

EXPERIMENTAL STUDIES OF ILLITE¹

by

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ABSTRACT

Investigations in the system K_2O - MgO - Al_2O_3 - SiO_2 - H_2O were made in an attempt to synthesize micas similar to illite and to determine their upper stability limits. These are representative of materials referred to by many clay mineralogists as illite, hydromuscovite and K-bentonite. Gels of these compositions were treated hydrothermally at temperatures above 250°C and at pressures above 10,000 lb/in.². Natural illites and related minerals were also treated under the same conditions.

It is possible to prepare phases having the properties of illite. This is achieved below 500°C but above this temperature well-crystallized micas plus other phases are obtained. The partially disordered micas formed from K-deficient compositions give the x-ray diffraction pattern of the 3T polytype, whereas the well-crystallized micas obtained with more K_2O or at higher temperatures are the 1M polytype. Once formed at lower temperatures, however, the 3T mica is persistent and not readily transformed at higher temperatures. The 2M polytype, which is reported to be the stable form for pure muscovite at the temperatures of this investigation, was not obtained.

Compositions with the same alumina : silica ratio as muscovite but with less potassium do not yield a mica-type mineral as a single phase under the conditions of these experiments. However, those in which the lower potassium content is compensated by less substitution and lower layer charge do yield illite alone. These studies indicate that the differences in properties between illites and well-crystallized micas are a function of composition as well as of the temperature of formation.

INTRODUCTION

Illite, a clay mineral substance structurally related to the micas, is the dominant constituent of many fine-grained sediments. Much has been written about its possible formation by degradation or aggradation processes (Griffiths, 1952 ; Yoder and Eugster, 1955 ; Mackenzie, 1955). The formulation of the low-temperature reactions involved has been based on much geologic evidence and on a limited number of experimental studies of cation exchange and "potassium fixation" by expanding-type clay minerals.

The present investigation was undertaken in order to learn whether material with the properties of natural illites can be synthesized readily from amorphous gels and to determine the upper temperature stability limits of such phases. Such information would be of value in considerations of the aggradation process postulated for the formation of illite.

"Illite" was proposed by Grim, Bray and Bradley (1937) as a "general term for the clay mineral constituents of argillaceous sediments," and presumably also of soils, "belonging to the mica group." They stated that,

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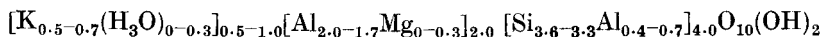
as more data accumulated, specific names could be given to some of the clay micas and "illite" would remain the group name.

Later, as specific names were given to various clay micas, they were no longer considered "illite" and this term became restricted almost entirely to substances resembling in almost every detail the illite from the Illinois occurrences. It became necessary to use a different group name, and "hydrous mica" was proposed by Brown (1951) to include all the clay micas, including those with interstratified layers of montmorillonite. "Illite" was limited to those whose 10 Å reflections were not significantly affected by mild thermal or chemical treatments. These, of course, could contain minor amounts of interstratified layers, which is one of the principal reasons for the subsequent confusion described by Yoder and Eugster (1955).

It should be noted that one of the valid reasons for the proposal of "illite" as a general term was that "hydromica" had been badly defined, and "hydrous mica" scarcely differs from "hydromica." This term has been avoided in the proposals made by the Clay Minerals Group Sub-Committee on Nomenclature of Clay Minerals (Brown, 1955a), in which "illite" is broadly defined as containing less potassium and more water than muscovite, as being generally fine grained and as giving x-ray patterns usually poorer in lines than muscovite. This definition, while being ambiguous enough to avoid the usual arguments, is too vague to be of practical use.

The most recent review of the nomenclature and classification of the micas and related clay minerals is that by Taboada and Ferrandis (Mackenzie, 1957). These authors divide the mica family into two groups: the "true micas" and the "clay micas." "Illite," in its restricted sense, is included in the latter. The "clay mica" of this classification apparently refers to the same materials as "illite" of the Clay Minerals Group Nomenclature Sub-committee, but the former has been defined more satisfactorily. In the first place, it is mentioned that these materials contain more silica, as well as more water, than do muscovites. Secondly, it emphasizes the following features of the x-ray diffraction patterns of clay micas: the basal reflections are not alterable with mild treatments; there may be some asymmetry of the basal reflections due to interstratification; and there may be some asymmetry of "general" reflections due to stacking irregularities.

For the purpose of the present investigation, "illite" is used in a broad sense: It is clay grade material of which the chemical composition may be expressed by the formula:



Its x-ray diffraction patterns show it to be a mica with small but significant amount of montmorillonite-like layers. This definition, which is based on the examination of a number of illites for which published data are available, includes hydromuscovite but excludes the sodium mineral brammallite, all those clay micas with large amounts (> one-fourth) of interstratified layers of other silicates, and all micas with sharp 001 reflections corresponding to $d < 10.1 \text{ \AA}$. In natural illites, of course, iron may occur in octahedral sites.

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METHOD OF INVESTIGATION

Equipment

The crystallization of gels and the decomposition of natural materials were carried out in "test tube" bombs of the type described by Roy and Osborn (1952). These were heated in chromel-wound furnaces, the temperatures of which were regulated by Brown Pyr-O-Vane controllers. The reaction vessels were attached by pressure tubing to a Sprague pump, which was used to obtain the desired pressure during the initial heating period. After attaining the desired temperature, each vessel, together with a Bourdon type gauge, was isolated from the pump by means of a valve. The accuracy of temperature measurements was about $\pm 5^\circ\text{C}$, and of pressure measurements about ± 5 percent.

Starting Materials

Gels of the desired composition (Table 1) were prepared by adding 1 N KOH solution and "Ludox" colloidal silica (E. I. du Pont de Nemours & Co.) to solutions of the nitrates of the other elements. In some instances nitric acid was added to prevent the precipitation of aluminum hydroxide. The suspensions were then evaporated on a steam bath until clear, rigid gels were formed, and the heating was continued until much of the water was removed. The gels were then ignited at 400° or 500°C overnight to decompose the nitrate, and finally were ground in a mullite mortar to insure intimate mixture.

TABLE I.—COMPOSITIONS OF GELS INVESTIGATED

No.	Composition	Mineral (anhydrous)
1.	$\text{K}_{0.1}\text{Al}_{2.0}\text{Si}_{3.9}\text{Al}_{0.1}\text{O}_{11}$	—
2.	$\text{K}_{0.3}\text{Al}_{2.0}\text{Si}_{3.7}\text{Al}_{0.3}\text{O}_{11}$	K-aluminian montmorillonite
3.	$\text{K}_{0.5}\text{Al}_{2.0}\text{Si}_{3.5}\text{Al}_{0.5}\text{O}_{11}$	"illite"
4.	$\text{K}_{0.7}\text{Al}_{2.0}\text{Si}_{3.3}\text{Al}_{0.7}\text{O}_{11}$	"illite"
5.	$\text{K}_{1.0}\text{Al}_{2.0}\text{Si}_{3.0}\text{Al}_{1.0}\text{O}_{11}$	muscovite
6.	$\text{K}_{1.3}\text{Al}_{2.0}\text{Si}_{2.7}\text{Al}_{1.3}\text{O}_{11}$	—
7.	$\text{K}_{0.7}\text{Al}_{2.0}\text{Si}_{3.0}\text{Al}_{1.0}\text{O}_{10.85}$	hydromuscovite
8.	$\text{K}_{0.5}\text{Al}_{2.0}\text{Si}_{3.3}\text{Al}_{0.7}\text{O}_{10.9}$	hydromuscovite
9.	$\text{KAl}_2\text{Si}_3\text{AlO}_{11} + 1.8\text{SiO}_2$	—
10.	$0.05\text{K}_2\text{O} : 2.4\text{Al}_2\text{O}_3 : 3\text{SiO}_2$	—
11.	$\text{K}_{0.7}\text{Al}_{1.7}\text{Mg}_{0.3}\text{Si}_{3.6}\text{Al}_{0.4}\text{O}_{11}$	"illite"
12.	$\text{K}_{0.5}\text{Al}_{1.9}\text{Mg}_{0.1}\text{Si}_{3.6}\text{Al}_{0.4}\text{O}_{11}$	"illite"
13.	$\text{K}_{0.5}\text{Ca}_{0.2}\text{Al}_{1.8}\text{Mg}_{0.2}\text{Si}_{3.3}\text{Al}_{0.7}\text{O}_{11}$	"illite"

Some experiments also were carried out on the following natural samples.

(1) Illite, Fithian, Illinois; $<0.2\mu$ fraction. Obtained from Gulf Research & Development Co. If crystalline impurities are present, the amounts are too small to be detectable by x-ray diffraction.

(2) Illite, Ballater, Scotland; $1.4-0.4\mu$ fraction. Obtained from R. C. Mackenzie, Macaulay Institute, Aberdeen. If crystalline impurities are present, the amounts are too small to be detectable by x-ray diffraction. Chemical analysis given by Mackenzie, Walker and Hart (1949).

(3) Hydromuscovite; $<0.4\mu$ fraction. Obtained from R. C. Mackenzie. Contains trace of 7 \AA mineral.

(4) K-bentonite, Oak Hall, Pennsylvania; no. N2, $0.3-0.2\mu$ fraction. Obtained from Gulf Research & Development Co. If crystalline impurities are present, the amounts are too small to be detectable by x-ray diffraction.

Technique

Between 15 and 25 mg of sample and 6–7 mg of de-ionized water were sealed in gold tubing of 2.5 mm inside diameter. The volume of the sealed tubes was about 0.05 ml. These were weighed before and after the hydrothermal treatment to determine whether leakage had occurred. Some experiments were carried out with gold envelopes instead of sealed tubes; the sample in a small envelope was placed in a larger envelope containing more of the sample as a buffer. The contents of both the inner and outer envelopes were examined to determine the effects of leaching which was found to occur.

The tubes or envelopes were placed in a reaction vessel, which was then filled with de-ionized water, attached to the pressure system, and heated to the desired temperature under pressure. The thin-walled tubes collapsed partially so that the pressure in the tubes was equivalent to that in the bomb. After a sufficient length of time, the furnace was removed and the bomb quenched in water.

Identification of Phases

After removal from the tubes or envelopes, portions of the hydrothermal products were ground in two drops of water, smeared on glass slides, and allowed to dry at room temperature. x-Ray diffraction patterns of these sample preparations were obtained with a Norelco High Angle Diffractometer using filtered copper radiation. Identification of the phases and indications of the degree of crystallinity, disorder and mixed-layering were obtained from the diffractometer traces.

Adsorption and Desorption Studies

Some of the slide preparations were x-rayed under variable humidity conditions to determine whether the layered structures contained some layers that could be hydrated and dehydrated. Variable humidity was obtained with the apparatus described by Gillery (1959). A few slides were x-rayed in a dry atmosphere after being heated.

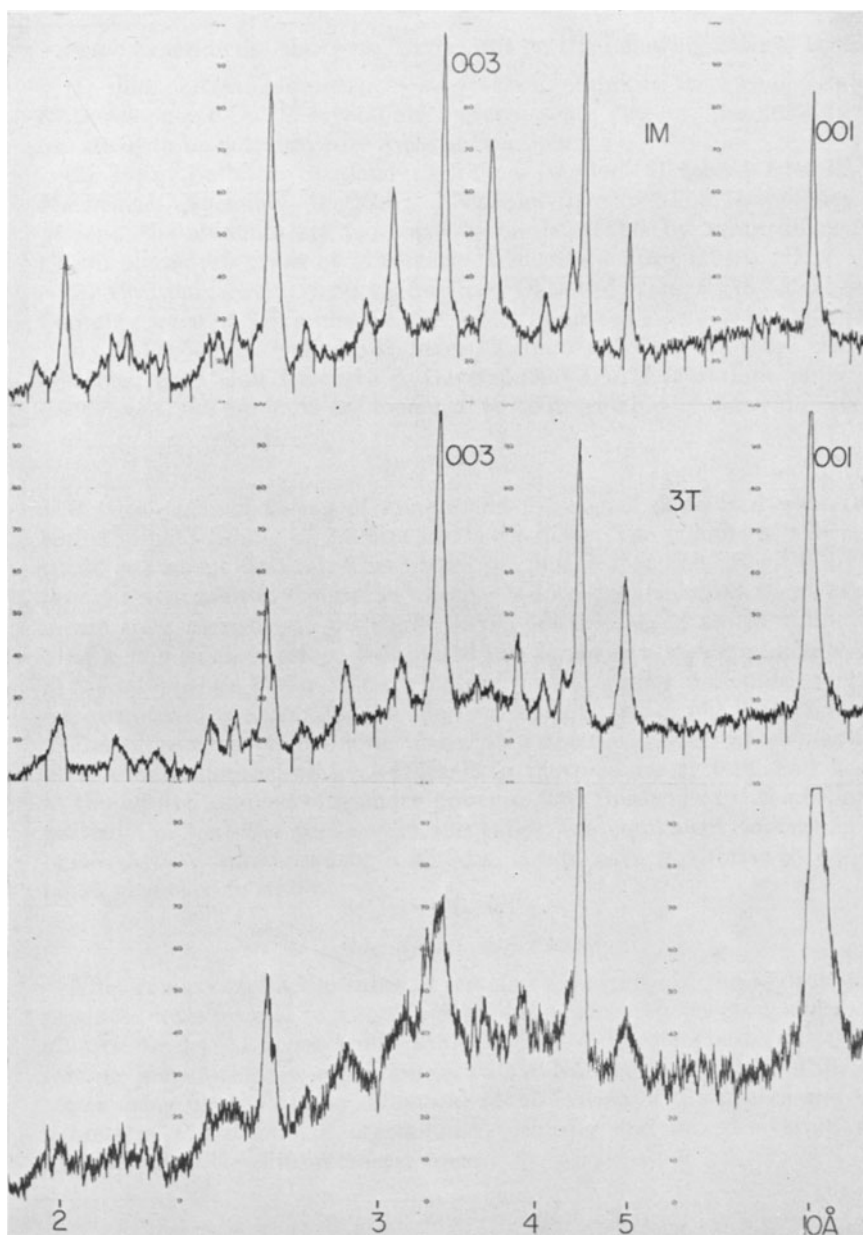


FIGURE 2.—X-Ray diffractometer traces of synthetic micas. Filtered copper radiation, scanning speed = $1^\circ 2\theta/\text{min}$. Upper pattern: IM muscovite, serial no. 9101, see Table 2; scale factor = 4. Middle pattern — 3T muscovite, serial no. 9096, see Table 2; scale factor = 4. Lower pattern: poorly crystallized 3T muscovite plus minor montmorillonite (= "illite"), serial no. 9051, gel no. 4 treated hydrothermally at 385°C ; scale factor = 2.

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Additional portions of many samples were solvated with ethylene glycol on glass slides, allowed to dry enough to lose the excess glycol, and then x-rayed to determine whether the layers could thus be expanded, as is done with montmorillonite.

RESULTS

The compositions investigated are listed in Table I with the proportions given in terms of an anhydrous mica. Most of them are in the system $K_2O-Al_2O_3-SiO_2-H_2O$ and are projected, in Fig. 1, on to the anhydrous base of the tetrahedron representing this system.

Since this investigation is concerned primarily with illite or potassium-deficient micas, the gel compositions and hydrothermal conditions were

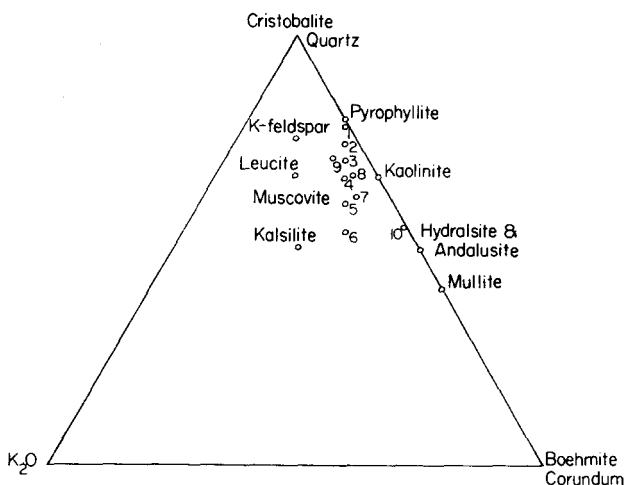


FIGURE 1.—Anhydrous base of system $K_2O-Al_2O_3-SiO_2-H_2O$ showing projected compositions (mole percent) of the gels and their hydrothermal products. Gels numbered as in Table I.

such that a mica-type phase is the dominant constituent in most of the hydrothermal products. It was necessary also to make some runs outside the illite composition and stability ranges. The mica-type phases obtained in the majority of runs were studied in some detail.

Variations in x-ray Patterns of Micac

The most obvious variation among the x-ray patterns obtained from the micas prepared under different conditions lies in the sharpness and number of reflections, both of which generally increase with temperature of treatment. Some of the variation in x-ray diffraction patterns is illustrated in Fig. 2.

The variations in the basal reflections are particularly notable. Broad 001

reflections (Fig. 2(c)), some of which have the asymmetry characteristic of illite, have spacings between 10.1 and 10.7 Å while the sharp 001 reflections (Fig. 2(a)) are close to 10.0 Å. The 003 and 005 reflections show less variation in spacing than the 001 peak which is the most sensitive for detecting the presence of expanded layers. The evidence for nonintegral orders of basal reflections is fairly strong. In general, the sharpness of the basal reflections can be correlated with the crystallinity of the mica as shown by the pattern as a whole.

The intensity of the 003 reflection relative to that of the 001 reflection normally increases with the sharpness of the whole pattern, but the large differences in the relative intensities of these two reflections can be correlated with the potassium content of the gel, the ratio I_{003}/I_{001} increasing with K_2O in general agreement with the calculations of basal intensities by Brown (1955b).

The 060 reflection is found to vary from 1.492 to $1.499 \text{ \AA} \pm 0.001 \text{ \AA}$ for micas and aluminian montmorillonites containing only aluminum in octahedral positions, the spacing apparently increasing with tetrahedral substitution of aluminum for silicon. The spacing is from 1.497 to $1.501 \text{ \AA} \pm 0.001 \text{ \AA}$ for micas containing magnesium.

At an early stage of the investigation, it was obvious that two distinctly different polytypes of mica were being encountered, namely, the single-layer monoclinic, 1 M, and the three-layer trigonal, 3 T. A comparison of the 1 M and 3 T diffraction patterns is given in Table 2 and shown in Fig. 2. These polytypes are most readily distinguished by the spacings and relative intensities of the reflections in the following regions: 3.87 Å, 3.59–3.66 Å, 3.07–3.13 Å, 2.84–2.93 Å. A poorly crystallized 3 T mica (Fig. 2(c)) is difficult to distinguish from a disordered one, which will be called "mica-D," because of the low intensity of the *hkl* reflections of the former.

All the above features were noted in examining the diffraction patterns of the hydrothermal products.

$K_2O-Al_2O_3-SiO_2-H_2O$ System

Compositions 1–5 (Table 1 and Fig. 1) lie on a straight line between muscovite and pyrophyllite. This is not a binary join, for treatment of these gels does not yield a mixture of these two phases. In this area, this system bears a strong resemblance to the system $Na_2O-Al_2O_3-SiO_2-H_2O$ (Sand, Roy and Osborn, 1957) in that, at temperatures below 500°C, one of the phases is represented by a composition field rather than a point composition. In the soda system, the field is montmorillonite, whereas in the present investigation a field is obtained for illite. Thus, at temperatures up to 500°C, hydrothermal treatment of gels 3, 4 and 5 (representative of muscovite and illite) yields only mica. The K-aluminian montmorillonite composition (no. 2) lies outside this field and yields only aluminian montmorillonite below 400°C but this phase plus mica at 400°C and above. Water-adsorption studies indicate the presence of two aluminian montmorillonites, one with potassium and the other with aluminum in the interlayer position, in the products obtained

TABLE 2.—X-RAY DIFFRACTION PATTERNS OF IM AND 3T MUSCOVITES

Synthetic IM Micas				Synthetic and Natural 3T Micas			
Serial No. 9101 ¹		Yoder and Eugster (1955)		Serial No. 9096 ¹		Sultan Basin, Wash. Levinson (1955)	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
10.0	60	10.077	>100	10.1	75	9.98	s
5.01	30	5.036	37	5.01	35	4.98	m
4.48	80	4.488	90	4.47	65	4.47	s
4.34	15	4.349	27	4.27	10	4.29	vw
4.10	10	4.115	16	4.10	10	4.11	vw
				3.87	20	3.87	m
3.65	40	3.660	60	3.58	5	3.60	m
3.34	70	3.356	>100	3.34	70	3.34	vs
3.07	35	3.073	50	3.12	15	3.10	m
2.93	10	2.929	6	2.86	20	2.87	m
2.68	10	2.689	16	2.68	5		
2.578	35	2.582	50	2.578	20		
2.557	60	2.565	90	2.557	35	2.57	vs
		2.550	22				
2.442	10	2.450	11	2.455	10	2.47	mb
2.392	5	2.405	4				
2.362	5	2.380	12	2.380	10	2.38	m
2.243	10	2.246	8	2.227	5	2.24	w
2.212	5	2.219	7				
		2.191	4	2.191	5	2.20	w
2.149	10	2.156	20	2.132	10	2.13	m
2.113	5	2.109	6				
2.090	2					2.05	vw
2.010	30	2.013	32	2.002	15	2.00	ms
1.953	5	1.957	7	1.961	2	1.96	w
		1.900	4				
1.719	2					1.72	vw
1.670	10	1.668	18				
		1.653	12	1.65	5b	1.65	m
1.637	10	1.635	12			1.61	vw
		1.514	4			1.52	vw
1.499	20	1.499	33	1.495	15	1.50	m

Note: $\text{CuK}\alpha = 1.5418 \text{ \AA}$. b = broad or diffuse.

¹ Serial No. 9101: Gel no. 6, 14,000 lb/in², 495°C, 7 days, gold envelope.

Serial No. 9096: Gel no. 4, 13,500 lb/in², 450°C for 14 days, followed by 555°C for 8 days, sealed gold tube.

from this gel; thus, it may not be possible to prepare a pure, single-phase K-aluminian montmorillonite hydrothermally.

The micas obtained below 500°C from the muscovite composition (no. 5) and from compositions with less potassium and aluminum (nos. 3 and 4) exhibit variations related to both temperature and composition, as shown in Table 3, which gives the mica polytype, the spacing and character of the 001 reflection, and the additional phases. The muscovite composition yields

TABLE 3.—PRODUCTS OF HYDROTHERMAL TREATMENT OF GELS IN THE SYSTEM $K_2O-Al_2O_3-SiO_2-H_2O$

No.	Composition of Gel	375°C	400°C	500°C	600°C
(5)	$K_{1.0}Al_{2.0}Si_{3.0}Al_{1.0}O_{11}$	10.1 sharp 1M	—	10.0 sharp 1M	10.1 vsh. 1M
(4)	$K_{0.7}Al_{2.0}Si_{3.3}Al_{0.7}O_{11}$	10.3 sl.b. 3T	10.1 sl.b. 3T	10.1 sharp 3T, 1M	10.1 vsh. 1M crist., chlor.
(3)	$K_{0.5}Al_{2.0}Si_{3.5}Al_{0.5}O_{11}$	10.7 broad mica-D	10.1 broad mica-D	10.1 broad 3T	10.1 vsh. 1M chlor., crist.
(2)	$K_{0.3}Al_{2.0}Si_{3.7}Al_{0.3}O_{11}$	10.8 broad beid	10.2 and 12 beid., 3T	9.9 broad C-beid	10.1 sharp chlor., crist., mica, hydral.

a good 1 M mica, with the 003 reflection larger than the 001, from 250° to 500°C. The composition with only two-thirds of the theoretical potassium of muscovite (no. 4) yields a good 3T mica, with the 003 intensity equal to that of the 001, below 500°C, even with runs of 3 week duration, but at 500°C, some 1 M mica is obtained in addition to the 3T. The 001 reflection changes gradually with temperature from a slightly broad 10.3 Å peak at 385°C to a sharp 10.1 Å peak at 460°C. When only one-half of the theoretical potassium of muscovite is present (no. 3), only the 3T polytype is obtained at 500°C. Below this temperature a disordered mica, possibly a very poorly crystallized 3T, is formed. The 001 peak, which remains broad at 500°C and below, varies from 10.7 Å at 375°C to 10.1 Å at 500°C. With this composition also, the intensity of the 003 reflection is equal to that of the 001.

Above 500°C, the muscovite field decreases to a point. The muscovite composition (no. 5) continues to yield only the one phase, 1 M mica, up to its decomposition temperature, but the compositions with less potassium (nos. 3 and 4) yield other well crystallized phases. These are cristobalite, hydralsite, and a phase having the first basal maximum at 13.7 Å, presumably an aluminian chlorite. These may well be metastable phases, but they appear persistently under the conditions of this investigation. Stability conditions have not been established, but it appears that the "chlorite" phase is a higher temperature one than hydralsite. Quartz appears in addition to cristobalite above 650°C.

The mica from all three compositions under discussion improves in crystallinity with increasing temperatures. The 1 M polytype is obtained above 500°C, and small amounts of the 2 M polytype are observed just below the decomposition temperature of muscovite. The 3T mica formed below 500°C is not readily converted to the 1 M polytype above this temperature and improves in crystallinity.

As was mentioned above, the K-aluminian montmorillonite composition (no. 2) behaves differently from those with more potassium. Below 400°C, aluminian montmorillonite is obtained having a broad peak at 10.8 Å under

normal humidity conditions. At 400°C, two basal spacings are obtained under these conditions, 10.2 Å and 12 Å. The whole diffraction pattern suggests that a very poorly crystallized 3T mica is present in addition to aluminian montmorillonite. At 500°C, only one layer-silicate phase is present in addition to minor cristobalite. This appears to be a collapsed aluminian montmorillonite with a broad 001 reflection at 9.8–9.9 Å. Above 500°C, other crystalline phases gradually become dominant. These are, as above, cristobalite, hydralite, the 13.7 Å phase and quartz. The 13.7 Å phase is the dominant one above 600°C. At this temperature also, mica-D replaces the collapsed aluminian montmorillonite. This statement is based on the observation that the broad 001 reflection which was, up to this temperature, much greater in intensity than the 003, as with montmorillonite, gives way to a sharp 001 reflection which has the same intensity as the 003. It is believed that this change takes place primarily in the interlayer position, a replacement of potassium for aluminum, since the 060 reflection, which is here related to the amount of tetrahedral substitution, remains at 1.492 Å which is much smaller than that of muscovite, 1.499 Å. Thus, this mica-D is possibly a fully collapsed K-aluminian montmorillonite.

Two mica compositions were prepared in which the potassium deficiency was not accompanied by a deficiency of tetrahedral aluminum (gels no. 7 and 8). The existence of hydronium micas with such compositions has been proposed by Brown and Norrish (1952). The neutralization of the layer charge in such micas and the filling of interlayer positions not occupied by potassium is accredited to hydronium (H_3O^+) ions. Hydrothermal treatment of these gels does not yield hydronium micas. Even at 375°C, these compositions are outside the muscovite field and boehmite is obtained in addition to mica. However, the micas obtained at this temperature are 3T and not 1M, indicating that they are not pure muscovite but have compositions somewhere in the illite field. At higher temperatures, the same additional phases are obtained as with the other potassium-deficient compositions. The results indicate that, if hydronium micas do exist in nature, they are probably formed under conditions different from those of this investigation.

Compositions Containing Mg and Ca

In general, the results of treating illite gels containing small amounts of magnesium (nos. 11 and 12) were similar to those obtained with the other illite compositions. Only a mica phase was obtained below 500°C. Above this temperature the major phase in addition to mica was cristobalite.

Calcium was included in one gel (no. 13) in order to detect readily any mixed-layering that might be present among the hydrothermal products of runs made below the decomposition temperature of montmorillonite. The basal spacing should be greater than that of mica when the sample is x-rayed under normal humidity conditions at room temperature, since interlayer calcium, unlike potassium, is hydrated under such conditions. Below 500°C two separate layer phases are formed. Apparently true mixed-layering is not obtained under these experimental conditions, but mixtures are formed.

Adsorption and Desorption Studies

The basal reflections of mixed-layer minerals consisting of interstratified mica and montmorillonite layers vary appreciably in spacings and intensities with the moisture content of the air in contact with the specimen during the recording of the x-ray diffraction pattern (see for example Milne and Warsaw, 1956). The same kind of variation is shown by illites, which consist mostly of mica layers with minor amounts of randomly interstratified layers of variable spacing. In this instance, however, it is usually necessary to record the pattern at a slow scanning speed in order to detect significant differences.

A few of the hydrothermal products of this investigation were x-rayed under variable humidity conditions. The only samples selected for this study were those which would give significant results with the usual scanning speed, but these were checked with slow speed patterns. The results are compared in Table 4 with those for Fithian illite and two mixed-layer minerals, K-bentonite and glauconite from California. Data are given only for the 001 reflection although the other basal reflections also show variations.

The natural materials all decrease in spacing with decreasing humidity; however, less decrease is shown by the glauconite, which may contain significant amounts of divalent cations in interlayer positions, as shown by chemical analysis (Warsaw, 1957). The least variation in intensity is exhibited by the illite sample, which has fewer montmorillonite-like layers than the mixed-layer minerals.

TABLE 4.—VARIATION IN SPACINGS (IN Å) AND INTENSITIES OF FIRST-ORDER BASAL REFLECTIONS OF ILLITES AND RELATED MINERALS WITH ADSORPTION AND DESORPTION OF POLAR COMPOUNDS

Composition and Hydrothermal Treatment	Glycol Sat.	About 85% ¹		Normal 20–50% ¹		Dry < 1% ¹		After 110°C Overnight	
	d_{001}	d_{001}	Peak Hgt.	d_{001}	Peak Hgt.	d_{001}	Peak Hgt.	d_{001}	Peak Hgt.
K-bentonite, Oak Hall, Pa.	9.9	10.4	35	10.3	45	9.9	59	9.9	60
Illite, Fithian, Ill.	9.9	10.4	45	10.3	48	10.10	45	10.05	53
Mixed-layer Glauconite ²	9.9	10.4	23	10.4	30	10.3	33	10.1	33
$K_{0.5}Al_{2.0}Si_{3.5}Al_{0.5}O_{10}(OH)_2$ (no. 3)									
9022–375°C, 2 weeks	12.8								
	9.5	10.8	35	10.6	40	10.6	40	10.3	35
9007–500°C, 1 week	9.8	10.1	25	10.1	25	10.1	25	10.1	25
$K_{0.3}Al_{2.0}Si_{3.7}Al_{0.3}O_{10}(OH)$ (no. 2)									
9050–385°C, 2 weeks	13.0	11.8	15	10.8	35				
	9.3	10.4	10			10.2	37		
9004–400°C, 2 weeks		12.3	20	12.1	25	11.8	13		
	9.5	10.2	15	10.1	15	10.2	22		

¹ Relative humidity.

² Warsaw (1957).

The hydrothermal products of the gel (no. 3) with 0.5 mole potassium per formula unit are similar to the illite in some respects. A nonexpandable mica is obtained at 500°C, but the layer silicate prepared below 400°C has a variable 001 reflection. This does not collapse as readily as that of the natural illite, which may be due to the presence of some aluminum in interlayer positions.

Hydration studies reveal the presence of two phases in both products synthesized from the K-aluminian montmorillonite composition (no. 2). Both phases obtained below 400°C collapse in dry air. However, there

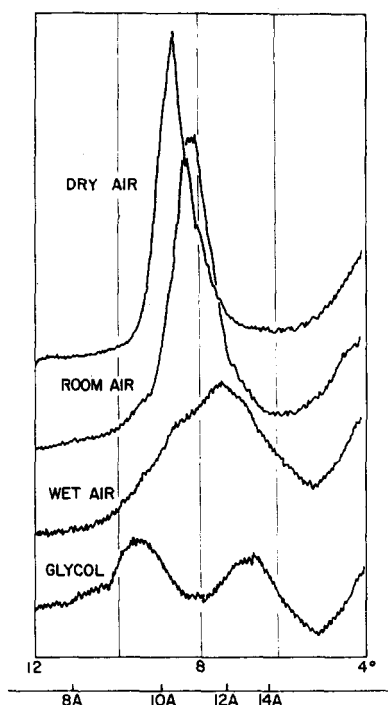


FIGURE 3.—First-order basal reflections obtained from the same sample of K-aluminian montmorillonite (no. 2, Table 1) under different conditions during recording of x-ray diffraction pattern. Filtered copper radiation, scanning speed = $1^\circ 2\theta/\text{min}$.

appears to be a greater difference between the two phases obtained at 400°C, since two 001 reflections are obtained under all three humidity conditions. The intensity variations suggest that three phases may be present in this product: mica, K-aluminian montmorillonite, and a hydrated aluminian montmorillonite, perhaps Al or H-aluminian montmorillonite.

Some of the samples were dehydrated by heating overnight at 110°C. As shown in Table 4, no further change takes place when dehydration at room temperature has already collapsed the basal spacing to 9.94 Å. However,

further collapse, with little intensity change, is exhibited by the glauconite and the "illite" synthesized at 375°C.

All the hydrothermal products which gave broad 001 reflections were treated with ethylene glycol and all showed evidence of glycol saturation, which is further evidence that the hydrothermal products similar to natural illite are mixtures of mica and expandable layers.

Fig. 3 shows the 001 reflections obtained from the same sample under different conditions. The same scale factor was used for the upper three. This is the K-beidellite (no. 2) mixture crystallized at 375°C. Unless varying humidity and glycol treatments were used, one would perhaps consider this simply a poorly ordered mica. The glycol peak at 7° is probably due to one of the phases adsorbing only one layer of glycol.

Natural Minerals

Fithian illite.—The $<0.2\mu$ fraction of the mica-type clay mineral from Fithian, Illinois, was used in this investigation. x-Ray diffraction patterns of this material do not have the *hkl* reflections characteristic only of 1M, 2M or 3T muscovites. Such material has been designated 1Md by Yoder and Eugster (1955, p. 244). It is a disordered mica, but it is not two-dimensional like montmorillonite. There is some short-range order in the manner of stacking, for x-ray powder films clearly show the presence of reflections related to the pseudohexagonal lattice, the 20 l and 13 l reflections of the monoclinic mica structures, as shown in Table 5. Because of this short range order in stacking, this disordered mica is possibly no more 1Md than 2Md or 3Td and should probably be designated merely mica-D.

TABLE 5.—X-RAY DATA FOR DISORDERED MUSCOVITES

Serial No. 9083 ¹			Fithian Illite <0.2 μ		Yoder and Eugster (1955) X = Presence of Reflection
<i>d</i>	<i>I</i>	<i>hkl</i> ²	<i>d</i>	<i>I</i>	
10.2	50	001	10.2	100	X
4.96	15	002	4.98	20	X
4.46	80	020, 110	4.49	80	X
3.31	40	003	3.33	60	X
2.56	60	200, 130	2.58	80	X
2.45	10	20 $\bar{2}$, 131	2.46	5b	
2.39	10	201, 13 $\bar{2}$	2.38	20b	
2.22	5b	040, 220	2.26	10	
2.14	10	202, 13 $\bar{3}$	2.14	10	
1.99	5	005	2.00	10b	X
1.65	5b	310, 240	1.67	5b	
1.492	15	060	1.50	60	X

¹ Gel no. 12, 14,000 lb/in², 400°C, 16 days, sealed gold tube.

² Calculated for 1M unit cell; do not agree completely with those given by Yoder and Eugster (1955).

By hydrothermal treatment, this Fithian sample is converted partially to vermiculite at temperatures below 400°C and then to mica plus chlorite from 400 to 550°C.

Ballater illite and K-bentonite.—The mica-type clay mineral from Ballater, Scotland, first described by Mackenzie, Walker and Hart (1949) is the 3T polytype and appears to be a mixed-layer mineral containing montmorillonite layers. The only result of the hydrothermal treatment is the collapse of the expandable layers. Similar results are obtained with a K-bentonite from Oak Hall, Pennsylvania, which is also 3T.

Hydromuscovite.—The investigation of a natural hydromuscovite, believed to be a hydronium mica, was of particular interest since attempts to synthesize such micas had not been successful. This sample is a mixed-layer mineral with the 1M type of stacking. With a very well oriented sample it is possible to detect the presence of a minor amount of a 7 Å mineral. An increased amount of the 7 Å material is present after hydrothermal treatment. This is believed to be a variety of serpentine, rather than kaolinite, since it persists to at least 550°C. Some andalusite is also formed at 500°C and mullite at 550°C and higher temperatures.

Thus, the results of treatment of the hydromuscovite differ from those obtained with the 3T illites. Not only are the expandable layers collapsed but other phases are crystallized readily. It is believed that extraneous material is probably present but not readily detectable in the sample before hydrothermal treatment. The presence of the constituents of an Al-rich serpentine would account for the fact that a hydromuscovite contains more alumina and structural water than other K-deficient micas.

SUMMARY

Natural illites and gels of illitic composition were treated hydrothermally. The gel of muscovite composition yields only 1M mica with d_{001} close to 10.0 Å and no other phases from 250°C up to the decomposition temperature. The high temperature runs were probably not long enough to develop the 2M polytype. The illite compositions, that is, those with less K and Al than muscovite, give only an illite phase below 500°C. This is the 3T polytype and gives broad, nonintegral basal reflections which are affected by hydration and glycol saturation. Thus, at least two phases are present, montmorillonite or aluminian montmorillonite and a mica that is not pure muscovite. The phases are distinct and probably not mixed-layered, as shown by preparing a Ca-illite. When good muscovites are synthesized from the illite compositions above 500°C, other phases also crystallize.

Compositions with the same alumina/silica ratio as muscovite but with less potassium do not yield a mica as a single phase under the conditions of these experiments, although those in which the lower potassium content is compensated by less substitution and lower layer charge do yield micas similar to natural illites. Hydrothermal treatment of a natural hydromuscovite used in this investigation readily yields other phases in addition to muscovite. Possibly extraneous material rich in aluminum and structural

water is present, but not detectable, in many samples of hydromuscovite.

When Fithian illite is treated just below 400°C, some vermiculite is formed in addition to illite. From 400°C to 550°C, the hydrothermal products consist of mica plus chlorite, an assemblage characteristic of low-grade metamorphism of shales.

The x-ray diffraction patterns of the potassium-deficient micas synthesized below 500°C resemble those of natural illites in that the 001 reflections are broad and frequently asymmetrical and the *hkl* reflections are relatively weak. Moreover, the 001 spacing is frequently greater than 10.1 Å while the 003 spacing is less than 3.33 Å, the former being of greater intensity than the latter. The broad 001 peaks of both the synthetic and the natural materials vary in spacing with changes in humidity and mild heat-treatment indicating variation in the water content of some layers. These layers also adsorb ethylene glycol. The presence of expandable layers along with nonexpandable mica layers does not necessarily mean that they are intimately interstratified but that the intimacy of mixture is not discernible when potassium is the only interlayer cation.

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