

## Layer deformation and crystal energy of micas and related minerals. I. Structural models for 1M and 2M<sub>1</sub> polytypes

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### Abstract

Tetrahedral rotation, flattening of the octahedral layer, and counter-rotation of oxygen triads in dioctahedral layers are used to construct models for (trioctahedral) 1M micas and (dioctahedral) 2M<sub>1</sub> micas. The tetrahedral rotation is taken to be the only deformation 'in plan' in the ideal 1M mica. The octahedral rotation in 2M<sub>1</sub> micas flattens the hexagon formed by the apical oxygens of the tilting tetrahedra, and increases the monoclinic angle  $\beta$ . The interlayer K-O bondlength is estimated with a coordination correction which depends on the tetrahedral rotation. The octahedral thickness in 1M micas can be deduced from chemical analysis, but the octahedral rotation in 2M<sub>1</sub> micas prohibits such an approach.

The comparison of structure refinements with the 2M<sub>1</sub> model shows a lower observed potassium shift, due to a lower observed tilting. The tilting is suggested to be counteracted by the tendency of the highly-charged tetrahedral cations to equalize their mutual distances.

### Introduction

The misfit of ideal octahedral and tetrahedral layers in sheet silicates gives rise to deformations from the ideal coordination units. An ideal octahedron with equilateral faces has an edge-length of  $r_{M^{(6)}O}\sqrt{2}$  and a height of  $r_{M^{(6)}O}/\sqrt{3}$ , where  $r_{M^{(6)}O}$  = length of cation-oxygen bond in six-coordination. Likewise, an ideal tetrahedron, also with equilateral faces, has an edge-length of  $r_{M^{(4)}O}\sqrt{8/3}$ , and a height of  $r_{M^{(4)}O}/3$ . The mica unit-cell with ideal geometrical units then should have a  $b$  dimension, of 3 octahedral side-lengths, varying from 8.15Å to 9.03Å for Al and Fe<sup>2+</sup> respectively. The ideal tetrahedral  $b$  dimension, with two side-lengths multiplied by  $\sqrt{3}$ , varies in a similar way from 9.07Å to 9.40Å, for Si and Si<sub>2.5</sub>Al<sub>1.5</sub> respectively.

These differences are compensated by the following distortions:

- The octahedra are flattened into trigonal antiprisms, increasing the edge-length with constant  $r_{M^{(6)}O}$  (Donnay *et al.*, 1964).
- In dioctahedral forms, a counter-rotation of upper and lower oxygen triads of the octahedral layer diminishes cation-cation repulsion, and  $b$  is increased even more (Newnham, 1961; Radoslovich, 1963a).
- The tetrahedra are lengthened along  $c'$ , thus shortening the basal edge-length, but, more importantly,

they are rotated along  $c'$ , thereby allowing an increase in the basal edge-length with constant  $b$  (Radoslovich and Norrish, 1962).

These deviations from ideality have been found to be present in all sheet-silicates, and have been used to explain general compositional and structural variations (Radoslovich, 1963b), trace-element variations (Hazen and Wones, 1972), and have been used to predict the 1M structure from composition and cell dimensions (Franzini and Schiaffino, 1963; Donnay *et al.*, 1964; Tepikin *et al.*, 1969). The distortions permit a wide range of substitutions, which make mica chemistry complex and obscure. If, however, the crystalline form is the reflection of ordering and more favorable substitution series, the distortions should be an expression of an energy advantage in the natural system. An investigation is thereby proposed into the geochemistry of micas and related minerals by means of crystal-energy calculations on the structural models suggested here (*cf.* Appelo, 1977). Two polytypes are considered: the 1M form for trioctahedral phlogopites and biotites, and the 2M<sub>1</sub> form for dioctahedral muscovites and phengites.

### 1M micas

All structural models are based on the original definition for the tetrahedral rotation  $\alpha$  by Radoslov-

ich and Norrish (1962), *i.e.* the Si-Si-O angle in orthoprojection along  $c'$ . If the basal oxygen triads remain equilateral when rotated around the ortho-projected Si position, this angle can be found as the deviation of the basal edge from the undeformed hexagonal network of basal oxygens. In terms of cell dimensions, it is found as  $\alpha = \arccos(a/2O_{bb})$ , where  $O_{bb}$  is the basal edge-length, see Figure 1. The coordinates of the ions can be estimated from unit-cell dimensions and chemical analysis, which gives  $r_{M-O}^{(4)}$  and  $r_{M-O}^{(6)}$ .

Donnay *et al.* (1964) take the tetrahedra to be regular and find the tetrahedral thickness  $t_t$  and  $\alpha$  as described before. The octahedral thickness can be estimated if the octahedral layer is flattened only, and remains regular in projection along  $c'$ . With this information and known unit-cell dimensions, the structure is wholly defined. Franzini and Schiaffino (1963) use a one-dimensional Fourier synthesis along  $c'$  to obtain the thicknesses of the different units, and also calculate the tetrahedral rotation from the interlayer thickness with a constant K-O distance. Their model was applied again by Tepikin *et al.* (1969), who extended it with additional geometrical relationships.

There is a general agreement between mica-model predictions and observed structures. Differences exist, however, depending on the choice of the variables. The tetrahedra for example are elongated along  $c'$ , which gives smaller basal edge-lengths than predicted from  $r_{M-O}^{(4)}$ , and results in too large an estimated  $\alpha$ , especially at smaller angles. McCauley and Newnham (1971) have proposed an empirical relation between  $r_{M-O}^{(4)}$  and  $\alpha$ , which fits the smaller angles as well. The interlayer K-O distance was found to be highly variable (Donnay *et al.*, 1964), and consequently the interlayer thickness has to be considered as a dependent variable, although Drits (1969) suggested a constant interlayer volume for trioctahedral micas. In the present study an effort is made to define the 1M structure from chemical analysis and unit-cell data, using the results of new structure refinements to estimate  $t_t$  and  $t_i$  as dependent variables.

#### Interlayer thickness $t_i$

As a result of the tetrahedral rotation, the coordination around the interlayer cation changes from 12-coordination with  $\alpha = 0^\circ$  to 6-coordination at the maximal  $\alpha = 30^\circ$ . To correct for such coordination effects, Pauling (1960) has used a formula derived from the Born model for the lattice energy:

$$r_{M-O}^{(x)} = r_{M-O}^{(y)} \left\{ \frac{A_x B_y}{A_y B_x} \right\}^{1/(n-1)}$$

where  $A_y$  and  $B_y$  are the Madelung constant and the repulsive coefficient of structure  $y$  respectively, and  $n$  the Born exponent. Pauling then takes the ratio of the coefficients  $B$  to be equal to the ratio of the coordination numbers, and neglects small differences in the Madelung sums (which, in our case, ought to be replaced by the lattice-site potentials of the interlayer cation and surrounding oxygens).

Using the values of  $r_{K-O_i}$  of 18 structure refinements, quoted in Table 1, the following regression equation is obtained, with  $R^2 = 0.945$ :

$$r_{K-O_i}^{(\alpha)} = 3.15 (\sqrt{3} - \tan \alpha) / (\sqrt{3} + \tan \alpha)^{0.40} \quad (1)$$

where the term  $(\sqrt{3} - \tan \alpha) / (\sqrt{3} + \tan \alpha)$  is the ratio of the orthoprojected distances to the inner and outer oxygens. The low value of the Born exponent,  $n = 3.5$ , which should be about 8, is possibly caused by the neglect of existing potential differences. Also, the equation leads to improbable values for  $\alpha > 15^\circ$ , *i.e.*  $r_{K-O} < 2.78\text{A}$ .

The interlayer thickness is now found from the orthoprojection

$$r'_{K-O_i} = (\sqrt{3} - \tan \alpha)b/6, \quad \text{and}$$

$$t_i = 2\sqrt{r_{K-O_i}^2 - (r'_{K-O_i})^2}.$$

As a result of the decreasing K-O bondlength, the interlayer separation decreases slightly with increasing tetrahedral rotation. The constancy of the interlayer volume, as stated by Drits (1969), is in good agreement with the present model, although a somewhat larger value was suggested:  $173\text{A}^3$  *vs.*  $\sim 164\text{A}^3$  here.

#### Tetrahedral thickness $t_t$

Takeda and Burnham (1969) suggested that the tetrahedral elongation is the result of electrostatic interactions with the octahedral layer. As such, the elongation is considered the result of a relatively low (positive) potential at the apical oxygen site, making the tetrahedral lengthening a function of the octahedrally-offered positive charge. We found that the difference in oxygen site potentials is compensated if the tetrahedra are lengthened and at the same time rotated less to keep a constant  $r_{M-O}^{(4)}$ . Thereby, the Madelung sum of the structure also decreases for all effective charges on silicon.

We thus rely on experimental observations from

Table 1. K-O bondlengths and tetrahedral rotations from structure refinements

mica, polymorph	$r_{K-O_i}$ (Å)	$\alpha$ (degrees)	reference
biotite, 1M	3.13	1.0	Tepikin et al. (1969)
biotite, 1M	3.144	1.54	Hazen and Burnham (1973)
lepidolite, 2M <sub>2</sub>	2.980	5.30	Takeda et al. (1971)
synt. F-phlogopite, 1M	3.004	5.88	McCauley et al. (1973)
phengite, 2M <sub>1</sub>	2.970	6.02	Güven (1967)
synt. Li,F-phlogopite, 1M	2.995	6.22	Takeda and Donnay (1966)
lepidolite, 2M <sub>1</sub>	2.97	6.4	Sartori (1977)
lepidolite, 2M <sub>2</sub>	2.976	6.45	Sartori et al. (1973)
lepidolite, 1M <sup>2</sup>	2.942	7.41	Sartori (1976)
phlogopite, 1M	2.969	7.54	Hazen and Burnham (1973)
phlogopite, 1M	2.970	7.67	Joswig (1972)
Al-mica, 1M	2.93	8.3	Soboleva and Zvyagin (1969)
phlogopite, 1M	2.965	8.65	Rayner (1974)
mica, 2M <sub>2</sub>	2.86	11.3	Zhoukhlstov et al. (1973)
muscovite, 2M <sub>1</sub>	2.855	11.37	Güven (1967)
muscovite, 2M <sub>1</sub>	2.857	11.42	Rothbauer (1971)
muscovite, 3T <sup>1</sup>	2.868	11.84	Güven and Burnham (1967)
muscovite, 2M <sub>1</sub>	2.85	13.0	Birle and Tettenhorst (1968)

which an average lengthening of 0.03 to 0.05 Å is found to be satisfactory. From this follows that the edge-lengths to the apical oxygen can be calculated as  $O_{ab} = \sqrt{t_i^2 + O_{bb}^2/3}$ , and with the tetrahedral cation at equidistance from the four oxygens  $r_{M^{(4)}O} = O_{ab}^2/2t_i$ . The amount of tetrahedral Al substituting for Si can be found from above value using the linear relationship, e.g. from Jones (1968):  $f_{Al} = (r_{M^{(4)}O} - 1.603)/0.158$ .

#### Octahedral thickness $t_o$

It has been shown by several authors (Brindley and MacEwan, 1953; Faust, 1957; Radoslovich, 1962; Drits, 1969), that the  $b$  dimension of the mica unit cell can be expressed as a function of the octahedral cations (with different ionic radii). The coefficients in such equations are not, however, directly related to the crystal radii (Radoslovich, 1962), because of

Table 2. Intercepts of regression of  $b$  on octahedral cations in 1M micas

cation "M <sup>(6)</sup> "	intercept	crystal-radius	$t_o$	O-O shared
Mg <sub>2+</sub>	3.135 ± .004	2.08	2.18	2.81
Fe <sub>2+</sub>	3.224 ± .01	2.12	2.25	2.88
Fe <sub>3+</sub>	3.14 ± .04	2.04	2.0	2.7
Al	3.05 ± .04	1.92	1.6	2.4

changing octahedral thicknesses and additional distortions in dioctahedral micas. The octahedral thickness can be estimated as the remaining term, when  $t_t$  and  $t_i$  are calculated from cell dimensions and tetrahedral Al. Another approach would be to proceed from regression equations on the  $b$  axis in which a variable  $t_o$  is implicitly accounted for. For 1M micas this leads to:

$$b^2/27 = (r_{M^{(6)}O}^2)^2 - t_o^2/4 + \sum_{n \neq m} f_n (b_n^2/27 - b_m^2/27)$$

in which  $f_n$  stands for the fraction of cation  $n$  in the octahedral layer, and the intercept of the regression equation gives  $(r_{M^{(6)}O}^2)^2 - t_o^2/4$ , for the cation  $m$  not included in the regression. This exclusion is, in fact, necessary to do the regression on variables which are at least theoretically independent. The independency largely determines the stability of the intercept. Using part of the data given by Radoslovich (1962), supplemented by structure refinements of 1M micas and data by Hall (1968), we found the intercepts for 38 trioctahedral micas (Table 2).

The very stable intercepts found of Mg and Fe<sup>2+</sup> lead to values  $t_o$  and oxygen distances over shared edges of the octahedra which agree with values found in structure refinements. The very short O-O distances found for Fe<sup>3+</sup> and Al point to distortions

which we shall discuss in the section on  $2M_1$  micas. Due to these distortions, it is necessary to have the cell dimensions from which the octahedral thickness can be calculated as dependent variables (Hazen and Wones, 1972).

As a result of comparatively short O4–O4 shared distances of hydroxyls and fluorine, the O4 ion is depressed into the octahedral layer. It is difficult to account for this, although one may propose a constant O4–O4 distance of 2.64Å for phlogopites.

For the OH distance 1.0Å is taken, consistent with the value found by Joswig (1972) through neutron diffraction. Rayner (1974), using the same technique, found a somewhat shorter distance of 0.93Å in a sample which contained less fluorine. This may indicate a random location of H and F, if present, contrary to a suggestion by Wones (in Hazen and Burnham, 1973), but consistent with the 1M cell (and the very low  $R = 0.020$  obtained by Joswig).

#### Structural model for 1M micas

With the thickness of the structural units defined, or found from cell dimensions, only the  $a$  and  $b$  coordinates of the basal oxygens of the tetrahedral sheet need further definition in terms of  $\alpha$ . This is done most easily from the ideal O3 positions in the octahedral sheet, the projected distance between O3

and O1,2 without rotation being  $b/6$  (see Fig. 1). From this the  $X$  displacement of O2 is found to be  $\Delta X_{O_2} = -b \tan(\alpha)/6$ . This displacement is separated in a  $X$  and  $Y$  direction for O1, giving respectively  $\Delta X_{O_1} = b \tan(\alpha)/12$ , and  $\Delta Y_{O_1} = b\sqrt{3} \tan(\alpha)/12$  (cf. also Donnay *et al.*, 1964). Table 3 summarizes the model. Comparisons between estimated and known structures will be given in a later paper.

#### $2M_1$ micas

In the dioctahedral micas, the plane of the oxygens in the octahedral layer can no longer be considered ideal, because of an additional shortening of O–O distances over shared edges. From a geometrical point of view, this shortening has been described as opposite rotations of the upper and lower oxygen triads around the filled cation site (Newnham, 1961). The rotation results in two smaller cation sites, and one larger empty site in the dioctahedral micas (Veitch and Radoslovich, 1963). The rotation angle  $\omega$  can now be defined both from the deviation from  $30^\circ$  of the Al–Al–O angle in plan, and from the corners of the hexagon formed by the apical oxygens, four corners being deformed to  $120^\circ - \omega$ , and two corners to  $120^\circ + 2\omega$ , see Figures 2 and 3a. Note that the hexagon is flattened by the rotation, and that the angle  $\omega$  is not to be found from the average deviations of

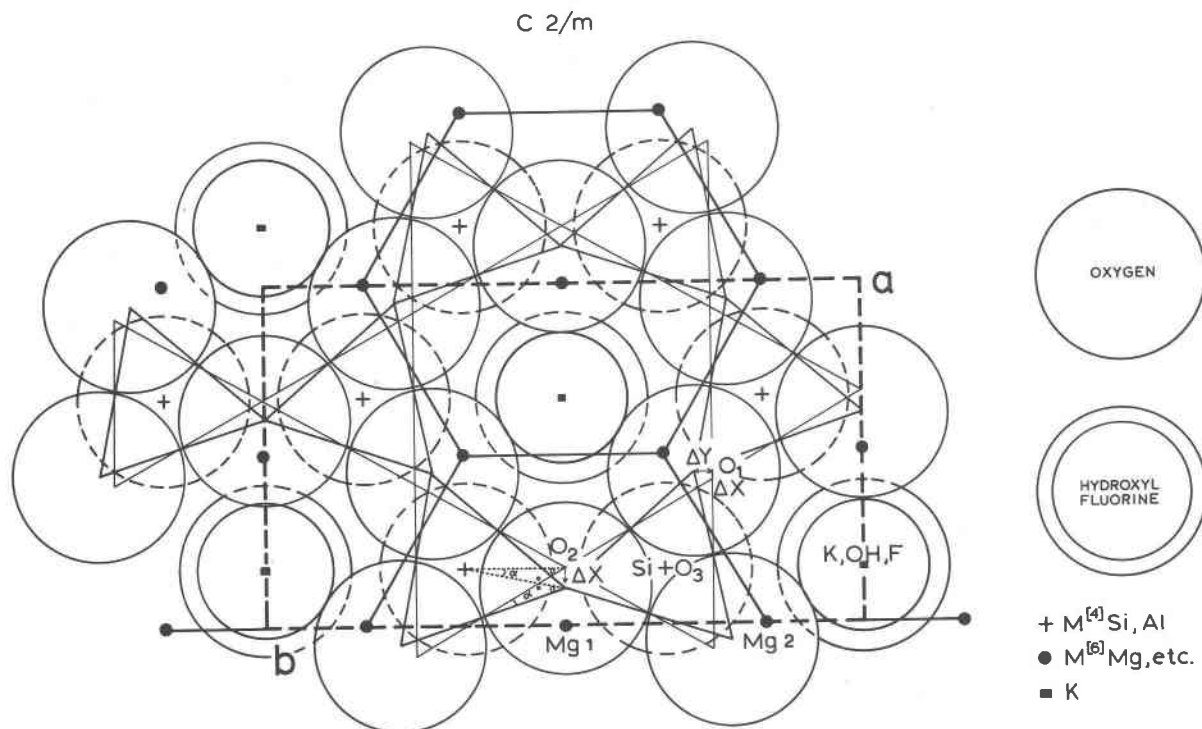


Fig. 1. 1M mica unit cell, projected along  $c'$ , with oxygens drawn approximately to scale.

Table 3. Structural model for 1M micas, space group C2/m

	X/a	Y/b	Z/c
K	0	0	0
M1 (6)	0	1/2	1/2
M2 (6)	0	1/6	1/2
M (4)	$-Z\cos(\beta)/a$	1/3	$(t_t - r_{M-O}^{(4)} + t_i/2)/c'$
O1	$Y/b - Z\cos(\beta)/a$	$1/4 + \tan(\alpha)\sqrt{3}/12$	$t_i/2c'$
O2	$-\tan(\alpha)\sqrt{3}/6 - Z\cos(\beta)/a$	1/2	$t_i/2c'$
O3	$-Z\cos(\beta)/a$	1/3	$1/2 - t_o/2c'$
O4	$-Z\cos(\beta)/a$	0	$1/2 + (\Delta - t_o/2)/c'$
H	$-Z\cos(\beta)/a$	0	$Z_{O4} - 1/c'$

Data:  $b, c', f_{Al}^{(4)}$

$$a = b/\sqrt{3} \quad \beta = 90^\circ + \arctan(a/3c')$$

$$c = c'/\sin \beta$$

$$r_{M-O}^{(4)} = 1.603 + 0.158f_{Al}^{(4)} = (t_t^2 + O_{bb}^2/3) / 2t_t$$

$$\text{tetrahedral thickness } t_t = O_{bb} \sqrt{2/3} + 0.03$$

$$\text{tetrahedral basal edge-length } O_{bb} = a/2\cos \alpha$$

$$\text{interlayer thickness } t_i = 2\sqrt{r_{K-O_i}^2 - \{(\sqrt{3} - \tan(\alpha))b/6\}^2}$$

$$\text{octahedral thickness } t_o = c' - t_i - 2t_t$$

$$\text{hydroxyl depression } \Delta = t_o/2 - \sqrt{(1.32)^2 - (a/6)^2}$$

(suggested value for phlogopite)

} Iteration used to calculate  $t_t, O_{bb}, \alpha$ .

interatomic angles from  $120^\circ$ . The flattening of the apical hexagon is accompanied by a shift along [110]. This results in a markedly larger monoclinic angle  $\beta = 90^\circ + \arctan(a/3c')$ . This divergence between the observed and calculated value of  $\beta$  can in fact be used to estimate the octahedral rotation, although some difficulties appear in the tetrahedral and interlayer region which will be discussed later.

It has been noted that the different distances between the apical oxygens lead to a tilting of the tetrahedra towards the longer distance (Newham, 1961). However, the planes (220) remain equally spaced, because the octahedral rotation does not affect the hexagonal relation  $a = b/\sqrt{3}$ . It follows then that the tilting cannot compensate for the different distances between the apical oxygens if the basal triangles are to remain equilateral. Rather, the tilting is the result of a redistribution of repulsive forces among the tetrahedral oxygens, equalizing their mutual distances as far as is expedient. Structure refinements of 2M<sub>1</sub> micas generally show a slightly larger distance from the apical oxygen towards the depressed oxygen than towards the outward bulging oxygens. The difference is significant but small, and

we will assume that the tetrahedral edge-lengths towards the apex remain equal, elongating the basal triangle towards the depressed oxygen. All tetrahedra are taken to be of similar shape, and hence the basal face becomes equilateral again in the orthoprojection along  $c'$ .

Just as in the 1M structural model, we consider the octahedral thickness and the depression of hydroxyl and fluorine as given quantities which can be estimated, however, from known values of  $b$ , the crystal radii of the ions in the octahedral sheet, and the octahedral rotation  $\omega$ . The displacements of the ions as a result of the different distortions can now be found from simple geometrical calculations (Figs. 2 and 3).

#### Octahedral oxygens

The displacement of O5 (Fig. 3a) is in the  $X$  direction only, being  $\Delta X_{O5} = -\{\tan 30^\circ - \tan(30^\circ - \omega)\}b/6$ . For O4, this displacement is separated in an  $X$  and  $Y$  direction, giving  $\Delta X_{O4} = -\Delta X_{O5} \cos 60^\circ$ , and  $\Delta Y_{O4} = -\Delta X_{O5} \sin 60^\circ$ . The same displacements are found for the hydroxyl position O6, with the exception that  $\Delta Y_{O6} = -\Delta Y_{O4}$ .

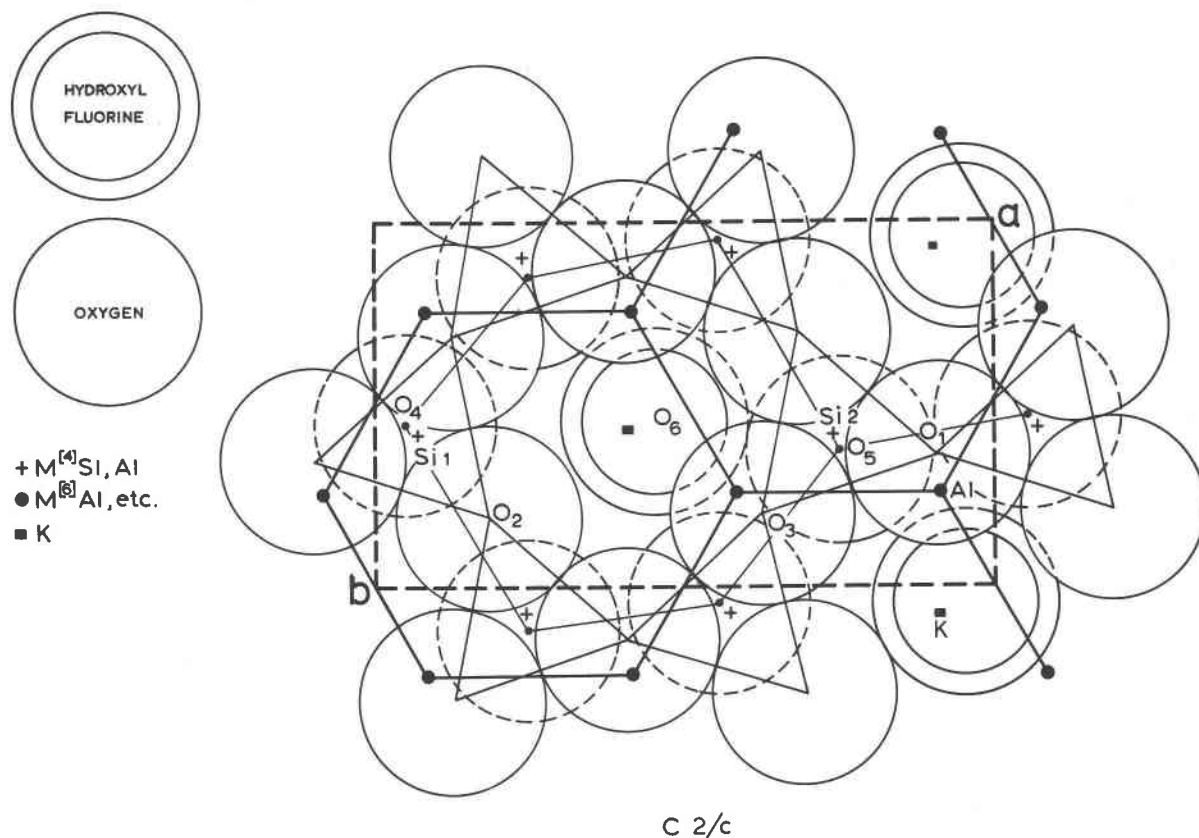


Fig. 2. 2M<sub>1</sub> mica unit cell, projected along  $c'$ , with oxygens drawn approximately to scale.

The hydrogen position is presumably a function of the octahedral rotation, but data are lacking, the only values being from infrared absorption studies and Rothbauer's (1971) neutron-diffraction refinement. Giese (1971) has calculated angles for Radoslovich's (1960) muscovite refinement from electrostatic energy calculations. With the present state of knowledge, we take the hydrogen position at fixed distance and angles to O<sub>6</sub>, using the values given by Rothbauer, who found it positioned along [110], and O<sub>6</sub>-H at an angle of 78° with  $c'$ .

#### Basal oxygens

The  $X/Y$  displacements of the basal oxygens can be found most easily from the orthoprojection onto the octahedral sheet. Because the basal faces become equilateral upon projection along  $c'$ , the tetrahedral rotation  $\alpha$  can be described from the positions of the apical oxygens. This follows from O<sub>5</sub> being midway between O'1-O'3, with a projected distance changing as  $1/\cos \alpha$ , just like the basal edge-length O<sub>1</sub>-O<sub>3</sub>, which holds the angle O<sub>5</sub>-O'1-O'3 equal. With O<sub>4</sub> and O<sub>5</sub> remaining at equal distances to both Al posi-

tions and to the projected O'1 and O'3 positions, the tetrahedral rotation shifts O'1 and O'3 towards the Al positions along the projection of Al onto O'5-O'4. The shorter distance between the apical oxygens O<sub>5</sub> and O<sub>4</sub> is seen (Fig. 3a) to be  $b\sqrt{3}/6\cos(30^\circ - \omega)$ , and the Al-O'1, O'3 distances are calculated to be  $\text{Al-O}'_{1,3} = (\tan 30^\circ - \tan \alpha)b/12 \cos(30^\circ - \omega)$ . Multiplication by  $\cos \omega$  and  $\sin \omega$  respectively gives the  $X$  or  $Y$  component of O<sub>1</sub> relative to the (fixed) Al site. The  $X$  and  $Y$  components of the O<sub>3</sub> site are found in a similar way with reference to the next Al along  $b$ , by multiplying Al-O'3 by  $\cos(60^\circ - \omega)$ , and  $\sin(60^\circ - \omega)$  respectively.

The displacement of O<sub>2</sub> is elucidated in Figure 3b. The octahedral rotation shifts this ion site the amount  $b\sin\omega/6\sqrt{3}\cos(30^\circ - \omega)$ , and rotation of the tetrahedra moves this ion in just the opposite direction the amount  $\{1 + \sin\omega/\cos(30^\circ - \omega)\}b\tan(\alpha)/6$ . The net displacement is along [110], and is simply related to  $X$  and  $Y$  components.

The  $c'$  coordinates of the basal oxygens can be calculated from the apical edge-length  $O_{ab} = \sqrt{(O_{bb}\sqrt{2/3} + 0.07)^2 + O_{bb}^2/3}$ , and the ortho-

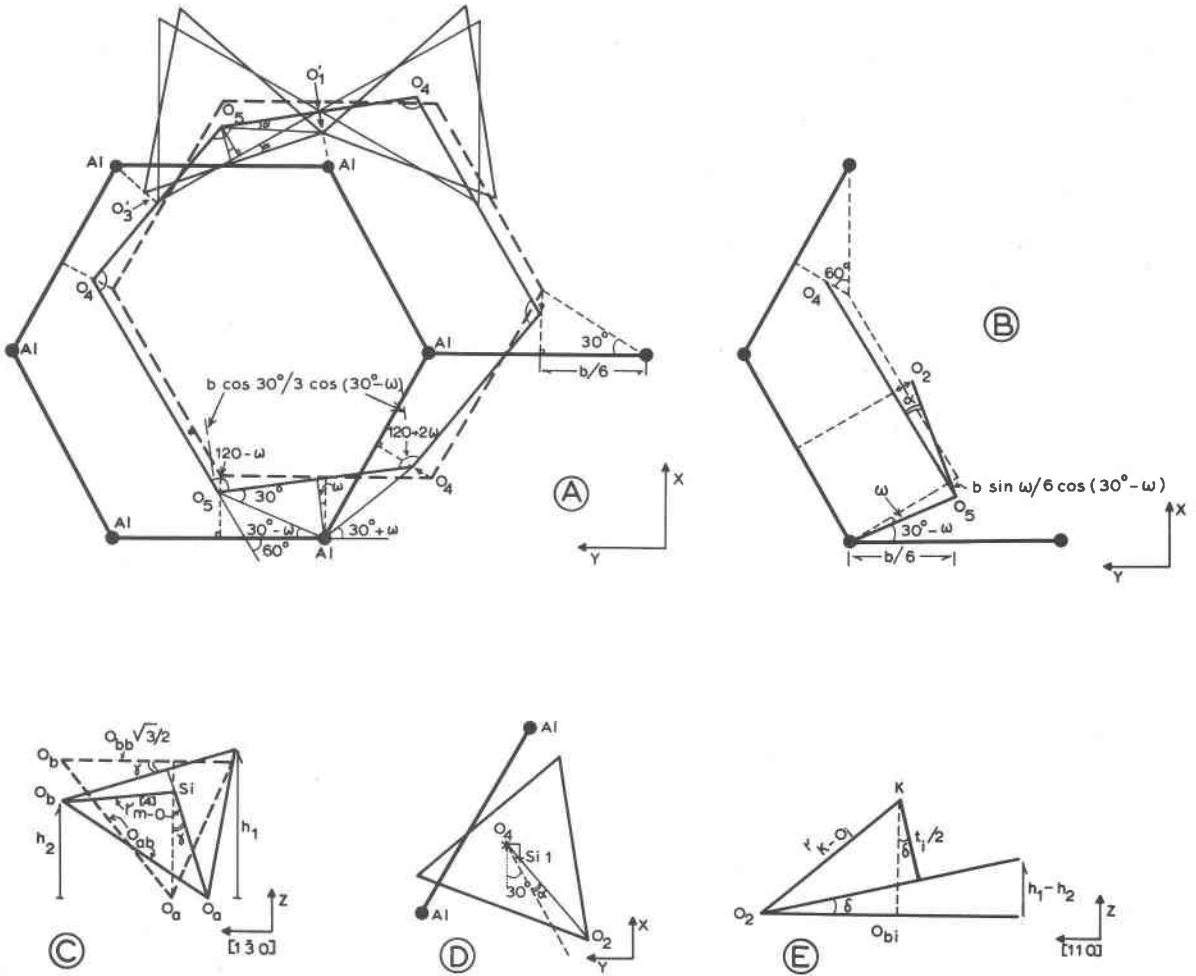


Fig. 3. Geometrical relationships in 2M<sub>1</sub> micas.

projected distances to the apical oxygen. The latter are found as illustrated in Figures 3a,b:

$$O'1,3-O5 = b/6\sqrt{3}\cos(30^\circ-\omega)\cos\omega \text{ and}$$

$$O'2-O5 = \{1 + \sin\omega/\cos(30^\circ-\omega)\}b/6\cos\alpha.$$

The height of O1 and O3 above the apical oxygens is then:  $h_1 = \sqrt{O_{ab}^2 - (O'1,3 - O5)^2}$ , and, similarly of the depressed O2:  $h_2 = \sqrt{O_{ab}^2 - (O'2 - O5)^2}$ . The equal height of O1 and O3 allows the shorter basal edge-length  $O_{bb}$  to be found as  $O_{bb} = a/2\cos\alpha$ , as in 1M micas. The relation to the size of the tetrahedral cation is somewhat more complex, and iteration is necessary when the tetrahedral rotation is to be estimated from chemical analysis and  $b$ . The same holds for the tetrahedral tilting, which can be expressed as the height-difference  $h_1 - h_2$ , or as the angle of tilting  $\gamma = \arctan \{2(h_1 - h_2)/O_{bb}\sqrt{3}\}$  (Fig. 3c).

*Tetrahedral cation*

The tetrahedral cation site is assumed to be equidistant from the oxygens, and the cation-oxygen distance can be found, as before, from  $r_{M-O}^{(4)} = O_{ab}^2/2t_t$ , where the tetrahedral thickness is now calculated from:

$$t_t = \sqrt{O_{ab}^2 - (O_{bb} \{ \cos^2\gamma + 3 \} / 4\cos\gamma)^2} / 3,$$

see Figure 3c. The X/Y displacements are along the line O'2-O4,5, and can be expressed simply from the orthoprojected position above the apical oxygens, e.g. for Si1 above O4 (cf. Fig. 3d):

$$\Delta X_{Si1} = -r_{M-O}^{(4)} \sin\gamma\cos(30^\circ+\alpha)$$

$$\Delta Y_{Si1} = -r_{M-O}^{(4)} \sin\gamma\sin(30^\circ+\alpha)$$

and in a similar way for Si2 above O5.

*Interlayer cation*

The interlayer cation also is assumed to remain centered between the coordinating (inward-rotating) basal oxygens. It is thus shifted along [110] due to the octahedral rotation, additionally by the tilting over the interlayer plane, and back again due to tetrahedral rotation. It is easy to proceed from the angle of interlayer tilting  $\delta$ , defined from the tetrahedral tilt  $h_1 - h_2$  over the interlayer coordination triad:  $\delta = \arctan \{(h_1 - h_2)/O_{bi}\}$ , where  $O_{bi} = O_{bb}\sqrt{3}\cos(30^\circ + \alpha)$  is the distance of O2 projected onto O1-O3 around the interlayer cation.

It is now a simple matter to find the interlayer thickness, if equation (1) holds, which gives  $r_{K-O_i}$ . Figure 3e shows that

$$t_i/2 = \sqrt{r_{K-O_i}^2 - (O_{bi}\cos^2\delta + 3/6\cos\delta)^2}$$

and the additional shift due to tilting is found as

$$t_i\sin(\delta)/2 + 2O_{bi}\{1 - (\cos^2\delta + 3)/4\}/3 \quad (2)$$

The shift due to octahedral and tetrahedral rotation can be found from the  $b$  shift of the O1 site, projected onto [110]. The O1 oxygen forms the top corner of the projected equilateral triangle formed by the apical oxygens, and shifts along [110] the amount:

$$bsin\omega\{\tan 30^\circ - \tan \alpha\}/6\cos(30^\circ - \omega). \quad (3)$$

The net displacement of the K ion from its ideal position with respect to an undistorted octahedral layer then is  $\Delta K = (2) + (3)$ . This shift is along [110], and thus results in  $\Delta Y_K = \Delta K \cos 30^\circ$  and  $\Delta X_K = -\Delta K \sin 30^\circ$ . Coming at the end now, the height of the interlayer cation with respect to O2 is:  $t'_i/2 = t_i\cos(\delta) + 2 + O_{bi}\tan\delta(\cos^2\delta + 3)/6$ , and the structure is wholly defined, with the monoclinic angle  $\beta$  calculated from the  $X$  shift of the K ion over two layers:

$$\beta = 90^\circ + \arctan(\{(a/3) - 4\Delta X_K\}/c'). \quad (4)$$

Table 4 presents a summary of the estimated positions of the ions. It is of interest that the structure can be calculated from the cell parameters and the chemical analysis giving Al<sup>(4)</sup>, from which  $r_{M^{(4)}-O}$  is obtained. An iterative procedure has to be used, in which the octahedral rotation  $\omega^*$  is first estimated from the  $X$  shift of K due to octahedral rotation along, *i.e.* assuming tetrahedral distortions to be absent. This value of  $\omega^*$  can then be used to calculate the tetrahedral tilting and rotation from  $r_{M^{(4)}-O}$ , which is incorporated in a new value of the octahedral rotation, *etc.* The shift of  $\beta$  due to octahedral rotation alone can be found from (2), (3), and (4),  $\delta$  and  $\alpha = 0$ :

$$\beta = 90^\circ + \arctan(\{(a/3) + b\{\tan 30^\circ - \tan(30^\circ - \omega)\}/6\}/c'),$$

which gives, with  $a = b/\sqrt{3}$ :

$$\omega^* = 30^\circ - \arctan(\sqrt{3} - 6c'\tan(\beta - 90^\circ)/b).$$

With  $\beta \simeq 95.7^\circ$ , this formula gives values for  $\omega^* \simeq 8^\circ$  which are close to the values (6.9–8°) found in the refinements by Güven (1967) and Rothbauer (1971). Incorporation of the backward shift due to tetrahedral rotation and forward shift due to tilting gives less satisfactory results, the values found in an iterative procedure being  $\sim 5^\circ$ . The reason lies in the overestimated tilting of the interlayer region, which is somewhat smaller than estimated due to lengthening of O4,5-O2 distances, and also has less effect in the term  $t_i\sin(\delta)/2$  because of shorter K-O<sub>i</sub> distances to the outward bulging oxygens.

For a comparison between the predicted and observed structure it was decided to take the actual value of  $\omega$ , and compare ion sites in an orthogonal cell along  $c'$ . Table 5 gives the results for Güven's phengite refinement and the neutron-diffraction refinement of muscovite by Rothbauer. The observed value of  $\alpha$  leads to coincident values for  $r_{M^{(4)}-O}$ , both for muscovite and the disordered tetrahedra in phengite. If in this way  $r_{M^{(4)}-O}$  was estimated in a reliable manner from chemical analysis, practically identical results would have been obtained. However, the comparisons presented here are given to validate the abstraction of the 2M<sub>1</sub> structure into formal geometrical relationships.

Several interesting features can be observed from the discrepancies between predicted and observed structures. Thus, apart from the shortening of the shared edges of the octahedra described as octahedral rotation, the oxygens also shift along Al-Al, shielding the octahedral cations still more with already very short O-O distances at  $\sim 2.4\text{Å}$ . More significant are the discrepancies in the tetrahedral and interlayer region, notably of K, which is far less shifted along [110] than predicted, resulting thus in too high  $\beta$  in the predicted structure. Neither the use of the observed K-O distance nor of the observed tetrahedral tilting, or both, decrease the predicted  $\beta$  to any great extent, because K is shifted towards the O1,3 oxygens.

The overestimate of the tetrahedral tilting gives a rather low estimated octahedral thickness, especially in phengite, where however the tetrahedral ordering has not been accounted for. The lower observed tilting is possibly due to the observed shift of the tetrahe-



Table 4. Structural model for 2M<sub>1</sub> micas, space group C2/c

	X/a=0		
K	Y/b=1/12 + √3/2 { sin ω(tan 30°-tan α)/6cos(30°-ω) + cos(30°+α){1-(cos <sup>2</sup> (δ)+3)/4}/3cos α + t <sub>1</sub> sin(δ)/2b}		
	Z/c=1/4		
	X/a=1/4		
M (6)	Y/b=1/12		
	Z/c=0		
	X/a=(X/a) <sub>O4</sub> - r <sub>M-O</sub> <sup>(4)</sup> sin(γ)cos(30°+α)/a - (Z <sub>M1</sub> -Z <sub>O4</sub> )cos(β)/a		X/a=1/2 - tan(30°-ω)/4√3 - Z <sub>O4</sub> cos(β)/a
M1 (4)	Y/b=(Y/b) <sub>O4</sub> - r <sub>M-O</sub> <sup>(4)</sup> sin(γ)sin(30°+α)/b	O4	Y/b=1 - tan(30°-ω)/4√3
	Z/c={r <sub>M-O</sub> <sup>(4)</sup> cos γ + t <sub>O</sub> /2}/c'		Z/c=t <sub>O</sub> /2c'
	X/a=(X/a) <sub>O5</sub> + r <sub>M-O</sub> <sup>(4)</sup> sin(γ)cos(30°-α)/a - (Z <sub>M2</sub> -Z <sub>O5</sub> )cos(β)/a		X/a=1/4 + tan(30°-ω)/2√3 - Z <sub>O5</sub> cos(β)/a
M2 (4)	Y/b=(Y/b) <sub>O5</sub> + r <sub>M-O</sub> <sup>(4)</sup> sin(γ)sin(30°-α)/b	O5	Y/b=1/4
	Z/c={r <sub>M-O</sub> <sup>(4)</sup> cos γ + t <sub>O</sub> /2}/c'		Z/c=t <sub>O</sub> /2c'
	X/a=1/4 + cos ω(tan 30°-tan α)/4cos(30°-ω) - Z <sub>O1</sub> cos(β)/a		X/a=1/2 - tan(30°-ω)/4√3 - Z <sub>O6</sub> cos(β)/a
O1	Y/b=1/12 + sin ω(tan 30°-tan α)/4√3cos(30°-ω)	O6	Y/b=1/2 + tan(30°-ω)/4√3
	Z/c={√o <sub>ab</sub> <sup>2</sup> - (o <sub>bb</sub> /2cos(30°-ω)) <sup>2</sup> + t <sub>O</sub> /2}/c'		Z/c=(t <sub>O</sub> -Δ)/2c'
	X/a=1/6 + {tan α - sin ω(tan 30°-tan α)/cos(30°-ω)}/4√3 - Z <sub>O2</sub> cos(β)/a		X/a=(X/a) <sub>O6</sub> - 0.93sin(78°)/2a - (Z <sub>H</sub> -Z <sub>O6</sub> )cos(β)/a
O2	Y/b=5/6 - {tan α - sin ω(tan 30°-tan α)/cos(30°-ω)}/4√3	H	Y/b=(Y/b) <sub>O6</sub> + 0.93sin(78°)/3/2b
	Z/c={√o <sub>ab</sub> <sup>2</sup> - (b(1 + sin(ω)/cos(30°-ω))/6cos α) <sup>2</sup> + t <sub>O</sub> /2}/c'		Z/c=(Z/c) <sub>O6</sub> + 0.93cos(78°)/c'
	X/a=1/4 - cos(60°-ω)(tan 30°-tan α)/4cos(30°-ω) - Z <sub>O3</sub> cos(β)/a		
O3	Y/b=5/12 - sin(60°-ω)(tan 30°-tan α)/4√3cos(30°-ω)	Data:	b, c, β, f <sub>A1</sub> (4)
	Z/c={√o <sub>ab</sub> <sup>2</sup> - (o <sub>bb</sub> /2cos(30°-ω)) <sup>2</sup> + t <sub>O</sub> /2}/c'		
	a=b/√3		c'=c sin β
	tetrahedral basal edge-length o <sub>bb</sub> =a/2cos α		
	tetrahedral apical edge-length o <sub>ab</sub> =√(o <sub>bb</sub> <sup>2</sup> /2/3 + 0.07) <sup>2</sup> + o <sub>bb</sub> <sup>2</sup> /3		
	tetrahedral tilt Δh=√(o <sub>ab</sub> <sup>2</sup> - {o <sub>bb</sub> /2cos(30°-ω)} <sup>2</sup> ) - √(o <sub>ab</sub> <sup>2</sup> - (b(1+sin(ω)/cos(30°-ω))/6cos α) <sup>2</sup> )		Iteration used to calculate α
	tetrahedral tilt-angle γ=arctan(2Δh/o <sub>bb</sub> √3)		
	r <sub>M-O</sub> <sup>(4)</sup> =1.603+0.158f <sub>A1</sub> (4)=o <sub>ab</sub> <sup>2</sup> /2√o <sub>ab</sub> <sup>2</sup> - (o <sub>bb</sub> <sup>2</sup> (cos <sup>2</sup> (γ)+3)/4cos γ) <sup>2</sup> /3		
	tilt-angle over interlayer-region δ=arctan(Δh/o <sub>bb</sub> √3cos(30°+α))		Iteration used to calculate ω
	interlayer-thickness t <sub>i</sub> =2√r <sub>K-O</sub> <sup>2</sup> - (o <sub>bb</sub> cos(30°+α){cos <sup>2</sup> (δ)+3}/2√3cos δ) <sup>2</sup>		
	Potassium-shift ΔK=b sin ω(tan 30°-tan α)/6cos(30°-ω) + 2o <sub>bb</sub> cos(30°+α){1-(cos <sup>2</sup> (δ)+3)/4}/3 + t <sub>1</sub> sin(δ)/2		
	β=90° + arctan{(2ΔK + a/3)/c'}		
	octahedral thickness t <sub>O</sub> =c'/4 - √(o <sub>ab</sub> <sup>2</sup> - (b(1+sin(ω)/cos(30°-ω))/6cos α) <sup>2</sup> ) - o <sub>bb</sub> cos(30°+α)tan δ{cos <sup>2</sup> (δ)+3}/4√3 - t <sub>1</sub> cos(δ)/2		

dral cations towards O2 positions. This has the effect of equalizing the distances between these cations—an indication of high charge indeed, at a distance of ~3Å, with oxygens in between—and would push O2 ions upward if cation-oxygen distances are to remain equal. As somewhat shorter Si-O2 bondlengths are observed, the O2 oxygen would require less charge-

compensation from the interlayer cation, which moves towards O1/O3, and hence decreases β. The upward push of O2 is in contrast with the possibility that tilting is induced by O6-H. . . O<sub>2</sub> bonding (Takeda *et al.*, 1971). This is doubtful anyhow, since it can be calculated, using a model by Pauling (1960, p. 453), that the O2. . . H bond would have only 0.2

Table 5. Comparison between observed and estimated orthogonal structure of 2M<sub>1</sub> micas

Muscovite (Rothbauer, 1971). Data: $\alpha=11.42^\circ$ ; $\omega=8.04^\circ$ ; $c'=19.9454$ ; $b=9.0153$									
	X/a	Estimated Y/b	Z/c'	$\Delta(\text{est.}-\text{obs.}) \times 10^4$				estimated	observed
K	-0.1027 ,	0.1034 ,	0.25	-67 ,	54 ,	-	$\beta$	96.15 <sup>o</sup>	95.735 <sup>o</sup>
M (6)	0.25 ,	0.0833 ,	0	2 ,	2 ,	-	a	5.205	5.1918
M1 (4)	0.4168 ,	0.9291 ,	0.1351	41 ,	0 ,	-4	$r_{K-O_i}$	2.868	2.857
M2 (4)	0.3980 ,	0.9291 ,	0.1351	-17 ,	-20 ,	-5	$r_{M-O}^{(4)}$	1.646	1.644
O1	0.3502 ,	0.0915 ,	0.1685	-20 ,	-12 ,	2	$f_{Al}$	0.272	?
O2	0.1876 ,	0.8123 ,	0.1561	-24 ,	16 ,	-17			
O3	0.1876 ,	0.3706 ,	0.1685	20 ,	3 ,	-2			
O4	0.4418 ,	0.9418 ,	0.0530	13 ,	-14 ,	-4			
O5	0.3664 ,	0.25 ,	0.0530	10 ,	-15 ,	-5			
O6	0.4418 ,	0.5582 ,	(0.0502)	45 ,	-45 ,	(-)			
Phengite (Güven, 1967). Data: $\alpha=6.02^\circ$ ; $\omega=6.9^\circ$ ; $c'=19.846$ ; $b=9.0383$									
	X/a	Estimated Y/b	Z/c'	$\Delta(\text{est.}-\text{obs.}) \times 10^4$				estimated	observed
K	-0.1010 ,	0.1016 ,	0.25	-53 ,	52 ,	-	$\beta$	96.10 <sup>o</sup>	95.769 <sup>o</sup>
M (6)	0.25 ,	0.0833 ,	0	30 ,	8 ,	-	a	5.218	5.2112
M1 (4)	0.4155 ,	0.9288 ,	0.1338	42 ,	-9 ,	-17	$r_{K-O_i}$	3.000	2.970
M2 (4)	0.3989 ,	0.2566 ,	0.1338	-18 ,	-15 ,	-16	$r_{M-O}^{(4)}$	1.626	(1.622+1.633)/2
O1	0.3773 ,	0.0922 ,	0.1665	-11 ,	-9 ,	-13	$f_{Al}$	0.146	0.1525
O2	0.1730 ,	0.8270 ,	0.1561	-29 ,	13 ,	-40			
O3	0.1730 ,	0.3574 ,	0.1665	48 ,	0 ,	-17			
O4	0.4384 ,	0.9384 ,	0.0522	24 ,	-12 ,	-22			
O5	0.3731 ,	0.25 ,	0.0522	4 ,	4 ,	-15			
O6	0.4384 ,	0.5616 ,	(0.0526)	54 ,	-40 ,	(-)			

percent of the strength of the O6-H bond in Rothbauer's muscovite, and tilting should not change this to any notable amount.

**Conclusions and some remarks on mica polymorphism**

The formal geometrical relationships which have been derived to describe the 1M and 2M<sub>1</sub> structures are related to mica polymorphism. As a result of larger lateral dimensions of the tetrahedral sheet, the tetrahedra rotate, because this is favored electrostatically above elongation of the tetrahedra. Qualitative reasoning now suggests that the 1M structure is the more stable if the basal oxygens are coplanar, both from mutual repulsion of basal oxygens from successive layers, and from the best approximation towards hexagonal coordination around the interlayer cation. Potassium seems to be quite pliable in this respect, however, since its bondlength with oxygen is dependent on its coordination number.

In dioctahedral micas the octahedral sheet is distorted, which is formalized here as rotation  $\omega$  of the octahedral oxygens. It leads to unequal distances between the apical oxygens, and forces the tetrahedra to

tilt. Outward bulging oxygens are front to front at two sites only in the 2M<sub>1</sub> and 2M<sub>2</sub> structures, and the coordination (or repulsion) polyhedron around K seems to be the next determining step, being 60° from perfectly hexagonal in 2M<sub>2</sub> micas to 30° near perfectly hexagonal in 2M<sub>1</sub> micas. The latter are clearly favored in the natural environment.

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**References**

Appelo, C. A. J. (1977) Layer-deformation and crystal-energy of trioctahedral 1M-micas and related minerals. *Proc. Int. Symp. Water-Rock Interaction, Strasbourg, IV*, 218-229.  
 Birle, J. D. and R. Tettenhorst (1968) Refined muscovite structure. *Mineral. Mag.*, 36, 883-886.  
 Brindley, G. W. and D. M. C. MacEwan (1953) Structural aspects of the mineralogy of clays and related silicates. In A.T. Green and G.H. Stewart, Eds., *Ceramics, a Symposium*, p. 15-59. British Ceram. Soc.  
 Donnay, G., J. D. H. Donnay and H. Takeda (1964) Trioctahedral one-layer micas, II. Prediction of the structure from composition

- and cell dimensions. *Acta Crystallogr.*, **17**, 1374–1381.
- Drits, V. A. (1969) Some general remarks on the structure of trioctahedral micas. *Proc. Int. Clay Conf., Tokyo*, 51–59.
- Faust, G. T. (1957) The relation between lattice parameters and composition for montmorillonite-group minerals. *J. Washington Acad. Sci.*, **47**, 146–147.
- Franzini, M. and L. Schiaffino (1963) On the crystal structure of biotites. *Z. Kristallogr.*, **19**, 297–309.
- Giese, R. F. (1971) Hydroxyl orientation in muscovite as indicated by electrostatic energy calculations. *Science*, **172**, 263–264.
- Güven, N. (1967) The crystal structures of 2M<sub>1</sub>-phengite and 2M<sub>1</sub>-muscovite. *Carnegie Inst. Wash. Year Book*, **66**, 487–492.
- and C. W. Burnham (1967) The crystal structure of 3T muscovite. *Z. Kristallogr.*, **125**, 163–183.
- Hall, A. (1969) The micas of the Rosses granite complex, Donegal. *Proc. R. Dublin Soc.*, **A3**, 209–217.
- Hazen, R. M. and C. W. Burnham (1973) The crystal structures of one-layer phlogopite and annite. *Am. Mineral.*, **58**, 889–900.
- and D. R. Wones (1972) The effect of cation substitutions on the physical properties of trioctahedral micas. *Am. Mineral.*, **57**, 103–129.
- Jones, J. B. (1968) Al–O and Si–O tetrahedral distances in aluminosilicate framework structures. *Acta Crystallogr.*, **B24**, 355–358.
- Joswig, W. (1972) Neutronenbeugungsmessungen an einem 1M-Phlogopit. *Neues Jahrb. Mineral. Monatsh.*, 1–11.
- McCauley, J. W. and R. E. Newnham (1971) Origin and prediction of ditrigonal distortions in micas. *Am. Mineral.*, **56**, 1626–1638.
- , ——— and G. V. Gibbs (1973) Crystal structure analysis of synthetic fluor-phlogopite. *Am. Mineral.*, **58**, 249–254.
- Newnham, R. E. (1961) A refinement of the dickite structure and some remarks on polymorphism of the kaolin minerals. *Mineral. Mag.*, **32**, 683–704.
- Pauling, L. (1960) *The Nature of the Chemical Bond*, 3rd. ed. Cornell University Press.
- Radoslovich, E. W. (1960) The structure of muscovite, KAl<sub>2</sub>(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>2</sub>. *Acta Crystallogr.*, **13**, 919–930.
- (1962) The cell dimensions and symmetry of layer-lattice silicates. II. Regression relations. *Am. Mineral.*, **47**, 617–636.
- (1963a) The cell dimensions and symmetry of layer-lattice silicates. IV. Interatomic forces. *Am. Mineral.*, **48**, 76–99.
- (1963b) The cell dimensions and symmetry of layer-lattice silicates. V. Composition limits. *Am. Mineral.*, **48**, 348–367.
- and K. Norrish (1962) The cell dimensions and symmetry of layer-lattice silicates. I. Some structural considerations. *Am. Mineral.*, **47**, 599–616.
- Rayner, J. H. (1974) The crystal structure of phlogopite by neutron diffraction. *Mineral. Mag.*, **39**, 850–856.
- Rothbauer, R. (1971) Untersuchung eines 2 M<sub>1</sub>-Muskovits mit Neutronenstrahlen. *Neues Jahrb. Mineral. Monatsh.*, 143–154.
- Sartori, F. (1976) The crystal structure of a 1M lepidolite. *Tschermaks Mineral. Petrol. Mitt.*, **23**, 65–75.
- (1977) The crystal structure of a 2M<sub>1</sub> lepidolite. *Tschermaks Mineral. Petrol. Mitt.*, **24**, 23–37.
- , M. Franzini and S. Merlino (1973) Crystal structure of a 2M<sub>2</sub> lepidolite. *Acta Crystallogr.*, **B29**, 573–578.
- Soboleva, S. V. and B. B. Zvyagin (1968) Crystal structure of dioctahedral Al–mica 1M. *Kristallogr.*, **13**, 605–610. [transl. *Soviet Phys.-Crystallogr.*, **13**, 516–520].
- Takeda, H. and C. W. Burnham (1969) Fluor-polyolithionite: a lithium mica with nearly hexagonal (Si<sub>2</sub>O<sub>5</sub>)<sup>2-</sup> ring. *Mineral. J.*, **6**, 102–109.
- and J. D. H. Donnay (1966) Trioctahedral one-layer micas. III. Crystal structure of a synthetic lithium fluor mica. *Acta Crystallogr.*, **20**, 638–646.
- , N. Haga and R. Sadanaga (1971) Structural investigation of polymorphic transition between 2M<sub>2</sub>-, 1M-lepidolite and 2M<sub>1</sub>-muscovite. *Mineral. J.*, **6**, 203–215.
- Tepikin, E. V., V. A. Drits and V. A. Alexandrova (1969) Crystal structure of iron biotite and construction of structural models for trioctahedral micas. *Proc. Int. Clay Conf., Tokyo*, 43–49.
- Veitch, L. G. and E. W. Radoslovich (1963) The cell dimensions and symmetry of layer-lattice silicates. III. Octahedral ordering. *Am. Mineral.*, **48**, 62–75.
- Zhoukhlistov, A. P., B. B. Zvyagin, S. B. Soboleva and A. F. Fedotov (1973) The crystal structure of the dioctahedral mica 2M<sub>2</sub> determined by high voltage electron diffraction. *Clays Clay Minerals*, **21**, 465–470.

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