

# EXPERIMENTAL STUDIES ON MICAS : A SYNTHESIS

*by*

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## ABSTRACT

The principal end members of the micas believed to be common in sediments have been synthesized and some of their stability relations determined. The polymorphs of muscovite and paragonite, the principal dioctahedral end members, obtained were 1Md, 1M and 2M<sub>1</sub>, and those of phlogopite and annite, the principal trioctahedral end members, 1Md and 1M or 3T. The range of stability of each of the polymorphs could not be fixed accurately because of the slow rate of transformation ; however, the transformations 1Md → 1M → 2M<sub>1</sub> were effected for muscovite and paragonite and 1M → 1Md or 3T and 2M<sub>1</sub> → 1M or 3T for phlogopite. The growth characteristics of these micas in the laboratory are believed to be analogous to the formation of micas in sediments.

Knowledge of the synthetic micas contributes greatly to an understanding of the natural materials called illite, hydromica, and high-silica sericite. The dioctahedral members of these materials and related minerals may be delineated accurately in the system muscovite—Al-celadonite—pyrophyllite and their iron analogues. The trioctahedral members of some of the same materials may be outlined in the system phlogopite—eastonite—talc and their iron analogues. The postulated substitution schemes in these systems are mainly  $\text{MgSi} \rightleftharpoons \text{Al}^{\text{VI}}\text{Al}^{\text{IV}}$ ,  $\text{KAl} \rightleftharpoons \text{Si}$ , and  $\text{H}_3\text{O} \rightleftharpoons \text{K}$ . In materials intermediate between these systems, such as most biotites and vermiculites, the substitution of  $3\text{Mg} \rightleftharpoons 2\text{Al}^{\text{VI}}$  is of major importance. The mixed-layer structures involving micas are elucidated.

## INTRODUCTION

The micas are among the most common rock-forming minerals. They show great compositional variation and can form under a wide range of physical and chemical conditions. Members of the mica group are found in all rock types—sedimentary, metamorphic, and igneous. Because of their wide range of stability and variations in properties, the micas are potentially useful indicators of the environmental conditions at the time of their formation or recrystallization. The synthesis of micas in the laboratory under controlled conditions analogous to those in nature was undertaken so that a correlation of the properties of the micas with environmental conditions could be made. The results of the experimental studies on the micas bear on many petrological problems, and in particular on the problems of the clay minerals.

The experimental approach to these problems has several advantages not realized in the study of naturally occurring clays. The principal advantages are that the bulk composition is known, quantitative information on the stability of the phases can be ascertained, growth characteristics can be observed at various stages, and the physical properties of the final products

in some cases are more amenable to study than those of the materials obtained in nature. Because the bulk composition is known, the synthetic products may be identified by many techniques not applicable to natural products of complex or unknown composition. The isolation and identification of single phases, often the principal problem of the clay mineralogist, is thereby greatly simplified by the experimental approach.

It is the purpose of this synthesis of recent studies on micas to outline the experimental method used at the Geophysical Laboratory, indicate how some of the results bear on clay mineral problems, and delineate several important areas for future work. The data on which most of the conclusions are based may be found in Yoder and Eugster (1954, 1955) and Smith and Yoder (1956). Brief synopses of additional work on the micas by the same investigators may be found in the Annual Reports of the Director of the Geophysical Laboratory (Morey, 1953, pp. 64-69; Abelson, 1954, pp. 111-114; 1955, pp. 124-129; 1956, pp. 158-161; 1957, in press). It is anticipated that detailed reports will be forthcoming on the "Stability and occurrence of paragonite" (Eugster and Yoder, abstr. 1954), "Muscovite-paragonite join and its use as a geologic thermometer" (Eugster, abstr. 1956) and "Stability of iron-rich biotites and the petrological significance of redox reactions" (Eugster, abstr. 1956a, 1957, and in Abelson, 1957). The comments and criticisms of Drs H. P. Eugster, D. M. Foster, and particularly D. B. Stewart were of considerable help in the preparation of the present synthesis.

### MICA END MEMBERS

The first step in the experimental study of the micas, or any mineral group, is to determine the principal end members. The source of this information is, of course, the published analyses of the naturally occurring micas from all environments, and knowledge of the structure based on single-crystal or powder diffraction techniques. Some of the compositions of mica investigated are listed with other simple end members of the principal dioctahedral, trioctahedral, and intermediate micas in Table 1. Natural micas close to the composition of annite, eastonite, iron-eastonite, and Al-celadonite have not been found in nature; yet these compositions as components have been found to comprise a large part of some natural micas and, therefore, serve as reasonable end members. Siderophyllite has been considered as analogous in composition to eastonite (see Winchell, 1925, p. 323); however, those micas described as siderophyllite appear to be more closely related in composition to lepidomelane. The intermediate end members<sup>1</sup> of the mica group were chosen from analyzed natural specimens as limiting compositions: they are

<sup>1</sup> The intermediate micas are those *end members* which have more than two-thirds and less than all the octahedral positions filled. It is not intended that the term "intermediate" be used to describe the *natural* micas having both dioctahedral and trioctahedral character in that practically all micas would fall into this group and the compositions of the end members are arbitrary. It has yet to be demonstrated that the intermediate end members are true compounds and not just maximum members of a discontinuous solid solution series.

the result of at least two types of solid solution ( $\text{MgSi} \rightarrow \text{Al}^{\text{VI}}\text{Al}^{\text{IV}}$ ;  $2\text{Al}^{\text{VI}} \rightarrow 3\text{Mg}$ ) whose limits have not been accurately determined.

TABLE 1.—PRINCIPAL END MEMBERS OF THE MICA GROUP

Dioctahedral				
Muscovite	K	$\text{Al}_2$	$\text{AlSi}_3$	$\text{O}_{10}(\text{OH})_2$
Paragonite	Na	$\text{Al}_2$	$\text{AlSi}_3$	$\text{O}_{10}(\text{OH})_2$
Margarite	Ca	$\text{Al}_2$	$\text{Al}_2\text{Si}_2$	$\text{O}_{10}(\text{OH})_2$
Celadonite	K	$\text{MgFe}^{+3}$	$\text{Si}_4$	$\text{O}_{10}(\text{OH})_2$
Al-celadonite	K	$\text{MgAl}$	$\text{Si}_4$	$\text{O}_{10}(\text{OH})_2$
Trioctahedral				
Phlogopite	K	$\text{Mg}_3$	$\text{AlSi}_3$	$\text{O}_{10}(\text{OH})_2$
Annite	K	$\text{Fe}_3$	$\text{AlSi}_3$	$\text{O}_{10}(\text{OH})_2$
Clintonite	Ca	$\text{Mg}_3$	$\text{Al}_2\text{Si}_2$	$\text{O}_{10}(\text{OH})_2$
Polyolithionite	K	$\text{Li}_2\text{Al}$	$\text{Si}_4$	$\text{O}_{10}\text{F}_2$
Eastonite	$\text{K}_2$	$\text{Mg}_5\text{Al}$	$\text{Al}_3\text{Si}_5$	$\text{O}_{20}(\text{OH})_4$
Iron-castonite	$\text{K}_2$	$\text{Fe}_5\text{Al}$	$\text{Al}_3\text{Si}_5$	$\text{O}_{20}(\text{OH})_4$
Intermediate				
Siderophyllite	K	$\text{Fe}^{+2}_{1.66}\text{Al}$	$\text{Al}_{1.33}\text{Si}_{2.67}$	$\text{O}_{10}(\text{OH})_2$
Lepidomelane	K	$\text{Fe}^{+2}_{1.66}\text{Fe}^{+3}$	$\text{Al}_{1.33}\text{Si}_{2.67}$	$\text{O}_{10}(\text{OH})_2$

In general, the natural muscovites, most common of the dominantly dioctahedral micas, lie close to the join muscovite–Fe-muscovite–Al-celadonite–celadonite shown in Fig. 1. Beginning with  $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$  the principal substitution schemes on this join are  $\text{MgSi} \rightleftharpoons \text{Al}^{\text{VI}}\text{Al}^{\text{IV}}$  and  $\text{Fe}^{+3} \rightleftharpoons \text{Al}^{+3}$ . The first scheme leads to high-silica sericite (see Schaller, 1950), which is believed to be the most important mica in sediments and low-grade metamorphic rocks. The high-silica sericites appear to merge into the glauconites with increasing substitution of  $\text{MgSi} \rightleftharpoons \text{Al}^{\text{VI}}\text{Al}^{\text{IV}}$ . In the glauconites the substitution of  $\text{Fe}^{+3} \rightleftharpoons \text{Al}^{+3}$  and  $\text{Fe}^{+2} \rightleftharpoons \text{Mg}^{+2}$  become important, in general, iron increasing from the muscovites to the celadonites. The latter substitutions are of paramount importance in many sedimentary and metamorphic problems; however, for the present synthesis Mg and  $\text{Fe}^{+2}$  will be considered together and occasionally it will be convenient to combine  $\text{Fe}^{+3}$  and  $\text{Al}^{+3}$ . The glauconites consist in bulk composition of approximately two-thirds of the celadonite components and one-third of the muscovite components (see Hendricks and Ross, 1941, p. 708). As will be seen below, the value one-third often appears in the composition of other micas and clays related to the micas. It is the opinion of the writer that the glauconites may have some trioctahedral character; however, the substitution of  $3\text{Mg} \rightleftharpoons 2\text{Al}^{\text{VI}}$ , for example, appears to be very limited. It is possible that a dioctahedral glauconite may break down to a trioctahedral lepidomelane and other products through iron reduction according to a recent suggestion of J. F. Burst (personal communication, 1957).

Other substitutions may lead to a high-silica series such as found along the muscovite–celadonite join. One possible substitution is  $\text{Si} \rightleftharpoons \text{KAl}$  trending

towards montmorillonite. In addition, the limited substitution of  $\text{Li}_2\text{Si} \rightleftharpoons \text{Al}^{\text{VI}}\text{Al}^{\text{IV}}$  has been shown to lead to a high-silica mica, the lithian muscovite of Levinson (1953). Of particular significance in this substitution is the fact that slightly more than two-thirds of the octahedral sites may be filled. That is to say, *the muscovites as a group need not be exactly dioctahedral and may have some trioctahedral character*. If the substitution of  $\text{Li}_2\text{Si} \rightleftharpoons \text{Al}^{\text{VI}}\text{Al}^{\text{IV}}$  is carried on, two phases develop, a lithian muscovite and a polyolithionite. Finally, when carried to completion, the product is polyolithionite, the chief lepidolite and a common member of the trioctahedral micas. It is to be noted

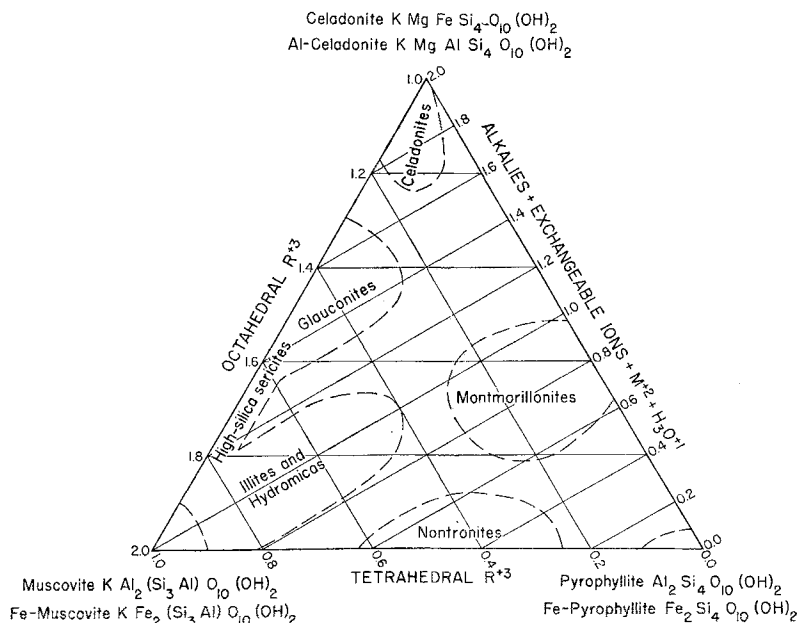


FIGURE 1.—Plot of tetrahedral  $\text{R}^{3+}$  and octahedral  $\text{R}^{3+}$  in atom proportions of dioctahedral micas and related minerals (Yoder and Eugster, 1955, p. 257).

that the lepidolites are primarily fluoromicas (Stevens, 1938). Polyolithionite has been synthesized in the laboratory, but its hydroxyl analogue has not. At one time the series muscovite–polyolithionite was considered as a continuous solid solution series; however, the x-ray evidence presented by Levinson (1953) indicates that a two-phase region exists. To the best knowledge of the writer *there is no known continuous solid solution series between a dioctahedral and a trioctahedral mica*.

Another important substitution in muscovite is  $\text{Na}^{+1} \rightleftharpoons \text{K}^{+1}$  leading to paragonite, a mica that appears to be common as means of recognition are improved. This substitution is not continuous and a two-phase region of muscovite and paragonite solid solutions exists. Other minor substitutions

may occur in the muscovite group, such as:  $\text{CaAl} \rightarrow \text{KSi}$ , trending towards margarite;  $\text{H}_3\text{O} \rightarrow \text{K}$  (which has yet to be established), trending toward the hydrous micas; and  $\text{Fe}^{+3} \rightarrow \text{Fe}^{+2}\text{H}^{+1}$ , trending toward the oxymicas of low OH content.

The biotites, the chief trioctahedral micas, lie in a general way on and between the joins phlogopite-lepidomelane and phlogopite-iron-eastonite, including their respective analogues as shown in Fig. 2. Here the substitution schemes are dominantly  $\text{Al}^{\text{VI}}\text{Al}^{\text{IV}} \rightleftharpoons \text{MgSi}$  and  $2\text{Al}^{\text{VI}} \rightleftharpoons 3\text{Mg}$ , as well as  $\text{Fe}^{+2} \rightleftharpoons \text{Mg}$  and  $\text{Fe}^{+3} \rightleftharpoons \text{Al}$ . In the natural biotites, the iron content usually increases from phlogopite to lepidomelane and to iron-eastonite. Critical information about the conditions of formation of biotite may be obtained, therefore, from the relative  $\text{Al}^{\text{VI}}$  and  $\text{Al}^{\text{IV}}$  content as well as the relative Mg and  $\text{Fe}^{+2}$  content. Gower (1957) has demonstrated a useful x-ray technique for estimating the iron-magnesium ratio in biotite; however, a rapid method for determining the aluminum content and distribution has not as yet been developed.

Lithium enters the trioctahedral structure as in polyolithionite,  $\text{KLi}_2\text{AlSi}_4\text{O}_{10}\text{F}_2$ ; zinnwaldite,  $\text{K}(\text{LiFe}^{+2}\text{Al})(\text{AlSi}_3)\text{O}_{10}\text{F}_2$ ; or taeniolite,  $\text{K}(\text{Mg}_2\text{Li})\text{Si}_4\text{O}_{10}\text{F}_2$ . In these micas fluorine principally occupies the OH positions where  $\text{F} \rightleftharpoons \text{OH}$ . The substitution of  $\text{H}_3\text{O} \rightleftharpoons \text{K}$  and  $\text{Mg} \rightleftharpoons 2\text{K}$  (see Barshad, 1948) have been proposed for the biotites, and these in part are thought to bring about changes in composition toward the vermiculites, which are currently classed with the montmorillonite group. Other minor substitution schemes in the trioctahedral micas may take place involving such atoms as V, Cr and Mn.

It is clear according to the studies of Foster (1957) that the biotites which are dominantly trioctahedral have some dioctahedral character. It is to be noted that there are no natural dominantly trioctahedral micas which result solely from the substitution  $2\text{Al}^{\text{VI}} \rightleftharpoons 3\text{Mg}$ . In other words, no natural micas lie wholly on the join phlogopite-muscovite. The mica mahadevite, which was believed to lie on this join, has since been shown to lie near the join phlogopite-eastonite (Yoder and Eugster in Morey, 1953, p. 67).

### POLYMORPHISM

The main features of the fundamental mica structure are well known (see, for example, Bragg, 1937, pp. 205 ff.), and several polymorphs have been described (Hendricks and Jefferson, 1939; Axelrod and Grimaldi, 1949; Amelineckx and Dekeyser, 1953). Polymorphism occurs because the atomic arrangement of the fundamental sub-cell has monoclinic symmetry whereas the surface of the sub-cell has hexagonal or pseudo-hexagonal symmetry. Rotation of the sub-cell by  $60^\circ$  does not affect the packing of the surfaces but does affect the position of the sub-cell. The various shifts of position resulting from rotation of the sub-cell can be represented by a vector, and the different simple ways of stacking the sub-cell can be enumerated (Smith and Yoder, 1956). On the condition that only one angle of rotation

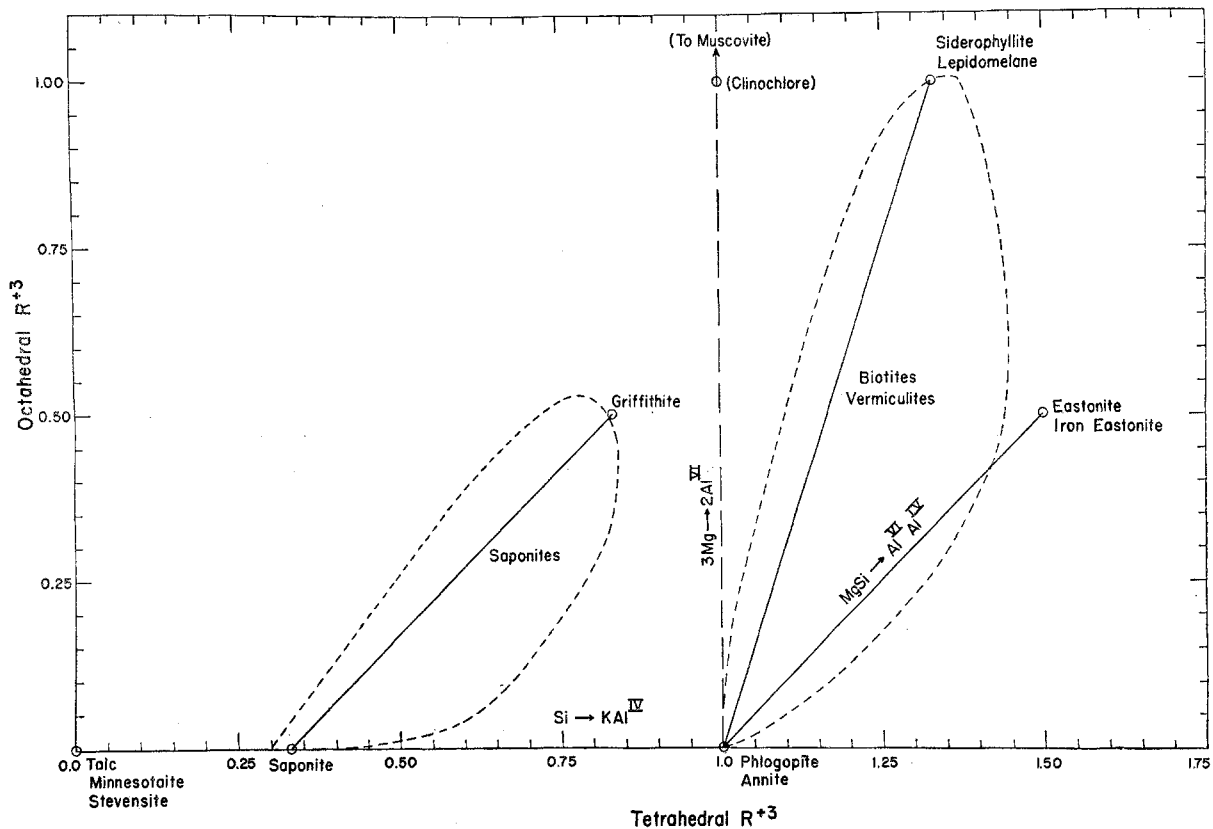


FIGURE 2.—Plot of tetrahedral  $R^{+3}$  and octahedral  $R^{+3}$  in atom proportions of dominantly trioctahedral micas and related minerals. Compiled mainly from Foster (1957) and Ross and Hendricks (1945).

occurs in a given polymorph, six simple regular polymorphs may be constructed as shown in Fig. 3. The symbols adopted give first the number of layers in the repeat unit and second the symmetry: where M is monoclinic; O, orthorhombic; T, trigonal; and H, hexagonal. Of these 1M, 2M<sub>1</sub>, 2M<sub>2</sub>,

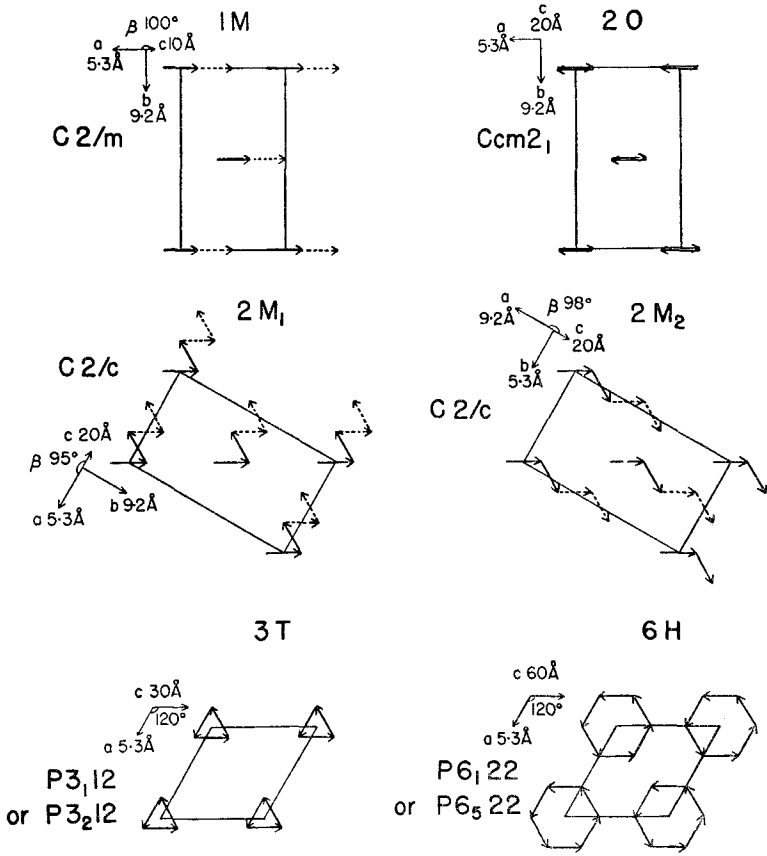


FIGURE 3.—The six simple regular polymorphs of mica deduced by assuming only one angle of rotation occurs in the stacking of sub-cells. The arrows are the interlayer stacking vectors: solid vectors show the layer stacking in one unit cell, and the dashed vectors show the layer stacking in the next unit cell. The base of the unit cell is shown by thin lines, and the space group and lattice parameters are listed by the left side of each diagram (Smith and Yoder, 1956, p. 213).

and 3T have been found in nature. The 2O and the 6H polymorphs have not been observed in either natural or synthetic products. More complex stacking of the micas is, of course, possible and those observed include 8Tc (triclinic), 12M and 18M. In addition to these regularly stacked micas, there exist in nature, particularly in the clays, randomly stacked micas in which the

stacking angles occur in random sequence. These have been designated by the symbol 1Md.<sup>2</sup>

Of these general structures the biotites prefer 1M, but they are also found with 1Md, 2M<sub>1</sub>, 3T, and the more complex structures. The muscovites are most often found as the 2M<sub>1</sub> polymorph, less commonly as 1Md and 1M and rarely 3T. Lepidolite is usually 2M<sub>2</sub> and sometimes is 1M and 3T (Levinson, 1953). Glauconite is only known to the writer as 1Md and 1M. The crystal chemical reasons for these preferences are not well understood because of the lack of precise structure determinations. The departure from hexagonal character of the (Al, Si) sheets which arises from the difference in Al–O and Si–O bond lengths is greatly enhanced in the dioctahedral micas (the celadonites excluded) because of vacant sites in the octahedral layers. As W. F. Bradley (personal communication, 1957) has pointed out, the deviations from the ideal structure are expected to be even more pronounced in micas such as margarite, CaAl<sub>2</sub>(Al<sub>2</sub>Si<sub>2</sub>)O<sub>10</sub>(OH)<sub>2</sub>, where the tetrahedral layer has equal portions of Al and Si and the octahedral layer has the maximum vacant sites. The resulting distortions are believed to have a great influence on the stacking sequence.

It appears, therefore, that the composition of a mica plays a dominant role in determining the polymorphic structure. As will be seen below, temperature and to a lesser extent pressure also influence the structure.

## SYNTHESIS OF DIOCTAHEDRAL MICAS

### *Muscovite*

With the knowledge gained from the composition of the natural micas and the study of their structures, it was possible to select the common end members for synthesis. Since many of the micas could be developed from the principal dioctahedral mica muscovite or the principal trioctahedral mica phlogopite, these compositions were the first to be studied in detail. The techniques for achieving synthesis have been described in detail by Yoder and Eugster (1954, 1955). In brief, various synthetic and natural materials of the requisite composition are held in a pressure vessel and subjected to a fixed pressure and temperature for various periods of time. The products are identified by means of the petrographic and electron microscopes and x-ray or electron diffraction techniques.

The region of pressure and temperature in which muscovite was found to be stable is given in Fig. 4. The curve represents the maximum stability for *pure* muscovite, which breaks down to sanidine + corundum + gas. In general, the curves for reactions of muscovite with other phases will lie at different temperatures and pressures, but will be of similar shape. For example, the reaction curve for muscovite + quartz  $\rightleftharpoons$  sillimanite + ortho-

<sup>2</sup> The small letter "d" was originally taken from the word disordered. The writer prefers to describe the stacking of *layers* as regular or random and the distribution of *ions* over lattice sites in the sub-cell as ordered or disordered. No change in the symbol is suggested.



clase + gas is believed to lie somewhat below that of pure muscovite. In another example, the reaction curve of muscovite + clinocllore  $\rightleftharpoons$  phlogopite + cordierite + gas was found to lie at much lower pressures and temperatures. Note that the reaction curve is dashed in the low-pressure

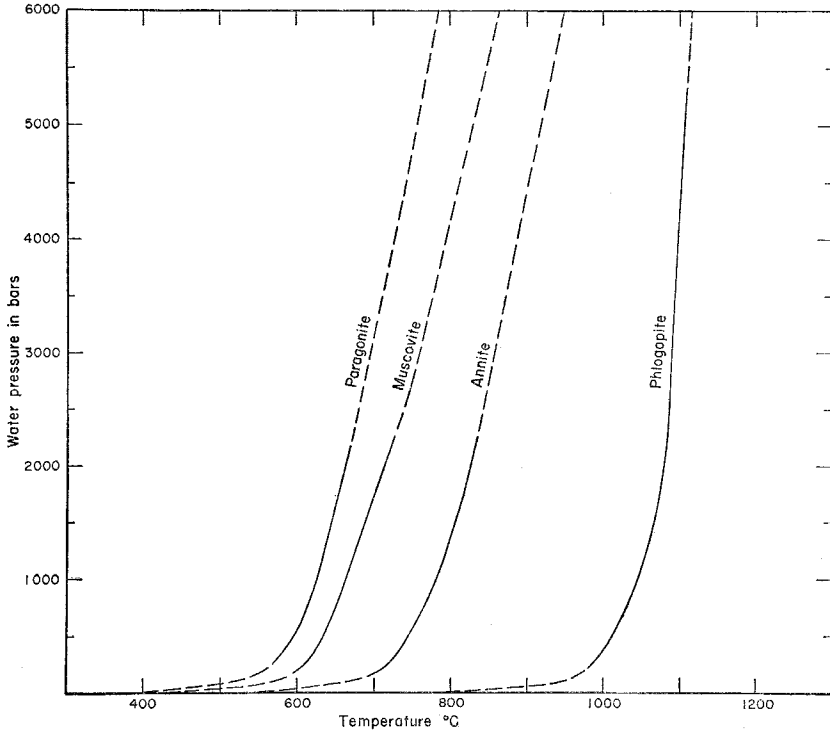
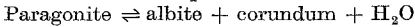
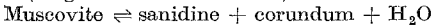


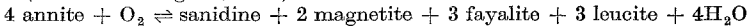
FIGURE 4.—Univariant equilibrium curves for the reactions :



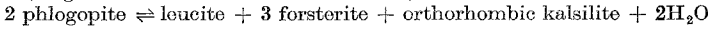
(Eugster and Yoder, 1954)



(Yoder and Eugster, 1955)



(Eugster, 1956a ; and in Abelson, 1957)



(Yoder and Eugster, 1954)

These curves represent the upper stability limit of the pure micas indicated.

The dashed portions of the curves are obtained by calculation. A pressure of 5000 bars obtains at a depth of approximately 20 km (= 12.4 miles).

region and turns to lower temperatures. The reaction rates are exceptionally slow at low pressures and the curve is obtained by calculation (see Yoder and Eugster, 1955, pp. 259–262) using the data obtained at higher pressures. By this means it was found that muscovite would decompose at 395°C at 1 atm water pressure and at 290°C under 0.015 atm of water vapor

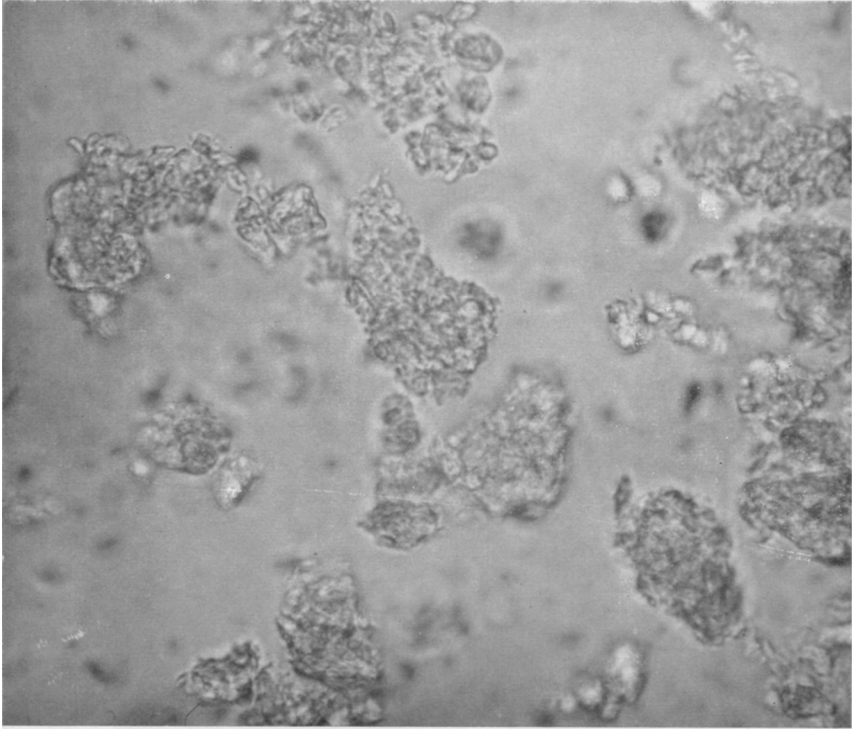


FIGURE 5.—Photomicrograph of a representative sample of synthetic muscovite (Yoder and Eugster, 1955, fig. 7).

*(To face p. 50)*

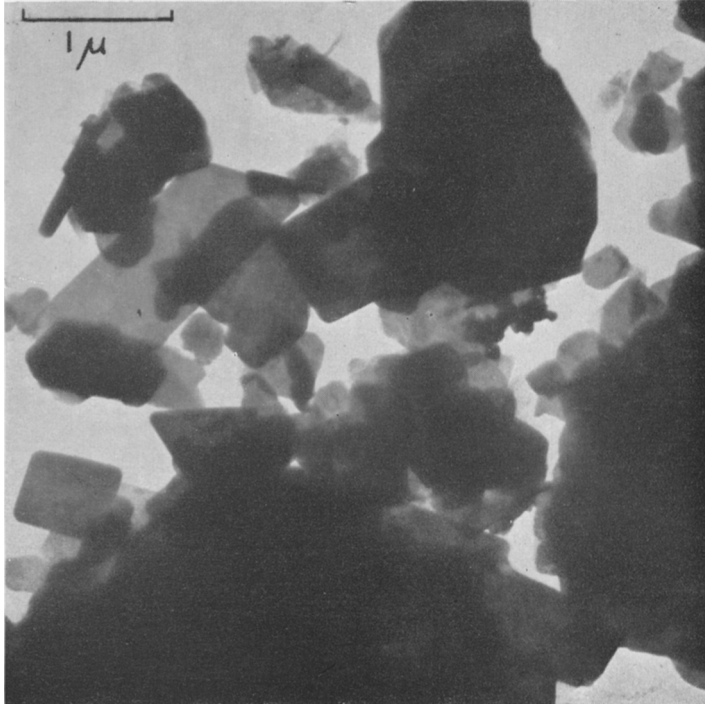


FIGURE 6.—Electron micrograph of synthetic 1M muscovite taken by Max Swerdlow, National Bureau of Standards (Yoder and Eugster, 1955, fig. 8a).

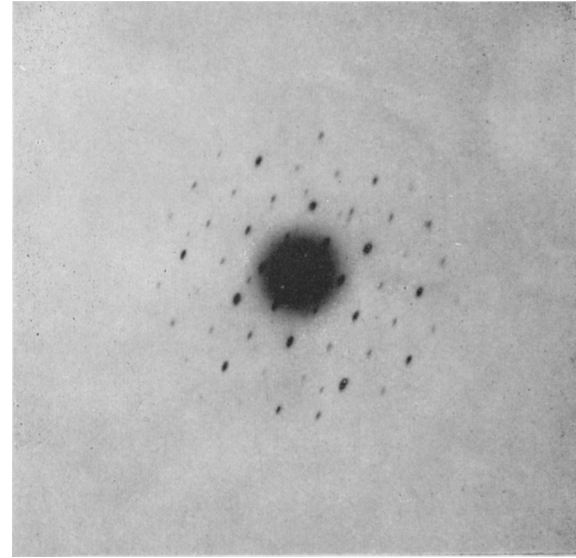


FIGURE 7.—Transmission selected-area diffraction pattern of synthetic 1M muscovite taken by Max Swerdlow, National Bureau of Standards (Yoder and Eugster, 1955, fig. 8d).

pressure, the water vapor pressure at 25°C in an atmosphere 50 percent saturated with water. In differential thermal analysis the endothermic peak marking the decomposition of muscovite under the vapor pressure of water in the atmosphere is approximately 750–900°C, depending on grain size and other factors (Grim and Bradley in Brindley, 1951, p. 147). The discrepancy emphasizes the point that differential thermal analysis is primarily a rate process involving non-equilibrium conditions, and the results from such studies cannot be used in the construction of equilibrium diagrams.

A photomicrograph of a representative sample of synthetic muscovite obtained from the hydrothermal treatment of various mixtures is seen in Fig. 5. The optical study of such material is not too informative; however, under the electron microscope the details of the crystals can be seen (Fig. 6). The largest crystals are about  $1 \times 2\mu$  and about 100Å thick. The electron diffraction pattern of this particular group of crystals gives spacings in accord with those of a natural 1M muscovite. The transmission, selected-area, diffraction pattern of an isolated aggregate clearly demonstrates the hexagonal character of the product (Fig. 7).

The growth of these crystals may be followed readily by means of x-ray powder diffraction patterns. At the bottom of Fig. 8 is given the pattern of the type of material formed in short runs or in runs at very low temperatures. With increasing length of run or at higher temperatures growth proceeds in the manner indicated by the selected patterns arranged consecutively from bottom to top. The growth sequence  $1M_d \rightarrow 1M \rightarrow 2M_1$  is believed to obtain in the progressive metamorphism of materials of the requisite composition in a sediment, initiating perhaps as early as the stage in which diagenesis begins. It is for this reason that the writer believes the  $2M_1$  polymorph in recent sediments is of detrital origin. It was not possible to fix the stability ranges of the polymorphs because of the sluggish nature of the transformation. The first transformation,  $1M_d \rightarrow 1M$ , is probably, but not necessarily, dependent on factors affecting reaction rate. The second transformation,  $1M \rightarrow 2M_1$ , may be expressed by a univariant curve of equilibrium (i.e. an isograd). The structures of these materials were deduced by comparison with micas whose structure had been previously determined by single-crystal methods or by indexing powder patterns. In Fig. 9 it is seen by comparison that the 1M and  $2M_1$  muscovites have been produced. The synthesis of the 3T polymorph was suspected in one run but could not be substantiated.

### *Paragonite*

Closely related to muscovite is the mica paragonite, the sodium analogue. Its stability curve is given in Fig. 4. Note its close relationship to the breakdown curve of muscovite. It seems to be impossible to distinguish these two micas optically (Schaller and Stevens, 1941, p. 595). When both micas are present in a rock, the coarser grained mica is usually muscovite (see for example, Rosenfeld, 1956). They are, on the other hand, readily identified by x-ray powder diffraction patterns (Fig. 10). The 0010 spacing at about 46 degrees  $2\theta$  ( $CuK_\alpha$ ), for example, is quite different in the two micas and the

spacing may be used as a measure of the sodium or potassium content of a muscovite or paragonite, respectively. The limits of solid solution have been determined in part in the laboratory and the preliminary results are presented in Fig. 11. The sodium content of muscovite in equilibrium with another sodium-bearing mineral such as albite has been used as a geothermometer by Grootemaat and Holland (1955, p. 1569). The investigation

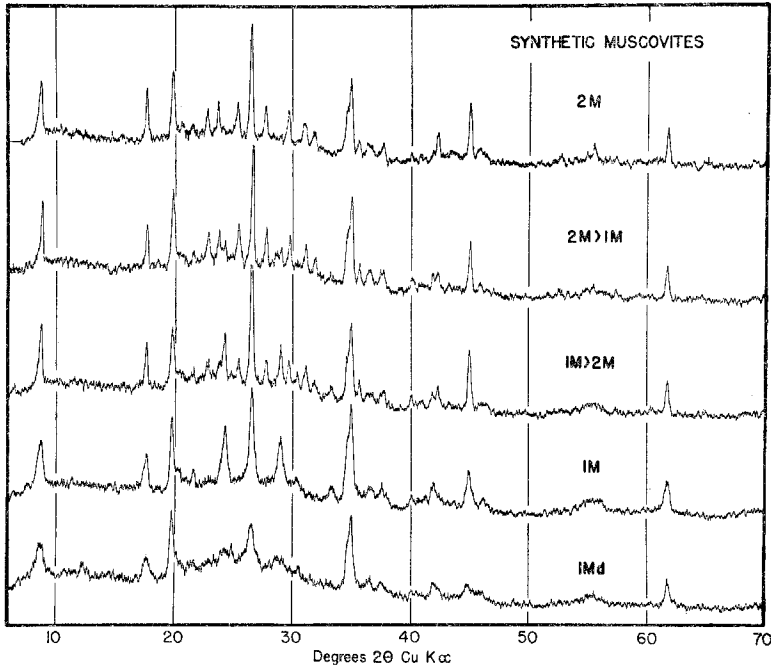


FIGURE 8.—Photograph of x-ray powder diffraction patterns of synthetic micas (Yoder and Eugster, 1955, fig. 10). The 1Md pattern is obtained at low temperatures and at high temperatures in short runs. With increasing length of run at high temperatures the growth usually proceeds in the manner indicated by the patterns arranged from bottom to top. This sequence of growth is believed to obtain in the metamorphism of materials of the requisite composition in sediments.

of other mica joins, such as muscovite-polythionite, may also produce equally useful geothermometers. The polymorphs of paragonite which have been synthesized include 1Md, 1M and  $2M_1$ . The  $2M_1$  polymorph is found in nature, and it has been established as a common rock-forming mineral. The occurrence of a 3T polymorph of paragonite was reported by Dietrich (1956); however, a comparison of his published spacings with those obtained from the synthetic products suggests that his sample has a 1M structure.

## MICAS AND CLAYS RELATED TO MUSCOVITE

The 1M and the 1Md muscovite shown in Fig. 8 are of particular interest to the clay mineralogist. These structures had not been previously recognized among natural muscovites. A thorough study of natural materials indicated that the 1Md and 1M muscovites were of common occurrence. They are found among materials called illite, sericite, sarospatakite, potash bentonites,

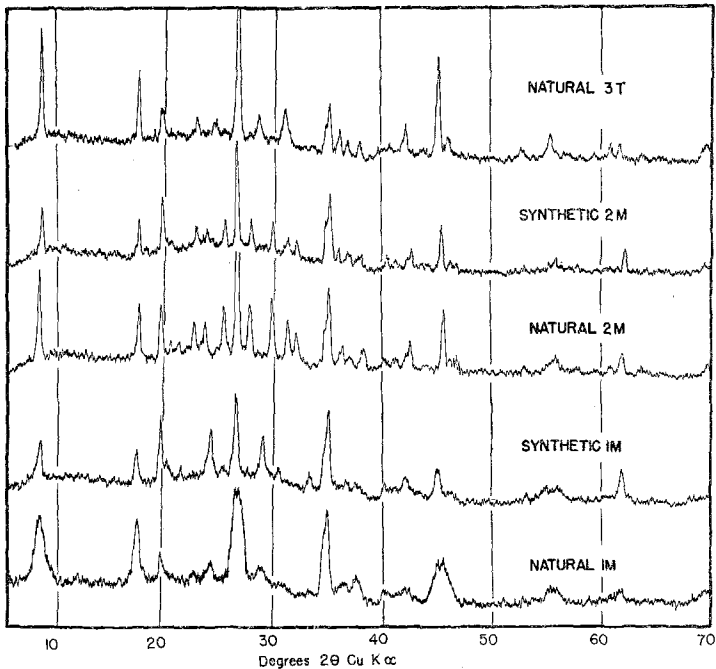


FIGURE 9.—Photograph of x-ray powder diffraction patterns of synthetic and natural muscovites (Yoder and Eugster, 1955, fig. 9). Note the region 22–32° 2θ for comparative purposes.

secondary mica, pinite, mariposite, glauconite, gieseckite, hydromica, celadonite and “glimmerartiger Ton.”

In Fig. 1 is plotted the composition of dioctahedral minerals related to the muscovites. Grim (1953) and his colleagues clearly defined illite as a general term and not as a specific mineral name. Recent studies of illite indicate that such material usually consists of mixed layers of 1Md or 1M muscovite and montmorillonite and may contain 2M<sub>1</sub> or 3T muscovite as an additional phase. The bulk compositions, for example, of these mineral assemblages suggest the presence of montmorillonite, which may account for the low potash and high water content of many illites. The existence of these *bulk*

compositions should not, however, be cited as evidence of a solid solution series between muscovite and montmorillonite; the limits of substitution of  $\text{Si} \rightleftharpoons \text{KAl}$  have yet to be demonstrated. It is suggested that illite should be used only as a field term as Grim *et al.* intended, and, after identification of the various phases is made in the laboratory, the polymorph of the mica should be specified and the nature of the mixed-layer mineral and the other phases present should be indicated.

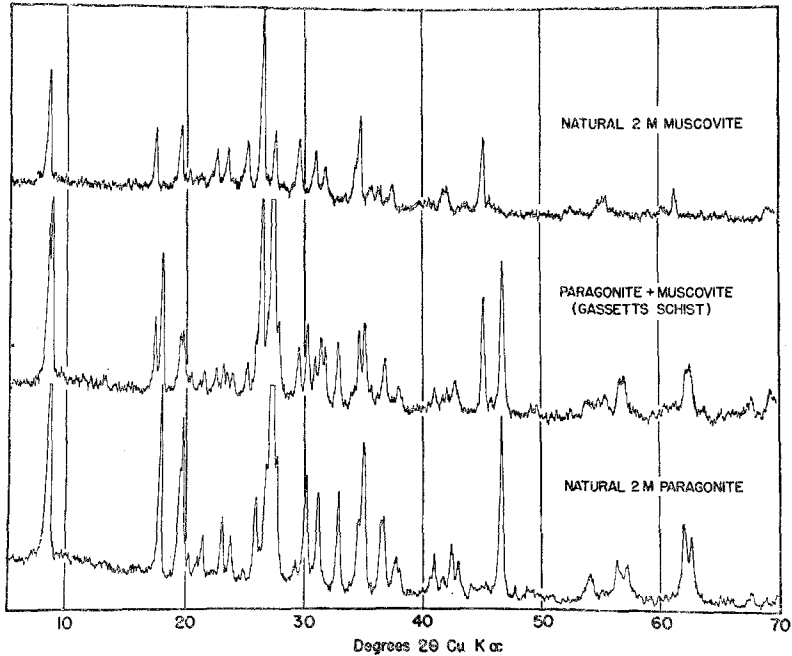


FIGURE 10.—Photograph of x-ray powder diffraction patterns of natural  $2M_1$  muscovite, a mixture of  $2M_1$  muscovite and  $2M_1$  paragonite from the Gassetts, Vermont, schist, and a natural  $2M_1$  paragonite (unpublished data, see Eugster and Yoder, 1954).

The glauconites are of special interest in that they lie approximately one-third of the way from the celadonites, having a  $1M$  structure, to the muscovites, which may also have a  $1M$  structure. The glauconites known to the writer have a  $1Md$  or a  $1M$  structure on the basis of x-ray powder diffraction patterns, and are dominantly dioctahedral. The question arises whether glauconite is a true compound or a mixed-layer structure. Since neither muscovite nor celadonite expands with glycolation, it would not be possible to distinguish a random mixed-layer mineral assemblage from a true compound on the basis of x-ray powder diffraction patterns. A single-crystal study of glauconite would, of course, resolve this problem and

attempts are now being made to obtain a suitable single crystal for study. It is interesting to note that other members of the dominantly dioctahedral micas and clays and some dominantly trioctahedral micas and clays occur at about one-third positions on the principal joins, e.g. montmorillonite, nontronite, saponite, siderophyllite and lepidomelane. The reason for this is not clear; however, a detailed study of the bond lengths may indicate that these compositions may be accommodated in a unique structural arrangement.

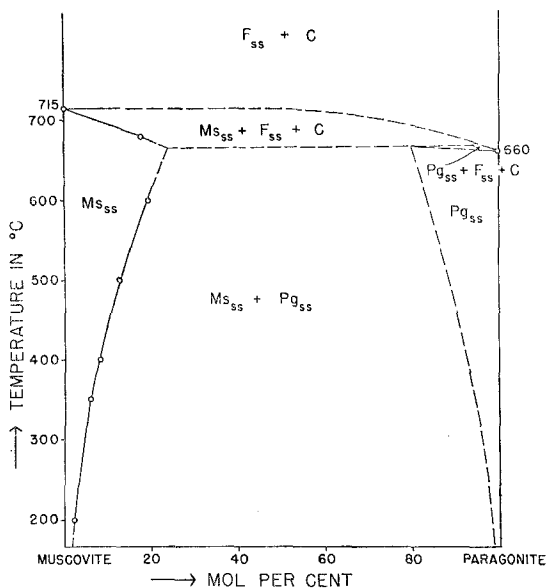


FIGURE 11.—Preliminary phase diagram for the subsolidus region of the join muscovite-paragonite (Eugster, in Abelson, 1955, p. 125).

Attention is again directed to the high-silica sericites (Fig. 1), which lie on the same join as the glauconites. They are presumably far more abundant than presently recognized. One recent study by Lambert (unpublished thesis; personal communication from C. E. Tilley, 1957) points up the necessity of having some Mg or Fe<sup>+2</sup> in addition to high silica in the muscovites of the lowest grade metamorphic rocks and presumably in the muscovites in sediments as well. According to Lambert (Fig. 12) the muscovites change in composition from a high-silica sericite to a mica richer in the muscovite component with increasing grade of metamorphism. The formation of biotite, represented here by eastonite, during metamorphism from the reaction of a high-silica sericite and an aluminous chlorite yields in addition a muscovite containing less of the celadonite component. The pairs of reactants and products are connected schematically by tie lines to illustrate the nature of the reaction. The synthesis of the micas along the join muscovite-celadonite would make a very rewarding study.



## SYNTHESIS OF TRIOCTAHEDRAL MICAS

The experimental results on two trioctahedral micas will now be presented. The maximum stability curve of phlogopite, as well as that of its iron analogue, annite, is given in Fig. 4 with the others previously described. The synthetic crystals of phlogopite and annite are much more amenable to optical study than those of synthetic muscovite or paragonite (Fig. 13). The growth

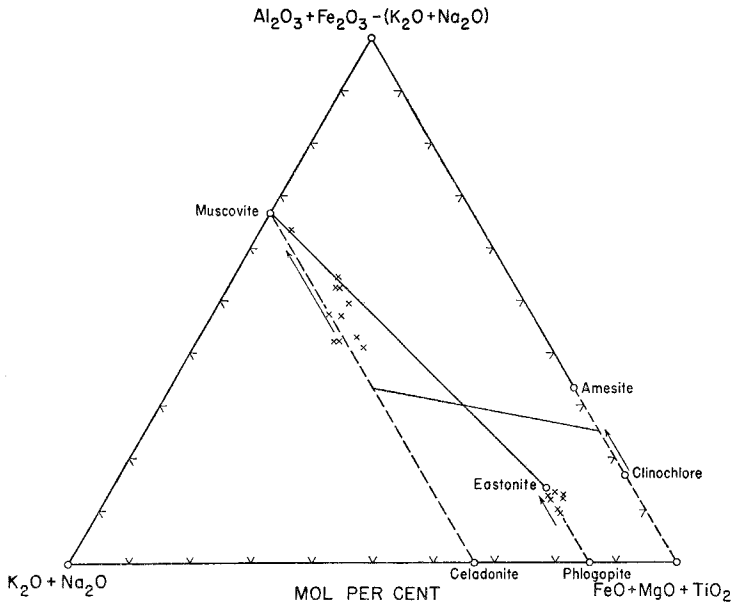


FIGURE 12.—Plot of analyzed muscovites (on and near the join muscovite–celadonite and their analogues) and biotites (on and near the join eastonite–phlogopite and their analogues). The heavy lines illustrate schematically the pairs of reactants and products in the reaction high-silica sericite + chlorite  $\rightleftharpoons$  muscovite + biotite. The arrows indicate the direction of change of composition with increasing grade of metamorphism. After Lambert (unpublished data, 1957).

sequence is 1Md  $\rightarrow$  1M or 3T judging from the x-ray powder diffraction diagrams given in Fig. 14. The reason for the uncertainty in the final product, indicated as 1M or 3T, is apparent from Fig. 15. In x-ray powder diffraction patterns the 1M and 3T polymorphs can not be distinguished. The 2M<sub>1</sub> polymorph has not been synthesized, and the natural 2M<sub>1</sub> material slowly transforms to a 1M or 3T at high temperatures. The stability range of the polymorphs could not be ascertained because of the sluggish nature of the transition.



FIGURE 13.—Photomicrograph of synthetic phlogopite (Yoder and Eugster, 1954, fig. 3).

*(To face p. 56)*

### CLAYS AND MICAS RELATED TO TRIOCTAHEDRAL MICAS

A trioctahedral clay mica has been identified by Walker (1950). It appears to be a mixed-layer mineral consisting of a 1Md mica structure and a montmorillonite, judging from the published x-ray powder pattern, the listed spacings, and the partial chemical analysis. Such trioctahedral clay micas should be more common, particularly among the clays in limestones and dolomites, which often yield phlogopite on metamorphism. The 1Md or 1M

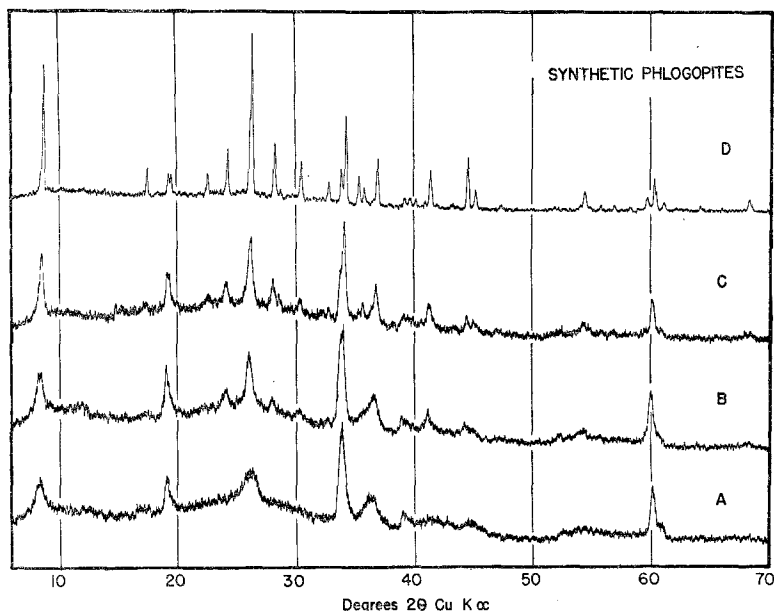


FIGURE 14.—Photograph of x-ray powder diffraction patterns showing growth characteristics of synthetic phlogopite from low temperatures (A) to high temperatures (D) (Yoder and Eugster, 1954, p. 174).

trioctahedral mica may be difficult to recognize in mixtures or mixed-layer aggregates including vermiculite, montmorillonite and chlorite. In Fig. 2 it is to be noted that the vermiculites have the same distribution of octahedral and tetrahedral  $R^{+3}$  atoms as the biotites. It has long been thought that the biotites are the source material for the vermiculites, and Barshad (1948) describes vermiculite as a biotite in which K has been replaced with  $H_2O$  and Mg. The relationship of the biotites to other dominantly trioctahedral minerals may also be delineated in Fig. 2.

Some experiments have been made on the join phlogopite–muscovite. Because of the common occurrence of a biotite and a muscovite, it was pre-

dicted that there was only limited solid solution between the two phases. The preliminary experiments yielded some rather surprising results. Based solely on shifts of the 060 (60–62 degrees  $2\theta$   $\text{CuK}\alpha$ ) spacing in x-ray powder diffraction patterns, there was an *apparent* increase in solid solution with a decrease in temperature! Although the products were poorly crystallized, it is believed that the *apparent* solid solution is the result of mixed layering of a 1Md phlogopite and a 1Md muscovite. It suggests that some of the poorly organized materials such as illite may consist of random mixed layers of

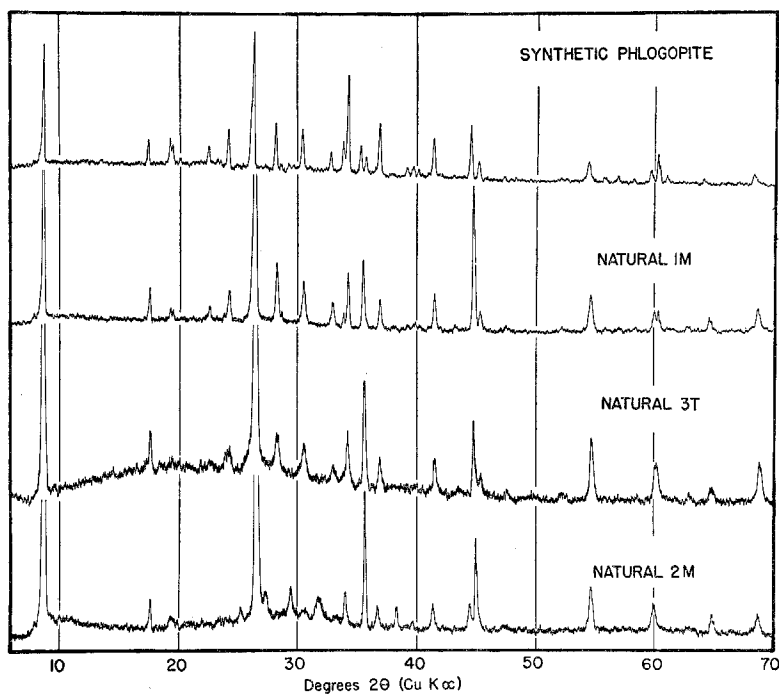


FIGURE 15.—Photograph of x-ray powder diffraction patterns of synthetic, natural 1M, natural 3T, and natural 2M<sub>1</sub> phlogopites (Yoder and Eugster, 1954, p. 169).

biotite and muscovite. Careful measurement of the 060 spacing in x-ray powder diffraction patterns of natural materials may yield information on this problem.

Only a brief resume of some of the experimental work on the micas has been given. It is clear that further experimental studies on the principal micas joins will be most rewarding, and it is hoped that some of the clay mineralogists will have an opportunity to pursue their mica problems in the laboratory.

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