

*Experimental and theoretical studies of the  
mica polymorphs.*

(With Plates VIII and IX.)

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*Summary.*—An experimental and theoretical study has been made in order to determine the number and the structure of the possible polymorphs and to determine the structural relations between them. The simplest structures are 1M, 2M<sub>1</sub>, 2M<sub>2</sub>, 3T, 2O, and 6H polymorphs, and more complicated types can be developed. Some of the previously described polymorphs were not contained in the theoretical list and were re-examined. The 6M structure was found to be a 2M<sub>2</sub> polymorph, the 6-layer triclinic type was found to be a 2M<sub>1</sub> polymorph, and the 3M structure was shown to be a 3T type. The 24-layer triclinic structure could be described on a simpler 8-layer cell. This type together with a new 12-layer monoclinic structure, as well as other structures of higher periodicity, presumably consists of complex stacking and results from spiral-growth mechanism. Two extreme types of layer-disordered crystals may be built and a disorder of individual ions may also occur. Single stacking faults result in twinned crystals. A new twin relation (180° rotation about the [100] axis) has been recognized. Twenty specimens from extreme geological environments have been examined in order to evaluate the control of environment on the stacking. The type of stacking could not be attributed solely to the influence of pressure and temperature. Composition appears to play a dominant role in the type of stacking, and semi-quantitative structural arguments appear to support this contention. The influence of growth mechanism is discussed. A scheme for the identification of the mica polymorphs by X-ray powder and single-crystal methods is given.

**I**N the course of an experimental investigation of the stability ranges and relations of phlogopite and muscovite by Yoder and Eugster (1954, 1955), it was found difficult to identify some mica polymorphs from X-ray powder patterns and it was necessary to establish a standard X-ray powder pattern for each polymorph. Although a large number of specimens had been examined in the past, especially in the extensive study of Hendricks and Jefferson (1939), it was not certain that all possible polymorphs had been discovered. For these reasons it was desirable to develop a theory which would permit the prediction of all the possible polymorphs. This theoretical study led to an examination

of the factors which govern the growth of the polymorphs. An understanding of these factors required study of the growth mechanism and twin laws as well as of the effect of the environment and the crystal structure. Since the polymorphs could not all be synthesized by Yoder and Eugster it was necessary to augment the synthetic studies by the identification of polymorphs obtained from a wide range of geological conditions. In the absence of detailed crystal-structure data an evaluation of the structural controls from semi-quantitative considerations was required.

#### *Possible polymorphs.*

The structure of a mica polymorph was first established by Jackson and West (1930, 1933) for a 2-layer monoclinic muscovite. Hendricks and Jefferson (1939) demonstrated the existence of other polymorphs and determined their structures. They showed that all the polymorphs were based on the same sub-cell. Polymorphism in the micas occurs because the atomic arrangement in the sub-cell has monoclinic symmetry, whereas the symmetry of the surface of the sub-cell is hexagonal or pseudo-hexagonal. Rotation of a sub-cell by  $60^\circ$  does not affect the packing of the surfaces but does affect the position of the sub-cell.

The features of the mica structure important to this study are given in fig. 1*a*, *b*, *c*. A more complete set of diagrams of the mica structure may be found in the 'Atomic Structure of Minerals' by W. L. Bragg (1937, pp. 205 ff.). All ions in the mica structure are in parallel pseudo-hexagonal arrays. In each mica layer there are two sheets of oxygen tetrahedra containing silicon and aluminium. Each sheet consists of tetrahedra linked at each of three corners to form an hexagonal array with all the bases parallel and all the vertices pointing the same way. The two silicon-aluminium sheets that are contained in each mica layer are parallel and have opposing vertices. They are held together by Mg or other ions in octahedral coordination. For convenience, the basal oxygen ions of the Si and Al tetrahedra will be denoted  $O_B$  and the oxygen atoms at the apices,  $O_A$  (see fig. 1*b*). The  $O_A$  atoms form an hexagonal array and the centres of the array are filled by OH or F ions (fig. 1*a*). Each Mg ion is linked to  $2O_A + 1OH$  from the upper silicon-aluminium sheet and  $2O_A + 1OH$  from the lower sheet. Although all atoms are in hexagonal arrays, the linkage at the Mg ions reduces the layer symmetry to monoclinic with a layer stagger of  $1.7 \text{ \AA}$ . Each layer has a vertical plane of symmetry passing through the OH ions (fig. 1*a*), and the layer is face centred, giving a symmetry of  $Cm$ . The layers are linked by K

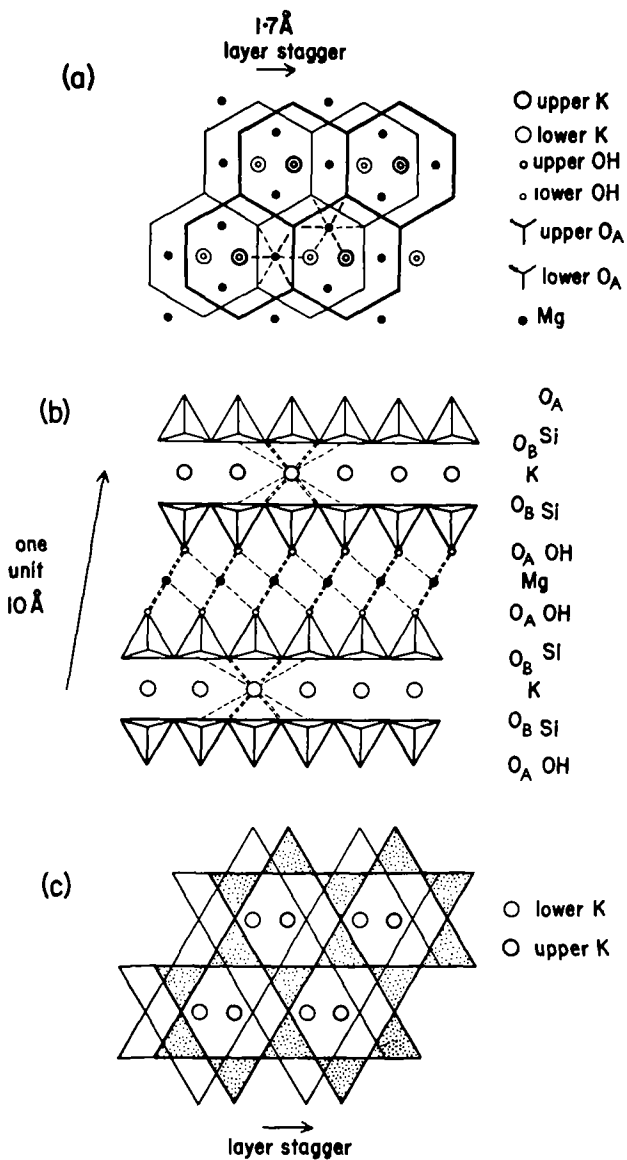


FIG. 1. (a) A projection normal to one mica layer showing the K (○), Mg (●), and OH (○) ions. The  $O_A$  oxygen atoms are at the corners of the hexagons. The thick and thin lines and circles in this figure and in fig. (c) represent the upper and lower layers of atoms in the unit. (b) A projection on (010) showing one layer together with the adjacent parts of the two adjoining layers. The  $O_A$  oxygen atoms overlap with the OH ions. The  $O_A$  and  $O_B$  oxygen atoms are at the vertices of the tetrahedra. The K, Si, Mg, and OH ions may be replaced by other ions. (c) A projection normal to one mica layer showing only the K (○) and  $O_B$  atoms. The  $O_B$  atoms are at the corners of the hexagons.

ions in 12-fold coordination (six  $O_B$  atoms from each layer). The  $O_B$  atoms form two hexagonal arrays and each K ion sits symmetrically in the centre of an hexagonal prism. The  $O_B$  atoms above and below the K ions superpose exactly, giving no layer stagger at the interface (fig. 1*b*).

The different ways of stacking two adjacent mica layers will now be enumerated. As the layer stagger is equal to the horizontal displacement of either the  $O_B$  atoms or the K atoms and the interlayer stacking is concerned only with these atoms, it is only necessary to consider these atoms for the present purpose. When a new layer is added to the top of the first layer, the six lower  $O_B$  atoms of the new layer superpose directly on the six upper  $O_B$  atoms of the first layer. Because of the hexagonal symmetry of these oxygen sheets there are six possible orientations of the new layer which are related by  $60^\circ$  rotations. Correspondingly, the directions of stagger of the two layers may be at any one of the six angles  $0^\circ$ ,  $60^\circ$ ,  $120^\circ$ ,  $180^\circ$ ,  $240^\circ$ , and  $300^\circ$ . Because of the plane of symmetry of the layer that is parallel to the layer stagger, angles  $60^\circ$  and  $300^\circ$  are equivalent, as also are angles  $120^\circ$  and  $240^\circ$ . There are, therefore, four different ways of stacking two adjacent layers. The simplest way of depicting the stacking sequence is to show the positions of the K atoms on a projection taken normal to the mica layer. It is convenient to draw vectors from one K atom to a K atom in the next layer with the arrowhead showing the direction of increasing height of the mica layers (see fig. 2).<sup>1</sup> From the positions of the K atoms the positions of the other atoms may be reconstructed. The angle between two interlayer vectors, the *interlayer stacking angle*, is measured in the counterclockwise direction in this paper.

If there is no control over the choice of the interlayer stacking angle, disordered crystals will result, whose stacking angles occur in random sequence. Each layer will have its atoms in fixed positions: this is random stacking of *whole layers*, not of *individual atoms*. Different sorts of disordered crystals may be obtained by restricting the possible stacking angles. For example, two extreme types of disordered crystals can be built; one containing a random mixture of  $0^\circ$ ,  $120^\circ$ , and  $240^\circ$  stacking angles, and the other containing a random mixture of  $60^\circ$ ,  $180^\circ$ , and  $300^\circ$  stacking angles.

If there is complete control over the layer stacking, fully ordered crystals will result. By taking all combinations of the stacking methods,

<sup>1</sup> Ramsdell (1947) has used a similar method for describing the polymorphs of SiC, and Dekeyser and Amelinckx (1953) have used this method for describing the mica structures.

an infinity of structures may be constructed. However, it may be expected that, if layers start growing with a particular stacking angle,

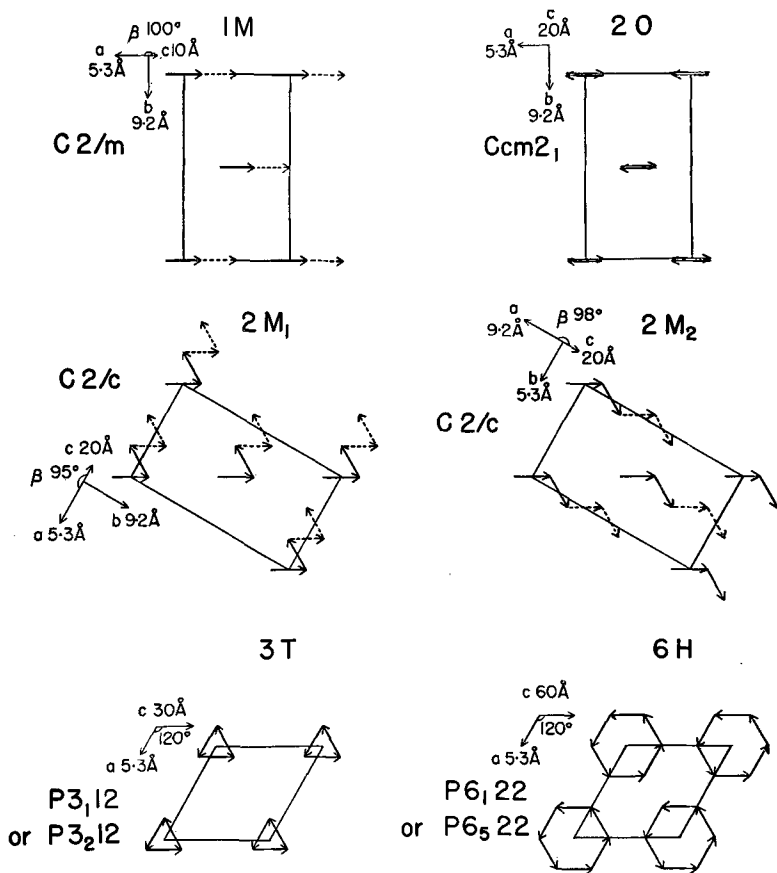


FIG. 2. The six simple ways of stacking mica layers in an ordered manner. The arrows are the interlayer stacking vectors. Full line vectors show the layer stacking in one unit cell, whereas the broken line vectors show the positions of layers in the next unit cell. The base of the unit cell is shown by thin lines, and the space group and lattice parameters are listed by the side of the diagram. Note that there are two possible directions of screw of the stacking vectors in the 3T and 6H polymorphs corresponding to the two space-groups listed for each polymorph. Pabst (1955) has recently shown that the ideal structure of a 1M mica has the space-group  $C2/m$ .

additional layers will also have this stacking angle. On the condition that only one stacking angle occurs, six polymorphs may be built as

shown in fig. 2. For convenience, a simple nomenclature has been adopted in which the first symbol gives the number of layers in the repeat unit and the second gives the symmetry. The polymorphs are 1M, 2M<sub>1</sub>, 2M<sub>2</sub>, 2O, 3T, and 6H. As there are two 2-layer monoclinic (2M) polymorphs, the subscripts 1 and 2 are used. The letter O represents orthorhombic; T, trigonal; and H, hexagonal. The derivation of the six simple polymorphs is as follows. The only polymorph that can be built solely from the 0° stacking angle is the 1M structure. Similarly the 2O structure is the only one that can be built solely from 180° stacking angles. If 120° and 240° stacking angles are used, three simple arrangements can be found, two of which are merely mirror images. They are: a continuous sequence of 120° angles; a continuous sequence of 240° angles, which gives rise to a mirror image of the 120° sequence; and a continuous alternation of 120° and 240° angles. The first two give the 3T polymorph and its mirror image; the third gives the 2M<sub>1</sub> structure. The derivation of the polymorphs based on the 60° and 300° angles is identical. The three structures formed are: a continuous sequence of 60° angles; a continuous sequence of 300° angles, which gives rise to a mirror image of the 60° sequence; and a continuous alternation of 60° and 300° angles. The first two are the 6H polymorph and its mirror image and the remaining one is the 2M<sub>2</sub> polymorph. It should be noted that the 2M<sub>1</sub> and 2M<sub>2</sub> polymorphs have quite different stacking arrangements even though they belong to the same symmetry system and have the same repeat unit.

If only an occasional stacking fault—that is, a mistake in the repeated sequence of layers—occurs in ordered crystals, twinned crystals result, as described in a later section.

#### *Observed polymorphs.*

Mauguin (1927, 1928) showed that the *c*-axis of a biotite was apparently one-half that of a muscovite. Pauling (1930) proposed a structure for the micas, and Jackson and West (1930, 1933) independently established the structure of a muscovite (now called 2M<sub>1</sub>). Hendricks and Jefferson (1939), in an important and extensive survey of about 100 micas, identified and gave detailed structures for six polymorphs, which may be denoted in the new nomenclature, 1M, 2M, 3T, 6M, 6Tc (triclinic or anorthic), and 24Tc. Axelrod and Grimaldi (1949) described a 3M muscovite, and Amelinckx and Dekeyser (1953) demonstrated the existence of an 18-layer monoclinic biotite. Levinson (1953), in a study of lepidolites, confirmed the existence of 1M, 2M, 3T, and 6M poly-

morphs. The 1M, 2M, and 3T<sup>1</sup> micas are identical with the theoretical polymorphs 1M, 2M<sub>1</sub>, and 3T described in this paper.

Axelrod and Grimaldi (1949) described the first example of a 3-layer muscovite and they showed that the geometry of the sharp reflections was trigonal. They suggested, however, that it might be monoclinic because of the finite value of  $2V$  and the asymmetry of the diffuse streaks observed in the Weissenberg photographs. This specimen (Sultan Basin) was re-examined, and it was found that the sharp reflections have intensities and interaxial angles corresponding to exact trigonal symmetry. The interaxial angles were measured on a precession camera with an accuracy of 5' of arc. The diffuse streaks were not asymmetric in intensity, and moreover they are caused by stacking faults in the crystal and do not reflect the symmetry of the ordered portions. There is, therefore, no evidence from the X-ray photographs that the symmetry of the ordered portions is other than trigonal. The finite values of  $2V$  may be caused by strain or by some other factors. It is well known that the 'optical' symmetry can differ from the 'X-ray' symmetry, and this may be attributed to the difference of wave-length of the two radiations. Structural deviations of approximately the wave-length of X-rays will result in observable X-ray phase changes; whereas deviations much greater than these wave-lengths may result in uncorrelated and consequently unobservable phase changes. Therefore, deviations that affect light (wave-length  $\sim 6000$  Å.) need not affect X-rays (wave-length  $\sim 1$  Å.).

Examination of the 6M structure given in fig. 6c and table 10 of the paper of Hendricks and Jefferson (1939) shows that a smaller unit cell may be taken. This new unit cell is identical with that for the theoretical 2M<sub>2</sub> polymorph and one-third as large as the original 6M cell. That this new cell is not a pseudo-cell is shown both by the systematic absences recorded by Hendricks and Jefferson and by a new set of X-ray photographs of a specimen (Stevens, no. 7) described as having the 6M structure by Hendricks and Jefferson. All reflections could be indexed on the smaller unit cell. The 6M mica (found so far only in lepidolites) is therefore renamed 2M<sub>2</sub>, for its true repeat is only two layers. The 6M cell has symmetry  $Cc$  with  $a = 9.2$ ,  $b = 5.3$ ,  $c = 60$  Å.,  $\beta = 90^\circ$ ; the smaller 2M<sub>2</sub> cell has symmetry  $C2/c$  with  $a = 9.2$ ,  $b = 5.3$ ,  $c = 20$  Å., and  $\beta = 98^\circ$ .

<sup>1</sup> Called rhombohedral by Hendricks and Jefferson and hexagonal by Levinson. The term trigonal is preferred in accordance with the 1952 edition of 'International Tables for X-ray Crystallography'.

The existence of the 6-layer triclinic structure described by Hendricks and Jefferson was not confirmed. X-ray examination of the biotite from Sterling Hill, N.J. (U.S.N.M. C3675), showed that it has a  $2M_1$  structure, and not the 6Tc structure assigned by Hendricks and Jefferson. The X-ray photograph which Hendricks and Jefferson describe as a zero-layer, *a*-axis Weissenberg photograph (reproduced by them as fig. 4*i*) is identical with a zero-layer, [110]-axis Weissenberg photograph of a  $2M_1$  crystal. By taking new *a*- and *b*-axes, the 6Tc unit cell may be transformed into a  $2M_1$  unit cell. It is concluded, therefore, that the 6Tc structure is a  $2M_1$  structure described on different axes.

Re-examination of the 24-layer triclinic mica described by Hendricks and Jefferson (biotite, U.S.N.M. 34476) confirmed the triclinic symmetry. Weissenberg photographs about all three of the 5.3 Å. axes, however, could be indexed on an 8-layer unit cell, and could not be interpreted as twinning of a crystal containing a smaller number of layers. This 8Tc polymorph is not included in the list of the 'simple' polymorphs deduced from the theoretical study and it must have, therefore, a complex stacking scheme.

From Laue photographs Amelineckx and Dekeyser (1953) have demonstrated the coexistence in a biotite crystal from Monte Somma of a 1-layer monoclinic portion with another monoclinic part consisting of some 18 layers (the exact number of layers is difficult to determine when the number is so large, for indexing is uncertain).

A crystal of 'ephesite' from Postmasburg, South Africa, kindly supplied by Dr. W. T. Schaller, was examined by Weissenberg methods, which revealed the existence of a further polymorph. The symmetry is monoclinic and the strong reflections agree closely, both in position and in intensity, with those from a  $2M_1$  polymorph. Weak reflections at distances corresponding to one-third of the separation of the strong reflections indicate that the repeat unit is at least 6 layers; in addition, very faint reflections appear approximately midway between the weak reflections. Although the reflections are so weak that it is difficult to be sure that they lie exactly at the midway points, the unit cell probably consists of 12 layers.

Disordered polymorphs have been observed by Hendricks and Jefferson in natural materials and by Yoder and Eugster (1954, 1955) in synthetic micas. Hendricks and Jefferson, as well as Yoder and Eugster, have described all variations from ordered to disordered polymorphs. The partially disordered materials contain a large number of stacking faults, the percentage of faults increasing with disorder until



finally the stacking is random. The effect on the X-ray pattern is explained by Hendricks and Jefferson in the following way:

Inspection of the various drawings and tables of coordinations will perhaps make it evident that translation of one-half of a mica layer by  $nb/3$  with respect to the other half leaves the layer unchanged but results in a change of relationship of successive layers. This is really the factor which permits the polymorphism of the octophyllite micas. Now if this process is carried out in a random instead of a regular manner there will be no definite  $c$  periodicity unless the  $k$  index is a multiple of three, in which case the periodicity is that of a single layer. As a result diffuse scattering of the observed type will necessarily appear, and its intensity will depend on the number of the random shifts.

It is thus found that of the simple polymorphs only the 2O and 6H polymorphs have not been found so far in nature. The other four simple ordered polymorphs 1M,  $2M_1$ ,  $2M_2$ , and 3T and the disordered polymorphs are found in nature. If the 6H polymorph does occur in nature it probably occurs in the lepidolite group, since this is the only mica group to produce the  $2M_2$  polymorph, whose stacking is related to that of the 6H polymorph. In addition to the four simple ordered polymorphs, three more ordered polymorphs have been identified: 12M, 18M, and 8Tc. These polymorphs occur only very rarely in nature, probably under conditions that favour the operation of the spiral-growth mechanism. The great majority of the micas fall into the four structural types 1M,  $2M_1$ ,  $2M_2$ , and 3T, whose structures consist of the simplest stacking of mica layers. The structures of the 8Tc and 12M micas must be closely similar to those of the  $2M_1$  polymorphs in view of the similarities between the X-ray patterns that have been found. Only with much effort would it be possible to determine the exact structure of these complicated polymorphs, for the number of possible polymorphs containing a certain layer periodicity increases very rapidly with the number of layers. It is possible that other factors operate besides interlayer stacking; for example, two polymorphs may have the same layer stacking but different distribution of the ions in the layers. Only very detailed intensity calculations would permit evaluation of such factors.

#### *Twinning.*

Frequent random stacking faults result in disordered crystals; the occurrence of a single stacking fault in an ordered block of crystal gives rise to a twinned crystal. The possible twin laws may be enumerated by introducing all the possible stacking faults into an

ordered structure, using a vector diagram. A complete list need not be given here.

Twinning on a  $[310]$  axis, with composition plane  $(001)$ , has been known for a long while and is referred to as the common mica twin law. A search of the literature reveals that this type of twin law has been found in all the common micas. This suggests that the same twin law operates for several polymorphs, although careful determinations of both the twin law and the type of stacking for a series of specimens would be needed before this could be definitely established.

The introduction of a single mistake in the stacking of a  $2M_1$  polymorph may lead to twinning about the  $[310]$  axis in two ways (fig. 3*a, b, c*). The interlayer stacking vectors of a  $2M_1$  structure bear alternately an angular relation of  $240^\circ$  and  $120^\circ$  (the angular rotation is taken counterclockwise throughout this paper). If a single fault occurs in which the  $240^\circ$  angular relation replaces a  $120^\circ$  angular relation (fig. 3*b*), a twin about the  $[310]$  axis results (fig. 3*a*). In detail, the sequence of angles in fig. 3*b* is  $120^\circ, 240^\circ, 120^\circ, 240^\circ, 120^\circ, 120^\circ$  (fault),  $120^\circ, 240^\circ, 120^\circ, 240^\circ$ . If a single fault occurs in which a  $0^\circ$  angular relation replaces a  $120^\circ$  angular relation (fig. 3*c*), a twin about the  $[310]$  axis also results (fig. 3*a*). Similarly, in fig. 3*d, e, f* the introduction of a single mistake may lead to a twin about the  $[3\bar{1}0]$  axis. In fig. 3*e* a  $240^\circ$  angle replaces a  $120^\circ$  angle, and in fig. 3*f* a  $0^\circ$  angle replaces a  $240^\circ$  angle; the stereogram for the  $[3\bar{1}0]$ -axis twin is given in fig. 3*d*. For a 1M polymorph (fig. 3*g, h*) a stacking error of  $240^\circ$  again leads to the same twin law; this stacking error involves replacement of one of the  $0^\circ$  angles by either a  $120^\circ$  or a  $240^\circ$  angle. It may be shown that a displacement of the upper half of a layer by  $nb/3$  with respect to the lower half is equivalent to a change of  $120^\circ$  in the interlayer stacking angle. A displacement of  $nb/3$ , therefore, would lead to twinning about the  $[310]$  axis in a 1M or  $2M_1$  polymorph. (It is interesting to note that the fault in a  $[310]$  twin axis of a 1M, a  $2M_1$ , or a 3T polymorph is used in one of the other polymorphs as a stacking element.)

This type of twinning was found in a 1M crystal of phlogopite from Chester, Vermont. A zero-layer,  $a$ -axis Weissenberg photograph contained reflections lying near the positions of reflections from a 3T polymorph; the anomalous intensity distribution, however, indicated that this specimen of phlogopite has a 1M structure and is twinned about both the  $[310]$  and  $[3\bar{1}0]$  axes. The spots on the photographs, instead of lying on smooth curves with a uniform variation of intensity, lie on a slight zigzag with every third reflection staggered in the same direction

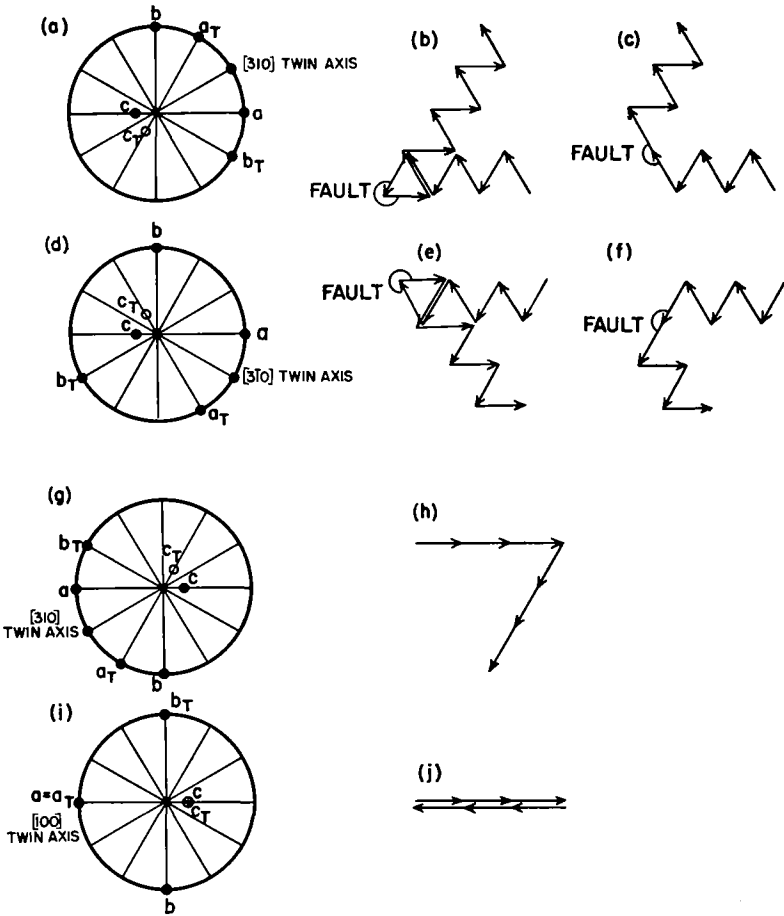


FIG. 3. (a) and (d) are stereograms showing the angular relations between the two twin components and (b), (c), (e), and (f) show the stackings which lead to the twinning of a  $2M_1$  structure on the  $[310]$  and  $[3\bar{1}0]$  axes. Notice that replacement of a  $120^\circ$  by a  $240^\circ$  or a  $0^\circ$  stacking angle leads to the same twin law but by a different method. Both (b) and (c) give the angular relation in stereogram (a); similarly with stereogram (d) and stacking diagrams (e) and (f). Stereogram (g) and stacking diagram (h) show the twinning of a 1M structure about the  $[310]$  axis. Stereogram (i) and stacking diagram (j) show the twinning of a 1M structure about the  $[100]$  axis.

and having the same intensity anomaly. Other crystals from the same hand specimen contained an untwinned 1M structure and still others the 3T structure.

Examination by Weissenberg methods of a mahadevite crystal from Racha Konda, India, contributed by Professor C. Mahadevan, has revealed the occurrence of a new twin law. The crystal has a 1M structure and is twinned about the [100] axis with (001) as the composition plane. The crystals were not suitable for an examination of the surface morphology and the twin law could not be confirmed from the morphology. This type of twinning can be explained (fig. 3*i, j*) by postulating the existence of a 180° stacking angle in the ordered sequence of 0° angles that forms the 1M type of structure. This type of twinning is related to the theoretical 2O polymorph, which is built solely from 180° stacking angles.

*Factors governing the growth of polymorphs.*

If the stacking of the layers in the mica structure were uncontrolled, completely disordered structures should always result. In the majority of the natural and synthetic specimens examined so far, the structure is reasonably well ordered, thus demonstrating the existence of controlling bond forces. The presence of stacking disorder, either partial or complete, in some of the micas shows that the controlling bond forces may be weak and may be rendered inactive under some thermodynamic conditions. In this section an attempt is made to evaluate the relative dominance of the various structural factors which control the stacking of the mica layers.

Observations on the mechanics of growth contribute to an understanding of the structural controls. Two mechanisms of growth have been recognized: growth of perfect crystals by secondary nucleation of each individual layer (Kossel, 1927; Stranski, 1928; Stranski and Kaischew, 1931); and growth of imperfect crystals (Burton, Cabrera, and Frank, 1949) by propagation of one nucleus into many layers of identical structure by spiral growth arising from a dislocation (cf. Frank, 1952). Several workers have examined the surface topology of micas by the method of multiple-beam interferometry developed by Tolansky. Tolansky (1945, 1946*a*, 1946*b*) showed that the surface of a mica sheet is violently contorted and crossed by cleavage steps, the heights of which appeared to be multiples of the *c*-spacing. According to Courtney-Pratt (1950), these cleavage steps were multiples of 10 Å. It was also shown by Tolansky that micas can be cleaved true to a single layer over large areas of many square centimetres. Tolansky and Morris (1947) investigated the surface topology of cleaved natural micas by an interferometric method which measures the thickness of the sheets. They

found that muscovites exhibited large areas of uniform thickness which contain very few inclusions; the average size of the uniform areas was 1 sq. cm. and the number of inclusions was about 10 per sq. cm. The phlogopites and biotites exhibited only small areas of uniform thickness and contained many inclusions, about 100 per sq. cm. The absence of spirals is consistent with either secondary nucleation of perfect crystals or spiral growth with the original dislocations having extended themselves over all the examined faces of the crystal so that they can no longer be detected. Amelinckx (1952) and Amelinckx and Dekeyser (1953) have demonstrated that cleavage faces of muscovite contain emerging screw dislocations and that growth spirals occur on a biotite crystal. It appears certain, therefore, that at least some micas have grown by the dislocation mechanism of Frank. The other micas may have grown by either method. It should be noted that these experimental observations apply only to large, well-developed crystals suitable for use in a multiple-beam interferometer. Fine-grained micas have not been examined in this apparatus and may have quite different surface topologies.

If growth proceeds by secondary nucleation of each additional layer there is no necessity for the added layers to adopt a fixed orientation unless other factors control the orientation. However, if growth proceeds by the spiral mechanism, the added layers must adopt the orientation of the primary nucleus and the resultant crystal will consist of a single ordered type of stacking. The type of stacking will thus be governed by the structural bond forces of the primary nucleus.

The second consideration involves the nature of the mica structure itself, and some of its properties will now be examined for evidence of specific structural bond controls. The pseudo-hexagonal stacking of the atoms in the mica structure results in weak structural control between adjacent sheets. The larger the deviation from hexagonal symmetry of the sheets of atoms, the larger will be the structural bond forces that control the orientation of adjacent layers. It should be noted, however, that even if all the atoms lie in arrays whose symmetry is exactly hexagonal there should still be a small controlling bond force, for the hexagonal sheets of atoms in any one layer are arranged in such a way as to give monoclinic symmetry. This bond force is probably quite small, for it arises in the stagger of the two halves of the mica layer that adhere at the octahedrally coordinated ions and it must operate through hexagonal arrays of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra, which act as an electrostatic screen. In addition, asymmetry will arise from the

distribution of Si and Al atoms in the tetrahedral sheet unless the Si and Al atoms are disordered.

Unfortunately, accurate structure determinations of the micas have not yet been made, and it is necessary to use qualitative arguments to evaluate the nature of the structural bond forces. As mentioned by Hendricks and Jefferson (1939), the (06*l*) reflections with *l* odd have zero intensity if all the ions occupy the ideal sites of hexagonal arrays. Muscovite and other dioctahedral micas give fairly large intensities for these reflections, showing that there is considerable deviation from the ideal structure. As shown by Jackson and West (1930), the observed angle  $\beta$  for a 2M<sub>1</sub> muscovite is 95° 30', which deviates considerably from the value of 94° 55' calculated for an ideal structure. Similarly the angle  $\beta$  for a 1M muscovite is 101° 35' (Yoder and Eugster, 1955) instead of the ideal value of 99° 41'. For natural 1M phlogopites, however, measurements of  $\beta$  with a precession camera have agreed within the experimental error of 5' with the ideal value of 99° 49'. The lengths of the *a*- and *b*-axes should be controlled dominantly by the linked array of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra, for these provide the strongest linkages in the micas. Using the value 1.645 ± 0.01 Å. for the distance Si<sub>3</sub>Al<sub>1</sub>—O (Smith,

TABLE I. Measurement of *b* (Å.) for muscovite and phlogopite polymorphs.

	Muscovite.	Phlogopite.
Natural 1M	—	9.20*
Synthetic 1M	9.00†	9.20‡ (or 3T)
Natural 2M <sub>2</sub>	9.02*	9.23‡
Synthetic 2M <sub>2</sub>	9.00†	—
Natural 3T	9.01†	9.21*

\* Present work.

† Yoder and Eugster (1955).

‡ Yoder and Eugster (1954).

1954) and assuming an ideal parallel array, *b* should equal 9.30 ± 0.06 Å. and *a* = *b*/√3. Both muscovite and phlogopite satisfy the condition *a* = *b*/√3. The measurements of *b* for the muscovite and phlogopite polymorphs are given in table I. The values for phlogopite fit quite well with the ideal value, thus suggesting that the tetrahedra are in closely parallel arrays. The values for muscovite, however, are 3% smaller than the ideal value, suggesting that the sheets of tetrahedra are buckled. It is plausible to suppose that in muscovite the sheets of tetrahedra collapse about the vacant octahedral sites. It is concluded from this evidence that there is considerable bond control over the stacking of dioctahedral micas and a smaller bond control over the stacking of trioctahedral micas.

In addition to the evidence provided by observations of the mechanics of growth and the properties of the mica structure itself, observations obtained on the synthesis of micas by Yoder and Eugster (1954, 1955) contribute to the problem of the nature of the controlling bond forces. They found that at high temperatures, hydrothermal growth of synthetic mica is relatively rapid and equilibrium can be demonstrated. Synthetic muscovite (which may be taken as a typical example of a dioctahedral mica) crystallizes with the  $2M_1$  structure; whereas phlogopite (a typical trioctahedral mica) crystallizes with the 1M, 3T, or both 1M and 3T structures (the identity of the powder patterns of 1M and 3T phlogopite precludes identification of the fine-grained synthetic crystals). Equilibrium at the high temperatures has been approached by converting a 1M and a 3T muscovite into a  $2M_1$  muscovite, and a  $2M_1$  phlogopite into a 1M, 3T, or both 1M and 3T phlogopite. These results are in agreement with those found by examination of natural micas from high-temperature environments. The muscovites from geologically high-temperature environments almost invariably have the  $2M_1$  structure; whereas the phlogopites generally have the 1M structure, but occasionally the 3T and other structures. The trioctahedral biotite often has a wide variety of structures including very complex ones such as the 8Tc and 12M already mentioned. The larger size of natural crystals allows the use of single-crystal methods, and all workers who have used this technique agree that stacking disorder does not occur in  $2M_1$  muscovites but is common in phlogopites and biotites—sometimes amounting to almost completely random stacking.

According to Yoder and Eugster, at low temperatures a different situation occurs with regard to the relative dominance of the polymorphs. In the laboratory, muscovite first crystallizes with the completely disordered structure (1Md), which changes into the 1M structure during longer runs or at higher temperatures. On raising the temperature the 1M structure can be converted into the  $2M_1$  structure. The reactions are so sluggish that equilibrium cannot be demonstrated. It is possible that the 1M structure is stable at low temperatures and it is probable that the transformation 1Md to 1M depends on the reaction rate. At low temperatures phlogopite also grows with the 1Md structure, which transforms into the 1M, 3T, or both 1M and 3T structures in the course of time or at higher temperatures. It is again probable that this reaction depends on factors affecting the reaction rate. It is believed that in nature the progressive metamorphism of sediments leads to the transformation  $1Md \rightarrow 1M \rightarrow 2M_1$  for muscovite in accordance with the

laboratory results. For phlogopite both 1Md (trioctahedral clay mica) and 1M structures have been found in low-temperature environments.

With this review of the experimental evidence, the relative merits of the hypotheses of growth by secondary nucleation and by the spiral mechanism, and the extent to which growth is controlled by structural factors, can now be examined:

If growth proceeds by secondary nucleation and there is no structural bond control, randomly stacked structures should result. If there is a little structural control, partially ordered crystals containing large regions of 1Md should occur.

If growth proceeds by the spiral mechanism and there is no structural bond control, ordered crystals should occur because the spiral mechanism provides a 'memory'. All polymorphs should occur in all possible environments since there is no structural control over the selection of the polymorph. It would be expected that the simpler ones would predominate, and that the order of abundance would be 1M; 2M<sub>1</sub>, 2M<sub>2</sub>, and 2O; 3T, 6H, &c.

If growth proceeds by secondary nucleation and there is complete structural control, ordered crystals should occur. Only one polymorph should occur for any one composition, temperature, and pressure. Different compositions could give different polymorphs and different polymorphs could be stable at different pressures and temperatures, for the crystal structure is a function of composition, pressure, and temperature. If the structural control is not complete, disorder can occur. This will not result in complex polymorphs, for the secondary nucleation growth mechanism has no 'memory'.

If growth proceeds by the spiral mechanism and there is complete structural control, the same result will occur as for growth by secondary nucleation with complete structural control. If the structural control is not complete, faults will occur sometimes and these will give complex polymorphs which retain their high repeat distances from the 'memory' of the spiral.

The growth of 1Md phlogopites and muscovites at low temperature fits most easily with the hypothesis of secondary nucleation and no structural control. The growth of 2M<sub>1</sub> muscovites at high temperature, with the absence of disorder and polymorphism, is explained by complete structural control and growth by either mechanism.

The growth of phlogopites and biotites at high temperatures, with the observed tendency to give 1M, 3T, or both 1M and 3T polymorphs, suggests a moderate structural control that can often be overwhelmed.



The presence of complex polymorphs, although rarely observed, definitely suggests operation of the spiral mechanism. The presence of random stacking disorder suggests that crystals containing this disorder grew by the method of secondary nucleation.

These two suggestions of complete control of the muscovites and moderate structural control of the phlogopites and biotites agree well with the semi-quantitative deductions concerning the distortion of the mica layers. It is highly desirable that accurate determinations of the atomic coordinates of these structures be carried out in order that the structural controls can be more fully evaluated. From these determinations it should be possible to determine why muscovite adopts the  $2M_1$  structure and phlogopite and biotite tend to adopt the  $1M$  structure.

Dekeyser and Amelinekx (1953) believe that the ions in the octahedral sites are not able to control the stacking of the mica layers, for they would have to influence the fourth nearest neighbours. It is the view of the present writers that the inferred distortion of the sheets of tetrahedra in the muscovite structure gives a direct linkage between the upper and lower surfaces of each mica layer, and hence the stacking is controlled without recourse to direct interaction between fourth neighbours. In trioctahedral micas there should be a small force arising from the monoclinic nature of each layer which requires interaction only between second neighbours.

Rejecting structural control (p. 26) Dekeyser and Amelinekx state in their English abstract that:

1. . . . The high frequency of polytypes in the trioctahedral types is correlated with growth conditions. For concision order and disorder are used in the sense of strict regularity resp. irregularity in the superposition of layers.

2. Order of micas and related clay minerals results from growth following the *mechanism of Frank*, as exemplified by the biotite considered in Part 1. This means growth at low supersaturations. Disorder occurs when growth proceeds by secondary nucleation.

3. Partial order means that the crystal has developed through different stages of supersaturation. Such crystals must generally be considered formed by the juxtaposition of a disordered part and one or more highly ordered ones.

4. The high percentage of order present in dioctahedral clay minerals (when their dimensions are superior to those of the primary nuclei) and the absence of polytypes indicates formation in conditions chemically not too complex, and at low supersaturation.

5. High degree of disorder, frequent polytypism, characteristic for trioctahedral minerals (with same restrictions as above) are the result of growth at higher temperatures and (or) complex chemical environment. In fact these conditions seem to be only compatible with the dioctahedral<sup>1</sup> type.

[<sup>1</sup> Misprint for trioctahedral?]

While it is agreed that disorder can occur when growth proceeds by secondary nucleation, it does not follow that order must always result from growth following the mechanism of Frank. It is considered by the writers that order may also result from growth by secondary nucleation if the structural control is strong. Furthermore, partial order may result either from development through different stages of supersaturation or from growth in which the structural control is only moderate so that the structural control may sometimes be overwhelmed by environmental conditions. Under the second hypothesis it is not necessary to consider that partially ordered crystals must be formed of the juxtaposition of a disordered part with one or more ordered ones; the ordered and disordered regions may be so intermixed that no separation of blocks can be made. The high order of dioctahedral micas formed *at high temperatures* results from strong structural control and not from the supersaturation. As cited above the dioctahedral micas contain considerable disorder when grown at low temperatures. The high degree of disorder and frequent polymorphism result from the presence of only moderate structural control. Since partially ordered phlogopites and biotites occur in the same hand specimen as fully ordered muscovites, it is clear that temperature does not have the dominant role ascribed by Dekeyser and Amelinckx.

It should be obvious from the frequent resort to qualitative and semi-quantitative evidence in the arguments presented in this section that much additional work is needed in order to resolve fully the issues discussed here. Further studies by interferometric and X-ray methods (such as those carried out by Amelinckx and Dekeyser, 1953) on crystals from a wide range of geological environments should be made. Detailed study of the ionic distribution in the mica structures is needed in order that accurate estimates of the structural forces can be made. Combination of the data from the two methods should result in more quantitative conclusions.

#### *Polymorphism in natural micas.*

In order to test the semi-quantitative deductions presented in the previous section, single crystals were selected from geological occurrences believed to represent a wide range of environmental conditions. They were obtained from intrusive and extrusive igneous rocks, low- and high-grade metamorphic rocks, alteration and contact zones, veins and pegmatites, and sediments.

*Extrusive.* Two specimens were examined from extrusive rocks.

Biotite 49-34 was collected by Dr. O. F. Tuttle at Camp Hale, Eagle Co., Colorado, from a flow rhyolite containing phenocrysts of biotite and quartz, the latter showing high-temperature morphology and inversion characteristics (Keith and Tuttle, 1952); the feldspars in the groundmass were also indicative of high temperatures. Biotite B399 is from a flow rock in the Leucite Hills, Wyoming (Kemp, 1897); the specimen was collected by Dr. J. F. Kemp and contributed by Dr. Arie Poldervaart from the Columbia University collection. Both specimens gave a 1M structure, and it is for this reason that the synthetic phlogopite made at high temperatures (Yoder and Eugster, 1954) is believed to be 1M rather than 3T.

*Intrusive.* The biotite F2-183 from the Beinn an Dubhaich granite of the Isle of Skye was selected because the rock has the textural and compositional features of a granite, but with mineralogical features attributed to the rhyolites; it is considered by Tuttle and Keith (1954) to be a link between granites and rhyolites. One crystal was examined and found to have a 1M structure. Studies by X-ray powder diffraction of biotites and muscovites from a collection of common granites gave in all cases the 1M and  $2M_1$  structures, respectively. For those granites that formed from a liquid, it has been shown that biotite is one of the first phases to appear. On the other hand, the appearance of muscovite in granites may be primary or secondary, depending on the pressure and temperature (Yoder and Eugster, 1954, 1955).

*Pegmatites.* The pegmatites yield the greatest variety of mica polymorphs, 1M,  $2M_1$ ,  $2M_2$ , 3T, 8Tc, and larger units, as well as mixed-layer types. The phlogopites from the Burgess, Ontario, mica deposit gave, for example, 1M and  $2M_1$  (U.S.N.M. 82459 and U.S.N.M. C3679, 1M; U.S.N.M. 106758,  $2M_1$ ). Hendricks and Jefferson (1939, p. 765) cite the Ambulawa, Ceylon, pegmatite as one containing the  $2M_1$ ,  $2M_2$ , and 8Tc polymorphs. The mahadevite specimen, (1M), a gift of Professor C. Mahadevan, is now considered, on the basis of the published analyses, to be close to eastonite in composition and does not lie midway between muscovite and phlogopite; it is described as occurring in a 'pegmatite vein which cuts through a band of micaceous schists in the khondalites (sillimanite garnet gneiss)' (Ramaseshan, 1945). The lepidolite ( $2M_2$ ) from the Brown Derby Claim at Ohio City, Colorado (Stevens, 1938, U.S.N.M. 97893), was examined mainly because of its importance as an end member of what Levinson (1953) stated to be a complete series between lepidolite and muscovite. Levinson found that those micas having bulk compositions in the middle of the range actually had mixed-

layer structures of muscovite ( $2M_1$ ) and lepidolite ( $2M_2$ ) in contradiction to his concept of a complete series of solid solutions between muscovite and lepidolite. It is impossible for different structural types (e.g.  $2M_1$  and  $2M_2$ ) to form a complete series of solid solutions since it is not possible to turn one mica structure into another by a continuous displacive<sup>1</sup> transformation, but only by a reconstructive transformation.

*Replacement.* An example of a selective replacement mica is the Sultan Basin, Washington, muscovite collected by Dr. A. C. Waters and contributed by Mr. J. M. Axelrod (Axelrod and Grimaldi, 1949). According to Waters, the muscovite occurs as veinlets and replacements in granodiorite, and he visualizes the mica as forming from hot gases following the sheeting in the granite rock. The structure was found to be  $3T$ . Another example of a replacement mica is from Postmasburg, South Africa, where it was formed in argillaceous sediments along with the manganese ore minerals. The occurrence is described by Hall (1927) and the crystals by Phillips (1931). The mica was described as an ephesite (soda-margarite), but it may also be described as a lithium paragonite for the analysis shows large amounts of lithium. It is of special importance because it is the first mica high in soda that has been found in crystals suitable for single-crystal study. The one crystal examined was mainly  $2M_1$ , but gave indication of the presence of a  $12M$  polymorph.

*Contact.* Two specimens described as having grown in contact zones were also studied. Palache (1935, p. 116) described a biotite (U.S.N.M. C3675) in the skarn zones where pegmatites cut the limestones at the Sterling Hill, New Jersey, zinc deposits and he thought that the mica would best be described as a manganophyllite. The mica from the Wissahickon schist near its contact with Baltimore gneiss near Germantown, Pennsylvania, is noteworthy for its low  $2V$  and is described in detail by Postel and Adelhelm (1944). Both specimens have the  $2M_1$  structure.

*Hydrothermal alteration.* One specimen representing growth by hydrothermal alteration also gave a  $2M_1$  structure. It is a muscovite formed at the expense of a topaz crystal (U.S.N.M. 45075) from Stoneham, Maine, and classed with the rather ill-defined variety damourite (Clarke and Chatard, 1884).

*Metamorphic.* Micas from both high- and low-grade metamorphic rocks were examined. The muscovite (C-16) from the sillimanite zone

<sup>1</sup> A transformation in which atoms are merely displaced, in contrast to a reconstructive transformation, in which the structure breaks down and is rebuilt (M. J. Buerger, Amer. Min., 1948, vol. 33, p. 101 [M.A. 10-380]).

(Barrow, 1912) in Glen Clova, Scotland, was found to have a  $2M_1$  structure. The phlogopite (149) in a tremolite marble near Chester, Vermont, exhibited both the 1M and 3T polymorphs. A very large collection of biotites and muscovites from an area in which all grades of metamorphism may be found was examined by Dr. Vernon J. Hurst (unpublished, 1954) using powder X-ray diffraction techniques. The results indicated that all the biotites were 1M or 3T and all the muscovites were  $2M_1$ .

*Sedimentary* (?). Only one example of a mica believed to have grown diagenetically in a sediment and of a size suitable for single-crystal study was obtained. Carr, Grimshaw, and Roberts (1953) described a mica from a Yorkshire fireclay as a hydrous mica or an illite. Their published X-ray powder pattern was noted by them to be a mixture of mica and kaolinite. The presence of kaolinite would account for the excess water and low potassium obtained in the chemical analyses. The single-crystal study, as well as close examination of their X-ray powder pattern, indicates that the mica has a  $2M_1$  structure. Although materials called illite and hydrous mica may contain micas having any structure or may even be mixtures, only that portion of the micas having a 1Md or a 1M structure is believed by Yoder and Eugster (1954) to be indicative of a low-temperature environment. One might suspect, therefore, that the  $2M_1$  mica in the Yorkshire fireclay is of detrital origin and did not grow in the sediment.

It is concluded from these data on natural micas that there are factors other than environmental that determine the type of polymorph. Composition clearly has a strong influence on the structure. Aside from the obvious structural preferences of the common dioctahedral and trioctahedral micas, muscovite and biotite, respectively, there are compositional preferences within each of these groups, as exemplified by the limited solid solution between muscovite and lepidolite. Ordering forces are evident in the natural micas, particularly in the low-grade environments. The variation of structure in the natural micas cannot, therefore, be attributed solely to changes in pressure and temperature.

#### *Identification of the mica polymorphs.*

The structures of the mica polymorphs have many elements in common, resulting in difficulties in identifying the mica polymorphs from X-ray patterns. A rapid X-ray method of identification consists of taking a powder record either by photographic means or by the use of a Geiger counter focusing diffractometer. However, the dominant basal

cleavage results in preferred orientation, which is especially serious for the focusing diffractometers, and some care is needed in order to obtain satisfactory powder records. A more serious objection to the powder method is that 1M and 3T phlogopites (or other trioctahedral micas) give powder patterns that are indistinguishable (see below) and these polymorphs can only be distinguished by the use of single-crystal methods. The other common polymorphs, dioctahedral 1M and 3T, and the  $2M_1$  and  $2M_2$  polymorphs, however, can be identified from their powder patterns. It is doubtful whether the complex polymorphs such as the 12M can be identified by powder methods, for the strong reflections are similar to those for one of the simple polymorphs and the weak reflections are liable to be obscured in powder patterns. Table II

TABLE II. Data for identification of mica polymorphs from powder patterns; see also Levinson (1953).  $d$  in Å.

1M		$2M_1$		3T		1M and 3T		$2M_1$	
muscovite.†		muscovite.†		muscovite.†		phlogopite.‡		phlogopite.§	
<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>
vs	10.08*	vs	10.04*	vs	9.99*	vs	10.05*	vs	10.13*
w	5.04*	m	5.02*	s	4.99*	w	5.02*	w	5.06*
s	4.49	m	4.48	w	4.49	vw	4.59	w	4.61
		m	4.46	w	4.46	vw	4.55	vw	4.52
w	4.35	vw	4.39						
		w	4.30						
vw	4.12	vw	4.11					vw	4.08
		vw	3.97			vw	3.93		
		w	3.89	w	3.87			w	3.81
m	3.66	w	3.74	w	3.60	vw	3.66		
		m	3.50			m	3.39	m	3.54
vs	3.36*	vs	3.35*	vs	3.33*	vs	3.35*	vs	3.36*
m	3.07	m	3.21	w	3.11	w	3.14	m	3.28
vw	2.93	m	3.00			w	2.92	vw	3.16
		w	2.87	w	2.88			s	3.04
		w	2.80			vw	2.71	vw	2.93
vw	2.69	m	2.59	w	2.59	vw	2.64	w	2.82
m	2.58	m	2.58			m	2.62	w	2.65
s	2.56	s	2.56	m	2.56			vs	2.62
w	2.55	w	2.51*	vw	2.50*	m	2.51*	w	2.52*

\* Basal reflections.

† Yoder and Eugster (1955).

‡ Present work, Table III.

§ Yoder and Eugster (1954).

contains the  $d$  values and intensities for the powder patterns of  $2M_1$ , 1M, and 3T polymorphs of muscovite, the identical patterns of 1M and

3T phlogopite polymorphs, and the  $2M_1$  phlogopite polymorph. Data for the 1M,  $2M_2$  (described as 6M by Levinson), and 3T polymorphs of lepidolite and the  $2M_1$  of lithian muscovite have been given by Levinson (1953, p. 100, table 3). In his table 3, column 1, 3·20 should read 3·32, and in column 2, 4·94 should read 4·49. Muscovite and phlogopite may be taken as typical representatives of the dioctahedral and trioctahedral mica groups. In using table II for the identification of the polymorphs it should be realized that deviations of composition from the ideal muscovite and phlogopite formulae will result in small variations from the  $d$  values listed. As an example one may refer to the differences between a hydroxyl-bearing phlogopite and a fluorine-bearing phlogopite (Yoder and Eugster, 1954, pp. 170, 177). Preferred orientation in the powder specimen will give considerable variation in intensities from those listed in table II, for preferred orientation results in an increase of intensity for reflections whose planes are nearly parallel to (001) with a corresponding decrease for reflections whose planes are nearly normal to (001). The basal reflections (00 $l$ ) are starred in table II; these are enhanced most by preferred orientation.

The reason for the identity of the 1M and 3T phlogopite patterns is that the 1M and 3T polymorphs are based on the same sub-cell and that the 1M unit cell may be transformed into a cell with trigonal geometry. It can easily be shown that the  $2\theta$  values of the X-ray reflections are the same for the two polymorphs if:  $a_M = a_T$ ;  $b_M = b_T$ ;  $3c_M \sin \beta_M = c_T$ ;  $\cos \beta_M = -a_M/3c_M$  or  $\cot \beta_M = -a_T/c_T$ .

Since the structure of the sub-cell is ideally hexagonal for phlogopite, as revealed by (06 $l$ ) reflections, the intensities of the X-ray reflections will also be identical. Measurements of the lattice parameters of 1M and 3T natural phlogopites show that the geometrical conditions given above hold true within experimental error. In particular, the measured value of  $\beta_M$  agrees within the experimental error of about 5' of arc with the calculated value. In addition, the intensities of corresponding reflections measured from Weissenberg photographs are equal within experimental error for 1M and 3T phlogopite crystals.

Table III contains measurements of the powder patterns of a natural 1M and a natural 3T phlogopite together with the indices of the reflections. The agreement between the  $2\theta$  values and intensities is very close and the small differences in  $2\theta$  may be ascribed to small variations in the chemical composition. (A small amount of F replacing OH, for example, results in a large change in the  $c$  dimension without affecting the geometrical conditions governing the relation between the 1M and 3T unit

TABLE III. Powder records of 1M and 3T natural phlogopites. Cu- $K\alpha$  radiations. Intensities on an arbitrary scale.

1M			3T		
<i>I.</i>	$2\theta_{\text{obs.}}$	Indices.	<i>I.</i>	$2\theta_{\text{obs.}}$	Indices.
> 100	8.87	001	> 100	8.730	0003
6	17.67	002	23	17.660	0006
7	19.345	020	8	19.310	10 $\bar{1}$ 0
5	19.495	110	8	19.525	10 $\bar{1}$ 1
3	22.665	111	3	22.560	1014
7	24.360	11 $\bar{2}$	7	24.300	10 $\bar{1}$ 5
20	26.3 ?	022	45	26.255	10 $\bar{1}$ 6
> 100	26.625	003	> 100	26.575	0009
10	28.385	112	25	28.350	10 $\bar{1}$ 7
7	30.655	11 $\bar{3}$	21	30.645	10 $\bar{1}$ 8
3	33.075	023	12	33.050	10 $\bar{1}$ 9
7	33.935	{ 130 20 $\bar{1}$	10	33.910	11 $\bar{2}$ 1
30	34.305	{ 200 13 $\bar{1}$	30	34.255	11 $\bar{2}$ 2
15	35.705	{ 004 113 131 20 $\bar{2}$	52	35.730	{ 0.0.0.12 1.0. $\bar{1}$ .10 11 $\bar{2}$ 4
15	36.985	{ 13 $\bar{2}$ 201	17	36.970	11 $\bar{2}$ 5
3	39.305	22 $\bar{1}$	3	39.245	20 $\bar{2}$ 1
?	39.8	{ 220 132 203	2	39.900	11 $\bar{2}$ 7
?	40.3	041	2	40.200	20 $\bar{2}$ 3
15	41.610	{ 133 202	21	41.590	11 $\bar{2}$ 8
30	45.05	005	> 100	45.090	0.0.0.15
7	45.47	{ 204 133	12	45.450	1.1. $\bar{2}$ .10
2	47.60	{ 134 203	4	47.655	1.1. $\bar{2}$ .11
?	52.335	{ 205 134	3	52.350	1.1. $\bar{2}$ .13
15	54.825	{ 135 204	35	54.820	1.1. $\bar{2}$ .14
15	60.285	060	25	60.235	30 $\bar{3}$ 0
2 ?	61.1	{ 061 330	2 ?	61.12	30 $\bar{3}$ 3



cells.) The powder pattern of a synthetic phlogopite (given in Yoder and Eugster, 1954) can be indexed equally well on a 1M or a 3T unit cell.

On the other hand the 1M and 3T dioctahedral powder patterns (as exemplified by muscovite, table II) are not identical because the monoclinic unit cell cannot be transformed into a unit cell of the same shape as the trigonal cell. Measurements of  $\beta$  for a 1M muscovite differ by about  $1^\circ 51'$  from the value required for geometrical equality. Furthermore, the intensities of corresponding reflections are not identical in accordance with the inferred distortion of the sub-cell.

As mentioned earlier, the 1M and 3T polymorphs may be readily identified from single-crystal moving-film photographs, but even with this method some care is needed; for example, a 1M crystal twinned on the  $[310]$  and  $[3\bar{1}0]$  axes gives a photograph similar to that of a 3T crystal.

Plates VIII and IX contain zero-layer  $5.3 \text{ \AA}$ . axis Weissenberg photographs of 1M and 3T crystals. There are three axes of  $5.3 \text{ \AA}$ . translation for each polymorph and only for the 3T polymorph are they identical. For the 1M polymorph the axes are  $[100] \neq [110] \neq [1\bar{1}0]$ ; whereas for the 3T polymorph the axes are  $[2\bar{1}\bar{1}0] = [\bar{1}2\bar{1}0] = [\bar{1}\bar{1}20]$ . Plate VIII, a and b are zero-layer photographs about the  $[100]$  and  $[110]$  axes of a 1M phlogopite. The  $[100]$  axis photograph shows the presence of a plane of symmetry. A 1M muscovite pattern differs only slightly in position and intensity of the reflections. Plate IX, c and d are zero-layer photographs about the  $[2\bar{1}\bar{1}0]$  axis of a 3T phlogopite and muscovite. These have closely similar positions of the reflections but the intensities differ considerably. It will be seen that the 1M and 3T photographs are quite different and may be readily distinguished.

But a  $5.3 \text{ \AA}$ . axis rotation photograph of a 1M phlogopite twinned on  $[110]$  or  $[1\bar{1}0]$  will contain reflections on or very close to the positions occupied by the 3T reflections. If  $\beta$  is exactly equal to the ideal value, there will be no displacement from positions consistent with 3T symmetry. If  $\beta$  deviates from the ideal value, the reflections will lie on zigzags. If no displacement from trigonal geometry is visible, the twinning can still be detected if the three components connected by the twinning do not have equal volumes, for the intensities of the reflections will not agree with those for a 3T polymorph. If the volumes are equal the intensities will be equal to those for a 3T crystal. On the other hand a twinned 1M muscovite cannot give a photograph identical with a 3T muscovite, for the positions of the reflections will be considerably different since  $\beta$  does not have the value necessary for pseudo-trigonal geometry as described above.

The zero-layer  $b$  (9.2 Å.) axis Weissenberg (or precession) photographs of 1M and 3T phlogopite crystals are identical and cannot be used for identification purposes, because the reflections arising from the 3-layer repeat depend on distortion of the sub-cell and in the ideal trioctahedral structure have zero intensity. First- and second-layer  $b$ -axis photographs are suitable for identification purposes.

For routine identification of the mica polymorphs it is recommended that a powder photograph be taken first. This powder specimen may be obtained by grinding selected crystals or, if a focusing diffractometer is available, a slab of a fine-grained rock, cut perpendicular to the schistosity, serves as a suitable X-ray mount. The 1M and 3T structures of trioctahedral crystals will give identical powder patterns but can be resolved by single-crystal study. Complex polymorphs will be mistaken for simpler polymorphs since they give similar X-ray powder patterns, and the weak reflections that serve to identify them in single-crystal patterns will be lost in the background of a powder pattern. As the complex polymorphs appear to be rare and independent of specific pressure and temperature conditions, it may not be critical to obtain a positive identification in routine work. If identification or knowledge of twinning is desired, single-crystal photographs must be taken.

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## EXPLANATION OF PLATES VIII AND IX.

Zero-layer Weissenberg photographs of micas about rotation axes with 5.3 Å. repeat distance. Filtered  $\text{Co-K}\alpha$  radiation. The straight rows contain the basal reflections.

## PLATE VIII.

FIG. A. 1M phlogopite, [100] axis; specimen 149.

FIG. B. 1M phlogopite, [110] axis; specimen 149.

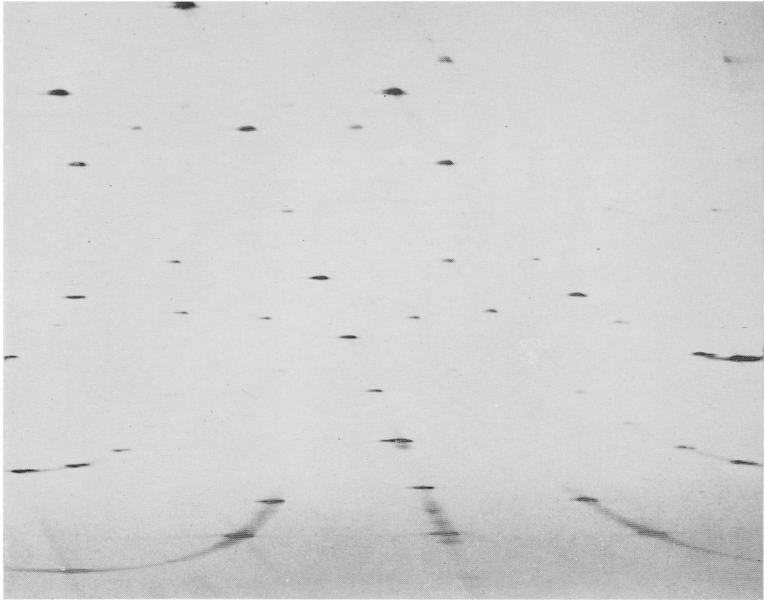
The most striking difference between figs. A and B is the plane of symmetry in A. In these two figures the diffuse reflections between the (00 $l$ ) reflections are probably caused by parallel growth of another layer mineral. In the first curved row there are also some weak reflections from another layer mineral, or reflections from a small amount of a complex mica polymorph in parallel orientation with the 1M crystal, but they are somewhat irregular in position and no certain identification was possible.

## PLATE IX.

FIG. C. 3T phlogopite,  $[2\bar{1}10]$  axis; specimen R4463.

FIG. D. 3T muscovite,  $[2\bar{1}10]$  axis; specimen Sultan Basin.

In figs. C and D note the uniform rise and fall of intensities in the rows of the 3T phlogopite, C, in contrast to the irregular sequence for the 3T muscovite, D.



A



B



C



D