

ART. XIX.—*Studies in the Mica Group*—PART I; by A. N. WINCHELL.

For many years the study of mineral groups has been hampered by the theory that in an isomorphous series one element can take the place only of another element of the same valence. This theory is doubtless correct in simple binary compounds, but its application to complex silicates, such as the micas, has led only to confusion. The related theory that two monovalent atoms can take the place of one divalent atom, three monovalent atoms the place of one trivalent, etc., is still more misleading, and probably false for all compounds, whether simple or complex.¹ Of course, all valences must be satisfied in each molecule, but the writer believes that, in building crystals, atoms of one element can take the places of those occupied by atoms of another element in other crystals of the same isomorphous series only in case the atoms are similar in volume.² This proposition, which is so simple that it seems almost self-evident, was accepted by occasional mineralogists in the past, but lack of knowledge of the sizes of atoms made it impossible to apply it to concrete cases, and the theory that atoms in solids were separated by distances much greater than their own diameters prevented the general acceptance of the proposition. At the present time it is believed that the atoms of crystals are close-packed, if not in actual contact, and measurements based on this theory have been made of the diameters of the atoms of most of the elements. Therefore, it is now possible to discard the idea that valence determines what elements can take the place of others in an isomorphous series of crystals of complex composition, and at least test the proposition that the volume of the atoms is one of the determining factors.

X-ray measurements give directly and quite accurately the distances between the centers of any two adjacent

¹ An exception was suggested in the case of H, and Mg in amphiboles, this Journal, 7, 291, 1924, but this was explained as due to probable volume equivalence rather than to equal valences. Artificial zeolites seem to furnish another exception.

² For the purposes of this article an atom is assumed to occupy all the space from the nucleus to the outer shell of electrons.

atoms in any crystal, but to deduce the sizes of the atoms from these measures it is necessary to assume, first, that the atoms are "close-packed" or in contact, an assumption which is in harmony with the present views of most physicists; and, second, that half the atomic-center distance in a crystallized metal is equal to the radius of an atom of the same element in any compound. The second assumption is probably only an approximation, and Davey,³ on the basis of a substitute assumption, has obtained results which are decidedly different from those of Bragg,⁴ but they are not quoted in the following table because they are measurements of ions rather than of atoms.

In order to convert atomic diameters, or radii, thus obtained, into atomic volumes it is necessary, at present, to make a third assumption, namely, that atoms are spherical in shape. According to current theories of atomic structure this assumption is a rough approximation for the atoms of all elements except hydrogen, which may be considered to be disc-shaped, provided its electron travels always in a single plane. If atoms are in contact in all crystals, it is evident that they must vary in size, since the atomic-center distances are distinctly different in such cases as diamond and graphite, sphalerite and wurtzite, calcite and aragonite, etc. It is considered probable that atoms do vary in size under differing physical conditions, perhaps as much as thirty per cent, but this variation may be expected to be roughly uniform for all kinds of atoms, so that *relative* size would not change so much under varying conditions. Furthermore, according to measures of Bragg and others, atoms of certain elements differ in volume by amounts much greater than thirty per cent.

The most important available data are summarized in the following table, in which the volumes are computed from atomic diameters given by the authors quoted by means of the approximate formula: $V = 4.2r^3$. The elements are arranged in the order of increasing size and the unit of measure is the cubic ångström or one cubic centimeter $\times 10^{-24}$. For comparison atomic volumes derived from atomic weights divided by density are added.

¹ Phys. Rev., 22, p. 211, 1923.
² Phil. Mag., 40, p. 169, 1920.

TABLE I. Approximate Atomic Volumes of Elements.

Element	Atomic Volume from X-ray Data.				Atomic Weight divided by Density
	Atoms in various compounds.		Uncombined.		
	Bragg ¹	Huggins ²	Wherry ³	Davey ⁴	
Oxygen	1.2	1.2	1.2		
Fluorine	1.3		2.6		
Hydrogen		1.6 (in ice)	3.6		
Hydrogen		2.4 (in haloids)			
Carbon	1.9	1.9	1.4		
Sulphur	4.5	4.7	4.9	4.5	
Chlorine	4.9	3.7	10.3		
Beryllium	6.4	4.8	6.4	8.6	4.8
Silicon	6.8	6.8	6.4	6.7	11.4
Zinc	9.7	9.6	10.	12.	9.2
Aluminum	10.		12.	12.	10.6
Nickel	10.		10.	8.	6.6
Copper	11.	12.	6.	9.	7.1
Iron	12.	8.	9.	8.	7.2
Chromium	12.				7.7
Titanium	12.		13.	13.	13.6
Magnesium	12.	9.	13.	17.	14.0
Manganese	13.	11.	14.		7.4
Lithium	14.		8.	16.	13.1
Calcium	21.		22.	31.	25.2
Sodium	23.		14.	27.	23.7
Lead	29.		24.	22.	18.3
Strontium	31.		29.	42.	32.6
Potassium	37.		24.	49.	45.3
Barium	39.		39.	64.	36.6
Cesium	56.		45.	97.	70.4

It is worthy of note that, in general, the atoms of electro-negative or acid elements are much smaller than those of electro-positive or metallic elements.

If the hydrogen atom consists of a nucleus with only one electron it is possible that its volume is only a small fraction of $4.2r^3$, since the electron may remain more or less exactly in one plane.

Crystals are now known to be built out of atoms arranged in very definite and regular space lattices, illustrated by that of halite shown in fig. 1. It is important to note that the halite space lattice consists of two parts—a regular space lattice of Na atoms interpenetrated with a regular space lattice of Cl atoms. Neither one of these space lattices can exist alone, but if it could, it would make a crystal of the same symmetry as the inter-

¹ Phil. Mag., 40, p. 169, 1920.

² Phys. Rev., 21, p. 205, 509, 1923.

³ Mineral. Mag., 9, p. 165, 1924. Wherry has used the formula: $V = \frac{4}{3}\pi r^3$.

⁴ Phys. Rev., 23, p. 318, 1924.

penetration of the two, and just as perfect a crystal, except for the voids occupied in the halite crystal by the atoms of the other space lattice. If a crystal of halite contained some NaBr, not mechanically mixed, but as an integral part of the crystal, the Na space lattice would not be changed at all, but the Cl space lattice would be

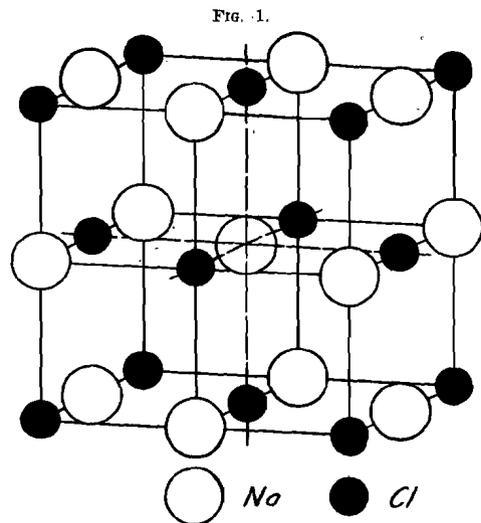


Fig. 1.—Space lattice of halite.

different in that some of the points occupied by Cl atoms in a pure halite crystal would be occupied by Br atoms. Furthermore, since chemical and optical tests would indicate homogeneity, it is probable that the Br atoms would be just as regularly arranged (with respect to each other) as the Na atoms. When certain atoms thus take places which would otherwise be occupied by certain other atoms they may be said to *proxy*⁹ for the latter, and this *proxation* (to coin a word) of one element by another is the characteristic feature of every isomorph-

⁹ Adopting a term used by Johannsen, Jour. Geol., 30, p. 640, 1922.

ous series. It is customary to speak of the "replacement" of one element by another in an isomorphous series, but this term is incorrect,¹⁰ since the one element does not take a place formerly occupied by the second, but rather a place which could be occupied by the latter. It is not possible for Br atoms to proxy for Na atoms in halite; they can occupy only places of Cl atoms; also, it is not possible for Cl atoms to proxy for Na atoms, or vice versa.

With the possible exception of those of elements, all crystals whose detailed structure has been worked out by X-ray studies are similar to halite in consisting of two (or more) interpenetrating space lattices. Any one of these is just as definite and regular as any other.

The table of volumes of atoms of the common elements shows that O and F are nearly equal in volume; it is believed that F proxies for O in many silicates. The volume of the hydroxyl group, OH, is not known, but it has been suggested¹¹ that it is not equal to the sum of the volumes of O and H, but may be even less than that of H; in the humite, apatite, and other groups it has been known for years that hydroxyl (and Cl) may proxy for fluorine. Therefore, in silicates the oxygen space lattice may include F, Cl, and OH, but no other common elements. Furthermore both chemical properties and relative volumes indicate that these elements cannot proxy for any other common elements; therefore, all the hydroxyl groups, and fluorine and chlorine atoms, will occur in the oxygen space lattice. No O, F or OH can proxy for Si or any of the bases, nor can the latter proxy for O atoms.

It has been suggested¹² that 2H may proxy for Mg in amphiboles, since the volumes concerned are not very unequal, but it is clear that H can not proxy for K since the volumes are far different. This is contrary to the view of many writers who have based their opinion on the equality of valence of H and K. In this study of

¹⁰ In the normal growth of some crystals belonging to isomorphous series, like the plagioclase feldspars, crystals first formed have their composition changed by a real replacement of certain atoms by others, but this process is not referred to in the ordinary discussions of "replacement" in isomorphous crystals.

¹¹ This Journal 7, 291, 1924.

¹² This Journal, 7, 291, 1924.

micas it has been assumed that all the H in them is in hydroxyl, and therefore, it is referred to the O space lattice. Both chemically and by means of the decided difference in size of the atoms the oxygen space lattice

TABLE II. Summary of Composition of Biotite System.

Doelter's Best Analyses.

Percentage of Atoms, omitting O, H, F.

Doel- ter's No.	Analyst	Date	Si	Al	Fe ⁺	Fe ⁺	Mg	Ca	Na	K	Ti	Mn	Mg+ Fe+ Mn	Si+
10	Schneider	1891	34.7	17.5	0.2	0.2	34.7		1.1	11.1	0.4		34.9	35.1
11	Hillebrand	1897	36.5	12.3	1.8	0.7	30.4	0.2	0.8	12.4	1.4		31.1	29.9
12	Catlett	1890	34.5	16.5	0.4	0.6	35.5	0.3	1.1	11.1			35.1	34.6
29	Egleston	1904	34.5	17.9	0.7	0.3	38.8		0.4	10.0	0.1		36.3	34.4
49	Egleston	1904	35.0	15.9	3.6	2.9	32.6		1.6	8.8	0.2	0.5	35.5	35.2
50	Dittorich	1904	35.0	12.7	2.9	10.4	21.2		0.5	10.0	1.8	Tr.	36.7	36.9
70	Schneider	1890	32.6	21.8	2.2	3.9	28.8	0.3	1.4	9.4	0.8	0.1	31.1	33.6
71	Rosenbusch	1910	35.4	14.1	5.0	4.5	21.0	0.7	2.8	11.0	5.2		25.5	30.9
79	Rosenbusch	1910	34.9	15.3	12.2	7.5	12.4	1.0	1.3	10.4	2.6		20.2	27.5
79	Schmalz	1894	34.5	18.4	11.5	8.5	14.4	1.0	0.6	7.1	3.2	0.4	28.2	37.8
80	Schmalz	1894	35.5	25.0	9.0	8.9	15.4	0.7	2.0	8.4	1.3		30.2	35.0
81	Herrmann	1901	34.5	24.4	19.8	7.4	9.7		4.6	10.4		4.6	18.3	24.6
100	Egleston	1904	37.9	21.5	9.3	10.4	6.7	0.2	1.7	4.8	0.4	0.5	17.4	33.3
101	Rosenbusch	1910	35.1	14.2	0.5	9.1	20.7		1.6	10.4	7.4		29.8	42.7
102	Rosenbusch	1910	35.6	16.4	0.7	8.5	19.4		2.6	9.3	8.5		27.4	42.3
105	Valentine	1899	35.0	17.5	5.4	11.2	15.6	1.0	0.9	9.7	1.9	0.6	30.4	36.9
105	Parsons	1918	34.0	17.1	4.2	10.2	15.9	2.3	2.3	9.8	2.6	0.5	27.6	36.6
112	Balyankin	1909	35.8	21.9	3.4	9.7	24.0	0.6	1.2	12.0	0.9	0.5	34.2	34.7
116	Glarum	1889	35.5	20.1	15.5	12.2	6.1	0.9	2.8	8.9		0.8	17.1	35.5
128	Weyberg	1909	35.1	20.2	8.3	12.2	8.3	0.8	3.7	10.8	1.4	0.4	18.9	36.7
128	Weyberg	1909	35.8	23.0	5.7	11.4	14.1	1.1	2.9	4.8	2.1	0.5	24.2	34.7
124	Weyberg	1909	35.5	19.7	2.9	12.2	12.3	0.9	4.0	11.2	2.2	0.5	24.0	34.7
140	Valentine	1899	34.5	21.2	4.0	11.9	14.1	0.9	0.7	11.4	0.8	0.6	26.5	35.3
141	Hillebrand	1899	35.0	14.9	8.4	11.5	15.2	0.2	0.6	11.5	2.3	0.4	30.1	37.5
142	Stokes	1899	35.6	14.0	5.9	11.5	18.1		0.2	11.6	2.6	0.1	29.5	36.2
145	Valentine	1899	36.3	16.7	5.0	14.1	14.4	1.5	0.8	10.4	2.3	0.4	26.9	36.4
145	Schmalz	1896	32.3	22.9	2.1	14.4	12.7	1.0	0.9	11.0	2.2	0.2	27.5	34.9
150	Hempel	1896	32.8	21.7	2.0	15.0	12.2	1.3	0.8	10.4	1.4	0.4	25.5	34.9
164	Schneider	1890	36.5	15.9	4.1	19.0	8.9		0.4	11.3	2.1	0.4	28.5	37.5
164	Egleston	1904	31.8	25.9	4.4	25.5	4.5	1.4	3.6	8.4	Tr.	1.4	29.5	31.8
171	Walt	1898	35.4	17.2	3.5	22.5	7.2	1.4	5.9	8.5	0.7	0.2	19.9	34.5
181	Harrington	1905	35.7	15.1	7.1	24.5	1.2	0.7	2.1	10.6	2.3	2.5	28.2	35.0
221	Lots	1910	37.4	15.7	0.9		35.7			8.5	9.7		38.7	37.4
222	Grimm	1904	35.1	19.6	5.0	12.4	14.1	0.2	1.7	10.0	0.9	0.8	27.3	36.0
223	Quibbert	1912	35.2	19.0	6.2	20.5	5.9		4.7	8.5	1.4	0.8	25.5	36.5

Minor amounts of certain elements are reported in the preceding analyses as follows:-

0.2 Ba in 10, 0.4 Ba and 0.5 Cr in 11, 0.3 Cr in 50, 0.5 Si in 70, 0.6 Ba in 101, 0.7 Ba in 102, 0.1 Ba in 103, 0.1 Ba in 122, 0.6 Li in 123, 0.2 Li in 124, 0.5 Ba in 142, 0.1 Ba in 145, 0.3 Li in 150, 0.2 Si and 0.1 Li in 154, 0.1 Li in 161, 1.9 Li in 221. The last three analyses are from Doelter, (pages 716, 723, 725) but not in his numbered series.

is quite distinct from the others, which are not nearly so sharply separable from one another. Therefore, no attempt will be made to separate them as a preliminary to the following study, though this may be possible at its conclusion.

The minerals commonly included in the mica group are the following: biotite, phlogopite, lepidolite, zinnwaldite, muscovite and paragonite. The composition and relationships of these types are only vaguely known. Even

TABLE III. Summary of Composition of Biotite System.

Recent Analyses.

Percentage of Atoms, omitting O, H, F.

No.	Analyst	Date	Si	Al	Fe ⁺	Fe ⁺	Mg	Ca	Mn	K	Ti	Mn
1	Seidel	1906	34.2	15.8	2.7	7.9	21.5	0.8	4.1	11.8	1.3	
2	Seidel	1906	33.0	18.3	3.3	12.7	14.4	0.6	3.0	11.9	4.6	
3	Seidel	1906	34.9	17.7	5.6	5.4	22.6	0.7	2.8	7.7	1.2	
4	Seidel	1906	35.7	18.6	5.4	15.3	11.7	0.2	2.5	11.6	1.9	
5	Seidel	1906	32.4	19.4	10.8	2.4	12.3	0.6	3.6	11.0	1.5	
6	Seidel	1906	34.0	21.2	2.2	9.9	19.6	0.2	1.6	9.3	1.3	
7	Philpenko	1915	39.0	22.7	1.4	3.8	19.5		2.7	10.6		
8	Stanley	1916	36.2	19.0	6.9	4.5	20.9		5.0	6.6	0.4	
9	Zambonini	1919	33.0	19.5	1.5		14.6	15.8	6.5	9.1		0.3
13	Koto	1919	34.4	18.9	14.9	11.5	4.0	0.9	0.3	9.7	0.1	5.1
14	Thomassen	1920	33.8	19.8	0.8	5.8	22.7	0.1		12.4	2.8	
15	Sahlbom	1922	35.4	15.4	1.8		22.7	0.1		11.3		
16	Kunitz 1	1924	30.1	14.2	0.2	0.5	26.5	0.2		1.1	10.8	
17	Kunitz 2	1924	35.0	17.2	1.0	0.5	34.7			0.5	9.7	
18	Kunitz 3	1924	35.5	15.9	0.7	0.4	34.3			1.7	10.5	
19	Kunitz 4	1924	35.0	17.1	0.9		34.1			2.3	9.8	
20	Kunitz 5	1924	34.9				35.1			2.2	10.1	
21	Kunitz 6	1924	35.7	16.5	1.3	0.3	31.0	0.8		2.2	11.0	0.3
22	Kunitz 7	1924	34.0	17.2	0.8	1.5	28.4			2.0	9.3	0.3
23	Kunitz 8	1924	35.7	18.8	1.5	9.8	20.5	0.7		3.5	9.3	0.2
24	Kunitz 9	1924	35.4	20.8	1.5	17.0	12.9			2.3	10.4	
25	Kunitz 10	1924	33.5	19.4	4.3	18.9	8.0	0.3		1.7	10.2	2.9
26	Kunitz 11	1924	34.1	14.8	7.2	16.6	10.2			1.8	10.5	2.4
27	Groat 1	1924	35.4	15.5	5.3	6.1	23.4	1.9		0.7	11.1	1.2
28	Groat 2	1924	35.8	19.3	5.0	12.4	15.2	2.5		1.3	6.9	1.7
30	Groat 3	1924	34.5	16.6	2.2	16.7	13.4	1.2		0.9	10.0	2.4
31	Groat 4	1924	35.9	20.2	0.8	19.7	9.2	1.8		9.2	2.0	0.3

Minor amounts of certain elements are reported in the preceding analyses as follows:-

0.2 Ca in 7, 0.4 Cr in 6, 2.0 Li in 9, 0.2 Ba in 14, and 0.9 Zr in 31.

the existence of paragonite has been called in question by Kunitz,¹³ and it is true that no satisfactory samples have ever been studied. It will, therefore, be omitted in this discussion.

THE BIOTITE OR OCTOPHYLLITE SYSTEM.

The formula of biotite has been discussed repeatedly by such able chemists and mineralogists as Rammels-

¹³ N. Jahrb. Mineral., Beil. Bd. L., p. 364, 1924.

berg,¹⁴ Tschermak,¹⁵ Clarke,¹⁶ Boeke,¹⁷ and Doelter.¹⁸ Detailed studies of biotite have been made by Hirschi,¹⁹ Daub,²⁰ Malt,²¹ Seidel,²² Zschimmer.²³ Important recent contributions have been made by Kunitz²⁴ and Grout.²⁵ The writer believes that further progress is now possible by applying to the problem the principles and data deduced from X-ray studies and already outlined.

In 1917 Doelter¹⁸ assembled 214 analyses of fresh biotite, and at the same time Boeke¹⁷ made a statistical study of 175 analyses, about 30 of which differ from those given by Doelter. Of these, only 54 are modern analyses, that is, made within the last thirty years; and analytical methods have been so much improved that earlier analyses must be regarded as inferior. However, three analyses by Schneider, one by Clarke, and one by Catlett, made about 1890, are remarkably complete, and may be added to the list of preferred analyses, while 22 (of the 54) are clearly inferior²⁶ in quality or must have been made on impure or abnormal material, and are therefore excluded. Two analyses of "anomite" by Simpson are not of a mica which belongs to the biotite system; on the contrary, they were made from material belonging to the lithia mica system, as defined elsewhere in this article. The remaining 35 analyses are assembled in Table II; they are believed to be the most accurate analyses of biotite at present available. In Table III are assembled all analyses of this mica known to the writer which have

¹⁴ Sitzber. Akad. Wiss. Berlin, Feb. 1889; Erg. Heft, I, 1887, p. 112, and II, p. 404. See note 18 below.

¹⁵ Zeit. Kryst. 3, p. 122, 1879.

¹⁶ This Journal, 34, p. 131, 1887 and 37, p. 384, 1889.

¹⁷ N. Jahrb. Mineral., 1916, I, p. 83.

¹⁸ Hdb. Mineralch., II, 2, 1917, p. 680.

¹⁹ Diss. Zurich, 1901.

²⁰ Diss. Freiburg, 1912; N. Jahrb. Mineral., 1913, I, p. 214.

²¹ Diss. Leipzig, 1913; N. Jahrb. Mineral., 1914, II, p. 357.

²² Diss. Zurich, 1906; Zs. Kryst. 57, p. 415, 1923.

²³ Diss. Jena, 1898; Zs. Kryst. 33, p. 491, 1900.

²⁴ N. Jahrb. Mineral., Beil. Bd. L., 1924, p. 364.

²⁵ Amer. Mineral., 9, p. 159, 1924.

²⁶ Many of these are excluded on the basis that biotite so commonly (if not always) contains F, TiO, and MnO that analyses which do not report at least two of these are inferior. Three analyses quoted by Rosenbusch are included even without F and MnO because they are remarkably rich in TiO; one by Morozewicz without F and TiO, is likewise included because it is high in MnO.

been made since the date (1917) of Doelter's study, and also those of Seidel, made in 1906, but omitted in the "Mineralchemie."

In preparing these tables the weight percentages of

TABLE IV. The role of Ti and Fe^{III} in Biotite.
Doelter's Best Analyses.

No.	Si ⁺ Ti	Al ⁺ Ti	Al ⁺ Fe ^{III}	$\frac{Al^{+}}{Ti}$	Mg ⁺ Fe ^{III}	Mg ⁺ Fe ^{III}	Mg ⁺ Fe ^{III}	Mg ⁺ Fe ^{III}
10	35.1	17.9	17.9	16.3	34.9	35.1	35.5	
11	35.9	18.5	14.9	16.1	31.1	32.9	34.5	
12	34.6	16.8	16.9	16.9	36.1	36.5	36.5	
29	34.4	18.0	18.6	16.7	36.3	37.0	37.1	
49	35.2	14.5	17.5	17.7	36.1	40.4	40.6	
50	36.9	14.6	15.5	15.5	35.7	37.5	39.5	
70	33.6	22.6	24.0	24.6	31.1	33.3	34.1	
71	36.9	21.4	21.2	25.4	25.5	30.5	35.6	
78	37.5	19.4	22.0	31.6	20.2	38.4	35.0	
79	37.7	21.6	30.2	33.4	23.3	35.1	38.3	
80	33.8	24.3	34.0	33.3	20.1	29.2	30.8	
81	34.6	14.4	35.7	33.7	16.8	35.6	35.6	
100	36.3	31.7	35.5	35.9	17.6	19.8	20.2	
101	42.7	21.8	14.8	22.4	29.6	30.4	36.0	
102	42.3	24.9	17.1	25.6	27.4	28.1	35.6	
103	36.9	19.4	30.9	33.8	29.4	33.8	33.7	
105	34.4	19.7	21.5	25.9	27.6	31.5	34.4	
112	35.7	12.3	15.3	16.2	34.2	37.5	38.5	
116	35.3	20.1	35.7	35.7	17.1	32.7	32.7	
132	36.7	21.6	27.0	26.5	20.9	27.7	29.3	
133	34.7	25.1	26.7	30.8	25.2	31.9	34.0	
134	34.7	21.9	22.5	24.8	25.0	28.9	31.1	
140	35.3	22.0	25.2	26.0	25.0	30.5	31.5	
141	37.3	19.2	20.5	22.6	30.1	33.5	35.8	
142	36.2	16.6	19.9	22.5	29.5	33.4	36.0	
143	36.6	19.0	19.7	20.0	26.9	31.3	34.2	
146	34.5	25.1	25.0	27.2	27.5	29.6	31.8	
150	34.9	23.1	23.7	25.1	26.6	30.6	32.0	
168	37.6	16.0	22.0	24.1	26.5	34.6	36.7	
168	31.8	25.9	26.3	28.3	29.5	33.9	35.9	
171	34.5	17.9	20.7	21.4	29.9	33.4	34.1	
181	38.0	15.4	20.2	22.6	28.2	35.3	37.6	
221	37.4	13.7	14.6	14.6	35.7	36.6	36.6	
222	36.0	20.5	24.6	25.5	27.3	32.3	33.2	
223	36.6	20.4	25.3	24.7	26.8	33.1	34.5	

each oxide have been divided by the respective molecular weights,²⁷ after doubling the numbers thus obtained for molecules such as Al₂O₃, Na₂O, etc., and omitting numbers for H₂O and F, the total has been reduced to one hundred.

²⁷ To reduce the labor involved in the calculations, molecular weights expressed in nearest whole number have been used.

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- 27, 28, 30, 31. F. F. Grout, Am. Mineral. 9, p. 159, 1924.
221. Analysis 12, page 713, C. Doelter, loc. cit.
222. Analysis 8, page 723, C. Doelter, loc. cit.
223. Analysis 19, page 725, C. Doelter, loc. cit.

The data of Table II form the best basis at present available from which to determine the constitution of biotite. In this Table it should be noted that the percentage of silicon atoms is not constant, as it would be if biotite were a silicate of any definite and simple formula. It is, therefore, incorrect and misleading to write any such formula for this mineral.

The percentage of silicon varies from 31.8 to 38.5, which differs only a little from a variation from 5/16 or 31.25 to 6/16 or 37.5.

The percentage of Al ranges from 11.9 to 31.2, or with two exceptions (Nos. 100 and 112) from 12.7 to 25. The average of the three lowest values (Nos. 11, 50 and 112) is 12.4+. The minimum tenor is, therefore, reasonably placed at 12.5, or 2/16, and the maximum at 25. or 4/16. (Trifling percentages of Cr are considered to be equivalent to Al in the crystal structure.)

Omitting ferric iron for the moment, it is easily seen from Table 2 that ferrous iron and magnesium proxy for each other in biotite as in many other minerals, since one increases as the other decreases, at least in general. It may be assumed that Mn, and also Ni and Cu, play the same role as ferrous iron. These elements are brought together in column 6 of Table 4 from which it appears that the maximum tenor of $Mg+Fe''+Mn+Ni$ is 36.8, and the minimum is 16.5. This is approximately a variation from 6/16 (37.5) to 3/16 (18.75).

The next abundant constituent is potassium. The evidence favors decidedly the view that Na proxies for K, although it seems possible that it plays a dual role in some cases in which the tenor is considerable, some portion taking the place of Mg. From relative valences Ba would be expected to proxy for Mg, but, since it proxies for K in feldspar and is almost unknown in pyroxene and amphibole, it is here assumed that it plays a similar role in biotite; this is in harmony with present knowledge of the atomic volumes of Ba, K, and Mg. It is more difficult to determine what part is played by Ca. Does it proxy for Na, as in feldspar, or for Mg, as in pyroxene and amphibole? The tenor of Ca in ordinary biotite is so small that it is difficult to settle this point; it is evident that in Zambonini's *calcibiotite* (No. 9, Table III) Ca must proxy for Mg, but a study of the eleven analyses of biotite in Table II made by members of the U. S. Geological Survey, which are probably the best analyses yet made of black mica, and of the eleven analyses just reported by Kunitz, leads to a different conclusion for the Ca of ordinary biotite, as may be seen in the following table:

TABLE V. Potassium and its proxies in biotite.

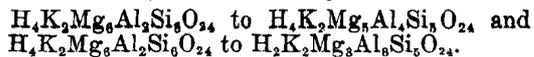
No.	Analyst	K + Na + Ba	K + Na + Ba + Ca
10	Schneider	12.4	12.4
11	Hillebrand	13.6	13.8
12	Catlett	12.2	12.5
70	Schneider	11.0	11.3
103	Valentine	10.7	11.7
116	Clarke	10.3	11.9
140	Valentine	12.1	13.0
141	Hillebrand	12.1	12.3
142	Stokes	12.3	12.3
143	Valentine	11.3	12.8
166	Schneider	11.7	11.7
16	Kunitz	10.3	10.6
17	Kunitz	11.6	11.6
18	Kunitz	12.2	12.2
19	Kunitz	12.1	12.1
20	Kunitz	12.3	12.3
21	Kunitz	13.2	14.0
22	Kunitz	11.8	11.8
23	Kunitz	12.8	13.5
24	Kunitz	12.7	12.7
25	Kunitz	11.9	12.2
26	Kunitz	12.2	12.2

It seems probable to the writer that $K(+Na+Ba+Ca)$ is essentially constant in biotite, as maintained by Kunitz²⁸ and others. Potassium taken alone exceeds 12.5 percent in no case; in most of the best analyses the variation from 12.5 percent (of $K+Na+Ba+Ca$) is little, if any, greater than the possible error of the determinations.

In summary, Si varies from 5/16 to 6/16, Al from 2/16 to 4/16, Mg from about 3/16 to very nearly 6/16, and K is apparently invariable at 2/16. All these conditions indicate that the biotite unit cell (or smallest group of atoms which is complete) consists of 16 atoms, excluding O, H, and F. Studying those analyses which are lowest in tenor of iron and titanium, it appears that the chief variation is from the well known phlogopite formula ($K_2Mg_3Al_2Si_6$,—omitting O, H, and F) toward a formula richer in Al, namely $K_2Mg_3Al_4Si_5$. Another important variation is from these molecules toward their iron equivalents, that is, toward $K_2Fe_3Al_2Si_6$ and $K_2Fe_3Al_4Si_5$.

However, the role of ferric iron and titanium remains unsettled. It will be shown later that Ti probably does not proxy for Si; if both Fe''' and Ti proxy for Al then Al must vary to Al_6 (doubtless in the formula $K_2Mg_3Al_6Si_5$), but if they proxy for Mg then Al probably varies only to Al_4 and the end molecule is $K_2Mg_5Al_4Si_5$.

Adopting the ordinary view regarding the O and H present in biotite, these series may be written as follows:



In the hope that detailed tests of the analyses would aid in solving these uncertainties Tables VI and VII were prepared. The purpose of these tables is to show the discrepancies between the best analyses and the two interpretations here suggested with various assumptions regarding the roles of Fe''' and Ti.

Column 2 in Table IV compared with column 4 of Table II shows that $Si + Ti$ is less constant than Si alone, the range for the former being from 31.8 to 42.7 and for the latter from 31.8 to 38.5. This makes it improbable that Ti proxies for Si, but such a role for Ti is further tested

²⁸ N. Jahrb. Min., Beil. Bd. L., p. 364, 1924.

in Tables VI and VII. From these it is clear that, if either proposal is correct for the range in composition of the mineral, Ti does not proxy for Si, unless the analyses are seriously defective. However, the true role of Ti is not so easily determined. The smallest discrepancies result from assuming that biotite varies only to H_4K_2 -

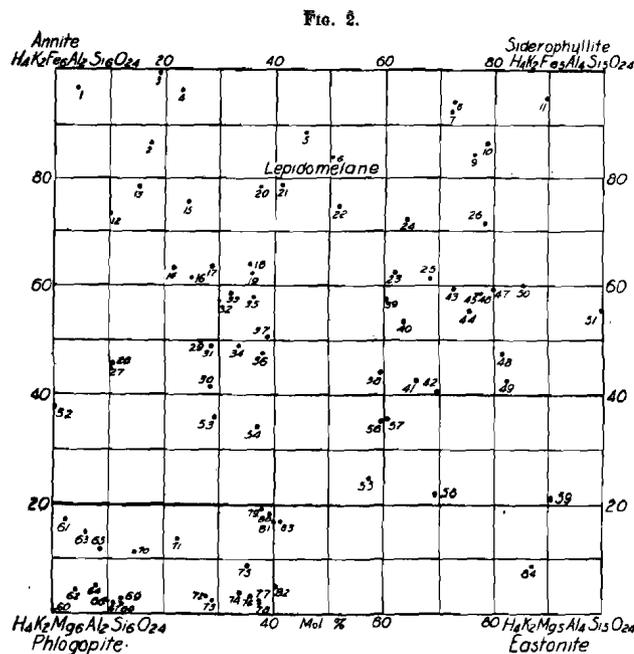


Fig. 2.—The biotite or octophyllite system; each dot represents an analysis.

$Mg_5Al_4Si_5O_{24}$, and that both Ti and Fe''' proxy for Mg, but the discrepancies are not much larger if it be assumed that the mineral varies to $H_4K_2Mg_3Al_6Si_5O_{24}$ and that both Ti and Fe''' proxy for Al. In the first case all the elements (Ti, Fe''' , and Fe'') which are most important

in their effects on the optical properties, come together in a single variable (Mg + Fe²⁺); in the second case Fe²⁺ proxies for Mg and the others for Al. The first case is easily represented in a diagram (see fig. 2), while the second case needs a three-dimension model.

The writer knows of no way to show all possible mixtures of more than three wholly independent components in a plane figure, but, fortunately, the four chief components of biotite are not wholly independent. Assuming the series H₄K₂Mg₆Al₂Si₆O₂₄ to H₄K₂Mg₅Al₄Si₆O₂₄, they are shown at the corners of fig. 2. Everywhere on the square the horizontal axis expresses the percentage of di-alumina (2Al₂O₃) molecules, while the vertical axis expresses the percentage of ferri-ferrous²⁹ molecules.

REFERENCES FOR FIG. 2.

No. 1 of the figure is Doelter's (Hdb. Mineralch. II, 2, 1917, p. 680) No. 181; No. 2 = Doelter's 81; 3 = D. 178; 4, S. Weidman, Wis. Geol. Surv. Bull. 16, p. 295, 1917 and F. F. Grout, Am. Mineral. 9, p. 159, 1924; 5, B. Koto, Jour. Geol. Soc. Tokyo, 26, p. 407, 1919; see also p. 7; 6 = D. 19 (p. 725); 7 = D. 116, 8 = D. 115; 9 = D. 128; 10 = D. 168; 11 = D. 114; 12 = Kunitz's No. 11 (N. Jahrb. Min., Beil. Bd. L, p. 412, 1924); 13 = D. 165; 14 = D. 113; 15 = D. 166; 16 = D. 98; 17, F. F. Grout, Am. Mineral. 9, p. 159, 1924, No. 3; 18 = D. 78; 19 = D. 79; 20 = D. 172; 21 = D. 171; 22 = Kunitz No. 10; 23, P. Seidel, Diss. Univ. Zurich, 1906; Zs. Kryst. 57, p. 416, 1923, No. III; 24 = Grout's No. 4; 25 = D. 134; 26 = D. 132; 27 = Grout's No. 1; 28 = D. 101; 29 = D. 142; 30 = D. 71; 31 = D. 102; 32 = Seidel's No. IV; 33 = D. 2 (p. 722); 34 = D. 141; 35 = D. 143; 36 = D. 103; 37 = D. 105; 38 = Seidel's No. VI; 39 = D. 8 (p. 723); 40 = Grout's No. 2; 41 = D. 6 (p. 722); 42 = Seidel's No. V; 43 = Kunitz 9; 44 = D. 140; 45 = D. 150; 46 = D. 133; 47 = D. 149; 48 = D. 86; 49 = D. 139; 50 = D. 148; 51 = D. 80; 52 = D. 112; 53 = Seidel's No. I; 54 = Seidel's No. II; 55, W. C. Broegger, Vid. Skr. Mat. Nat. Kl., 1, 1920-21, No. 9, Zs. Kryst., 57, p. 421, 1923, No. XIV; 56 = Kunitz No. 8; 57, E. R. Stanley, Trans. Roy. Soc. Australia, 40, p. 268, 1916, Zs. Kryst. 57, p. 421, 1923, No. XI; 58 = D. 70; 59, P. Filipenko, Nach. Univ. Tomsk, 62, p. 653, 1915, Zs. Kryst., 57, p. 421, 1923, No. XV; 60 = D. 9; 61 = D. 49; 62, H. v. Eckeremann, Geol. För. Förh. Stockholm, 44, p. 384, 1922; 63 = D. 50; 64 = D. 19; 65 = D. 52; 66 = D. 12 (p. 718); 67 = D. 17; 68 = Kunitz No. 1; 69 = D. 28; 70 = D. 11; 71 = D. 32; 72 = Kunitz No. 3; 73 = D. 12; 74 = Kunitz No. 2; 75 = Kunitz No. 6; 76 = D. 29; 77 = Kunitz No. 4; 78 = D. 10; 79 = Kunitz No. 7; 80 = D. 82; 81 = D. 51; 82 = Kunitz No. 5; 83 = D. 67; 84 = D. 196.

²⁹The "ferri-ferrous" molecules are considered to include the titaniferous and manganeseiferous, and ferric iron, Fe₂O₃, is used as equivalent to ferrous iron, 2FeO.

³⁰A name suggested here for the pure magnesian di-alumina mica; the name is derived from the locality (Easton, Pa.) where Eyerman (Amer. Geol. 34, p. 46, 1904) found a sample which approaches this composition very closely.

Any point in the square represents a definite and easily determined mixture of the four components. For example, point 26 of fig. 2 represents a biotite with 72 percent of ferri-ferrous molecules (H₄K₂Fe₆Al₂Si₆O₂₄ = annite or Ann and H₄K₂Fe₅Al₄Si₆O₂₄ = siderophyllite or Sd) and 28 percent of non-ferri-ferrous molecules (H₄K₂Mg₆Al₂Si₆O₂₄ = phlogopite or Pg and H₄K₂Mg₅Al₄Si₆O₂₄ = eastonite³⁰ or Es); further, it represents 78 percent of di-alumina molecules (Sd and Es) and 22 percent of mon-alumina molecules (Ann and Pg); therefore,

TABLE VI. Discrepancies in the total for Si and its proxies in biotite, assuming the series:

Anal- ysis No.	H ₄ K ₂ Mg ₆ Al ₂ Si ₆ O ₂₄ to H ₄ K ₂ Mg ₅ Al ₄ Si ₆ O ₂₄					H ₄ K ₂ Mg ₆ Al ₂ Si ₆ O ₂₄ to H ₄ K ₂ Mg ₅ Al ₄ Si ₆ O ₂₄				
	Si	Al	Mg	Fe ²⁺	Fe ³⁺	Si	Al	Mg	Fe ²⁺	Fe ³⁺
	as as	as as	as as	as as	as as	as as	as as	as as	as as	as as
10	+0.2	+0.0	-0.2	-0.1	-0.5	-1.1	-1.4	-1.5	-1.5	-1.6
11	+8.7	+2.0	+2.8	+2.1	+1.4	+8.0	+2.0	+1.8	+1.8	+1.8
12	-0.7	-0.7	-0.7	-0.9	+0.5	-1.8	-1.9	-1.8	-1.9	-1.9
18	-0.1	-0.1	-0.2	-0.5	-0.5	-1.6	-1.7	-1.7	-1.8	-1.9
49	+0.2	+0.1	0.0	-1.7	-1.0	-1.1	-1.2	-1.5	-2.1	-2.1
50	+2.1	+1.1	-0.2	+0.7	-0.5	+1.7	+0.8	-0.2	+0.1	-0.4
70	+1.9	+1.4	+1.0	+0.8	0.0	-1.0	-1.6	-1.8	-2.2	-2.3
71	+8.7	+8.0	+0.4	+0.6	+6.1	+8.5	+0.4	-1.8	-1.7	-2.0
72	+8.2	+6.9	+5.8	-0.8	-0.4	+4.1	+2.2	+1.5	+0.9	-1.5
73	+9.0	+7.5	+5.8	+1.5	0.0	+4.6	+2.2	+1.4	-0.7	-1.5
81	+7.7	+6.4	+5.7	+1.9	+1.2	+1.7	+0.7	+0.4	-1.6	-1.3
81	+7.7	+7.7	+7.7	-0.9	-1.9	+2.4	+2.4	+2.4	-2.4	-2.4
100	+11.8	+11.1	+10.9	+10.0	+9.6	+6.0	+5.6	+5.6	+5.1	+5.1
101	+8.8	+8.8	+1.8	+2.8	+1.8	+8.8	+0.1	-1.8	-0.1	-2.0
102	+7.1	+2.9	+1.4	+2.5	+1.8	+6.0	-0.3	-2.5	-0.6	-2.7
103	+2.4	+2.5	+1.7	+0.9	0.0	+1.8	+0.1	-0.4	-0.6	-1.8
106	+8.8	+8.2	+0.9	+0.1	+1.8	+2.3	-0.7	-1.8	+0.7	+0.4
114	+0.5	+0.1	-0.2	-1.8	-1.7	-0.1	-0.8	-1.0	-1.6	-1.7
116	+9.4	+9.4	+9.4	+1.4	+1.8	+5.6	+5.5	+5.5	-0.5	-0.5
122	+6.4	+5.6	+4.8	+2.2	+1.4	+2.8	+1.6	+1.2	-0.1	-0.5
123	+2.5	+5.5	+4.4	+2.4	+1.8	+2.5	+0.9	+0.4	-0.5	-1.1
124	+2.2	+1.1	0.0	-0.5	-1.4	-0.2	-1.9	-2.6	-2.7	-3.2
140	+4.1	+6.7	+2.3	+1.7	+1.2	+1.0	+0.4	+0.2	-0.4	-0.8
141	+2.7	+2.5	+1.4	+0.8	-0.5	+1.6	0.0	0.4	-0.8	-1.4
142	+4.4	+2.1	+1.8	+1.1	-0.1	+2.8	+0.5	-0.1	-0.4	-1.0
143	+4.7	+5.8	+2.4	+2.0	+0.3	+2.9	+1.2	+0.4	+0.4	-0.2
148	+2.2	+2.1	+1.0	+2.1	0.0	+0.1	-1.6	-2.1	-2.1	-2.5
150	+2.0	+2.3	+1.4	+1.3	+0.4	+0.2	-0.9	-1.2	-1.4	-1.7
166	+4.2	+2.8	+2.7	+0.7	-0.2	+2.5	+0.9	+0.4	-0.4	-1.2
169	+2.2	+2.2	+2.2	0.0	0.0	-1.7	-1.8	-1.7	-2.9	-2.9
171	+0.9	+0.8	+0.2	-1.2	-1.4	-1.2	-1.7	-1.9	-2.6	-2.7
181	+4.2	+2.8	+2.0	-0.4	-1.5	+2.4	+0.7	+0.1	-1.1	-1.6
221	+0.9	+0.9	+0.9	+0.8	+0.5	+0.4	+0.4	+0.4	+0.2	+0.2
222	+4.5	+4.1	+2.6	+1.4	+1.1	+1.5	+0.6	+0.6	-0.4	-0.6
223	+2.5	+4.6	+4.1	+1.4	+0.9	+2.3	+1.2	+0.9	-0.4	-0.7
Total	149.2	117.8	92.8	80.9	41.8	78.0	45.7	48.2	45.9	52.5
Aver.	4.2	3.4	2.6	1.4	1.2	2.2	1.5	1.5	1.5	1.7
+ Total	149.7	118.0	93.4	81.4	42.2	80.1	47.9	51.5	48.5	55.5
- Total	0.5	0.2	0.6	0.5	0.4	2.1	2.2	2.7	2.6	3.0
Diff.	+147.2	+118.7	+92.8	+80.9	+41.8	+78.2	+46.1	+48.9	+46.3	+52.5
Aver.	+ 4.2	+ 3.5	+ 2.6	+ 1.0	+ .066	+ 1.6	+ 0.5	+ 0.2	+ 1.0	+ 1.3

it represents 78 percent of 72 percent or 56 percent of Sd, 22 percent of 72 percent or 16 percent of Ann, 28 percent of 78 percent or 22 percent of Es, and 28 percent of 22 percent or 6 percent of Pg.

Besides the chief molecules shown in the figure there are many other molecules present in biotite in limited amount, such as: $H_2Na_2Mg_6Al_2Si_6O_{24}$, $H_4K_2Mn_2Al_2Si_6O_{24}$ and $H_4K_2Mg_6Cr_2Si_6O_{24}$. Other subordinate molecules, whose exact composition is uncertain, may be written tentatively as follows: $H_2Ca_2Mg_6Al_2Si_6O_{24}$, $H_2Ba_2Mg_6Al_2Si_6O_{24}$, $K_2Mg_6Al_2Si_6O_{20}F_4$. In fig. 2 the following molecules are also assumed: $K_2Mg_4Ti_2Al_2Si_6O_{24}$ and $HK_2Mg_3Fe'''_3Al_2Si_6O_{24}$. Finally, all of these molecules may be written also in such a way as to end in Si_6O_{24} .

In the preparation of fig. 2 no attempt has been made to calculate and plot all available analyses since it seemed unnecessary to carry the work beyond the status shown; it is believed that enough points (about 80) have been found to show that nearly all parts of the system are represented in natural crystals although the pure di-alumina types are rare, especially the pure $H_4K_2Mg_6Al_2Si_6O_{24}$. A careful study of the 240 known analyses has disclosed only 8 which contain too much alumina to belong to this system; it seems reasonable to suggest that in these few cases the excess alumina may be due to impurities or inaccuracies.

In case the biotite series extends from $H_4K_2Mg_6Al_2Si_6O_{24}$ to $H_2K_2Mg_6Al_2Si_6O_{24}$, it has been shown that Ti and Fe''' proxy for Al; the molecules in which they occur are assumed to be $H_2K_2Mg_6Ti_2Si_6O_{24}$ and $H_4K_2Mg_6Fe'''_2Si_6O_{24}$.

There are various objections to the idea that the second term of this series is correct for biotite. First, the molecule last named, which is a corollary of this conception, is unknown in mica in anything like the pure state. Second, very few analyses are known in which Al_2O_3 alone (without Fe''') appreciably exceeds the amount in $H_4K_2Mg_6Al_2Si_6O_{24}$. Third, a graph can be drawn (see fig. 3) showing the relation between variations in composition and variations in indices of refraction for the system $H_4K_2Mg_6Al_2Si_6O_{24}$ to $H_4K_2Mg_6Al_4Si_6O_{24}$ but for the system $H_4K_2Mg_6Al_2Si_6O_{24}$ to $H_2K_2Mg_6Al_4Si_6O_{24}$ the relations between these variations can only

be shown in a three-dimension model; on some sections through such a (cubic) model the optic data available may be satisfactorily graphed, but the results are unsatisfactory and even contradictory on other sections, as

TABLE VII. Discrepancies in the total for Mg and its proxies in biotite, assuming the series:

Anal- ysis No.	to					to				
	$H_4K_2Mg_6Al_2Si_6O_{24}$ $H_2K_2Mg_6Al_4Si_6O_{24}$					$H_4K_2Mg_6Al_2Si_6O_{24}$ $H_2K_2Mg_6Al_4Si_6O_{24}$				
	Ti	Ti	Ti	Ti	Ti	Ti	Ti	Ti	Ti	Ti
10	0.0	+0.2	+0.4	+0.2	+0.2	+1.2	+1.4	+1.7	+1.6	+1.7
11	-5.1	-4.4	-5.7	-6.5	-2.8	-4.4	-5.3	-5.0	-2.8	-2.5
12	+0.3	+0.8	+0.3	+1.0	+1.0	+1.9	+1.9	+1.9	+2.0	+2.0
29	+1.8	+1.9	+1.9	+2.2	+2.2	+5.4	+5.4	+3.6	+3.6	+3.6
48	+1.8	+1.9	+2.0	+2.7	+2.8	+5.0	+5.2	+3.2	+4.1	+4.1
60	-0.1	+0.0	+1.0	+1.8	+2.2	+0.2	+1.6	+2.1	+1.9	+2.4
70	+0.7	+0.5	+0.1	+0.2	+1.2	+2.2	+2.2	+2.0	+2.4	+2.5
71	-7.7	-5.1	-2.4	-2.6	+0.1	-5.6	-1.6	-0.2	-0.2	+1.0
78	-9.1	-7.4	-6.5	-1.7	+0.4	-4.9	-3.0	-2.2	+0.1	+0.7
79	-5.4	-3.8	+2.2	+2.1	+3.7	-0.9	+1.5	+2.3	+4.4	+5.2
80	-6.6	-5.9	-5.3	-1.6	-0.8	-1.2	-0.2	+0.1	+2.0	+2.4
81	+10.4	+10.4	+10.4	+8.8	+8.8	+2.2	-5.1	-5.5	-0.3	-0.3
100	-3.4	-2.2	-2.0	-2.1	-7.9	-4.2	-3.9	-3.8	-3.3	-3.2
101	-6.6	-2.8	-1.0	-2.5	+1.3	-6.0	-0.3	+1.6	-0.2	+1.6
102	-7.0	-3.6	+0.7	-3.2	+1.0	-5.7	-0.3	+1.0	-0.1	+2.0
102	-2.9	-2.0	-1.0	-0.5	+0.7	-0.5	+0.6	+1.1	+1.5	+1.9
102	-2.5	-4.2	-2.9	-2.1	-0.8	-2.3	-1.4	-0.7	-0.2	+0.5
112	-1.9	-1.5	-1.0	+0.2	+0.7	-1.2	-0.5	-0.5	+0.3	+0.6
116	-0.5	-2.8	-0.8	-1.0	-1.0	-2.0	-3.0	-3.0	+0.9	+0.9
122	-9.4	-8.6	-7.9	-5.2	-4.4	+5.7	-4.5	+4.1	-2.8	-2.5
125	-2.2	-2.2	-1.1	+0.7	+1.7	+0.2	+2.4	+2.9	+3.9	+4.4
124	-6.5	-5.4	-4.5	-3.9	-2.8	-3.9	-2.3	-1.7	-1.6	-1.0
140	-4.7	-4.3	-3.9	-2.4	-1.9	-1.5	-0.9	-0.7	-0.0	+0.3
141	-2.5	-2.4	-1.2	-0.7	+0.5	-1.6	+0.2	+0.7	+1.0	+1.6
142	-4.2	-2.0	-1.7	-1.1	+0.2	-2.5	-0.5	+0.1	+0.5	+1.1
143	-5.0	-3.9	-2.7	-2.4	-1.2	-2.2	-1.5	-0.9	-0.7	-0.2
148	-3.8	-2.7	-1.6	-1.6	-0.5	-0.6	+1.0	+1.4	+1.5	+2.1
150	-2.3	-2.4	-1.9	-1.6	-0.9	-0.5	+0.5	+0.9	+1.0	+1.4
166	-4.3	-3.2	-2.2	-2.2	+0.9	-1.9	-0.3	+0.2	+1.1	+1.7
168	-0.1	-0.1	+0.1	+2.1	+2.1	+0.9	+2.8	+2.8	+4.9	+4.9
171	-3.5	-3.2	-2.8	-1.4	-1.1	-1.5	-0.9	-0.8	-0.0	+0.1
181	-5.5	-4.3	-3.2	-0.6	+0.4	-3.5	-1.8	-1.2	0.0	+0.8
221	-0.8	-0.8	-0.8	-0.3	-0.3	-0.2	-0.2	-0.2	0.0	0.0
222	-4.2	-3.7	-3.3	-1.2	-0.9	-1.1	-0.4	-0.2	+0.8	+1.2
223	-4.8	-3.6	-2.9	-0.5	+0.2	-1.1	0.0	+0.3	+1.5	+1.9
Total	156.6	129.4	103.4	64.9	55.0	92.0	60.4	61.2	56.4	54.9
Total	4.5	5.4	3.0	1.9	1.5	2.6	1.7	1.7	1.5	1.8
Total	4.4	5.3	2.7	2.4	2.5	2.3	2.5	2.9	2.0	2.2
Total	-124.0	-123.8	-94.9	-50.5	-28.5	-70.5	-55.9	-54.3	-12.4	-9.7
Diff.	-180.0	-118.2	-96.0	-36.1	-4.0	-48.2	-11.4	+12.6	+29.6	+45.5
Ave.	-4.2	-3.3	-2.5	-1.0	-0.1	-1.4	-0.3	+0.4	+0.6	+1.3

deduced from all available data. For these reasons no graphs of this system are presented.

For the system $H_4K_2Mg_6Al_2Si_6O_{24}$ to $H_4K_2Mg_6Al_4Si_6O_{24}$ all available data showing the relations between com-

position and optic properties are assembled and interpreted in fig. 3. Since the lines showing optic properties are approximately parallel and horizontal in the lower part of the drawing, they give very little help in determining the percentage of di-alumina molecules in biotites containing little iron; it is to be hoped that some other

FIG. 3.

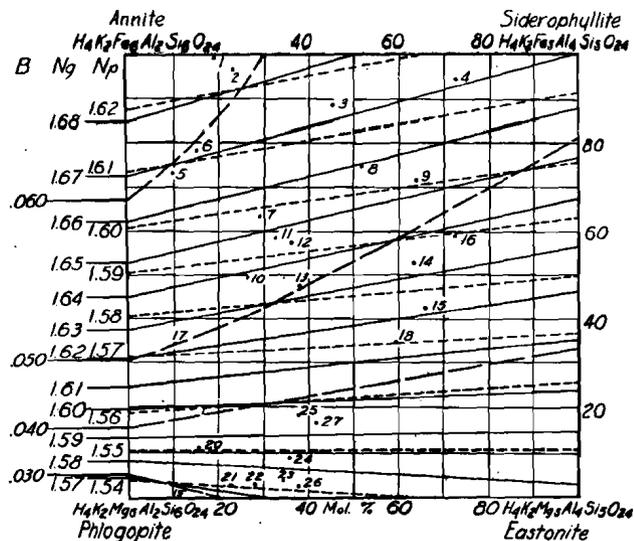


Fig. 3.—Relations between optic properties and composition in the biotite system. B = birefringence = $N_g - N_p$.

property may be discovered which will serve this purpose. Also, there is no close relationship between the variations in composition on which the diagram is based and variations in the optic angle and the change reported to occur in position of the optic plane. These optic properties must depend chiefly upon some other variation in composition. It is possible that this other variable is to be found in the relations between hydroxyl

and fluorine; present data indicate that biotites with much hydroxyl have the optic plane in 010 while those with much fluorine have the optic plane normal²¹ to 010; but more accurate and complete data are necessary to establish this relationship and permit its presentation in graphic form.

There are many subordinate molecules commonly present in biotite in addition to the chief molecules shown on fig. 3; therefore, it is impossible to prepare a diagram that will give the exact indices of refraction of each crystal. However, the maximum known discrepancy between the diagram and measured crystals is about ± 0.01 and the average discrepancy is much less.

REFERENCES FOR FIG. 3.

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(To be continued in the May number.)

²¹ It is suggested later in this article that such micas are not really biotites at all, but belong to another division of the mica group both chemically and optically.