THE MINERALOGICAL MAGAZINE

AND

JOURNAL OF

THE MINERALOGICAL SOCIETY.

No. 116. March, 1927. Vol. XXI.

On the chemical classification of the mica group. III. The molecular volumes.

By A. F. Hallimond, M.A., F.G.S.
Assistant Curator, Museum of Practical Geology, London.[1]

[Read March 16, 1926.]

IT is unfortunate that so many published analyses of mica are not accompanied by the physical data for the material used. Nevertheless, enough information is available to permit a general comparison of the density relations for the group. This is most conveniently made in terms of the specific volume, for, in most isomorphous series, the volume is an additive property even when the molecular volumes of the end-minerals differ appreciably. Such a relationship will be shown to hold good approximately for the micas; the volume can be calculated from constants assigned to the constituent oxides, the difference from the observed value being rarely more than 2 per cent. This result does not, of course, imply the adoption of any particular chemical theory; but it is convenient to work in terms of molecular volumes, and for that purpose

[1] Communicated by permission of the Director.

the theory outlined in the earlier parts of the present paper[1] has been adopted. The micas are regarded as salts of an acid with a constant number (6) of silicon atoms; and the volume associated with $6SiO_2$ is accordingly taken as the 'molecular volume' (mean); for formulae based on $3SiO_2$ the volumes would, of course, be one-half the values given. The group has already been divided into sections of differing chemical composition, and the several divisions are reflected in the scheme of molecular volumes now obtained (fig. 6). This, however, is simply the consequence of the fact that the volume is an additive property, and is true whatever formulae are adopted; but the present formulae are to a certain extent supported by the fact that the molecular volumes derived from them are such as would be expected in an isomorphous group; they are all of the same order of size, but differ sufficiently to agree with the view, already advanced on grounds of chemical composition, that the various sections have limited miscibility.

The fact that the volume is an additive property will be used in discussing the state of combination of titanium. In the micas that element (as TiO_2) is assumed to replace silica, and the amount present is frequently high enough for the volume data to afford good evidence in favour of this view. But several authors have considered the possibility that titanium is present as Ti_2O_3 or in some other form, and in one outstanding case it will be shown that the volume data can best be explained by the presence of titanium in a form not isomorphous with silica; for chemical reasons it would seem to be present as TiO_2 rather than as Ti_2O_3.

Calculation of the molecular volumes.—If, as in the present theory, the mica molecule contains the same number (n) of silicon atoms in all members of the group, it becomes possible to calculate the 'molecular volume' (V), i.e. the volume occupied by the matter associated with $nSiO_2$, directly from the silica percentage (a) and the density (ρ), by means of the following formula

$$V(\text{obs.}) = \frac{n \times 60 \times 100}{a \times \rho}.$$

The result is independent of all theory as to the nature of the substituent groups (provided they do not contain silica), and includes matter present in solid solution. It can, indeed, be applied in any mineral group for the purpose of investigating whether, for a proposed set of formulae, the scheme of molecular volumes is consistent with the

[1] Min. Mag., 1925, vol. 20, pp. 305–318, and 1926, vol. 21, pp. 25–33. Figures 1–5 and Tables I–IV were given in those parts.

isomorphous relationship known to exist between the members of the group.

All the volumes for the micas to be given below are referred to $6SiO_2$. For trisilicic molecules the values would of course be halved. If titanium

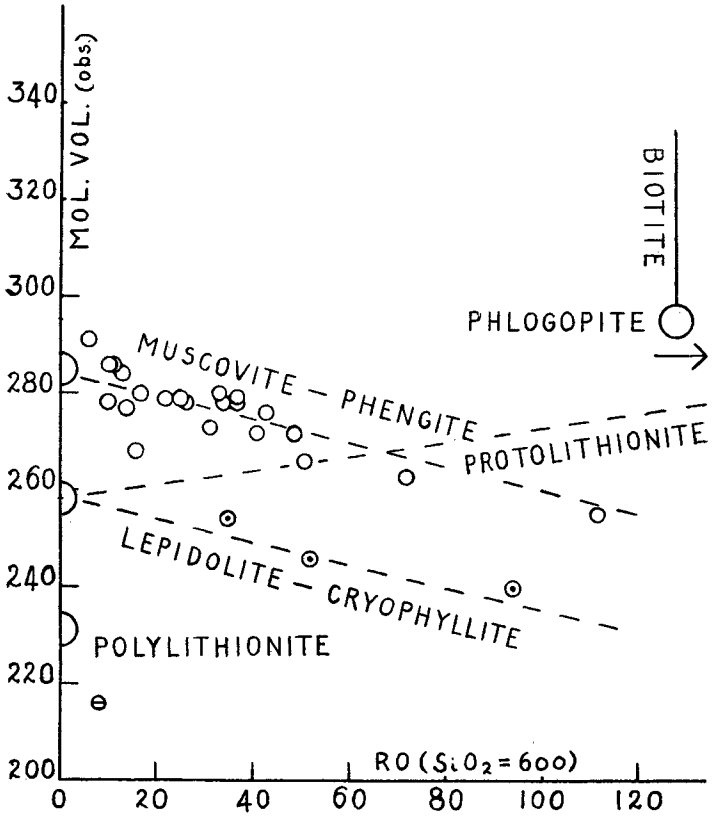

FIG. 6. Molecular volumes for the mica group. The points shown represent observed values, the large circles being the values calculated for the pure compounds. Biotite and phlogopite if plotted against their RO-content would lie far to the right of the diagram; their range of volume has been indicated for comparison with that of the acid micas.

is present as TiO_2 replacing silica it is necessary to correct the silica percentage by adding $\frac{3}{4}$ of the TiO_2 percentage, while the total material is reduced from 100 to $(100 - \frac{1}{4}TiO_2)$. In some analyses the silica

percentage is given for material dried at 105°C., while the density refers to air-dried material; for mica, however, this source of error is not serious and has been ignored. The 'observed' molecular volumes in the following pages are those obtained by the above formula. The 'calculated' values are derived from the molecular proportions of RO, R_2O_3, and Li_2O by means of constants according to the following equation (see p. 200):

$$V\,(\text{calc.}) = 165 + 0{\cdot}40\ (R_2O_3) + 0{\cdot}15\ (RO) + 0{\cdot}13\ (Li_2O),$$

(R_2O_3), &c., being the equivalent numbers for the respective oxides when $SiO_2 = 600$, as given in the present tables. Observed and calculated values show close agreement throughout the whole group, as will be seen from the data for the various sections below.

(*a*) *Muscovite-phengite.*—

Analysis.[1]	RO.	*V* (obs.).	*V* (calc.).	Analysis.	RO.	*V* (obs.).	*V* (calc.).
Dana, 3 ...	6	291	288	Kunitz, 11 ...	33	280	285
Kunitz, 1 ...	10	286	290	,, 6 ...	34	278	280
,, 4 ...	10	278	282	,, 7 ...	37	278	278
Dana, 4 ...	11	286	289	,, 5 ...	37	279	278
Kunitz, 2 ...	13	284	286	,, 9 ...	41	272	279
Boeke, 38 ...	14	277	279	Dana,			
Dana, 8 ...	16	268	279	'biotite' 6 ...	43	276	288
Kunitz, 3 ...	17	280	283	,, 15 ...	49	272	279
Dana, 1 ...	22	279	286	,, 10 ...	51	266	278
Kunitz, 8 ...	25	279	279	,, 17 ...	72	263	262
Dana, 2 ...	26	278	284	,, 18 ...	112	255	262
Kunitz, 10 ...	31	273	276				

These values indicate a progressive contraction as the proportion of phengite increases, a result that might be anticipated for the replacement of Al_2O_3 by the small group RO. The decrease in volume is about 25 units for the introduction of 100RO; this is the value used to ascertain the constant for Al_2O_3 (p. 200). The volume of pure muscovite is taken to be 285.

(*b*) *Lepidolite.*—The older analyses yield the following values:

Analysis.	*V* (obs.).	*V* (calc.).	Analysis.	*V* (obs.).	*V* (calc.).
Dana, 1	250	260	Dana, 4	259	258
,, 2	249	262	Kunitz, 3	244	246

The rather high difference in Dana (2) corresponds with a deficiency in $(K,Na)_2O$.

[1] See Part I of this paper, p. 317.

Additional lepidolites (not given in Part I).—

	R_2O_3.	RO.	R_2O_3+RO.	Li_2O.	$(K,Na)_2O$.	H_2O.	F_2.	H_2O+F_2.	V (obs.).	V (calc.).
Genth[1] ...	131	27	158	103	95	24	138	162	234	235
Hall[2] ...	153	5	163	114	97	—	—	—	240	243
Simpson[3] ...	159	19	178	135	95	17	150	167	245	249
Gibson[4] ...	167	12	179	141	106	7	145	152	257	253

The first two analyses from Dana are incomplete; unfortunately there seems to be no record of the density of a normal lepidolite, though the formula is supported by a series of good analyses. In the analyses last quoted the alkalis agree well with the ratio $K_2O:6SiO_2$, but in all cases except one the amount of lithia exceeds the simple value 100, so that these minerals are presumably mixed with polylithionite; while the analyses of Genth and Hall show a deficiency of bases and can be represented as belonging to the series lepidolite–irvingite. Thus in all these cases the volumes will be somewhat below that for the simple formula. The volume 13 has been assigned to Li_2O since this yields satisfactory calculated values for all the lithia micas, including those given above; the calculated volume of true lepidolite is then 258.

(*c*) *Lepidolite–cryophyllite* (Part I, p. 317).—

Analysis.	RO.	V (obs.).	V (calc.).	Analysis.	RO.	V (obs.).	V (calc.).
Lepidolite (theory) ...	0	—	258	Kunitz, 5 ...	52	246	249
Kunitz, 4 ...	35	254	257	Dana, 3 ...	94	240	240

The replacement of R_2O_3 by RO is marked by a contraction analogous with that in the muscovite–phengite series. (See fig. 6.)

(*d*) *Polylithionite* (Part I, p. 318).—The only density available yields the volume 216. Potash has largely been replaced by soda (p. 201), so that this value will no doubt be lower than that of the potash compound, which has the calculated volume 231; allowing for this, it is clear that the further substitution of lithia for the alumina in lepidolite has again diminished the volume by about 27 units for the introduction of $100Li_2O$.

[1] F. A. Genth, Amer. Journ. Sci., 1892, ser. 3, vol. 44, p. 388; Japan.

[2] A. G. Hall, Victoria Mines Report for 1908, 1909, p. 66; Coolgardie.

[3] E. S. Simpson in A. N. Winchell, Amer. Journ. Sci., 1925, ser. 5, vol. 9, p. 424; Coolgardie.

[4] C. G. Gibson in A. N. Winchell, ibid., Coolgardie, Western Australia.

(*e*) *Lepidolite-protolithionite* (Part I, p. 318). The analyses discussed in Part I indicate that this series is derived from lepidolite by addition of RO; at the basic end of the series Li_2O is replaced by RO.

Analysis.	V (obs.).	V (calc.).	Analysis.	V (obs.).	V (calc.).
Kunitz, 8	264	266	Stelzner	306	305
,, 9	266	268	Kunitz, 10 ...	286	279
Dana, 8	328	305	,, 11 ...	296	290

In obtaining the 'calculated' volumes allowance is not made for the high alkali-content which has no doubt raised the observed values for Dana (8) and Kunitz (10).

(*f*) *Irvingite* (Part I, p. 318).—Unfortunately the density is not recorded, but two analyses already given under lepidolite suggest the existence of a continuous series of mixtures between the two minerals. The calculated volume is 206 (11 units being deducted since only $1H_2O$ is present).

(*g*) *Phlogopite.*—The observed volumes are :—Dana ('System', p. 633) (1) 289, (2) 293, (8) 288, (11) 297, (12) 293. These indicate for pure phlogopite the value $V = 295$. Phlogopite is derived from muscovite by the substitution of 2RO for $2Al_2O_3$, coupled with the addition of 4RO. The molecular volume of muscovite is 285. If we assume that the replacement of Al_2O_3 here produces the same volume-change (25 units) as in the muscovite-phengite series, the molecular volume V of the 'additional' RO can be calculated as follows:

$$295 = 285 - 25 \times 2 + V \times 4.$$

The volume of 'additional' RO is therefore 15. This is really the value for MgO, but it will be shown that in the biotites the substitution of FeO for MgO does not produce any marked disturbance in the volumes.

If the volume of substituent RO is also 15, and $V(Al_2O_3 - RO) = 25$, the molecular volume 40 must be assigned to Al_2O_3. The volume of the common mica-nucleus $K_2O \cdot 6SiO_2 \cdot 2H_2O$ (i. e. muscovite $- 3Al_2O_3$) is therefore $285 - 3 \times 40 = 165$, and the volume of any given mica is to be calculated by adding to this nucleus the volumes due to R_2O_3, RO, and Li_2O according to the following equation

$$V(\text{mica}) = 165 + 0{\cdot}40(R_2O_3) + 0{\cdot}15(RO) + 0{\cdot}13(Li_2O),$$

(R_2O_3), &c., being the equivalent numbers for the respective oxides when $SiO_2 = 600$, as given in the tables appended to Parts I and II of this paper. The values so obtained are the 'calculated' values given in the present note. Throughout the whole group the difference between

observed and calculated values rarely exceeds 2 per cent., and nearly every instance of greater deviation is at once seen to be related to the presence of an abnormal amount of alkali or of water.

(*h*) *Other basic micas.*—Observed and calculated volumes for the new analyses have already been given in Table III (Part II, p. 31). The agreement is very satisfactory, the only serious differences (except no. 44) being explained by the presence of additional water (1), excess or deficiency of potash (17, 19, 20, 22, 43), and the replacement of potash by soda (24). In the same way the following results from older data show good agreement.

Analysis.	*V* (obs.).	*V* (calc.).	Diff.	Analysis.	*V* (obs.).	*V* (calc.)	Diff.
Dana, 1 ...	314	317	−3	Boeke, 76 ...	336	332	4
,, 2 ...	310	307	3	,, 99 ...	326	325	1
,, 5 ...	326	321	5	,, 133 ...	311	307	4
,, 7 ...	309	312	−3	,, 134 ...	293	295	−2
,, 11 ...	312	317	−4	,, 135 ...	282	290	−8
,, 22 ...	314	306	8	,, 136 ...	312	305	7
,, 29 ...	330	326	4	,, 137 ...	300	302	−2
,, 31 ...	317	313	4	,, 190 ...	307	303	4

It is clear from the close agreement throughout the group that the substitutions of Fe_2O_3 for Al_2O_3, and of FeO for MgO, cause no great disturbance in the molecular volume. This accords with the close isomorphous relations between those oxides.

Substitution of sodium for potassium.—The 'calculated' volumes given are based on the assumption that all the alkali is present as potash. Calculated values for the soda micas will therefore differ from the observed values by an amount equal to $V(K_2O) - V(Na_2O)$. Thus:

Paragonite (Part I, p. 317).—

Analysis.	*V* (obs.).	*V* (calc.).	Diff.
Dana, 2	279	295	16
,, 4	259	280	21
,, 6	267	288	21

Allowing for the low water content in Dana (4), $V(K_2O) - V(Na_2O)$ is approximately 15. This agrees with the data for polylithionite, where the replacement of two-thirds of the potash by soda together with the loss of $1H_2O$ corresponds with a deficiency of 15 units in the observed volume.

Volumes of H_2O and F_2.—Considerable variation in the amount of these constituents has but little effect on the molecular volume, so that their volume cannot be large. Consideration of a number of extreme

cases, like biotite (new) no. 1, points to a value between 10 and 15 for H_2O, while it is clear from the phlogopites (p. 200) that replacement of $(OH)_2$ by F_2 causes but little alteration.

Valency of titanium.—In calculating the molecular ratios for the present tables it has been assumed that titanium is present as the dioxide, isomorphous with SiO_2. This is the view taken by Kunitz, and the older analyses in general yield simpler values for the ratio $K_2O : SiO_2$ if titanium is included with the silica. Here the molecular volumes afford a more sensitive indication than do the molecular ratios, as will be seen from the analyses of titaniferous micas tabulated in full below (Table V). For each analysis the upper line (*a*) shows the result of including titania with silica in the usual way, while the second line (*b*) gives the values when titania is taken along with the group R_2O_3. The first four micas, which are representative of those tabulated earlier in this paper, give quite normal values by the first method (top lines), and the observed and calculated values agree; but the volumes obtained by the second method (lower lines) show throughout a larger difference from the calculated values, and in two cases lie outside the usual limits for biotite. The agreement between observed and calculated volumes for the titaniferous micas in the tables already given would thus seem to imply that the titanium has been correctly assigned to TiO_2 replacing silica. The last analysis in this group of Table V appears, however, to indicate a transition to those of the second group.

The analyses in the second group of Table V were not included in the general tables. They show an unusually high content of titanium, and normal values are found in the *second* lines. If the titanium is included with SiO_2 (top lines) the volumes are well outside the usual limits for biotite, there is a marked difference between the observed and calculated values, and the other data are less consistent with the values for ordinary biotites. It would seem, therefore, that the titanium cannot be regarded as replacing silica, but must be placed either in the group R_2O_3 or as an independent constituent. There are serious chemical difficulties in admitting the presence of Ti_2O_3 in a mineral containing ferric iron, but the case may be comparable with the admixture of $(Mg,Fe)O.TiO_2$ in haematite.

Further light on the behaviour of titanium is afforded by the data for the mineral astrophyllite given in the third section of Table V. In this mineral, which is evidently closely allied to the micas, the content of alumina is small; but the total value for R_2O_3 (including the titanium) is still about 100, as in phlogopite, and the other data resemble those for

Table V. Biotite: molecular ratios and volumes when (*a*) (Si,Ti O_2 = 600 *and* (*b*) SiO_2 = 600.

	TiO_2 %.		R_2O_3.	RO.	$(K,Na)_2O$.	H_2O.	F_2.	$H_2O + F_2$.	*V* (obs.).	*V* (calc.)	Diff.
1. Typical biotites with TiO_2 replacing SiO_2.—											
Kunitz, 11 ...	3·06	(*a*)	199	464	99	217	—	—	315	314	1
		(*b*)	243	505	108	236	—	—	345	338	7
Kunitz, 12 ...	2·56	(*a*)	180	489	101	239	—	—	314	310	4
		(*b*)	216	525	108	257	—	—	339	330	9
Boeke, 190 ...	3·16	(*a*)	164	482	97	191	5	196	307	303	4
		(*b*)	193	513	104	203	5	208	330	319	11
Dana, 22 ...	4·73	(*a*)	179	459	104	119	—	—	314	306	8
		(*b*)	230	508	115	129	—	—	351	333	18
Boeke, 135 ...	7·68	(*a*)	164	395	107	50	—	—	282	290	−8
		(*b*)	238	457	124	58	—	—	333	329	4
2. Abnormal biotites from the shonkinite of Katzenbuckel, Baden; TiO_2 replacing R_2O_3.—											
Doelter, 101...	10·86	(*a*)	104	418	82	76	—	—	248	270	−22
		(*b*)	193	509	103	96	—	—	310	318	−8
Doelter, 102...	12·02	(*a*)	121	388	89	48	—	—	251	271	−20
		(*b*)	224	487	111	60	—	—	324	328	−4
Rosenbusch[1] .	12·56	(*a*)	84	370	84	32	14	46	—	—	—
		(*b*)	177	459	104	39	18	57	—	—	—
3. Astrophyllite; titanium replacing R_2O_3.—											
Dana,[2] 1 ...	7·09	(*b*)	108	502	104	104	—	—	296	284	—
„ 5 ...	11·11	(*b*)	98	559	110	200	26	226	—	—	—
„ 6 ...	13·58	(*b*)	134	421	95	198	—	—	295	282	—
„ 7 ...	11·4	(*b*)	95	485	117	233	—	—	—	—	—

Small amounts of zirconium (*up to 5 per cent.*) have been included with SiO_2 and the volumes are calculated accordingly.

the micas. When plotted on the diagram given in figure 5, the four points lie along the lower boundary of the biotite area. The volumes agree fairly well, but the unusual composition prevents a close comparison, since the volumes of zirconium and titanium are not accurately known. Physically, though closely resembling a biotite, the mineral is brittle with a pseudo-tetragonal percussion figure, and has distinctive optical characters. It constitutes, therefore, an independent species, but is

[1] H. Rosenbusch (A. Osann), 'Gesteinslehre', 5th edit., 1923-24, p. 224. 'Wodanite.' The other two analyses are given in the 3rd edition, 1910, p. 201. [Min. Abstr., vol. 2, p. 11.] It will be noted that these micas have an abnormally low content of water.

[2] Dana's 'System', 1892, p. 719. Small amounts of CaO, &c., are omitted.

apparently related to the biotites in somewhat the same way as the biaxial mineral bassetite is related to the uniaxial torbernite. Structural modifications of this kind are often accompanied by little or no change in the molecular volume. The Katzenbuckel mica, on the other hand, would seem to be a true biotite in physical properties as well as in general composition.

True molecular volumes.

The values given represent the volume in cubic centimetres occupied by the molecular weight in grams. Since an atom of hydrogen is known to weigh $1{\cdot}66 \times 10^{-24}$ grams, the real volumes occupied by the respective atoms or groups can at once be ascertained. These volumes include the interspaces, and the partition of a crystal into separate domains for the constituent oxides appears at first sight purely arbitrary. But the volumes given are based, not upon any arbitrary form of cell, but upon the expansion effect due to the introduction of a known amount of the oxide into a space-lattice common to the mica group. The lattice behaves within certain limits like a liquid or an extensible network, and the volume-constant for an oxide in mica can be as precisely defined, though it is not so accurately known, as that for a salt dissolved in a liquid. The following table summarizes the data here ascertained for the micas:

Oxide.	Molecular volume V.	True molecular volume $= V \times 1{\cdot}66 \times 10^{-24}$
R_2O_3	40	$66{\cdot}4 \times 10^{-24}$
RO	15	24·9 „
Li_2O	13	21·6 „
$K_2O.6SiO_2.2H_2O$ ...	165	274 „
Also (less accurately known):		
K_2O	41	68 „
Na_2O	26	43 „
SiO_2	17	28 „
H_2O	11	18 „