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EXPERIMENTAL DETERMINATION OF MUSCOVITE POLYMORPH STABILITIES

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ABSTRACT

Relative stabilities of the muscovite polymorphs have been determined by hydrothermal experiments with the result that $2M_1$ was found to be the only stable form. The kaolinite+KOH→muscovite reaction is used to demonstrate this conclusion by means of variations in the experimental parameters of time, temperature, and pressure.

A discussion of the significance of this result in application to natural micas is given in the belief that polymorph relations of natural micas will be of significance in determining their genesis.

INTRODUCTION

Muscovite and other potassic dioctahedral micas are common and abundant constituents of sedimentary and metamorphic rocks. These micas are also frequent but less abundant in plutonic igneous rocks. The range of geologic occurrence in which dioctahedral potassium micas are found could be expected to result in quite different mica compositions and structures. The main compositional variations can be described as being between the minerals muscovite and celadonite (Foster, 1956). The structural variations (polymorphs) are described by Smith and Yoder (1956) as being variously ordered sequences in stacking of the mica "sheet" units. Radoslovich (1960) and Radoslovich and Norrish (1962) have indicated that composition can significantly affect the mica structure and may influence the polymorph. The commonly occurring natural polymorphs are designated as 1Md, 1M, $2M_1$, and 3T (Yoder and Eugster, 1955).

By grouping these micas into similar geologic occurrences the following generalizations can be made about structure and composition of potassic dioctahedral micas:

1. Micas in sedimentary rocks have the 1Md, 1M, and more rarely $2M_1$ polymorphs. The most abundant of these micas is the mineral group illite in which the 1Md polymorph predominates with $2M_1$ forming generally a minor constituent. It is probable that the $2M_1$ portion is in part detrital and therefore should not be considered as having a genesis in common with the major portion of the illite (Velde and Hower, 1963).
2. The sedimentary mica glauconite and the alteration product celadonite both have a 1M polymorph (Hower, 1961; Wise and Eugster, 1964). These minerals characteristically have a high content of magnesium and ferrous and ferric iron relative to muscovite (Foster, 1956).
3. Sericites formed as hydrothermal alteration products of acidic rocks can have 1Md, 1M, and $2M_1$ polymorphs (Burnham, 1956). Such materials, called high-silica sericite or hydromuscovite, often have variable compositions, either non-mica, *i.e.* low in alkali con-

tent, or non-muscovite, *i.e.* high in SiO_2 and MgO relative to muscovite (Grim 1953; Schaller, 1950). Cases where these micas are muscovites will be discussed later.

4. Micas in metamorphic rocks have 1M, 3T, and $2M_1$ polymorphs. Their compositions are generally closer to that of muscovite and they are often given the name phengite (Lambert, 1959; Ernst, 1963; Van der Plas, 1959). The micas described by Lambert (1959) appear to change composition with increasing metamorphic grade. Higher-grade metamorphic rocks then appear to contain micas whose compositions are closer to muscovite. Phengites from low-grade metamorphics (commonly associated with glaucophane and other minerals indicative of high pressures) have compositions about half way between muscovite and celadonite. Smith and Yoder (1956) state that muscovite in high-grade metamorphics is $2M_1$ in most instances whereas phengites have 1M, $2M_1$ and 3T forms.

5. The remaining group of dioctahedral micas is of igneous occurrence. These micas can have highly variable compositions with ions such as Mn, Cr, etc., present when considered as a whole but in general their compositions are probably close to muscovite and their structures are generally $2M_1$. Wide variations in composition and structure exist in rather specialized instances such as ore deposits and pegmatites (Foster, 1956; Yoder and Eugster, 1955).

In summary, dioctahedral potassic micas have variable compositions and structures. Obviously hydrothermal data for one species can be applied to that species only.

Previous hydrothermal studies have been conducted for the muscovite composition, and three polymorphs were synthesized—1Md, 1M, and $2M_1$ (Yoder and Eugster, 1955). The syntheses were made for the $KAl_2Si_3AlO_{10}(OH)_2$ composition only. The 1Md polymorph was determined to be a metastable product; 1M appeared to be stable below 200°–350° C. and $2M_1$ above this range. This was consistent in general with natural occurrences of micas cited by Yoder and Eugster. However, if compositional variations affect mica polymorphs as suggested by Radoslovich and Norrish (1962), the application of polymorph stability data for pure muscovite to dioctahedral micas in general is not valid.

Problem of Polymorph Stabilities

The synthesis of minerals is often fraught with difficulties of metastability. An excellent example is found in the anthophyllite synthesis. Greenwood (1963) demonstrated that anthophyllite was formed synthetically as a breakdown product of talc. Apparently portions of the talc structure were inherited in the formation of anthophyllite. The difficulty regarding experimental work was that anthophyllite could only be grown in the P–T range above its stability. Thus experimental runs in the P–T range where it was first formed (and metastable) would give varying results with varying duration of the experiments. Greenwood demonstrated metastability by means of a rate study of the persistence of anthophyllite above its stability range.

In the case of muscovite polymorphs Yoder and Eugster (1955) ob-

observed a sequence of phases 1Md→1M→$2M_1$ at temperatures above 200°–350° C. Below this range they believed 1M to be stable, and thus the sequence would be 1Md→1M. At all temperatures where muscovite was considered stable 1Md was the first product formed. Thus at higher temperatures 1Md and 1M are metastable steps in the formation of $2M_1$ muscovite. The 1M→2M transformation was never reversed at low temperatures. If 1M is stable, the $2M_1$→1M transformation should be feasible. Yoder and Eugster stated that the reaction rates were too slow for the reversal ($2M_1$→1M) to be accomplished experimentally.

In such a study, if there is a problem of multiple metastable forms preceding the stable form, a reaction should be chosen that would result in a rapid production of the desired form from the starting materials. This would permit observation of the metastable steps in the reaction within times realistic for experimental work. The reaction kaolinite$+$KOH $+H_2O\rightleftarrows$muscovite was chosen in the present study because it fulfills the above requirement. In this way the relations of metastable and stable phases were demonstrated in the problem of muscovite polymorphism.

PROCEDURE

Experiments were carried out in "cold seal" bombs (Tuttle, 1949) externally heated by insulated electrical resistance furnaces. The furnace temperatures were regulated by on-off type controllers (Minneapolis-Honeywell "Pyrovanes") or resistance sensitized-controllers that were regulated by motor-driven variable resistance units (made at the Geophysical Laboratory). Temperatures were measured during the runs by sheathed chromel-alumel thermocouples. Resulting errors were estimated to be ±6° C. from the values stated in Table 1. Confining pressure was transmitted to the container statically with water; control was ±100 bars. Solid materials were placed in gold or platinum capsules with known amounts of water and then arc-welded shut. The capsules were weighed before and after the experiments to determine whether leakage occurred. If leakage occurred, the run was discarded.

Natural kaolinite was used as a source of silicon and aluminum. The impurities were $K_2O=0.06$, $Na_2O=0.15$, and $TiO_2=0.30$ weight per cent. Potassium was derived from Fischer's solid KOH ($Na_2O=0.02$ weight per cent impurity). The two materials were dried for at least 24 hours at 120° C. and weighed as solids. Longer periods of drying gave no further loss in weight. Weighing was done in a desiccated balance. The materials were then combined in aqueous solution, which was then evaporated to dryness. The residue was ground for 2 hours in a mechanical mortar under alcohol. The resulting material had a muscovite composition that may have varied up to an excess of 8 per cent in KOH content due to difficulties in drying and weighing.

TABLE 1. EXPERIMENTAL DATA

Temperature, ° C.	Pressure, kb	Time, days	Product
Staring Materials: Kaol+KOH			
570	1	2	1M+Δ-kaol
570	1	3	1M+2M?
580	1	1	1M+2M??+Δ-kaol
600	1	2	1M+2M
600	1	1	1M+Δ-kaol
630	1	1	1M+2M tr
150	2	6	Kaol
150	2	21	1Md
150	2	10	Kaol+mica?
175	2	2	Δ-kaol
190	2	10	Kaol+mica tr
200	2	2	Kaol+mica tr
200	2	10	1Md+kaol+Δ-kaol
220	2	1	Kaol+mica?
230	2	6	1Md+mica tr+kaol+Δ-kaol
240	2	6	1Md+1M tr+kaol+Δ-kaol
250	2	1	Kaol+mica
250	2	0.8	Kaol
250	2	2	1Md
270	2	1	1M tr+1Md+kaol+Δ-kaol
270	2	2	1M+Δ-kaol
285	2	0.8	1Md+1M tr+kaol+Δ-kaol
285	2	1	1Md+1M+kaol+Δ-kaol
300	2	1	1Md+1M+kaol
350	2	0.5	1M+kaol+Δ-kaol
380	2	0.2	1M+kaol+Δ-kaol
400	2	10	1M+2M tr
510	2	6	1M+2M?
550	2	2	1M+2M tr
550	2	6	1M+2M
570	2	2	1M+2M
600	2	0.5	1M
600	2	1	1M+2M tr
630	2	0.5	1M+2M tr+S+C
225	4.5	10	1M tr+2M ?+1Md+kaol+Δ-kaol
275	4.5	10	1M+2M+1Md+kaol+Δ-kaol
300	4.5	4	1M+1Md+kaol+Δ-kaol
350	4.5	4	1M+1Md+Δ-kaol
380	4.5	4	1Md+1M+2M+Δ-kaol
400	4.5	2	1M+2M tr+Δ-kaol
Starting Material: Synthetic 1M muscovite			
125	4.5	14	1M+2M
Starting Material: Δ-kaol+KOH			
190	2	1	Kaol
200	2	1	Kaol+m
450	2	1	1Md+Δ-kaol
500	2	1	1Md+1M tr
Starting Material: D-kaol			
235	2	1	Kaol+Δ-kaol+mica tr
285	2	1	1Md+kaol+Δ-kaol
325	2	1	1Md+1M tr+kaol+Δ-kaol
Starting Material: Natural 2M Muscovite			
675	2	73	2M
570	.01	10	2M+S+C
600	.1	73	2M
660	1	20	2M+S+C

D-kaol, partially hydroxylated kaolinate; kaol, kaolinate; Δ-kaol, metakaolin; M, mica (no polymorph discernible); 1Md, 1M, $2M_1$, polymorphs of muscovite (Yoder and Eugster, 1955); tr, traces; S, sanidine; C, corundum; ?, questionable identification.

During all stages of this process the kaolinite appeared to be unchanged, as determined by *x*-ray and optical methods. It is possible that some of the kaolinite was dissolved in the KOH solution, but this amount could not be detected from a change in intensities of the *x*-ray reflections. No detectable amount of muscovite was formed during any of these operations.

In order to determine the importance of the structure of the starting materials in the kaolinite+KOH→muscovite conversion, two modifications of the aluminosilicate were prepared. This was accomplished by heating the kaolinite+KOH solids at 560° C. and 1 atm. pressure for periods of 5 minutes and more than 10 minutes. Partially dehydroxylated kaolinite resulted from heating for the short period and a metakaolin (Brown, 1961) from the longer period. The metakaolin was identified from a single *x*-ray reflection at about 3.54 Å over the range of 10 to 2.5 Å d values. No muscovite was detected in these products by *x*-ray diffraction studies. It is assumed that KOH dehydrated to K_2O during heating.

In some of the runs a natural $2M_1$ muscovite from a Harney Peak granite, Black Hills, South Dakota, was used. *X*-ray and optical examination revealed it to be very close to a muscovite composition. Chemical composition is as follows (weight per cent): SiO_2, 45.10; Al_2O_3, 36.46; TiO_2, 0.05; total iron, 0.77; MgO, trace; Na_2O, 1.01; K_2O, 9.64. Optical properties and unit cell dimensions[1] are: $\gamma=1.596\pm0.001$, $\alpha=1.560\pm0.003$, $2V=46°\pm2°$; $a=5.155\pm0.016$ Å, $b=8.919\pm0.027$ Å, $c=20.064\pm0.038$ Å, $\beta=96.33\pm0.29°$; volume$=916.930\pm0.049$ Å^3.

EXPERIMENTAL DATA

Run data are presented in Table 1. (Runs of similar pressure and temperature are given by Yoder and Eugster, 1955, pp. 237–238.) Most of the runs represent stages in the reaction kaolinite+KOH→muscovite. This reaction and the control of its equilibrium by variations in temperature and K^+/H^+ ratios in the fluids is discussed by Hemley (1959). Using Hemley's data, the starting materials were prepared to produce muscovite, *i.e.* the equilibrium of the reaction as written was shifted to favor the muscovite product as much as possible. Thus problems of the reversal of the reaction were not considered, and all products of experiments represent various stages in completion of the reaction.

The results of the present investigation regarding the production of various muscovite polymorphs can best be seen in a time-temperature plot (Fig. 1). Three muscovite polymorphs can be identified: 1 Md, 1M, and $2M_1$. The identifications follow Yoder and Eugster (1955); using

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[1] Seventeen reflections used, diffractometer data. IBM program for refinement (Burnham, 1962).

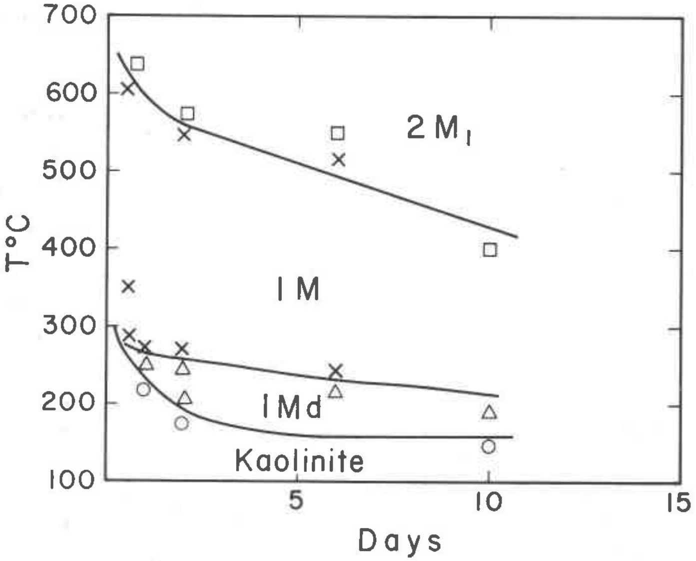

FIG. 1. Time-temperature relations of the stages in the kaolinite+KOH→$2M_1$ muscovite reaction. Runs were made at 2 kb water pressure. Crosses, 1M present; squares, $2M_1$ present; triangles, 1Md present; circles, only kaolinite; no mica present.

Cu Kα radiation 1Md has only 4.48, 3.33, and 2.58 Å reflections. The 1M polymorph has 3.66 and 3.07 Å reflections in addition to these. The $2M_1$ polymorph has major reflections at 4.48, 4.29, 3.89, 3.74, 3.54. 3.33, 3.21, 3.01, 2.87, 2.80, and 2.58 Å. In all cases at least two reflections unique to a polymorph were considered necessary for its identification. The reflections were not always obvious, and identification of a new phase over small temperature ranges of 10° or 15° C. was arbitrary. However, since the relations of 1Md and 1M polymorph occurrence deal with metastable forms, exact measurements of their occurrence with respect to temperature, pressure, or duration of the experiments do not have general significance. Persistence of metastable forms can be influenced by mechanical conditions of each individual experiment (grain size, etc.), and therefore each experiment could give slightly different results for the same pressure-temperature-duration variables. Also, because conversions of metastable phase are involved, reversibility could not be demonstrated. The sequence of polymorph transformation appears as 1Md →1M→2M with an increase of either time, temperature, or pressure.

CONCLUSIONS FROM EXPERIMENTAL DATA

The information from work at 4.5 kb (Table 1) shows that $2M_1$ is the stable polymorph at temperatures as low as 125° C. The sequence of 2 kb and 1 kb curves indicates that the conversion is slower at lower pressure, as could be expected, but from the parallelism of the curves it could also be expected that $2M_1$ is the stable polymorph at low temperatures in these pressure ranges (Fig. 2). At all three pressures $2M_1$ was preceded by 1Md and 1M polymorphs. These forms were never produced from $2M_1$ muscovite, *i.e.* the conversions were not reversed. It is concluded that $2M_1$ is the only stable polymorph of muscovite at low and moderate temperatures.

The possibility does exist, however, that the sequence $1Md \rightarrow 1M \rightarrow 2M_1 \rightarrow 1M$ is the succession at high temperatures and low pressures. Runs were made at the upper stability of muscovite at 1, 160, and 1000 atmospheres water pressure using a natural $2M_1$ muscovite. This material was used because an exclusively $2M_1$ mica was never produced from non-mica starting materials. The conversion $2M_1 \rightarrow 1M$ did not take place in the experiment.

However, natural micas are very slow to react in hydrothermal experiments (Yoder and Eugster, 1955). In order to examine the possibility of 1M stability, natural materials were collected from geologic situations

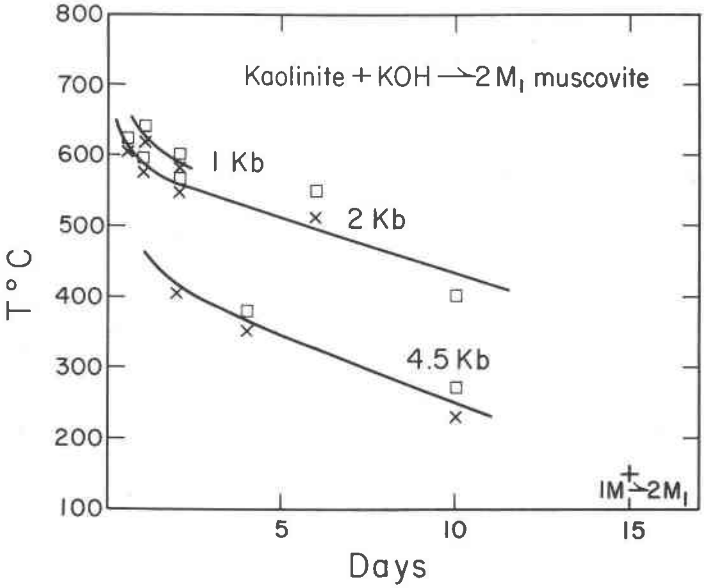

FIG. 2. Formation of $2M_1$ polymorph at various pressures for given times and temperatures. The sequence indicates that $2M_1$ is probably stable at all temperatures and pressures. Crosses, 1M only; squares, $1M+2M_1$; plus sign, 1M starting material converting to $2M_1$.

where high temperatures and low pressures existed. The important criteria for these samples were that a $2M_1$ muscovite mica experienced local thermal metamorphism as its last phase of metamorphism. The following two series were collected:

1. Pennsylvanian Fountain arkose intruded by a rhyolite sill of Laramide age (near Lyons, Colorado). A sharp contact indicates little hydrothermal metamorphism of the intruded arkose. Thin sections show no recrystallization of the rhyolite groundmass, and hence the rocks are interpreted as having experienced no major post-emplacement metamorphism. The rhyolite sill is greater than 100 feet thick. Arkose country rock contains $2M_1$ muscovite.
2. Mica pegmatite (Paleozoic?) intruded by a Triassic diabase dike (Slippery Elm mica mine, Plum Tree, North Carolina). No post-emplacement metamorphism influenced the rocks. The dike is $1\frac{1}{2}$ feet thick. The pegmatite contains a $2M_1$ mica.

Both intrusives were believed to produce primarily thermal metamorphism of the country rock. Samples taken in sequence from less than 1 inch to 2 feet from the dikes show no evidence of a 1M polymorph; only $2M_1$ micas appeared. In these two geologic situations conditions of high temperature and low pressure were very likely to have occurred. If such conditions are necessary for proposed 1M stability it can be concluded from the presence and persistence of $2M_1$ muscovite that 1M does not have a field of stability under these conditions. As no stable occurrence of 1M muscovites was found in the field studies or in the laboratory, 1M is concluded to be a metatable polymorph of muscovite.

THE KAOLINITE+KOH→MUSCOVITE REACTION

A few words may be said about the reaction that was used to produce the muscovite polymorphs, kaolinite+KOH→muscovite. Fundamentally, the equilibrium is controlled by the K^+/H^+ ratio of the solution that is in contact with the solid kaolinite (Hemley, 1959). The use of KOH shifted the equilibrium in the direction of a muscovite product. However, the rapid rate of ordered polymorph[2] formation, and especially the rapid rate of $2M_1$ formation, should be explainable in terms of crystal structure since the same type of equilibrium control should pertain for other starting materials. The work of Yoder and Eugster (1955) bears this out as they used various forms of K-Al-Si oxide mixtures with varying rates of mica formation. In their work it was pointed out that a starting material of kaolinite and $KAlSiO_4$ glass formed muscovite at the greatest rate, yet this was very slow. The present study used the same aluminosilicate, kaolinite, but the source of potassium was notably different. Yoder and Eugster used a potassium aluminosilicate glass whereas the present study had essentially K^+ ions in the hydrothermal fluid of the

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[2] See Yoder and Eugster (1955) for a discussion of order in polymorph structures.

starting material. It is believed that the kaolinite structure is partially inherited by the muscovite product in the conversion. A source of potassium readily available to the kaolinite structure permits rapid conversion and thereby preservation of the structure before it is destroyed.

In order to test this hypothesis three variations of the basic material were used, each with a different structure—kaolinite, partially dehydroxylated kaolinite, and metakaolin (for a detailed discussion of these structures see Brown, 1961; Taylor, 1962; Gastuche *et al.*, 1963). Runs were made for 1 day at 2 kb pressure with all three starting materials. Figure 3 shows the products for different temperatures. The temperature range over which the 1Md metastable mica is found for each starting material is significant.

Assuming that reaction rates for a conversion are roughly proportional to temperature the following can be said: Persistence of a metastable phase involved in a reaction will indicate the rate at which that reaction is proceeding (greater persistence≅slower rate). The persistence of a metastable phase can be measured by fixing the duration and varying the temperature of the experiments. The largest temperature interval at which the metastable phase occurs indicates greatest persistence of that phase and therefore a slow reaction rate; that is, it persists even when large amounts of thermal energy are in the system.

Figure 3 shows that the metastable 1Md has greatest temperature

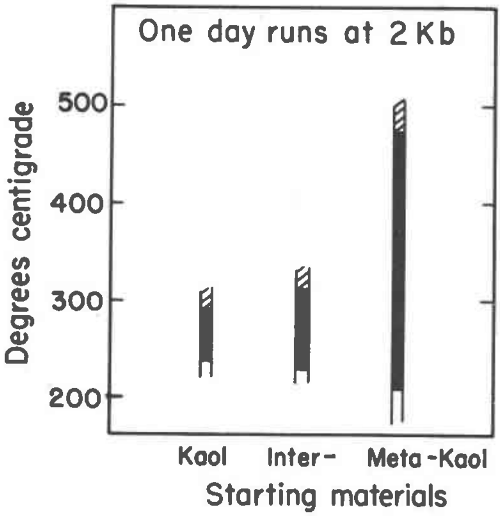

FIG. 3. Variations in reaction rate (persistence of 1Md, see text) due to variation in starting material. Blank area, kaolinite; solid, 1Md mica; diagonal line, 1M mica. Kaol, kaolinite; Inter-, partially dehydroxylated kaolinite; Meta-Kaol, metakaolinite.

range for a metakaolin starting material. The partially dehydroxylated kaolinite has a smaller range, and kaolinite starting material results in the smallest temperature range for 1Md occurrence after 1 day runs. Considering the above, the reaction utilizing kaolinite has the fastest rate of conversion to 1M because it has the smallest temperature range of 1Md occurrence.

An explanation can be given on a structural basis. According to Yoder and Eugster (1955), 1Md is a disordered structure involving random stacking of the mica layers; 1M and 2M are ordered arrangements. If a portion of the kaolinite structure is inherited by muscovite this could be expected to facilitate formation of an ordered structure, 1M. This appears to be the case (Fig. 3). The material with a disordered structure, metakaolin, could not provide an ordered structure for the formation of muscovite and, therefore, an ordered muscovite was slow to form. It is believed that the experiments of Yoder and Eugster were the result of such a phenomenon in that their kaolinite starting material was destroyed before the potassium was released from the glass in which it was initially held. The inheritance of a portion of the kaolinite structure was then impossible, and therefore a slow rate of ordered polymorph formation was observed.

In accordance with Ostwald's step rule, the sequence $1\text{Md}\rightarrow 1\text{M}\rightarrow 2\text{M}_1$ was then dependent upon the rate of the $1\text{Md}\rightarrow 1\text{M}$ conversion before the final 2M_1 product was formed. For this reason, in the experiments of Yoder and Eugster the $1\text{M}\rightarrow 2\text{M}$ conversion was not observed at low temperatures because of the slowness of the total reaction. It should be noted that the present study included higher pressures than were available to Yoder and Eugster, which resulted in more rapid reaction rates (Fig. 2).

An examination of *x*-ray diffraction patterns demonstrates a structural continuity between kaolinite and mica. *X*-ray diffraction reflections, common to kaolinite, 1Md muscovite, and 1M muscovite are the 4.48 and 2.58 Å reflections. In kaolinite these represent the (020)(110) and (130) $(1\bar{3}0)$ reflections and in 1M muscovite the (020) and (130) respectively; all are (*hk*0) reflections. This continuity of reflections through the intermediate stage of the conversion, 1Md, indicates a similarity in the *a–b* plane of the structures which could be interpreted as inheritance of the kaolinite layer network by muscovite. Inheritance of a portion of its structure greatly facilitates the formation of an ordered mica structure (1M). The above demonstrates the importance various starting materials can have in forming a product under hydrothermal synthesis.

Crowley and Roy (1964) have recently published a study involving determinations of muscovite polymorph stabilities which requires special consideration. They did not publish any run data with their article, nor did they explain in any detail their methods of phase identification. The information can be found by securing a copy of the senior author's Ph.D. thesis (Crowley, 1959).

Two pertinent points can be made about this work. Identification was made from *x*-ray diffractometer traces only. The present author believes that microscopic identification is essential to work on synthetic silicate systems. Amounts up to 20 per cent of a phase can go undetected using *x*-ray identifications. Complete identification is particularly important in studies where solid solutions do not differ radically in bulk compositions so that an intermediate mixture giving no solid solution would only give 15 or 20 per cent of another phase which could be overlooked in an *x*-ray diffractometer trace.

The second important factor involved in the study by Crowley and Roy is the short duration of the experiments. Only one run in the muscovite series lasted for 22 days. Other runs were generally on the order of 5 days in length. This determination hardly demonstrates equilibrium.

Crowley and Roy (1964, Fig. 3) indicate that 1M muscovite is stable at temperatures as high as 620° C. at 1 kb pressure. Above this temperature 1M and $2M_1$ are present. These relations can be compared with results in the present paper (Fig. 1), given a run duration of about 1 day. It can be deduced from comparison with the present study that the published results of Crowley and Roy (1964) are based on runs of duration inadequate to demonstrate stability.

Geologic Interpretation

The experimental and field studies of this paper have shown that $2M_1$ is the stable polymorph of muscovite; however, 1M potassic dioctahedral micas do exist in nature. Most of these can be explained if, as Radoslovich and Norrish (1962) assume, structure is controlled by composition. Low-temperature micas such as illite, celadonite, glauconite, and hydrothermal sericite, which have 1M and 1Md polymorphs, do not have a muscovite composition. Low- and medium-grade metamorphic rocks contain micas (phengites) with compositions closer to but not actually those of muscovite. Micas from ore deposits and pegmatite occurrences have quite variable compositions and structures. These are generally not muscovites but can be rather close to that composition, such as some of the micas reported by Glass (1935), the 1M and 3T muscovites. Explanation of 1Md, 1M, or 3T polymorphism can then generally be attributed to compositional variation.

In two particular instances 1M micas can be explained as metastable stages in the kaolinite→muscovite transformation. One has been mentioned earlier as the case of hydrothermal alterations of feldspars in acidic rocks that host ore mineralizations (Burnham, 1956). Many of these sericite micas are products of the kaolinite$\rightleftarrows$muscovite$\rightleftarrows$K feldspar reactions that depend upon the K^+/H^+ constitution of the hydrothermal fluids (Hemley, 1959). Since temperature greatly affects the Na/K ratio of fluid in contact with alkali feldspars (Orville, 1963), the potassium content of the fluid could be expected to change and thereby the K^+/H^+ ratio would fluctuate causing great variability in the equilibria of the system involving kaolinite, muscovite, and K feldspar. These conditions could be expected to produce metastable products because of rapid fluctuations in equilibrium and low temperatures. It is in such cases that 1M and 1Md sericites are often found as alteration products. If they are muscovites their polymorph could be explained as being a metastable step in the production of $2M_1$ muscovite.

Droste (1961) reported 1M dioctahedral micas in clay minerals of playa deposits in California. These micas, called illite, were always mixtures of polymorphs. Because illites in Paleozoic sediments very rarely have 1M polymorphs (Velde and Hower, 1963), this case seems rather anomalous. However, kaolinite is a common constituent of the detrital material supplied to the basins. In the highly saline waters (when present) of the playa, the kaolinite$\rightarrow$muscovite conversion could be expected to proceed rapidly. This might offer an explanation for the scarcity of potassium salts of the evaporites reported by Droste. Much of the incoming potassium was probably used in the formation of muscovite. A part of the mica so formed appears to have remained in the metastable 1M mm.

Previously Grim (1953) pointed out that the conversion of kaolinite to muscovite in ocean sediments seemed probable on the basis of studies of clay minerals in recent and ancient sediments. Since then several other explanations and alternative arguments have been advanced to explain the situation encountered (Weaver, 1959). Looking at the geochemical abundance of potassium, however, one may conclude that the reaction reported in the present paper could be important in natural sedimentary processes and thus bear out the original hypothesis of Grim. Goldschmidt (1958) lists the following average potassium-sodium atomic ratios: magmatic rocks, 0.54; rivers, lakes, 0.23; sea water 0.02; recent marine clays, 21.4 The argument can be made that relative potassium depletion in sea water is due to the incorporation of potassium into clay structures upon their diagenetic formation. It has been noted (Velde and Hower, 1963) that illite or potassic micas form a large part of marine sedimentary materials, and it is known that kaolinite is common in many soil types and is a rather abundant detrital material (Jackson *et al.*, 1952; Griffin: 1962). Thus the conversion of kaolinite to muscovite during sedimentation of detritus in littoral and near shore marine environment seems quite probable as a partial contributor to the formation of these sedimentary micas. There are other methods of arriving at such a product that are probably important, but the kaolinite→muscovite reaction should be considered in the genesis of sedimentary micas. The laboratory investigations reported here emphasize the fast rate at which the reaction proceeds.

SUMMARY

Investigations were made on selected natural muscovites and synthetic products from hydrothermal experiments to determine the stabilities of the muscovite polymorphs 1M and $2M_1$. It is concluded from these data that $2M_1$ is the only stable polymorph of ideal muscovite, $KAl_2Si_3AlO_{10}(OH)_2$. Both 1Md and 1M muscovite are metastable forms. Dioctahedral micas (alkali "interlayer" ions having a total charge near +1 per formula weight) which have either 1Md or 1M polymorphs are either metastable muscovite forms or are micas with a composition differing from muscovite, e.g. glauconite, celadonite, and illite. The latter 1Md and 1M micas are common in nature and form a large part of the minerals in sedimentary and low-grade metamorphic rocks.

The reaction kaolinite+KOH→muscovite, which was used in the polymorph study, proceeded rapidly in the laboratory. Considerations should be given to the importance of similar reactions in common sedimentary and lithification processes. The common occurrence of kaolinite in detrital materials, its absence in older sedimentary rocks, and the low potassium content of sea water indicate that the reaction is probably important in the formation of the very abundant dioctahedral micas in sediments.

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