TOPOTACTIC TRANSFORMATION OF MUSCOVITE UNDER MILD HYDROTHERMAL CONDITIONS*

by

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ABSTRACT

Studies have been made on muscovite single crystals treated under dry and hydro-thermal conditions at temperatures above 800°C. The course of reaction is markedly affected by the amount of water present in the system. In the presence of a large excess of water, appreciable reaction commences at 800°C with the formation of kalsilite and corundum. The kalsilite may bear an epitaxial relationship to the muscovite, but the corundum is quite unoriented. Reaction appears to proceed by solution of part of the muscovite and reprecipitation on unreacted areas. In the presence of low pressures of water the reaction course appears to be similar to that under dry conditions. Above 900°C a new phase has been identified which is similar to the spinel phase reported by Eberhart at temperatures above 1050°C. The phase is monoclinic and probably represents an intermediate stage between dehydrated muscovite and the spinel phase. A tentative mechanism is proposed for the dehydration of muscovite based on an inhomogeneous mechanism.

INTRODUCTION

ALTHOUGH muscovite is a very important and a very common mineral with reactions of interest both to geochemists and to workers interested in reaction kinetics and mechanisms, virtually no studies have been made of the high temperature transformations using single crystal techniques. Such studies are indispensable in any attempt to explain the mechanisms of such reactions and they can also shed light on possible interrelationships between minerals in the various metamorphic faces by indicating, probably more accurately than with powders, the conditions under which large crystals may be expected to react and the nature and probable morphology of the product minerals. Conversely, an unusual morphology for a mineral may indentify it as a reaction product and a knowledge of possible topotactic reactions leading to this species might aid in identifying the parent mineral. The application of the results to the extension of our knowledge of reaction mechanisms and the degree of control exercised by the original structure on the course of the reaction has been discussed by many workers,

notably Brindley and Nakahira (1959), Brindley (1961), Taylor (1962), and Dent-Glasser, Glasser and Taylor (1962).

From the work of Hawkins and Roy (1963) it appeared that the formation of most clay minerals from gels took place via a solution phase when hydrothermal conditions were used. It was decided, therefore, to see whether any topotactic reactions could be observed in a favourable case.

The present study, which is concerned primarily with the reactions of muscovite under hydrothermal conditions, was undertaken as part of a general study of weathering and transformation reactions in clay minerals, under contract with the American Petroleum Institute, Project 55: "Preparation, Structure and Properties of Synthetic Clay Minerals." The problem was suggested by Professor Rustum Roy who gave much valuable assistance with the work and also kindly read the manuscript.

PREVIOUS WORK

Previous work on muscovite under hydrothermal conditions has been done exclusively on powders. Yoder and Eugster (1954) and Crowley (1959) have studied the decomposition of muscovite to give feldspar, corundum and water and the latter has shown that this occurs reversibly and rapidly at 715°C and at 1 kilobar pressure. Thus muscovite crystals would be expected to decompose at temperatures above 715°C under hydrothermal conditions.
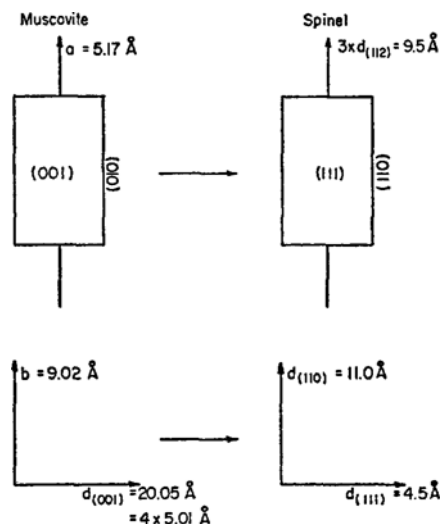

FIGURE 1.—Relative orientations of real cells of muscovite and spinel phase, after Eberhart.

Eberhart (1962, 1963a, b) has recently studied the structural details of the dehydration process of muscovite at low water pressures. When heated dry at 700°C the product gives an X-ray pattern which is very closely similar to that of the original mica. There are slight expansions in the axial lengths, the β angle has decreased from 95° 20′ to 94° 30′ and the intensities of certain reflections have changed. The basic structure, therefore, appears only slightly affected by the dehydration process. Above 1050°C Eberhart reports the formation of a spinel phase topotaxially oriented relative to the original mica. The cubic cell dimension is 7.97 Å, intermediate between values for λ-Al$_2$O$_3$ (7.84 Å) and MgAl$_2$O$_4$ (8.1 Å), and varies with the Mg content of the starting material. The spinel (111) is oriented parallel to muscovite (001) and the spinel (110) to muscovite (010). Figure 1 has been constructed from these data. No work exists to the writer's knowledge on the reactions under water pressure.

EXPERIMENTAL

Pieces of muscovite, about 5 mm × 2 mm × 0.2 mm, cut from a large sheet of the mineral were sealed into gold tubes along with a predetermined amount of distilled water and treated hydrothermally under the appro-

TABLE 1.—Phases Formed from Muscovite under Various Conditions

Crystal	Temp.°C	Pressure (bars)	Time	Results
19	800	1000	120 hr	Musc.
1	810	700	70 hr	Musc., Kal.
5	850	1000	5 hr	Musc., Kal.
6	870	1000	6 hr	Musc., Kal.
9	900	700	3 hr	Musc., Jal.
10	900	800	17 hr	18Å Product
10(a)	900	800	17 hr	Musc., Kal., Cor.
11	910	1000	27 hr	Kal., Cor.
18	850	100	72 hr	Musc., Kal.
12	887	200	17 hr	Musc., Phase 1
17	910	100	48 hr	Musc., Phase 1
16	980	100	48 hr	Musc., Phase 1
3	900	Dry	14 days	Musc.
7	1000	Dry	15 min	Musc.
13	1020	Dry	30 min	Musc., Phase 1
20	1090	Dry	90 min	Spinel
21	1090	Dry	16 hr	Spinel
4	1100	Dry	60 min	Spinel
4(a)	1350	Dry	60 min	Mullite

Abbreviations: Musc.—Muscovite, Kal.—Kalsilite, Cor.—Corundum.

priate pressure–temperature conditions. Dry runs were made by heating the crystals in a standard quench furnace.

RESULTS

Table 1 lists the products formed from muscovite under various conditions. The results fall into three groups corresponding to hydrothermal treatment in the presence of a large excess of water, treatment in the presence of very little water, and dry heating. In general in the Table, pressures above 700 bars indicate a large excess of water and those around 100 bars represent very little water; these conditions will be considered separately.

Excess water.—These conditions probably approximate most closely to the majority of natural situations. The products formed above $800^{\circ}C$, i.e. appreciably above the temperature of reaction of powders, are mainly kalsilite with corundum as a minor phase. After treatment the muscovite crystals, while still retaining much of their original shape, had lost much of their mechanical strength and the originally transparent, light-brown sheets were opaque and bluish-grey. The loss in strength was first thought to be due to the effect of the high pressure on the flakes, but in run 19, where there was very little reaction, the flakes had not lost strength and so this cannot be the cause. The reactivity, as was expected, appeared to increase as the particle size decreased.

In the X-ray diffraction photographs of the treated crystals, reflections from the unchanged muscovite showed marked streaking along powder lines indicating that the crystallites, and even the sheets, of the mica were rotating relative to one another in the (001) plane. In rotation photographs, the kalsilite lines were very "spotty" whereas the corundum lines were quite smooth showing that the kalsilite is less randomly oriented than is the corundum. In some 10° oscillation photographs, moreover, the kalsilite reflections showed some evidence of layer development, although so complex as to suggest the presence of more than one orientation of the material. The reflections were again markedly streaked along powder lines. The X-ray data indicate that the kalsilite is formed with some orientation relative to the mica, but that the relationship is probably not topotactic, but rather epitaxial.

Little water.—When insufficient water is present to dissolve an appreciable amount of the mica, the reaction appears to follow a course quite different from that described above. After treatment at temperatures above $900^{\circ}C$ and pressures around 100 bars, the crystals were opaque and generally colourless with little or no loss in mechanical strength. The product was an almost perfect pseudomorph after the original muscovite. A new phase, which has been called Phase 1, has been formed. The X-ray diffraction pattern shows a high degree of orientation relative to the

muscovite, suggesting that the reaction is topotactic, and is very similar to that of Eberhart's spinel phase, which is formed at temperatures above 1050°C (*loc. cit.*). Dry heating of a crystal of muscovite at 900°C for 14 days did not produce any evidence of Phase 1 and the temperature had to be raised to about 1020°C before the phase appeared. Thus water appears to play a catalytic role in the mechanism of the reaction, since its presence lowers the temperature necessary for the transformation by about 100°C.
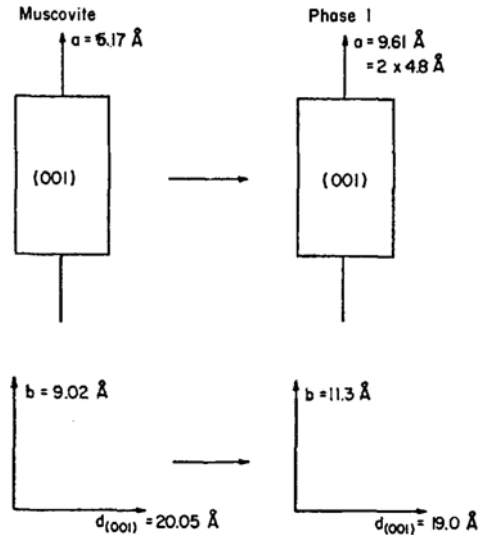

FIGURE 2.—Relative orientations of real cells of muscovite and Phase 1.

Figure 2 shows the relative orientations of the axes of muscovite and Phase 1, derived from 10° oscillation X-ray photographs in which reflections were present from both muscovite and Phase 1, and are correct to within ± 2 per cent. The a, b and c^* directions coincide in the two phases and the β angle has shrunk to approximately 92°. The length of the a-axis of Phase 1 is slightly less than double that of muscovite a and the $d_{(001)}$ spacing also has shrunk. The b-axis of Phase 1 appears to be strongly pseudo-halved. General hkl reflections indicate that its length is somewhat more than half the original muscovite b, but the presence of the (032) reflection at 3.43 Å indicates that the true length may be 11.3 Å.

The mullite formed at 1350°C gave an X-ray diffraction pattern in which there was slight layer development, showing that this phase possesses a slight degree of residual orientation from the mica. Thus, although the ratio of Al_2O_3 to SiO_2 has increased from 1 : 2 in the mica to 3 : 2 in mullite, the orientation and formation of this phase appears to depend on con-

trol transferred from the muscovite structure through the intermediate phases.

DISCUSSION

Excess water.—The loss in strength of the mica, the higher reactivity of smaller particles and the X-ray data all lead to the conclusion that the mechanism of reaction involves initial solution of part of the muscovite, possibly as complex ionic species. Such a process will weaken the residual material and permit rotation of adjacent sheets in a book of mica. Subsequent precipitation and growth of kalsilite occurs on the residual mica. The mica thus acts both as a nucleating agent and as a controller of the initial growth and orientation of the product. In this case the oxygens, since they are the largest and most abundant ions, will probably exercise the principal control, which means that at least three orientations could be produced because of the symmetry of the packing. As the growth continues the initial control is maintained to give a product oriented relative to the starting material but not necessarily in one unique position. Subsequent breakdown of the kalsilite may occur, again in an ordered fashion, to give rise to the intergrowths of mica and feldspar which are found in nature.

Little water.—The marked similarity between the patterns of Phase 1 and Eberhart's spinel has led the writer to consider that Phase 1 is an intermediate between the dehydrated form of muscovite and the spinel. There is no direct evidence to support this in that no crystal has been found in which all the phases could be identified, largely because of limitations in the apparatus used. It is thought, however, that the X-ray evidence combined with the observation that the phase can be made by dry heating at temperatures below that at which the spinel phase is formed make this a reasonable assumption.

Table 2 lists the cell dimensions and d spacings for the various phases and compares them in the experimentally observed orientations. The regularity with which the spacings change and the progressive decrease of β

TABLE 2.—COMPARISON OF SPACINGS IN EXPERIMENTALLY OBSERVED
ORIENTATIONS OF THE SEPARATE PHASES

Muscovite	Dehydrated Muscovite	Phase 1	Spinel		
$2 \times a = 10.40$ Å	$2 \times a = 10.46$ Å	$a = 9.61$ Å	$3 \times d_{(112)} = 9.5$Å		
$b = 9.20$ Å	$b = 9.20$ Å	$b = 11.3$ Å	$2 \times d_{(110)} = 11.0$Å		
$d_{(001)} = 20.05$ Å	$d_{(001)} = 20.20$ Å	$d_{(001)} = 19.0$ Å	$4 \times d_{(111)} = 18.0$ Å		
$\beta = 95°20'$	$\beta = 94°30'$	$\beta = 92°$	$\beta = 90°$		
Vol. $= 1900$ Å³	Vol. $= 1940$ Å³	Vol. $= 2060$ Å³	Vol. $= 1970$ Å³		

in the sequence muscovite→dehydrated muscovite→Phase 1→spinel is very striking. Thus, after a general expansion to form dehydrated muscovite, the original a and $d_{(001)}$ spacings progressively contract, the b direction expands and the cell becomes less skew. The maximum change in the volume of the cell common to all the phases is about 8 per cent—a relatively insignificant amount.

Eberhart (1963a) has discussed the formation of dehydrated muscovite and considers that it arises by elimination of a water molecule between two Al–OH groups to give a new Al–O–Al linkage in the structure. He quotes, in support of this theory, his observation that, in a one-dimensional Fourier synthesis along the normal to (001), the electron density of the octahedral layer is appreciably reduced after heating and hence that the water lost is liberated from this layer. This idea corresponds to the homogeneous mechanism of dehydration whereby the elements of water are lost uniformly from all parts of the crystal and water molecules, as such, from the structure.

This hypothesis can be criticized on several counts.

(1) It is difficult to see how a relatively large water molecule of radius about 1.8 Å can be removed from an almost close-packed array of oxygens, such as there is in muscovite, without destroying the structure completely. The X-ray evidence indicates, however, that the mica structure is affected in only a minor way in the transformation.

(2) The observation concerning the electron density can be interpreted in terms of the inhomogeneous mechanism. Such a mechanism involves migration of, probably Al^{+3} and/or Si^{+4} through a relatively unchanged lattice of oxygens to replace H^+, with the formation of "acceptor" regions, into which the cations migrate, and "donor" regions, into which the hydrogen ions migrate, in the same crystal. Taylor (1962) has discussed this mechanism and considers that the acceptor regions form the crystalline products while the water given off is lost from the donor regions, which are largely destroyed, and not from the bulk of the crystal. Since these regions will be intimately mixed in any crystal, any X-ray intensities obtained will be a statistical average from both parts so that the observed reduction in electron density of the octahedral layers in muscovite may arise not from a uniform loss of water from all parts of the crystal but from the destruction of the octahedral layers in the donor regions. It is reasonable to assume that Al^{+3} ions, particularly in the octahedral sites, migrate during the transformation since they are small and probably less strongly covalently bound to oxygens than are the Si^{+4} ions, because of their lower polarizing power, so that counterdiffusion of Al^{+3} and H^+ would be set up in the octahedral layer. Also, in the donor regions the hydrogens are already bound to oxygens in the octahedral layer and so this layer will be more likely to be destroyed than will the tetrahedral. It would, therefore, appear that the overall effect of such a process would be to reduce the total observed electron density of the layer, but it is im-

portant to note that the electron density in the acceptor regions may have increased by virtue of the inward migration of the aluminums.

(3) Elimination of water would appear to suggest that the resulting cell should be smaller, but the dehydrated cell is, in fact, larger. Replacement of H^+ by a larger cation will explain the increase.

(4) The b dimension quoted by Eberhart for the dehydrated cell closely approaches the theoretical value of 9.3 Å given by Radoslovich and Norrish (1962) for the unstrained tetrahedral layer in muscovite, suggesting that the strain present in the muscovite structure is being released during the dehydration.   This strain is caused by the misfit between the octahedral and tetrahedral dimensions in the b direction, that of the octahedral being the smaller. Elimination of water and the formation of a new Al–O–Al linkage suggests that this layer should contract, thus increasing the strain on the tetrahedral layer and reducing b. Migration of Al^{+3} into the layer, on the other hand, should expand the octahedral layer sufficiently to release much of the strain. The resulting decrease in the rotation of the tetrahedra away from the ideal position in the tetrahedral layer also will mean that the oxygens around the interlayer cation are approaching more closely to a coplanar arrangement, that the packing round this cation will become closer and that the layers will be pushed apart by a form of "squeezing out" process on the potassium, giving the observed increase in the (001) spacing. The potassium can no longer penetrate so deeply into the tetrahedral layer.

This mechanism explains also the transformations to Phase 1 and the spinel phase. At the higher temperatures of these transformations migration of both Al^{+3} and Si^{+4} occurs simultaneously with repacking of the oxygen framework. It is impossible to be more definite than this since the compositions of the high temperature phases are unknown. The overall effect, however, is movement of cations through a relatively unchanged lattice of oxygens. Taylor (1958) and Nicol (1962) have both observed that transformations in the calcium silicates which involve this migration of silicons through an oxygen lattice occur, under hydrothermal conditions, at temperatures appreciably below those at which the reactions occur in dry conditions. The same reduction in reaction temperature has been observed here. The role of the potassiums in these transformations is not known. They may be incorporated into the phases formed and may even play an integral part in their structures.

CONCLUSION

A mechanism has been proposed whereby the formation of naturally occurring topotactic assemblages of muscovite and kalsilite may be explained in terms of transformation from the mica. The similarities in structure between kalsilite and the feldspars suggest that assemblages of muscovite

and feldspar may arise by a similar mechanism. The reaction appears to involve solution of the mica and is governed by classical chemical rules.

The discovery that, in the presence of only a small amount of water, the transformations of muscovite appear to follow a path closely similar to those under dry conditions has led to the conclusion that these transformations take place by an inhomogeneous rather than by a homogeneous mechanism. Although the available data on these transformations are insufficiently definitive for distinguishing between the two reaction mechanism schemes, it is thought that the inhomogeneous scheme explains the observed data at least as well as the homogeneous one, which has been generally accepted as correct. This theory is presented in the hope that it will stimulate further work on this question.

REFERENCES

Brindley, G. W. (1961) The role of crystal structure in the dehydration reactions of some layer-type minerals (In English): *J.Min. Soc. Japan*, v.5(4), pp.217–237.

Brindley, G. W. and Nakahira, M. (1959) The kaolinite-mullite reaction series: *J. Amer. Ceram. Soc.*, v.42, pp.311, 314, 319.

Crowley, M. S. (1959) The effect of solid solubility on the synthesis, stability and polytypism of the micas: Ph.D. Thesis, The Pennsylvania State University.

Dent-Glasser, L. S., Glasser, F. P. and Taylor, H. F. W. (1962) Topotactic reactions in inorganic oxycompounds: *Quart. Revs.*, v.16, pp.343–360.

Eberhart, Jean-Pierre (1962) Étude de cristaux de muscovite deshydratés: *Comptes Rendues*, v.254, pp.2391–2392.

Eberhart, Jean-Pierre (1963a) Étude de la muscovite déshydratée: *Comptes Rendues*, v.256, pp. 3711–3714.

Eberhart, Jean-Pierre (1963b) Étude de la phase type spinelle: *Comptes Rendues*, v.256, pp.3860–3863.

Hawkins, D. B. and Roy, Rustum (1963) Experimental hydrothermal studies bearing on rock weathering and clay mineral formation: *Amer. Miner.*, (In Press).

Nicol, A. W. (1962) Oriented transformations in the system $CaO–SiO_2–H_2O$: Ph.D. Thesis, University of Aberdeen.

Radoslovich, E. W. and Norrish, K. (1962) The cell dimensions and symmetry of layer-lattice silicates: Part 1: *Amer. Miner.*, v.47, pp.599–615.

Taylor, H. F. W. (1958) The dehydration of tobermorite: *Clays and Clay Minerals*, 6th conf. Pergamon Press, N.Y., pp.101–109.

Taylor, H. F. W. (1962) Homogeneous and inhomogeneous mechanisms in the dehydroxylation of minerals: *Clay Min. Bull.*, v.5, pp.45–55.

Yoder, H. S. and Eugster, H. P. (1954) Synthetic and natural muscovites: *Geochim et Cosmochim. Acta*, v.8, pp.225–280.