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Trioctahedral One-Layer Micas. II. Prediction of the Structure from Composition and Cell Dimensions*

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Atomic trimetric coordinates are predicted for $1M$ trioctahedral micas of known compositions from the following data: tetrahedral and octahedral metal–oxygen distances, taken from the literature; b and $d(001)=c\sin\beta$, determined experimentally; $a=b/\sqrt{3}$, assumed. Predictions for ferri-annite and ferriphlogopite compare well with the known structures.

Introduction

The crystal structures of 'ferri-annite' (Donnay, Morimoto, Takeda & Donnay, 1964) and of other trioctahedral $1M$ micas (Steinfink, 1962; Zvyagin & Mishchenko, 1962) indicate that the essential structural features of $1M$ polymorphs might be predicted from known composition and cell dimensions, because suitable assumptions can be made. Various assumptions have already been made by previous authors working on related problems (*e.g.* Radoslovich, 1959–1963). As we re-examine the problem, we will state, or restate, those assumptions that are necessary and sufficient for our purpose.

We shall show how, in order to match the experimental value of b, tetrahedra must be rotated through angle α about c^* and the octahedra must be flattened into trigonal antiprisms. We define ψ as the angle between c^*, the normal to the basal octahedral face, and the line that connects opposite vertices of the octahedron. Before flattening $\psi=54°\,44'$; it exceeds that value after flattening. (The angle α has been used by previous authors, but as far as we know, the flattening of the octahedra has not heretofore been expressed in terms of ψ, although it has been discussed in terms of thickness of the octahedral layer, by Bradley, 1958.)

Trimetric atomic coordinates $x'/a, y/b, z'/c'$ can be calculated in a rectangular system of axes Ox, Oy, Oz', in which Ox and Oy are the usual monoclinic axes, Oz' is normal to the cleavage plane (001), and $c'=c\sin\beta^*$ is the interplanar distance $d(001)$. As consequences we have:

$$z/c=z'/c',$$
$$x=x'+z'\cot\beta^*=x'+z\cos\beta^*,$$
$$x/a=x'/a+(z/c)(c/a)\cos\beta^*.$$

A trioctahedral $1M$ mica structure can be derived from the idealized biotite structure, in which the sheets of tetrahedra and octahedra have hexagonal symmetry. The rearrangements and deformations that are involved are of two kinds as they affect the structure: (1) *in plan*, that is, in its orthogonal projection on the cleavage plane; and (2) *in elevation*.

The structure in plan

We need the following assumptions:

1. The basal oxygen atoms of each tetrahedral sheet are coplanar and their plane is (001).
2. The basal faces of the tetrahedra are equal, rigid, equilateral triangles.
3. These triangles are articulated at their vertices.
4. The orthohexagonal relation $a=b\tan 30°$ (Table 1) is rigorously obeyed; it holds approximately for all micas (Sadanaga & Tekéuchi, 1961).

Note that the structural rearrangements must preserve the observed monoclinic mirror. Note also that we need *not* assume the holohedral symmetry, which has actually been observed in all the $1M$ micas that have been studied until now. It is not necessary to assume, at this time, that the sides of the basal faces of the tetrahedra must be equal to the apical edges. This additional assumption will be made later on, when the tetrahedra are taken to be regular.

The purpose of the rearrangements of the tetrahedra is to reduce the idealized length b to the observed value.* In the plane of the basal oxygen atoms of the tetrahedra, consider (Fig. 1) three triangles in the hexagonal network of the idealized biotite structure (before rearrangement). The oxygen atoms CA_0D_0 on the one hand, CB_0E_0 on the other, are collinear;

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* The misfit between an oversize tetrahedral sheet and an undersize octahedral sheet was observed in dickite by Newnham & Brindley (1956).

the y axis bisects the 60° angle D_0CE_0 at C, which point we shall choose as origin for the purpose of calculations. Obviously D_0E_0 is perpendicular to the y axis, which it intersects at K_0. Since $D_0K_0=a/2$ and $CK_0=b/2$, the well-known relation $a=b \tan 30°$ is obeyed.

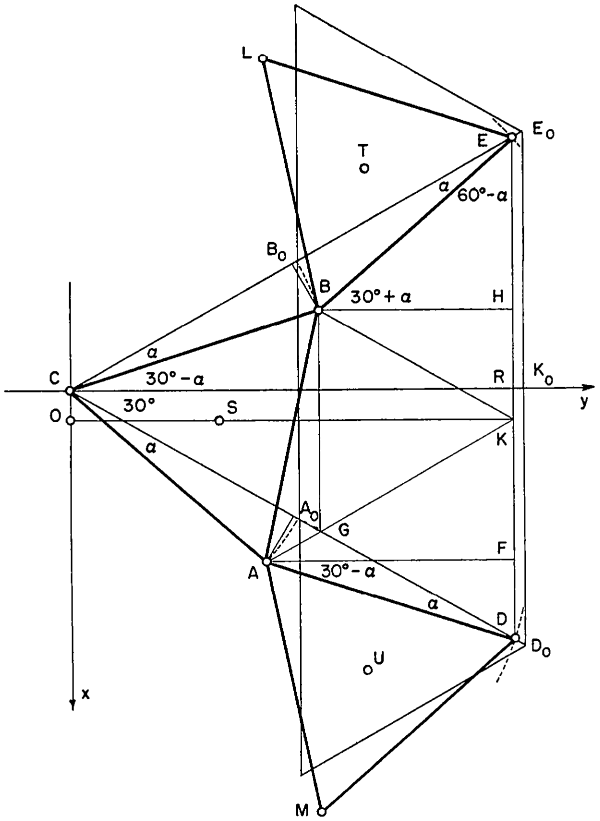

Fig. 1. Projections of tetrahedral sheet onto (001), before rotation of tetrahedra (thin line) and after rotation (thick line).

Let e be the length of the O–O edge of the tetrahedron.

Keeping C fixed, let us rotate triangle CA_0B_0 clockwise through an angle α around C. It comes to CAB. We shall prove that *the oxygen atoms* D_0 *and* E_0, *which must remain at distance e from A and from B, respectively, will come to the points D and E, located at the intersections of* CD_0 *and* CE_0 *with arcs of circles with radius e drawn from A and B respectively*: since triangles CAD and CBE are isosceles, triangle CDE is also isosceles; CK_0 intersects DE in its midpoint R; DE is perpendicular to the y axis, so that the monoclinic mirror is preserved; $a_{\text{obs.}}=DE$ and $b_{\text{obs.}}=2CR$, so that the orthohexagonal relation $a_{\text{obs.}}=b_{\text{obs.}} \tan 30°$ holds true. Any other pair of points, say $D'E'$ or $D''E''$, that would lie on the arcs of circles, but either to the right or to the left of DE, must be rejected: any line $D'E'$ perpendicular to the y axis would decrease $a_{\text{obs.}}$ and increase $b_{\text{obs.}}$; any line $D''E''$ would increase $a_{\text{obs.}}$ and decrease $b_{\text{obs.}}$ thus destroying the orthohexagonal relation. This proof also shows that *if triangle CAB is rotated clockwise through angle* α, *then the connected triangles ADM and BEL rotate counterclockwise through the same angle* α. We have

$$CD=CE=2e \cos \alpha$$

and

$$CD=CR/\cos 30°=b_{\text{obs.}}/2 \cos 30°,$$

whence

$$\cos \alpha=b_{\text{obs.}}/4e \cos 30°.$$

Since the b before rearrangement (b_t of Radoslovich) is equal to $2CK_0=4e \cos 30°$, we derive* the known relation $\cos \alpha=b_{\text{obs.}}/b_t$. In terms of the tetrahedral cation-to-oxygen distance d_t, we have

$$\cos \alpha=b_{\text{obs.}}/4d_t\sqrt{2}\ .$$

Before the rotations of the tetrahedra take place, the projection of the potassium atom falls at K_0. After the rearrangement, the potassium atom will be projected in the center K of the ditrigonal ring of oxygen atoms: $DABE$.... In particular we must have $KD=KB$ and $KA=KE$. Join BD and AE. Triangles ABD and ABE are isosceles. We will show that their altitudes AK and BK meet at K, and that the angles at K, AKD, AKB, BKE, are equal to 60°. Angle $BAD=180°-60°-2\alpha=120°-2\alpha$ is bisected by AK, so that angles BAK and DAK are equal to $60°-\alpha$. Since $ADK=60°+\alpha$, $AKD=60°$. Likewise $ABK=EBK=60°+\alpha$, $BEK=60°-\alpha$, and $BKE=60°$. Finally $AKB=180°-(60°-\alpha)-(60°+\alpha)=60°$. It follows that the rearrangement of the tetrahedra leaves the lines KD, KA, KB, KE, ... at 60° to each other, and the symmetry† of this figure (in plan) is $3l$. This result was to be expected from the combination of the trace of the monoclinic mirror with the point K of 3-fold rotational symmetry.

Another way of treating the problem is to take the projection of K as the origin and let the sides AB and BE turn (in opposite senses) in such a way that A and E move away from K, and B moves toward K, while staying on the symmetry lines KA, KB, KE, ..., in such a way that $AB=BE=e$ remains constant. We can then calculate the inward and outward displacements, Δ_{in} and Δ_{out}, of atoms like B and A, respectively. We find

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* In order to compare the predicted value of α with the experimental value, it is necessary to define the latter. We take it to be the average of six values. For each of the six lines AB, BC, CA, SA, SB, SC (Fig. 1), we measure the angle (on the ab projection) between the original direction in idealized biotite and the actual direction in the determined structure.

† Mathieson & Walker (1954) rotated the oxygen triangles in vermiculite; Steinfink (1958), in chlorite; Takéuchi & Donnay (1959), in hexagonal $CaAl_2Si_2O_8$; Takéuchi & Sadanaga (1959), in xanthophyllite; Radoslovich (1960), in muscovite. In all these cases ditrigonal symmetry is observed.

$$\Delta_{\text{in}}/e = (\sqrt{3}/3)\sin\alpha + 1 - \cos\alpha$$

and

$$\Delta_{\text{out}}/e = (\sqrt{3}/3)\sin\alpha - (1 - \cos\alpha)\ .$$

On Fig. 1 it can be seen that $\Delta_{\text{in}} = K_0B_0 - KB$ and $\Delta_{\text{out}} = KA - K_0A_0$.

The centers of the equilateral triangles are the orthogonal projections of the Si (and O_{III}) atoms onto the (001) plane. We shall now prove that *the six projected* Si *atoms form a regular hexagon*. To this end we shall show (Fig. 1) that they are equally distant from (projected) K, on radial lines from K that bisect the 60° angles between the symmetry lines AKB, BKE, AKD. The center S of triangle ABC lies on the y axis, at $y = b/6$; hence, distance $KS = b/3$. Since $BKE = 60°$, $SKB = 30°$; likewise, since $AKD = 60°$, $SKA = 30°$, and KS bisects AKB. Now, in triangle KET, where T is the center of the BEL triangle, we know: $KE = e\,(\cos\alpha + (\sqrt{3}/3)\sin\alpha)$, $TE = (\sqrt{3}/3)e$, angle $KET = 60° - \alpha + 30° = 90° - \alpha$. We derive $KT = (2/\sqrt{3})e\cos\alpha = b/3$ and $\sin EKT = \frac{1}{2}$, whence $EKT = 30°$, so that KT bisects angle BKE. Likewise, $KU = b/3$ and KU bisects angle DKU. Note that the hexagon of the projected silicon atoms is smaller after rearrangement of the tetrahedra than before. It has shrunk in the same ratio as b, that is, $1/\cos\alpha$.

The next layer up is composed of oxygen atoms (O_{III}), which are projected exactly above the silicon atoms, and of hydroxyl groups, which are projected in the centers of the hexagons.* The OH groups thus form a hexagonal net, with the shortest OH–OH distance equal to $b/\sqrt{3}$. The oxygen atoms occupy the H-centering positions in the OH net. The smaller hexagonal net, the nodes of which are occupied by OH groups or by oxygen atoms, has an a period (OH–O distance) $u = b/3$.

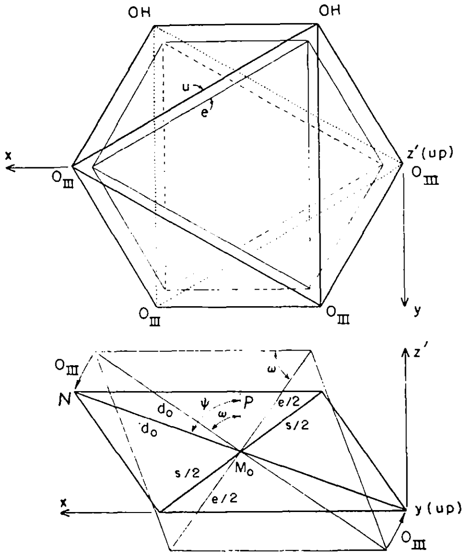

Fig. 2. Projections of octahedron onto (001), before flattening (thin line) and after flattening (thick line), with corresponding cross-sections.

The octahedra are built on this layer. The octahedral cations are projected at the centers of the equilateral triangles that form the bottom and top faces of the octahedra. The coordinates of the cations in the plane $x'y$ will be (Fig. 2): $x' = -a/6$, $y = 0$; $x' = -a/6$, $y = b/3$.

The structure in side elevation

We will need the following assumptions:

(1) The tetrahedra remain regular after rearrangement.

(2) The apical oxygen ions of the tetrahedra are coplanar with the monovalent anions (OH, or F, or both).

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* If the OH groups and O atoms were in disorder, the geometrical argument would not be affected. Of course F can replace OH.

Table 1. *Observed facts on which our assumptions rest*

Composition	b/a	$(c/a)\cos\beta$*	β	b (Å)	Reference
Annite:					
SACW100B	1·7317	0·3315	100° 0′ ± 15′	9·334	Eugster & Wones, 1962
762	1·7338	0·3315	99° 59′ ± 15′	9·328	Eugster & Wones, 1962
$AnFe_4$	1·7339	0·3297	99° 56′ ± 15′	9·330	Eugster & Wones, 1962
$AnFe_7$	1·7312	0·3345	100° 5′ ± 15′	9·324	Eugster & Wones, 1962
$AnFe_6$	1·7340	0·3223	99° 42′ ± 15′	9·348	Eugster & Wones, 1962
Ferri-annite	1·731	0·330	100° 0′ ± 10′	9·40	Donnay, Morimoto, Takeda & Donnay, 1964.
Ferri-annite	1·7319	0·3329	100° 4′ ± 10′	9·404	Wones, 1963*a*, *b*
Ferriphlogopite	1·733	0·337	100° 0′ ± 10′	9·29	Steinfink, 1962
Fluorphlogopite	1·7316	0·3336	100° 4′	9·195	Yoder & Eugster, 1954
Fluorphlogopite	1·7339	0·3294	99° 55′	9·188	Kohn & Hatch, 1955
Phlogopite	1·7320	0·3337	99° 54′	9·204	Yoder & Eugster, 1954
Taeniolite	1·732	0·338	100° 0′ ± 15′	9·13	Yamzin, Timofeyeva, Shashkina, Belowa & Gliki, 1955
Xanthophyllite	1·731	0·334	100° 3′	9·02	Sanero, 1940
Xanthophyllite	1·7283	0·3302	100° 4′	9·013	Forman, 1951
Xanthophyllite	1·734	0·329	100·1° ± 0·2°	9·00	Takéuchi & Sadanaga, 1959
Assumptions	$\sqrt{3}$	$\frac{1}{3}$	100° 0′		

(3) If M_o is an octahedrally surrounded cation, the M_o–O distance is equal to the M_o–OH distance and the octahedron is deformed into a trigonal antiprism, which fulfils the condition that row [103] is *exactly* perpendicular to (001) or $(c/a)\cos\beta^* = \frac{1}{3}$ (see Table 1).

Consider a cation M_o in octahedral coordination, and let d_o be its distance to one of the neighboring oxygen ions,

$$d_o = M_o\text{–O} .$$

Consider (Fig. 2) the plan and side elevation of this (regular) octahedron lying on one of its faces. In the plane xz' the line $O_{III}O_{III}$ makes an angle* $\omega = 54°\,44'$ with the vertical z'. This angle may be increased, say to ψ, by rotating the line $O_{III}O_{III}$ counterclockwise around the y axis. The octahedron can thus be deformed into a trigonal antiprism, whose height o is given by

$$o = 2d_o \cos\psi$$

and is smaller than that of the original octahedron, $2d_o \cos\omega$. The result of this flattening of the octahedral layer is to increase the size of the top and bottom faces, which remain equilateral triangles. A clockwise rotation of $O_{III}O_{III}$ (Fig. 2) would increase the height o and would result in smaller equilateral triangles.

Noting that the altitude t of the regular tetrahedron is

$$t = 4d_t/3 ,$$

where d_t is the cation-to-oxygen distance,

$$d_t = M_t - O ,$$

we can express the thickness i of the interlayer

$$i = c' - o - 2t$$

or

$$i = c\sin\beta - 2d_o\cos\psi - (8/3)d_t .$$

The period b can be expressed in terms of ψ. It is equal to three times the edge of the equilateral triangles in the antiprism. This *unshared edge u* is given by the triangle M_oNP (Fig. 2):

$$\tfrac{2}{3}u \sin 60° = d_o \sin\psi ,$$

whence

$$u = \sqrt{(3)}\,d_o \sin\psi$$

and

$$b = 3u = 3\sqrt{(3)}\,d_o \sin\psi.$$

In the preceding section we have expressed b in terms of one of the basal edges e of the tetrahedron, $b = 2\sqrt{(3)}\,e\cos\alpha$. If we make the assumption that the tetrahedra are regular, e becomes a tetrahedral edge, and we have

$$e = 2d_t \sin\omega ,$$

whence

$$b = 4\sqrt{(2)}\,d_t \cos\alpha .$$

Prediction of the crystal structure

Given the observed b value and knowing the two cation-to-oxygen distances, we can calculate the angles α and ψ:

$$\cos\alpha = b_{\text{obs.}}/4\sqrt{(2)}\,d_t$$

and

$$\sin\psi = b_{\text{obs.}}/3\sqrt{(3)}\,d_o .$$

A nomogram (Fig. 3) can be prepared allowing for a range of values of d_o and d_t. It illustrates the effect which b length and cation size have on α and ψ. It can also be used to predict a range for b when values of d_o and d_t are assumed. Under the discussion of K–O bond lengths, at the end of the paper, we shall show how the K–O bond further limits the range of

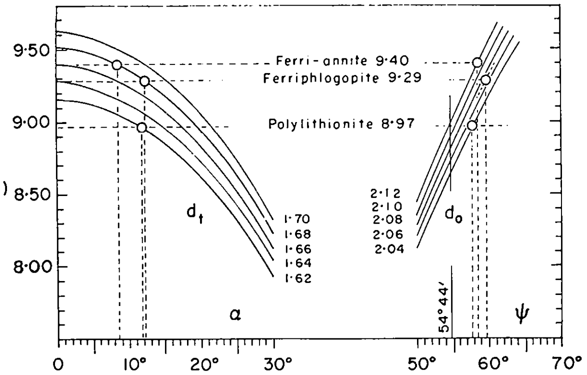

Fig. 3. Nomogram giving α and ψ from observed b and literature values of d_t (tetrahedral metal–oxygen distance) and d_o (octahedral metal-to-anion distance) for any given composition.

Table 2. *Atomic trimetric coordinates in rectangular axes Ox, Oy, Oz′*

$d_t = M_t - O,\ d_o = M_o - O,\ c' = c\sin\beta,\ \beta^* = 180° - \beta$

$$\tan\alpha = 4\sqrt{2}\sqrt{\left(\left(\frac{d_t}{b}\right)^2 - \frac{1}{32}\right)},\quad d_o\cos\psi = b\sqrt{\left(\left(\frac{d_o}{b}\right)^2 - \frac{1}{27}\right)}$$

	x'/a	y/b	$z'/c' = z/c$
K	0	1/2	0
O_I	$-\frac{\sqrt{3}}{6}\tan\alpha$	0	$\frac{1}{2} - \frac{d_o\cos\psi + \frac{4}{3}d_t}{c\sin\beta}$
O_{II}	$\frac{1}{4} + \frac{\sqrt{3}}{12}\tan\alpha$	$\frac{1}{4} - \frac{\sqrt{3}}{12}\tan\alpha$	$\frac{1}{2} - \frac{d_o\cos\psi + \frac{4}{3}d_t}{c\sin\beta}$
M_t	0	1/6	$\frac{1}{2} - \frac{d_o\cos\psi + d_t}{c\sin\beta}$
O_{III}	0	1/6	$\frac{1}{2} - \frac{d_o\cos\psi}{c\sin\beta}$
OH	0	1/2	$\frac{1}{2} - \frac{d_o\cos\psi}{c\sin\beta}$
M_{oI}	−1/6	0	1/2
M_{oII}	−1/6	1/3	1/2

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* The angle ω is the cube–octahedron angle. The following values are useful: $\sin\omega = \sqrt{(2/3)}$, $\cos\omega = \sqrt{(1/3)}$, $\tan\omega = \sqrt{2}$. They can be read off directly from a diagonal plane of symmetry of the cube.

Table 3. *Predicted ferri-annite structure*

Data: $a = 5·43$, $b = 9·40$, $c = 10·32$ Å, $\beta = 100° \, 0'$; (Si, Fe^{3+})–O = 1·68; Fe^{2+}–(O, OH) = 2·12 Å

Position	Atom	x'/a	x/a	$10^3\Delta(x/a)$	y/b	$10^3\Delta(y/b)$	z/c	$10^3\Delta(z/c)$
2(*b*)	K	0	0	—	1/2	—	0	—
4(*i*)	O_I	−0·043	0·014	1	0	—	0·171	−5
8(*j*)	O_{II}	0·271	0·328	−8	0·229	7	0·171	−4
8(*j*)	Si, Fe^{3+}	0	0·075	0	1/6	0	0·226	−2
8(*j*)	O_{III}	0	0·130	3	1/6	−1	0·391	0
4(*i*)	OH	0	0·130	4	1/2	—	0·391	10
2(*c*)	Fe_I^{2+}	−1/6	0	—	0	—	1/2	—
4(*h*)	Fe_{II}^{2+}	−1/6	0	—	1/3	0	1/2	—

	(Si, Fe^{3+})–O	Fe^{2+}–O	Fe^{2+}–OH	$(O–O)_s$	$(O–O)_u$	s/u	K–O	K–O	α	ψ
Predicted	...	...	...	2·86	3·13	0·91	3·42	3·03	8° 28′	58° 35′
Observed	1·685	2·123	2·075	2·814	3·136	0·90	3·347	3·054	6° 24′	59° 7′

Δ = observed–predicted.

Table 4. *Predicted ferriphlogopite structure*

Data: $a = 5·36$, $b = 9·29$, $c = 10·41$ Å, $\beta = 100° \, 0'$ (Steinfink, 1962); (Si, Fe^{3+})–O = 1·68, Mg–(O, OH) = 2·07

Position	Atom	x'/a	x/a	$10^3\Delta(x/a)$	y/b	$10^3\Delta(y/b)$	z/c	$10^3\Delta(z/c)$
2(*b*)	K	0	0	—	1/2	—	0	—
4(*i*)	O_I	−0·062	−0·002	−2	0	—	0·180	−10
8(*j*)	O_{II}	0·281	0·341	−7	0·219	4	0·180	−11
8(*j*)	Si, Fe^{3+}	0	0·078	−1	1/6	1	0·234	−8
8(*j*)	O_{III}	0	0·133	−6	1/6	1	0·398	−8
4(*i*)	OH	0	0·133	2	1/2	—	0·398	−2
2(*c*)	Mg_I	−1/6	0	—	0	—	1/2	—
4(*h*)	Mg_{II}	−1/6	0	—	1/3	0	1/2	—

	(Si, Fe^{3+})–O	Mg–O	Mg–(OH)	$(O–O)_s$	$(O–O)_u$	s/u	K–O	K–O	α	ψ
Predicted	...	...	...	2·75	3·10	0·89	3·53	2·98	12° 10′	59° 44′
Observed	1·681	2·115	2·079	2·85	3·10	0·92	3·458	2·942	11° 2′	58° 11′

Δ = observed–predicted

b values to be expected. The atomic coordinates can then be computed (Table 2) in terms of α, ψ, d_t, and d_o. If the perpendicularity condition $(c/a) \cos \beta^* = \frac{1}{3}$ does not hold rigorously true for the observed cell dimensions, the observed value of $c' = c \sin \beta$ should be used (see Table 2) in the calculations. A program has been written for the IBM 7094 computer, in which cell dimensions together with d_t and d_o are the input data. More than three predicted structures are computed per millisecond and, in addition to all atomic coordinates, the print-out gives the interatomic distances and angles α and ψ as shown on the last line of Tables 3 and 4.

At this juncture we must take up the question of symmetry. Although we started with a minimum of assumptions in this respect, the way in which we have built our structural model carries space-group implications. We have listed the atomic coordinates (Table 2) on the assumption of space group *C*2/*m*, which is the one found in determined structures.

We shall now prove that our model actually requires holohedral symmetry, that is, space group *C*2/*m*.

Below the sheet of O_I and O_{II} oxygen atoms, at half the interlayer distance, lie the potassium atoms, which are projected in the centers of the ditrigonal rings. Consider one such potassium atom. Below it is another O_IO_{II} sheet, whose tetrahedra have (like those of the sheet just above) also rotated through the same angle α, either clockwise or counterclockwise. (Otherwise the *b* length would not be preserved.) We rule out the possibility of a clockwise rotation, as in the upper O_IO_{II} sheet, because it would lead to prismatic coordination of potassium. With counterclockwise rotation (in the treatment of Fig. 1) the lower O_IO_{II} sheet will have its ditrigon inverted in the plane and the center of the ditrigon would fall above the line *CR*, instead of below, but by the same amount. Since the potassium atom is already fixed, with respect to the upper O_IO_{II} sheet, the lower O_IO_{II} sheet must be centrosymmetrically related to the upper one, and the potassium atom occupies the symmetry center. It is easy to check that the successive layers of our model, from potassium to the octahedral cations, on either side of potassium, do obey the centrosymmetry.

Although the model is centrosymmetric, the refinement can, of course, be conducted as though it were not. This is, in fact, how Steinfink (1962), with appropriate change of origin, refined the ferriphlogopite structure and showed that there was no evidence for ruling out the center. The lattice complexes of potassium and octahedral cations, M_{oI} and M_{oII}, are the same in *Cm* as in *C*2/*m*. Every one of the other complexes splits into two.

After deformation of the octahedron into a trigonal antiprism, two kinds of edges can be distinguished: the top and bottom edges, unshared edges, which have a length u; the lateral zigzag edges, shared edges, which have a length s. Calculation shows that the ratio of shared to unshared edge can be written

$$\frac{s}{u}=\sqrt{\left(\frac{4}{3\sin^2\psi}-1\right)}\,,\ \text{whence}\ \sin^2\psi=\frac{4}{3}\frac{u^2}{s^2+u^2}\,.$$

According to one of Pauling's rules, we should have $s<u$, and therefore, we should not expect ψ to exceed ω or even to be equal to it. (For $\psi=\omega$, we have $s/u=1$.)*

Prediction of the cell dimensions

Inasmuch as the angle β may be taken as 100° in trioctahedral one-layer micas (Table 1), we have three relations between the four unknowns: a, b, c, β. The required fourth relation is provided by the measured density, together with the known chemical composition and cell contents.

Under our simplifying assumptions (Table 1), all trioctahedral one-layer micas should have the same axial elements ($a/b, c/b, \beta$), the various cells differing only by a scale factor.

Discussion of the ferri-annite structure

The assumption that Fe–O and Fe–OH distances are equal is not borne out; the shift of 0·010 in z_{OH} reduces the Fe–OH distance from the assumed 2·12 to 2·07 Å (standard deviation 0·01). This can perhaps be ascribed to the one-directional bonding of the hydroxyl ions — each OH^- receives bonds of strength $\frac{1}{3}$ from three Fe^{2+} ions lying on one side of it. Each $O^=$, on the other hand, receives one additional bond of average strength 15/16 from the tetrahedral cation on the opposite side.

The maximum difference between predicted and observed coordinates is found (Table 3) for one of the basal oxygen atoms of the tetrahedral sheet, O_{II}, which is shifted by 0·36 Å. As a result, the basal triangle of the tetrahedron is scalene with sides of lengths 2·770, 2·696 and 2·727, not equilateral as was assumed. It turns out that the tetrahedral cation is found (in horizontal projection) exactly where it is predicted to be. The three lines that connect this point to the vertices of the triangle and the three sides of the triangle each give an experimental value for α (*cf.* footnote p. 1375). The average of the six values is compared with the predicted value and the agreement is reasonably good; α is extremely sensitive to departure from regularity of the tetrahedra.

Predicted and observed K–O bond lengths agree to better than one per cent; they exceed the reported maximum value for six-coordinated K–O by 0·14 Å (*International Tables for X-ray Crystallography*, 1962). The present example thus demonstrates that the K–O bond length cannot be assumed to predict the structure. It is one of the variables in a mica structure.

Discussion of the ferriphlogopite structure*

In ferriphlogopite (Table 4) we have used the same origin as in ferri-annite and recalculated Steinfink's data accordingly. Steinfink's value of 12° for the *observed* α was roughly estimated from the drawing (Steinfink, 1962, Fig. 2), on which he labels three angles (12°, 12°, and $10\frac{1}{2}$°); we have calculated his observed α from his published atomic coordinates and find an average value of 11° 2′ (the six values are: 10° 9′, 10° 57′, 12° 1′, obtained from the projected Si–O directions; 10° 36′, 11° 10′, 11° 21′, from the O–O directions).

Our recalculations of interatomic distances confirm, within rounding-off errors, the values published by Steinfink (1962, Table 3), with two exceptions: (1) the Mg(1)–OH distance should be 2·065 (instead of 1·975), much closer to the Mg(2)–OH distance of 2·094; (2) the Mg(2)–O(3) distance should be the average of 2·098 and 2·123, equal to 2·110 (instead of 2·097), closer to the Mg(1)–O(3) value of 2·119.

The Mg–(O, OH) distance, which was estimated from the literature, is too short and results in too large a value for the predicted ψ. As a consequence the thickness of the octahedral layer is too small and the predicted z values of O_{III}, OH and all the remaining atoms of the tetrahedral layer are too large.

The difference in the Mg–OH and Mg–O bond lengths is equal to only twice Steinfink's estimated standard deviation of 0·02 Å; it is not as significant as in the case of ferri-annite. The basal oxygen atom, O_{II}, of the tetrahedral sheet is again the atom whose observed coordinates differ most from the predicted ones. But the basal triangle of the tetrahedron has sides 2·751, 2·717 and 2·727 Å, thus departing only slightly from the assumed equilateral character. Predicted and observed K–O bond lengths agree. The observed value of 2·94 Å is 0·03 Å in excess of

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* Veitch & Radoslovich (1963) appear to have reached a different conclusion. They write: *It has been necessary to abandon the simplest geometrical model (which assumes that the octahedra remain essentially regular) for one in which the expansion due to the substitution of larger ions is several-fold greater in the direction normal to the layers than it is in the a–b plane.* We know from the determined structures of ferri-annite and ferriphlogopite (see discussion below) that in the case of Fe^{2+} substituting for Mg^{2+}, the opposite effect, namely a flattening of the octahedra, takes place even though the ionic radius of ferrous iron exceeds that of magnesium by 0·07 Å.

* The structure of phlogopite, determined by electron diffraction (Zvyagin & Mischenko, 1962), is known only through two projections: the $h0l$ reflections give $R=17{\cdot}2\%$; the $0kl$ projections, $R=20{\cdot}4\%$. It is not accurate enough to warrant comparison with a predicted structure.

the reported maximum (*International Tables*, 1962) for potassium with coordination number 6.

K-O bond lengths

In ferri-annite, as in ferriphlogopite, the predicted K–O bond length agrees reasonably well with the observed average. It therefore seemed worthwhile to explore the effect that changes in b, d_t, and d_o have on the K–O bond length in our structural model. Using the IBM program mentioned above, K–O distances were computed for 28 values of b from 8·56 to 9·26 Å, for five values of d_t (1·62 to 1·70 Å), and five of d_o (2·04 to 2·12 Å). For each pair of values (d_t, d_o) the curve of K–O *versus* b can thus be plotted by points. The curves group themselves in families of five corresponding to one value of d_t and the five d_o values that go with it. We show here (Fig. 4) only the curves for the limiting values of d_o (2·04 and 2·12 Å) within the expected range of K–O bond length, namely 2·72 to 3·25 Å (*International Tables*, 1962). For a given b the K–O bond length decreases much more rapidly with increasing d_t and fixed d_o than with increasing d_o and fixed d_t. Likewise, for a given K–O value, b increases more rapidly with d_t than with d_o.

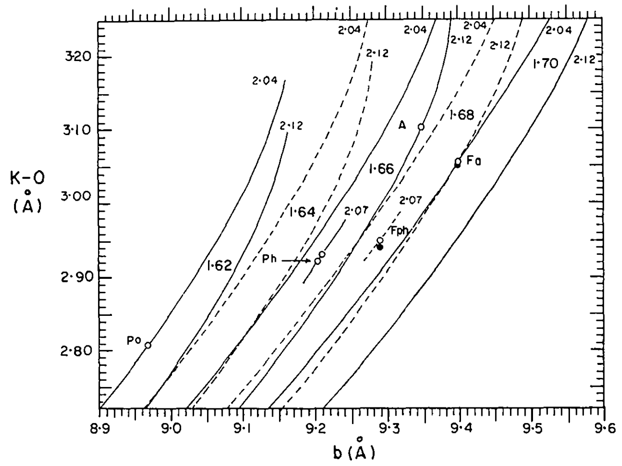

Fig. 4. Nomogram giving the K–O bond length from observed b and literature values of d_t (1·62 to 1·70) and d_o (2·04 to 2·12) for any given composition. Examples shown by white circlets: A = annite (Eugster & Wones, 1962, $\mathrm{AnFe_6}$), Fa = ferri-annite, Ph = phlogopite (lower point, Yoder & Eugster, 1954; upper point, Wones, 1963*b*), Fph = ferriphlogopite (Steinfink, 1962), Po = polylithionite (Munoz & Takeda, private communication). Black circlets indicate experimental K–O values for ferriphlogopite (Steinfink, 1962) and ferri-annite (Donnay *et al.*, 1964).

Let us use the ferri-annite composition to show that the K–O bond length restricts the range of possible b values more severely than does either d_t or d_o. From Fig. 3 we find that b can range from 9·00 Å (for $d_o = 2{\cdot}12$ and $\psi = 54° 44'$, which corresponds to $s/u = 1{\cdot}00$) to 9·51 Å (for $d_t = 1{\cdot}68$ and $\alpha = 0$). Fig. 4 shows that, within the permissible range of K–O, b can range only from 9·15 to 9·49 Å.

Another use to which Fig. 4 can be put is to estimate the relative importance of d_t and d_o in controlling the cell size. Radoslovich (1963*d*), in a recent summary of his mica publications, concluded that ... *the tetrahedral layers play a secondary role in determining the b-axis, not the co-equal role previously assumed. The cell dimensions of micas appear to be controlled largely by their octahedral layers and by the interlayer cations.* Let us consider a 0·02 Å decrease in d_t starting again with the ferri-annite composition ($d_t = 1{\cdot}68$) and leaving K–O and d_o unchanged. The value of b drops from 9·40 to 9·33 Å. If now the value of d_o (2·12 Å) is decreased by 0·02 Å, with K–O and d_t remaining unchanged, b drops only to 9·385 Å. We must conclude that, on the basis of the present structural model, the size of the tetrahedra plays a more important role in determining the b length than the size of the octahedra.

Finally, can we find an explanation for the surprisingly large K–O distances, especially in ferri-annite? The particular combination of d_t and d_o cannot be held responsible, because the corresponding curve (Fig. 4) would give the normal K–O bond length of 2·83 Å for $b = 9{\cdot}24$ Å, which is quite a reasonable b value. The predicted K–O for annite ($b = 9{\cdot}348$ Å, Eugster & Wones, 1962, sample $\mathrm{AnFe_6}$) is even larger,* namely 3·10 Å. Thus $\mathrm{Fe^{2+}}$ in the octahedral layer seems to have a lengthening effect on the K–O bonds even though the iron sheet is more than 5 Å away from the potassium sheet. The substitution of Mg for $\mathrm{Fe^{2+}}$ is accompanied by a shortening in K–O bonds as is well demonstrated by the data on synthetic biotite (Wones, 1963*b*) (Fig. 5) for which d_t remains 1·66 Å throughout. The substitutions in the tetrahedral layer are not as readily interpretable. In the $\mathrm{Fe^{2+}}$ micas, K–O distances in annite exceed those in ferri-annite by 0·5 Å, whereas in the Mg micas, K–O distances in phlogopite are less by 0·3 Å than what they are in ferriphlogopite. We are planning to refine the structure of a synthetic fluopolylithionite ($b = 8{\cdot}968$ Å, Munoz & Takeda, private communication), which is most intriguing because its predicted K–O bond length is as short as 2·81 Å (Fig. 4). Since only silicon fills the tetrahedra, the basal oxygen atoms have their charge completely satisfied by two Si–O bonds of strength +1 each and, in this clay-like environment, the potassium would not be expected to get so close to its oxygen neighbors.

Our purely geometric approach to detailed predic-

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* The curves of Figs. 4 and 5 have been calculated on the assumption that the cells of all 1*M* micas have a constant shape. As shown by Wones (1963*b*), c decreases in his series of synthetic biotites, from phlogopite to annite, instead of increasing as postulated by our model. The K–O values read off our Fig. 5 for biotites are therefore known to be high and get worse as the Fe/Me ratio increases.

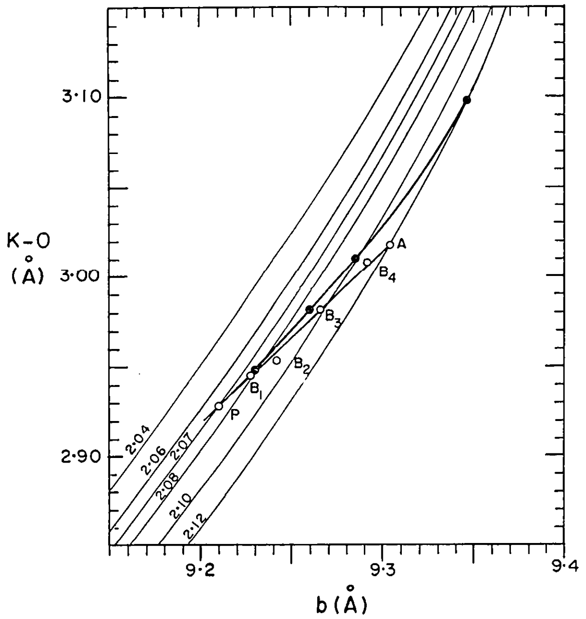

Fig. 5. Nomogram giving K–O from observed b and literature value of d_o (2·04 to 2·12) for $d_t = 1{\cdot}66$. P = phlogopite, B_1 to B_4 = biotites, A = annite. Synthetic. Data from Wones (1963b, Table 4); white and black circlets indicate two series of experiments with differing oxygen fugacities.

tions of the crystal structures in solid-solution series need not be restricted to micas or even to sheet structures. Tourmalines, pyroxenes, amphiboles, possibly also silicon-framework structures, might be tackled in a similar fashion once a few of their structures have been refined for known compositions. This approach should be of some help to structural mineralogists who want to understand the reasons for observed solid-solution ranges and changes in properties with compositions, but who cannot hope to determine *all* the structures in the range they wish to consider.

Note added in proof. — The paper on the crystal structure of biotites by Franzini & Schiaffino (1963) reached us after we submitted our manuscript for publication.

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References

Bradley, W. F. (1958). *Proc. Sixth Nat. Conf. Clays and Clay Minerals*, 18.

Donnay, G., Morimoto, N., Takeda, H., and Donnay, J. D. H. (1964). *Acta Cryst.* **17**, 1369.

Eugster, H. P. & Wones, D. R. (1962). *J. Petrology*, **3**, 82.

Forman, S. A. (1951). *Amer. Min.* **36**, 450.

Franzini, M. & Schiaffino, L. (1963). *Z. Kristallogr.* **119**, 297.

International Tables for X-ray Crystallography (1962). Vol. III, p. 258. Birmingham: Kynoch Press.

Kohn, J. A. & Hatch, R. A. (1955). *Amer. Min.* **40**, 10.

Mathieson, A. McL. & Walker, G. F. (1954). *Amer. Min.* **39**, 231.

Newnham, R. E. & Brindley, G. W. (1956). *Acta Cryst.* **9**, 759.

Radoslovich, E. W. (1959). *Nature, Lond.* **183**, 253.

Radoslovich, E. W. (1960). *Acta Cryst.* **13**, 919.

Radoslovich, E. W. (1961). *Nature, Lond.* **191**, 67.

Radoslovich, E. W. (1962). *Amer. Min.* **47**, 617.

Radoslovich, E. W. (1963*a*). *Amer. Min.* **48**, 76.

Radoslovich, E. W. (1963*b*). *Amer. Min.* **48**, 348.

Radoslovich, E. W. (1963*c*). *Amer. Min.* **48**, 368.

Radoslovich, E. W. (1963*d*). *Proc. Int. Clay Conf.*, Stockholm, Sweden. In the press.

Radoslovich, E. W. & Norrish, K. (1962). *Amer. Min.* **47**, 599.

Sadanaga, R. & Takéuchi, Y. (1961). *Z. Kristallogr.* **116**, 406.

Sanero, E. (1940). *Period. Miner.* **11**, 53.

Steinfink, H. (1958). *Acta Cryst.* **11**, 191.

Steinfink, H. (1962). *Amer. Min.* **47**, 886.

Takéuchi, Y. & Donnay, G. (1959). *Acta Cryst.* **12**, 465.

Takéuchi, Y. & Sadanaga, R. (1959). *Acta Cryst.* **12**, 945.

Veitch, L. G. & Radoslovich, E. W. (1963). *Amer. Min.* **48**, 62.

Wones, D. R. (1963*a*). *Amer. J. Sci.* **261**, 581.

Wones, D. R. (1963*b*). *Amer. Min.* **48**, 1300.

Yamzin, I. I., Timofeyeva, V. A., Shashkina, T. I., Belova, E. N. & Gliki, N. V. (1955). *Mém. Soc. russe Min.* ser. 2, **84**, 415. (*Min. Abst.* **13**, 419).

Yoder, H. S. & Eugster, H. P. (1954). *Geochim. Cosmochim. Acta*, **6**, 157.

Zvyagin, B. B. & Mishchenko, K. S. (1962). *Kristallografiya*, **7**, 623.