compound was formed. The solid, the properties of which were in every respect identical with those of the body above described, gave on analysis—

	Calculated for $SiP_2O_6Cl_2$.	Found.		
		I.	II.	III.
Si.................	10·92	9·92	10·05	10·21
P	24·15	25·52	25·63	25·84
Cl	27·59	29·66	29·90	....

The reaction is, therefore, represented by the equation—

$$Si(OC_2H_5)_4 + 2POCl_3 = SiP_2O_6Cl_2 + 4C_2H_5Cl.$$
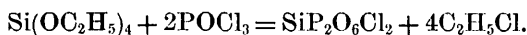
The constitution of the silico-phosphoryl chloride is possibly very complex. The simplest constitutional formula, deduced from the last equation, would be

$$Si \begin{cases} O \\ O \end{cases} > POCl \\ \begin{cases} O \\ O \end{cases} > POCl \; ;$$
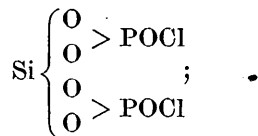
but as this would give no pyro-phosphoric acid on decomposition with water, we must assume that it is

$$SiO < {O.PO.Cl \atop O.PO.Cl} > O;$$
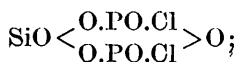
or a polymer containing the group—O.PO.O.PO.O—, which makes it a derivative of metasilicic acid. The cause of the formation of silicon tetrachloride from the chlorhydrines is not clear. It is obviously not due to a direct replacement of ethoxyl by chlorine, for then it should be obtained in the same amount from each chlordydrine, or from the ether; whereas the latter does not give it, and the amount obtained from the former is proportional to the amount of chlorine they already contain. Besides, no phosphoric ethers are formed. Nor does the supposition explain the formation of silico-pyrophosphoryl chloride in quantities inversely as the amount of chlorine. A possible explanation is the following: The chlorhydrines[1] are formed by heating mixtures of ortho-silicic ether with silicon tetrachloride, or of either of these with other chlorhydrines, that one being formed in largest amount which corresponds in compósition to the mean composition of the mixture; for example—

$$3Si(OC_2H_5)_4 + SiCl_4 = SiCl(OC_2H_5)_3.$$
$$2SiCl_3(OC_2H_5) + Si(OC_2H_5)_4 = 3SiCl_2(OC_2H_5)_2.$$
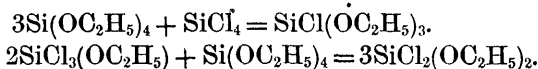
These reactions take place below 200°; partial dissociation occurring, the products reuniting to form that body which tends to give the liquid a homogeneous composition. Doubtless the reverse process takes place at the same time; for example—

$$4SiCl(OC_2H_5)_3 = 3Si(OC_2H_5)_4 + SiCl_4;$$

and if phosphorus oxychloride be present—which, as just shown, destroys the ether—this can go on until all the chlorhydrine has been converted into ether and tetrachloride. This explanation is simple enough, but, as shown by the action of phosphorus oxychloride on *disilicic* chlorhydrines, the actual process is possibly more complicated.

By heating a mixture of trichlorhydrine, phosphorus and iodine, a solid of similar properties was obtained, and silicon tetrachloride was formed. The reaction was not followed further.

ACTION OF PHOSPHORUS OXYCHLORIDE ON DERIVATIVES OF DISILICIC ACID.

Hexethyl disilicate,[2]

$$O<{Si(OC_2H_5)_3 \atop Si(OC_2H_5)_3},$$
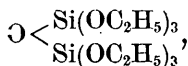
was heated with an excess of phosphorus oxychloride in sealed tubes at 180-200° for two or three hours. The tubes contained a white solid, outwardly resembling silico-pyrophosphoryl chloride and much ethyl-chloride. No volatile silicon compound was formed. The solid resembled in its general properties the one described. It was completely soluble in alcohol, and therefore contained no free silica. The solution

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[1] Friedel and Crafts: Ann. chim. phys. [4], vol. 9, pp. 11, 14, 15,
[2] Ibid, p. 24,

gave the reactions of pyro-phosphoric acid. It differed markedly in composition from the orthosilicic derivative, the analysis giving—

	Calculated for $SiP_2O_6Cl_2$.	Found.
Si	10·92	17·02
P	24·15	23·91
Cl	27·59	21·04

This corresponds to no probable formula, but contains 4 atoms Si to 5 atoms P, instead of 1 atom Si to 2 atoms P. Phosphorus pentachloride converts it readily (at 100°) into silicon tetrachloride and phosphorus oxychloride. No silicon oxychloride is formed, the product passing over entirely below 112°. The tetrachloride was isolated and converted into the tetrethyl ether (boiling at 165.5°).

The ease with which the ortho-chlorhydrines give, with phosphorus oxychloride, silicon tetrachloride, led to an analogous experiment with ·the *disilicic chlorhydrines*, in the hope that in this way silicon oxychloride might be obtained. On the above hypothesis, we should have, in the presence of phosphorus oxychloride, the following reaction:

$$6O <^{SiCl_3}_{SiCl_2(OC_2H_5)} = 5O <^{SiCl_3}_{SiCl_3} + O <^{Si(OC_2H_5)_3}_{Si(OC_2H_5)_3};$$
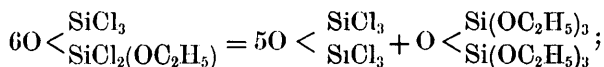
and analogous reactions with the other chlorhydrines.

The disilicic chlorhydrines, which have not hitherto been prepared, are formed by heating disilicic ether with an excess of silicon tetrachloride for several hours at 200°. A gradual exchange of ethoxyl and chlorine occurs, disilicic chlorhydrines and ortho-silicic trichlorhydrine being formed. After distilling off the latter, the residue is again heated with silicon tetrachloride, whereby the conversion is carried further. In this way a mixture of disilcic chlorhydrines was obtained, which, after freeing from all ortho-silicic compounds by repeated distillation, boiled at 170–220°. A chlorine determination showed that it contained the equivalent of 65 per cent Si_2OCl_6. No attempt was made to isolate any of these chlorhydrines, as no less than eight are theoretically possible, and it was presumed that they would all act in the same way toward phosphorus oxychloride. The mixture was heated with excess of phosphorus oxychloride (based on the amount of chlorine shown by analysis) for two and a half hours at 180–200°; after which no further action was observed. The appearance of the product was the same as in previous experiments. The liquid product was distilled off and fractioned. It was found to consist of an excess of phosphorus oxychloride, of *silicon tetrachloride*, which was recognized through conversion into the ether, and ethyl chloride. The liquid boiled entirely below 112°, and therefore none of the expected silicon oxychloride was formed. The solid product was markedly different from those before obtained. It

was only partly soluble in alcohol, and on boiling out with the solvent a large residue of *silica* was left. Besides a soluble silico-phosphoryl chloride and ethyl chloride the only products were silicon tetrachloride and silica. If the oxychloride be formed at all, it is at once decomposed in the presence of phophorus oxychloride—

$$2Si_2OCl_6 = 3SiCl_4 + SiO_2$$
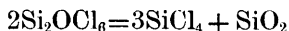
Whether this actually occurs is questionable, as the oxychloride and all the other substances concerned are, by themselves, stable at a much higher temperature than that employed. I am unable to give any satisfactory explanation of the reaction.

Amorphous silica, prepared from water-glass and dried at 100°, gives with phosphorus oxychloride a small amount of silico-phosphoryl chloride, soluble in alcohol: 3·5 per cent of the silica was converted into this compound.

The silicon tetrachloride used as the starting-material of these experiments was made by the admirable method of Gattermann.[1] For preparing the silicon mixture I used, instead of test tubes, sheet-iron crucibles of about 200^{cc} capacity. These are nearly filled with an intimate mixture of three parts quartz powder and one part magnesium powder, tightly pressed down. On heating over a blast lamp, the reaction starts in a few seconds, and is indicated by the whole crucible suddenly becoming red-hot. During the reaction the lid must be held down firmly. I prefer to extract the magnesia from this product before using it, as less care has to be used in regard to temperature when passing chlorine over it. By using ice alone, to condense the chloride, nearly the theoretical yield is obtained; the crude product loses about 15 per cent in the process of purification.

The *orthochlorhydrines* were prepared essentially according to the method of Friedel and Crafts.[2] Any mixture may be used which coincides in composition with that of the chlorhydrine desired. The yield is never theoretical, no matter how long the heating may be continued. The yields of pure substance, obtained after six distillations, were as follows: Monochlorhydrine, 65 per cent; dichlorhydrine, 40 per cent; trichlorhydrine, 47 per cent. More can, of course, be obtained by uniting and heating the residues.

Friedel and Crafts[3] obtained the disilicic ether by adding to silicon tetrachloride, drop by drop, alcohol containing the calculated amount of water. They claim that the yield is nearly theoretical. I am not able to confirm this statement. By following their directions exactly, I obtained a mixture of ortho- and disilicic ethers, with ethers of much higher boiling points. After repeated fractioning, only 33 per cent of the theoretical yield of disilicic ether was obtained, and the amount of

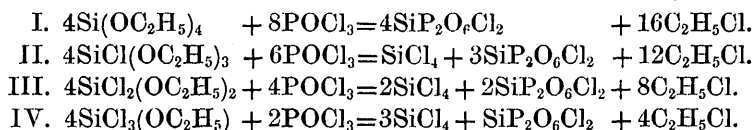[1] Ber. d. deutsch. chem. Ges. vol. 22, pp. 186–188.
[2] Loc. cit.
[3] Ann. chim. phys. [4] vol. 9, p. 26.

ortho-ether was much greater. This is due to the fact that the added water acts on the disilicic ether already formed, giving more complex bodies, so that there is an excess of tetrachloride, which is converted into ortho-ether.

The essential results of these experiments may be summed up as follows:

Phosphorus oxychloride acts on orthosilicic ether and its chlorine derivatives according to the following equations:

$$I. \quad 4Si(OC_2H_5)_4 \quad + 8POCl_3 = 4SiP_2O_6Cl_2 \qquad + 16C_2H_5Cl.$$
$$II. \quad 4SiCl(OC_2H_5)_3 + 6POCl_3 = SiCl_4 + 3SiP_2O_6Cl_2 + 12C_2H_5Cl.$$
$$III. \quad 4SiCl_2(OC_2H_5)_2 + 4POCl_3 = 2SiCl_4 + 2SiP_2O_6Cl_2 + 8C_2H_5Cl.$$
$$IV. \quad 4SiCl_3(OC_2H_5) + 2POCl_3 = 3SiCl_4 + SiP_2O_6Cl_2 + 4C_2H_5Cl.$$

The body $SiP_2O_6Cl_2$ is the chloride of a silico-pyrophosphoric acid, is decomposed by water into silica and pyrophosphoric acid and is easily converted by phosphorus pentachloride into silicon tetrachloride and phosphorus oxychloride.

The ether of disilicic acid acts similarly, giving a silico-phosphoryl chloride of different composition but analogous properties.

The chlorhydrines of disilicic acid do not give with phosphorus oxychloride, as might be inferred, a silico-phosphoryl chloride and silicon oxychloride, but a mixture of the first with free silica and silicon tetrachloride.

Phosphorus trichloride also acts on orthosilicic ether at 200°, giving a white solid, and liquid products, which will be further studied.

ON THE COLLOIDAL SULPHIDES OF GOLD.

BY E. A. SCHNEIDER.

The credit of having definitely established the proportions in which gold and sulphur combine is due to L. Hoffmann and G. Krüss.[1] They found, as a result of many elaborate experiments, that gold can form with sulphur only aurous sulphide Au_2S and auroauric sulphide Au_2S_2, but not auric sulphide Au_2S_3. It must be observed, however, that lately Antony and Lucchesi[2] have stated that they succeeded in pre-paring auric sulphide by passing dry hydrogen sulphide over lithium aurochloride.

While studying both the sulphides, which were prepared in a pure state by Krüss, I repeatedly noticed their tendency to form colloidal solutions. I have found in chemical literature some suggestions bearing on this behavior, but no special investigation upon the subject has been recorded. Consequently it seemed desirable to look into the matter.

COLLOIDAL AUROUS SULPHIDE.

Hoffmann and Krüss state that freshly precipitated aurous sulphide forms with water a clear brown solution, without, however, laying any stress on its colloidal nature. Although some of the properties of the solution mentioned by Hoffmann and Krüss, for instance, coagulation by hydrochloric acid and by neutral salts (sodium chloride, potassium chloride), indicate clearly its colloidal character. I have, nevertheless, made an experiment to prove it directly. The brown, clear solution was placed in a dialyser and after the lapse of several days the liquid in the outer jar did not contain a trace of any gold compound. Consequently the aurous sulphide solution is colloidal, and to compare it with sodium sulphide, as Hoffmann and Krüss have done, in order to characterize the position of gold in the periodic system, is not admissible, particularly as it is well known that the sulphides of the heavy metals in general can form colloidal solutions. This subject Spring and Boeck[3] and later Winssinger[4] have investigated. In order to prepare colloidal aurous sulphide in sufficient quantity the directions of Hoffmann and Krüss should mainly be followed, but with the following changes:

[1] Ber. d. deutschen chem. Gesell., vol. 20, pp. 2369 and 2704.
[2] Gazzetta chimica italiana, vol. 20, pp. 601–607.
[3] Bull. de la société chimique, vol. 48, p. 165.
[4] Ibid., vol. 49, p. 452.

Aurous cyanide isolated from potassium aurocyanide by means of hydrochloric acid is dissolved in the least possible quantity of potassium cyanide; the solution is then saturated with sulphuretted hydrogen. Hydrochloric acid is now added and the liquid gently warmed until it becomes distinctly brown and cloudy, but the heating should be discontinued as soon as a heavy precipitate begins to form. This solution is next subjected to a prolonged dialysis. In the dialyser remains a dark brown colloidal solution of aurous sulphide, which can be separated by decantation and filtration from solid aurous sulphide, which latter is usually present in considerable quantities.

The strongest solution obtained by this method contained 1·740 grammes aurous sulphide in the liter. An attempt was made to concentrate this liquid in vacuo to half of its bulk. A small quantity, however, of aurous sulphide separated out when this degree of concentration was reached.

When a solution of aurous sulphide is heated to a temperature of 200–230° gold separates out and simultaneously sulphuric acid is formed. On freezing and subsequent thawing aurous sulphide is deposited in solid form. The same behavior has been observed in the case of many other colloidal solutions.[1] It appeared to be of some interest to ascertain whether colloidal aurous sulphide possesses the property to undergo mutual decompositions similar to those of sulphuretted hydrogen and of the soluble sulphides of the alkalies and alkaline earth metals; and particularly whether it would react with other colloidal solutions, such as colloidal ferric hydrate, according to the following equations:

$$2Fe(OH)_3 + 3Au_2S = Fe_2S_3 + 3Au_2O * + 3H_2O$$
$$2Fe(OH)_3 + 3Au_2S = 2FeS + S + 3Au_2O + 3H_2O$$
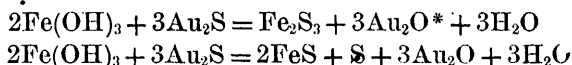
Some time ago Wright[2] studied the action of sulphuretted hydrogen on ordinary ferric hydrate. I find that colloidal ferric hydrate behaves in the same way. If sulphuretted hydrogen is conducted into a solution of colloidal ferric hydrate at ordinary temperatures iron sulphide immediately separates out. The reaction proceeds probably according to the equations—

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O$$
$$2Fe(OH)_3 + 3H_2S = 2FeS + S + 6H_2O$$
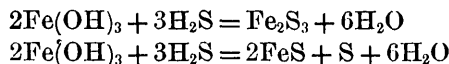
which Wright has demonstrated to be probable in the case of the ordinary compound. If solutions of colloidal ferric hydrate and colloidal aurous sulphide are mixed no reaction takes place either at ordinary or at higher temperatures. This fact confirms the hypothesis[3] that in

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[1] Zeitschrift f. phys. Chem., vol. 4, p. 480.

[2] Jour. Chem. Soc., 1883, vol. 43, p. 156.

[3] C. Barus and E. A. Schneider: On the nature of colloidal solutions. Zeitschrift f. phys. Chem., vol. 8, p. 278.

* The soluble aurous oxide has been described by Krüss; Ann. Chem. Pharm., vol. 237, p. 283.

colloidal solutions extremely small solid particles are held in suspension, for solid substances do not react among themselves, excepting possibly when very high pressure is used.

COLLOIDAL AUROAURIC SULPHIDE.

Weak solutions of colloidal auroauric sulphide have been already prepared by Winssinger.[1] Comparatively concentrated solutions of auroauric sulphide may be obtained easily and in large quantity when the freshly precipitated compound is boiled with potassium cyanide or potassium polysulphide until about half of the gold salt has gone into solution. The undissolved sulphide is rinsed now with water in a dialyser and subjected to dialysis. After removal of all the crystalloids there remains in the dialyser a dark brown liquid, together with some solid auroauric sulphide, which can be easily separated by decantation and filtration.

The yield is equally good whether potassium cyanide or potassium polysulphide is used. In the second case, however, it seems to be more difficult to remove the crystalloids, even by protracted dialysis.

The colloidal auroauric sulphide solutions are perfectly transparent to both transmitted and reflected light (the latter is not always the case with colloidal solutions).

When the solution is frozen it behaves like the solution of aurous sulphide and most of the other colloids. It undergoes no change when heated to 240° in a sealed tube.

The strongest solution which I was able to obtain, according to the above described method, contained 0·8 gramme auroauric sulphide in the liter. Its color is dark brown and a layer of about 2 centimeters thickness is almost opaque.

In order to ascertain whether the auroauric sulphide had undergone change on dissolving, a liquid containing the compound in colloidal condition was coagulated.

The precipitated sulphide was reddish brown when moist; black when dried. The analysis gave data which corresponded well with the formula Au_2S_2.

Colloidal solutions of *aurous* sulphide can be obtained by treating aurous sulphide with potassium polysulphide, but the yield is much smaller than in the case of auroauric sulphide.

That colloidal solutions are formed by prolonged washing with water of a precipitate which has been already acted on by a solvent has been observed several times. Wright[2] states that ferrous sulphide changes to the colloidal condition if washed with water after previously having been boiled with enough potassium cyanide to effect partial solution. I have repeated the experiment and can fully confirm this statement.

[1] Bull. de la société chimique, vol. 49, p. 452.

[2] Jour. Chem. Soc., 1883, vol. 43, p. 163.

Without knowing of Wright's experiments I found several years ago that ordinary ferric hydrate may be converted into its colloidal form by a similar process.[1]

Freshly precipitated ferric hydrate is easily dissolved by a neutral solution of aluminum chloride. Now, if an excess of ferric hydrate is present which does not further dissolve, and if the same is placed on a filter and washed with water until all salts present are removed it goes into a solution which seems to be in its properties almost identical with ordinary dialysed ferric hydrate.

The following explanation can be given of this behavior: If a solvent acts on a finely divided precipitate, single molecules throughout the whole mass of the latter go into solution. Thus the large aggregates of molecules are broken up into smaller ones. These aggregates of molecules may become, under certain conditions, so small that they remain permanently suspended in the liquid and form a so-called "colloidal" solution. It must be added, however, that this happens only in certain cases and with certain substances. If, for instance, silver sulphide is treated exactly in the same way as ferrous sulphide or auroauric sulphide with potassium cyanide and then washed with water no trace of a colloidal solution is formed.

An unsuccessful experiment, which was made with the intention of obtaining colloidal auroauric sulphide by another method, may be mentioned, as it gave rise to an interesting observation. If sulphureted hydrogen is conducted at ordinary temperatures into a solution of auric chloride, very little precipitate is formed as long as undecomposed chloride is present; the color of the solution becomes at the same time dark brown; thin layers of the liquid remain still transparent. This behavior seemed to indicate that at first only colloidal auroauric sulphide is formed. In order to confirm this assumption by experiment a solution of auric chloride was incompletely precipitated by sulphureted hydrogen and then placed in a dialyser. After the lapse of a few hours the unchanged chloride of gold was diffused; in the dialyser, however, remained finely divided gold instead of colloidal auroauric sulphide as had been expected.

It appears that the gold chloride had acted on the auroauric sulphide according to the following equation:

$$Au_2S_2 + (AuCl_3)_4 + 8H_2O = Au_6 + 2H_2SO_4 + 12HCl.$$
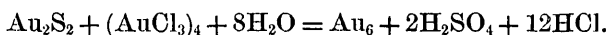
And, indeed, if a mixture of the solutions of colloidal auroauric sulphide and gold chloride is gently heated gold immediately separates out. The following quantitative experiment definitely confirms this view. 1·4140 grammes auroauric sulphide (one molecule Au_2S_2) were heated on the water bath with four molecules auric chloride, corresponding to 2·8280 grammes gold. After the lapse of four hours the liquid had become entirely colorless and the brownish black color of

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[1] Ann. Chem. Pharm., vol. 257, p. 374.

auroauric sulphide had changed entirely to the yellowish brown of metallic finely divided gold. The gold which had thus separated out was carefully washed, dried, digested with carbon bisulphide for some time and ultimately dried at a temperature of 110°. Its weight after this treatment amounted to 4·2708 grammes—on heating and calcining the same a sulphur flame was noted, and a loss of 0·0327 grammes or 0·77 per cent was found; consequently found 4·2381 grammes gold, instead of 4·2420 grammes.

The presence of sulphuric acid as required by the above equation was only qualitatively proved. The presence of a small quantity of sulphur in the gold can be explained by the fact that the auroauric sulphide used was not freed originally from the sulphur which is always formed when gold chloride solution is precipitated by sulphureted hydrogen. Consequently it was possible for the metal to be contaminated with traces of sulphur, which are removed only with great difficulty by carbon bisulphide.

By a second, but not strictly quantitative experiment it was shown that gold chloride reacts with auroauric sulphide in the above described manner even at ordinary temperatures, but the reaction proceeds more slowly. The reduction of boiling solutions of auric chloride by sulphureted hydrogen, which has been already observed by Levol,[1] can be explained by the above reaction.

Finally, colloidal auroauric sulphide was prepared by prolonged treatment of freshly precipitated auroauric sulphide with sulphureted hydrogen water. Freshly precipitated auroauric sulphide was suspended in a few hundred cubic centimeters of water and placed in a dialyser. Sulphureted hydrogen was conducted into the latter for a week, and the water in the outer jar was frequently renewed. After the lapse of this time a light brownish yellow solution had formed in the dialyser. This solution contained 0·023 gramme auroauric sulphide per liter.

It is evident that more concentrated solutions could be obtained if the treatment with sulphureted hydrogen were continued for a longer period. If, however, we compare this method with the preceding it appears long and tedious. Some of the facts mentioned may possibly throw light on certain chemico-geological problems.

It appears probable—

(1) That the separation of free gold in the upper strata of the earth's crust may have been effected by the action of sulphureted hydrogen on chloride of gold;[2] for the constant associate of gold, pyrites, owes its formation, as Doelter[3] has shown in his investigation on that subject, to the action of sulphureted hydrogen water on the various oxides of iron at temperatures below 100°.

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[1] Annal. Chim. Phys. (3), vol. 30, p. 356.

[2] The original formation of gold chloride in the earth-crust can be explained by the action of chlorine on gold at a considerable depth.

[3] Zeitschrift f. Kryst. und Min., vol. 11, p. 30.

(2) That the formation of gold could have taken place at no very great depth, for we have seen that already at much lower temperatures auric chloride effects the separation of gold from auroauric sulphide solutions.

(3) That the formation of pyrites has taken place in strata nearer the surface than those in which the formation of gold took place, for it is necessary to assume that the mineral acids which are formed, when gold is separated out by sulphureted hydrogen from gold chloride solution, had to be first neutralized by the bases of strata of considerable thickness in order to make possible the formation of pyrites by the action of sulphureted hydrogen on ferric oxide.

In connection with this investigation I have tried the action of high pressures on some colloidal solutions.

A colloidal solution of ferric hydrate (0·64 per cent F_2O_3) was subjected at temperatures of 17° and of 100° to a pressure of 1,700 atmospheres. No visible action was observed. A colloidal solution of silicic acid (1·22 per cent) also remained at 17° and at 100° under the same pressure entirely unchanged.

MISCELLANEOUS ANALYSES.

THREE MINERALS FROM COLORADO.

[Collected by Whitman Cross, analyzed by L. G. Eakins.]

A. Heulandite, from Anthracite creek, Gunnison county.
B. Diaspore, from Mount Robinson, Custer county.
C. Alunite, from Knickerbocker hill, Custer county.

	Heuland-ite.	Diaspore.	Alunite.
SiO_2	57·38	....	2·82
Al_2O_3	17·18	83·97	38.91
Fe_2O_3	trace	....	....
CaO	8·07	....	·35
MgO	....	....	trace
K_2O	·40	....	4·03
Na_2O	·82	....	4·32
H_2O	16·27	15·43	13·03
SO_3	....	....	35·91
	100·12	99·40	99·37
Sp. gr	2·24, 21°		

YELLOW SMITHSONITE FROM ARKANSAS.

[Collected in Marion county by W. P. Jenney, and analyzed by H. N. Stokes.]

Bright golden yellow in color. Takes a fine polish. Known locally as "turkey-fat ore."

SiO_2	·06
CO_2	34·68
Cu	trace
CdS	·25
CdO	·63
ZnO	64·12
FeO	·14
CaO	·38
	100·26

ROCKS AND CLAYS FROM THE ZINC REGION OF MISSOURI AND KANSAS.

[Collected by W. P. Jenney.]

First. Two dolomites from the Oswego land, Joplin, Missouri.

[Analyzed by L. G. Eakins.]

	A.	B.
CaO	21·46	28·72
MgO	14·79	17·26
Al_2O_3, Fe_2O_3	1·32	1·03
Insoluble	29·77	11·66
CO_2 (calculated)	33·13	41·55
	100·47	100·22

Second. Seven cherts.

A. Partly altered, from East Hollow, Belleville, Jasper county, Missouri.

B. Altered to "cotton rock," same locality.

C. Unaltered, same locality.

D. Surprise mine, Joplin, Missouri.

E, F. Bonanza shaft, Galena, Kansas.

G. Altered, same locality.

[Analyzed by E. A. Schneider.]

	A.	B.	C.	D.
SiO_2	98·92	98·71	98·17	99·46
Al_2O_3, Fe_2O_3	·48	.43	·83	·29
CaO	·03	·03	·05	·04
MgO	.02	·02	·01	trace
Ign	·42	·50	·78	·34
	99·87	99·69	99·84	100·13

	E.	F.	G.
SiO_2	99·23	98·60	99·13
Al_2O_3, Fe^2O_3	·22	·52	·16
CaO	·02	·10	trace
MgO	trace	trace	.01
Ign	·50	·40	·20
	99·97	99·62	99.50

Third. "Jasperite" and "tripoli."

A. Jasperite, from Joplin, Missouri.

B. Jasperite, from Galena, Kansas.

C, D. Tripoli, from Seneca, Newton county, Missouri.

[Analyses by L. G. Eakins.]

	A.	B.	C.	D.
SiO₂	95.77	97·33	98.29	98·93
Al₂O₃, Fe₂O₃	1·84	1·89	·62	·63
CaO	·54	·11	·09	.04
MgO	·24	·09		
H₂O	1·17	·77	1·11	·68
	99·56	100·19	100·11	100·28

Fourth. Eleven "tallow clays."

A, B, C, D. From Joplin, Missouri.

E. From Aurora, Missouri.

[Analyzed by T. M. Chatard.]

	A.	B.	C.	D.	E.
Ign	17·19	16·74	17·63	16·95	16·96
Insoluble	40·64	43·07	39·34	39·62	34.04
Soluble Al₂O₃	5·72	7·60	6·17	6·45	10·01
Soluble Fe₂O₃	1·30	1·12	1·16	1·53	3·62
Soluble ZnO	32·46	29·43	34·28	33·55	33·49
Soluble CaO	1·80	1.70	2.13	1.77	2·09
Soluble MgO	.27	·32	·27	·30	·25
	99·38	99·98	100·98	100·17	100.46

F. Cave Springs mine, Jasper county, Missouri.

G. Coon hollow, Boone county, Arkansas.

H. Great Western mine, Granby, Missouri.

I, J, K. Woodcock mine, Granby.

[Analyses by H. N. Stokes.]

	F.	G.	H.	I.	J.	K.
Ign	10·37	8·36	8·22	7·99	9·19	7·52
Insoluble	51·64	47·20	44·14	39·12	44·79	40·93
Soluble Al₂O₃	7·38	6·34	10·78	8·21	8·93	6·46
Soluble Fe₂O₃	10·34	4·40	3·89	2·75	5·98	3·49
Soluble ZnO	14·35	30·50	29·54	38·59	26·23	38·90
Soluble CaO	1·55	1·91	2·65	2·77	2·01	2·56
Soluble MgO	·35	·75	·90	·78	·46	·42
	95·98	99·46	100·12	100·21	97·59	100·28

In these analyses the terms insoluble and soluble refer to solubility of the material in aqueous hydrochloric acid,

TWO FELDSPARS.

[Separated from the eleolite-syenite of Litchfield, Maine, by W. S. Bayley; analyzed by W. H. Melville.]

	Sp. gr., 2·56.	Sp. gr., 2·622.
H₂O	·17	·09
SiO₂	65·14	68·28
Al₂O₃	18·19	19·62
FeO	·25	·23
CaO	·33	·31
MgO	·16	·09
K₂O	14·14	·39
Na₂O	1·68	10·81
	100·06	99·82

SIX SANDSTONES.

A, B, C. "Peebles-Henley stone," from Portsmouth, Ohio.

[Analyzed by H. N. Stokes. Alkalies probably present, but not sought for.]

	A.	B.	C.
SiO₂	90·40	89·32	87·12
Al₂O₃	5·15	5·52	5·96
Fe₂O₃	·65	·87	·85
FeO	·27	·35	·85
MgO	·28	·51	·73
Ign	·99	1·49	2·00
	97·74	98·06	97·51
Insoluble in HCl	98·00	96·90	95·52

D. Brown sandstone, Hummelstown, Pennsylvania.
E. Potsdam sandstone, Sauk county, Wisconsin.
F. Banded sandstone, Peoa, Utah.

[Analyses by E. A. Schneider.]

	D.	E.	F.
SiO₂	88·13	99·42	96·60
Al₂O₃	5·81	} ·31	2·02
Fe₂O₃	1·77		
FeO	·31	....	....
CaO	·20	....	·04
MgO	·53	....	·08
K₂O	2·63	....	....
Na₂O	·06	....	....
H₂O	·49	·18	·40
	99·93	99·91	99·14

SEVEN MARBLES AND DOLOMITES.

A and B. From Happy valley, Georgia.
C. From Rutland, Vermont.

[Analyses by L. G. Eakins.]

	A.	B.	C.
CaO	53·91	53·69	50·79
MgO..........................	·83	·83	trace
Al₂O₃	·17	·15	·39
FeO	·05	·06	·14
CO₂.............	43·16	43·13	39·80
H₂O	·13	·17	1·01
Insoluble	1·84	2·01	8·00
	100·09	100·04	100·13

Analyses of portion insoluble in hydrochloric acid.

	A.	B.	C.
SiO₂	58·21	55·48	56·69
Al₂O₃	7·37	15·58	31·16
FeO	·31	trace	2·13
CaO	12·53	14·52	2·68
MgO.........................	20·42	12·88	3·27
	98·84	98·46	95·93

D. Marble from Lee, Massachusetts.
E. Compact gray limestone, from Greason, Pennsylvania.
F. Dolomite, from Cockeysville, Maryland.
G. Crystalline limestone, Eureka, Nevada.

[Analyses by E. A. Schneider.]

	D.	E.	F.	G.
CaO	30·88	39·26	29·08	30·60
MgO.........................	21·42	9·00	20·30	21·69
Al₂O₃, Fe₂O₃	·24	....	·40	....
CO₂.................	46·72	38·82	44·26	47·13
H₂O, 105°	....	·18	....	....
Insoluble	·19	11·07	5·57	·53
Organic matter	....	·75	....	....
	99·45	99·08	99·61	99·95

NINE ROCKS FROM MARYLAND.

[Collected by G. H. Williams; analyzed by W. F. Hillebrand.]

A. Granite, from Guilford.
B. Granitite, Sykesville.

C. Hornstone, from contact with limestone, Sykesville.

D. Dissolved inclusion, Sykesville.

	A.	B.	C.	D.
SiO$_2$	72·57	71·45	67·02	47·35
Al$_2$O$_3$	15·11	14·36	13·77	29·76
Fe$_2$O$_3$	·59	3·07	4·64	2·94
FeO	1·02	2·78	1·02	3·15
CaO	1·65	1·58	11·09	2·20
MgO	·30	1·17	·65	1·60
K$_2$O	4·33	3·28	·09	6·83
Na$_2$O	3·92	1·95	·66	2·84
H$_2$O	·47	1·30	1·16	3·15
	99·96	99·94	100·10	99.82

E, F, G. Granitites.

H, I. Gneisses.

E. From Woodstock, the remainder from Dorsey's run.

	E.	F.	G.	H.	I.
SiO$_2$	71·79	62·91	70·45	57·33	48·92
Al$_2$O$_3$	15·00	19·13	15·98	15·31	16·57
Fe$_2$O$_3$	·77	·98	·75	3·39	4·21
FeO	1·12	3·20	1·84	8·19	9·18
CaO	2·50	4·28	2·60	3·95	9·69
MgO	·51	1·69	·77	4·36	5·98
K$_2$O	4·75	3·38	3·59	4·57	1·56
Na$_2$O	3·09	3·94	3·83	1·22	2·47
H$_2$O	·64	·63	·45	1·80	1·68
	100·17	100·14	100·26	100·12	100·26

Manganese and traces of lithia present in all. SrO and BaO not looked for. TiO$_2$ and P$_2$O$_5$, if present, are included with the alumina.

ERUPTIVE ROCK FROM KENTUCKY.

From a dike in Crittenden county.

[Analyzed by W. F. Hillebrand. Material dried at 100°.]

SiO$_2$	33·84
TiO$_2$	3·78
Al$_2$O$_3$	5·88
Cr$_2$O$_3$	·18
Fe$_2$O$_3$	7·04
FeO	5·16
MnO	·16
NiO	·10
CoO	trace
CaO	9·46
BaO	·06
MgO	22·96
K$_2$O	2·04

Na_2O	·33
H_2O	7·50
P_2O_5	·89
Cl	·05
CO_2	·43
	99·86

FOUR GRANITES FROM MISSOURI.

From NE. ¼ Sec. 6, T. 33, R. 5 E.

[Analyses by W. H. Melville.]

	A.	B.	C.	D.
SiO_2	69·94	72·35	71·33	71·88
TiO_2	·25	·44	·55	·22
P_2O_5	·13	·13	·16	·15
Al_2O_3	15·19	13·78	12·55	12·88
Fe_2O_3	1·88	1·87	3·75	3·05
FeO	·60	·36	·85	1·05
NiO	trace	·20	·15	·02
MnO	·03	·06	·04	trace
CaO	1·15	·87	·94	1·13
MgO	·92	·42	·58	·33
Na_2O	3·95	4·14	4·52	4·21
K_2O	4·29	4·49	4·20	4·46
H_2O, 100°	·14	·22	·12	·17
H_2O, ignition	·85	·54	·30	·26
	99·32	99·87	100·04	99·81

THREE ROCKS FROM MINNESOTA.

A. Hypersthene gabbro from SE ¼ Sec. 20, T. 65 N., R. 4 W.
B. Olivine gabbro, SE. ¼ Sec. 19, T. 63, R. 9 W.
C. Olivine gabbro, S. quarter post, Sec. 35, T. 61 N., R. 12 W.

[Anaylses by H. N. Stokes.]

	A.	B.	C.
SiO_2	46·96	45·66	46·45
TiO_2	·62	·92	1.19
P_2O_5	·03	·05	·02
Al_2O_3	14·13	16·44	21·30
Fe_2O_3	·76	·66	·81
Cr_2O_3	trace	trace	....
FeO	14·95	13·90	9·57
NiO	·06	·16	·04
MnO	·93	trace	trace
CaO	2·32	7·23	9·83
MgO	15·97	11·57	7·90
K_2O	1·68	·41	·34
Na_2O	·35	2·13	2·14
H_2O, 105°	·07	·07	·14
H_2O, above 105°	1·26	·83	1·02
	100·09	100·03	100·75

ROCKS FROM COLORADO.

A, B, C. Three rocks from Gunnison county; A, Mount Marcellina; B, Storm ridge; C, Mount Carbon.

[Analyses A and C by T. M. Chatard; B by L. G. Eakins.]

	A.	B.	C.
SiO$_2$	62·85	61·42	65.36
TiO$_2$	·41	·37	·52
P$_2$O$_5$	·48	·14	·25
Al$_2$O$_3$	16·21	17·69	15·48
Fe$_2$O$_3$	3·08	4·24	3·09
FeO	1·46	1·74	1·21
MnO	·15	·19	·19
BaO	·11	·09	·08
CaO	4·72	5·29	4·14
MgO	1·47	1·81	1·53
K$_2$O	3·10	3·19	3·41
Na$_2$O	3·49	3·14	3·58
H$_2$O, 105°	·29	} ·97	{ ·82
H$_2$O, ignition	2·03		·70
	99·85	100·28	100·36

D. Rhyolite from Mount Robinson, Custer county.

[Analysis by L. G. Eakins. Contains much diaspore.]

	D.
SiO$_2$	69·67
Al$_2$O$_3$	13·72
CaO	·07
MgO	trace
K$_2$O	2·44
Na$_2$O	·34
H$_2$O	4·73
SO$_3$	9·27
	100·24

E, F, G, H, I. Spherulites from Custer county; E, G, H, from Rosita; F, I, from Silver cliff.

[Analyses by L. G. Eakins.]

	E.	F.	G.	H.	I.
SiO$_2$	74·47	83·91	80·61	79·21	78·77
Al$_2$O$_3$	13·87	9·54	10·94	12·24	12·46
CaO	·51	·19	·26	·43	·34
MgO	trace	trace	·09	·11	·09
K$_2$O	7·46	5·06	3·02	5·26	5·84
Na$_2$O	2·10	·62	2·90	2·58	2·12
H$_2$O	1·88	·69	2·20	·66	·70
	100·29	100·01	100·02	100·49	100·32

ROCKS FROM MONTANA.

Received from G. P. Merrill. A, from hills northwest of Red Bluff; B, between Antelope and South Bowlder creeks; C, hills east of South Bowlder creek; D, near North Meadow creek; E, near North Meadow creek; F, northwest of Red Bluff.

[Analyzed by L. G. Eakins.]

	A.	B.	C.	D.	E.	F.
SiO_2	48·95	50·82	50·03	46·13	51·83	59·48
TiO_2	·81	·59	·61	·73	·29	.93
Al_2O_3	5·69	11·44	14·08	4·69	7·98	16·37
Cr_2O_3	·05	·03	trace	·04	.31	.03
Fe_2O_3	1·20	·25	2·92	.73	1·48	3·21
FeO	12·11	8·94	6·11	16·87	8·28	3·17
MnO	·08	·19	.08	trace	trace	·19
NiO	·16	trace	trace	·09	·11	trace
CaO	5·33	8·14	7·46	4·41	5·26	4·88
MgO	23·49	14·01	10·73	25·17	24·10	3·29
BaO	trace	·06	.04	trace	....	·13
K_2O	·79	3·45	2·64	trace	·06	2·81
Na_2O	1·58	1·79	1·46	·08	·35	3.30
H_2O	·18	·58	3·70	1·38	·29	2·01
P_2O_5	·12	·20	·42	·07	·09	·41
S	....	....	....	·24	....	....
	100·54	100·49	100·28	100·63	100·43	100·21

Rock and separations from top of Square butte, Bear Paw mountains.

[Analyses by W. H. Melville.]

	Rock.	Hornblende.	Sp. gr. 2·265.	Sp. gr. 2·255.
SiO_2	56·45	38·41	41·56	49·54
TiO_2	·29	....	....	....
P_2O_5	·13	....	....	....
Cl	·43	....	4·79	1·67
Al_2O_3	20·08	17·65	29·48	25·07
Fe_2O_3	1·31	3·75	....	....
FeO	4·39	21·75	.49	·40
NiO	trace	trace	....	....
MnO	·09	·15	....	....
CaO	2·14	10·52	·49	·22
MgO	·63	2·54	·15	.20
Na_2O	5·61	2·95	19·21	·15·32
K_2O	7·13	1·95	·91	·89
H_2O, 100°	·26	....	·45	undet.
H_2O, above 100°	1·51	·24	3·73	undet.
	100.45	99·91	101·26	93·31
Less O=Cl	·10	....	1·08	·38
	100·35	....	100·18	92·93

Two rocks from the Crazy mountains: A, theralite, Gordon's butte; B, porphyritic theralite, Elbow creek.

[Analyzed by E. A. Schneider.]

	A.	B.
SiO$_2$	44·31	47;67
Al$_2$O$_3$	17·20	18·22
Fe$_2$O$_3$	4·64	3·65
FeO	3·73	3·85
CaO	10·40	8·03
MgO	6·57	6·35
MnO	·10	·28
K$_2$O	3·64	3·82
Na$_2$O	4·45	4·93
H$_2$O, 105°	·77	·38
H$_2$O, ign	3·30	2·97
	99·11	100·15

Four rocks from the Crazy mountains: A, green dike parallel to theralite; B, divide between first and second large creeks west of Smith's; C, Peaked butte; D, green dike north of long theralite dike.

[Analyzed by W. H. Melville.]

	A.	B.	C.	D.
SiO$_2$	58·70	62·17	59·66	64·33
TiO^2	trace	trace	trace	trace
P$_2$O$_5$	·10	·11	·14	trace
Al$_2$O$_3$	19·26	18·58	16·97	17·52
Fe$_2$O$_3$	3·37	2·15	3·18	3·06
FeO	·58	1·05	1·15	·94
MnO	·10	trace	·19	·35
CaO	1·41	1·57	2.32	·56
MgO	·76	·73	·80	·34
Na$_2$O	8·55	7·56	8·38	7·30
K$_2$O	4·53	3·88	4·17	4·28
H$_2$O, 105°	·07	·07	·07	.04
H$_2$O, ign	2.57	1·63	2·53	·95
	100·00	99·50	99·56	99·07

ROCKS FROM ARIZONA.

A series of four from the Santa Maria basin.

[Analyzed by W. F. Hillebrand.]

	1.	2.	3.	4.
SiO_2	49·36	55·35	57·04	57·48
TiO_2	·98	·87	·94	·94
Al_2O_3	16·35	12·71	13·66	14·09
Fe_2O_3	2·93	4·67	4·96	5·21
FeO	8·55	2·06	1·77	1.35
MnO	·19	.08	·17	·09
(NiCo)O	.05	·05	·07	·08
CaO	10.08	5·77	6·23	6·05
SrO	none	trace	trace	trace
BaO	·04	·19	·22	·23
MgO	7·06	6·29	4·43	3·49
K_2O	·82	4·86	4·95	4·69
Na_2O	2·67	2·65	3·08	3·00
H_2O, 100°	·22	2·67	1·11	1·20
H_2O, above 100°	·65	1·18	1·10	1·37
P_2O_5	·30	·58	·63	·65
Cl	undet.	undet.	undet.	undet.
Li_2O	none	trace	trace (?)	none
	100·25	99·98	100·36	99·92

ROCK FROM EUREKA, NEVADA.

An andesitic pearlite.

[Analysis by W. H. Melville.]

SiO_2	65·13
TiO_2	·58
P_2O_5	·23
Al_2O_3	15·73
Fe_2O_3	2·24
FeO	1·86
NiO	·07
MnO	trace
CaO	3·62
MgO	1·49
K_2O	3·96
Na_2O	2·93
H_2O, 105°	·52
H_2O, above 105°	1·91
	100·27

ROCKS FROM CALIFORNIA.

Three from Mount Diablo: A, diabase, somewhat altered; B, diabase, fresh; C, pyroxenite.

[Analyzed by W. H. Melville.]

	A.	B.	C.
SiO_2	51·58	52·06	53·25
TiO_2	1·05	·47	trace
P_2O_5	·24	·13	....
Al_2O_3	14·99	14·34	2·80
Cr_2O_3	....	....	·54
Fe_2O_3	2·04	2·11	·69
FeO	8·36	7·74	5·93
NiO	....	....	·07
MnO	trace	trace	·09
CaO	8·59	8·05	16·22
MgO	6·51	9·26	19·91
Na_2O	3·08	1·74	·19
K_2O	·31	·73	trace
H_2O, 100°	·34	·59	·05
H_2O, above 100°	2·67	2·90	·24
	99·76	100·12	99·98

Four collected by H. W. Turner: A, Table mountain, basalt, Tuolumne county; B, basalt, Plumas county; C, dolerite, Plumas county; D, quartz porphyrite, Plumas county.

[Analyzed by W. F. Hillebrand.]

	A.	B.	C.	D.
SiO_2	56·19	50·56	53·91	73·25
TiO_2	·69	1·71	·52	trace
Al_2O_3	16·76	14·71	17·95	13·25
Fe_2O_3	3·05	3·54	2·21	....
FeO	4·18	8·90	4·80	1·74
MnO	·10	·13	·10	trace
CaO	6·53	7·58	10·40	2·23
BaO	·19	·25	.05	trace
MgO	3·79	4·07	5·52	·28
K_2O	4·46	2·10	1·34	3·79
Na_2O	2·53	2·94	2·90	2·69
H_2O, 100°	·34	1·06	·20	·07
H_2O, above 100°	·66	1·12	·20	1·03
P_2O_5	·55	1·14	·21	trace
CO_2	....	....	....	1.05
FeS_2	....	....	....	·58
	100·02	99·81	100·31	99·96

Also traces of lithia and strontia.

SINTER FROM QUEENSLAND.

From the Mount Morgan gold mine. Analyzed for comparison with the sinters from the Yellowstone National Park.

[Analysis by E. A. Schneider.]

SiO_2	94·02
$Al_2O_3 + Fe_2O_3$	2·27
CaO	·07
MgO	trace
H_2O, 105°	1·07
H_2O, ignition	2·29
	99·72

TWO CLAYS FROM FLORIDA.

A, from Tampa; B, from Lakeland.

[Analyses by L. G. Eakins.]

	A.	B.
SiO_2	70·78	80·39
$Al_2O_3 + Fe_2O_3$	11·33	15·03
CaO	2·18	1·22
H_2O	14·55	4·34
	98·84	100·98

IRON ORES FROM WEST VIRGINIA.

[Analyses by H. N. Stokes.]

First, from Cherry run, near the Potomac river.

H_2O, 105°	·81
Fe	50·16
Mn	·04
S	·06
P	·80
Insoluble	14·43

Second, a series from Tazewell county.

	Taylor.	Hornets Nest.	Dial Rock.	Boulder.	Adds Ridge.
Moisture, 105°	1·67	1·59	1·10	3·17	1·24
Fe	36·81	56·48	54·01	56·07	40·75
Mn	5·42	·47	·26	trace	....
S	·09	·03	·09	·25	·08
P	·04	1·08	·95	·91	trace
Insoluble	26·19	1·85	4·26	2·63	32·37

COAL AND COKE FROM WEST VIRGINIA.

From the Thomas Vein, Davis. A, upper coal; B, middle coal; C, lower coal; D, 48-hour coke; E, 72-hour coke.

[Analyses by L. G. Eakins.]

	A.	B.	C.	D.	E.
Fixed carbon	65·60	65·99	72·76	87·08	90·05
Volatile hydrocarbons	22·87	23·88	22·90	·95	1·16
Moisture	·64	·68	·96	·23	·15
Ash	10·89	9·45	3·38	11·74	8·64
	100·00	100·00	100·00	100·00	100·00
Sulphur	·64	1·39	·59	·63	·70
Phosphorus	·06	·02	·01	·06	·04

TWO COALS FROM UTAH.

A, Little Cottonwood gulch, near Salt Lake city; B, Wasatch mountains.

[Analyses by L. G. Eakins.]

	A.	B.
Fixed carbon	85·83	42·81
Volatile hydrocarbous	7·15	24·60
Moisture	2·98	25·57
Ash	4·04	7·02
	100·00	100·00

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