ART. XLVI.—*Experiments upon the Constitution of certain Micas and Chlorites;* by F. W. CLARKE and E. A. SCHNEIDER.

SHORTLY after the publication of our first joint paper upon the constitution of the natural silicates,* we received from Mr. A. Lösch, curator of minerals in the Imperial School of Mines at St. Petersburg, some highly important material bearing upon our researches. Our work upon leuchtenbergite, it will be remembered, was defective, on account of impurity in the specimens at our disposal; and Mr. Lösch therefore sent us a supply of the perfectly pure mineral, selected with extreme care, and in the very best condition for study. To this gift he added four other minerals which he thought would be of interest to us, and upon these five specimens our present communication is founded.

The minerals, and the analyses are as follows:

A. Xanthophyllite, var. Waluewite, from the Nikolai-Maximilian mine, District of Slatoust, Ural.
B. Clinochlore from the same locality. Green, broadly foliated, closely resembling the mineral from West Chester, Pennsylvania.
C. Leuchtenbergite from Slatoust.
D. "Diallage serpentine" from the River Poldnewaja, District of Syssert, Ural.
E. White mica from Miask, Ural.

	A.	B.	C.	D.	E.
SiO_2	16·85	30·84	30·00	42·55	44·17
TiO_2	trace	----	----	----	----
Al_2O_3	42·33	18·31	20·43	1·25	37·35
Fe_2O_3	2·35	1·94	1·68	1·56	1·29
FeO	0·20	1·08	0·14	1·52	0·20
MnO	----	----	----	----	0·10
CaO	13·30	----	0·21	none	----
MgO	20·77	34·38	34·26	40·05	----
K_2O	----	----	----	----	10·00
Na_2O	----	----	----	----	1·14
Chromite	----	----	----	0·37	----
F	----	----	----	---	0·90
H_2O, 105°	0·04	0·55	0·55	0·21	1·06
" 250°–300°	0·12	0·49	0·35	0·11	0·53
" ignition	4·44	12·84	12·85	12·15	4·14
	100·40	100·43	100·47	99·77	100·88
Less O=F	----	----	----	----	·37
					100·51

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* This Journal, Oct., Nov., and Dec., 1890.

The molecular ratios deducible from these analyses, rejecting water given off below 300°, and the chromite contained in the serpentine, are as follows:

	A.	B.	C.	D.	E.
SiO_2	·281	·516	·500	·709	·736
R_2O_3	·430	·192	·211	·022	·374
RO	·759	·874	·861	1·022	·004
R_2O	----	----	----	----	·124
H_2O	·247	·713	·714	·675	·230
F	----	----	----	----	·050

Hence we get the following empirical formulæ, in which all R‴=Al, all R″=Mg, etc.

Waluewite,	$Al_{86}Mg_{76}H_{50}(SiO_4)_{28}O_{174}$
Clinochlore,	$Al_{38}Mg_{87}H_{143}(SiO_4)_{52}O_{113}$
Leuchtenbergite,	$Al_{42}Mg_{86}H_{143}(SiO_4)_{50}O_{121}$
Serpentine,	$Al_4Mg_{102}H_{135}(SiO_4)_{71}O_{35}$
Mica,	$Al_{75}K_{25}H_{46}(SiO_4)_{74}O_9F_5$

The last of these minerals is evidently an ordinary muscovite, possibly a little altered, and will receive no further consideration in this paper. The other minerals were examined more in detail, with very interesting results. As in our previous work, all experiments upon each mineral were made upon a uniform sample of the powdered material, so that direct comparisons with the analyses might be possible. The analyses themselves agree closely with the published analyses made by others, and are noteworthy only in the fractional determinations of the water.

Towards dry, gaseous hydrochloric acid, at the temperature interval 383°–412°, the minerals under investigation were somewhat refractory. From the waluewite, after nine hours heating in the gas, only 0·22 per cent of lime and 0·10 per cent of magnesia were extractable by water. Hence we may fairly infer that the species contains practically no –Mg–OH groups, a result which is in accordance with theory, as will be seen later. The chlorites and the serpentine, however, gave anomalous results, as follows; there being two experiments on each.

	Clinochlore.		Leuchtenbergite.		Serpentine.	
Hours heated,	8½	13	16½	18½	28½	7
MgO extracted,	7·34	5·48	7·33	5·62	3·66	2·66

In each case the heating was continued to constant weight, but the amount of action was much less than in the American clinochlore and serpentines which we formerly investigated. The leuchtenbergite behaves much like the impure material discussed in our earlier paper, from which 6·29 per cent of magnesia was removable; but more than double that amount is required to represent the MgOH which must be present under any recognized theory.

These results were so unsatisfactory that further work seemed to be desirable, but the tediousness of the process was discouraging. As a possible abbreviation of the method a new device was tried, which, although as yet unconclusive in its outcome, is nevertheless interesting. Ammonium chloride, as is well known, dissociates upon vaporization into ammonia and hydrochloric acid. Will it then, dissociating in presence of a silicate, act in any way by virtue of the acid so liberated ? This question is still under investigation; but some preliminary data may here be given. In each experiment the mineral was intimately mixed with ten times its weight of sal ammoniac, and then heated in a platinum crucible, well below redness, until all the ammonium salt had been vaporized and driven off. The residue was then leached out with water, and the soluble magnesia determined. Upon olivine and waluewite there was very little action, as in the case of the treatment with gaseous hydrochloric acid; but upon the chlorites and serpentine there was a vigorous attack. The magnesia thus rendered soluble was as follows:

	Clinochlore.	Leuchtenbergite.	Serpentine.
Percent MgO,	2·12	3·98	4·93

In a second series of experiments the minerals were heated as before with ammonium chloride until the latter was driven off. Then a fresh charge of chloride was added to the contents of the crucible and expelled like the first. Finally a third charge was added and likewise expelled. By this means more magnesia was converted into chloride than in the first experiments, as the subjoined figures show:

	Clinochlore.	Serpentine.	
	3 heatings.	2 heatings.	3 heatings.
Soluble MgO,	3·80	14·30	10·63

The irregularities in all these data remain to be explained. So far the results have only qualitative value. In those minerals which must contain the group MgOH, some action takes place, but in variable amount. But the magnesium silicates which cannot contain MgOH are practically unattacked, and so far all the evidence is harmonious and clear. Contrary to our earlier expectations, however, we cannot trust the dry hydrochloric acid reaction quantitatively, at least until its conditions and its nature are more fully understood. We can determine when the group MgOH is present as an essential part of a silicate, but not its actual amount. Probably the hydroxyl is first replaced by chlorine, converting the group –MgOH into the chlorhydrin-like group –MgCl. The latter, by continued action of the gaseous acid is then possibly split off as $MgCl_2$, but with secondary reactions to which the anomalous and irregular results may be due. The question is still open, and we hope by further experiments to get at something more conclusive. The problem is, to measure basic hydroxyl by its replacement with chlorine; and there seems to be no good reason why it should not be solvable.

By strong aqueous hydrochloric acid the chlorites and the serpentine were easily decomposed; but by previous ignition they were split up into soluble and insoluble portions. This splitting up is, in the case of serpentine, already well understood; the products being as Daubreé has shown, olivine and enstatite. For the waluewite and the chlorites, however, the existing data were scanty, and accordingly new experiments were undertaken. In each case the powdered mineral was ignited over a blast for several hours. It was then digested with strong hydrochloric acid, and after evaporation to dryness and re-solution, the residue was filtered off. Then, after drying and ignition, it was boiled with aqueous sodium carbonate to remove the silica which had been released from the soluble silicates, and the final residue was weighed and analyzed. As this process was followed in our first investigation with the Pennsylvania ripidolite, the results are included here for comparison with the Siberian material. The percentages of insoluble residue were as follows:

	Waluewite.	Clinochlore.	Leuchtenbergite.	Ripidolite.
Found,	45·01	17·56	19·24	19·74
Corrected,	43·96	16.63	18·05	18·49

In the second line the silica found in the residues, being presumably extraneous, is deducted. The composition of the residues is given below.

	Waluewite.	Clinochlore.	Leuchtenbergite.	Ripidolite.
SiO_2	2·34	5·25	6·16	6·32
R_2O_3	71·12	67·20	68·52	67·81
MgO	26·75	27·89	25·12	25·67
CaO	trace	----	----	----
	100·21	100·34	99·80	99·80

In these analyses the silica ranges from 0·93 to 1·25 per cent of the original mineral, and the remainder has quite sharply the composition of spinel. This point was noticed in our former paper, in the case of the West Chester ripidolite; but since then it has acquired new significance, and it is emphasized by the new analyses. Leaving the waluewite for separate consideration, it is to be noted that the three chlorites studied by us are all typical members of Tschermak's orthochlorite series; which, according to him, are mixtures of two end compounds, serpentine and amesite. How amesite may behave upon ignition, we do not know; but serpentine splits up, as is well known, into olivine and enstatite; the latter being insoluble in hydrochloric acid. Under Tschermak's theory of the chlorites, a clinochlore of the composition SpAt, should upon ignition yield about 18 per cent of enstatite; or in other words, the insoluble residue should contain *at least* one third of all the silica in the mineral. Since no enstatite is actually formed, or practically none, it is plain that the three chlorites here considered contain no serpentine molecules; and hence, so far at least as these minerals are concerned, Tschermak's theory falls to the ground.

Approximately, but not exactly, the formation of spinel from the waluewite and the chlorites, seems to follow a single quantitative law. To illustrate this the empirical formulæ may be reproduced here.

Waluewite,	$Al_{86}Ca_{24}Mg_{52}H_{50}(SiO_4)_{28}O_{174}$
Clinochlore,	$Al_{38}Mg_{87}H_{143}(SiO_4)_{52}O_{113}$
Leuchtenbergite,	$Al_{42}Mg_{86}H_{143}(SiO_4)_{50}O_{121}$
Ripidolite,	$Al_{38}Mg_{86}H_{140}(SiO_4)_{50}O_{113}$

Upon ignition, of course, water is expelled, and the ignited residue is empirically as follows:

Waluewite,	$Al_{86}Ca_{24}Mg_{52}(SiO_4)_{28}O_{149}$
Clinochlore,	$Al_{38}Mg_{87}(SiO_4)_{52}O_{41}$
Leuchtenbergite,	$Al_{42}Mg_{86}(SiO_4)_{52}O_{49}$
Ripidolite,	$Al_{38}Mg_{86}(SiO_4)_{50}O_{43}$

Here we have in each mineral an excess of oxygen over SiO_4, and to that excess the amount of spinel residue is approximately proportional, thus:

	Found corrected.	Calculated.
Waluewite,	43·96	43·15
Clinochlore,	16·63	14·80
Leuchtenbergite,	18·05	17·62
Ripidolite,	18·49	15·83

Considering the impurities in the original materials, and the unavoidable inaccuracies of manipulation, the agreement here is as close as could be expected. The calculation assumes that the excesses of oxygen represent quantitatively the amount of spinel formed, and all the errors of analysis are accumulated in the final result. If we deduct the spinel from the composition of each mineral, the soluble portion is expressible as a mixture of olivine and magnesian garnet; two species which are among the commonest progenitors of the chlorite group. That olivine and garnet are actually formed is certainly not proved; but it seems highly probable that the chlorites studied do split up in the manner indicated, yielding water, spinel, garnet and olivine as the final products of decomposition. Other chlorites may behave differently; and it is quite likely that the species or varieties rich in iron may diverge widely from the types considered here. Speculation upon this theme would be premature.

As to the chemical structure of the leuchtenbergite and clinochlore, the evidence now available is quite in harmony with the general theory of the chlorite group recently advanced by one of us.* Again including the Pennsylvania ripidolite, the three chlorites reduce to compositions as follows:

Clinochlore,	$Mg_{50}(SiO_4)_{52}(AlH_2O_2)_{38}(MgOH)_{37}H_{30}$
Leuchtenbergite,	$Mg_{49}(SiO_4)_{50}(AlH_2O_2)_{42}(MgOH)_{37}H_{22}$
Ripidolite,	$Mg_{49}(SiO_4)_{50}(AlH_2O_2)_{35}(MgOH)_{37}H_{27}$

Condensing, by union of the univalent factors, these become—

Clinochlore,	$Mg_{50}(SiO_4)_{52}R'_{105}$
Leuchtenbergite,	$Mg_{49}(SiO_4)_{50}R'_{101}$
Ripidolite,	$Mg_{49}(SiO_4)_{50}R'_{102}$;

or, in general, all three examples have nearly identical composition, and conform to the typical expression—

$$Mg_2(SiO_4)_2R'_4,$$

in accordance with the theory which represents them as substitution derivatives of the normal salt $Mg_4(SiO_4)_2$. We may interpret the minerals in detail as was done in the case of our earlier discussion of the West Chester ripidolite, or we may regard them as mixtures of the two salts—

$$Mg_2(SiO_4)_2(AlH_2O_2)_2(MgOH)_1H$$
and $Mg_2(SiO_4)_2(AlH_2O_2)_1(MgOH)_2H$

In either case the juxtaposition of the groups AlH_2O_2 and $MgOH$ renders the formation of spinel intelligible.

In the waluewite, or more properly xanthophyllite, we have the first example of a true brittle mica met with in the course of our investigations. Being the most basic known member of the clintonite series, it has peculiar interest; and it deserves a somewhat detailed discussion. In the empirical formula deduced from our analysis,

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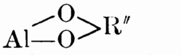
* This Journal, March, 1892.

$$\mathrm{Al_{86}Ca_{24}Mg_{52}H_{60}(SiO_4)_{28}O_{174}},$$

the most noticeable feature is the great excess of oxygen compared with the possible hydroxyl and the small amount of SiO_4. This excess is accounted for in part by the general formula which we have heretofore assigned to the clintonite group,

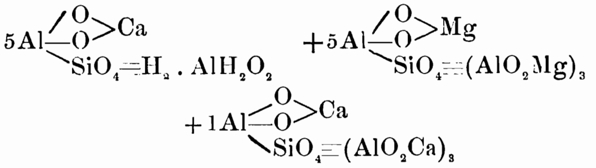


$$\mathrm{Al}\begin{array}{l}\begin{matrix}\diagup\mathrm{O}\\ —\mathrm{O}\end{matrix}\!>\mathrm{R''}\\ \diagdown\mathrm{SiO_4\equiv R'_3};\end{array}$$

which formula, however, needs some extension along a new line. In that formula the group of atoms $-AlO_2R''$ appears, an equivalent obviously of the group AlO_2H_2; and this group may fairly be repeated among the components of R'_3. With such a group, the extreme member of the clintonite series should have the composition $(AlO_2R'')_4SiO_4$; and a molecule of that type is theoretically capable of splitting up into olivine and spinel in the ratio of 1:2, when each mineral is given its lowest possible formula:

$$(\mathrm{AlO_2R''})_4\mathrm{SiO_4} = \mathrm{R''_2SiO_4} + 2\mathrm{R''Al_2O_4}$$

In the case of xanthophyllite, if such a molecule is contained in it, the olivine formed should be partly monticellite. At Monzoni, monticellite is found associated with spinel; and brandisite, a member of the clintonite series, occurs in the same region. In fact, all three of the true clintonite micas are commonly associated with spinel, a fact of much interest when considered in its relations to our experiments. In the light of the foregoing argument the composition of waluewite and its manner of decomposition by heat, may be represented as follows:



$$5\mathrm{Al}\begin{array}{l}\begin{matrix}\diagup\mathrm{O}\\ —\mathrm{O}\end{matrix}\!>\mathrm{Ca}\\ \diagdown\mathrm{SiO_4\equiv H_2\,.\,AlH_2O_2}\end{array} + 5\mathrm{Al}\begin{array}{l}\begin{matrix}\diagup\mathrm{O}\\ —\mathrm{O}\end{matrix}\!>\mathrm{Mg}\\ \diagdown\mathrm{SiO_4\equiv(AlO_2Mg)_3}\end{array} + 1\mathrm{Al}\begin{array}{l}\begin{matrix}\diagup\mathrm{O}\\ —\mathrm{O}\end{matrix}\!>\mathrm{Ca}\\ \diagdown\mathrm{SiO_4\equiv(AlO_2Ca)_3}\end{array}$$

These three molecules are all of the general type heretofore assigned to the clintonite series, and two of them are presumably capable of yielding spinel. Reducing the original analysis to 100 per cent with consolidation of like bases as usual, we get the following comparison between experiment and theory; the calculated composition being in accordance with the structural formula above cited.

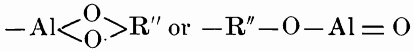
	Found, reduced.	Calculated.
SiO_2	16·97	17·02
Al_2O_3	44·14	44·71
CaO	13·50	13·00
MgO	20·92	20·63
H_2O	4·47	4·64
	100·00	100·00
Spinel formed,	43·96	43·94

Reckoned on a similar basis, clintonite, according to the analysis published by Sipöcz, may be written—

$$AlO_2R''.\,SiO_4\,.\,H_3 + (AlO_2R'')_4\,.\,SiO_4$$

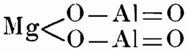
and brandisite is of the same general character, with a small admixture of the first of the three xanthophyllite molecules given in our structural expression. Whether chloritoid is a true member of this group, seems to be uncertain; but if it is, its composition may be written $AlO_2Fe\,.\,SiO_4\,.\,H\,.\,AlOH$; the last factor being a bivalent group related to the univalent AlO_2H_2.

As for the ultimate structure of the group AlO_2R'', it may be written in two ways, thus:



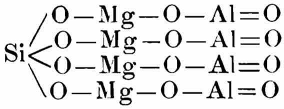
$$-\mathrm{Al}\mathord{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\mathord{>}\mathrm{R}'' \text{ or } -\mathrm{R}''-\mathrm{O}-\mathrm{Al}=\mathrm{O}$$

The first form corresponds to the group $-Al(OH)_2$, the second to the formula commonly assigned to spinel,

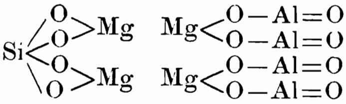


$$\mathrm{Mg}\mathord{<}\begin{array}{l}\mathrm{O-Al=O}\\ \mathrm{O-Al=O}\end{array}$$

In either case two of the groups AlO_2R'' coalesce to form one molecule of spinel, with removal of a single magnesium atom. Such a coalescence is easiest comprehended when the second form of the radical is chosen; but the first form is more harmonious with the constitution of the mica series in general. If the xanthophyllite compound $(AlO_2R'')_4SiO_4$ be regarded independently of the micas, it is most simply written as follows, with its splitting up into olivine and spinel as indicated:

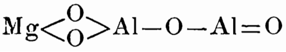


$$\mathrm{Si}\left\langle\begin{array}{l}\mathrm{O-Mg-O-Al=O}\\ \mathrm{O-Mg-O-Al=O}\\ \mathrm{O-Mg-O-Al=O}\\ \mathrm{O-Mg-O-Al=O}\end{array}\right.$$



$$\mathrm{Si}\left\langle\begin{array}{l}\mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\end{array}\right.\begin{array}{l}\mathord{>}\mathrm{Mg}\\ \\ \mathord{>}\mathrm{Mg}\end{array}\quad\begin{array}{l}\mathrm{Mg}\mathord{<}\begin{array}{l}\mathrm{O-Al=O}\\ \mathrm{O-Al=O}\end{array}\\ \mathrm{Mg}\mathord{<}\begin{array}{l}\mathrm{O-Al=O}\\ \mathrm{O-Al=O}\end{array}\end{array}$$

If, however, for the sake of preserving harmony with the mica formulæ we adopt the first expression for $-AlO_2R''$, then spinel would seem to have the constitution



$$\mathrm{Mg}\mathord{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\mathord{>}\mathrm{Al-O-Al=O}$$

Although the last formula is somewhat novel, it is not altogether improbable; but between it and its alternative we cannot yet certainly decide. Another open question is furnished by the chlorites, in which the formation of spinel may possibly be due to the presence of $\cdot AlO_2Mg$ groups. Upon this supposition, however, the chlorites do not reduce to simple formulæ, and therefore the suggestion has slight value. Apart from all theoretical considerations, the spinel reaction, as it may fairly be called, is one of an entirely new order in mineral chemistry, and it opens up a noteworthy line of attack upon the difficult problems before us.

Laboratory U. S. Geological Survey, Washington, Jan. 14, 1892.