STRUCTURES OF BRITTLE MICAS

by

Y. TAKÉUCHI

Mineralogical Institute, University of Tokyo

ABSTRACT

THE CRYSTAL structures of xanthophyllite, $CaMg_2Al(Al_3Si)O_{10}(OH)_2$ (a 1M structure) and margarite $CaAl_2(Al_2Si_2)O_{10}(OH)_2$ (a $2M_1$ structure), have been refined by three-dimensional least squares. Ordering of Mg and Al has been observed in the octahedral layers of xanthophyllite. There is no significant evidence for ordering among cations in the silicate layers of margarite. The tetrahedra are rotated about 23° in xanthophyllite and about 21° in margarite. The configuration of the octahedral layers in margarite has the same features as those in muscovite and dickite.

The mode of deformation of the silicate layer is roughly similar in both structures, but there are important differences. These differences are caused by the different configurations of the octahedral layers and are a common feature among micas. In the aluminum octahedral layer, the oxygen hexagons whose corners are apices of tetrahedra have short edges of 2.81Å and a pair of longer edges of 3.35Å (distances are averages obtained from the structures of margarite, muscovite and dickite). Because of these longer edges, the tetrahedra in the dioctahedral micas are tilted in addition to having rotations caused by the short edges. The z-parameters of the basal oxygen atoms in the tetrahedra thus show maximum deviations of 0.19 ± 0.03Å in margarite and 0.12 ± 0.03Å for muscovite. On the other hand, in trioctahedral micas, the edges of the oxygen hexagons are almost the same length, with a maximum deviation of 0.05Å. The silicate layers in trioctahedral micas are accordingly almost free from tilting of tetrahedra. The difference in z-parameters in dioctahedral micas causes a corrugation of layers and also causes a shift of interlayer cations.

It is known that in trioctahedral micas, the direction of the OH bond is perpendicular to (001), while in muscovite it is inclined to the b-axis. Taking into account this asymmetrical orientation of the OH bond, together with the above-mentioned interlayer cation shifts, it is possible to show that a layer stacking by the operation of the twofold axis in the space group of the $2M_1$ structure is no longer identical with that produced by rotations of $\pm 120°$ about an axis perpendicular to (001). A more restricted number of operations would therefore be possible in the generation of polytypes.

An index, D, has been defined that is a direct measure of the misfit between octahedral and tetrahedral layers. It will be shown that the layer silicates may be classified into three categories with the aid of this index.

INTRODUCTION

BELOV (1963, p. 14) has shown that silicate chains adopt various configurations in accordance with the size of coexisting octahedral chains. The layer silicates are not exceptions. Results for the layer silicates hitherto reported by various authors (Mathieson, 1958; Radoslovich, 1960; Newnham, 1961; Steinfink, 1962; Brown and Bailey, 1963) suggest that the configurations

1

of the octahedral layers and that of individual tetrahedra are fairly constant for a given chemical composition and that the dimensional misfit between octahedral and tetrahedral layers is achieved primarily by a distortion of tetrahedral layers. The size of the interlayer cations is also responsible for distortion of tetrahedral layers (Takéuchi, 1958; Takéuchi and Donnay, 1959).

The distortion of the tetrahedral layers is of special importance in layer silicates because it is related to various properties of layer silicates, especially the morphology of clay minerals (Bates, Hildebrand and Swineford, 1950) and mica polytypism (Radoslovich, 1959; Sadanaga and Takéuchi, 1961). In spite of accumulated knowledge on the structures of layer silicates, the difficulties encountered in explaining the abundant polytypes of dioctahedral micas have been left unsolved.

The chemical formulae of brittle micas suggest that they are the calcium analogue of micas, potassium in ordinary micas being replaced by calcium in brittle micas. The structure analysis of xanthophyllite has shown that xanthophyllite really has a mica-type structure (Takéuchi and Sadanaga, 1959). The excess positive charge introduced by divalent calcium atoms is balanced by the replacement of Si by Al in tetrahedral layers. The Al : Si ratio amounts to 3 : 1 in xanthophyllite. The size of tetrahedral layers is thus greater than that of ordinary micas, giving an extreme case of misfit between octahedral and tetrahedral layers among the mica structures. Brittle micas are, accordingly, well suited for an investigation of the modes of distortions of tetrahedral layers. A refinement of the structure of xanthophyllite was made by Takéuchi and Sadanaga and that of margarite by Takéuchi, Kawada and Sadanaga. It is not the purpose of the present paper to give a detailed description of the refinements but rather to give the descriptions of these structures and discussions based upon the new results. Details of the refinements of these structures will be published elsewhere.

CRYSTAL DATA

Dioctahedral brittle mica is known as margarite, with the ideal chemical formula of $CaAl_2(Al_2Si_2)O_{10}(OH)_2$. Optical studies have shown that the trioctahedral brittle micas are divided into two subgroups, xanthophyllite and clintonite. The chemical formula of xanthophyllite is close to $CaMg_2Al$ $(Al_{2.8}Si_{1.2})O_{10}(OH)_2$, in which the Al content in octahedral sites is fairly constant (Forman, 1951). Chemical analyses show no significant differences between xanthophyllite and clintonite (Deer, Howie and Zussman, 1962, p. 100) but Mg may be replaced by Fe to some extent. The crystal data for brittle micas that are available to date are listed in Table 1.

The Table shows that the xanthophyllites from different localities have the 1M structure and seybertite, a variety of clintonite, has the 3T structure. X-ray photographs of most of the trioctahedral brittle micas show diffuse reflections for hkl with $k \neq 3n$, suggesting poor structural control between layers. These parallel the case of trioctahedral micas.

TABLE 1. CRYSTAL DATA OF BRITTLE MICAS

		Lattice constants				Structure type	Reflections $k \neq 3n$
		a (Å)	b (Å)	c (Å)	β		
Triocta-hedral							
Xantho-phyllite	Crestmore[1]	5.215	9.013	9.853	100°04′	1M	
	Achmatovsk[1]	5.25	8.998	9.810	100°10′	1M	
	Adamello[2]	5.21	9.02	9.97	100°03′	1M	Drawn out
	Chichibu[3]	5.194	9.003	9.802	100.1°	1M	Sharp + weak diffuse streak
Clintonite (Seybertite)	Amity, N.Y.[4]	5.19	8.99	28.76		3T	Drawn out
Diocta-hedral							
Margarite	Chester, Mass.[3]	5.123	8.886	19.221	95.5°	2M$_1$	Sharp
	Lukmanier[5]	5.11	8.87	19.18	95°26′	2M$_1$	Sharp

[1] Forman (1951). [2] Sanero (1940). [3] Sadanaga & Takéuchi (1961) (The constants given by Takéuchi & Sadanaga (1959) have been revised in this paper). [4] Takéuchi & Sadanaga (1959). [5] Present work.

X-ray data on margarite are available only for material from two localities. The specimens of Lukmanier margarite (Niggli, 1955) were kindly furnished by Prof. E. Niggli for the present work. Crystals of margarite from both localities show a 2M$_1$ structure, and no evidences of stacking disorder were observed. Although X-ray data on margarite are limited to these two cases, they are consistent with the characteristics of muscovites, which tend to crystallize in 2M$_1$ structures. For the present structural investigations, xanthophyllite from Chichibu, Japan, whose chemical formula is $Ca_{1.10}Mg_{2.18}Al_{0.72}(Al_{2.95}Si_{1.05})O_{10}(OH)_2$ and margarite from Chester, Mass., were used. Based upon the chemical analysis by Koch (1935), the chemical formula of the latter was approximated to $(Ca_{0.87}Na_{0.13})Al_2(Al_2Si_2)O_{10}(OH)_2$.

DESCRIPTION OF THE STRUCTURES

The refinement of the atomic parameters of xanthophyllite (Takéuchi and Sadanaga, 1959) was begun with a three-dimensional Fourier synthesis. The improved parameters were further refined by three-dimensional least squares. The final R value is 0.108 for all observed hkl. The accuracies of these parameters were estimated from atom peaks in the final three-dimensional Fourier synthesis. The mean $\sigma(x_n)$ is 0.012Å for oxygen, 0.008Å for M_{II} and 0.007Å for tetrahedral cations. The atomic parameters of margarite were first derived by two-dimensional Fourier methods. They were then refined by three-dimensional least squares. The final parameters give $R = 0.165$ for all observed reflections. Estimated errors in parameters are: $\pm$ 0.008Å for Al; $\pm$ 0.005Å for Si, Al; $\pm$ 0.009Å for Ca; and $\pm$ 0.02Å for oxygen.

Xanthophyllite

The atomic parameters of xanthophyllite are given in Table 2; and the bond lengths, bond angles and interatomic distances are listed in Table 3. The structure is shown in Fig. 1. The Al_3Si—O bond lengths vary from 1.71_0 to 1.75_4Å, giving a mean value of 1.73_0Å. In spite of the very high aluminum content, the tetrahedra are fairly regular. The deviations of O—Al_3Si—O angles from their mean value are in the range of $\pm 2.5°$. For the bond to the apical oxygens the bond length is slightly shorter than the others. Since $\sigma(l)$ for the bond is ± 0.014Å, the difference may be significant. In muscovite, however, the corresponding bond is longer than its nonapical bonds (Rado-slovich, 1960).

TABLE 2. ATOMIC PARAMETERS OF XANTHOPHYLLITE

	x	y	z	B	$z*$†	
M_I	0	0.5	0.5	1.13	0	⎫
M_{II}	0.5	0.330	0.5	0.96	0	⎬ Octahedra
OH	0.632	0.5	0.400	1.90	0.050	
O_3	0.617	0.165	0.383	2.04	0.0585	⎭
Al_3Si	0.564	0.168	0.208	0.83	0.1460	⎫
O_1	0.427	0	0.150	1.34	0.1750	⎬ Tetrahedra
O_2	0.857	0.188	0.144	1.46	0.1780	
Ca	0.5	0.5	0	0.97	0.25	⎭

† To compare z-parameters with those of margarite (Table 4) the values $z* = |z-0.5|/2$ are given in the last column.

The octahedral cations M_I and M_{II} are not related by symmetry. The mean bond lengths are 2.01_6Å for M_I—O and 2.072Å for M_{II}—O. Since the standard deviations of these bond lengths are ± 0.011Å for M_I—O and ± 0.014Å for M_{II}—O, this difference is significant. The mean value for M_{II}—O is very close to that of the Mg—O bond lengths observed in Mg-vermiculite (Mathieson, 1958) and Cr-chlorite (Brown and Bailey, 1963), suggesting that the sites of M_{II} are almost fully occupied by Mg atoms. The mean value for Mg—O found in phlogopite (Steinfink, 1962) is 2.07_3Å, which also shows very good agreement with the M_{II}—O bond lengths. As a consequence, it is very likely that most of the aluminum atoms are distributed over the M_I sites. Since the distance for the pure Al—O bond is close to 1.92Å (Table 6), the mean bond length 2.01_6Å for M_I—O corresponds approximately to the value for $Mg_{0.5}Al_{0.5}$—O.

The most notable feature in the structure of xanthophyllite is the configuration of the tetrahedral layers, which show the highest deformation so far observed in layer silicates (Fig. 1). In spite of this deformation, the maximum deviation in the z-parameters of the basal oxygens of the tetrahedra is only 0.06 ± 0.02Å, and therefore these oxygens define a practically flat surface. This suggests that the deformation is mainly caused by the rotations of tetrahedra around an axis perpendicular to (001). The angle of the rota-

tions amounts to about 23° and is close to the maximum value 30°. Because of this large amount of rotation, the tetrahedral layers are "shrunk" by about 10 per cent from the ideally hexagonal case. The tetrahedral cations in a
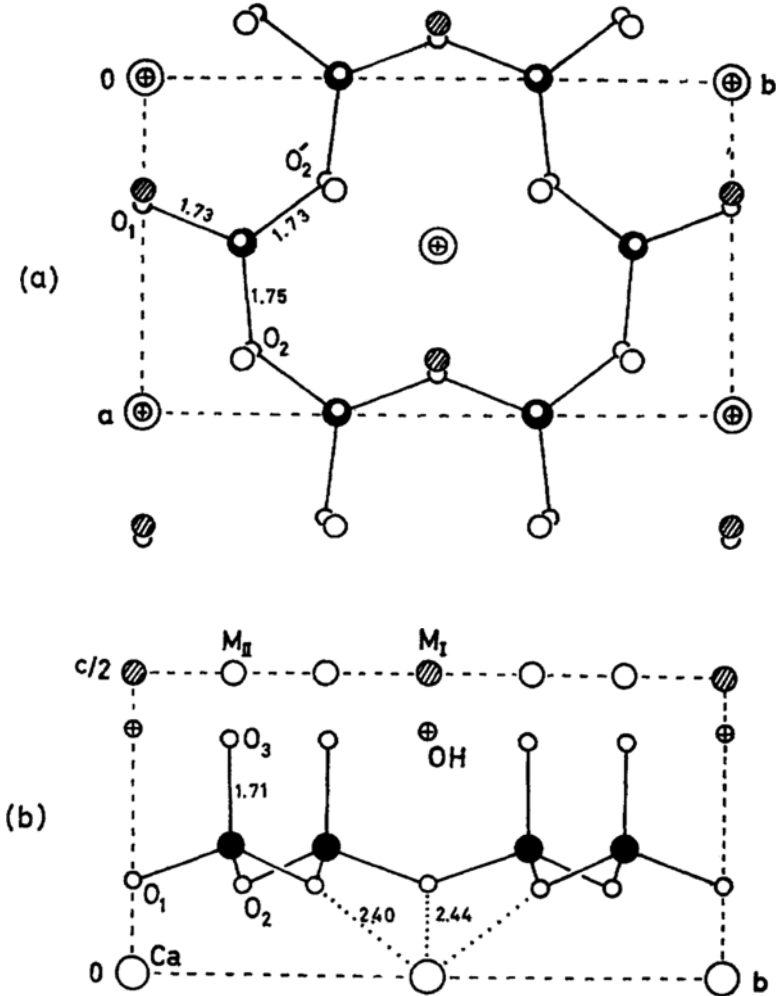

FIG. 1. The structure of xanthophyllite: (a) the projection on (001); (b) the projection along the a-axis.

layer are, accordingly, much closer than those in the ordinary micas. The effect is probably to increase the energy of the crystal compared to ordinary micas. The compacted layers form fairly regular octahedra around the sites of the interlayer cations. The mean value of the edges of the octahedra is

3.41$_7$Å and, thus, the size of the octahedra is just suited for Ca atoms. If the dimensions of the octahedra formed by the shrinking of the tetrahedral layers were not of the correct size for Ca atoms. further deformation of the layers would be expected. But this is not the case for the brittle micas.
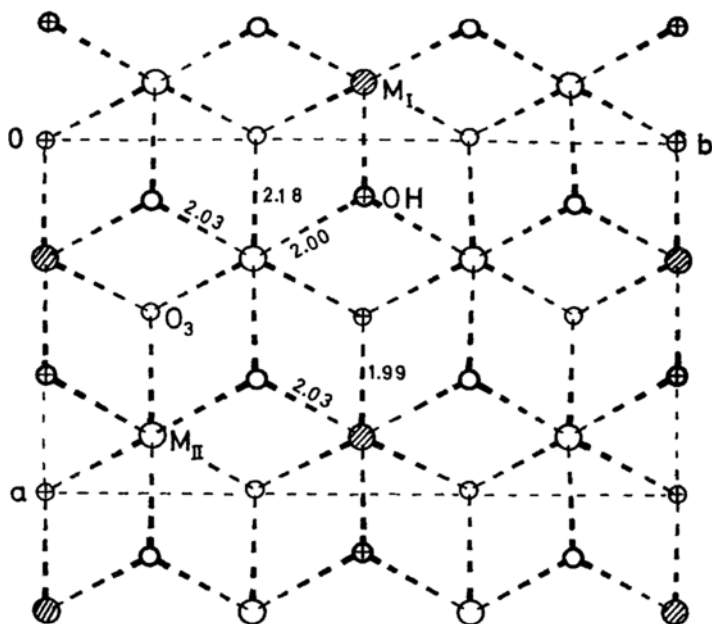

FIG. 2. The octahedral layer of xanthophyllite projected on (001).

Margarite

The atomic parameters of margarite are given in Table 4; and bond lengths, bond angles and interatomic distances are listed in Table 5. The structure is shown in Fig. 3. The dimensions of the aluminum octahedral layers are seen to be slightly smaller than those of muscovite (Radoslovich, 1960) and similar to those of dickite (Newnham, 1961). However, as will be mentioned later, the general characteristic features of the aluminum octahedral layers are common among layer silicates.

The two tetrahedra that are not related by symmetry are almost the same size. It appears therefore that the Al and Si are randomly distributed over the tetrahedral sites. For margarite, complete ordering of the tetrahedral cations means that one tetrahedron should be occupied solely by Al and the other by Si. If this occurs, the sum of the electrostatic bonds to the apical oxygens of Al-tetrahedra will be somewhat less than that to other oxygens. For the apical oxygens the Al,Si—O bond lengths do not show significant differences from those for basal oxygens. Like xanthophyllite, the tetra-

TABLE 3. BOND LENGTHS, BOND ANGLES AND INTER-
ATOMIC DISTANCES IN XANTHOPHYLLITE

OCTAHEDRA

M_I—O $\sigma(l) = 0.011$Å
  M_I—OH $1.98_9(2)$,* M_I—O_3 $2.03_4(4)$
  mean 2.01_6
M_{II}—O $\sigma(l) = 0.014$Å
  M_{II}—OH $2.00_1(2)$, M_{II}—O_3 $2.03_4(2)$
  M_{II}—O_3 $2.18_2(2)$,
  mean 2.07_2
O—O $\sigma(l) = 0.017$Å
  shared edges
  OH—OH 2.58_2, O_3—O_3 $2.82_9(2)$
  O_3—O_3 2.77_8, O_3—OH $2.73_1(2)$
  mean 2.74_7
  nonshared edges
  (M_I–octahedra)
  O_3—OH $2.95_4(4)$, O_3—O_3 $2.97_1(2)$
  mean 2.96_0
  (M_{II}–octahedra)
  O_3—O_3 $3.01_4(2)$, O_3—OH $3.07_2(2)$
  O_3—OH $3.03_9(2)$
  mean 3.04_1

TETRAHEDRA

(Al,Si)—O $\sigma(l) = 0.014$Å
  Al,Si—O_1 1.72_5,   Al,Si—O_2 1.75_4
  Al,Si—O_3 1.71_0,   Al,Si—O_2 1.73_0
  mean 1.73_0
O—O $\sigma(l) = 0.017$Å
  O_1—O_2 2.81 O_1—O_3 2.75_8
  O_1—O_2 2.83_2, O_2—O_3 2.82_0
  O_2—O_3 2.82_7 O_2—O_3 2.86_2
  mean 2.81_8
O—(Al,Si)—O $\sigma(\theta) = 0.6°$
  O_1—Al,Si—O_2 $107.8°$
  O_1—Al,Si—O_2 $110.1°$
  O_2—Al,Si—O_2 $108.4°$
  O_1—Al,Si—O_3 $106.8°$
  O_2—Al,Si—O_3 $111.4°$
  O_2—Al,Si—O_3 $110.1°$
  mean $109.1°$
(Al,Si)—O—Al,Si $\sigma(\theta) = 0.9°$
  Al,Si—O_2—Al,Si $118.0°$
  Al,Si—O_1—Al,Si $122.5°$
  mean $120.3°$

Ca–OCTAHEDRA

Ca—O $\sigma(l) = 0.012$Å
  Ca—O_1 $2.43_5(2)$,   Ca—O_2 $2.40_3(4)$
  mean 2.41_0
O—O $\sigma(l) = 0.017$Å
  O_2—O_2 $3.38_0(2)$, O_2—O_1 $3.40_1(4)$
  O_1—O_2 $3.44_3(4)$, O_2—O_2 $3.41_3(2)$
  mean 3.41_7

* Numbers in parentheses indicate the number of
equivalent bonds.

2

hedral layers are highly deformed from hexagonal to trigonal symmetry. The rotations of tetrahedra are about 21°, which is very close to the value predicted by Radoslovich and Norrish (1962). For this case, however, the z-parameters in the basal oxygens of tetrahedra show a maximum deviation of 0.01, which corresponds to 0.19Å. Thus, the basal oxygens do not form a flat
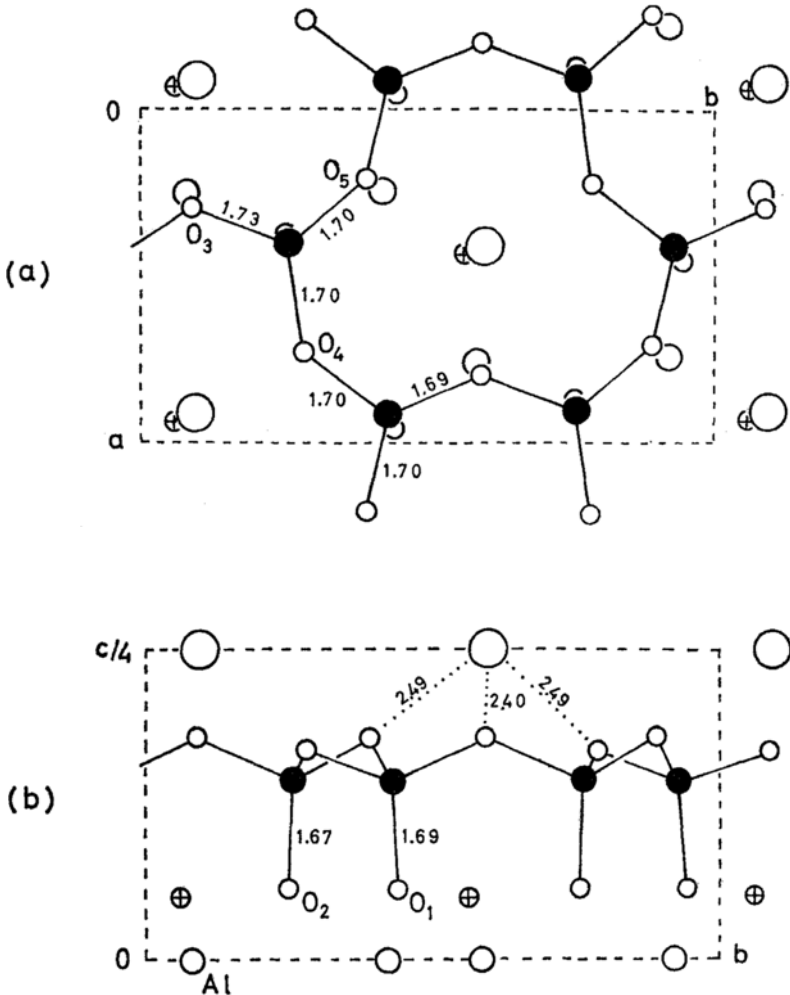

FIG. 3. The structure of margarite : (a) the projection on (001); (b) the projection along the a-axis.

TABLE 4. ATOMIC PARAMETERS OF MARGARITE

	x	v	z	B	
Al	0.251_8	0.081_5	0.000_0	0.29	⎫
OH	0.449_2	0.562_4	0.050_5	0.87	⎬ Octahedra
O_1	0.954_7	0.443_0	0.055_3	1.25	⎭
O_2	0.387_4	0.252_4	0.056_9	1.12	
Si,Al_1	0.462_8	0.928_3	0.143_2	0.53	
Si,Al_2	0.454_3	0.257_5	0.143_8	0.71	
O_3*	0.359_7	0.088_4	0.178_8	0.40	⎬ Tetrahedra
O_4*	0.278_6	0.783_9	0.169_5	1.46	
O_5*	0.270_0	0.390_3	0.179_7	0.45	
Ca	0	0.094_2	0.25	1.14	

* These oxygens define the basal planes of tetrahedral layers. Their z-parameters should be compared with $z*$ of O_1 and O_2 in xanthophyllite (Table 2).

TABLE 5. BOND LENGTHS, BOND ANGLES AND INTERATOMIC DISTANCES IN MARGARITE

Al-OCTAHEDRA

Al–O $\sigma(l) = 0.02$Å

Al—OH	1.91_4,	Al—OH	1.85_7
Al—O_2	1.96_0,	Al—O_2	1.93_2
Al—O_1	1.87_4,	Al—O_1	1.93_5
mean 1.91_2			

O—O $\sigma(l) = 0.03$Å

shared edges

OH—OH	2.33_8,	O_1—O_1	2.43_9
O_2—O_2	2.48_5		
mean 2.42_1			

non-shared edges

OH—O_1	2.79_2,	OH—O_2	2.80_3
OH—O_2	2.82_9,	OH—O_2	2.75_6
O_2—O_1	2.94_1,	O_2—O_1	2.78_7
O_2—OH	2.77_6,	O_1—OH	2.76_0
O_1—O_2	2.77_2		
mean 2.80_2			

TETRAHEDRA

Si,Al—O $\sigma(l) = 0.03$Å

Si,Al_1—O_1	1.69_2,	Si,Al_1—O_3	1.68_5
Si,Al_1—O_4	1.69_8,	Si,Al_1—O_5	1.69_6
mean 1.69_3			
Si,Al_2—O_2	1.67_4,	Si,Al_2—O_3	1.73_4
Si,Al_2—O_4	1.70_3,	Si,Al_2—O_5	1.69_7
mean 1.70_2			

O—O $\sigma(l) = 0.03$Å

Si,Al_1–tetrahedra

O_3—O_4	2.74_1,	O_4—O_5	2.68_1
O_5—O_3	2.74_2,	O_1—O_3	2.78_6
O_1—O_4	2.83_1,	O_1—O_5	2.79_5
mean 2.76_3			

Si,Al_2–tetrahedra

O_3-O_4	2.78_0,	O_4-O_5	2.79_4
O_5-O_3	2.72_2,	O_2-O_3	2.77_4
O_2-O_4	2.81_9,	O_2-O_5	2.77_5
mean 2.77_7			

$O-Si,Al-O$ $\quad \sigma(\theta) \simeq 1°$

O_1-Si,Al_1-O_3	$111.2°$
O_3-Si,Al_1-O_4	$108.2°$
O_4-Si,Al_1-O_5	$104.4°$
O_5-Si,Al_1-O_1	$111.1°$
O_5-Si,Al_1-O_3	$108.4°$
O_1-Si,Al_1-O_4	$113.2°$
mean $109.4°$	
O_2-Si,Al_2-O_3	$109.0°$
O_3-Si,Al_2-O_4	$107.9°$
O_4-Si,Al_2-O_5	$110.5°$
O_5-Si,Al_2-O_2	$110.8°$
O_2-Si,Al_2-O_4	$113.2°$
O_3-Si,Al_2-O_5	$105.0°$
mean $109.4°$	

$Si,Al-O-Si,Al$

Si,Al_2-O_5-Si,Al_1	$120.1°$
Si,Al_1-O_4-Si,Al_2	$124.9°$
Si,Al_2-O_3-Si,Al_1	$117.7°$
mean $\quad 121.0°$	

Ca-OCTAHEDRA

$Ca-O$ $\quad \sigma(l) = 0.02Å$

$Ca-O_3$	$2.39_9(2)*$,	$Ca-O_4$	$2.48_7(2)$
$Ca-O_5$	$2.48_8(2)$		
mean 2.45_8			

$O-O$ $\quad \sigma(l) = 0.03Å$

O_3-O_5	$3.49_6(2)$,	O_5-O_4	$3.50_3(2)$
O_4-O_3	$3.43_0(2)$,	O_3-O_5	$3.36_1(2)$
O_3-O_4	$3.52_4(2)$,	O_5-O_5	3.40_9
O_4-O_4	3.65_7		
mean 3.47_5			

* Numbers in parentheses indicate the number of equivalent bonds.

surface as in xanthophyllite but a corrugation running parallel to [110] and [1$\bar{1}$0] in alternate layers (Fig. 4). Fig. 3b shows that the corrugation of the layers is caused by the tilting of tetrahedra. For margarite, therefore, the configuration of the tetrahedral layers is defined by the tilting of tetrahedra in addition to the rotations. A similar configuration of tetrahedral layers was first pointed out by Newnham (1961) in his study of dickite. For this case, the maximum deviation in the parameters of the basal oxygens is 0.17Å. A closer examination of the structure of muscovite also reveals a similar corrugation of the layers. For muscovite, the maximum deviation amounts to 0.12Å. This evidence suggests that the corrugation of the tetrahedral layers is a characteristic feature of the dioctahedral layer silicates.
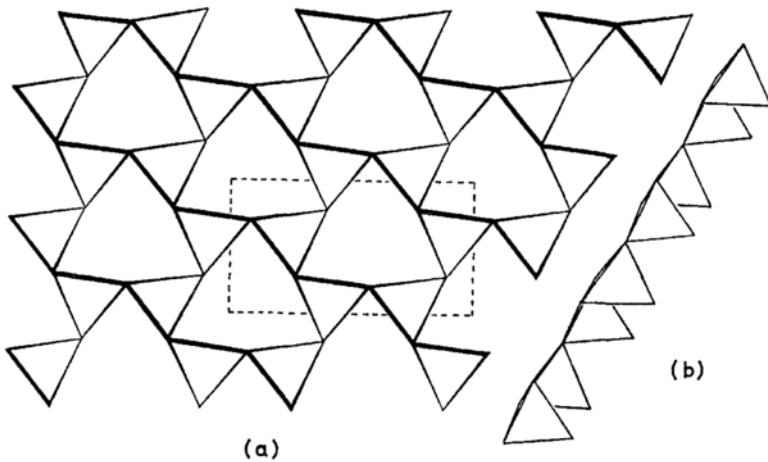
FIG. 4. A single tetrahedral layer of margarite, showing corrugation of the layer. Heavy lines indicate the elevated edges of basal oxygen triangles. The projection at (a) is on (001) and at (b) a view along [110].
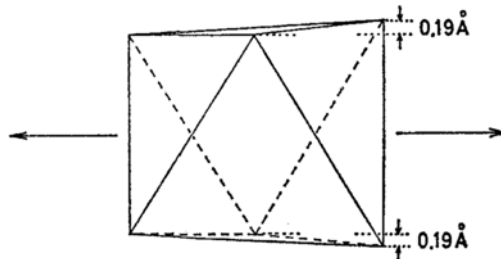

FIG. 5. Oxygen configuration around interlayer cations of dioctahedral micas as seen along the a-axis (the case of margarite is shown). As compared to the trioctahedral micas, where the planes of the basal oxygen triads are coplanar and parallel to the twofold axis, the basal oxygen planes in dioctahedral micas are tilted slightly, causing a displacement of the interlayer cations along the twofold axis.

The corrugation of tetrahedral layers in trioctahedral layer silicates is almost negligible for many cases. The importance of the layer corrugations in the structures of dioctahedral micas is that they cause a small shift of the interlayer cations to a certain direction specified by the orientation of the layers (Figs. 5 and 11). In Fig. 6, the oxygen configurations around Ca atoms are compared for the cases of xanthophyllite and margarite. The difference in bond lengths may be related to the difference in the configuration of tetrahedral layers.
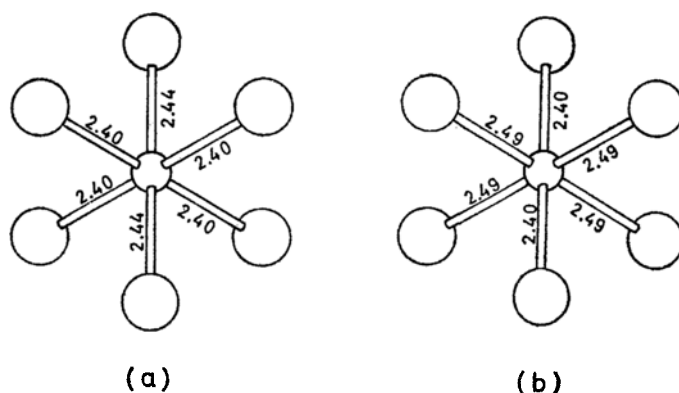
(a)   **(b)**

FIG. 6. The bond lengths in Ca—octahedra of (a) xanthophyllite, and (b) margarite.

CONFIGURATIONS OF OCTAHEDRAL LAYERS

The difference between the configuration of tetrahedral layers in dioctahedral micas and that in trioctahedral micas, as shown in the previous section, can be explained primarily by the difference between the configuration of dioctahedral layers and that of trioctahedral layers. The characteristic features of dioctahedral layers are the existence of vacant sites and the shortening of shared edges. The mean values of interatomic distances of aluminum octahedra in some layer silicates that have been studied to date with high accuracy are compared, in Table 6, together with those of gibbsite. In spite of different chemical compositions, the lengths of nonshared edges and those of the Al—O bond show good coincidence. There are some deviations among lengths of shared edges, but they are unexceptionally shorter than nonshared edges by about 10–14 per cent.

An important point in the configuration of the dioctahedral layers is that the shortening of the shared edges causes considerable distortion in the arrangement of surface oxygens of the layer. It is convenient to show the distortion by taking oxygen hexagons that consist of O—O edges of aluminum

TABLE 6. INTERATOMIC DISTANCES AND BOND LENGTHS OF ALUMINUM OCTAHEDRA

	Shared edge (Å)	Nonshared edge (Å)	Al—O(Å)
Gibbsite[1]	2.49±0.05	2.79	1.89±0.05
Dickite[2]	2.36±0.02	2.80	1.90±0.02
Kaolinite[3]	2.48±0.04	2.83	1.93±0.04
Muscovite[4]	2.55±0.03	2.83	1.95±0.02
Margarite	2.42±0.03	2.80	1.91±0.02

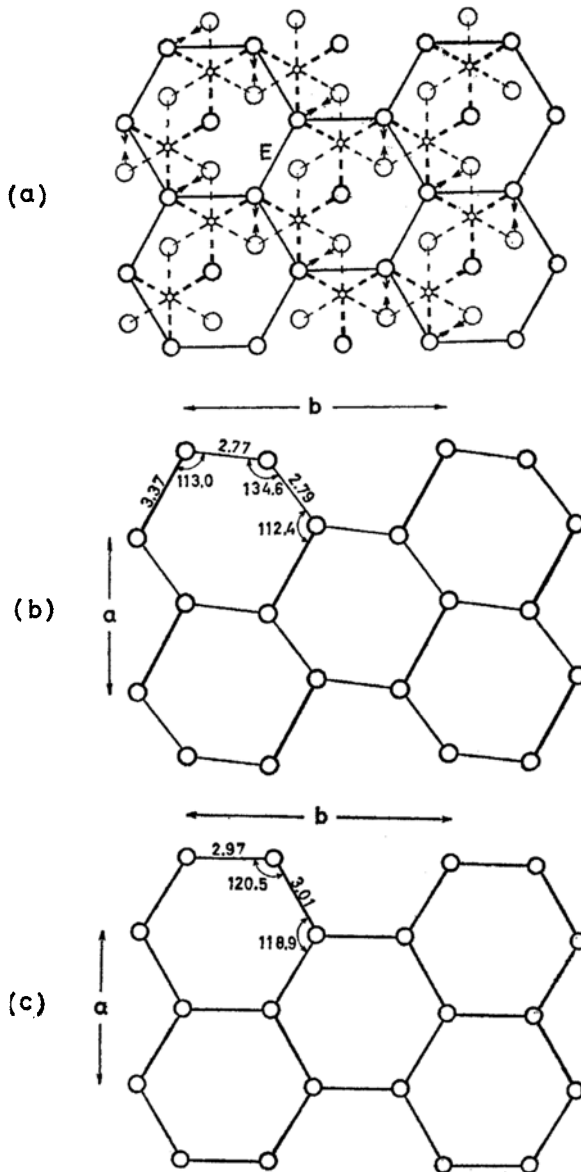[1] Megaw, 1934. [2] Newnham, 1961. [3] Zvyagin, 1960. [4] Radoslovich, 1960

FIG. 7. (a) Al-octahedral layer. The hexagonal network of oxygen hexagons is outlined. The arrows indicate the directions of the shifts of oxygens due to shortening of shared edges. (b) The network of oxygen hexagons in margarite. (c) The network of oxygen hexagons in xanthophyllite.

octahedra (Fig. 7a). If shortening of edges does not occur, the oxygen hexagons should have perfect hexagonal symmetry. If shortening actually occurs, the oxygen atoms of shared edges are shifted from their ideal positions as shown by arrows in Fig. 7a, thus causing a stretching of edges parallel to E, which corresponds to an edge of vacant octahedra. The shifts of oxygen atoms of shared edges do not cause such an effect in the other edges of the oxygen hexagons but merely cause twisting of the edges. As a result, the oxygen hexagons are deformed as shown in Fig. 7b, which shows the case for margarite. The deformation is characterized by the presence of stretched-out longer edges parallel to one direction. The dimensions of the oxygen hexagons of some layer silicates are compared in Table 7 together with those of gibbsite. Each hexagon in the hexagonal net of oxygens is symmetrically equivalent for kaolinite, dickite, muscovite and margarite, but there are two non-equivalent hexagons in gibbsite. The longer edge of one of the hexagons in gibbsite is considerably shorter, but that of the other hexagon has a length similar to those of others. It is interesting to note that the dimensions of oxygen hexagons for dickite are very similar to those of margarite, while those for muscovite and kaolinite show higher values. Nevertheless, the presence of stretched-out longer edges in the oxygen hexagons is a common characteristic of the dioctahedral layers, and the fact that similar values are maintained for these edges throughout various kinds of layer silicates strongly suggests that the octahedral layers are a fundamental feature of the structures of layer silicates. It should be noted that the length of the longer edges is as large as the edges of Fe^{2+} or Mn octahedra.

TABLE 7. EDGE LENGTHS OF OXYGEN HEXAGONS IN SOME ALUMINUM OCTAHEDRAL LAYERS

	Short edge (Å)	Longer edge (Å)
Gibbsite	2.92	3.32
	2.76	2.94
Dickite	2.76	3.41
	2.81	
Kaolinite	2.84	3.22
	2.86	
Muscovite	2.84	3.26
	2.91	
Margarite	2.77	3.37
	2.79	

Since the oxygen atom at each corner of the hexagons forms a bond with cations of the tetrahedral layer in layer silicates, the dimensions of the oxygen

hexagons should be compared with those of oxygen hexagons formed by apical oxygens of the tetrahedral layer. The calculated values of edge l_t of oxygen hexagons that are formed by apical oxygens with ideal hexagonal symmetry are listed in Table 8. The values for tetrahedral bond lengths were obtained from the work by Smith and Bailey (1963). It should be noted that the values of l_t lie between those of short edges and those of longer edges of oxygen hexagons of the octahedral layer. It is not likely that l_t exceeds the values of the longer edges of the oxygen hexagons of the octahedral layer, the mean value of the longer edges for dickite, kaolinite, muscovite and margarite being 3.32Å. As a consequence, to fit the dimensions of the longer edges of oxygen hexagons in a dioctahedral layer, the dimensions of the hexagons of apical oxygens must be expanded. This is done only by the tilting of tetrahedra, providing no deformation of the tetrahedra themselves. On the other
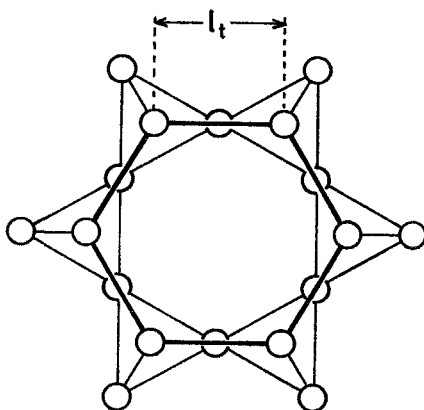

FIG. 8. A component hexagonal ring of ideal tetrahedral layers. Edge l_t of apical oxygen hexagon is indicated.

TABLE 8. TETRAHEDRAL CATIONS AND EDGE LENGTH, l_t, OF OXYGEN HEXAGONS FORMED BY APICAL OXYGENS OF TETRAHEDRAL LAYERS WITH IDEALLY HEXAGONAL SYMMETRY

Tetrahedral cations Si : Al		Bond length d(Å)	l_t*(Å).
1	0	1.620	3.055
3	1	1.659	3.130
1	1	1.696	3.206
1	3	1.732	3.262
0	1	1.77	3.338

* Using the tetrahedral angle 109°28′20″, l_t is derived by the formula $l_t = 1.8856 \times d$.

hand, the presence also of shorter edges in oxygen hexagons of a dioctahedral layer requires shrinkage of the apical oxygen hexagons. Uniform shrinkage of apical oxygen hexagons can be achieved by rotations of tetrahedra. The combination of these two effects determines the configurations of tetrahedral layers in dioctahedral micas. Thus, in dioctahedral micas, tiltings of tetrahedra are inherent, giving rise to a corrugation of basal oxygens of tetrahedral layers.

On the other hand, in trioctahedral layers, all octahedral sites are occupied mainly by magnesium (magnesium may be replaced by Fe, Mn, Ca or by some amount of Li or Al) and the shortening of shared edges contracts the layers uniformly. Accordingly, the deformation of oxygen hexagons of surface oxygens is very small, and the symmetry of the hexagons is nearly or perfectly hexagonal (Fig. 7c). The edge lengths of the hexagons in some trioctahedral layer silicates are listed in Table 9, which shows that the difference in the edge lengths is very small for each substance. The difference shown in the Table for xanthophyllite is due to the ordering of existing aluminum atoms. For some other minerals not listed in the Table, like amesite (Steinfink and Brunton, 1956) and Cr-chlorite (Brown and Bailey, 1963), the difference is either exceedingly small or zero by symmetry. This evidence supports the theory that the configurations of the trioctahedral layers are, as in the case of dioctahedral layers, fairly regular, regardless of the chemical composition of the tetrahedral layers, and that this governs the configurations of the tetrahedral layers.

TABLE 9. EDGE LENGTHS OF OXYGEN HEXAGONS IN SOME
TRIOCTAHEDRAL LAYERS

	Octahedral cation	Edge length (Å)	
Brucite[1]	Mg_3	3.12	—
Xanthophyllite	Mg_2Al	3.01	2.97 ± 0.02
Phlogopite[2]	Mg_3	3.08	3.13 ± 0.03
Mg-vermiculite[3]	Mg_3	3.07	3.06 ± 0.03
Iron-mica[4]	Fe_3	3.14	3.12 *

[1] Aminoff, 1919 (in Bragg, 1937, p. 107). [2] Steinfink, 1962.
[3] Mathieson, 1958. [4] Morimoto et al.. 1963.
    * Not stated but probably less than ± 0.02Å.

In trioctahedral micas (Table 9), the apical oxygen hexagons are always larger than the oxygen hexagons of the octahedral layers. Accordingly the misfit between these layers is mainly adjusted by the rotations of tetrahedra. Therefore, z-parameters of basal oxygens of tetrahedra show no appreciable deviations. The maximum values of the deviations for some trioctahedral layer silicates are compared with those of dioctahedral layer silicates in Table 10. An exceptional case has been observed in the structure of "phlogopite–biotite" for which the maximum deviation is 0.1Å (Zvyagin and

Mischenko, 1963). However, a closer examination of the structure revealed that this is caused by deformation of tetrahedra and not by tilting. Because the accuracy of the parameters is less than that for other cases cited above, further refinement of the structure is desirable to confirm this point.

TABLE 10. THE MAXIMUM DEVIATIONS IN z-PARAMETERS OF TETRAHEDRAL BASAL OXYGENS

Dioctahedral (Å)		Trioctahedral (Å)	
Dickite	0.17 ± 0.03	Iron-mica	0.01
Kaolinite	0.15 ± 0.04	Mg-vermiculite	0.00 ± 0.03
Margarite	0.19 ± 0.03	Phlogopite	0.01 ± 0.03
Muscovite	0.12 ± 0.03	Xanthophyllite	0.06 ± 0.02

SYMMETRY OF DIOCTAHEDRAL MICA LAYERS

The structure of natural muscovite is unique in that the existence of disorder and of stacking polytypes is very rare. Although an exceptional case has been reported (Axelrod and Grimaldi, 1949), natural muscovites tend to adopt the $2M_1$ structure and to give sharp hkl reflections with $k \neq 3n$. The 1M structure is known for synthetic muscovite (Yoder and Eugster, 1955). In both natural and synthetic cases, the 3T polytype is rare. As has been discussed in the previous sections, the mode of distortion of tetrahedral layers in dioctahedral micas is different from that in trioctahedral micas. This fact may suggest that relative abundances of polytypism in the dioctahedral micas could be ascribed to the inherent distortions of the mica layers. It appears, however, that no reasonable explanation of the problem can be deduced from the goemetrical features of the distorted layers alone. This suggests that a thorough investigation of the bond forces between the layers is desirable.

However, one thing that would be worth noting here is that the orientations of the O—H bond of the OH groups in dioctahedral micas is somewhat different from that of trioctahedral micas. Because of the different nature of polarization of OH groups between dioctahedral and trioctahedral layers, the O—H bond is nearly perpendicular to (001) for trioctahedral micas, while it is considerably inclined from the c'-axis [an axis perpendicular to (001)] for dioctahedral micas (Serratosa and Bradley, 1958). The orientation of O—H bond in muscovite has been investigated in detail by Tsuboi (1950) and Vedder (1963) by using polarized infrared radiation. Using the notations of conventional stereographic projections, their results compare as follows:

	ρ	ϕ
Tsuboi	70°	−39°
Vedder	74°~71°	~ −32°

In spite of the considerable deviations in these results, one conclusive thing is that the value of $|\phi|$ is not 30° but has, according to Vedder, a " definitely"

larger value. The orientation of the bond obtained by Vedder is shown in Figs. 9 and 10a. Also illustrated in Fig. 9 are the hexagon formed by basal oxygens of tetrahedra, the potassium atom center and the geometrical center G of the O_E, O_C, O_D triangles in projection onto (001). The notation of oxygens is that originally assigned by Radoslovich (1960). The actual geometrical center of the potassium polygon formed by three oxygens (O_E, O_C,
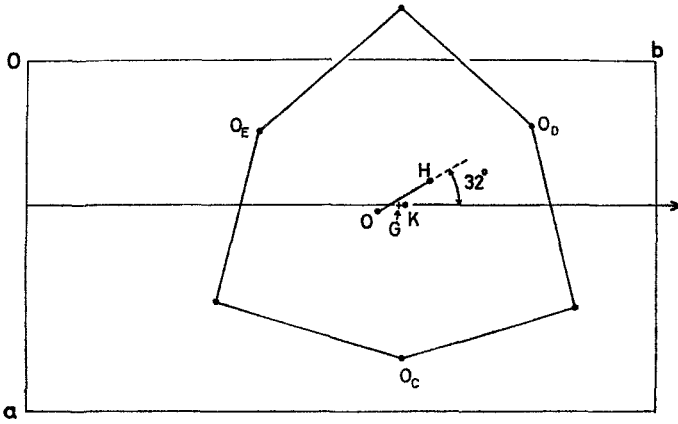

FIG. 9. Orientation of the O—H bond in muscovite. G shows the geometrical center of the oxygen triangle O_E, O_C, O_D in the projection on (001).
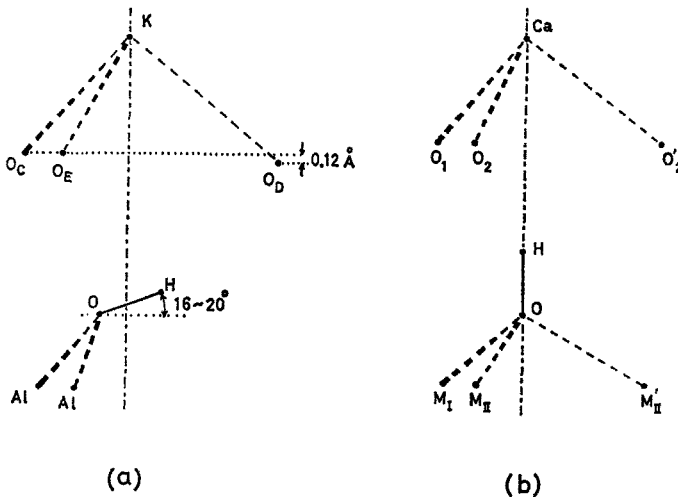

(a)   (b)

FIG. 10. (a) Orientation of the O—H bond in muscovite as seen approximately along [310]. (b) For the case of trioctahedral micas like xanthophyllite, the O—H bond is nearly perpendicular to (001).

O_D) and their symmetrical pairs should be shifted from G toward K because of the deviations of z-parameters, as mentioned above.

It should be noted that the O—H bond does not pass through G. On the assumption, therefore, that the deviation of O—H direction from $|\phi| = 30°$ is characteristic of muscovite and, hence, possibly of other dioctahedral micas, then the symmetry of the diotahedral mica layers is not C_{2h} because the mirror plane is missing in the strictest sense. The symmetry will be C_i, because it would be reasonable to suppose that the O—H bond in the upper half of a layer is related to that in the lower half by a center of symmetry, rather than a twofold axis.

A mica layer is related to its successive layers by a rotation of multiples of 120° (Radoslovich, 1959). The relation is also expressed by twofold operations about an axis [010], [310] or [3̄10] (axes are referred to the $2M_1$ structure). By these operations, no appreciable changes occur in the surroundings of the interlayer cations. A rotation of a layer with respect to successive layers is equivalent to one of the twofold operations if the symmetry of the layer is C_{2h}. In Table 11, the rotations and corresponding twofold operations are listed together with related polytypes. For the symmetry C_i, however, there is no equivalency between these two kinds of operations. The oxygen configurations and arrangements of OH groups around K resulting from various operations are compared in Fig. 11. The cases obtained by rotations of $\pm$ 120°, which are the generating operations of 3T structure locations of H in the upper layer and in the lower, are not symmetrical about K. They are symmetrical in other cases. It would seem, therefore, that this situation is correlated with an abundance of polytypes of muscovite. However, it is not quite clear whether the interaction between the weak positive charge of H and

TABLE 11. TWOFOLD OPERATIONS AND ROTATIONS AROUND THE c'-AXIS. ANGLES ARE GIVEN COUNTERCLOCKWISE AND AXES ARE REFERRED TO THOSE OF THE $2M_1$ STRUCTURES

| Symmetry of composite layer | Symmetry operation | | Related polytypes |
	Twofold axis	Rotation around c'-axis	
C_{2h}	[010] [3̄10]	120° 240°(−120°)	$2M_1$, 3T
	[310]	360°	1M
C_i	[010] [3̄10]		$2M_1$
		120° 240°(−120°)	3T
	[310]	360°	1M* 1Tc†

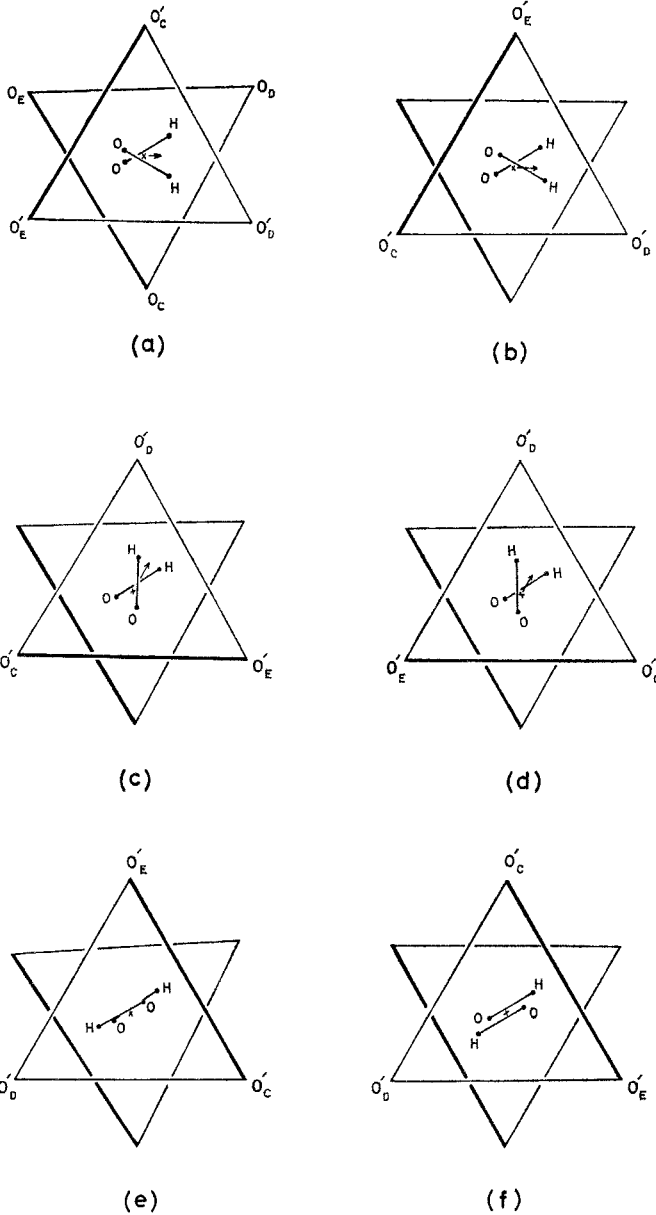* Symmetry is lower than $C2/m$.   † One-layer triclinic.

FIG. 11. Comparison of oxygen configurations and arrangements of O—H bonds around potassium resulting from various symmetry operations. The orientations of O_E, O_C, O_D triangles are the same throughout this figure. The

K is significant enough to have an effect on the equilibrium position of K. This problem requires further investigation. The distance between H and K is about 3.7Å on the assumption that the position of H is fixed and that the O—H bond length is 0.9Å. Similar discussion can be applied to margarite. However, for this case, the oxygen octahedra around Ca are more contracted than the octahedra around K in muscovite, and the O—H bond, if $\phi = -32°$, is closer to G.

It has been suggested by Bradley (1959) that the ordering of tetrahedral cations may be the determining factor in the crystallization of the dioctahedral micas. It should be noted that the ordering of Al and Si in tetrahedral sites as revealed by Radoslovich (1960) also lowers the possible symmetry of the composite layer to C_i. In any case, therefore, in the discussion of layer stackings in dioctahedral micas, the above six operations should be considered.

CONFIGURATIONS OF TETRAHEDRAL LAYERS IN LAYER SILICATES

In view of the fact discussed above, it would be convenient to define a measure of the degree of the dimensional difference between octahedral and tetrahedral layers. A convenient quantity may be defined by

$$D = (l_0 - l_t)/l_0$$

where l_0 is the edge length of the oxygen hexagons in octahedral layers and l_t is that of the oxygen hexagons formed by apical oxygens of the tetrahedral layers with ideal hexagonal symmetry. Thus, D provides a direct measure of misfit. For the case of the dioctahedral layers, it is meaningless to take an average of the values for longer edges and short ones. Therefore, for this case D is expressed by two values, one negative and the other positive. Among trioctahedral layer silicates, if tetrahedral cations contain aluminum like micas, chlorites and vermiculite, D is always negative, ranging from -8.7 to zero. If the tetrahedral cations are mainly Si and octahedral sites are occupied by Mg or cations of larger size like Fe^{2+}, Mn or Ca, D is positive. In this way, the layer silicates may be classified into three types, listed in Table 12. Positive D values imply distortions of tetrahedral layers by the tilting of tetrahedra and negative ones imply rotations. The D's of type II are simply related to the rotation angles of tetrahedra, but the negative D's of type I are not explainable in a simple way because the tilting of the tetrahedra causes shortening of

---

heavy lines of these triangles indicate elevated edges. The O'_E, O'_C, O'_D triangles are related by the symmetry operations to the O_E, O_C, O_D triangles and for these heavy lines indicate depressed edges. The directions of the shifts of interlayer cations are shown by arrows (refer to Fig. 6). Crosses indicate G (Fig. 9). The symmetry operations are: (a) Twofold operation about [010] (the case of the $2M_1$ structure). (b) Rotation of 120°. (c) Twofold operation about [3$\bar{1}$0]. (d) Rotation of 240°. (e) Twofold operation about [310]. (f) Rotation of 360°.

other edges of apical hexagons. Consequently, muscovite and xanthophyllite, for instance, have similar D's but the rotations of tetrahedra in muscovite are much smaller than those in xanthophyllite. Similarly, among the minerals in type I, muscovite and dickite have almost same negative D values but the rotation of the tetrahedra in muscovite is larger than that of dickite. This is because the $+D$'s of dickite are much larger than those of muscovite, less rotation being required. In either case of types I and II, brittle micas show the largest negative D values.

TABLE 12. MISFIT INDEX, D, AND CLASSIFICATION OF LAYER SILICATES

Type	Layer silicate	Main tetra. cation	Main octa. cation	$D\%$
	Dioctahedral micas	Si,Al	Al	−15.3, +4.9
	Margarite			
	Muscovite			− 8.9, +4.0
	Paragonite			
I	Pyrophyllite	Si	Al	
	Kaolinite group	Si	Al	
	Dickite			− 8.8, +11.6
	Smectite			
	Montmorillonite	Si	Al	
	Trioctahedral micas	Si,Al		
	Xanthophyllite		Mg,Al	− 8.7
	Lepidolite		Li,Al	
II	Phlogopite		Mg	
	Biotite		Mg,Fe	⏜−0.5
	Chlorite	Si,Al	Mg,Al,Fe	|
	Vermiculite	Si,Al	Mg,Fe,Al	⏜zero
	Smectite			
	Hectorite	Si	Mg	
	Talc	Si	Mg	
	Serpentines			+2.0
III	Chrysotile	Si	Mg	
	Palygorskite group	Si	Mg	
	Bementite	Si	Mn	
	Pyrosmalite	Si	Mn	+8.8
	Zeophyllite	Si	Ca	+13.4

In the case of type III, the tetrahedral layers are primarily matched with octahedral layers through tilting of tetrahedra. If the misfit is significantly large, the tetrahedral layers can no longer maintain their two-dimensional extended planar configurations and take various configurations to relieve the strain due to misfit. In Fig. 12b, an example of pyrosmalite, $D = 8.8$, (Takéuchi, Kawada and Sadanaga, 1963) is shown. The six-membered

tetrahedral rings are alternatively inverted in two dimensions. In the actual structures, tetrahedra of each ring show considerable tilting. The largest value of D for layer silicates may be given by those containing Ca-octahedral layers ($D = 13.4$). The structure of zeophyllite proposed by Chalmers, Dent and Taylor, (1958) (but not definitely confirmed) is shown in Fig. 12a where six-membered rings are connected by bridge tetrahedra. When the misfit is smaller, the tetrahedral layers tend to stretch in one direction and the resulting strain in the directions perpendicular to the stretching is released by corrugation or inversion of tetrahedra. Examples of these cases are serpentines (Kunze, 1956 and 1958) and palygorskites (Fig. 12d) (Bradley, 1940; Preisinger, 1959; Caillère and Hénin, 1961). An interesting example has been given by the structure of astrophyllite (Woodrow, 1963) in which the dimensional difference between tetrahedral and Fe,Mn-octahedral layers is mainly adjusted by having Ti-octahedra in the tetrahedral layers (Fig. 12c). Talc has D values similar to chrysotile and palygorskites. Nevertheless, the structure of talc consists of micalike layers. The further study of the details of this structure should reveal more interesting features.
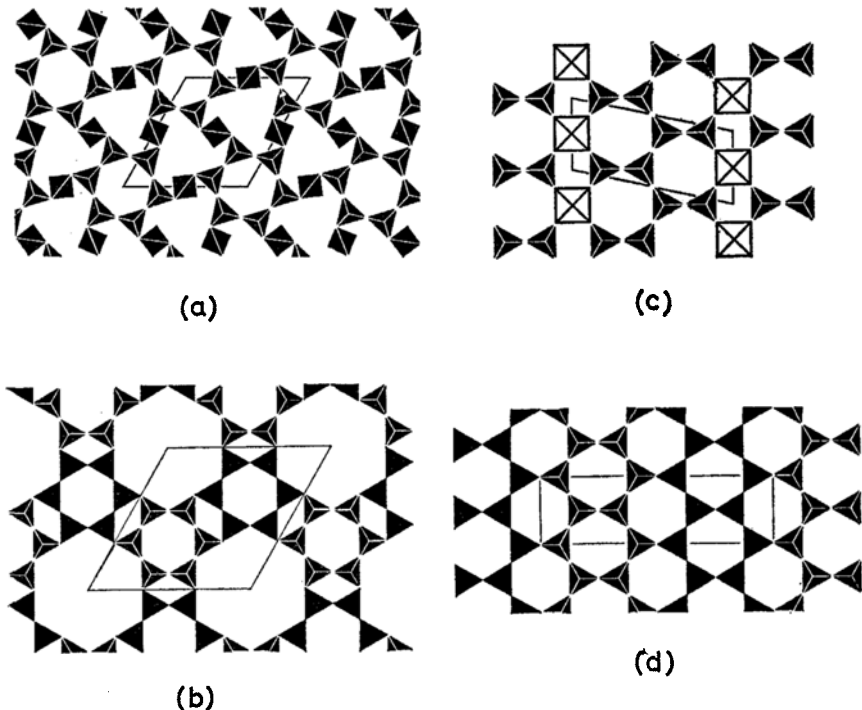

(a)

(c)

(b)

(d)

FIG. 12. Various configurations of tetrahedral layers in the layer silicates of type III. (a) Zeophyllite. (b) Manganopyrosmalite. (c) Astrophyllite. (d) Palygorskite.

3

By an extensive survey of 1 : 1 layer silicates, Bates (1959) has assigned a similar misfit index M. Since it is based upon the ionic radii of octahedral and tetrahedral cations, it gives an indirect measure of misfit. From a structural view point, the index D provides more detailed information about misfit, especially for the dioctahedral cases.

ACKNOWLEDGMENTS

REFERENCES

AXELROD, J. M., and GRIMALDI, F. S. (1949) Muscovite with small optic axial angle, *Am. Mineralogist* **34**, 559–72.

BATES, T.F., HILDEBRAND, F. A., and SWINEFORD, A. (1950) Morphology and structure of endellite and halloysite, *Am. Mineralogist* **35**, 467–84.

BATES, T. F. (1959) Morphology and crystal chemistry of 1 : 1 layer lattice silicates, *Am. Mineralogist* **44**, 78–114.

BELOV, N. V. (1963) *Crystal Chemistry of Large-Cation Silicates*, Consultant Bureau, New York.

BRADLEY, W. F. (1940) Structure of attapulgite, *Am. Mineralogist* **25**, 405–10.

BRADLEY, W. F. (1959) Current progress in silicate structures, *Clays and Clay Minerals*, 6th Conf. [1957], pp. 18–25, Pergamon Press, New York.

BRAGG, W. L. (1937) *Atomic Structure of Minerals*, Cornell University Press, Ithaca, New York.

BROWN, B. E., and BAILEY, S. W. (1963) Chlorite polytypism, II, Crystal structure of a one-layer Cr-chlorite, *Am. Mineralogist* **48**, 42–61.

CAILLÈRE, S., and HÉNIN, S. (1961) Palygorskite, *X-ray Identification and Crystal Structures of Clay Minerals*, (edited by T. Brown), pp. 343–53, Mineralogical Society, London.

CHALMERS, R. A., DENT, L. S., and TAYLOR, H. F. W. (1958) Zeophyllite, *Mineral. Mag.* **31**, 726–35.

DEER, W. A., HOWIE, R. A., and ZUSSMAN, J. (1962) *Rock-Forming Minerals*, vol. 3, (Sheet Silicates), Longmans, London.

FORMAN, S. A. (1951) Xanthophyllite, *Am. Mineralogist* **36**, 450–7.

KOCH, G. (1935) Chemische und physikalisch-optische Zusammenhänge innerhalb der Sprödglimmergruppe, *Chem. Erde* **9**, 453–63.

KUNZE, G. (1956) Die gewellte Struktur des Antigorites, I, *Z. Krist.* **108**, 82–107.

KUNZE, G. (1958) Die gewellte Struktur des Antigorites, II, *Z. Krist.* **110**, 282–320.

MATHIESON, A. McL. (1958) Mg-vermiculite, a refinement and re-examination of crystal structure of the 14.36Å phase, *Am. Mineralogist* **43**, 216–27.

MEGAW, HELEN D. (1934) The crystal structure of hydragillite, $Al(OH)_3$, *Z. Krist.* **87**, 185–204.

MORIMOTO, N., DONNAY, G., TAKEDA, H., and DONNAY, J. D. H. (1963) Crystal structure of synthetic iron mica, *Acta Cryst.* **16**, A 14.

NEWNHAM, R. E. (1961) A refinement of dickite structure and some remarks on polytyp-ism in kaoline minerals, *Mineral. Mag.* **32**, 683–704.

NIGGLI, E. (1955) Zum Vorkommen von Kalkglimmern (Margarit, Clintonit) in der Schweizer Alpen, *Leidse Geol. Mededel.* **20**, 165–70.

PREISINGER, A. (1959) X-ray study of the structure of sepiolite, *Clays and Clay Minerals*, 6th Conf. [1957], pp. 61–7, Pergamon Press, New York.

RADLOSLOVICH, E. W. (1959) Structural control of polymorphism in micas, *Nature* **183**, 253.

RADOSLOVICH, E. W. (1960) The structure of muscovite, $KAl_2 (Si_3Al)O_{10}(OH)_2$, *Acta Cryst.* **13**, 919–32.

RADOSLOVICH, E. W., and NORRISH, K. (1962) The cell dimensions and symmetry of layer-lattice silicates. I. Some structural considerations, *Am. Mineralogist* **47**, 599–616.

SADANAGA, R., and TAKÉUCHI, Y. (1961) Polysynthetic twinning of micas, *Z. Krist.* **116**, 406–29.

SANERO, E. (1940) La struttura della xantofillite, *Periodico Mineral. (Rome)* **11**, pp. 53–77.

SERRATOSA, J. M., and BRADLEY, W. F. (1958) Infra-red absorption of OH bonds in micas, *Nature* **181**, 111.

SMITH, J. V., and BAILEY, S. W. (1963) Second review of Al—O and Si—O tetrahedral distances, *Acta Cryst.* **16**, 801–11.

STEINFINK, H., and BRUNTON, G. (1956) The crystal structure of amesite, *Acta Cryst.* **9**, 487–92.

STEINFINK, H. (1962) Crystal structure of a trioctahedral mica, phlogopite, *Am. Mineralogist* **47**, 886–96.

TAKÉUCHI, Y. (1958) A detailed investigation of the structure of hexagonal $BaAl_2Si_2O_8$ with reference to its $\alpha-\beta$ inversion, *Mineral. J.* **2**, 311–32.

TAKÉUCHI, Y., and DONNAY, G. (1959) The crystal structure of hexagonal $CaAl_2Si_2O_8$ *Acta Cryst.* **12**, 465–70.

TAKUÉCHI, Y., and SADANAGA, R. (1959) The crystal structure of xanthophyllite, *Acta Cryst.* **12**, 945–6.

TAKUÉCHI, Y., KAWADA, I., and SADANAGA, R. (1963) The crystal structure and poly-types of manganpyrosmalite, *Acta Cryst.* **16**, A 16.

TSUBOI, M. (1950) On the positions of the hydrogen atoms in the crystal structure of muscovite, as revealed by the infra-red absorption study, *Bull. Chem. Soc.* Japan **23**, 83–8.

VEDDER, W., and McDONALD, R. S. (1963) Vibrations of the OH ions in muscovite, *J. Chem. Phys.* **38**, 1583–90.

YODER, H. S. JR., and EUGSTER, H. P. (1955) Synthetic and natural muscovite, *Geochim. Cosmochim. Acta.* **8**, 225–80.

WOODROW, P. J. (1963) The crystal structure of astrophyllite, *Acta Cryst.* **16**, A 16–17.

ZVYAGIN, B. B. (1960) Electron-diffraction determination of the structure of kaolinite, *Soviet Phys.—Cryst.* **2**, 388–94.

ZVYAGIN, B. B., and MISHCHENKO, K. S. (1963) Electronographic data on the structure of phlogopite-biotite, *Soviet Phys.—Cryst.* **7**, 502–5.