THE CELL DIMENSIONS AND SYMMETRY OF LAYER-LATTICE SILICATES

I. SOME STRUCTURAL CONSIDERATIONS

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Abstract

The theoretical basis underlying accepted b-axis formulae (giving the sheet dimensions of layer-lattice silicates in terms of composition) has been re-examined. It is now proposed that in general the b-axis is determined by the octahedral layer together with (for micas) the interlayer cation. As a consequence of this most layer silicates will have ditrigonal, not hexagonal, surface networks; and the surface rotations may be easily calculated from b_{obs} and the known Al-for-Si substitution tetrahedrally. These ideas have implications for all layer structures; these implications are examined in detail for the micas and brittle micas.

Introduction

Various attempts have been made to predict the unit cell dimensions of the layer silicates, especially the b axes, from certain observations and assumptions about their structures, allowing for the expected differences due to different ionic radii. Cell sizes calculated from recent formulae generally agree well with experimental values; there are, however, some notable anomalies, especially among the micas and brittle micas.

A detailed analysis of the muscovite structure (Radoslovich, 1960), and other data, suggest that the previous b-axis formulae have been wrongly based for the micas, and also that the accepted "ideal" mica structure may usefully be modified (Radoslovich, 1961). New b-axis formulae for all the layer silicates, including the micas, are presented in Part II.

The most recent attempt to set up general formulae relating lattice parameters to composition in layer silicates appears to be that of Brindley and MacEwan (1953), who also summarize earlier work. Their semi-empirical formulae are based on the observed increase in the cell dimensions (with change of cation) of the hydroxides, $Al(OH)_3$, $Fe(OH)_3$, $Mg(OH)_2$ and $Fe(OH)_2$, though similar results may also be obtained by considering ionic radii. Brindley and MacEwan give several different formulae, *viz.*

(a) for the expected b dimensions of various tetrahedral networks, if they were not constrained.

(b) for the expected b dimensions of various di-octahedral and tri-octahedral layers, if they were not constrained.

(c) for the b axis of the unit cell, by considering the combined tetrahedral and octahedral layers.

TABLE 1

b dimension (Å)	Celadonite[1]	Xanthophyllite[2]
Tetrahedral, calculated[3]	9.20	9.84
Octahedral, calculated	9.19	9.19
Overall, calculated[3]	9.14	9.49
Observed	9.02	9.00

[1] *vide* Zviagin, 1957.

[2] *vide* Takéuchi and Sadanaga, 1959.

[3] Adjusted to the values, Si-O = 1.60 Å, Al-O = 1.78 Å (Smith, 1954).

When (c) is applied to some representative minerals (Table 2, Brindley and MacEwan) the results are surprisingly good; and more recent studies (*e.g.* Faust, 1957) have confirmed the general applicability of the formulae, within the limits of their premises. Recently, however, there has been increased interest in applying (a) and (b) to various minerals as a means of predicting strains between the layers, since such strains will cause departures from ideal structures and may account partially for observed properties such as polymorphism and morphology. When detail of this kind is sought some factors omitted by Brindley and MacEwan become important. In their formulation, for example,

(1) no account was taken of the effect of interlayer cations.

(2) no factor was introduced for varying octahedral layer thicknesses (Bradley, 1957).

(3) some correction may be required because the charge balanced by the interlayer cation is sometimes in the tetrahedral, and sometimes in the octahedral sites.

(4) the expansion due to increased ionic size is computed by comparing *e.g. di*octahedral Al(OH)$_3$, with two *tri*valent cations, with *tri*octahedral Mg(OH)$_2$, with three *di*valent cations, whereas some minerals either are intermediate in the number of octahedral cations, or differ in octahedral charge, or both.

(5) the three octahedral sites (per one-layer cell) are treated as similar, whereas the accepted space groups imply that they are crystallographically distinct for the common mica polymorphs.

The inadequacy of these formulae for micas is clearly shown by celadonite and xanthophyllite, for both of which the calculated tetrahedral, octahedral and overall b dimensions are each considerably larger than the observed b axis (Table 1).

The present paper is concerned with the structural model which is accepted by implication as the theoretical basis for calculating b-axis formulae; basic alterations to previous models are proposed. These alterations imply a number of changes in the current ideas of the mica structures especially, which are therefore discussed in the latter part of this paper.

Adequate *b*-axis formulae consistent with the new model have been constructed by trial and error, but somewhat better results are obtained by the regression analysis of *b* against composition, as Hey (1954) also has shown for the chlorites. In addition one aspect of the new model can be tested *only* by multiple regression analyses of an adequate number of minerals in each of the main groups. Such analyses are reported in Part II, in which the new *b*-axis formulae for the kaolins, chlorites, micas and montmorillonites (which follow from the regression analyses) are presented.

Calculation of the Rotation of "Silica" Tetrahedra in Layer Silicates

For most of the layer silicate structures now known in some detail the network of "silica" tetrahedra—ideally hexagonal—is "distorted" to a ditrigonal surface symmetry, by the opposed rotation of alternate tetrahedra. The amount of this rotation varies from a few degrees to near the theoretical maximum of 30°. Minerals for which this has been reported include dickite, kaolinite, amesite, Mg-vermiculite, muscovite, celadonite, xanthophyllite, prochlorite, corundophyllite, and clinochrysotile. (Similar rotations have also been reported for the silicate network structures, tourmaline, crocidolite and hexagonal $BaAl_2Si_2O_8$ and $CaAl_2Si_2O_8$.)

The tetrahedral rotation is generally accepted as due to the misfit of a larger tetrahedral layer onto a smaller octahedral layer (*e.g.* Newnham and Brindley, 1956). The strain between these two layers is supposedly relieved by expansion of the octahedral layer, with an accompanying contraction in thickness, and partly by contraction of the tetrahedral layer by the rotation of the basal triads.

The average tetrahedral rotation from hexagonal symmetry, α, may be predicted from the observed *b* axis and known Al-for-Si substitution tetrahedrally. Let the actual 'Si'-O bond have an average length λ in projection along c^* (Fig. 1). The hexagon of 'Si' atoms has sides $= 2SO'$ $= 2\lambda \cos \alpha$, and it is easily shown that the observed *b* axis, b_{obs}, is three times this length, *i.e.* $6\lambda \cos \alpha$. The value of *b* for the same tetrahedral layer with zero rotations would be $b_{tetr} = 6\lambda$, whence

$$\alpha = \text{arc cos } (b_{obs}/b_{tetr}) \tag{1}$$

This equation applies to all layer silicates; the only assumptions are that the tetrahedra are approximately regular, and that contraction occurs simply by tetrahedral rotation. Calculated and observed values of α are discussed below for micas and in Part II for other layer silicates.

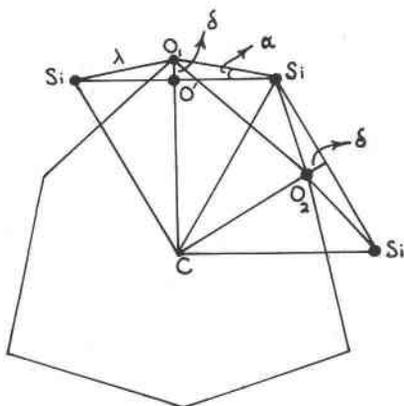It is noteworthy that calculated rotations of $<7°$ approx. are uncom-

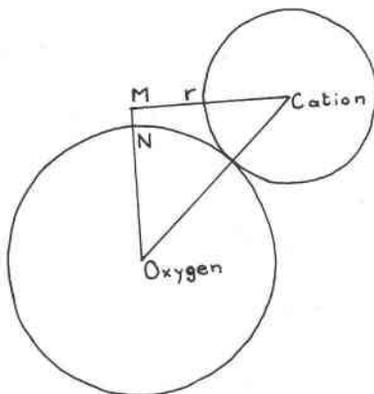FIG. 1. Calculations of angle, α, of rotation of tetrahedra.

FIG. 2. Calculation of layer separation.

mon for micas, although this requires caution, since the expression for α is very sensitive to small errors in b_{obs} and b_{tetr} when α is in this range.

The value of b_{tetr} may be calculated from the expected 'Si'-O bond length for a given Al-for-Si substitution from the curve by Smith (1954). If x is the number of Al atoms in *four* tetrahedral sites, T, and τ is the O_{apex}-T-O_{basal} angle, then

$$b_{tetr} = 6\lambda = 6 \left(1.60 + \frac{0.18x}{4} \right) \sin (180 - \tau) = (9.60 + 0.18x) \sin \tau \qquad (2)$$

which becomes, for the ideal value of $\tau = 109°28'$,

$$b_{tetr} = (9.051 + 0.254x) \qquad (2a)$$

Since τ can only be determined by a structure analysis (which also determines α), the validity of equation (1) rests on how far τ may depart from $109°28'$. A literature survey gave values from $107°$ for celadonite to $112°$ for dickite, *i.e.* $\pm 2\frac{1}{2}°$ from theoretical, which is serious when α is small but less important for $\alpha > 7$–$8°$. Observed values of α agree quite well with calculated values, *e.g.* muscovite, $13.7°$ $(14°42')$; dickite, $7.5°$ $(8°56')$; kaolinite, $10.9°$ $(10°48')$; kaolinite, $9°$ $(9°18')$; xanthophyllite, $23.2°$ $(23°19')$; and chrome chlorite, $6°$ $(5°58')$. The agreement is not quite so close for several other minerals, but in each case the O-Si-O angle is known to depart from $109°28'$ in the correct direction to account for any marked discrepancy. The observed values above have been obtained by plotting out the atomic parameters from the structure analyses, to which references are given in Table 3 and in Part II.

Factors Controlling the *b*-axis Dimension in Layer-Lattice Silicates

Recent structural analyses of micas strongly suggest that the tetrahedral layers play a secondary role in determining the *b* axis, not the dominant role previously assumed (*e.g.* Smith and Yoder, 1956). The *cell dimensions* of micas appear to be controlled largely by the octahedral layer and the interlayer actions, though micas for which the tetrahedral layer is smaller than the octahedral layer form (rare) exceptions to this. The *surface configuration*, however, depends primarily on the size of the "free" tetrahedral layer relative to the actual *b* axis.

This view of the mica structures led to a reconsideration of the role of the tetrahedral layer in determining the *b* axis of the other layer-lattice silicates. Whereas previous *b*-axis formulae (*e.g.* Brindley and MacEwan, 1953) have included a factor for the substitution of Al for Si tetrahedrally, the following hypothesis is now advanced, *viz.*

a) In *all the layer silicates* the "silica" tetrahedra can rotate fairly freely to *reduce* the dimensions of this layer; but the rigidity of the tetrahedral group prevents significant extension of the layer as, *e.g.* in the serpentine structures.

b) In *all the layer silicates* the octahedral layer can be extended or contracted with somewhat more difficulty, by changes in bond angles rather than bond lengths, and therefore with accompanying changes in thickness.

c) *For the micas* in particular the surface oxygen triads rotate until some (probably half) of the cation-oxygen bonds have normal bond-lengths, *i.e.* until half the oxygens "lock" onto the interlayer cation.

Note that if the octahedral layer of a mica tends to be *much* smaller than the tetrahedral layer the tetrahedra may rotate beyond this point (c); normal bond-lengths from the surface oxygens to the interlayer cation are then attained by the latter being held with its center slightly above the top of the oxygen layer, *i.e.* the oxygen surfaces are no longer in contact, *e.g.* muscovite (Radoslovich 1960).

The separate parts of this hypothesis may be supported as follows:

a) The inclusion of a tetrahedral term in the *b*-axis formulae was justified originally (*e.g.* Brown, 1951, p. 160) by comparing *b* for pyrophyllite (8.90 Å) and muscovite (9.00 Å). This was invalid as may be seen by likewise comparing pyrophyllite with paragonite (8.90 Å); the interlayer cation is the important factor in both cases. In fact it is not possible to find a mineral pair which differ *only* in tetrahedral substitution, since the necessity for charge balance requires an accompanying change either in the octahedral cations or interlayer region or both. The null effect of the tetrahedral layer may be inferred, however, if it is accepted that Li octahedrally does not increase *b*. Muscovite and polylithionite, both with

$b = 9.00$ Å, then effectively differ only in tetrahedral composition; and likewise for cookeite and kaolinite, both with $b = 8.92$ Å. In neither case does the substitution of Si_3Al for Si_4 change b.

The hypothesis is only *proved*, however, by determining by the multiple regression analysis of an adequate number of minerals the size and significance level of the coefficient for the tetrahedral Al term. This has been done (Part II); the coefficient is not significantly different from zero for each mineral group, kaolins, chlorites, and micas. The conclusion is that the tetrahedra rotate *so* freely that this layer does not effectively increase b at all, except possibly for the montmorillonites.

b) As a necessary consequence of a) it is now seen that the octahedral layers of only a minority of layer-lattice silicates are being stretched. For the dioctahedral micas the interlayer cation (especially the large K^+) appears to stretch the octahedral layer, and this may also happen in certain chlorites with pronounced ordering between octahedral layers. But for other layer-lattice silicates the regression analyses indicate virtually no stretching of this layer.

Octahedral layers are not generally contracted either, but the serpentines, saponites, talc and some talc analogues are exceptions to this. For all these except the saponites the octahedral layer so greatly exceeds the tetrahedral layer that the b axis is determined solely by the limit of stretching of the latter. For the saponites the octahedral layer only slightly exceeds the tetrahedral layer, and in this case the octahedral layer apparently contracts to the undistorted tetrahedral dimension; this is discussed further in Part II.

Bradley's discussion (1957) of octahedral layer thicknesses appears to be valid only under rather special circumstances, if the present hypothesis is correct.

c) Evidence to support this idea is found in the observed cation-oxygen bond lengths for muscovite, celadonite and xanthophyllite. In each case half of the total bonds are close to values predicted from ionic radii, the remainder being so great that these oxygens effectively are not bonded to the interlayer cation (Table 2).

TABLE 2. INTERLAYER CATION—OXYGEN BOND LENGTHS

Muscovite, K-O[1]	2.79_9	2.77_5	2.86_2	3.35_7	3.51_1	3.30_3 Å
Celadonite, K-O	2.77	2.85	2.77	3.27	3.27	3.34
Xanthophyllite, Ca-O[1]	2.35	2.39	2.39	3.49	3.49	3.52

[1] A reasonable value for the K-O bond is 2.81 Å, and for the Ca-O bond 2.35 Å.

Takéuchi and Donnay (1959) have shown that in the hexagonal framework structures $CaAl_2Si_2O_8$ and $BaAl_2Si_2O_8$ the networks are ditrigonal, with the nearer Ca-O bonds $= 2.39$ Å (contact distance for the effectively six-fold co-ordination); the rotation in α—$BaAl_2Si_2O_8$ is less than in $CaAl_2Si_2O_8$, because Ba is larger than Ca.

SEPARATION OF SUCCESSIVE LAYERS IN MICAS

It is possible to use the calculated α to make plausible predictions about the separation of the layers and/or the value of the O-T-O angle for individual micas as follows.

Let the interlayer cation-oxygen bond have length r ($= CO_2$ in Fig. 1) in projection along c^*, for an oxygen in contact with the cation, irrespective of whether the latter has its center at the surface of the oxygen layer or not. Then

$$r = CO' - \delta = (SiO' \cot 30°) - \delta = (b_{tetr}/6)(\sqrt{3} \cos \alpha - \sin \alpha) \tag{3}$$

For the general case (Fig. 2) the separation of the basal planes of successive layers will be

$$\eta = 2MO = 2(CO^2 - CM^2)^{1/2} = 2((\text{cation-oxygen bond})^2 - r^2)^{1/2} \tag{4}$$

Though equation (4) gives reasonable values of η for some micas it leads to an impossibly close approach of successive layers for other micas if the O-T-O angle is required to be $109°28'$ and the interlayer cation in contact with six oxygens. Where this occurs it may reasonably be assumed that the O-T-O angle changes and the layers are in contact, since the oxygen sheets can only interleave about 0.06 Å for $\alpha = 10°$, and for larger rotations than this the normal interlayer cations prevent any appreciable interleaving. On this basis new values of b_{tetr}, α, and τ are derived. From (1) and (3),

$$b_{tetr} = \left[36\left(\frac{\sqrt{3}}{6} b_{obs} - r \right)^2 + b_{obs}^2 \right]^{1/2} \tag{5}$$

in which r is given by (4) with $\eta = 0$. Corrected values of α and τ are then given by (1) and (2).

THE "IDEAL" MICA STRUCTURE

The observed layer silicate structures are usually discussed in relation to an "ideal" structure in which the surface oxygen configuration has hexagonal symmetry, *e.g.* the muscovite structure proposed by Jackson and West (1930) for which the y parameters are all multiples of $b/12$. In their classic work on the polymorphism of micas Hendricks and Jefferson (1939) pointed out that $2M_1$ muscovite departs considerably from this
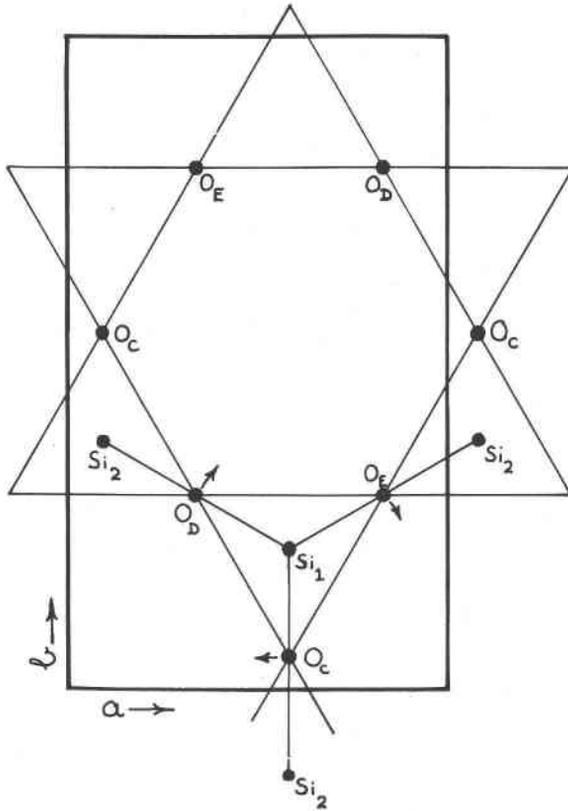
FIG. 3. Non-appearance of $o6l$, l odd reflections with tetrahedral rotations only.

arrangement because the $o6l$, l odd reflections (which are thereby for-bidden with spacegroup $C2/c$) are observed; this has been confirmed by Radoslovich (1960).

The erroneous implication, however, has been that two-layer micas for which the $o6l$, l odd reflections are *not* observed must have approxi-mately hexagonal symmetry. A simple calculation shows that the triads of oxygens on the mica surfaces may have all rotations from zero to the maximum of 30° without the $o6l$, l odd reflections appearing, provided that the tetrahedral centers are not displaced from their $y = nb/12$ posi-tions.

In the ideal hexagonal network (Fig. 3) any triad of oxygens consists of two oxygen atoms, O_D and O_E on the line in projection joining two sili-cons which lie at $\pm 60°$ to the b axis, together with O_C on such a line

parallel to the *b* axis. It is assumed that all triads are equal in size, and that their centers remain at $y = nb/12$ when *b* is decreased by tetrahedral rotations. The parameters of O_D and O_E before and after rotation are:

O_D, x, y, z→x + δx, y + δy, z and O_E, x + $\frac{1}{2}$, y, z→x + $\frac{1}{2}$ + δx, y − δy, z.

The y parameter of O_C remains at $y = nb/12$, since Si_1 and Si_2 also maintain $y = nb/12$; and hence the *o6l*, *l* odd reflections are solely due to O_D and O_E. For space group $C2/c$, the geometrical structure factor is

$$A = -8 \sin 2\pi lz \{ \sin 2\pi k(y - \delta y) + \sin 2\pi k(y + \delta y) \}$$
$$= 16 \sin 2\pi lz \cdot \sin 2\pi ky \cdot \sin 2\pi k \cdot \delta y \cdot$$
$$= 0 \text{ for } k = 6 \text{ and } y = \frac{n}{12}$$

For the 1M polymorph, spacegroup $C2/m$, these reflections may be present for all $y = nb/12$.

It appears probable that the tetrahedral networks in layer silicates may *readily* contract to a ditrigonal symmetry. Radoslovich (1961) has therefore suggested that the "ideal" mica structure be redefined as having ditrigonal surface symmetry, with the tetrahedral cations having y $= nb/12$; a hexagonal network is thus a special case of this structure. Muscovite is then a "distorted" structure because of tetrahedral displacements (due to the *partly*-filled octahedral layer).

APPLICATION TO VARIOUS MICAS

Calculated values of the rotation, α, and the expected interlayer separation η are given in Table 3; for several minerals average experimental values of α and η are also available for comparison. Since η_{calc} depends on the assumed bond length from the interlayer cation to the near oxygens, this is given in column 10, with the known observed average values in column 11.

(a) Biotites (no. 1–24), and phlogopites (no. 25–29)

It is noteworthy that α_{calc} varies between the narrow limits of $7-9\frac{1}{2}°$ approx., for these biotites having a considerable composition range (Table 4). Likewise the calculated separation η lies between 2.5 and 2.9 Å, suggesting that successive layers are generally in contact—in contrast with muscovites and lepidolites. This cannot be tested experimentally, however, because η cannot be estimated from $d(001)$, and the tetrahedral and octahedral thickness, since the latter is not precisely known for biotites and phlogopites. The substitution of F^- for OH^- introduces a further difficulty because Yoder and Eugster (1954) have shown

TABLE 3. TETRAHEDRAL ROTATIONS AND INTERLAYER DISTANCES IN SOME MICAS

No.	Mineral	b Å obs.	b Å tetr.	$\alpha°$ obs.	$\alpha°$ calc.	η Å obs.	η Å calc.	Cation-oxygen Å Obs.	Cation-oxygen Å Assume
1	Biotite, J-56-1	9.265*	9.355		7°57′		2.65		2.81
2	Biotite, J-56-1b	9.247*	9.355		8°42′		2.81		2.81
3	Biotite, J-56-5	9.268*	9.350		7°36′		2.68		2.81
4	Biotite, J-56-9	9.251*	9.320		7° 0′		2.64		2.81
5	Biotite, J-56-10	9.261*	9.358		8°15′		2.75		2.81
6	Biotite, J-56-11	9.251*	9.305		6°12′		2.55		2.81
7	Biotite, J-56-11b	9.257*	9.305		5°48′		2.51		2.81
8	Biotite, J-56-11b₁	9.225*	9.305		7°30′		2.72		2.81
9	Biotite, J-56-12	9.254*	9.391		9°48′		2.91		2.81
10	Biotite, J-56-12b	9.265*	9.391		9°24′		2.86		2.81
11	Biotite, J-56-13	9.262*	9.360		8°18′		2.76		2.81
12	Biotite, J-56-13b	9.206*	9.360		10°24′		2.93		2.81
13	Biotite, J-56-20	9.308*	9.410		8°21′		2.72		2.81
14	Biotite, J-56-21	9.246*	9.371		9°22′		2.87		2.81
15	Biotite, J-56-21b	9.255*	9.371		9° 1′		2.83		2.81
16	Biotite, J-56-22	9.253*	9.353		8°23′		2.67		2.81
17	Biotite, J-56-22b	9.215*	9.353		9°53′		2.99		2.81
18	Biotite, J-56-23	9.328*	9.360		4°51′		2.31		2.81
	For $\eta=2.60, \tau=108°41′$	9.328*	9.41		7°21′		2.60		2.81
19	Biotite, EL-38-134	9.266*	9.353		7°48′		2.63		2.81
20	Biotite, EL-38-167	9.300*	9.307		2°12′		2.00		2.81
	For $\eta=2.60, \tau=108°19′$	9.300*	9.37		7°41′		2.60		2.81
21	Biotite, EL-38-265	9.323*	9.305						
	For $\eta=2.60, \tau=107°49′$	9.323*	9.40		7°19′		2.60		2.81
22	Biotite, EL-230	9.260*	9.335		7°16′		2.66		2.81
23	Biotite, SLR-138	9.271*	9.360		7°54′		2.71		2.81
24	Biotite, Ra 135	9.265*	9.301		5° 2′		2.41		2.81
	For $\eta=2.60, \tau=109°2′$	9.265*	9.33		6°46′		2.60		2.81
25	Phlogopite, J-56-14	9.241*	9.292		6° 0′		2.54		2.81
26	Phlogopite	9.22	9.30		7°30′		2.72		2.81
27	Phlogopite	9.204	9.305		8°28′		2.83		2.81
28	Fluorophlogopite	9.195	9.395		8°48′		2.86		2.81
29	Fluorophlogopite	9.188	9.30		8°54′		2.88		2.81
30	Muscovite	8.995*	9.30	13.7°	14°42′	3.37	3.49	2.81	2.81
31	Iron-muscovite	9.06	9.24		11° 3′		3.17		2.81
32	Paragonite	8.90	9.30		16°52′		2.34		2.42
	For $\eta=2.60, \tau=106°51′$	8.90	9.45		19°36′		2.60		2.42
33	Lepidolite	9.006*	9.16		10°25′		3.16		2.81
34	Lepidolite	8.97	9.25		14°36′		3.51		2.81
35	Celadonite	9.02	9.12	12.0°	8°33′	3.30	3.12	2.78	2.81
	For $\tau_{obs}=107°0′$	9.02	9.28	12.0°	13°43′	3.30	3.30		2.78
36	Celadonite	9.05	9.05		0°		2.07		2.81
	For $\eta=2.60, \tau=108°58′$	9.05	9.08		4°30′		2.60		2.81
37	Celadonite	9.06	9.09		4°14′		2.55		2.81
38	Celadonite	9.08	9.09		2°42′		2.36		2.81
	For $\eta=2.60, \tau=109°33′$	9.08	9.11		4°54′		2.60		2.81
39	Zinnwaldite	9.12	9.23		9° 8′		2.97		2.81
40	Zinnwaldite	9.06	9.19		9°31′		3.04		2.81
41	Lithium biotite	9.21	9.32		8°44′		2.81		2.81
42	Lithium biotite	9.09	9.29		10°40′		3.08		2.81
43	Gümbelite	9.04	9.25		12°14′		3.28		2.81
44	Lepidomelane	9.29	9.41		9°10′		2.82		2.81
45	Margarite	8.92	9.56		21° 4′		2.57		2.38
46	Ephesite	8.896*	9.57		21°36′		2.78		2.42
47	Xanthophyllite	9.00	9.80	23.2°	23°19′	2.69	2.72	2.38	2.38
48	Xanthophyllite	9.01	9.77		22°45′		2.66		2.38
49	Xanthophyllite	9.00	9.76		22°46′		2.72		2.38
50	Xanthophyllite	9.02	9.77		22°36′		2.65		2.38
51	Bityite	8.713*	9.225		19°10′		2.55		2.38
52	Bityite	8.67	9.455		23°30′		2.93		2.38

* Original data, obtained using CoKα radiation, quartz internal standard, 19 cm diam. camera.

This table contains data on a few representative specimens of each of the micas, except for the biotites for which Dr. Jones supplied excellent data on twenty five specimens. All these data are included, partly to allow a discussion of interlayer separation, and partly because the same data are used subsequently in a regression analysis (Part II).

TABLE 4. COMPOSITIONS OF, AND REFERENCES TO, MICAS DESCRIBED IN TABLE 3

No.	Reference	K	Na	Ca		Fe^{2+}	Mg	Li	Mn	Fe^{3+}	Ti	Al^{VI}	Al^{IV}	Si	OH	F	Cl	O
1	Jones (1958) J-56-1	0.93	0.02	0.03		1.30	1.03		0.03	0.15	0.10	0.33	1.20	2.80	1.55	0.21	0.01	10.29
2	Jones (1958) J-56-1b	0.93	0.02	0.03		0.01	1.03	0.10	0.03	1.44	0.10	0.33	1.20	2.80	1.27	0.21	0.01	11.51
3	Jones (1958) J-56-5	0.85	0.02	0.04	0.01[2]	1.33	0.84	0.04	0.03	0.20	0.10	0.27	1.18	2.82	1.67	0.21	0.01	10.11
4	Jones (1958) J-56-9	0.80	0.10	0.01	0.01[2]	0.37	2.37	0.03		0.02	0.10	0.07	1.06	2.94	1.57	0.13	0.01	10.29
5	Jones (1958) J-56-10	0.92		0.02		1.13	1.11	0.07		0.18	0.15	0.25	1.21	2.79	1.72	0.09		10.19
6	Jones (1958) J-56-11	0.92	0.01	0.02		1.06	1.54	0.07	0.06	0.11	0.13	0.01	1.00	3.00	0.84	0.84	0.02	10.30
7	Jones (1958) J-56-11b	0.92	0.01	0.02		0.85	1.54	0.07	0.06	0.30	0.13	0.01	1.00	3.00	0.67	0.84	0.02	10.47
8	Jones (1958) J-56-11b₁	0.92	0.01			0.18	1.54	0.02	0.02	0.97	0.17	0.01	1.34	2.66	1.76	0.06	0.02	11.16
9	Jones (1958) J-56-12	0.92	0.04			1.33	0.68	0.02	0.02	0.08	0.16	0.50	1.34	2.66	0.43	0.06	0.01	11.50
10	Jones (1958) J-56-12b	0.92	0.02	0.01		0.01	0.68	0.02	0.02	1.41	0.17	0.26	1.34	2.66	1.61	0.06	0.01	11.17
11	Jones (1958) J-56-13	0.93	0.01	0.01		1.34	0.94	0.01	0.02	0.18	0.16	0.50	1.22	2.78	0.08	0.18	0.01	11.50
12	Jones (1958) J-56-13b	0.93	0.01	0.03		0.01	0.94	0.01	0.02	1.53	0.16	0.26	1.43	2.54	1.87	0.18	0.01	11.20
13	Jones (1958) J-56-20	0.95		0.01	0.01[2]	1.42	0.51		0.14	0.76	0.06	0.38	1.26	2.74	1.80	0.04		11.73
14	Jones (1958) J-56-21	0.92	0.03	0.01	0.01[2]	1.27	0.88	0.03	0.02	0.16	0.12	0.38	1.26	2.74	1.02	0.08	0.01	10.09
15	Jones (1958) J-56-21b	0.88	0.03	0.01		0.20	0.88	0.03	0.02	1.20	0.12	0.24	1.27	2.73	1.76	0.08		10.11
16	Jones (1958) J-56-22	0.88	0.01			1.19	1.24	0.01	0.01	0.09	0.14	0.13	1.27	2.73	0.95	0.13	0.01	10.89
17	Jones (1958) J-56-22b	0.73	0.01	0.04			0.28	0.04	0.01	1.25	0.14	0.36	1.22	2.78	1.62	0.13	0.01	10.09
18	Jones (1958) J-56-23	0.90	0.03		0.21[3]	1.72	1.05		0.03	0.44	0.18	0.40	1.19	2.81	1.01	0.09		10.90
19	Jones (1958) EL-38-134	0.92	0.08	0.05		1.05	1.05			0.26	0.19	0.37	1.01	2.99	1.60	0.33	0.02	10.27
20	Jones (1958) EL-38-167	0.85	0.02	0.01		1.82	0.69			0.09	0.33		1.01	2.99	0.72	0.60	0.02	10.66
21	Jones (1958) EL-38-265	0.80	0.08	0.11		1.80	0.51			0.23	0.19	0.38	1.01	2.99	0.31	0.22		11.34
22	Jones (1958) EL-230	0.71	0.07	0.20		1.00	1.18		0.01	0.26	0.31	0.30	1.12	2.88	0.70	0.31	0.02	11.06
23	Jones (1958) SLR-138	0.83	0.08	0.08		1.09	1.27			0.19	0.17	0.38	1.12	2.88	0.85	0.25	0.02	11.39
24	Jones (1958) Ra-135	0.99	0.02	0.01		1.33	0.93			0.23	0.21	0.30	0.99	2.99	0.92	0.08	0.02	11.25
25	Jones (1958) J-56-14	0.78	0.08	0.08	0.01[2]	0.23	2.15			0.12	0.48	0.16	0.95	3.01	0.55	0.15		11.07
26	Nagelschmidt (1937)	1.0				0.04	2.98			0.02		0.16	0.98	3.02	2.0			10.26
27	Yoder and Eugster (1954)[4]	1.0					3.0						1.0	3.0				10.0
28	Yoder and Eugster (1954)[4]	0.98	0.01				3.0						1.0	3.0	1.9	2.0		10.0
29	Kohn and Hatch (1955)	0.94	0.06				3.00					1.84	1.01	3.01	2.0	2.05		10.0
30	Radoslovich (1960)	0.94	0.02	0.01		0.15	0.06			0.12		1.27	0.89	3.11	2.0			10.1
31	Foster et al. (1960)		1.0		0.07[1]		0.19			0.42		1.32	0.73	3.27	0.57	1.53		10.0
32	Yoder (1958)[4]	0.82	0.10			0.01	0.02		0.03			0.82	1.0	3.0	4.34			10.0
33	Stevens (1938) no. 6	0.87	0.13			0.02	0.02	1.36		0.09			0.42	3.58	2.0			9.95
34	Nagelschmidt (1937)	0.82					0.7	1.35		1.4			0.79	3.21				9.66
35	Zviagin (1957)	0.98					0.77				0.01	0.07	0.4	3.6	2.0			10.0
36	Foster (1956) no. 17	0.83	0.07	0.03	0.25[3]	0.24	0.68			0.93		0.75		4.00	2.0			10.0
37	Maegdefrau and Hoffman (1937)	0.72		0.05		0.20	0.57			0.36		0.18	0.14	3.86	2.0			10.0
38	Malkova (1956) no. 41M	0.94				0.57		1.05		1.0		1.08	0.26	3.74	2.0			10.0
39	Cundy et al. (1960)	0.91	0.04	0.11		0.60	0.02	1.15	0.02	0.06	0.02	1.16	0.72	3.28	2.0			10.0
40	Cundy et al. (1960)	0.90	0.05	0.03		0.33	0.06	0.45	0.03	0.05	0.02	0.95	0.54	3.46	2.0			10.0
41	Cundy et al. (1960)	0.92	0.11			1.19	0.02	1.01	0.02	0.03		1.00	1.05	2.95	2.0			10.0
42	Mauguin (1913)	0.68	0.13	0.02		0.60	0.40		0.08			1.48	0.77	3.19	2.82			9.18
43	Aruja (1944)	0.81	1.11	0.07		1.46	0.68			0.35	0.04	0.07	1.43	2.57	2.01			9.99
44	Nagelschmidt (1937)			1.0				0.40			0.23	2.0	2.0	2.0	2.34			9.62
45	Takéuchi and Sadanaga (1959)			0.10		0.02	0.04			0.03		1.90	2.05	1.95	2.10			10.0
46	Phillips (1931)		0.12	1.1			2.18					0.72	2.95	1.05	2.0	0.04		9.92
47	Takéuchi and Sadanaga (1959)			0.98		0.02	2.09			0.15		0.70	2.83	1.17	1.92			10.16
48	Forman (1951)	0.01		1.00		0.06	2.23			0.04		0.76	2.78	1.22	2.07			10.0
49	Forman (1951)			0.98		0.04	2.14	0.63		0.08			2.84	1.16	2.17			9.97
50	Forman (1951)		0.04	1.01				0.71				2.09	0.69	2.17	2.0[6]			10.0
51	Rowledge and Hayton (1948)	0.01	0.04	0.99	1.14[5]		0.01					1.58	1.59	2.06				10.0
52	Strunz (1956)		0.05		0.35[6]													10.0

[1] Rb   [2] Ba   [3] (H₃O)⁺   [4] Synthetic specimen   [5] Be tetrahedrally   [6] Plus 0.8 H

that this substitution in phlogopite decreases $d(001)$, and Jones (1958) has suggested that similarly the substitution of both O^{2-} and F^- for OH^- in biotite decreases $d(001)$.

When b_{oct} is nearly as large as b_{tetr} the tetrahedra may not be sufficiently rotated for half the oxygens to be in contact with the interlayer cation. For these biotites (*e.g.* EL-38-167, Table 3) the tetrahedral angle is probably $< 109°28'$, and has therefore been adjusted to maintain both cation-oxygen contact and oxygen-oxygen contact across the interlayer region. It can be shown (*vide* Part II) that the ratio

$$\frac{Fe^{2+} + 0.853Fe^{3+} + 0.455Mg + 0.43Ti}{Al_{tetrahedral}}$$

(where Fe^{2+} etc. are the ionic proportions in the structural formulae) is a good measure of the ratio, b_{oct}/b_{tetr}. This ratio has been plotted against the η_{calc} in Figure 4, with values for muscovite, Fe-muscovite and three zinnwaldites added for comparison. The general trend (dotted line) shows that as the octahedral layer becomes smaller relative to the tetrahedral layer the increased tetrahedral rotation forces the layers apart.

There is a little evidence to confirm this trend for η_{calc}. The separation, η_{obs}, is known for muscovite; and if biotites are usually in interlayer contact this leads to the dashed line (Fig. 4). Secondly, $d(001)$ for muscovite, Fe-muscovite and the zinnwaldites is plotted on the same scale and shows a similar trend. Since, on the simplest hypotheses, the octahedral substitution of Fe^{3+}, etc. for Al^{3+} should *increase* $d(001)$ this observed *decrease* supports the present calculations of interlayer separations.

(For muscovite at least the substitution of F^- for OH^- does not decrease $d(001)$ (Yoder and Eugster, 1955). This may be expected if the decrease with the substitutions depends on the directed nature of the OH bond in relation to the K^+ ion. Bassett (1960) and others have shown by infrared spectroscopy that these bonds are normal to the sheets in phlogopite, nearly so in biotite, and at a low angle in muscovite. Zinnwaldite should be similar to muscovite; and this comparison of $d(001)$ with η_{calc} should be valid for these micas.)

(b) Muscovite, Fe-muscovite, paragonite (no. 30–32)

The correlation between $d(001)$ decreasing from 20.097 to 19.991, and the closer approach of successive layers due to the smaller tetrahedral rotation (*i.e.* greater K^+ penetration) is obvious for muscovite and iron-muscovite.

For paragonite $\eta_{calc} = 2.34$ is far too small, since oxygen layers across the interlayer region can scarcely interleave. It appears that the tetrahedra in paragonite must be somewhat "flattened," to give a greater ro-
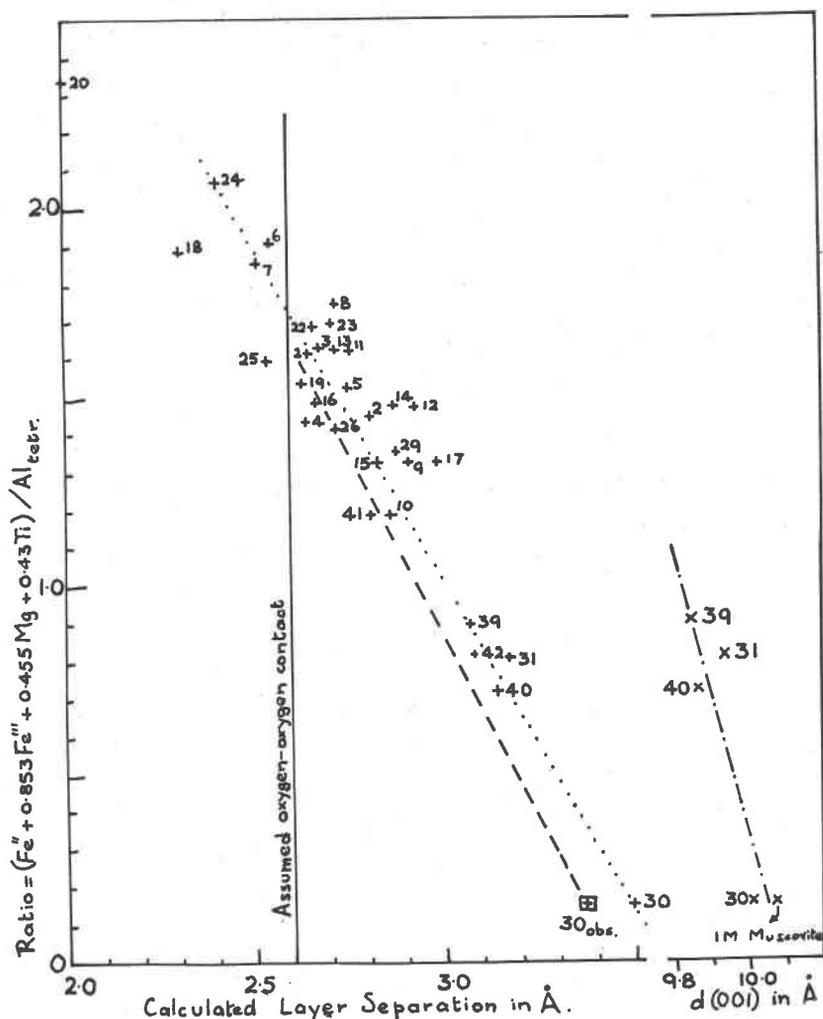
Fig. 4. Calculated layer separation as a function of composition; also (001) spacing as same function.

tation than ideal; and $\tau_{calc} = 106°51'$, close to $\tau_{obs} = 107°0'$ for celadonite (Zviagin, 1957).

An error in the discussion of the muscovite structure (Radoslovich, 1960) should be noted here. The octahedral layer in gibbsite was assumed to have a thickness equal to half the cell height (*i.e.* 2.53 Å), and the octahedral layer in muscovite (thickness, 2.12 Å) was supposed to be thinner because it was "stretched," *i.e.* $b = 8.995$ against 8.64 for gibbsite.

Megaw (1934) has studied gibbsite in detail, and gives the layer thickness as 2.12 Å, which is the same as that in muscovite. This, of course, is to be expected on the present hypothesis, that the tetrahedral layer exerts very little stretching force on the octahedral layer in micas. The b axis of gibbsite is shorter than that of muscovite because the surface OH-OH bonds result in a small contraction of the Al-O bonds (by 0.06 Å) and of the vacant site ("site"—0 distance less by 0.05 Å); and these contractions in bond length shorten the b axis *without* thickening the layer.

(c) Lepidolite (no. 33)

This lepidolite is a $2M_2$ polymorph (Levinson, 1953) which is surprising since $\alpha = 10\frac{1}{2}°$, and ditrigonal surfaces should not allow this polymorph (Radoslovich, 1959).

The surface would be nearly hexagonal ($\alpha = 2°8'$), if the layers were in contact at 2.6 Å, and the K-O bonds were 2.86 Å; then $\tau = 111°54'$, which is reasonable. But this lepidolite has the same c^* as $2M_1$ muscovite, so that the layers are probably separated by a similarly large distance. Crystallization in the $2M_2$ form is therefore very surprising; and a structural analysis of this is now being undertaken.

(d) Celadonite (no. 35)

The observed and calculated values of α and η do not agree well. Zviagin's structural analysis, however, shows that the O-T-O angle, $\tau = 107°0'$, instead of $109°28'$, which gives $\alpha_{calc} = 13°43'$, in better agreement with $\alpha_{obs} = 12°$ (aver. of 13.3°, 13° and 10°). Using α_{obs} and the observed K-O bond of 2.78 Å gives a calculated separation of layers of 3.30°, as observed.

This structure shows several unusual features for which tentative explanations may now be offered, *viz:*

(1) the observed octahedral layer thickness is 2.48 Å, compared with 2.12 Å for muscovite and 2.10 Å for brucite, $Mg(OH)_2$. This layer in celadonite is deficient in cationic charge, however, and can therefore more readily increase in thickness than other micas. This increased thickness completely accommodates the increase in octahedral cation-oxygen bonds in passing from muscovite to celadonite, by changing the bond angles; and the isomorphous replacement of Fe^{2+}, Mg^{2+} and Fe^{3+} for Al^{3+} does *not* therefore increase the b axis in this case.

(2) the O-T-O angle is 107°, rather than $109°28'$. The oxygen surfaces are separated (as in muscovite); this may possibly be a consequence of some mutual repulsion due to the K^+ charge being satisfied by the *octahedral* oxygens. For the nearer oxygens to maintain

TABLE 5. INTERATOMIC DISTANCES, OCTAHEDRAL CATION SITE TO OXYGENS

Celadonite		$2M_1$ Muscovite	
$Fe_{1.4}^{+3}$, $Mg_{0.6}^{2+}$-O (two sites)	2.06, 2.12, 2.15 Å	Al-O (two sites)	1.93_5, 1.93_2, 1.93_9 1.94_4, 2.04_8, 1.93_0
$Mg_{0.1}^{2+}$-O	2.11, 2.14, 2.14 Å	vacant-O	2.28_7, 2.23_3, 2.09

contact with the K^+ ion the tetrahedra must "over-rotate," which requires the basal triads to be enlarged; and since bond angles are changed more readily than bond lengths the tetrahedra "flatten out" by reducing τ to 107°0'.

(3) the β angle of celadonite is 100°6', nearly equal to $\beta = \cos^{-1}(-a/3c) = 99°44'$, and therefore contrasting with 1M muscovite for which $\beta_{obs} = 101°30'$ and $\beta_{calc} = 100°0'$. This is surprising since both structures are dioctahedral, with similar tetrahedral rotations (12° and $14\frac{1}{2}$°). In celadonite, however, the octahedral sites are similar in size, whereas in 1M muscovite (by deduction from $2M_1$ muscovite) the unoccupied site is significantly larger than the other two (Table 5). This leads to asymmetry in muscovite, *i.e.* to displacement of K^+ (and Si) from $y = nb/12$. The K^+ displacement contributes to the departure of β from theoretical for the 1M polymorph in muscovite, but does not occur in celadonite.

(e) Celadonite (no. 36)

Although this one mica theoretically has hexagonal symmetry this implies an impossibly close approach of successive layers (1.07 Å). If a more reasonable approach of 2.6 Å is assumed then $\alpha_{calc} = 4°30'$ (*c.f.* celadonite, ref. 5) with $b_{tetr} = 9.08$ and $\tau = 109°58'$, which is acceptable. A mica having $\alpha = 0$ may be expected to occur amongst the end-member celadonites, if at all; and this specimen suggests that micas with hexagonal surfaces do not occur in nature.

(f) Margarite, no. 45

The value of η_{calc} can be confirmed by comparison with muscovite and xanthophyllite for which structural data is available. The layers of margarite and xanthophyllite have the same thickness (9.56 and 9.59 Å); and the octahedral layer of margarite, $CaAl_2(Si_2Al_2)O_{10}(OH)_2$, should be comparable with muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$, *i.e.* 2.12 Å, which is close to that of xanthophyllite 2.20 Å. Hence the interlayer distances of margarite and xanthophyllite should be comparable, which they are, *viz.* 2.57 and 2.69 Å.

(g) Ephesite, no. 46

The regression analyses (Part II) suggested that the original value of b ($= 8.81$ Å) was far too small, and it was noted that ($\sqrt{3}$ a) ($= 8.95$ Å) was rather larger. An ephesite specimen from Postmasburg (U.S.N.M. 104815, kindly donated by the U. S. National Museum) was found to have $b = 8.896$ Å, using a 19 cm camera.

(h) Xanthophyllite, nos. 47–50

Even though xanthophyllite has an *excess* cationic charge octahedrally, the octahedral layer is nevertheless thicker (2.20 Å) than in brucite (2.10 Å). This confirms the dominant role of the interlayer cation-oxygen bonds in determining b axes in micas—in this case the Ca-O bonds apparently shorten the b axis to the extent of compressing and slightly thickening the octahedral layer against its excess charge effects.

(i) Bityite, nos. 51–52

Although the Be-O bond length in a layer-lattice silicate is not accurately known, this bond is quoted by Wyckoff (1948) for BeO, which has 4–4 tetrahedral co-ordination, as 1.64 Å. As an approximation, then, Be is treated as equivalent to Si in calculating b_{tetr}. For bityite no. 51 ("bowleyite") successive layers are in contact. For no. 52 the data suggest a small separation across the interlayer region. Strunz (1956) used a 5.73 cm diam. camera, however, and b_{obs} may easily be in error. A value of 8.77 Å, *e.g.*, makes $\alpha = 22°$ and $\eta = 2.75$ Å, and it is noteworthy that all the other brittle micas (nos. 45–51) are virtually in contact across the interlayer region. It is also interesting that the tetrahedral rotations are about 20° for each of the brittle micas, as would be expected because of their greater tetrahedral Al, and the dominating influence of Ca. The latter is illustrated by bityite in which the Ca contracts the octahedral layers from 8.9 Å to 8.7 Å, even against the excess charge effects on this layer. The comparable octahedral contraction in xanthophyllite (to which bityite is closely analogous) is from 9.2 Å to 9.0 Å, also due to interlayer Ca.

Summary

The hypotheses on which b-axis formulae for layer-lattice silicates have previously been based have been modified in ways suggested by the results of recent structure analyses. The new hypothesis carries structural implications for all these minerals; these are discussed in detail for the micas. This hypothesis also allows new b-axis formulae to be proposed (in Part II) which remove several anomalies, especially for the brittle micas.

More than ten structures are now known in which the tetrahedral

layers contract by the rotation of individual tetrahedra. The simple formula, $\alpha = \arccos(b_{obs}/b_{tetr})$ predicts the average rotation satisfactorily, though uncertainties arise in b_{tetr} when the O-Si-O angle departs from $109°28'$.

It is proposed that the sheet dimensions of layer-lattice silicates are controlled by the octahedral layer, and (for micas) the interlayer cation, except for those few minerals for which the tetrahedral layer is unduly stretched. Evidence is accumulating that the tetrahedral dimensions merely govern the surface configuration of these minerals.

A tentative formula is suggested for the separation of successive layers of micas across the interlayer region, and some evidence given for its general correctness.

A new ideal mica structure is proposed which has ditrigonal surface symmetry; this is consistent with the accepted space groups.

The new hypothesis is discussed in detail in relation to the micas and brittle micas, for which there are sufficient data to test its validity in some detail. A number of anomalies are explained thereby. It is emphasized, however, that the full validity of the model can be assessed only by comparison with the detailed analyses of key structures in the future.

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