THE CONSTITUTION OF THE LITHIA MICAS.

BY F. W. CLARKE.

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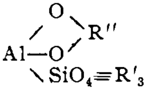
IN a series of papers published during the past eight or nine years,[1] I have sought to develop the theory that the complex natural silicates are chemically to be considered as substitution derivatives of simple normal salts. For the micas, in particular, a theory has been worked out in detail, partly on general principles, and partly on the basis of experimental evidence, in which the starting point of the series is the normal aluminum orthosilicate $Al_4(SiO_4)_3$, with occasional replacements of the orthosilicic groups by the feldspathic group Si_3O_8. Thus we have the following systematic scheme:

Normal salt	$Al_4(SiO_4)_3$
Muscovite	$Al_3(SiO_4)_3R'_3$
Biotite	$Al_2(SiO_4)_3R''_2R'_2$
Phlogopite	$Al(SiO_4)_3R''_3R'_3$
Clintonite	 $\mathrm{Al}\begin{cases}\mathrm{O}\searrow \\ \qquad\mathrm{R''} \\ \mathrm{O}\nearrow \\ \mathrm{SiO_4{\equiv}R'_3}\end{cases}$

This scheme is modified, however, not only by the assumption that SiO_4 may be replaced by Si_3O_8, as in the feldspars, but also by other considerations due to the presence of fluorine in many micas, etc., etc. In the cases of the lithia micas, lepidolite, zinnwaldite, cryophyllite, polylithionite, etc., such modification is absolutely necessary; and hitherto it has been covered by the supposition that the fluorine is represented by the univalent group AlF_2, among the components of R'.

Naturally, and almost necessarily, the development of any such theory is by process of evolution, in which details held provisionally at first are replaced by simpler conceptions, rendered possible by the acquisition of new evidence. A simplification of this order is the purpose of the present communication.

Structurally considered, the lithia micas are all characterized by two special features, an oxygen ratio lower than that of the orthosilicate, and the presence of fluorine. The first of these

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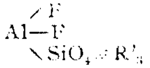
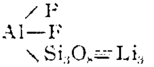
[1] Bulletins of the U. S. Geological Survey, Nos. 27, 42, 55, 60, 64, 78, and 90.

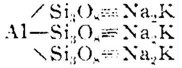
peculiarities has already been explained by the presence of the group Si_3O_8 replacing SiO_4, and the second is now rendered intelligible by assuming that the clintonite type may also be replaced by a molecule of the structure



or its equivalent in the corresponding polysilicate. For example, in the polylithionite described by Lorenzen, SiO_4 is entirely replaced by Si_3O_8, and the assumption of the latter group is thus fully vindicated. The analogy of the feldspars was strong evidence in its favor; but now we have what may fairly be regarded as positive proof. Polylithionite may now be considered as a mixture of the two molecules



and



in the ratio 5 : 1 ; whence we get the following comparison between observation and theory :

	Found.	Calculated.
SiO_2	59.25	59.80
Al_2O_3	12.57	12.70
FeO	0.93	. . . .
K_2O	5.37	5.85
Na_2O	7.63	7.72
Li_2O	9.04	9.34
F	7.32	7.93
	102.11	103.34
O=F	3.08	3.34
	99.03	100.00

The small amount of ferrous impurity, and the low summation of the analysis, fully account for all the variations between the two columns of figures, both as regards their magnitude and their direction.

In the light of the foregoing evidence, and of the mica theory in general, the lepidolites proper, such as occur in Moravia and in Maine, become easily explainable. All of their variations in composition are covered by the supposition that these micas consist of mixtures in different proportions, of two typical molecules; one the compound $AlF_2.Si_3O_8.R'_3$, with lithium as the principal constituent of R', and the other a muscovitic molecule,

$Al_3(SiO_4)_3R'_3$ in which R'_3 may be either K_2H or KH_2. Two such mixtures may be considered here: first, the two molecules $AlF_2.Si_3O_8.Li_3$ and $Al_3(SiO_4)_3K_2H$, in the ratio 1 : 1; and second, the three compounds $AlF_2.Si_3O_8.K_3$, $AlF_2.Si_3O_8.Li_3$, and $Al_3(SiO_4)_3KH_2$, commingled in the ratio 1 : 2 : 2. These mixtures correspond to the following percentage compositions:

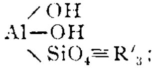
	First.	Second.
SiO_2	49.05	50.39
Al_2O_3	27.79	25.70
K_2O	12.81	13.16
Li_2O	6.13	5.04
H_2O	1.22	2.01
F	5.18	6.38
	102.18	102.68
Less O	2.18	2.68
	100.00	100.00

For purposes of comparison with these figures, the following analyses of typical lepidolites are quite sufficient, as they cover all important variations: A, Rozena, by Berwerth; B, Schüttenhofen, by Scharizer; C, Paris, Maine; D, Hebron, Maine; E, Norway, Maine; F, Rumford, Maine. The last four analyses are by Riggs.

	A.[1]	B.[2]	C.	D.	E.	F.
SiO_2	50.98	49.25	50.92	48.80	49.52	51.52
Al_2O_3	27.80	25.27	24.99	28.30	28.80	25.96
Fe_2O_3	....	....	0.30	0.29	0.40	0.31
FeO	0.05	0.84	0.23	0.09	0.24	....
MnO	....	0.85	trace	0.08	0.07	0.20
CaO	....	....	trace	0.10	0.13	0.16
MgO	....	....	trace	0.07	0.02	0.02
Li_2O	5.88	5.38	4.20	4.49	3.87	4.90
Na_2O	....	0.35	2.11	0.74	0.13	1.06
K_2O	10.78	13.85	11.38	12.21	8.82	11.01
Rb_2O	....		trace		3.73	....
Cs_2O	....		trace		0.08	....
H_2O	0.96	1.76	1.96	1.73	1.72	0.95
F	7.88	5.68	6.29	4.96	5.18	5.80
	104.33	103.23	102.38	101.86	102.71	101.89
Less O	3.32	2.39	2.64	2.02	2.18	2.44
	101.01	100.84	99.74	99.84	99.53	99.45

[1] Also contains 0.05 P_2O_5.
[2] Also contains 0.06 SnO_2.

In the first of these lepidolites, the mineral from Rozena, a slight variation from the scheme must be assumed, due to the excess of fluorine and the low proportion of alkalies. These peculiarities are easily accounted for by supposing a small admixture of the molecule $AlF_2.Si_3O_8.Al$; which corresponds to the type already indicated, and which is justified by other evidence. In the mineral cookeite, recently re-analyzed by Penfield,[1] we find what appears to be the vermiculite of the lepidolite series; with nearly all the alkalies but lithia removed, and with fluorine replaced by hydroxyl. Penfield's analysis of it reduces easily to the type



$$Al\begin{cases} OH \\ OH \\ SiO_4\equiv R'_3; \end{cases}$$

and in detail to a mixture of the three molecules $Al(OH)_2.SiO_4.Li_3$, $Al(OH)_2.SiO_4.H_3$, and $Al(OH)_2\ SiO_4.Al$, in the ratio 10 : 14 : 33. Reducing Penfield's analysis by uniting Fe with Al, the remaining bases with Li, and F with OH, and throwing out water lost at or below 300°, we get the subjoined comparison between observation and theory.

	Found.	Reduced.	Calculated.
SiO_2	34.00	35.01	34.68
Al_2O_3	45.06	46.71	46.53
Fe_2O_3	0.45		
CaO	0.04		
K_2O	0.14		
Na_2O	0.19		
Li_2O	4.02	4.29	4.56
H_2O below 300°	1.82	....	....
H_2O above 300°	13.14	13.99	14.23
F	0.46		
	99.32	100.00	100.00

In the lepidolite from Juschakova, analyzed by Rammelsberg, we find a connecting link between the lepidolites proper and the iron-lithia micas zinnwaldite and cryophyllite. The Juschakova mineral is easily represented as a mixture of molecules like the other lepidolites, except that a portion of the typical $AlF_2.Si_3O_8.R'_3$ is replaced by a similar molecule $AlF_2.Si_3O_8.MnLi$. In detail it

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[1] *Am. J. Sci.*, May, 1893.

seems to contain the molecules $Al_3(SiO_4)_3K_2H$; $AlF_2.SiO_4.Al$; $AlF_2.Si_3O_8.MnLi$, and $AlF_2.Si_3O_8.Li_2K$, in the ratio 2 : 1 : 3 : 6. Calculating its composition upon this basis, we get the following comparison with Rammelsberg's analysis:

	Found.	Reduced.	Calculated.
SiO_2	50.26	50.26	50.33
Al_2O_3	21.47	21.47	21.39
MnO	5.36	5.36	5.26
K_2O	11.08	11.08	11.60
Na_2O	0.54		
Li_2O	4.88	5.14	5.55
H_2O	0.66	0.66	0.44
F	8.71	9.33	9.38
Cl	1.16		
	104.12	103.30	103.95
Less O	3.92	3.92	3.95
	100.20	99.38	100.00

As for the iron-lithia micas, zinnwaldite and cryophyllite, a detailed discussion now would be premature; for the reason that alternative formulae, agreeing equally well with the recorded analyses, are possible. The complication is due to the iron, which may be regarded either as belonging to a molecule of the type $AlF_2.Si_3O_8.Fe''R'$; or to a biotitic molecule $Al_2(SiO_4)_3Fe''_2R'_2$. The zinnwaldite analyses of Berwerth and Rammelsberg are easiest interpreted as representing mixtures of $AlF_2.Si_3O_8.FeLi$, and $Al_3(SiO_4)_3K_3$, in the ratio 5 : 2, approximately. Cryophyllite, on the other hand, according to analyses by Riggs, is most simply represented by the composition

$$Al_3X_3KH_2+2(Al_2X_3Fe_2H_2)+3(AlF_2.X.K_3)+4(AlF_2.XLi_3);$$

in which X corresponds to the two acid groups SiO_4 and Si_3O_8 in the ratio 1 : 3. This interpretation is based in part upon the fact that cryophyllite occurs in margins upon plates of annite, which is a lepidomelane of the biotite type. The iron in cryophyllite, however, may also be regarded as present in the molecule $AlF_2.Si_3O_8.Fe''R'$, as in zinnwaldite; and between this interpretion and the other there are no adequate grounds for deciding. Taking the formulae as given above, Rammelsberg's analysis of zinnwaldite, and the mean of Riggs' three analyses of cryophyllite compare as follows:

	Zinnwaldite.		Cryophyllite.	
	Found.	Calculated	Found.	Calculated.
SiO_2	46.44	47.55	51.86	51.95
Al_2O_3	21.84	21.19	16.50	18.13
Fe_2O_3	1.27	....	2.98	....
FeO	10.19	13.60	6.65	7.52
MnO	1.57	....	0.21	....
CaO	....	....	0.04	....
MgO	0.18	....	0.07	....
Li_2O	3.36	2.84	4.89	4.71
Na_2O	0.54	....	0.79	....
K_2O	10.58	10.66	10.61	12.26
H_2O	1.04	....	1.29	1.41
F	7.62	7.18	7.08	6.94
	104.63	103.02	102.97	102.92

In general, it seems highly probable that the lithia micas are all characterized by the presence of the groups $AlF_2.X.R'_3$, $AlF_2.X.R''R'$, and $AlF_2.X.Al$; in which X may be either SiO_4 or Si_3O_8, and with the fluorine replaceable by hydroxyl in the process of vermiculitization. In the original form of the mica theory, the group AlF_2 was regarded as the equivalent of R' in a molecule of the muscovite type. It is now represented as belonging to a distinct molecule analogous to clintonite. So far as the evidence goes, this interpretation seems to be satisfactory; and it is an advance upon the earlier scheme in the direction of simplicity.

CHEMICAL NOTES FROM THE COLUMBIAN EXPOSITION.

I.

By J. H. Long.

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THE various exhibits of the Exposition in Chicago are grouped under twelve heads or departments. Those specially interesting from a chemical standpoint are found in the departments of Agriculture (A), Mines, Mining and Metallurgy (E), Manufactures (H), Electricity and Electrical Appliances (J), and Liberal Arts and Education (L). Certain departments occupy special buildings. The exhibits in several departments are scattered through a number of buildings.