THE HYDROTHERMAL TRANSFORMATION OF SODIUM AND POTASSIUM SMECTITE INTO MIXED-LAYER CLAY

Dennis Eberl

University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, U.S.A.

and

John Hower

Division of Earth Sciences, Geochemistry Program, National Science Foundation, Washington, D.C. 20550, U.S.A.

Abstract—The transformation of sodium and potassium smectite into mixed-layer clay was followed in hydrothermal kinetic experiments. Glasses of beidellite composition and the Wyoming bentonite were used as starting materials. Temperatures ranged between 260 and 490°C at 2 kbar pressure, and run times ranged between 6 hr and 266 days.

The course of the reactions was found to be strongly affected by interlayer chemistry. When potassium was the interlayer cation, increasing reaction produced the series: randomly interstratified illite/smectite–ordered interstratified illite/smectite–illite. This sequence is equivalent to that formed in shales during burial diagenesis. With interlayer sodium and temperatures above 300°C, an aluminous beidellite (Black Jack analog)–rectorite–paragonite series was realized. The difference between these two diagenetic families is discussed. Below 300°C, sodium beidellite formed randomly interstratified mixed-layer clay much like potassium beidellite, except that a higher layer charge was required to produce sodium mica-like layers. The higher charge resulted from sodium's higher hydration energy. The difference in hydration energy between potassium and sodium may account for the fixation of potassium rather than sodium in illite during burial diagenesis.

The appearance of ordered interlayering in mixed-layer phases is also related to interlayer chemistry. Ordering formed in sodium clays at high expandabilities, whereas it never appeared in the potassium clays above approximately 35% expandable. The appearance of ordering may be partly related to the polarizing power of the mica-like layers.

Phase diagrams, constructed from the kinetic experiments and from the composition and occurrence of natural clays, are presented for the systems paragonite and muscovite-2 quartz–kaolinite–excess water. This study also reports the first synthesis of a Kalkberg-type mixed-layer clay.

INTRODUCTION

It is well known that interlayer cations in smectite can be exchanged readily, and that exchange reactions, when performed at room temperature, do not appear to affect the chemistry of the 2:1 layers. At elevated temperatures, however, the 2:1 layers begin to react and chemically interact with the interlayer cations. Our experiments are addressed to these higher-temperature reactions.

The experiments study the difference in reaction between sodium and potassium smectites treated in an identical manner in hydrothermal bombs at 2 kbar pressure. Since the starting smectites initially have the same aluminosilicate composition, any difference in reaction must be ascribed to differences in the composition of the interlayers.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

There have been many hydrothermal studies of clay minerals. Partial summaries of previous work can be found in Grim (1968), and Millot (1970). It is fre-quently difficult, however, to draw petrologic conclusions from these studies because it is not known if the run products were in chemical equilibrium at the end of the experiments. Many of these studies also suffer from uncertainty with regard to the identification of run products, particularly mixed-layer clays. The present study used techniques designed to minimize these shortcomings. Rather than use single-run experiments at a given temperature, reactions were followed kinetically in an effort to discover the direction of the reaction and thereby predict end products. In addition, X-ray diffractograms of mixed-layer phases were identified by a detailed comparison with the computer-stimulated patterns of Reynolds and Hower (1970). Velde (1969) was the first to use these patterns to identify mixed-layer run products, and the present work is an outgrowth of this effort.

Details of the experimental and analytical techniques have been presented elsewhere (Eberl and Hower, 1975, 1976). Briefly, starting compositions (Table 1) were prepared by the Ludox gel method of Luth and Ingamells (1965). The ratios of the cations in the glasses are those of a beidellite, the structural formula for which can be written

Table 1. Glass starting compositions

Starting glass composition	Atomic proportions of			
	Si	Al	Na	K
II	1.0	0.64	—	0.093
III	1.0	0.64	0.019	0.074
IV	1.0	0.64	0.038	0.056
V	1.0	0.64	0.056	0.038
VI	1.0	0.64	0.074	0.019
VII	1.0	0.64	0.093	—

$Al_2(Si_{3.66}Al_{0.34})O_{10}(OH)_2(K,Na)_{0.34}$ after MacEwan (1961). Samples of Wyoming bentonite were also treated hydrothermally.

The starting compositions plus water were welded into gold capsules and reacted for various lengths of time in Tuttle bombs held at approximately 260, 300, 340, 390 and 490°C. The phases synthesized were, in part, identified by the X-ray peak positions given in Brown (1961). In addition, the expandability (per cent smectite) of the mixed-layer phase was determined by comparison between patterns of oriented, ethylene glycol-treated specimens and the previously mentioned patterns of Reynolds and Hower (1970). The peak positions found by Reynolds and Hower were calculated for mixed-layer illite/smectite (hereafter I/S). These positions were adjusted for clays synthesized from sodium composition VII to positions corresponding to a mixed-layer paragonite/smectite (hereafter Pa/S). The error in determining expandability is $\pm 5\%$. The presence of ordering at high expandabilities in the sodium clays was detected by the appearance of a superlattice reflection. The pH of the final run solutions was measured with a Beckman SS-3 pH meter from the damp to wet run product using a single-drop electrode.

TERMINOLOGY

A brief statement of terminology is presented because there is a confusion of usage. *Beidellite* is taken as a general name for dioctahedral smectites and mixed-layer clays in which the charge on the 2:1 structure is primarily tetrahedral (modified from Greene-Kelley, 1955). All the phases synthesized from glasses in this study are beidellites, since there were no divalent cations in the system. These beidellites include random and ordered mixed-layer I/S, random Pa/S, rectorite, and a highly-expandable smectite similar to the Black Jack beidellite.

Random and ordered I/S have been described by Reynolds and Hower (1970). They are an intimate interstratification of illite layers, in which the fixed interlayer cation is potassium, and smectite layers, with any exchangeable cation in the interlayer position. The *illite* layers are similar to muscovite, except that they do not have a full mica charge, and can have, for example, 0.8 equivalents of potassium/$O_{10}(OH)_2$ group (Hower and Mowatt, 1966). Natural occurrences of random and ordered I/S are closely

related. For example, in a study of shales from Gulf Coast oil wells, Perry and Hower (1970) found that I/S formed a series of clays that decreased in expandability with depth, going from a highly expandable randomly interstratified I/S near the surface, to an ordered I/S of low expandability at depth. The sodium analog of illite is called *brammallite* (Bannister, 1943).

Brown and Weir (1963a) have shown that *rectorite* is an ordered mixed-layer clay in which the mica-like layers are paragonite-like (the fixed interlayer cation is sodium), that the expanded layers are smectite-like, and that rectorite and allevardite are the same sodium aluminosilicate. Ideal rectorite is 50% expandable.
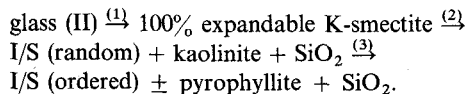
The *Black Jack beidellite* was studied by Weir and Greene-Kelley (1962). It is a 100% expandable smectite which has almost no octahedral substitution. Weir and Greene-Kelley recommended that it be regarded as a typical end-member beidellite, although it contains more aluminum than the ideal formula.

EXPERIMENTAL RESULTS

Results of the hydrothermal runs are presented in Table 2. The starting glasses were found to react according to Ostwald's step rule which, simply stated, says that the phase which involves the least change of entropy will form first, and then equilibrium will gradually be approached through a series of steps. In most cases, the initial phase to crystallize was a 100% expandable smectite which then reacted to form other phases. The mineralogy of the final products was a function of run time and temperature, and of whether the interlayer cation was potassium or sodium.

Reaction of the potassium glass (composition II)

Reaction for the K-rich starting composition II, observed for temperatures between 260° and 400°C with increasing run time, can be generalized as follows:

glass (II) $\xrightarrow{(1)}$ 100% expandable K-smectite $\xrightarrow{(2)}$
I/S (random) + kaolinite + SiO_2 $\xrightarrow{(3)}$
I/S (ordered) $\pm$ pyrophyllite + SiO_2.

The first step in this reaction went to completion in several days and will be ignored in the following discussion. The second and third steps, however, take place over months or years depending on the temperature.

The vital transformation in the second and third steps is the alteration of smectite layers into illite layers. This alteration is accomplished by the substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet. The resulting negative charge on the 2:1 layers is balanced by an increase in interlayer potassium. Generally speaking, the net result of this coupled substitution is to release aluminum and silicon to form kaolinite (or pyrophyllite) and SiO_2. The substitution of aluminum for silicon in a smectite layer continues until attraction between the negative 2:1 layers and the

Table 2. Hydrothermal runs at 2 kbar water pressure

Run No.	Starting comp.	Temp. (°C)	Run time (days)	Final pH at 25°C	Run products
1	II	260	99	5.0	I/S (85%), kao
2	II	260	266	—	I/S (65%), kao
3	II	300	31	4.2	I/S (85%), kao, Q, fspar
4	II	302	88	4.2	I/S (70%), kao, fspar (?)
5	II	343	1	—	poorly crystalline
6	II	343	5	—	I/S (90%)
7	II	343	23	4.6	I/S (80%), kao
8	II	347	88	3.8	(I/S) ord. (35%), Q (?)
9	II	338	99	4.7	(I/S) ord. (25%), Q (?)
10	II	393	1	—	poorly crystalline
11	II	394	3	4.4	I/S (70%), Q
12	II	392	14	4.2	I/S (70%), Q (?), py (?)
13	II	394	23	4.3	(I/S) ord. (35%), Q, py (?), fspar
14	II	394	169	—	(I/S) ord. (15%), Q, py
15	II	445	1	—	(I/S) ord. (?%)
16	II	492	6 hr	—	(I/S) ord. (33%)
17	II	492	11 hr	—	(I/S) ord. (33%)
18	II	492	16 hr	5.0	(I/S) ord. (35%), py
19	II	492	1 day	—	(I/S) ord. (30%)
20	II	492	3	—	(I/S) ord. (25%), Q (?), hyd
21	II	494	5	—	(I/S) ord. (30%), py, hyd. (?)
22	II	494	14	4.3	(I/S) ord. (10%), Q, py, fspar
23	II	492	24	4.8	(I/S) ord. (10%), crist, py, hyd
24	II	524	10	—	(I/S) ord. (5%), Q, hyd (?)
25	III	300	31	4.1	(I,Pa)/S (85%), kao, Q, fspar (?)
26	IV	260	99	4.4	(I,Pa)/S (80%), kao
27	IV	300	31	—	(I,Pa)/S (65%), kao, Q, fspar
28	V	260	99	—	(Pa,I)/S (90%), kao
29	V	260	266	3.8	(Pa,I)/S (75%), kao, Q
30	V	302	88	4.4	(Pa,I)/S (90%), kao
31	V	300	95	—	(Pa,I)/S (80%), kao
32	V	343	1	—	no reaction
33	V	343	5	—	(Pa,I)/S (95%)
34	V	343	23	4.2	(Pa,I)/S (90%)
35	V	347	88	4.1	(Pa,I)/S (85%)
36	V	338	99	5.1	(Pa,I)/S (80%), kao, Q (?), fspar (?)
37	V	350 (?) erratic	218	—	[(Pa,I)/S] ord (70%), kao, Q, fspar
38	V	393	1	—	poorly crystalline
39	V	394	3	4.4	(Pa,I)/S (95%)
40	V	392	14	4.3	[(Pa,I)/S] ord (90%), Q
41	V	394	23	4.5	[(Pa,I)/S] ord (85%), Q
42	V	394	169	4.5	[(Pa,I)/S] ord (50%), Q, illite
43	V	445	1	—	(Pa,I)/S (90%)
44	V	492	6 hr	—	(Pa,I)/S (95%)
45	V	492	11 hr	—	(Pa,I)/S (85%)
46	V	492	16 hr	5.5	[(Pa,I)/S] ord (55%), Q, fspar
47	V	494	1 day	—	[(Pa,I)/S] ord (55%), Q, fspar
48	V	492	3	—	[(Pa,I)/S] ord (50%), Q (?), fspar py (?), hyd (?)
49	V	494	5	—	[(Pa,I)/S] ord (45%), py, Q
50	V	494	14	5.1	[(Pa,I)/S]ord (40%), Q, py, fspar
51	V	492	24	4.9	[(Pa,I)/S]ord (30%), py, Q, fspar, hyd
52	VI	300	95	—	(Pa,I)/S (85%), kao
53	VI	343	123	4.3	smectite (100%), Q, fspar
54	VII	260	92	—	Pa/S (90%), kao
55	VII	260	259	4.6	Pa/S (70%), kao
56	VII	305	88	4.2	Pa/S (90%)
57	VII	300	95	—	Pa/S (75%), kao
58	VII	343	1	—	Pa/S (95%), kao
59	VII	343	5	—	Pa/S (85%), kao
60	VII	343	23	4.7	Pa/S (90%), Q (?)
61	VII	338	99	5.0	Pa/S (90%), kao, Q
62	VII	350 (?) erratic	218	—	(Pa/S) ord (70%), kao, Q
63	VII	393	1	—	poorly crystalline
64	VII	394	3	—	smectite (100%), kao
65	VII	393	5	—	smectite (100%), kao
66	VII	392	14	4.7	smectite (100%), Q (?)
67	VII	394	23	4.2	smectite (100%)

Table 2—*continued*

Run No.	Starting comp.	Temp. (°C)	Run time (days)	Final pH at 25°C	Run products
68	VII	394	169	4.6	smectite (100%), Q
69	VII	445	1	—	smectite (100%)
70	VII	492	16 hr	5.3	poorly crystalline
71	VII	494	1	—	Pa/S (85%)
72	VII	492	3	4.9	(Pa/S) ord (?) (90%), Q, fspar, Pa
73	VII	494	5	—	(Pa/S) ord (60%), Q, fspar
74	VII	494	14	—	(Pa/S) ord (40%), Q, fspar, py
75	VII	492	24	5.0	(Pa/S) ord (35%), Q, py
90	Wyo. bentonite (K-saturated)	215	167	5.0	(I/S) ord (35%), Q (?)
91	,,	250	167	4.9	(I/S) ord (20%), KCl
92	,,	493	1	—	(I/S) ord (20%), KCl
93	,,	285	74	4.1	(I/S) ord (35%), Q (?), KCl
94	,,	330	74	5.4	(I/S) ord (30%), kao, Q, KCl
95	,,	379	169	5.2	Kalkberg (15%), kao, Q
96	Wyo. bentonite (Na-saturated)	250	167	—	no reaction
97	,,	285	74	4.7	Pa/S (90%), NaCl
98	,,	330	74	5.1	Pa/S (90%), kao, Q, NaCl
99	,,	493	1	—	(Pa/S) ord (35%), chlorite, NaCl
100	,,	379	169	4.4	(Pa/S) ord (50%), kao, Q, fspar

I/S (85%) is an 85% expandable randomly mixed-layer illite/smectite; (I/S) ord (35%) is a 35% expandable ordered mixed-layer illite/smectite; Pa/S is a mixed-layer paragonite/smectite; (Pa, I)/S is mixed layer clay in which the mica-like layers may be either paragonitic or illitic; kao is kaolinite; Q is quartz; fspar is feldspar; py is pyrophyllite; crist is cristobalite; hyd is hydralsite.

positive interlayer potassium becomes greater than attraction between potassium and its shell of hydrating water. At this point potassium dehydrates. Water is expelled from the interlayers and potassium is fixed, converting the expandable smectite structure into that of an illite. The appearance of illite layers in the mixed-layer phase could be described with first order kinetic equations for most runs (Eberl and Hower, 1976). The longer the run time, the lower was the expandability of the I/S (see Runs 1–14, Table 2).

The first I/S to form in runs below 400°C had a random distribution of illitic and expanding layers. When the reaction had proceeded to approximately

similar to that written for composition II, except that the randomly interstratified mixed-layer phases presumably contained paragonite-like (or brammallite-like) layers as well as illite and smectite layers (runs 25–29, 54–55). Above 300°C, however, the simple conversion of smectite to mica-like layers was replaced by the remarkable appearance of a highly expandable and stable beidellite phase. At higher temperatures this phase was converted, with time, into rectorite. X-ray patterns of these phases are given in Figures 3 and 4. These reactions for the sodium end-member composition with increasing run time can be summarized as follows:

$$\text{glass (VII)} \xrightarrow{260°C} 100\% \text{ expandable smectite} \xrightarrow{260°C} \text{Pa/S (random)} + \text{kaolinite} + SiO_2$$

$$\text{glass (VII)} \xrightarrow{390°C} 100\% \text{ expandable smectite (Black Jack analog)} + SiO_2$$

$$\text{glass (VII)} \xrightarrow{490°C} 100\% \text{ expandable smectite} \xrightarrow{490°C} \text{rectorite} + \text{pyrophyllite} + SiO_2$$
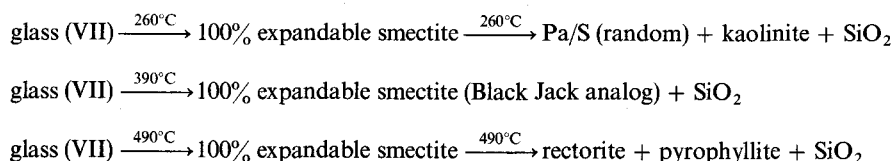
35% expandable layers, however, ordering could be detected. Above 400°C the glasses reacted directly to form a 35% expandable ordered I/S plus pyrophyllite and other phases (runs 16–24). X-ray patterns of random and ordered I/S synthesized from composition II are given in Figures 1 and 2.

Reaction of glasses that contained sodium (compositions III–VII)

Below approximately 300°C, the glasses that contained sodium followed a first-order reaction course

Reaction of Wyoming bentonite with excess Na *and* K

Potassium Wyoming bentonite with excess potassium (as KCl) reacted very quickly to form ordered mixed-layer structures and other phases between 250 and 490°C (runs 91–95). Run 95 is of special interest since it produced a Kalkberg-type clay (ISII ordering, see Reynolds and Hower, 1970), a diffraction pattern of which is shown in Figure 5. Potassium glass runs did not produce this phase.
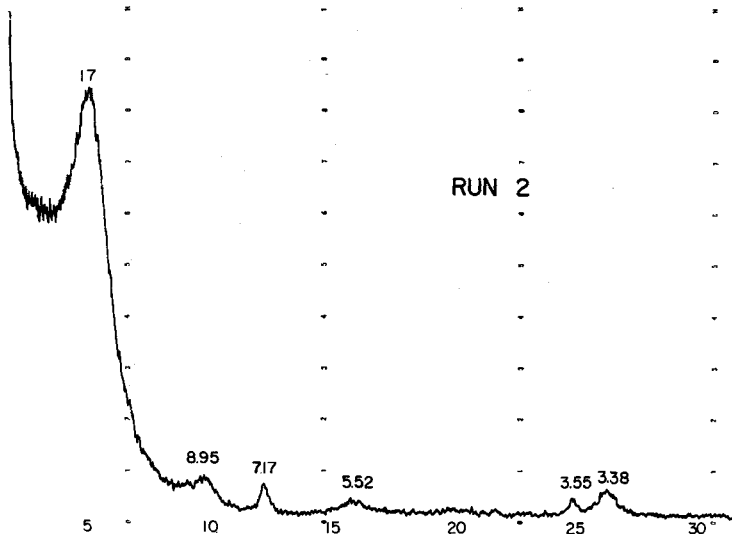
Figure 1. I/S (65%) and kaolinite formed from composition II at 260°C and 2 kbar water pressure after 266 days. Treated with ethylene glycol.
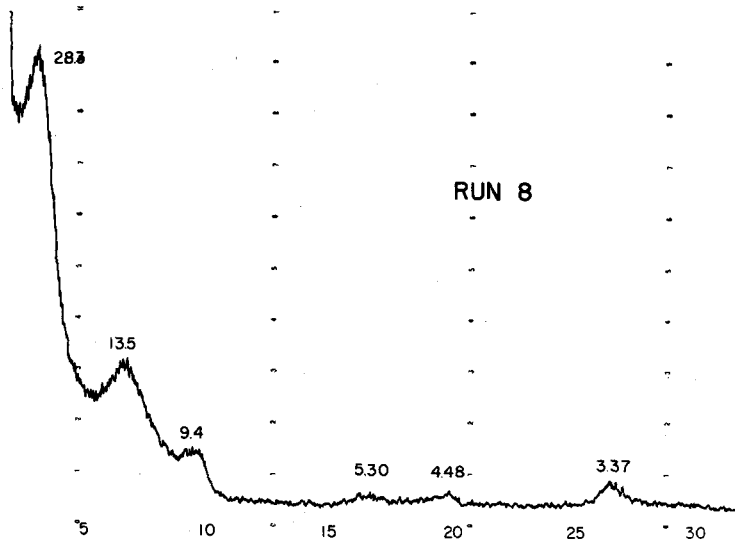

Figure 2. I/S ordered (35%), feldspar and quartz (?) formed from composition II at 347°C and 2 kbar water pressure after 88 days. Treated with ethylene glycol.
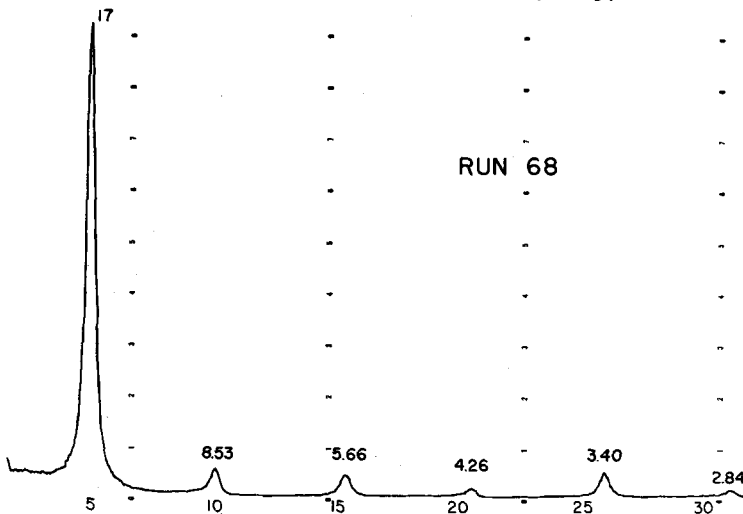

Figure 3. Black Jack analog and quartz formed from composition VII held at 394°C and 2 kbar water pressure for 169 days. Treated with ethylene glycol.
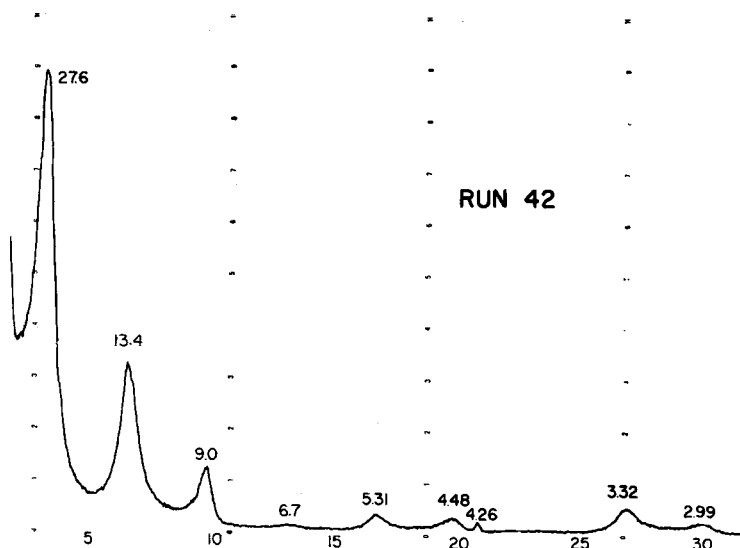
Figure 4. Rectorite (50%), quartz and illite (?) formed from composition V held at 394°C and 2 kbar water pressure for 169 days. Treated with ethylene glycol.

The sodium bentonite (run with excess NaCl) showed little tendency to react below approximately 350°C (runs 97–98). Above this temperature it formed rectorite and other phases (runs 99–100). An X-ray pattern of such a rectorite is given in Figure 6. Run conditions were identical for the products shown in Figures 5 and 6.

REACTIONS OF POTASSIUM AND SODIUM SMECTITES COMPARED

It was shown that the reactions of compositions II and VII to form randomly interstratified mixed-layer clay were similar: both initially reacted to form 100% expandable clay, and both subsequently formed mica-like layers with increasing run time. There were,

however, three important differences: (1) the potassium clay appears to have formed mica-like layers slightly faster (Table 3); (2) the sodium clay reacted to form more kaolinite (Figure 7); and (3) the sodium clay, for the most part, formed randomly interstratified clay only below 300°C, whereas the potassium clay formed it at all temperatures below 400°C.

In Figure 7 the appearance of kaolinite and the concomitant disappearance of smectite is followed from X-ray diffractograms by plotting the ratio of peak heights of the kaolinite 002 to the 003/005 of the mixed-layer phase. This ratio is used as an approximate measure of the relative proportions of kaolinite to I/S and Pa/S. The figure shows that as expandability decreased, the amount of kaolinite relative to I/S or Pa/S increased, as is to be expected
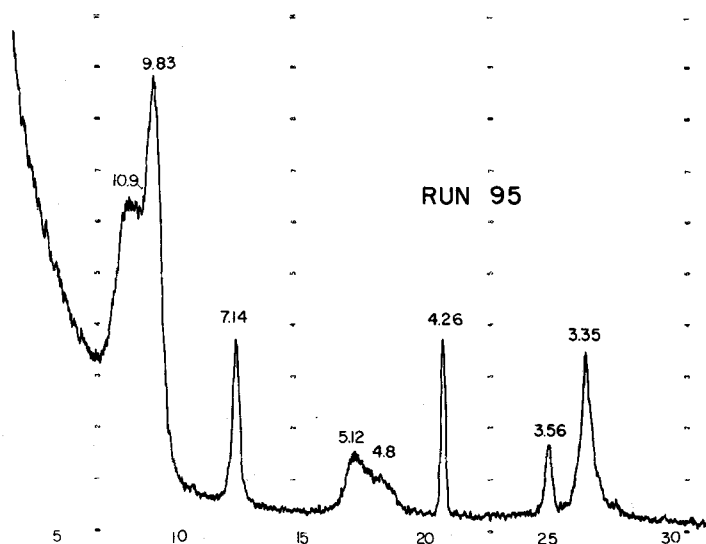

Figure 5. I/S (15%-Kalkberg ordering), kaolinite and quartz formed from K-saturated Wyoming bentonite held at 379°C and 2 kbar water pressure for 169 days. Treated with ethylene glycol.
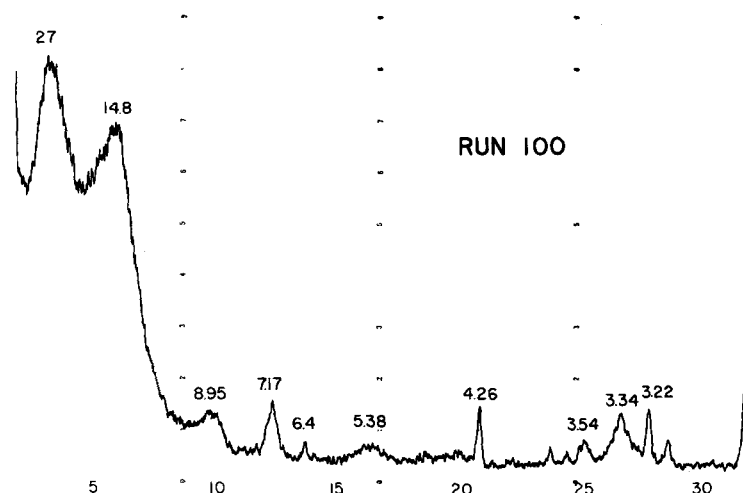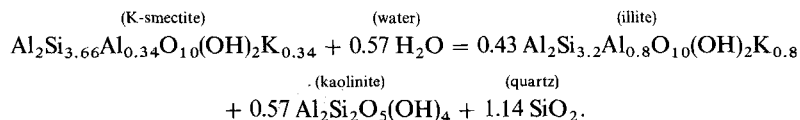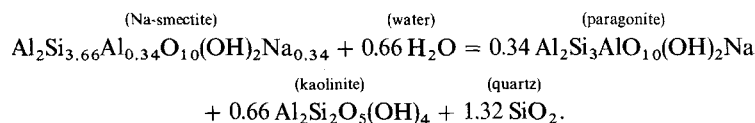
Figure 6. Rectorite (50%), kaolinite, quartz and feldspar formed from Na-saturated Wyoming bentonite held at 379°C and 2 kbar water pressure for 169 days. Treated with ethylene glycol.

from the reaction: smectite → I/S (or Pa/S) + kaolinite + quartz. It also shows that for reaction to a given expandability, the sodium composition VII produced more kaolinite than did the potassium composition II, and that the intermediate composition V produced an intermediate amount of kaolinite. The use of peak intensities as a measure of the relative amounts of kaolinite and mixed-layer clay is only an approximation, because differences in the structure factor between paragonite and illite will tend to suppress the 003/005 reflection of Pa/S relative to I/S, thereby apparently increasing the amount of kaolinite for the sodium clays. Calculations using the computer program of Reynolds and Hower (1970), however, show that the structure factors alone are insufficient to account for the observed differences in X-ray peak intensities.

In order to account for the first two of the aforementioned differences in reaction, namely, that the potassium composition produces less kaolinite and reacts faster, we assume that the mica-like layers in the sodium clay are more alkali-rich. Reactions for the transformation of a single smectite layer can be written as follows. For the potassium smectite:

group to form a non-expanded layer, whereas potassium smectite need only develop an illite charge of -0.8 equivalents/$O_{10}(OH)_2$. Thus the formation of paragonite layers yields 9 mole % more kaolinite than does the formation of illite layers.

The assumption that the mica-like layers in the sodium clay are more alkali-rich is justified by appealing to the difference in hydration energy between sodium and potassium. Sodium, with its larger hydration energy, will hold water molecules more tightly. Thus a greater negative charge must develop in the 2:1 lattice, with a concomitant greater amount of interlayer alkali, to dehydrate sodium and collapse a layer. In addition to producing more kaolinite, this mechanism also predicts that sodium smectites will decrease in expandability more slowly than potassium smectites since they require more tetrahedral substitution for collapse. The fact that sodium has a greater hydration energy than potassium in the interlayer region of smectite has been demonstrated by Shainberg and Kemper (1966).

The third difference in reaction is difficult to explain: below 300°C the sodium composition formed

(K-smectite)   (water)   (illite)
$$Al_2Si_{3.66}Al_{0.34}O_{10}(OH)_2K_{0.34} + 0.57 H_2O = 0.43 Al_2Si_{3.2}Al_{0.8}O_{10}(OH)_2K_{0.8}$$

(kaolinite)   (quartz)
$$+ 0.57 Al_2Si_2O_5(OH)_4 + 1.14 SiO_2.$$

For the sodium smectite:

(Na-smectite)   (water)   (paragonite)
$$Al_2Si_{3.66}Al_{0.34}O_{10}(OH)_2Na_{0.34} + 0.66 H_2O = 0.34 Al_2Si_3AlO_{10}(OH)_2Na$$

(kaolinite)   (quartz)
$$+ 0.66 Al_2Si_2O_5(OH)_4 + 1.32 SiO_2.$$

The important difference between these reactions is that the sodium-smectite must develop, for example, a full mica charge of -1.0 equivalents/$O_{10}(OH)_2$

randomly mixed-layer clay with time; yet at 390° there was a complete reversal in the reaction sequence and a highly expandable smectite appeared to be

Table 3. The expandability of mixed-layer phases produced from the reaction of compositions II and VII at 260°C and 2 kbar

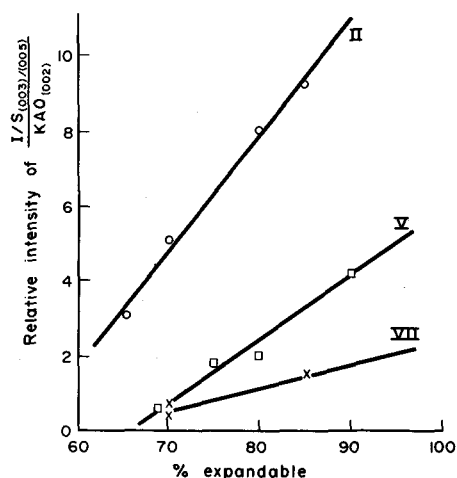| Run time (days-approximate)	Expandability of the mixed-layer phase K-smectite (II)	Na-Smectite (VII)	K Run No.	Na Run No.
95	85%	90%	1	54
260	65%	70%	2	55

Figure 7. The relationship between the expandability of the mixed-layer phase (here labeled I/S) and the relative proportions of the mixed-layer phase to kaolinite (based on the relative heights of their X-ray peaks) for three starting compositions.

stable. At higher temperatures this smectite reacted directly to form an ordered mixed-layer structure. This change in the nature of the reaction with temperature for the sodium clays may be related to a fundamental change in the crystal chemistry of the 2:1 layers formed above 300°C. Evidence will be presented that the high-temperature smectite and the higher-temperature ordered phase are analogous to the naturally occurring Black Jack beidellite and rectorite, and that they contain aluminum and hydroxyls in excess of that expected for dioctahedral clay minerals. Perhaps the incorporation of these extra components into the lattice leads to the change in behavior above 300°C.

The striking difference in reaction between the sodium and potassium clays at 390°C is summarized in Table 4. Here the potassium clay continued to form

mica-like layers with increasing run time, whereas the sodium clay remained 100% expandable. These runs demonstrate that the interlayer cation strongly affects reaction in the 2:1 layers. Temperature, for example, is not the sole factor determining the rate of Al^{3+} for Si^{4+} substitution in the tetrahedral layers.

Table 5 emphasizes the difference in expandabilities found for the appearance of ordering. Ordering developed at high expandabilities in the sodium clay, whereas in these experiments it never appeared above approximately 35% expandable at any temperature in the potassium clays. Reaction products for Wyoming bentonite with excess potassium and sodium, shown in Table 6, demonstrated reaction sequences analogous to those of the glasses.

Some insight into the difference in expandability for the appearance of ordering (Table 5) can be gained by appealing to the ordering mechanism of Sawhney (1967) for mica/vermiculite. Picture a mica-like layer in which interlayer cations are tightly bound in hexagonal holes between adjacent 2:1 layers. Two tetrahedral sheets, one from each 2:1 layer, face each other across the mica interlayer. The opposite tetrahedral sheets face expanded interlayers. For ordering to occur, the mica interlayer must somehow keep an adjacent expanded interlayer open as the reaction proceeds. Sawhney suggests that polarization of electron densities in the 2:1 layers towards the mica interlayer should take place because of the shorter cation-oxygen bond lengths. This polarization would make the tetrahedral sheets adjacent to the expanded interlayers effectively less negative. If they are less negative, then collapse of an adjacent expanded interlayer would be more difficult since more substitution of Al^{3+} for Si^{4+} would be required to develop sufficient negative charge to dehydrate the interlayer cation. Evidence also suggests that such polarization makes Al^{3+} substitution in adjacent expanded layers more difficult (Eberl, in preparation). According to this

Table 4. The expandability of mixed-layer phases produced from the reaction of composition II and composition VII at 390°C and 2 kbar

Run time (days)	Expandability of mixed-layer phase K-smectite (II)	Na-smectite (VII)	K Run No.	Na Run No.
1	poorly crystalline	poorly crystalline	10	63
3	70%	100%	11	64
5	—	100%	—	65
14	70%	100%	12	66
23	35% (ordered)	100%	13	67
169	15% (ordered)	100%	14	68

Table 5. The expandability and first appearance of ordering for mixed-layer phases produced from the reaction of composition II and composition VII at 490°C and 2 kbar

Run time (days)	Expandability of mixed-layer phase		K Run No.	Na Run No.
	K-smectite (II)	Na-smectite (VII)		
2/3	35% (ordered)	poorly crystalline	18	70
1	30% (ordered)	85% (random)	19	71
3	25% (ordered)	90% (ordered?)	20	72
5	30% (ordered)	60% (ordered)	21	73
14	10% (ordered)	40% (ordered)	22	74
24	10% (ordered)	35% (ordered)	23	75

model, an increase in the polarizing power of the mica interlayer would favor ordering.

It is reasonable to assume that a paragonite-like layer formed in a sodium mixed-layer clay has more polarizing power than an illite layer formed in a potassium clay. As was discussed previously, sodium mica-like layers contain more alkalis and are therefore more polar. In addition, the smaller sodium cation has a greater ionic potential than potassium and can penetrate more deeply into the 2:1 layers.

Whereas one paragonite layer may be sufficient to inhibit the formation of mica in neighboring layers, it may take groups of two illite layers to develop enough polarizing power to inhibit the formation of neighboring illite layers. In other words, partial ordering for sodium mixed-layer clays should occur at high expandabilities, with full ordering at 50% expandable. Full ordering would occur at $33\frac{1}{3}$% expandable for potassium clays. This situation is observed both in nature and in hydrothermal runs made above 300°C.

The model predicts that a fully ordered structure should first appear at expandabilities that are reciprocals of whole numbers. Glauconite appears to fit this model. In glauconite ordering appears at about 25% expandable (Thompson and Hower, 1975), a situation in which three collapsed layers are necessary to keep an adjacent layer open. Thompson and Hower have shown that mica-like layers in glauconite contain significantly less potassium than do those in an I/S. With less potassium they have less polarizing power.

Another factor leading to ordering, in addition to the polarization of electron densities, may be the rotation of octahedral hydroxyls due to repulsion between the interlayer cation and hydroxyl hydrogen. Giese (1974) has shown that this repulsion can affect interlayer bond energies in micas. Rotation of a hy-

droxyl away from mica-like layers would bring a positive hydrogen ion closer to an adjacent expanded layer, making the layer more difficult to collapse. A clay structure with extra hydroxyls, such as that postulated for rectorite, would thus more readily form ordered interstratification.

The above explanation for the development of ordering in mica/smectite minerals is offered in a tentative fashion. Clearly it is not the whole story because, as will be shown, ordering may develop in a clay that is 100% expandable before any interlayer collapse has occurred. The influence of interlayer cations on ordering has been emphasized. Undoubtedly the composition of the 2:1 layers is also influential, but this effect was not investigated.

APPLICATIONS OF THE EXPERIMENTAL RESULTS TO THE PETROLOGY OF NATURAL CLAYS

An origin for illite

A theory on the origin of illite must unite the following observations on the crystal chemistry of illite: (1) the charge on the illite structure is primarily tetrahedral (Grim, 1968); (2) illite contains less potassium per $O_{10}(OH)_2$ than does mica (Hower and Mowatt, 1966); and (3) the fixed interlayer cation in illite is primarily potassium (Grim, 1968).

One likely origin for illite is from the reaction of smectite during burial diagnesis. The mineralogic evidence of Perry and Hower (1970) for this origin has already been discussed, and the reaction sequence found by them was duplicated in the present experiments. Chemical evidence for this origin comes from the analyses of Weaver et al. (1971), Foscolos and Kodama (1974) and Hower et al. (1976). Their

Table 6. Differences in the mixed-layer phases produced by the reaction of K-saturated and Na-saturated Wyoming Bentonite at 2 kbar

Run temperature	Run time (days)	Expandability of mixed-layer phase		K Run No.	Na Run No.
		K-bentonite	Na-bentonite		
285	74	35% (ordered)	90%	93	97
330	74	30% (ordered)	90%	94	98
379	169	15% (ISII ordering)	50% (ordered)	95	100

analyses of illite/smectites from burial diagenetic sequences show that the charge necessary for illite formation is built in the 2:1 smectite layers by the substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet. The analyses of Hower et al. (1976) further demonstrate that the fixed interlayer cation in Gulf Coast I/S is almost entirely potassium, and that the mica-like layers have an illite charge rather than a full mica charge.

The mechanism of illite formation during burial can be related to the hydration energy of potassium. Geothermal heating drives a reaction which substitutes Al^{3+} for Si^{4+} in smectite's tetrahedral sheet. When a sufficient negative charge on the 2:1 layers have been developed, a charge which is somewhat less than that of a muscovite, interlayer potassium dehydrates and the 2:1 layers collapse irreversibly around it, forming illite. Cations with lower hydration energies than potassium, such as rubidium and cesium, should also be concentrated in illite. Sodium and other cations with higher hydration energies remain hydrated and are replaced by potassium in the collapsing layers. When the reaction has proceeded to completion, a situation which is found in geothermal wells at temperatures between 200° and 230°C (Eslinger and Savin, 1973), all of the smectite layers in I/S will have been converted into illite. Potassium for the reaction comes from the breakdown of detrital minerals such as muscovite and potassium feldspar, as has been demonstrated by Hower et al. (1976).

The relationship between the Black Jack beidellite and rectorite

The Black Jack beidellite is an extremely rare 100% expandable smectite which, as was discussed earlier,
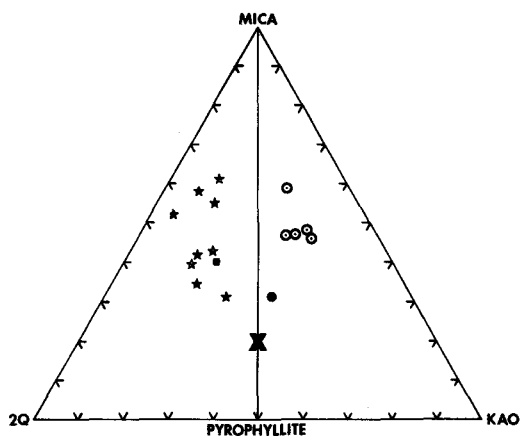

Figure 8. Compositions of some natural mixed-layer clays plotted in the system mica–2 quartz–kaolinite. The stars are I/S analyses from Hower and Mowatt (1966), Schultz (1969) and Hower et al. (1975). The solid square is the Beidel beidellite from Schultz (1969). The open circles are rectorite analyses from Brown and Weir (1963b) and Brindley (1956). The solid circle is the Black Jack beidellite from Weir and Greene-Kelley (1962). The "x" marks the ideal beidellite composition and is also the starting glass composition.

has almost no octahedral substitution. A chemical analysis of a Black Jack specimen made by Weir and Greene-Kelley (1962) is plotted as a solid circle in the system mica–kaolinite–2 quartz in Figure 8. In order to plot compositions in this system, magnesium and iron from the analyses were converted into equivalents of aluminum, and calcium into equivalents of sodium. All the alkalis were then converted into moles of mica. The aluminum left over from this step was converted to moles of kaolinite and the excess silica to quartz. The ideal beidellite composition falls where the X is plotted on the line joining pyrophyllite with mica. This composition is also the starting glass compositions for the hydrothermal experiments. The chemical analysis of the Black Jack beidellite falls to the right of this join, indicating that it is aluminum-rich.

As was mentioned previously, hydrothermal runs of composition VII made at 390°C (runs 66–68) produced a smectite (Figure 3) which is analogous to the Black Jack beidellite. Both the natural and the synthetic beidellites are 100% expandable and give similar diffraction patterns. Both are hydrothermal in origin and have sodium as the interlayer cation. Like the Black Jack, the synthetic smectite is thought to be aluminum-rich since the longest run (run 68) produced the smectite and quartz, indicating that the smectite's composition may also lie to the right of the pyrophyllite–mica join.

The structure of the Black Jack analog is closely related to that of rectorite. A particularly interesting feature of its diffraction pattern is a small peak at about 34 Å in the glycol-solvated sample which can be seen when the X-ray unit is run on a sensitive range. This peak indicates that the smectite has developed a rectorite-like super-lattice even though it is 100% expandable. This ordering may be between high- and low-charge 17 Å layers. The high-charge layers have not yet developed sufficient charge to form paragonite. On potassium saturation, however, the smectite converted into a 90% expandable mixed-layer clay, indicating that 10% of the layers had sufficient charge to form illite. Many naturally-occurring smectites that appear to have a distribution of interlayer charge behave in a similar manner.

The close relationship between the two structures was also evident in experiments in which the Black Jack analog converted into a rectorite-like phase with increasing run time and temperature. For example, at 390°C the analog appears to be stable, but at 490°C rectorite was synthesized (runs 70–75). A 99-day run of composition VII made at 338°C (run 61) produced the analog whereas a 218 day run with an erratic temperature which centered around 350°C (run 62) produced a rectorite-like 70% expandable structure. The best rectorite came from a 169 day run of composition V made at 390°C (run 42). The diffraction pattern shows that it has the ideal 50% expandable structure. The rate of formation of collapsed layers in runs 39–41 leading to the production of this rector-

ite shows that the formation of mica-like layers in run 42 had showed or stopped at 50% expandable, indicating that this phase may be stable.

The Black Jack beidellite and rectorite are related compositionally as well as structurally. The chemical compositions of some natural rectorites, plotted in Figure 8, also fall to the right of the pyrophyllite–mica join and appear to form a compositional trend with the natural Black Jack sample. The compositional similarity, and the fact that the Black Jack analog shows indications of ordering in the 100% expandable state and that it can be converted into rectorite, suggest that the Black Jack beidellite is a lower-temperature predecessor of rectorite for which alternate layers have not yet collapsed.

It is not known whether the Black Jack beidellite is a stable mineral or if it is a metastable phase, which, if given enough time, will always react to form rectorite. If such a smectite is stable, then its apparent rarity suggest that it forms under very limited physiochemical conditions. The hydrothermal experiments show that it forms at a lower temperature than rectorite in a system that contains more sodium than potassium. This type of high-temperature smectite may turn out to be more common than is presently thought. It is likewise unknown if natural rectorite can have a whole range of expandabilities as was found in the hydrothermal runs, or if it only exists in nature at 50% expandable layers. Since most of the rectorite analyses shown in Figure 8 plot in the same area, it is probable that the 50% expandable structure is the stable phase.

The difference between mixed-layer I/S and rectorite

The compositional difference between I/S and rectorite is evidence in Figure 8: illite/smectites plot along a trend of increasing mica content (decreasing expandability) to the left of the ideal beidellite, and rectorites plot along the previously discussed trend to the right of ideal beidellite. If mixed-layer I/S were simple mixtures of ideal beidellite and mica, then their compositions should fall along the line between pyrophyllite and mica in Figure 8. Their compositions may fall to the left of this line as a function of plotting. For example, a mixed-layer montmorillonite–mica such as $Al_{1.5}Mg_{0.5}Si_4O_{10}(OH)_2X_{0.5}^+$ has an Si/Al ratio of 2.2 after Mg has been converted into equivalents of Al. A mixed-layer beidellite/mica of equivalent expandability such as $Al_2Si_{3.5}Al_{0.5}O_{10}(OH)_2X_{0.5}^+$, however, has a Si/Al ratio of only 1.4. Thus, mixed-layer compositions can fall to the left

of the mica–pyrophyllite join if there is some octahedral as well as tetrahedral substitution. Moving from the mixed-layer I/S just discussed to the right in Figure 8, the pyrophyllite–mica join represents the minimum Si/Al ratio possible for an ideal 2:1 dioctahedral clay mineral. Dioctahedral 2:1 clays plotting to the right of this line have extra aluminum in their structure.

How this excess aluminum is held is not known, but Brindley (1956), in a comparison of calculated and observed structure factors and electron density distribution curves along c^* to the chemical analysis of the Allevard rectorite, concluded that the rectorite formula is best written based on $O_{9.7}(OH)_{2.3}$ rather than $O_{10}(OH)_2$. In this structure, excess aluminum could substitute for silicon in the tetrahedral layer and be electrically balanced by extra hydroxyls. Evidence for extra hydroxyls in beidellites has been presented by Schultz (1969). A second possiblity is that extra aluminum is held in the interlayer position.

A summary of the differences between I/S and rectorite mixed-layer families is presented in Table 7.

SUMMARY OF THE PHASE RELATIONS

The hydrothermal system $Al_2Si_{3.66}Al_{0.34}O_{10}$ $(OH)_2(K,Na)_{0.34}$–excess H_2O reacted according to Ostwald's step rule. Therefore a kinetic study was justified and could be used to predict end products. Whether or not these end products are equilibrium assemblages at the experimental temperatures is not known since synthesis experiments are necessarily limited to short reaction times and simple conditions. Ostwald's step rule, which leads to a prediction of the end assemblage, also limits that prediction since the end product itself may be metastable and, once reached, begin reacting towards another assemblage.

Between 260° and 490°C, potassium beidellite (composition II) reacted through a series of intermediate illite/smectites towards illite as a final product. Run times were not long enough to reach a purely non-expandable illite, but, as was mentioned earlier, Eslinger and Savin (1973) have presented evidence that mixed-layering disappears above 230°C in geothermal wells. Thus between 260° and 345°C the end assemblage is illite, kaolinite and quartz. Quartz is slow to crystallize, and so did not appear in the 260°C runs: here silica was amorphous. Quartz did begin to appear in the longer runs at 300°C. Trace amounts of feldspar also showed up in the reaction products

Table 7. I/S and rectorite families compared

| Property	I/S family	Rectorite family
fixed interlayer cation	K^+	Na^+
first appearance of ordering	35% expandable	at high expandabilities
charge on mica-like layers	<1.0 equivalent/O_{10} (OH)$_2$	≥1.0 equivalent/$O_{10}(OH)_2$
amount of aluminum	≤ ideal dioctahedral structure	> ideal dioctahedral structure
temperature of formation in nature	burial metamorphic temperatures (50°–200°C)	higher temperatures
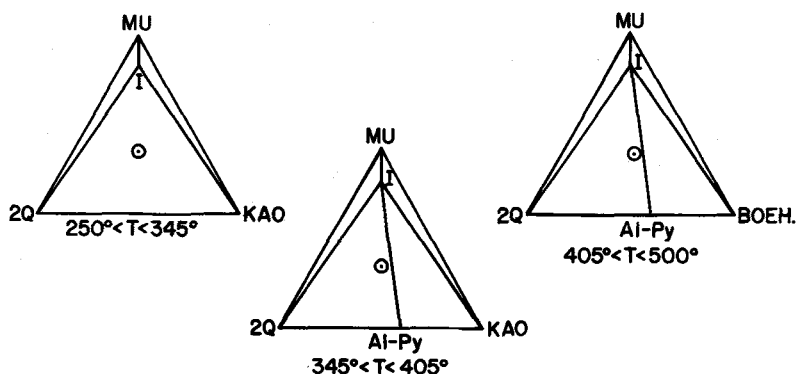
Figure 9. Phase relations in the system muscovite (MU)—2 quartz (Q)—kaolinite (KAO) or boehmite (BOEH), excess water. Al-Py is aluminum-rich synthetic pyrophyllite. I is illite. The dotted circle is starting glass composition II.

at 300°C; because they disappeared with increasing run time and temperature, the feldspar is considered unstable. At 345°C, pyrophyllite formed and the assemblage is illite, pyrophyllite and quartz.

The above interpretation for the reaction of potassium beidellite is at odds with that of Velde (1969). Starting with a similar run composition at 2 kbar, and using single-run experiments, Velde found mixed-layer I/S existing as a stable phase up to 400°C. The kinetic data casts doubt on this interpretation. I/S at these temperatures is most likely unstable and is reacting toward forming illite. Velde also has pyrophyllite appearing as a reaction product at about 300°C, whereas it was not found in our runs below 345°C. This discrepancy is unexplained.

The sodium composition VII formed a randomly interstratified mixed-layer clay at 260°C which continued to form mica-like layers with increasing run time. The final products at this temperature are thought to be brammallite, kaolinite and quartz. At 390°C the starting composition lies in a two-phase field quartz–beidellite. The beidellite is the 100%

expandable Black Jack analog. At 490°C this beidellite reacts to form an ordered mixed-layer structure which decreases in expandability with run time. A stable rectorite with the ideal 50% expandable layers was not realized from composition VII, but its stability field, which appears at lower temperatures with composition V, is thought to lie between 390° and 490°C. At 490°C rectorite has become unstable, and the system reacted toward forming a final assemblage of paragonite, pyrophyllite and quartz.

A summary of probable phase relations are presented in Figures 9 and 10. These diagrams are considered speculative. Furthermore, the temperatures given are probably somewhat higher than those found in nature due to the short reaction times and chemical purity of the synthetic systems. But the assemblages presented do seem to fit natural associations. The beidellite from Black Jack Mine, Colorado, for example, occurs with quartz, as is predicted from a composition which lies in the quartz–beidellite field in Figure 10. Henderson (1971) found an association of rectorite, illite, quartz and pyrophyllite in Paleozoic shales
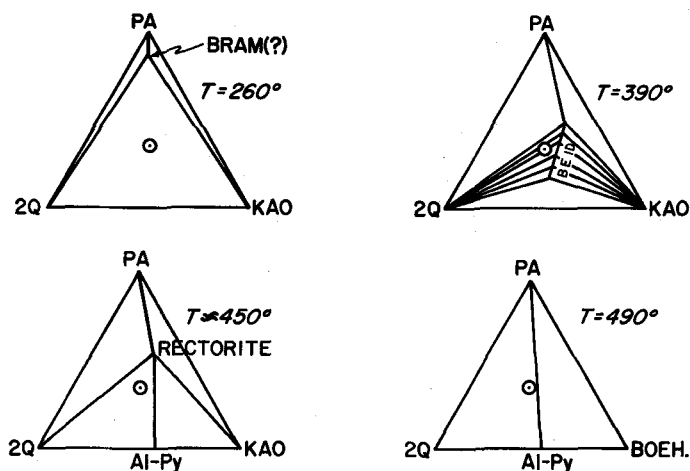

Figure 10. Phase relations in the system paragonite (Pa)–2 quartz (Q)–kaolinite (KAO) or boehmite (BOEH), excess water. BRAM is brammallite; BEID is the 100% expandable Black Jack beidellite analog; Al-Py is aluminum-rich synthetic pyrophyllite. The dotted circle is starting glass composition VII.

from Utah. Such an assemblage is predicted in combining Figures 9 and 10 into a tetrahedral diagram at about 450°C.

CONCLUSIONS

When a smectite is transformed by heat and pressure into a mixed-layer clay, the course of the reaction is influenced by the chemistry of the interlayers. Interlayer cations influence both the rate of substitution in the 2:1 layers, and the amount of substitution that must be accomplished to form a mica-like layer. Interlayer potassium gives rise to an illite/smectite series. This family forms in nature during burial diagenesis. Here potassium is preferentially fixed because potassium, of the abundant cations, is most easily dehydrated. Below 300°C, interlayer sodium gives rise to a family of mixed-layer clays similar to the illite/smectites. Above 300°C, however, sodium smectites react to form the rectorite series, which includes the Black Jack beidellite. The difference in reaction for sodium clays beginning at 300°C may result from the incorporation of extra aluminum and hydroxyls into the 2:1 layers.

The first appearance of ordering is also related to interlayer chemistry. With potassium, ordering never appeared in these experiments at expandabilities greater than about 35%. With sodium, however, ordering appeared at high expandabilities. A model based on the polarizing power of the collapsed layers can partly account for this difference in reaction.

Generally speaking, smectites studied here passed through three stages as they were transformed into a non-expandable structure. The first stage was a highly expandable clay, represented by randomly interstratified I/S if potassium is the interlayer cation, and by a Black Jack beidellite-type phase with sodium. With increasing reaction, these clays were transformed into regularly interstratified structures such as ordered I/S and rectorite. The third stage, never reached in our experiments, occurs when the ordered phases react to a final illite or paragonite mineralogy.

REFERENCES

Bannister, F. A. (1943) Brammallite (sodium illite), a new mineral from Llandebie, South Wales. *Mineralog. Mag.* **26**, 304–307.

Brindley, G. W. (1956) Allevardite, a swelling double-layer mica mineral. *Am. Miner.* **41**, 91–103.

Brown, G. (1961) *The X-ray Identification and Crystal Structure of Clay Minerals*, Mineral. Soc., London, p. 544.

Brown, G. and Weir, A. H. (1963a) The identity of rectorite and allevardite. *Int. Clay Conf. Proc.* **1**, Stockholm, 27–35.

Brown, G. and Weir, A. H. (1963b) An addition to the paper, The identity of rectorite and allevardite. *Int. Clay Conf. Proc.* **2**, Stockholm, 87–90.

Eberl, D. and Hower, J. (1975) Kaolinite synthesis: the role of the Si/Al and (alkali)/(H$^+$) ratio in hydrothermal systems. *Clays and Clay Minerals* **23**, 301–309.

Eberl, D. and Hower, J. (1976) The kinetics of illite formation. *Bull Geol. Soc. Am.* **87**, 1326–1330.

Eslinger, E. V. and Savin, S. (1973) Mineralogy and oxygen isotope geochemistry of the hydrothermally altered rocks of the Ohaki–Broadlands, New Zealand geothermal area. *Am. J. Sci.* **273**, 240–267.

Foscolos, A. E. and Kodama, H. (1974) Diagenesis of clay minerals from lower Cretaceous shales of northeastern British Columbia. *Clays and Clay Minerals* **22**, 319–336.

Giese, R. F. Jr. (1974) The effect of hydroxyl orientation on the interlayer bonding in di- and trioctahedral micas (abstr.). *23rd Ann. Clay Mineral Conf.*, Cleveland.

Greene-Kelley, R. (1955) Dehydration of montmorillonite minerals. *Mineralog. Mag.* **30**, 604–615.

Grim, R. E. (1968) *Clay Mineralogy*, McGraw Hill, New York. 576 pp.

Henderson, G. V. (1971) The origin of pyrophyllite and rectorite in shales of north central Utah: *Clays and Clay Minerals* **19**, 239–246.

Hower, J. and Mowatt, T. C. (1966) Mineralogy of the illite–illite/montmorillonite group. *Am. Miner.* **51**, 821–854.

Hower, J., Eslinger, E. V., Hower, M. E. and Perry, E. A. (1976) The mechanism of burial metamorphism of argillaceous sediments: 1. Mineralogical and chemical evidence. *Bull. Geol. Soc. Am.* **87**, 725–737.

Luth, W. C. and Ingamells, C. O. (1965) Gel preparation of starting materials for hydrothermal experimentation. *Am. Miner.* **50**, 255–260.

MacEwan, D. M. C. (1961) The montmorillonite minerals (montmorillonoids). In, *The X-ray Identification and Crystal Structure of Clay Minerals*, G. Brown, Ed., Mineral. Soc., London, Ch. 4.

Millot, G. (1970) *The Geology of Clays*. Springer-Verlag, New York, 429 pp.

Perry, E. and Hower, J. (1970) Burial diagenesis in Gulf Coast pelitic sediments. *Clays and Clay Minerals* **18**, 165–178.

Reynolds, R. C., Jr. and Hower, J. (1970) The nature of interlayering in mixed-layer illite–montmorillonites. *Clays and Clay Minerals* **18**, 25–36.

Sawhney, B. L. (1967) Interstratification in vermiculites. *Clays and Clay Minerals* **15**, 75–84.

Schultz, L. G. (1969) Lithium and potassium absorption, dehydroxylation temperature, and structural water content of aluminous smectites. *Clays and Clay Minerals*, **17**, 115–150.

Shainberg, I. and Kemper, W. D. (1966) Hydration status of absorbed cations. *Am. Proc. Soil Sci. Soc.* **30**, 707–713.

Thompson, G. R. and Hower, J. (1975) The mineralogy of glauconite. *Clays and Clay Minerals* **23**, 289–300.

Velde, B. (1969) The compositional join muscovite–pyrophyllite at moderate pressures and temperatures. *Bull. Soc. fr. Minér. Cristallogr.* **92**, 360–368.

Weir, A. H. and Greene-Kelley, R. (1962) Beidellite. *Am. Miner.* **47**, 137–146.

Weaver, C. E., Beck, K. C., and Pollard, C. O. (1971) Clay water diagenesis during burial: how mud becomes gneiss. *Geol. Soc. Am. Special Paper* **134**, 1–78.