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Note added in page proof: Dr. H.-U. NISSEN kindly informed us that his paper *Schweiz. Min. Petr. Mitt.* **48**, 53—55 demonstrates an unmixing gap between approx. 67 and 83 mol-% albite on the basis of lamellae oriented on (601) in bytownites from amphibolite and anorthosite rocks, and that the structure does not depend on potassium feldspar solid solution. In addition, he states (see p. 189) that the discussion is confused by a misunderstanding over identification of the texture. He and Dr. BOLLMANN suggest that the fine herring-bone texture may result merely from parallel alignment of evaporated chromium particles, but does not lead out a surface structure dependent on a domain structure.

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The A and B Mica Layers and the Crystal Structure of Sheet Silicates

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Abstract. A discussion of the transition from the “ideal hexagonal” mica structure to the “ideal ditrigonal” one, leads to the conclusion that the single mica layer may have two different structures (labelled A and B). The recent literature data show that both the A and B structures have been detected in some triocahedral layer lattice silicates found in nature. An examination of the structural stability of the A and B structures suggests that the last one may not be realized by dioctahedral layer lattice silicates. The concept of two structurally different mica layers, which however have the same lattice constants, greatly improves the understanding of polymorphism and twin laws in layer lattice silicates.

The structural features of the tetrahedral sheet, octahedral sheet and interlayer region are carefully examined. Thus we can reach the following conclusions: the tetrahedral sheet is not entirely free to reduce its lateral dimensions by the mechanism of tetrahedral rotation owing to the repulsion among O_{bas} atoms; the octahedral sheet in layer lattice silicates, may increase or reduce its lateral dimensions as compared to the lateral dimensions it has in the hydroxide minerals; the interlayer region is characterized by a regular octahedral coordination of the O_{bas} around the interlayer cation. On the ground of these conclusions, new structural models for some selected layer lattice silicates are proposed.

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Notations

- O_{bas} = basal oxygen atoms of the $(Al, Si)O_4$ tetrahedra.
 O_{ap} = apical oxygen atoms of the $(Al, Si)O_4$ tetrahedra.
 b_{tetr} = b dimension which the tetrahedral sheet would assume if unconstrained.
 b_{oct} = b dimension which the octahedral sheet has in the hydroxide minerals.
 b_{obs} = observed value of b .
 c_{oct}^* = thickness of the octahedral sheet.
 d_o = distance between an octahedral cation and an O_{ap} atom.
 d_{int} = distance between an interlayer cation and an O_{bas} atom.
 α = average tetrahedral rotation from ideal hexagonal symmetry.

Other notations with their usual meaning or with the meaning specified in the text.

Introduction

BAILEY (1966) points out that, owing to the research work of many authors during the past ten years, the structures of most of the hydrous layer lattice silicates are known with great detail. Thus a number of recent papers are devoted primarily to the discussion of the crystal chemistry of layer lattice silicates on the ground of very reliable experimental data.

In spite of this, it seems that some basic structural features of these minerals have not yet been explained satisfactorily. As an example we can mention the trigonal prismatic coordination around the interlayer cation assumed to be realized in the $2M_2$ micas, or the effect of the interlayer cation on the mica b_{obs} values.

FRANZINI e SCHIAFFINO (1963a, 1963b) have suggested on theoretical and experimental grounds that the single mica layer may have two different structures (which they labelled A and B) and that the coordination polyhedron around the interlayer cation may be an almost regular octahedron. These hypothesis have received great support from the many experimental data published in the last years.

The first part of the present paper will be devoted to a discussion in general terms of the newly acquired experimental data, in the light of what FRANZINI e SCHIAFFINO (1963a, 1963b) firstly suggested for the micas. Furthermore it will be proved that the two different structures of the single mica layer as well as the octahedral coordination around the interlayer cation are justified by taking into consideration the structural stability of the single mica layer. These two basic features of the layer lattice silicate structures, once recognized, allow a better understanding of the known experimental data about micas and other layer lattice silicates.

In the second part of the present paper the structural features of some selected layer lattice silicates will be discussed on the ground of the new ideas.

The basic structural feature of a mica is a composite 2:1 layer in which a sheet of octahedrally coordinated cations is sandwiched between two identical sheets of linked $(Si, Al)O_4$ tetrahedra. Between these composite layers lie the interlayer cations. In what follows the composite 2:1 layer in micas will be referred to as the "mica layer".

It would be better to label the composite 2:1 layer as "talc layer" or "pyrophyllite layer" according to its trioctahedral or dioctahedral character. However it will be shown that the interlayer cation has a great influence on the composite

2:1 layer. Therefore the composite 2:1 layer in talc and pyrophyllite may have a quite different structural arrangement (essentially a different α value) from the one realized in the composite 2:1 layer in micas. Thus we have preferred to indicate the composite 2:1 layer as "talc layer" (or "pyrophyllite layer") when speaking of chlorites and as "di- (or tri-) octahedral mica layer" when speaking of micas.

The Two Structures of the Mica Layer

Geometrical Considerations

RADOSLOVICH (1961) suggests that the "ideal" mica structure be redefined as having ditrigonal surface symmetry, with the tetrahedral cations having $y = nb/12$. This definition of the "ideal" structure has received great support from the data published by several authors since 1961.

The transition from the "ideal" hexagonal structure (JACKSON and WEST, 1930) to the "ideal" ditrigonal one (RADOSLOVICH, 1961) is fulfilled through an alternate clockwise and anticlockwise twist of the $(Si, Al)O_4$ tetrahedra about an axis perpendicular to (001). There are however two directions of rotation about an axis perpendicular to (001), and therefore the single "ideal" hexagonal structure originates two "ideal" ditrigonal structures. The two ditrigonal structures are not equivalent to each other because one of the directions of rotation (which will be indicated as "positive") approaches, and the other ("negative") removes all the O_{bas} from the octahedral cations (Fig. 1).

A mica layer contains two tetrahedral sheets so that we can build up four different mica layers, two with a centre of symmetry (positive-positive and negative-negative) and two without a centre of symmetry (positive-negative and negative-positive) (Fig. 2). These four combinations produce three nonequivalent structures being the two acentric combinations equivalent by a 180° rotation.

The possibility that the acentric structure (with the meaning previously defined) may be actually found in nature is ruled out taking into consideration the structural stability of this geometrically possible mica structure. Thus we can conclude that actually there are only two structurally different mica layers, labelled A and B in Fig. 2.

A more detailed discussion on this subject is reported by FRANZINI and SCHIAFFINO (1963b).

The A and B structures have the same lattice constants and space group and can be distinguished only taking into consideration the x parameter of the O_{bas} . Let x_A be the parameter of the O_{bas} in the A structure, and x_B the x parameter of the O_{bas} in the B structure, then (FRANZINI, 1966):

$$x_B = 2z/3c - x_A$$

assuming that $c \cos \beta^*/a = 1/3$ (DONNAY, DONNAY and TAKEDA, 1964).

The A and B mica layers have the same surface distribution of oxygen atoms and therefore they may be equally well joined to the interlayer cation. Thus we may have mica specimens whose structure contains only A layers, or only B layers, or A and B layers (FRANZINI and SCHIAFFINO, 1963b).

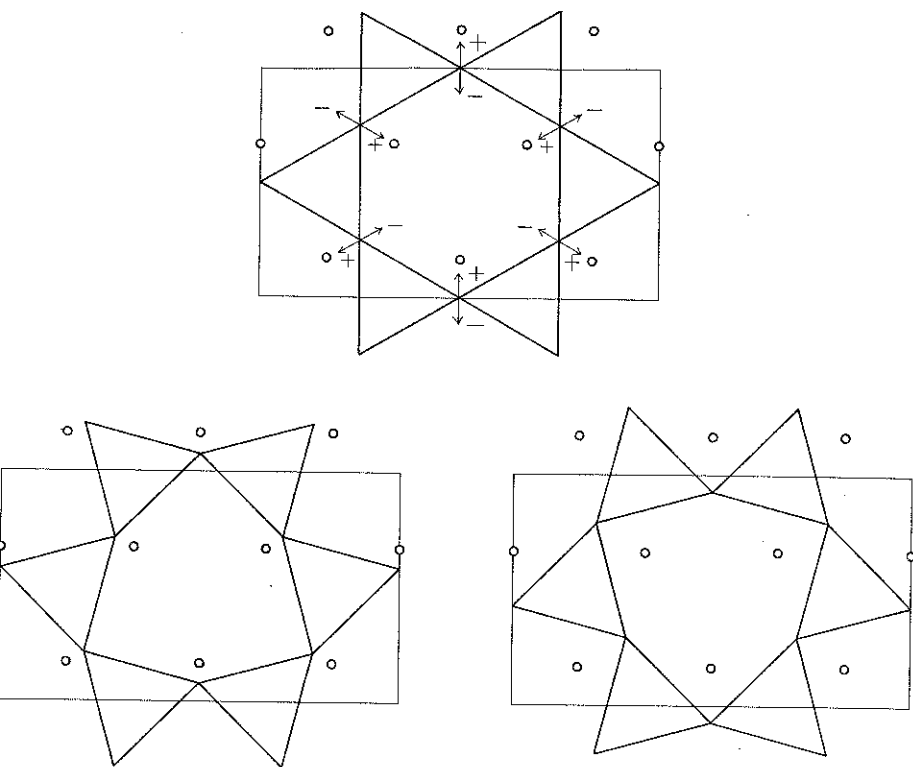


Fig. 1. Small circles represent octahedral cations. Upper: "ideal" hexagonal distribution of the O_{bas} atoms on the basal plane. Arrows point out "positive" and "negative" tetrahedral rotations. Lower: actual ditrigonal distribution, $\alpha = 15^\circ$; left: "positive" rotation; right: "negative" rotation

It is not possible on the whole to distinguish these different structures on the basis of their lattice constants. They can be distinguished only by taking into consideration the intensities of some selected x-ray diffractions or by solving the crystal structure.

The Actual Existence in Nature of A and B Layers

FRANZINI (1966) experimentally proved the actual existence in nature of the B layers measuring the intensities of the x-rays diffracted by a biotite crystal twinned on [100]. On the basis of the known experimental data we can state that usually the dioctahedral and trioctahedral micas are built up with A layers and that the B layers are only exceptionally found in some trioctahedral micas.

B layers, on the contrary, have been found in other layer-lattice silicates. As an example we can quote the chlorite studied by SHIROZU and BAILEY (1965) and the 9-layers serpentine studied by JAHANBAGLOO and ZOLTAI (1968). In this last mineral the 7 Å layer contains only one tetrahedral sheet whose tetrahedra show negative twist.

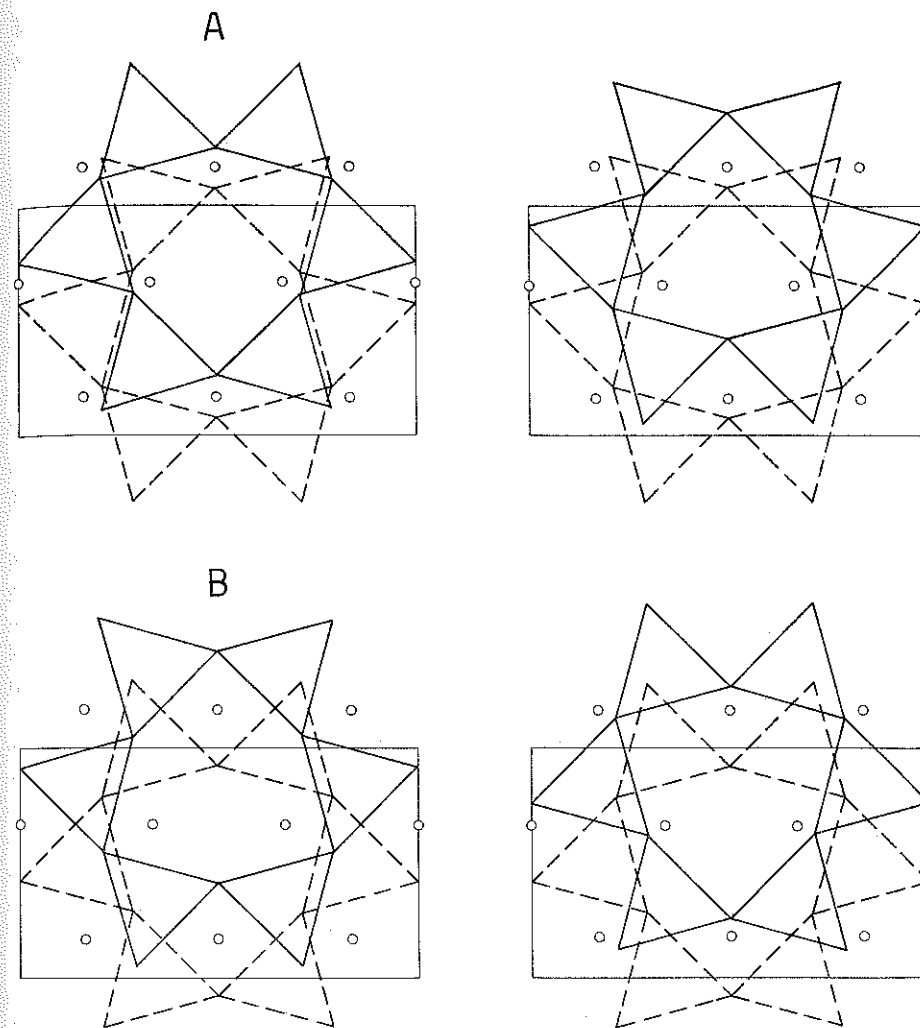


Fig. 2. The upper and lower (dashed lines) O_{bas} planes are represented. Small circles represent octahedral cations. $\alpha = 15^\circ$. Left: the two structures with centre of symmetry; upper: the A structure (positive—positive); lower: the B structure (negative—negative). Right: the two acentric structures

Structural Stability of A and B Layers

"Ideal" Trioctahedral A and B Layers. FRANZINI (1966) emphasizes that the A and B "ideal" trioctahedral layers are to be regarded as equivalent, with regard to their structural stability, because the bond lengths computed for the A layer are the same as the ones computed for the B layer. However we have to remember that in the A layers the basal oxygen atoms in both tetrahedral sheets move towards (and in the B layers away from) the nearest octahedral cations in the same layer. Therefore the trioctahedral A layer has to be regarded as more

table than the trioctahedral B layer, thus justifying the observed abundances of the two layer types. It is to be noted that the greater is the α value the more different are the A and B layers (Table 1).

Table 1

	Octahedral cation -O _{bas} distance	
	A-layer	B-layer
Biotite No. 5 ^a , $\alpha = 13.5^\circ$	3.40—3.37 Å	3.57—3.56 Å
Xanthophyllite ^b , $\alpha = 23^\circ$	3.44—3.38 Å	3.74—3.70 Å

FRANZINI and SCHIAFFINO (1963a).

TAKEUCHI (1966).

It is interesting to note that for $\alpha = 30^\circ$ (compare with xanthophyllite $\alpha = 23^\circ$, margarite $\alpha = 21^\circ$) the oxygen atoms in the A layer are in a close-packed cubic arrangement and in the B layer are in a close-packed hexagonal arrangement. The stabilization effect of the octahedral cation — O_{bas} interactions is to be regarded as a second order effect. As an example we can quote the 14 Å structures where the 2:1 talc portion of the structure may be of an A type or of a B type as a consequence of the additional influence of long hydrogen bonds to the basal oxygen atoms from adjacent interlayer OH (BROWN and BAILEY, 1963; SHIROZU and BAILEY, 1965).

Dioctahedral A and B Layers. A survey of the known experimental data points indicates that in nature only the dioctahedral A layer is found. A characteristic feature of dioctahedral layers is the existence of vacant sites that give origin to attractive and repulsive forces in the octahedral sheet that distort the hexagonal surface distribution of the O_{ap} and OH atoms. An important point in the configuration of the dioctahedral sheet is that the shortening of the shared octahedral edges causes a shift of the OH ion from the position they would occupy in the "ideal" structure.

FRANZINI (1966) suggests that the shift of the OH ion can not be realized in a dioctahedral B layer. This statement can be proved as follows. Table 2 lists the distances from an OH ion to the six nearest O_{bas} computed on the ground of the atomic parameters reported in literature. The data listed in Table 2 point out the following rules:

— the mean value of the three shortest OH—O_{bas} distances is inversely proportional to α values and directly proportional to b_{obs} values. On the contrary the mean value of the three longest OH—O_{bas} distances is directly proportional to both the α and b_{obs} values. It is not possible to use the α and b_{obs} values to make an accurate prediction about the value of the OH—O_{bas} distance because the OH ion is not exactly coplanar with the O_{ap} atoms.

— the deviation of any single value of the OH—O_{bas} distance from the mean value is about 0.03 Å for trioctahedral micas, and about 0.3 Å for dioctahedral micas.

The data of Table 2 permit us to compute the shortest OH—O_{bas} distance that will be realized in a dioctahedral B layer on the assumption that the OH shifts

Table 2

	OH—O _{bas} distances (Å)							
	shortest				longest			
	1	2	3	mean	1'	2'	3'	mean
Muscovite ^a	3.185	3.361	3.095	3.214	3.841	3.446	3.902	3.729
Muscovite ^b	3.303	3.341	3.203	3.282	3.933	3.379	3.864	3.725
Phengite ^b	3.269	3.448	3.274	3.303	3.695	3.297	3.705	3.566
Margarite ^c	3.10	3.21	3.13	3.147	4.08	3.67	4.07	3.940
Ferriphlogopite ^d	3.291	3.336	3.336	3.321	3.802	3.766	3.766	3.778
Ferriannite ^e	3.457	3.498	3.498	3.484	3.784	3.729	3.729	3.747
Li-fluormica ^f	3.423	3.419	3.419	3.420	3.671	3.670	3.670	3.670
Xanthophyllite ^c	3.121	3.162	3.162	3.147	4.045	4.077	4.077	4.066
Biotites 1—6 ^g				3.212				3.786
Chlorite ^h	3.410	3.408	3.408	3.409	3.616	3.620	3.620	3.619

^a RADOSLOVICH (1960).

^b GUVEN (1967).

^c TAKEUCHI (1966).

^d STEINFINK (1962).

^e DONNAY, MORIMOTO, TAKEDA and DONNAY (1964).

^f TAKEDA and DONNAY (1966).

^g FRANZINI and SCHIAFFINO (1963a).

^h SHIROZU and BAILEY (1965).

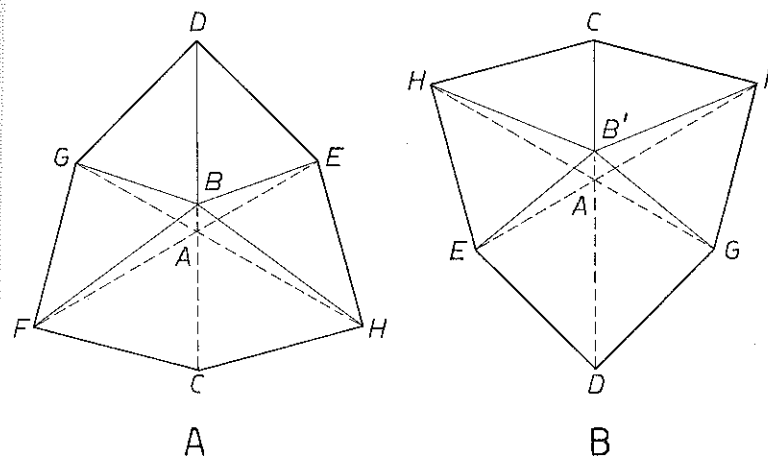


Fig. 3. Projection along c^* of six O_{bas} (C through H) and one OH in its "ideal" position (A) and in its actual position (B and B'). Dioctahedral layer, 1M orientation, $\alpha = 15^\circ$. Left: A structure; right: B structure

away from the ideal position by an amount equal to that actually observed in a dioctahedral A layer.

Fig. 3 shows a regularized projection along c^* of six O_{bas} atoms (labelled C through H) and one OH ion in its "ideal" position (labelled A) and after a shift (labelled B in a A layer and B' in a B layer) along a line joining two opposite O_{bas} atoms.

from the data of Table 2 and the z parameters of the O_{bas} atoms and OH ion it is possible to compute the distances in projection on (001) from the OH to the O_{bas} (BC, BD, . . . , BH). So we have

$$AB = AD - BD$$

$$AD = (BF + BG) \sin (30^\circ + \beta) / \sqrt{3}$$

$$\beta = \arcsin (BD / (BF + BG)).$$

$$AC = (EB + BH) \sin (30^\circ + \beta) / \sqrt{3}$$

$$\beta = \arcsin (BC / (EB + BH))$$

$$B'C = AC - AB.$$

Now it is possible to use the calculated $B'C$ value and the z parameters of the O_{bas} atoms and OH ion to compute the shortest O_{bas} —OH distance in a dioctahedral B layer (Table 3).

Table 3

	Distances in projection on (001) (Å)				O_{bas} —OH distances (Å)	
	AD	AB	AC	B'C	A-layer	B-layer
scovite ^a	2.946	0.296	2.246	1.950	3.140	2.951
scovite ^b	2.936	0.316	2.300	1.984	3.253	2.912
ngite ^b	2.770	0.257	2.452	2.195	3.272	3.032
rgarite ^c	3.110	0.243	2.004	1.761	3.115	2.903

^a RADOSLOVICH (1960).

^b HUYNH (1967).

^c TAKEUCHI (1966).

has been proved, from the data of the infrared absorption spectrometry, that there are not hydrogen bonds between the O_{bas} atoms and OH ion (JØRGENSEN, 1964; VEDDER and McDONALD, 1963). Therefore the smaller the distance between O_{bas} and OH, the stronger they repel each other.

Another proof of the intrinsic instability of the hypothetical dioctahedral layer, we can quote the following distances:

6 Å Brucite — between OH belonging to adjacent layers,

1 Å Dickite — between OH and O_{bas} belonging to adjacent layers,

5 Å Chlorite — between an OH belonging to the brucite layer and an O_{bas} belonging to the talc layer.

These data, taking into consideration that in dickite, as well as in chlorite it has been proved that there are long hydrogen bonds between OH and O_{bas} belonging to different layers, definitely suggest that the dioctahedral B layer would realize a very unstable atomic configuration. Therefore we conclude that the dioctahedral

Actual Trioctahedral A and B Layers. The same reasoning, utilized for the dioctahedral micas, may be applied to the trioctahedral ones. In a perfectly trioctahedral mica, containing three equal bivalent cations per formula unit, the OH ion occupies its "ideal" position. However a great many trioctahedral micas contain neither exactly three cations nor three equal cations: as a consequence the OH ion shifts from its "ideal" position.

Now we can observe that two small octahedra per one great octahedron are always present in the octahedral sheet of a dioctahedral mica. In trioctahedral micas, as a consequence of the possible presence in the octahedral sheet of different proportions of trivalent cations, bivalent cations, monovalent cations and vacancies, there may be as well as one small octahedron per two great octahedra, two small octahedra per one great octahedron.

In the first instance the OH shift would stabilize an B structure, whilst in the second instance a A structure.

Structural Features of the Mica Layers

FRANZINI and SCHIAFFINO (1963a) studying the crystal structure of six biotite specimens, concluded that in biotites an atomic configuration is favoured in which six out of twelve of the O_{bas} are at the corners of a regular octahedron and in contact with the K^+ ion. This conclusion is in disagreement with the current opinion that considers the octahedral sheet, instead of the interlayer cation, as the dominant structural element of the layer lattice silicates.

Let us consent to the hypothesis of the controlling influence of the octahedral sheet, then we have many experimental data that do not fit this structural model. Mentioning a few of them:

— the rotation angle α measured experimentally in some layer lattice silicates is greater than 0° even if the octahedral sheet is larger than the tetrahedral sheet. As an example, in biotites the octahedral sheet should have $b_{oct} > 9.40$ Å (i.e. greater than the b of brucite) and the tetrahedral sheet should have $b_{tet} = 9.27$ Å ($AlSi_3$): however, in biotites, α has a mean value of 10° .

— in the relation for micas the regression coefficients computed by RADOSLOVICH (1962) for the octahedral cations have about half of the value that the same coefficients have in the relation for kaolins. RADOSLOVICH (1962) assumes "that the regression coefficients (a_i) are linearly proportional to the difference between the ionic radii r_i and the hole filled r_h by the substituting cations, i.e. $r_i - r_h = ka_i$ ". The computed values of k are about 1 for kaolins and about 2 for micas, and this suggests that in kaolins the octahedral sheet is almost free to change its lateral dimensions as a consequence of isomorphous substitutions whilst in micas there is something that hampers the lateral expansion of the octahedral sheet.

Therefore it seems useful to briefly review our knowledges on the structural features of the three units that build up the mica layer (tetrahedral sheet, octahedral sheet, interlayer region) and to search for a new structural model that explains the known experimental data in a better way.

Tetrahedral Sheet

In most of the layer silicate structures known in detail the tetrahedra are not

tetrahedra are regular. Such an assumption leads to small errors in computing the α and b_{tetr} values (BAILEY, 1966), but these errors can be disregarded. Assuming perfectly regular tetrahedra, we have:

$$b_{\text{tetr}} = 9.04 + 0.23 x + 0.42 y \text{ \AA}$$

where x is the number of Al atoms and y the number of Fe^{+++} atoms in four tetrahedral sites.

The tetrahedral layer, ideally hexagonal, is usually distorted by the mechanisms of tetrahedral rotation and tetrahedral tilting. The tetrahedral rotation about the sheet normal reduces the lateral dimensions of the tetrahedral sheet according to the relation (RADOSLOVICH, 1961):

$$\cos \alpha = b_{\text{obs}}/b_{\text{tetr}}.$$

As a first approximation we can state that the tetrahedral tilting does not produce stresses in the tetrahedral sheet. The tetrahedral rotation, on the contrary, is counteracted by repulsive forces amongst O_{bas} atoms (see Fig. 4). Let us consider a tetrahedral sheet (Fig. 4); after a 30° tetrahedral rotation the shortest distance between two O_{bas} is only about 2.70 \AA.

Octahedral Sheet

The structural features of the dioctahedral sheet are very different from the ones of the trioctahedral sheet. Therefore it is very difficult to propose a single structural model which accounts for all the properties of the two different octahedral sheets. As it is well known, there is only a very limited isomorphous miscibility between dioctahedral and trioctahedral micas and therefore, to make things easier, we can make the assumption that there are only perfectly dioctahedral or perfectly trioctahedral micas.

Trioctahedral Sheet. All the octahedral sites are occupied and therefore all the octahedra are almost equal in size. The surface distribution of the O_{ap} and OH follows an hexagonal pattern. Shared octahedral edges are shorter than unshared ones and therefore the octahedra are thinned along the sheet normal and deformed into trigonal antiprisms.

Following DONNAY, DONNAY and TAKEDA (1964) the octahedral deformation may be represented by the value of the ψ angle. In a regular octahedron we observe $\psi = 54^\circ 44'$, whereas in trioctahedral sheets ψ has a value in the range from 57° to 59° .

The lateral dimensions of the trioctahedral sheets are very sensitive to small variations in the ψ value as is clearly shown by the nomogram (Fig. 3, p. 1377) given by DONNAY, DONNAY and TAKEDA (1964). Table 4 compares some relevant data about trioctahedral sheets in micas and in brucite and $\text{Fe}(\text{OH})_2$. The data of Table 4 suggest that the lateral dimensions of a free trioctahedral sheet may be computed by the following relation:

$$b_{\text{oct}} = 9.44 + 0.1 x \text{ \AA}$$

where x is the number of Fe^{++} ions in three octahedral sites.

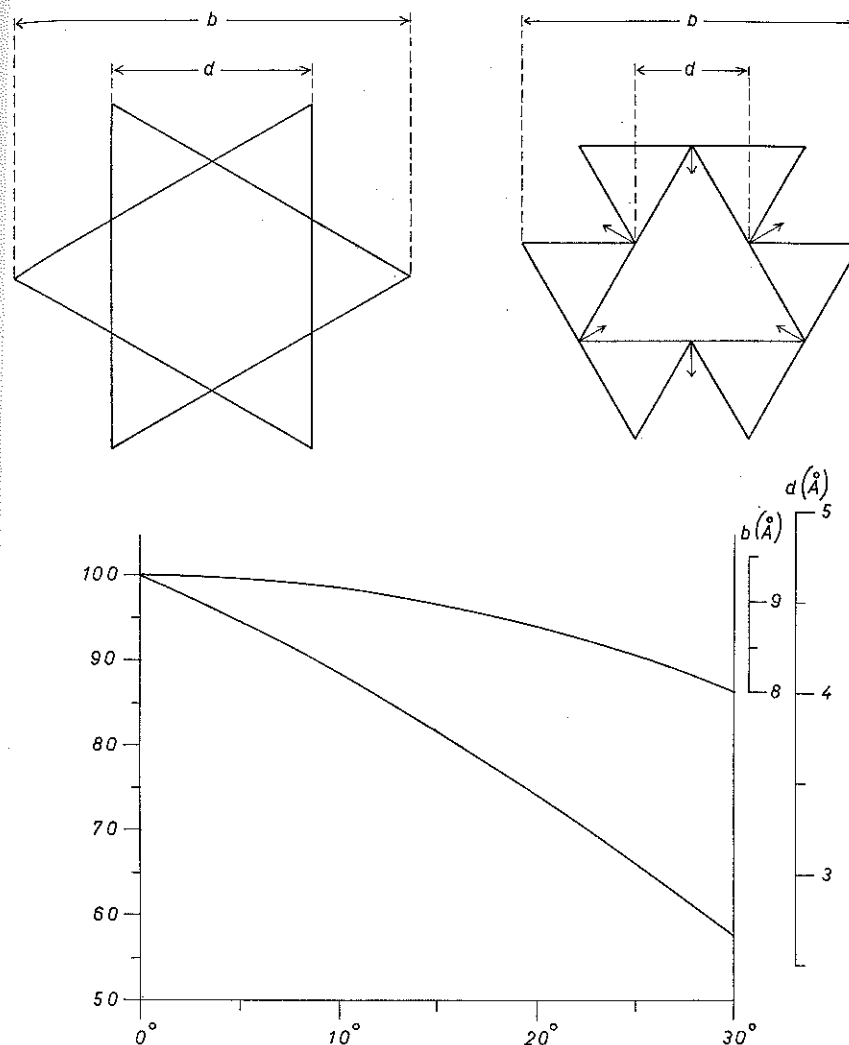


Fig. 4. Upper: O_{bas} distribution on the basal plane; $\alpha = 0^\circ$ (left) and $\alpha = 30^\circ$ (right); $d = \text{O}_{\text{bas}} - \text{O}_{\text{bas}}$ distance. Arrows represent repulsive forces among O_{bas} atoms. Lower: b (upper curve) and d (lower curve) values as a function of α (abscissae). The ordinate scale on the left gives the relative values of b and d as a function of α , having assumed $b = 100$ and $d = 100$ for $\alpha = 0^\circ$.

It is not possible to state a relation allowing computation of the octahedral thickness. In fact the lattice constants of brucite and $\text{Fe}(\text{OH})_2$ are to be regarded as essentially correct. The same is not true for what concerns the c_{oct}^* of $\text{Fe}(\text{OH})_2$. The value of c_{oct}^* has been computed utilizing the z parameters of the OH ions (0.27) given by NATTA e CASAZZA (1927). It seems however that the structural data reported by NATTA e CASAZZA (1927) are not precise enough for the sake of the present discussion. The very short distance between two OH belonging to adjacent octahedral layers (2.78 \AA, computed on the ground of the data of NATTA e CASAZZA, 1927) suggests the presence of strong hydrogen bonds that have never been detected in other analogous compounds. Assuming a bond distance $\text{Fe} - \text{O} = 2.17 \text{ \AA}$ (POVARENNYKH, 1964) the computed c_{oct}^* and ψ are respectively 2.16 \AA and 60° .

	$d_0(\text{\AA})$	$c_{\text{oct}}^*(\text{\AA})$	$b(\text{\AA})$	Ψ
phlogopite ^a	2.108	2.255	9.29	58° 11'
annite ^b	2.123	2.221	9.404	59° 07'
ferriphlogopite ^c	2.07	2.176	9.21	58° 52'
phyllosilicate ^d	2.07	2.259	9.003	56° 50'
phyllosilicate ^e	talc layer	2.15	9.247	58° 52'
	brucite layer	2.040		60° 42'
phyllosilicate ^f	g	2.24	9.75	56° 37'
	g	2.17		60° 02'
phyllosilicate ^h	2.08	2.069	9.44	60° 56'

FRANZINI (1962).

FRANZINI, MORIMOTO, TAKEDA and DONNAY (1964).

FRANZINI and DONNAY (1966).

FRANZINI (1966).

FRANZINI and BAILEY (1963).

FRANZINI and CASAZZA (1927).

Values computed assuming Fe—O = 2.17 Å.

FRANZINI (1965).

lateral dimensions of trioctahedral sheets computed by the foregoing relation are greater than the b values usually measured for trioctahedral micas, thus suggesting that the trioctahedral sheet in these minerals is "contracted" in comparison with what happens in brucite (see also the c_{oct}^* and ψ values in Table 4). Known experimental data further suggest that a trioctahedral sheet of a given composition may greatly change its lateral dimensions as is clearly demonstrated by the b_{obs} values of the following minerals all of which contain three octahedra in their trioctahedral sheet:

Brucite $b_{\text{obs}} = 9.44 \text{ \AA}$, Ferriphlogopite $b_{\text{obs}} = 9.29 \text{ \AA}$

Clintonite $b_{\text{obs}} \cong 9. \text{ \AA}$, Xanthophyllite $b_{\text{obs}} = 9.003 \text{ \AA}$.

These data point out that it is possible to stretch or to compress a trioctahedral sheet along every direction contained in the (001) plane.

The lateral dimensions of a free trioctahedral sheet represent an equilibrium between the repulsive forces amongst octahedral cations that stretch the sheet, and the repulsive forces amongst the oxygen atoms that compress the sheet. Assuming an Mg—O_{ap} distance equal to 2.08 Å, we can compute the following values of the O_{ap}—O_{ap} (shared edges) and Mg—Mg distances as a function of the ψ values:

O _{ap} —O _{ap} (shared edges)	Mg—Mg
2.72	3.15
2.88	3.00

The A and B Mica Layers

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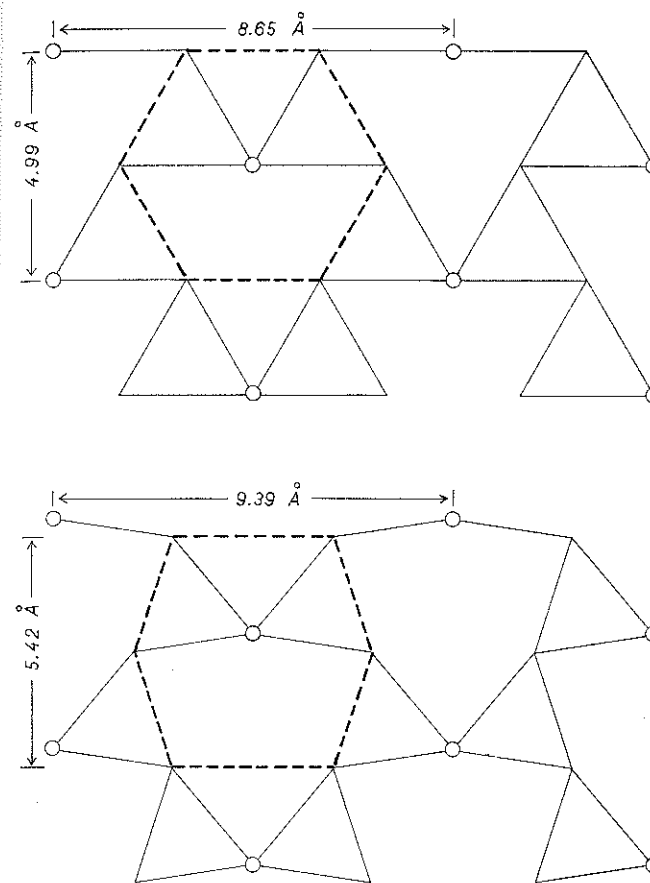


Fig. 5. O_{ap} and OH (small circles) distribution on the basal plane. Upper: "ideal" hexagonal distribution. Lower: actual ditrigonal distribution ($\epsilon = 10^\circ$)

From these data we can conclude that a Mg octahedral sheet may quite easily change its lateral dimensions at least in the range 9.45—9.00 Å.

Diocahedral Sheet. Only two of every three octahedral sites are occupied by cations. Therefore the diocahedral sheet is severely distorted as compared to the "ideal" hexagonal sheet.

It has been pointed out by TAKEUCHI (1966), it is convenient to show the distortion of the diocahedral sheet by taking O_{ap} hexagons that consist of O_{ap}—O_{ap} edges of Al octahedra. Owing to the shortening of shared octahedral edges the O_{ap} atoms are actually at the corners of a distorted hexagon characterized by two stretched out longer edges.

However it seems more useful to the aims of the present discussion, to describe the distortion of the diocahedral sheet from another point of view. Fig. 5 shows the distribution of the O_{ap} and OH on the basal plane; it represents the "ideal" hexagonal distribution as well as the actual one after the shifting of the OH ion from its ideal site. As it is clear from Fig. 5 that a transition occurs from a

hexagonal distribution to a ditrigonal one. The net effect of this distortion is an alternate clockwise and anticlockwise twist of those triads (two O_{ap} and one OH) that belong to filled octahedra.

The symmetry centre is not destroyed only if the upper and lower octahedral triads rotate in opposite directions (see Fig. 3, p. 6 in BAILEY, 1966).

As a consequence of the deformation, the lateral dimensions of the dioctahedral sheet, as well as its thickness, will be increased. This statement can be justified as follows. Let us define b_{hex} and c_{hex}^* as the lateral dimensions and thickness of an "ideal" hexagonal dioctahedral sheet and let us assume that, during the deformation, there be not any variation either in the octahedral cation — O_{ap} distance or in the octahedral edges lengths. No assumption is made about the regularity of the octahedra; on the contrary we can assume that the octahedra be thinned along the sheet normal so that the shared edges are shorter than the unshared ones.

On these hypotheses (ε is the angle of rotation of a triad from its ideal position, and t_s and t_u the lengths respectively of shared and unshared octahedral edges) we have:

$$b_{oct} = 2 b_{hex} \cos(30^\circ - \varepsilon) / \sqrt{3},$$

$$c_{oct}^* = c_{hex}^* \sqrt{((t_s^2 - 4 t_u^2 \sin^2(30^\circ - \varepsilon)/3) / (t_s^2 - t_u^2/3))}.$$

As an example, Fig. 5 has been drawn with $\varepsilon = 10^\circ$. Then we have:

$$b_{oct} = 1.085 b_{hex}$$

and, assuming $t_s = 2.40 \text{ \AA}$ and $t_u = 2.85 \text{ \AA}$:

$$c_{oct}^* = 1.21 c_{hex}^*.$$

These computed values indicate that the b_{oct} is very sensitive to the ε value (a 10° rotation produces an increase of about 0.8 \AA of the b_{oct} value) and justify that the dioctahedral sheets are nearly as thick as trioctahedral sheets.

Interlayer Region

In the "ideal" hexagonal structure, the interlayer cation is surrounded by twelve equidistant oxygen atoms arranged at the corners of a regular hexagonal prism. In all the refined mica structures however, an atomic configuration has been ascertained where, as a consequence of the tetrahedral rotation, six out of twelve of the O_{bas} are nearer to, and six farther from, the interlayer cation. The six nearest oxygen atoms are at the corners of an almost regular octahedron as it appears from the data of Table 5.

The mean value of the distances between two O_{bas} belonging to the same basal plane differs no more than 4% from the mean value of the distances between two O_{bas} belonging to contiguous basal planes. The mean value of all the independent distances between oxygen atoms in contact with the interlayer cation (mean observed O—O) is in practice equal to the value (mean calculated O—O) obtained multiplying the experimentally measured d_{int} values (see Table 5) by $1/\sqrt{2}$, i.e. to the length of the edge of a regular octahedron.

The data of Table 5 point out that the size of the O_{bas} octahedron is sensitive to the type of interlayer cation. The mean observed O—O distance is variable in the range from 4.318 to 4.037 \AA , when K is the interlayer cation, from 3.478 to

Table 5

	Independent distances (in Å) among two O_{bas} atoms in contact with the interlayer cation and belonging						Mean d_{int}	Mean obs. O—O	Mean calc. O—O			
	to the same basal layer			to contiguous layers								
	Mean value			Mean value								
Muscovite ^a	3.942	3.976	3.948	3.955	4.012	4.177	3.967	4.363	4.118	2.856	4.036	4.038
Muscovite ^b	3.962	3.989	3.968	3.973	3.983	4.151	4.288	3.934	4.089	2.855	4.039	4.037
Phengite ^b	4.230	4.271	4.244	4.248	4.086	4.211	4.243	4.076	4.154	2.970	4.194	4.199
Muscovite ^c										2.793		3.949
Muscovite ^c										2.641		3.734
3 T muscovite ^d										2.868		4.055
Margarite ^e	3.431	3.490	3.500	3.474	3.507	3.344	3.634	3.397	3.471	2.46	3.472	3.478
Ferriphlogopite ^f	4.11	4.14		4.12	4.21	4.22			4.21	2.94	4.165	4.157
Ferriannite ^g	4.38	4.44		4.40	4.23	4.25			4.237	3.054	4.318	4.318
Li-fluomica ^h	4.308	4.322		4.313	4.157	4.155			4.156	2.995	4.234	4.235
Xanthophyllite ^e	3.403	3.384		3.394	3.455	3.423			3.439	2.41	3.416	3.408
Biotites 1—6 ⁱ				4.13					4.13	2.92		4.13
Paragonite										2.45 ?		

^a GATINEAU (1963). ^b GUVEN (1967). ^c BURNHAM and RADOSLOVICH (1964). ^d GUVEN and BURNHAM (1967). ^e TAKEUCHI (1966). ^f STEINFINK (1962). ^g DONNAY, MORIMOTO, TAKEDA and DONNAY (1964). ^h TAKEDA and DONNAY (1966). ⁱ FRANZINI and SCHIAFFINO (1963a).

to overcome this difficulty some authors, observing for example that the $2M_2$ polymorph has been almost exclusively recognized in lepidolites, have suggested that the relative rotations of odd multiple of 60° may be possible only in micas having very low values of α . As a consequence the coordination polyhedron about the interlayer cation would shape as a hexagonal prism rather than a trigonal prism.

FRANZINI e SCHIAFFINO (1963b) have emphasized that the mica polymorphs characterized by relative rotations among adjacent mica layers of 60° , 180° , or 300° may preserve an octahedral coordination polyhedron about the interlayer cation provided that these polymorphs be built up by alternate A and B layers.

On the ground of the discussion of the features of the interlayer region we can state that the assumption of a trigonal prismatic coordination of the O_{bas} around the interlayer cation has no physical meaning. Thus we can conclude that polymorphs such as $2M_2$ or $2O$, which require B layer, will be realized only by trioctahedral micas.

Furthermore we can emphasize that there is no experimental evidence to support the trigonal prismatic coordination. In fact each N-layer mica polymorph is correspondent to a N-layer stacking sequence which may be identified in general by measuring its lattice constants. Another way of stating the problem is to say that the measured lattice constants of a given polymorph allow deduction of the stacking sequence, i.e. the values of the relative rotations among adjacent mica layers.

At this point we must emphasize, remembering that the A and B layers have the same unit of repeat, that from the lattice constants one can deduce only the values of the relative rotations among octahedral sheets belonging to adjacent mica layers: nothing can be said about the tetrahedral rotation (positive or negative) and hence about the coordination polyhedron around the interlayer cation (octahedron or trigonal prism).

In recent years the trend has spread to indicate the observed variety of mica structures (and in more general terms of layer lattice silicates) as "polytypism" rather than as "polymorphism". GUVEN and BURNHAM (1967) have criticized this tendency showing in a conclusive way that at least the $2M_1$ and $3T$ muscovite structures must be termed "polymorphs with derivative single layers". For what concerns the trioctahedral micas there are not, till to day, experimental data that allow to take up a definite position regarding "polytypism" or "polymorphism". However there are some data that suggest it is quite difficult to decide between the terms polytypism or polymorphism referring to the trioctahedral micas. Mentioning a few of them:

— the A and B structures are clearly polymorphs and not polytypes. However we must remember the possibility that the A and B layers develop as a consequence of a different chemical composition of the octahedral layer: in this instance, strictly speaking, the A and B layers can not even be regarded as polymorphs. FRANZINI (1966) proved experimentally that a biotite crystal twinned on $[100]$ is built up by two distinct portions one of which containing A layers and the other B layers. Assuming a constant chemical composition throughout the crystal it would seem proved that, at least in some instances, the A and B layers may be actually polymorphs. Although the assumption of a constant

chemical composition may be a quite reasonable assumption it is by no means an experimentally proved one. We can quote, as an example of chemical variability in a single crystal, the phlogopite studied by FRANZINI, MAZZUOLI e SCHIAFFINO (1967) and the biotites studied by BARBERI e INNOCENTI (1967).

— LEVINSON (1953) has pointed out that, in the muscovite — lepidolite series, a relation exists between chemical composition and polymorphic modification. From the data of LEVINSON (1953) it seems to be a constant characteristic that the trioctahedral lepidolites containing from 4.0 to 5.1% Li_2O have the $2M_2$ structure whilst those containing more than 5.1% Li_2O have the $1M$ or the $3T$ structure.

The foregoing discussion suggests that the terms "polytypism" and "polymorphism" must be used with care when applied to micas. In fact it seems proved beyond any doubt that sometimes a true polymorphism occurs (muscovite $2M_1$ and $3T$) whereas sometimes different polymorphic modifications correspond to different chemical compositions (trioctahedral lepidolites). Till to day no experimental proof of true polytypism in micas is known.

Kaolins, Pyrophyllite and Talc

The structure of the single kaolin layer represents an equilibrium between an octahedral and a tetrahedral sheet. The lateral dimensions of the free octahedral and tetrahedral sheets — respectively 8.65 and 9.05 Å — compared with the $b_{obs} = 8.93$ Å, suggest that both the octahedral and the tetrahedral sheets are somewhat deformed. The tetrahedral rotation angle α has a mean value of about 9° . This tetrahedral rotation is sufficient to reduce the shortest distance between two O_{bas} from 4.52 Å ($\alpha = 0^\circ$) to 4.05 Å ($\alpha = 9^\circ$). The repulsion between O_{bas} atoms does not permit a further reduction of the lateral dimensions of the tetrahedral sheet. Thus the octahedral sheet must adjust its lateral dimensions in order to fit the tetrahedral sheet, and an equilibrium is attained with $b_{obs} = 8.93$ Å.

The same arguments utilized for kaolins justify the observed dimensions of pyrophyllite. For what concerns talc, a comparison between the b_{oct} , b_{tetr} , and b_{obs} values (respectively 9.44, 9.05, 9.12 Å) suggests that in this mineral the angle α has a value of 0° . The severe strains imposed to the octahedral layer — which reduces its lateral dimensions from 9.44 to 9.12 Å — are counterbalanced partially by a deformation of the $(Al, Si)O_4$ tetrahedra. In fact an increase of the lateral dimensions of the tetrahedral sheet over the b_{tetr} value may be caused only by a deformation of the tetrahedra.

Structural Stability of Trioctahedral and Di/Trioctahedral Chlorites

SHIROZU and BAILEY (1965) pointed out that there are four chlorite layer types which they labelled Ia, Ib, IIa, IIb. Utilizing the nomenclature of the present paper, we observe that the Ia and IIb chlorite layers contain an A talc layer, whereas the Ib and IIa contain a B talc layer.

In chlorites the control on the structural arrangement of the talc layer (A structure or B structure) is essentially assumed by the overlying brucite sheet. In fact the

rection of tetrahedral rotation is regulated in such a way as the basal tetrahedral oxygens move toward the positions of the nearest hydroxyls in the adjacent muscovite sheet (SHIROZU and BAILEY, 1965).

BAILEY and BROWN (1962), BROWN and BAILEY (1963) SHIROZU and BAILEY (1965), on the ground of theoretical considerations and experimental data, have been able to forecast an order of stability of the four different chlorite layers that is in accord with the relative abundances in nature of layer types, namely IIb, Ib, Ia, and IIa. At first these authors have shown that the superposition of talc and brucite layers realized by the IIb and Ib chlorites is more stable than the one observed in the Ia and IIa chlorites. Further, taking into consideration other structural features, they have succeeded in explaining the greatest stability of the IIb and Ia layers in comparison to, respectively, the Ib and IIa layers.

As an alternative explanation we can state that the IIb and Ia layers are more stable in comparison to respectively the Ib and IIa layers because the former contain an A talc layer whilst the latter contain a B talc layer.

The same statement can be applied to the di/trioctahedral chlorites. These minerals contain a pyrophyllite-like layer which can not have a B structure. Thus we conclude that probably, the di/trioctahedral chlorites may be built up only by Ia and IIb layers. This last statement may be compared with the data reported by EGGLESTON and BAILEY (1967).

$2M_2$ Lepidolites

Lepidolites are a very interesting group of layer lattice silicates both from a structural and a chemical point of view. In fact lepidolites are the only mica group that exhibits both the $2M_2$ polymorph and a continuous chemical series between di- and trioctahedral end members (DEER, HOWIE and ZUSSMANN, 1963).

Let us examine firstly the structural meaning of the $2M_2$ polymorph. Because the structure of a $2M_2$ polymorph has not yet been determined, the only experimental data we can utilize are the lattice constants and the chemical data. From the measured values of the lattice constants it results that the $2M_2$ lepidolite unit repeat may be geometrically thought as built up by two superposed $1M$ unit repeat rotated by 60° on each other.

There is a 60° , or an odd multiple of 60° , relative rotation among adjacent layers, to preserve an octahedral coordination around the interlayer cation, one of the two $1M$ units must have an A structure and the other a B structure (FRANZINI e SCHIAFFINO, 1963b). It was pointed out that a dioctahedral layer may not have a B structure. Thus we can conclude that $2M_2$ lepidolites must be essentially trioctahedral.

Now let us suppose a mica with the following composition: $\text{KLi}_2\text{Al}[(\text{OH})_2(\text{Si}_4\text{O}_{10})]$. There is not any known lepidolite with such a composition. However we can predict that this mica would be built up by B layers (in its trioctahedral layer there are in fact two great octahedra occupied by Li, per one small octahedron occupied by Al). By similar arguments it can be argued that a lepidolite with composition $\text{KLiAl}_2[(\text{OH})_2(\text{Al}_2\text{Si}_2\text{O}_{10})]$ will be built up by A layers. Then a regular alternance of A and B layers, having the foregoing stated compositions, will originate a $2M_2$ lepidolite with composition: $\text{KLi}_{1.5}\text{Al}_{1.5}[(\text{OH})_2\text{AlSi}_3\text{O}_{10}]$.

The foregoing statement is, at the present, only an hypothesis whose structural meaning, particularly with respect to the mechanism that regulates the long range order amongst octahedral sheets belonging to adjacent layers, is not fully understood. However there are some chemical data that greatly support our interpretation. LEVINSON (1953) states that lepidolites with 4.0—5.1% of Li_2O generally crystallize with the $2M_2$ structure. This Li_2O content corresponds to 1.1—1.4 Li atoms per three octahedral sites, i.e. somewhat less than the assumed 1.5 value.

It must be observed that the value 1.5 Li atoms was deduced assuming a perfectly trioctahedral $2M_2$ lepidolite. Actually the high — Li lepidolites too are never perfectly trioctahedral. From a geometrical point of view the octahedral vacancies must be regarded as equivalent to Li atoms, meaning that an empty octahedron has almost the same size as a Li containing octahedron. Therefore the observed content of 1.1—1.4 Li atoms, summed for the vacancies, supports the proposed interpretation of the $2M_2$ lepidolite structure.

For what concerns the chemical continuity between di- and trioctahedral end members, nothing can be said on the ground of the structural considerations reported in this paper. We can observe only that it is beyond argument that many lepidolite hand specimens contain more than one polymorph. Thus it seems that a solution of this problem may be attained only by a careful examination of both the chemical composition and the structural features of selected lepidolite monocrystals.

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Über die Synthese von Albiten bei Temperaturen von 250 bis 700° C

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On the Synthesis of Albites at Temperatures in the Range 250 to 700° C

Abstract. A glass of composition $NaAlSi_3O_8$ with small contents of Fe has been crystallized in the presence of water vapor under 1000 bars, at temperatures in the range of 250 to 700° C for varying periods of time. The synthetic crystals were investigated microscopically and by x-ray powder diffraction methods. Most of the crystals are twinned according to the albite law, but other twins are found too. Size and form of the crystals seem to depend on the temperature of crystallization. The optic axial angles ($2V_x$) of the albites being measurable on the universal stage are in the range of 50 to 100 degrees. There seems to exist a linear relation between the $2\theta_{131}$ — $2\theta_{1\bar{3}1}$ values (used as an indicator for the degree of ordering) and the $2V_x$ values. The change of the lattice parameters from albite (D) to albite (O) is suggested to deviate slightly from linearity.

In contrast to previous investigations the steady value of $2\theta_{131}$ — $2\theta_{1\bar{3}1}$ which is characteristic of the temperature of crystallization was reached more rapidly. These results suggest that small content of Fe in the glass had a catalytic effect on the Al/Si ordering.

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1. Einleitung

Die vorliegenden Untersuchungen waren mit dem Ziel begonnen worden, möglichst große und optisch meßbare Albitkristalle unter verschiedenen *P-T*-Bedingungen hydrothermal zu synthetisieren, um die röntgenographischen Daten mit optischen zu korrelieren. Schon die ersten Versuche erbrachten Ergebnisse, die bezüglich der röntgenographischen Daten deutlich von denen ähnlicher Experimente anderer Autoren (MACKENZIE, 1957, und EBERHARD, 1967) abwichen.

MACKENZIE konnte zeigen, daß es eine unendliche Reihe stabiler und metastabiler Modifikationen von Na-Feldspat gibt, deren Strukturzustand von den Kristallisationsbedingungen abhängt. Als hierauf empfindlicher Parameter wurde von MACKENZIE die $2\theta_{131}$ — $2\theta_{1\bar{3}1}$ -Linienaufspaltung¹ im Pulverdiagramm benutzt. LAVES (1960) führt das Auftreten einer kontinuierlichen Reihe von Alkalifeldspat-Modifikationen auf Ordnungs-Unordnungsphänomene zurück. Danach ist zwischen

1. Im folgenden wird für die Differenz $2\theta_{131}$ — $2\theta_{1\bar{3}1}$ der Ausdruck 131—1 $\bar{3}$ 1 benutzt.