# THE MINERALOGICAL MAGAZINE

#### AND

## JOURNAL OF

## THE MINERALOGICAL SOCIETY.

No. 109.	June, 1925.	Vol. XX.

On the chemical classification of the mica group. I. The acid micas.

By A. F. HALLIMOND, M.A., F.G.S. Assistant Curator, Museum of Practical Geology, London.<sup>1</sup>

[Read June 19, 1923.]

IN a discussion of the composition of glauconite,<sup>2</sup> it was shown that the analyses of this substance can be represented in terms of simple molecular proportions, provided that the mineral is regarded as a mixture of a silicate containing the group  $R_2O_3$  with a similar compound in which one equivalent of  $R_2O_3$  is replaced with one equivalent of RO; the general formula being  $R_2O.4(R_2O_3, RO).10SiO_2.nH_2O$ .

Work on the sedimentary iron ores collected during the preparation of the 'Special Reports on Mineral Resources', recently issued by the Geological Survey, made it necessary to review the composition of some of the chlorites; but no evidence of similar replacement was found among the better-known minerals of that group. In the case of the micas, on the other hand, the adoption of the principle that  $R_2O_3$  can be replaced by RO results in a considerable simplification of the formulae; a brief

<sup>&</sup>lt;sup>1</sup> Communicated by permission of the Director.

<sup>&</sup>lt;sup>2</sup> A. F. Hallimond and E. G. Radley, Min. Mag., 1922, vol. 19, pp. 330-333.

account of this aspect of the group forms the subject of the present note.

To facilitate comparison, the analyses have been recalculated to approximate molecular proportions, with  $(Si,Ti)O_2 = 600$ , on the plan already adopted in the case of glauconite. This method is most useful in testing a set of formulae that have a constant number of atoms of silicon in the molecule; it is therefore less suitable for the formulae proposed by Tschermak or by Clarke, than for those used in the present discussion, where all the micas will be treated as derivatives of the same acid, having the group R<sub>2</sub>O.6SiO<sub>2</sub> in common. Tables showing the molecular composition for the chief constituents are given at the end of the paper;<sup>1</sup> the analyses used being those given by Dana, supplemented with later analyses. H. E. Boeke<sup>2</sup> has collected a very full list of mica analyses, from which the complete analyses later than 1890 are given in Table I. Unfortunately, the grouping of the oxides adopted by this author in calculating the molecular composition does not yield figures available for testing the grouping here adopted; moreover, it would seem that many altered micas, sericites, &c., must have been included in the list. Preference has, therefore, been given to the older tables by Dana, which are generally accepted as representative, and which have been fully confirmed by recent work, especially the extensive series of analyses by W. Kunitz.<sup>3</sup> The regularities shown by these analyses will first be

.<sup>1</sup> Calcium, which is present in unimportant amounts, is omitted except in the analyses by Kunitz, where it is included in the RO group.

<sup>2</sup> H. E. Boeke, Neues Jahrb. Min., 1916, vol. 1, pp. 83-117. [Min. Abstr., vol. 1, p. 245.]

<sup>3</sup> W. Kunitz, Neues Jahrb. Min., 1924, Beilage-Band 50, pp. 365-413. [Min. Abstr., vol. 2, p. 424.] This valuable paper was read at the annual meeting of the German Mineralogical Society in 1922, and a preliminary abstract was published in Zeits. Krist., 1923, vol. 57, pp. 559-561. The details of the 32 new analyses were published while the present paper was in manuscript. The analyses, recalculated to  $SiO_2 = 600$ , have been included in the present tables, and they fully confirm the earlier data. In many important respects the formulae assigned by Kunitz are in agreement with those here given. As regards the RO oxides, however, that author denies on 'valency-theoretical' grounds that RO can replace  $R_2O_3$  (p. 389); the phengites are explained as resulting from accidental inclusions (p. 378); and even the ferric oxide in lepidomelane is attributed to secondary alteration by reversible reaction between FeO and water (p. 389). Nevertheless it is recognized that lepidolite can be derived from muscovite by substituting Li<sub>2</sub>O for Al<sub>2</sub>O<sub>3</sub>; but phlogopite is derived from muscovite by putting 6RO in place of 2Al<sub>2</sub>O<sub>3</sub> (p. 396); and the author concludes that without synthetic experiments a complete explanation of the valency difference between Li and Al cannot be obtained. An attempt is made to deal with the question by means of complex groups such as [2 Li, Si], called discussed and a possible theory of the group, with a method of graphical representation, will then be outlined.

Ratio of  $SiO_2$  to  $R_2O$ .—The column (K,Na)<sub>2</sub>O in the various tables gives the sum of the equivalents for potash and soda. Lithia, when present in noteworthy amounts, is separately stated; for reasons which will be given in the discussion of the lithia micas, it will be treated as replacing the R<sub>2</sub>O<sub>2</sub> group and not R<sub>2</sub>O. On inspection of the tables it will be seen that throughout the whole group the equivalent for (K,Na),O is remarkably constant. This regularity has recently been observed by W. Kunitz, who finds a similarly constant value in a series of new analyses. The figures here given indicate variations somewhat beyond those usually assigned to experimental error in the determination of alkalis. It is clear, however, that the micas were formed in solutions of widely varying composition, and the approximate constancy of these values is therefore very strong evidence in favour of formulae having the fixed ratio  $K_{0}O: SiO_{0} = 1:6$ ; the small deviations being readily explained either by experimental errors or by the presence of small quantities of other molecules soluble to a very limited extent in the mica crystal.

The simplest possible formula would contain  $3SiO_2$ , but glauconite and several of the chlorites require formulae of greater complexity, so that there is no reason to retain the simplest form; it will be shown below that by doubling the formula it becomes possible to represent all the micas as symmetrical compounds of the same chain silicic acid.

Volatile constituents.—In glauconite the 'solid' oxides conform to simple molecular proportions, although the water content is variable. A similar relationship holds for the mica group, but allowance must be made for the exceptional difficulty of correctly estimating water and fluorine. It is clear from the recent analyses that  $H_2O$  and  $F_2$  are mutually replaceable, so that the water is to be regarded as hydroxyl. Further, the constancy of the 'solid' part of the molecule indicates that none of the 'solid' oxides is replaceable by water or fluorine. These constituents must therefore be combined either directly with the silica, forming an acid, or directly with alumina, in the form of basic radicles. Combination with the silica is improbable from the known unstable properties of silicic acid, and from the fact that in presence of water silicon fluoride is immediately decomposed, only the silico-fluorides being

307

<sup>&#</sup>x27;Le', thus the lithia micas are written  $KH_2Al_2Le[SiO_4]_2$ ; a formula which does not accord with the constant ratio  $K_2O:6SiO_2$ . The use of basic alumina radicles does not seem to have been considered, although early in the paper a reference is made to topaz. (See note on p. 318.)

stable. Basic alumina radicles, on the other hand, have already been postulated to explain minerals like topaz; there is no difficulty, therefore, in regarding the fluorine and water of the micas as due to the presence of groups such as  $-Al(OH)_2$ ,  $-AlF_2$ , =AlF, &c. Not all these, however, possess the valency required to make  $R_2O_3$  substitutable by  $Li_2O$  and by oxides of the RO group in the manner to be demonstrated below; and the possible forms for the alumina radicle can therefore be restricted within a narrow range. An interchange between  $-Al(OH)_2$ and -AlO would explain any outstanding irregularity in the water content of the micas.

Broadly speaking, the molecular proportion of water (and fluorine) to  $6SiO_2$  is 2 throughout the group. There is also always at least one equivalent of  $Al_2O_3$ , a fact which strongly supports the theory that the water is combined with alumina.

#### 1. Soda and potash micas.

#### Muscovite and phengite.

The ordinary muscovites approximate to the formula  $K_2O.3Al_2O_3$ .  $6SiO_2.2H_2O$ . Like glauconite, however, they generally contain substantial amounts of the RO oxides, particularly ferrous oxide and magnesia. The presence of these oxides can be explained if it is assumed that  $R_2O_3$  in the accepted formula for muscovite is substitutable by RO; the silica-rich varieties which were specially classed as 'phengite' then become merged in the ordinary muscovite group. The analyses are shown in Table I (p. 315), and it will be seen that while the amount of RO often approaches the value 50 and sometimes attains 100, the variation in the total of  $RO + R_2O_3$  is much smaller and rarely exceeds 20. The muscovites can therefore be represented as mixtures of

 $x[K_2O, 3R_2O_3, 6SiO_2, 2H_2O] (muscovite) + y[K_2O, RO, 2R_2O_3, 6SiO_2, 2H_2O] (phengite) + y[K_2O_3, 2H_2O_3, 2H_$ 

This relation between  $R_2O_3$  and RO in the muscovites is represented graphically in fig. 1, where the dotted line represents the theoretical values for mixtures of the above two molecules. The actual points are scattered along this line. That a certain number of muscovites will contain a small excess of RO is to be expected, for it can hardly be imagined that biotite will be entirely insoluble in muscovite; it is clear, however, that this solubility is very limited in extent even with a relatively high content of RO. The arrows on the right of fig. 1 indicate the direction in which the composition must have changed if RO had been present as biotite. A comparison of the proportion of ferrous oxide to magnesia in the original analyses shows that the more phengitic micas are often richer in magnesia, though no precise relation exists. This seems to correspond with a relationship in the biotite group, where the members with  $1Al_2O_3$ , approximating to phlogopite, are magnesian, while those with  $2Al_2O_3$  (the biotites) are relatively rich in ferrous iron. Apparently magnesia replaces  $R_2O_3$  more readily than does FeO.

The chrome micas and paragonite generally resemble muscovite, and show no features of special interest. As regards damourite and sericite



FIG. 1. Molecular proportions of  $R_2O_3$  and RO in muscovite and phengite. (Analyses from Table I. Points represent analyses from Dana's 'System', crosses those from Boeke, and points in circles the new determinations by Kunitz.)

it is generally recognized that the analyses are in many cases similar to ordinary muscovites, but it seems likely that these groups contain also some analyses of minerals derived from other than hexasilicic acid, some analyses of 'hydro-micas', and some of micas in which further substitution of alumina by alkalis has occurred. The few analyses available do not suffice for investigation of these alternatives and the two subordinate species have therefore been omitted from this paper.

#### 2. LITHIA MICAS.

Inspection of the analyses (Table II) shows that there are no analyses containing intermediate amounts of lithia. The value for  $\text{Li}_2\text{O}$  is approximately 100 throughout the whole of the lithia-bearing series; only in polylithionite does it greatly exceed that figure, and only at the extreme basic end of the protolithionite series does it diminish. Consequently, the acid micas can be divided into two classes, the first comprising the potash and soda micas already described, the second containing micas in which the ratio of  $\text{Li}_2\text{O}$  to  $\text{SiO}_2$  is at least 1:6. The observed immiscibility of lepidolite and muscovite thus extends throughout the whole series of acid micas. The lithia micas can be subdivided into the following species, of which the relationships are represented graphically in fig. 2.

#### Lepidolite.

This well-defined compound has been the subject of especially careful analyses (Table II), which lead to the formula R<sub>2</sub>O. Li<sub>2</sub>O. 2Al<sub>2</sub>O<sub>5</sub>. 6SiO<sub>2</sub>. 2II.O. A considerable part of the hydroxyl is replaced by fluorine. The formula resembles that assigned above to phengite, the alumina being replaced by lithia instead of by RO. This special property of lithia, in contrast with the other alkalis, may be explained by the fact that the molecular volumes of lithia and of alumina are similar and are smaller than that of soda and very much smaller than that of potash. Muscovite sometimes contains a little lithia, but is evidently almost completely immiscible with lepidolite; intergrowths of the two minerals have been described.<sup>1</sup> Under special conditions lithia might also, to a certain extent, replace soda in the molecule; indeed the sum of  $R_2O_3 + Li_2O + (K, Na)_2O$  for lepidolite is rather more nearly constant than that for (K,Na), O alone. The differences are, however, scarcely important enough to justify any final conclusion, for they might well result from imperfect separation of the alkalis in analysis; if the replacement occurs it is of extremely limited extent.

Most of the older lepidolite analyses are remarkably free from the RO metals, but the recent analyses by Kunitz are quite similar to those of average muscovites in this respect and indicate a continuous series between lepidolite and cryophyllite.

<sup>1</sup> H. L. Bowman, Min. Mag., 1902, vol. 13, p. 98; H. Baumhauer, Zeits. Kryst. Min., 1912, vol. 51, pp. 344-357.

#### Cryophyllite.

The sum of  $R_2O_3$  and RO approximates to 200, so that the natural mineral can be represented as a mixture of  $K_2O.Li_2O.2R_2O_3.6SiO_2.2H_2O$  (lepidolite) with  $K_2O.Li_2O.RO.R_2O_3.6SiO_2.2H_2O$  (cryophyllite).

Cryophyllite is thus related to lepidolite in the same way as phengite to muscovite. The lithia is slightly in excess of, and the  $R_2O$  slightly below, the exact value 100, so that there is again a possible indication that lithia is capable to a small extent of replacing soda.

#### Polylithionite.

Yet another molecule of  $R_2O_3$  would seem to be replaceable by lithia, yielding  $K_2O \cdot 2Li_2O \cdot R_2O_3 \cdot 6SiO_2 \cdot H_2O$ , a formula which approximately



FIG. 2. Molecular proportions of  $R_2O_3$  and RO in lithia micas. (Analyses from Table II. Two of the analyses fall outside the diagram. Lepidolite forms two series of mixed erystals—with cryophyllite and with protolithionite.)

represents the first analysis given for this mineral in Table II. If it is assumed that the substitution of alumina by lithia has proceeded a little farther than is indicated by the above simple formula, we obtain the calculated percentage composition shown in the first line of the table below (assuming partial substitution of  $K_2O$  by  $Na_2O$ , of  $Al_2O_3$  by FeO, and that  $H_2O = F_2$ ). Lorenzen's analysis of the mineral is given in the second line, while the third line shows the percentage composition calculated by Clarke<sup>1</sup> from the complex formula  $5AlF_2Si_3O_8Li_3 +$  $1Al(Si_3O_8Na_2K)_3$ . A comparison of this table with those given at the end of the paper will show the rather deceptive agreement that can be obtained by distributing the errors when formulae are recalculated to

<sup>1</sup> F. W. Clarke, Bull. U.S. Geol. Survey, 1914, no. 588, p. 55.

a percentage composition; the use of equivalents with  $SiO_2 = 600$  is a much more severe test of rationality.

	$SiO_2$ .	$Al_{2}O_{3}.$	FeO.	$K_2O$ .	$Na_2O$ .	Li <sub>2</sub> O.	F.
Calculated	60.0	12.7	1.0	5.2	6.8	11.0	6.3
Lorenzen's analysis	59.25	12.57	0.93	5.37	7.63	9.04	7.32
Calc. (Clarke)	59.79	12.74		5.85	7.72	9.34	7.88

#### Lepidolite-protolithionite (zinnwaldite).

Although there is a remarkable absence of analyses intermediate between muscovite and biotite, the ferrous lithia micas yield indications of wider miscibility. The two zinnwaldites from Dana might be regarded as consisting chiefly of the compound K2O.2Al2O3.RO.Li2O.6SiO2.2H,O, with other similar minerals in subordinate amount. Alternatively, they could be regarded as mixtures of lepidolite with a lithia biotite (protolithionite), having the formula K2O.2Al2O3.3RO.Li2O.6SiO2.2 H2O. The latter assumption would explain the new analyses as well as the two given by Dana, and it does not seem possible to go farther with the material at present available. Difficulty in distinguishing between an intermediate compound and a mixture arises in all isomorphous series; the matter could best be decided by detailed examination of the physical properties, for which material is at present lacking. This series is represented graphically in fig. 2; the lowering of the points may be explained as the result of admixture with cryophyllite. At the basic end of the series the content of lithia diminishes, presumably owing to the admixture of common biotite, K2O. 2Al2O3. 4RO. 6SiO2. 2H2O.

#### Other white micas.

Three other lithia-bearing minerals, irvingite, cookeite, and tainiolite, have been classed as micas. Cookeite resembles a chlorite or vermiculite; the others, however, contain  $R_2O: SiO_2 = 1:6$  and are presumably allied to the micas. Irvingite has the formula  $R_2O. R_2O_3. Li_2O. 6SiO_2. H_2O.$ Tainiolite lies between  $R_2O. 3RO. Li_2O. 6SiO_2. 3H_2O$ , and the similar formula with 4RO (the water-content is not accurately known); it can be represented as a mixture of irvingite with the compound  $R_2O. 4RO. Li_2O. 6SiO_2. n H_2O.$ 

Oellacherite and similar micas, containing alkaline earths, cannot easily be discussed in the absence of evidence as to the behaviour of barium and allied elements which are not usually present in the micas. A few micas, including euphyllite, show an excess of alumina over the

312

formula for muscovite, but the analyses are not sufficiently definite to permit any conclusion as to their formula.

#### GRAPHICAL FORMULAE.

In the first part of this paper attention was confined to obtaining the simplest rational formulae consistent with the analyses of the micas. It has also been found possible to represent the compounds so obtained by a series of simple graphical formulae, as salts of one silicic acid, while it will be shown in a later part of this paper that the same acid yields simple formulae for the basic micas (biotite, &c.) and for certain chlorites and vermiculites. The ordinary graphical notation of organic chemistry becomes rather unwieldy when employed for inorganic compounds of this kind, and a simpler notation will be used, which can be arrived at in the following way.

The silicates are characterized by the fact that they can in general be represented as the sum of the oxides of their constituent elements. No such rule applies to the carbon compounds, and it is clear that oxygen has in the silicates an essential role which is quite distinct from its subordinate part in organic chemistry. Compounds (salts) that can be represented as the sum of two oxides are derivable from the constituent hydrated oxides (acid + base) by reactions of which the following may be taken as a type:

$$A''(OH)_2 + R''(OH)_2 = A'' \langle O \rangle R'' + 2H_2O.$$

If we assume that all ordinary silicates are formed in this way, the direct union of R" and A" being excluded, we obtain a class of compounds fulfilling the condition that they are always representable as the sum of their constituent oxides. The normal role of the oxygen being thus reduced to that of a link between acidic and basic elements, it is no longer necessary to write the oxygen atoms separately, and the structural

formulae can be shortened by putting, in place of  $A'' \swarrow O R''$ , the notation A''=R'' where the heavy lines represent the connecting oxygen atoms. These will be termed oxy-bonds to distinguish them from ordinary valency bonds. Special acidic or basic groups such as  $-AI(OH)_2$  will still be written in the usual way except as regards the oxy-bond that joins them to the rest of the molecule.

It is further convenient to put an asterisk, in place of the letters Si, to represent the atom of silicon which occurs so frequently. A normal ferrous silicate 2FeO.  $SiO_2$  then becomes simply Fe=\*=Fe.

313

The oxy-bonds must throughout satisfy the valency of the elements or groups exactly as in the case of ordinary bonds, and if this condition is observed all the formulae obtained will represent possible oxidic compounds. The only other way of obtaining such compounds is to combine in the same molecule peroxidized groups with groups deficient in oxygen to an equivalent extent, a combination unlikely to occur except under the most unusual conditions, least of all at high temperatures.

After various trials it was found that the micas could be represented by a series of structural formulae based throughout upon the orthosilicic acid containing six atoms of silicon. The formulae are given below; it will be understood that the exact position of substituent groups could only be ascertained by considerable further investigation. That given appears to be the simplest arrangement consistent with the facts at present available.

1 and minun

1000 ma	
$\cdot$ [* represents Si, and -	represents -0]
Muscovite, ( $K_2O$ , $3Al_2O_3$ , $6SiO_2$ , $2II_2O$ )	$K = \frac{O}{K} = $
Phengite, $(\mathbf{K}_{2}\mathbf{O}, 2\mathbf{A}\mathbf{l}_{2}\mathbf{O}_{3}, \mathbf{RO}, \mathbf{6SiO}_{2}, \mathbf{2H}_{2}\mathbf{O})$	$K = \frac{\mathbf{C} \mathbf{C}}{\mathbf{K}} = \frac{\mathbf{C} \mathbf{C}}{\mathbf{K}} = \frac{\mathbf{C} \mathbf{C}}{\mathbf{K}} = \frac{\mathbf{C} \mathbf{C}}{\mathbf{C}} = \frac{\mathbf{C} \mathbf{C}}{\mathbf{C}} = \frac{\mathbf{C} \mathbf{C}}{\mathbf{C}}$
Lepidolite, (K <sub>2</sub> O. Li <sub>2</sub> O. 2Al <sub>2</sub> O <sub>3</sub> . $6 \text{SiO}_2 \cdot 2 \text{H}_2 \text{O} \dots$	$K \qquad Li \qquad \stackrel{\bigcirc}{\underset{\scriptstyle \downarrow}{\underset{\scriptstyle \downarrow}{\overset{\scriptstyle \downarrow}{\underset{\scriptstyle \downarrow}{\underset{\scriptstyle \downarrow}{\overset{\scriptstyle \downarrow}{\underset{\scriptstyle \scriptstyle \downarrow}{\underset{\scriptstyle \scriptstyle \scriptstyle}{\underset{\scriptstyle \scriptstyle \scriptstyle}{\underset{\scriptstyle \scriptstyle \scriptstyle}{\underset{\scriptstyle \scriptstyle \scriptstyle}{\underset{\scriptstyle \scriptstyle \scriptstyle}{\underset{\scriptstyle \scriptstyle}{\underset{\scriptstyle \scriptstyle}{\underset{\scriptstyle \scriptstyle}{\underset{\scriptstyle \scriptstyle}{\atop\scriptstyle}{\underset{\scriptstyle \scriptstyle}{\underset{\scriptstyle}{\underset{\scriptstyle}{\atop\scriptstyle}}{\underset{\scriptstyle}{\atop\scriptstyle}{\atop\scriptstyle}}{\underset{\scriptstyle}{\scriptstyle$
Cryophyllite, (K <sub>2</sub> O , Li <sub>2</sub> O , Al <sub>2</sub> O <sub>3</sub> , RO , 6 SiO <sub>2</sub> , 2 H <sub>2</sub> O)	$K = \frac{1}{K} = \frac{1}{K} = \frac{1}{K} = \frac{1}{K} = \frac{1}{K} = \frac{1}{K} = \frac{1}{K}$
Polylithionite, $(K_2O, 2Li_2O, Al_2O_3, 6SiO_2, 2H_2O)$	K Li Li Li Li Ah $(OH)_g$ *=*-*=*-*=* K Al $(OH)_g$
Zinnwaldite, (K <sub>2</sub> O, Li <sub>2</sub> O, 2Al <sub>2</sub> O <sub>3</sub> , RO, 6SiO <sub>2</sub> , 2H <sub>2</sub> O) (if a compound)	$K \qquad Li \qquad \bigcirc \bigcirc \bigcirc \bigvee \qquad Zi \qquad Li \qquad Al(OH)_2$ $* = * - * - * - * = *$ $K \qquad R \qquad Al(OH)_2$

Protolithionite,  

$$(K_{2}O. Li_{2}O. 2Al_{2}O_{3}. 3RO. 6SiO_{2}. 2H_{2}O)$$

$$K Li \stackrel{\bigcirc}{\leftarrow} \stackrel{\frown}{\leftarrow} Li Al(OH)_{2}$$

$$* - * - * - * - * - *$$

$$K \stackrel{\frown}{K} \stackrel{\frown}{K} \stackrel{\frown}{K} \stackrel{\frown}{K} Al(OH)_{2}$$

In these minerals, potash is replaceable by soda, alumina by ferric oxide and chromium oxide, while R = Mg, Fe, Mn.

The above formulae contain the anhydride grouping \*=\* (i.e.  $\operatorname{Si}_{2}O_{2}$ ), which is analogous with a 'double bond' in ordinary structural formulae. Protolithionite, the last mineral in the group, is really lithia biotite, and has accordingly a formula analogous with that which will be proposed for biotite. Formulae for minerals of the latter class will be derived from those for the acid micas by saturating the double bonds with oxides of the RO group. This results in a marked diminution of the silica-content, and the micas have accordingly been divided into two groups, termed 'acid' and 'basic'. As might be expected, the acidity of the mica corresponds with the degree of acidity of the rock-melt from which it is derived.

The group :\*  $\overset{\mathbf{R}}{\longrightarrow}$ : (i.e.  $\mathrm{RSi}_2O_3$ ) represents a six-atom ring analogous with the rarer heterocyclic rings of the carbon compounds, while the 'double oxy-bond' completes a four-atom ring. Neither structure demands any abnormal degree of stability such as is required in formulae with polyatomic rings, like those postulated in the 'hexite-pentite' theory of W. and D. Asch.<sup>1</sup>

# Acid Micas. Analyses recalculated to molecular proportions when $(Si,Ti)O_2 = 600.$

Table I. Potash and soda micas.

				muscou	<i>ie</i> •			
	No.	$R_2O_3$ .	RO.	$RO + R_2O_3$ .	(K,Na) <sub>2</sub> O.	$H_2O.$	$\mathbf{F}_{2}$ ,	$H_{2}O + F_{2}$
Dana, <sup>2</sup>	1	294	<b>22</b>	316	82	222	3	225
,,	<b>2</b>	288	<b>26</b>	314	87	211	S	214
,,	3	307	6	313	101	252	8	260
,7	4	307	11	318	99	279	4	283
"	6	289	12	301	113	246	15	261
,,	8	279	16	295	84	163	11	174
,,	9	247	32	279	95	148		
,,	10	264	51	315	90	174	15	189

<sup>1</sup> W. and D. Asch, The silicates in chemistry and commerce. London, 1913. <sup>2</sup> Dana's 'System', 6th edit., 1892, pp. 617-618.

	•							
	No.	$\mathbf{R}_{2}\mathbf{O}_{3}.$	RO.	$RO + R_2O_3$ .	(K,Na)20.	$H_2O.$	$\mathbf{F}_{2}$ .	$H_2O + F_2$ .
Dana,	11	<b>274</b>	54	328	97	175	<b>20</b>	195
,,	12	252	31	283	93	171	13	184
,,	13	247	<b>32</b>	279	109	258		
,,	14	244	39	283	118	274	27	301
,,	15	266	49	315	83	201		<u> </u>
,,	16	236	53	289	81	189		
"	17	215	72	287	94	170		
,,	18	200	112	312	102	143		
**	19	204	70	274	91	180		
Dana,1	6	280	43	323	74	172	20	192
Boeke, <sup>2</sup>	7	289	12	301	116	265	16	281
"	8	289	1	290	102	194	16	210
"	11	301	3	304	102	212	19	231
"	19	252	50	302	<b>64</b>	228	12	240
••	20	303	47	350	95	130	4	134
,,	<b>21</b>	294	<b>76</b>	370	80	91	10	101
,,	22	284	13	297	126	212		
,,	23	291	, 12	303	112	225		_
,,	<b>24</b>	276	12	288	128	187		
,,	38	280	14	294	87	216		<b></b>
,,	41	288	<b>49</b>	337	106	269		
<b>,</b> ,	44	242	61	303	89	227		
,,	<b>54</b>	201	<b>42</b>	243	97	184	_	
,,	65	321	17	338	89	346		
"	70	246	6	252	82	266		
,,	71	.294	<b>2</b>	296	80	213		
**	72	165	61	226	65	163		
Kunitz,	<sup>s</sup> 1	309	10	319	105	185	18	203
,,	<b>2</b>	298	13	311	106	146	23	169
,,	3	291	17	.308	102	193	11	204
,,	4	290	10	300	101	190	4	194
,,	<b>5</b>	268	37	305	113	187	<b>5</b>	192
,,	6	274	<b>34</b>	308	105	<b>1</b> 82	<b>14</b>	196
,,	7	268	37	305	101	211		
"	8	<b>274</b>	25	299	101	176	15	191
,,	9	269	41	310	99	189	61	250
,,	10	265	31	296	103	195	55	250
,,	11	288	33	321	100	188	8	196

 $^{\rm I}$  Biotite analysis no. 6 in Dana's 'System' (p. 630); a muscovite in composition.

<sup>2</sup> H. E. Boeke, Neues Jahrb. Min., 1916, vol. 1, pp. 86-89. Analyses later than 1890. Nos, 20 and 21 seem to require further investigation. Occasionally small amounts of lithia have been added to the  $R_2O_3$  group as representing lepidolite.

3 W. Kunitz, Neues Jahrb. Min., 1924, Beilage-Band 50, p. 376. The table on p. 412 apparently contains minor errors in printing.

Table I (continued):

14000 1	Com	<i>inau</i> ca).		Euchoi	10			
				Fuchsi				vr o m
	No.	$R_2O_3$ .	RO.	$RO + R_2O_3$ .	(K,Na) <sub>2</sub> O.	$H_{2}O.$	F <sub>2</sub> .	$H_2O + F_2$ .
Dana,1	55	282	13	295	87		—	
•,	56	255	44	299	86	235		
,,	57	256	65	321	94	256	—	
••	58	305	67	372	94	321		
,,	59	280	76	356	66	204		-
				Paragon	ite.			
Dana, <sup>2</sup>	1	300	12	312	79	206		
••	<b>2</b>	319	16	335	106			
.,	3	323			94	221		
	4	285	7	292	96	104		
Barbier,	<sup>s</sup> _	308		<del></del>	113	187	—	
				Euphyll	ite.			
Dana,4	1	384	13	397	104	415		·
Dana. <sup>5</sup>	2	327	õ	332	69	253		
	4	318			90	244	· -	
Dana,6	-	363		_	68	210		

#### Table II. Lithia micas, &c.

				Lepid	olite.				
	No.	$R_2O_3$ .	RO.	$R_2O_3 + RO.$	Li <sub>2</sub> O.	(K,Na) <sub>2</sub> O.	H <sub>2</sub> O.	$\mathbf{F}_2$ .	$H_2O + F_2$ .
Dana, <sup>7</sup>	1	197		197	121	94	94	97	191
	<b>2</b>	193		193	139	80	37	146	183
,,	3	150	(8)	—	116	90	26	164 9	190
,,	4	182	17	199	131	112	72	109	181
,,	5	179	4	183	114	94	<b>37</b>	106	143
••	6	174	<b>2</b>	176	99	110	134	117	151
••	7	206	1	207	110	104	71	96	167
,,	8	196	7	203	105	97	61	104	165
,,	9	176	<b>2</b>	178	117	100	37	120	157
,,	10	207	4	211	94	83	70	99	169
Kunitz, <sup>10</sup>	3	157	9	166	126	97	46	161	207
				Lepidolite-c	ryophylli	te.			
Kunitz,10	4	183	35	218	104	104	<b>43</b>	131	174
	5	152	52	204	113	97	37	142	179
Dana.11	6	129	61	190	115	84	56	127	183
	4	125	63	188	112	88	51	123	174
••	5	121	78	199	112	89	<b>43</b>	<b>138</b>	181
,,	3	123	94	217	94	97		—	

Dana, loc. cit., p. 619.
 <sup>2</sup> Dana, loc. cit., p. 623.
 P. Barbier, Compt. Rend. Acad. Sci. Paris, 1908, vol. 146, p. 1220.

<sup>4</sup> Dana, loc. cit., p. 623.

Table I (continued):

., p. 623. <sup>5</sup> Dana, loc. cit., p. 624.

<sup>6</sup> Dana, loc. cit., p. 624, from Pipra, India.

7 Dana, loc. cit., pp. 624-625.

\* Present; stated as MgO + MnO.

<sup>10</sup> W. Kunitz, loc. cit., p. 394. <sup>11</sup>

<sup>9</sup> Also Cl<sub>2</sub> 1.16% = 11 units.

<sup>11</sup> Dana, loc. cit., p. 627.

				Polylith	io <b>n</b> ite.				
	No.	$R_2O_3$ .	RO.	$\mathbf{R}_{2}\mathbf{O}_{3} + \mathbf{RO}.$	Li <sub>2</sub> O.	(K,Na) <sub>2</sub> O.	H <sub>2</sub> 0.	$\mathbf{F}_2$ .	$H_2O + F_2$ .
Dana,1	8	75	8	83	183	109	_	117	-
Flink, <sup>2</sup>	-	77	3	80	169	86	· <u> </u>	132	
			Lepid	olite-protolithic	mite (zir	(nwaldite).			
Dürrfeld, <sup>3</sup>	_	186	49		108	100	127	133	260
Schaller, <sup>4</sup>	-	187	82	·	96	96	38	175	213
Dana, <sup>5</sup>	<b>2</b>	173	129		87	94		155	_
Kunitz, <sup>6</sup>	8	167	<b>138</b>	_	94	96	48	172	220
Dana, <sup>5</sup>	1	176	146	-	85	93	40	164	204
Kunitz,"	. ð	173	149	_	89	95	<b>43</b>	170	213
Dana,7	8	271	168		55	135	64	107	171
Stelzner, <sup>8</sup>	-	245	192	_	103	90	164	_	
Kunitz, <sup>6</sup>	10	<b>19</b> 0	195		70	111	67	149	216
Stelzner, <sup>8</sup>	-	207	270	_	64	99	172	—	
Kunitz, <sup>6</sup>	11	190	286	—	46	105	76		—
				Irvin	gite.				
Weidman	<b>,</b> " -	114	<b>5</b>	119	93	112	43	75	118
				Taini	olite.				
Flink, <sup>2</sup>		17	327	_	87	104	883	-	

<sup>1</sup> Dana, loc. cit., p. 627.

<sup>2</sup> G. Flink, Meddel. om Grønland, 1901, vol. 24 (for 1899), p. 114.

<sup>3</sup> V. Dürrfeld, Zeits. Kryst. Min., 1909, vol. 46, p. 578.

<sup>4</sup> W. T. Schaller, Amer. Journ. Sci., 1907, ser. 4, vol. 24, p. 158.

<sup>5</sup> Dana, loc. eit., p. 626. <sup>6</sup> W. Kunitz, loc. eit., p. 394.

<sup>7</sup> Dana, loc. cit., p. 627 ('polylithionite'). Kunitz transfers the ferric iron to the RO group (loc. cit., p. 394, anal. 12).

<sup>8</sup> A. W. Stelzner, Zeits. prakt. Geol., 1896, p. 391.

<sup>9</sup> S. Weidman, Amer. Journ. Sci., 1907, ser. 4, vol. 23, p. 451.

Note.—An analysis of lithia mica quoted by W. Kunitz as evidence for his group 'Le' is one of three given by L. Duparc, M. Wunder, and R. Sabot (Mém. Soc. Phys. Hist. Nat. Genève, 1910, vol. 36, pp. 367-370). Although large amounts of fluorine are shown, the uncorrected totals are all very near 100%. These analyses have therefore been omitted from the present tables.

318

Table I1 (continued):