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REACTION SERIES FOR DIOCTAHEDRAL SMECTITES

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Abstract—Several dioctahedral clay minerals are related through reaction series. These series can be produced hydrothermally from beidellite gel and montmorillonite by making simple changes in interlayer and solution chemistry. The series are:

gel–K-beidellite–random illite/smectite–K-rectorite–illite;
K-montmorillonite–K-rectorite–illite;
Na-montmorillonite or beidellite–Na-rectorite–paragonite;
Li-montmorillonite–Li-tosudite–Li-rectorite–cookeite(?);
Mg-montmorillonite–Mg-rectorite–tosudite–sudoite(?);
Ca-montmorillonite–Ca-rectorite–margarite(?);
Al-Ca-montmorillonite–kaolinite/smectite–kaolinite (150°C);
Al-Ca-montmorillonite–pyrophyllite/smectite–pyrophyllite (320°C).

Assuming stability for the mixed-layer phases, paragenesis is a function of P, T, and X conditions. If the phases are considered to be metastable, paragenesis is a function of the speed and path of reaction.

Key Words—Beidellite, Cookeite, Hydrothermal, Mixed-layer, Rectorite, Sudoite, Tosudite.

INTRODUCTION

The crystal structure of phyllosilicates can be broadly described as an interlayering between three kinds of structural units: octahedral sheets, tetrahedral sheets, and hydrated or nonhydrated interlayer cations. Chlorite, for example, is composed of a regular alternation of octahedral and tetrahedral sheets, with no interlayer cations.

Because all clay minerals are composed of these units, different types of clay minerals can articulate with each other in a composite clay crystal, thereby forming mixed-layer structures. Tosudite, for example, is a regular alternation of chlorite and smectite layers.

Since clay minerals are so closely related structurally, it might be expected that they will also be closely related genetically. The present experiments show that different families of clay minerals can be formed hydrothermally from dioctahedral smectite by making simple changes in hydrothermal run conditions, including changes in the initial interlayer and solution chemistry.

TERMINOLOGY

The clays with which this study is concerned are represented schematically in Figures 1, 2, 3, and 4. The many names given these clays tend to obscure the underlying simplicity and relatedness of their structures. Generally, the clays can be divided into four structural trends: the mica trend, the chlorite trend, the pyrophyllite trend, and the kaolinite trend. The 2:1 or 1:1 layers for the minerals in all of these trends are dioctahedral. Three types of mica are represented on the right side of the mica trend in Figure 1 and are named illite, paragonite or margarite depending on whether the fixed interlayer cation is potassium, sodium or calcium. The term "illite" is preferable to "muscovite" because potassium micalike layers in clay minerals generally have a layer charge of -0.8 equivalents per $O_{10}(OH)_2$ rather than a full muscovite charge of -1.0 equivalent (Hower and Mowatt, 1966). "Paragonite" is used rather than "brammallite" (sodium illite; Bannister, 1943) because the latter material has not been well characterized. The left side of the figure depicts various types of montmorillonite which are named K-montmorillonite, Na-montmorillonite, etc., according to interlayer chemistry. Montmorillonite is a dioctahedral smectite in which the majority of the layer charge is developed by isomorphous substitutions in the octahedral layer. In beidellite, the main component of charge is tetrahedral. Smectite is the general term for swelling clay and can refer to either montmorillonite or beidellite. The name is used when the distinction between beidellite and montmorillonite is unnecessary or not possible. In the center of the figure are the mixed-layer mica/smectites which are intermediate in structure, although not necessarily exactly intermediate in composition (Eberl and Hower, 1977), between completely expanded montmorillonite and completely collapsed mica. The proportion of smectite layers in a mixed-layer clay determines the clay's expandability. If the distribution of smectite and mica layers in a clay crystallite is ordered (or regular), the clay is a rectorite, and is termed K-rectorite, Na-rectorite, etc. after the dominant interlayer cation in the micalike layers. Na-rectorite previously has been called allevardite (Brown and Weir, 1963a; Kodama, 1966), as has K-rectorite (Velde, 1972). There can be several types of ordering between layers (Reynolds and Hower, 1970). For example, K-rectorite can have "IS" ordering, in which "I" stands for illite layers and "S" for smectite. The pattern of layers in the c-axis direction in this case would be ISISIS. . . . ISI and ISII ordering are also

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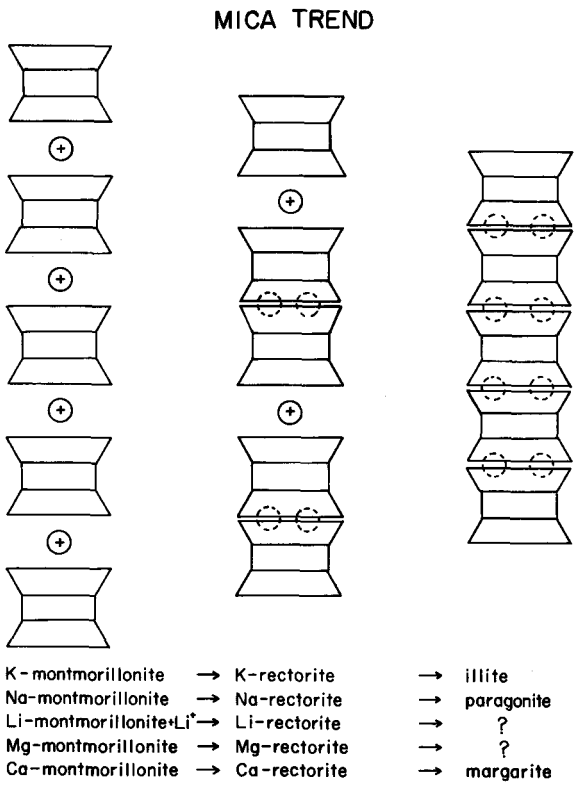


Fig. 1. Mica trend. The trapezoids are tetrahedral sheets. The rectangles are octahedral sheets. The circles with pluses are hydrated interlayer cations. The other circles are fixed interlayer cations.

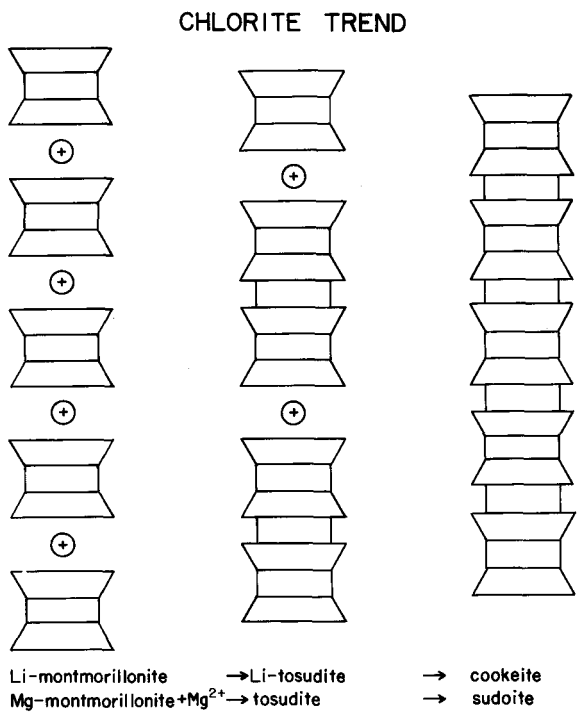


Fig. 2. Chlorite trend. Symbols as in Figure 1.

possible, as well as gradations between all three types. Mica/smectite may also be randomly interstratified, and is termed randomly interstratified illite/smectite, paragonite/smectite, etc. A complete gradation between a random and an ordered structure is possible, yielding a "partly ordered" clay. The different tendencies towards ordering can be described more precisely in terms of probabilities (Reynolds and Hower, 1970; Reynolds, in preparation).

The chlorite trend is shown in Figure 2. Two types of chlorite considered here are sudoite and cookeite. In ideal sudoite the 2:1 layer is dioctahedral and the interlayer hydroxyl sheet is trioctahedral (Pedro, 1970, as discussed in Bailey, 1975). Shirozu and Higashi (1976), however, have shown that the interlayer hydroxyl sheet may have an occupancy that is less than trioctahedral. They give the following probable structural formula for a sudoite from the Hanaoka Mine:

$$[(Mg_{1.3}Al_{1.5})(OH)_6]^{1.1+}$$

$$[(Mg_{0.3}Al_{1.7})(Si_{3.2}Al_{?.8})O_{10}(OH)_2]^{1.4-}.$$

A completely dioctahedral chlorite would be called donbassite (Bailey, 1975). Cookeite is similar to sudoite, except that the interlayer hydroxyl sheet contains lithium and aluminum rather than magnesium and aluminum. A structural formula for cookeite from the Jeffrey Quarry, Arkansas, calculated from the analysis of Miser and Milton (1964), is:

$$[(Al_{2.01}Li_{0.95})(OH)_6]^{0.98+}$$

$$[(Al_{2.00})(Si_{3.03}Al_{0.97})O_{10}(OH)_2]^{0.97-}.$$

A small amount of CaO (0.2%) found in the chemical analysis has been omitted. On the left side of Figure 2 are Mg- and Li-montmorillonites, and in the center are the ordered mixed-layer chlorite/smectites known as tosudite and lithium tosudite. Frank-Kamenetsky et al. (1963) and Shimoda (1969) restrict the name tosudite to a completely dioctahedral structure, in which case tosudite is an ordered mixed-layer donbassite/smectite; but Nishiyama et al. (1975) and Ichikawa and Shimoda (1976) use the name more generally to describe a clay in which the interlayer hydroxyl sheet is trioctahedral, in which case tosudite also could be an ordered mixed-layer sudoite/smectite. Kanaoka (1975) and Brown et al. (1974) note that both types, as well as intermediaries, have been discovered. In the present paper the name tosudite will be used in the more general sense to include both the di/di and the di/trioctahedral clays as well as intermediate forms. The completely trioctahedral analog of tosudite has been called corrensite (e.g., Lippmann, 1976), although this term was

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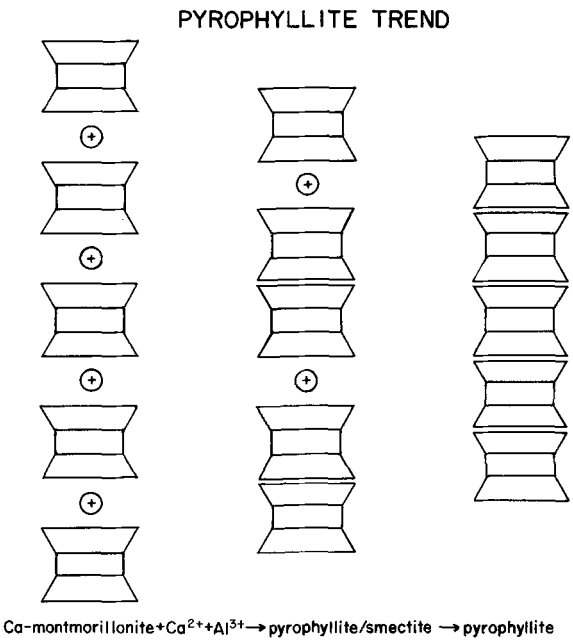


Fig. 3. Pyrophyllite trend. Symbols as in Figure 1.

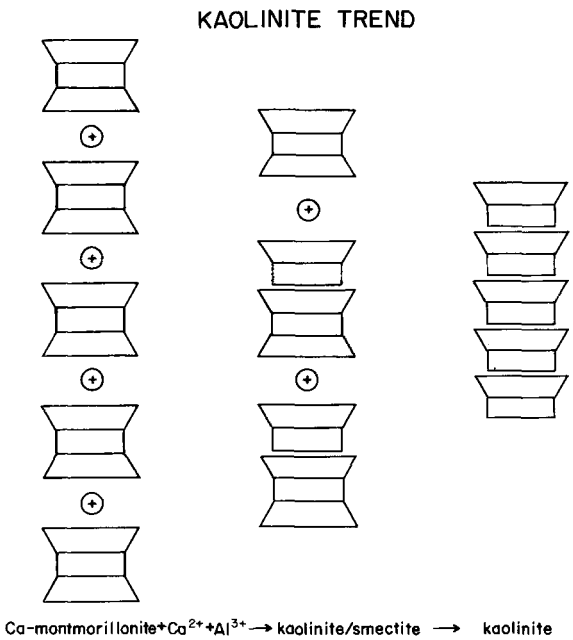


Fig. 4. Kaolinite trend. Symbols as in Figure 1.

originally used to indicate a regularly interstratified chlorite/swelling chlorite (Lippmann, 1954). Li-tosudite is a tosudite that contains lithium in the interlayer hydroxyl sheet. Ideally, it can be regarded as a regularly interstratified cookeite/smectite. A structural formula for Li-tosudite from the Hokuno Mine, written after the formula given by Ichikawa and Shimoda (1976), is:

$$[(Al_{1.67}Li_{0.38}Fe^{3+}{}_{0.14}Mg_{0.13})(OH)_6]^{0.07+}$$
$$[(Al_{2.00})(Si_{3.46}Al_{0.54})O_{10}(OH)_2]^{0.54-}$$
$$(Ca_{0.21}K_{0.06}Na_{0.02})^{0.50+}.$$

Octahedral occupancy for chlorites and chlorite/smectites that do not contain lithium can be determined roughly from the position of the 060 reflection. A completely dioctahedral structure will give an 060 around 1.49 Å. A trioctahedral 060 is at about 1.54 Å, and a mixed di/trioctahedral structure will give a peak at about 1.51 Å (Bailey, 1975). Li-tosudite and cookeite, however, may give a dioctahedral 060 around 1.49 Å even though the hydroxide interlayer may be trioctahedral. The problem lies in the small b-parameter of an (Al, Li)-hydroxide sheet. A chemical analysis is therefore required for identification.

Figure 3 presents the pyrophyllite trend, with pyrophyllite on the right, montmorillonite on the left and mixed-layer pyrophyllite/smectite in the center. Finally, Figure 4 presents a similar trend for kaolinite.

EXPERIMENTAL TECHNIQUES

Two types of starting materials were used in these experiments: 1) gels of K- and Na-beidellite composition (Eberl and Hower, 1977) prepared by the Ludox gel method of Luth and Ingamells (1965); and 2) samples of the <2-μm size fraction of the Wyoming montmorillonite source clay (Moll et al., 1975) which had been saturated with K^+, Na^+, Li^+, Ca^{2+} or Mg^{2+}. The montmorillonite was saturated 3 times over the course of 5 days with 1 N chloride solutions of these ions. The montmorillonites were then thoroughly washed and the supernatant solutions were checked for chloride with $AgNO_3$. Chemical analysis by atomic absorption, after solution preparation by the acid dissolution method of Jackson (1975), showed that cation exchange for the montmorillonites was essentially complete.

The starting materials were treated in standard hydrothermal apparatus using techniques described elsewhere (Eberl and Hower, 1976). Samples were run in welded gold tubes, with a solid:solution ratio of 1:1 by weight. Pressures were either autoclave pressure or 2 kbar. Temperatures ranged between 300 and 500°C. Run products were identified from X-ray diffractograms (Ni-filtered CuKα radiation) of air-dried and ethylene glycol-treated samples from peak positions and treatments given in Brown (1961), and in Reynolds and Hower (1970), and by using the computer program of Reynolds and Hower (1970) to model precisely some of the K-rectorites.

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Table 1. Hydrothermal run results.

Run No.	Starting Composition	Solution Composition	Temp. (°C)	Pressure (kb)	Time (days)	Run Products
1	K-beidellite gel	water	300	2	31	$(I/S)_{rand}$ (85), kao, Q, fs
2	" "	"	260	"	266	$(I/S)_{rand}$ (60), kao
3	" "	"	347	"	88	K-rect (32), Q, fs
4	" "	"	394	"	169	K-rect (15), Q, py
5	" "	"	492	"	24	K-rect (10), crist, py
6	K-montmorillonite	"	300	A	30	K-rect (40), Q
7	"	KCl	300	"	30	K-rect (25), Q, KCl
8	"	water	400	"	7	K-rect (20), kao, Q, fs
9	"	"	400	"	30	K-rect (20), kao, Q
10	"	KCl	379	2	169	K-rect (15), kao, Q
11	"	1.0 N KOH	400	A	30	K-rect (7), Q, fs
12	"	1.0 N KCl	400	A	30	K-rect (10), Q
13	Na-montmorillonite	water	300	A	30	Smectite, Q
14	Na-beidellite gel	"	350	2	218	Na-rect (70), kao, Q
15	Na-montmorillonite	"	400	A	30	Na-rect (50), kao, Q
16	"	1.0 N NaCl	400	A	30	Na-rect (50), Q, kao, albite
17	Na-beidellite gel	water	492	2	24	Na-rect (40), Q, py
18	Li-montmorillonite	water	300	A	30	Smectite, Q, kao (trace)
19	"	"	400	"	8	Smectite (high charge), kao, Q
20	"	"	"	"	30	Li-tosudite, kao, Q
21	"	"	500	"	7	" " " "
22	"	"	500	2	21	Smectite
23	"	"	600	A	9	Anthophyllite(?), mica(?), chlorite (cookeite?), Q, mullite
24	"	1.0 N LiCl	400	A	30	Smectite, Li-tosudite, Li-rect, kao, Q
25	Mg-montmorillonite	water	300	A	30	Smectite, kaolinite (trace)
26	"	"	400	A	8	Mg-rect, smectite, 7Å, Q
27	"	1.0 N $Mg(OH)_2$	"	"	30	Tosudite, Mg-rect, 7Å, Q
28	"	3.3 N $MgCl_2$	"	"	7	Tosudite, Mg-rect, 7Å, Q
29	"	1.0 N $MgCl_2$	"	"	30	Tosudite, 7Å, Q
30	Ca-montmorillonite	water	300	A	30	Smectite, Q
31	"	"	400	"	7	Ca-rect, smectite, kao, Q
32	"	"	"	"	30	Ca-rect, smectite, kao, Q
33	"	1.0 N $CaCl_2$	"	"	"	Ca-rect, kao, Q
34	"	1.0 N $Ca(OH)_2$	"	"	"	Ca-rect, smectite, kao, Q, chlorite(?), anorthite
35	Ca-montmorillonite	30 mg clay, 10 mg $AlCl_3 \cdot 6H_2O$, 40 µl 1.0 N $CaCl_2$	250	A	5	Smectite
36	"	30 mg clay 10 mg $AlCl_3 \cdot 6H_2O$, 50 µl 0.5 N $CaCl_2$	320	A	6	Py/smectite, kao, Q, anorthite
37	"	20 mg clay 10 mg $AlCl_3 \cdot 6H_2O$, 30 µl 1.0 N $CaCl_2$	400	A	7	Py, kao

All mixed-layer phases are regularly interstratified unless otherwise noted. $(I/S)_{rand}$ (85) is an 85% expandable randomly interstratified illite/smectite. Kao is kaolinite. Q is quartz. Fs is feldspar. Py is pyrophyllite. Crist is cristoballite. Rect is rectorite.

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EXPERIMENTAL RESULTS

In general the beidellite gels and the montmorillonites reacted to form mixed-layer clays according to the reaction series shown at the bottoms of Figures 1–4. The course of reaction was influenced strongly by interlayer cations and cations in solution. Therefore, the various reaction series are named after the dominant cations.

K-smectite series

Starting with a K-beidellite gel or with K-saturated Wyoming montmorillonite, two subseries of mixed-layer illite/smectites were formed which decreased in expandability with increasing run time and temperature (Table 1, runs 1–12). The K-beidellite composition reacted according to the following pattern with regard to the mixed-layer phase:

gel → K-beidellite → I/S(random) → K-rectorite → illite.

The K-montmorillonite reacted as follows:

K-montmorillonite → K-rectorite → illite.

Diffractograms of these subseries are shown in Figures 5 and 6. A modified version of the computer program of Reynolds and Hower (1970) was used to model expandabilities for the K-montmorillonite subseries, using a crystallite thickness of 14–15 layers, with maximum ordering. Expandabilities for the gel subseries were determined from peak positions and pattern shapes given in Reynolds and Hower (1970). Ordering did not appear until reaction had proceeded to about 32% expandable for the gel subseries (Figure 5C), the ordered phase being preceded by a randomly interstratified clay (Figures 5A, B). The K-montmorillonites, however, reacted very quickly to form an ordered structure approaching 50% expandable (Figure 6A). Within the K-montmorillonite subseries, extra K^+ in solution speeds reaction towards illite, as can be seen by comparing run 6 with run 7 (Table 1). A diffractogram of natural K-rectorite, a metabentonite from New York State, is shown in Figure 6D. It fits nicely into the structural series found for the synthetic samples. Pattern E (Figure 6) is comparable to a pattern of clay from the Kalkberg Formation shown by Reynolds and Hower (1970, figure 2). Patterns of the K-beidellite subseries (Figure 5) are comparable to diffractograms of natural illite/smectites from a burial diagenetic sequence in the Gulf Coast geosyncline (Perry and Hower, 1970, figures 3–10).

Na-smectite series

Smectites with Na^+ as the interlayer cation reacted to form the following series with increasing run time and temperature:

Na-smectite → Na-rectorite → paragonite.

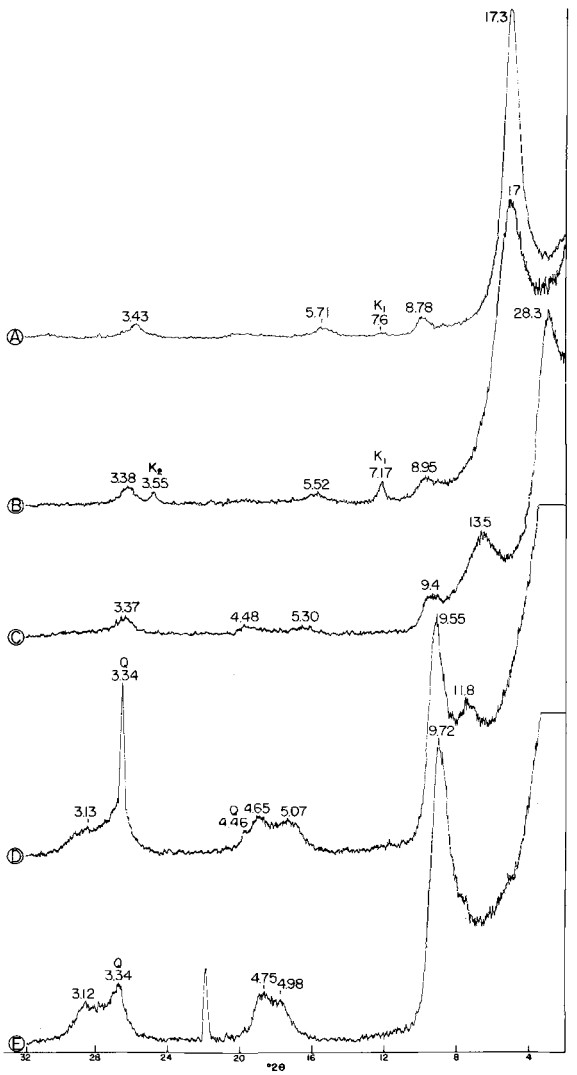


Fig. 5. K-beidellite subseries saturated with ethylene glycol. *K* is kaolinite. *Q* is quartz. The numbered peaks are attributed to mixed-layer illite/smectite. See Table 1 for run conditions. *Pattern A* is a 85% expandable random I/S formed in run 1. *Pattern B* is a 60% expandable random I/S formed in run 2. *Pattern C* is a 32% expandable K-rectorite formed in run 3. *Pattern D* is a 15% expandable K-rectorite from run 4. *Pattern E* is a 10% expandable IS from run 5. The peak between 20° and 24° is cristoballite.

Run results for the Na-series are given in Table 1, runs 13–17 and in Figure 7. The only observed difference in reaction between the two starting compositions (Na-beidellite gel and Na-montmorillonite) at the experimental temperatures reported here was that the montmorillonite reacted more quickly to the 50% expandable, well-ordered rectorite structure. At lower temperatures (260°C), however, the gel reacted to form randomly interstratified paragonite/smectite whereas the montmorillonite did not react (Eberl and Hower, 1977). Reaction beyond the 50% expandable structure proceeded very slowly for both compositions, and the

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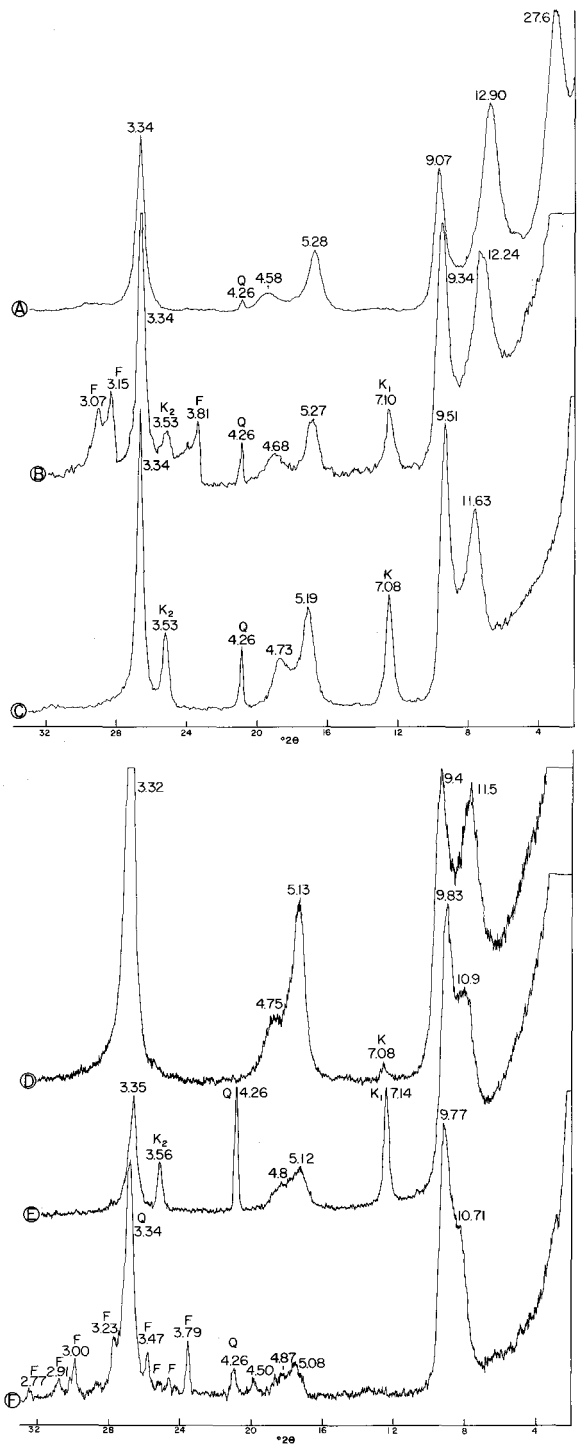


Fig. 6. K-montmorillonite subseries saturated with ethylene glycol. *F* is feldspar. The peaks which have numbers only are K-rectorites. Other symbols are given with Figure 1. *Pattern A* is a 40% expandable K-rectorite formed in run 6. *Pattern B* is 25% expandable K-rectorite from run 7. *Pattern C* is a 20% expandable K-rectorite from run 8. *Pattern D* is a natural K-rectorite (metabentonite) from the Ordovician Shoreham Formation of New York State. It is 15% expandable. *Pattern E* is an 11% expandable K-rectorite from run 10. *Pattern F* is a 7% expandable K-rectorite from run 11.

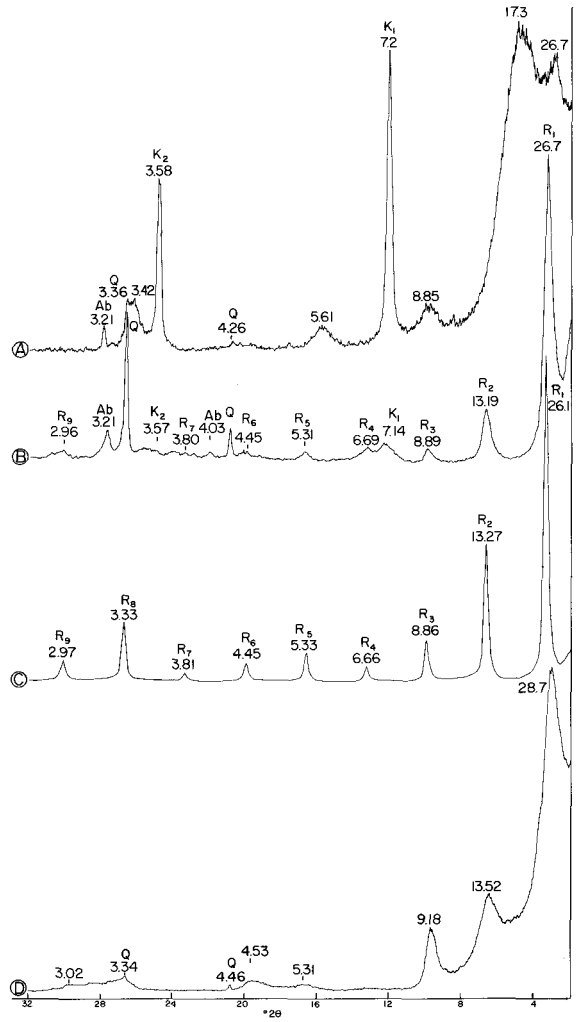


Fig. 7. Na-smectite series saturated with ethylene glycol. *Ab* is albite. *K* is kaolinite. *Q* is quartz. *R* is sodium rectorite. Peaks which have numbers only are attributed to Na-rectorite. *Pattern A* is a 70% expandable Na-rectorite formed in run 14. *Pattern B* is a 50% expandable Na-rectorite from run 15. *Pattern C* is a natural Na-rectorite from the Jeffrey Quarry, Arkansas. *Pattern D* is a 40% expandable Na-rectorite from run 17.

closest approach to paragonite was the 40% expandable clay shown in Figure 7D. Longer run times and higher concentrations of Na^+ in solution would probably have produced a nonexpanding paragonite. It should be noticed that whereas K-montmorillonites can react to form mixed-layer clay at 300°C and below (i.e., run 6), Na-montmorillonites react only at temperatures above about 350°C (compare runs 13 and 15). In general, montmorillonites with cations of low hydration energy (K^+, Cs^+, Rb^+) react to form mixed-layer clay at relatively low temperatures, whereas clays with interlayer cations of greater hydration energy (Na^+ and above) require higher temperatures (see runs 13, 18, 25, 30, and Eberl, 1978). A diffractogram of a natural Na-rectorite from Arkansas is given in Figure 7C for comparison.

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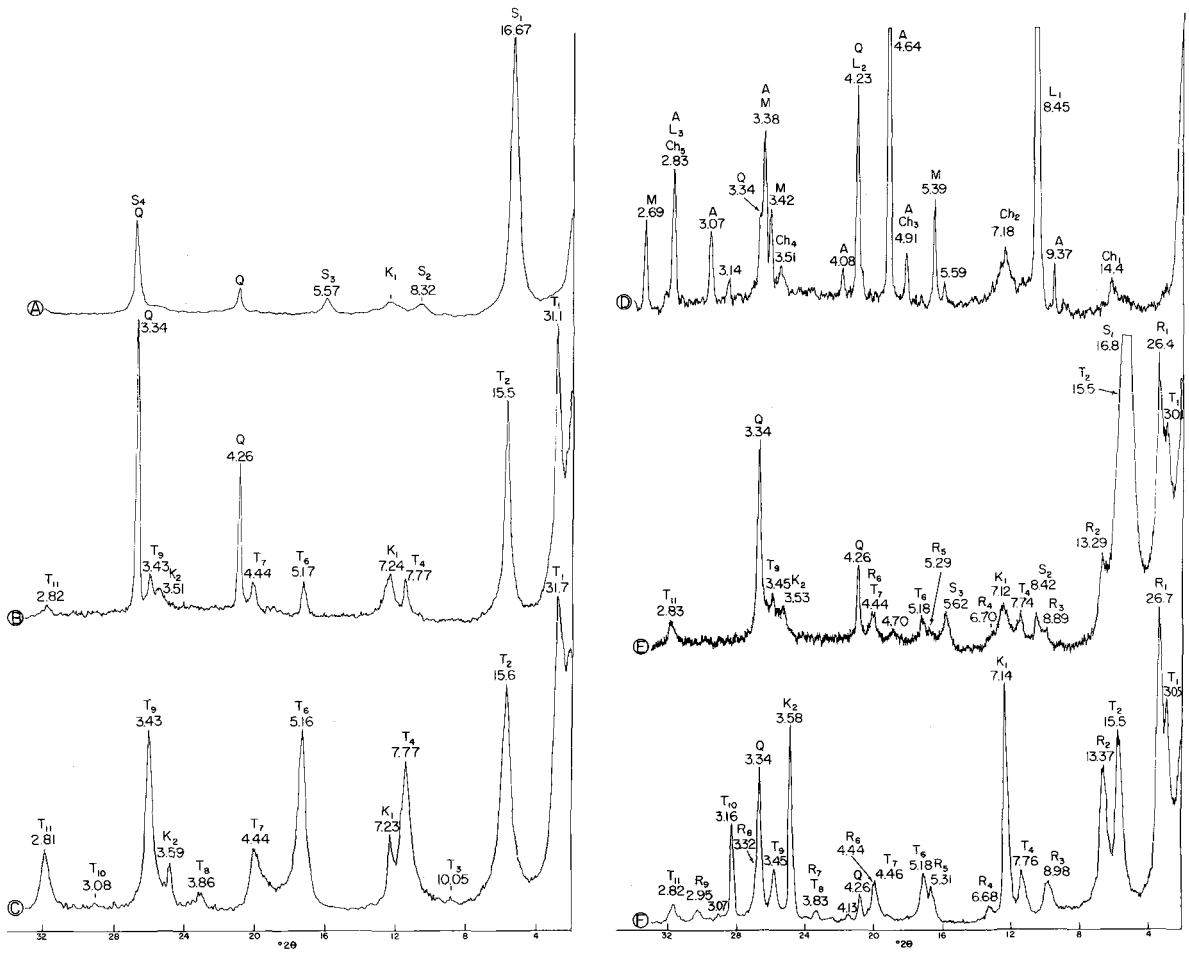


Fig. 8. Li-montmorillonite series saturated with ethylene glycol. *A* is an anthophyllitelike phase. *Ch* is a chlorite (cookeite?)like phase. *K* is kaolinite. *L* is an unidentified micalike phase. *M* is mullite. *Q* is quartz. *R* is a rectoritelike phase. *S* is smectite. *T* is lithium tosudite. *Pattern A* is a high charge smectite formed in run 19. *Pattern B* shows a Li-tosudite formed in run 20. *Pattern C* is a natural Li-tosudite from Huy studied by Brown et al. (1974). It is Ba-saturated. *Pattern D* shows products formed in run 23. *Pattern E* is Li-tosudite and rectorite formed in run 24. *Pattern F* is a natural Li-tosudite and rectorite (from the Roseki deposit) studied by Nishiyama et al. (1975).

Li-montmorillonite series

The Li-montmorillonites reacted as follows:

Li-montmorillonite → high charge smectite → Li-tosudite → cookeite(?);

Li-montmorillonite + Li^+ → Li-tosudite + Li-rectorite.

Li-saturated montmorillonite reacted to form a high-charge smectite after 8 days at 400°C under autoclave pressure (run 19; Figure 8A). A high layer charge was indicated by a shift of the 001 peak from about 16.9 Å for the untreated glycolated montmorillonite to 16.7 Å for the hydrothermal sample. The 00*l* reflections of smectite will shift to lower spacings with increasing layer charge (Suquet et al., 1977; Środoń, 1976). Additional evidence for increased charge is given by the appearance of kaolinite in the treated sample, indicating that layer charge may have increased according to the reaction:

montmorillonite → high charge smectite + kaolinite + quartz.

Upon saturation with K^+ at room temperature, about 20% of the layers in the sample collapsed, indicating that vermiculitic layers had been produced. With increased run time at 400°C, the high-charge smectite structure evolved into Li-tosudite (Figure 8B, run 20). Chlorite layers in the structure were distinguished from possible vermiculite layers by their lack of dehydration on dry heating for 1 hr at 550°C. The sample was X-rayed in dry air to prevent rehydration. A natural Li-tosudite studied by Brown et al. (1974) is shown in Figure 8C.

Increasing the run temperature from 400 to 500°C had little effect on the reaction products (compare runs 20 and 21), but increasing the pressure to 2 kbar prevented reaction (run 22). The effect of increased pressure on all of the reaction series was to inhibit reaction, as is

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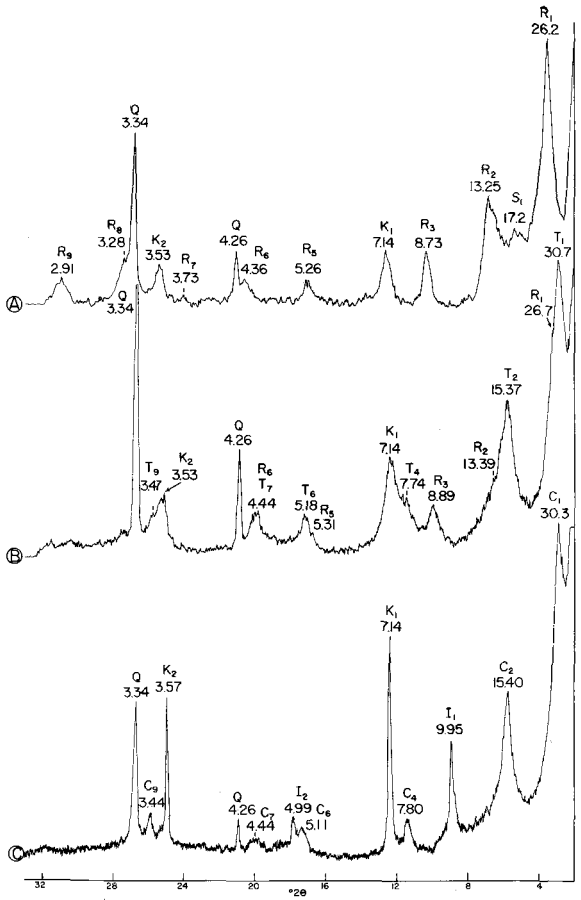


Fig. 9. Mg-montmorillonite series saturated with ethylene glycol. *C* is corrensite. *I* is illite. *K* is a kaolinitelike phase. *Q* is quartz. *R* is Mg-rectorite. *S* is unreacted smectite. *T* is tosudite. *Pattern A* is Mg-rectorite formed in run 26. *Pattern B* is Mg-rectorite and tosudite from run 27. *Pattern C* is a natural corrensite from a sandstone found in the Pecos Valley, New Mexico.

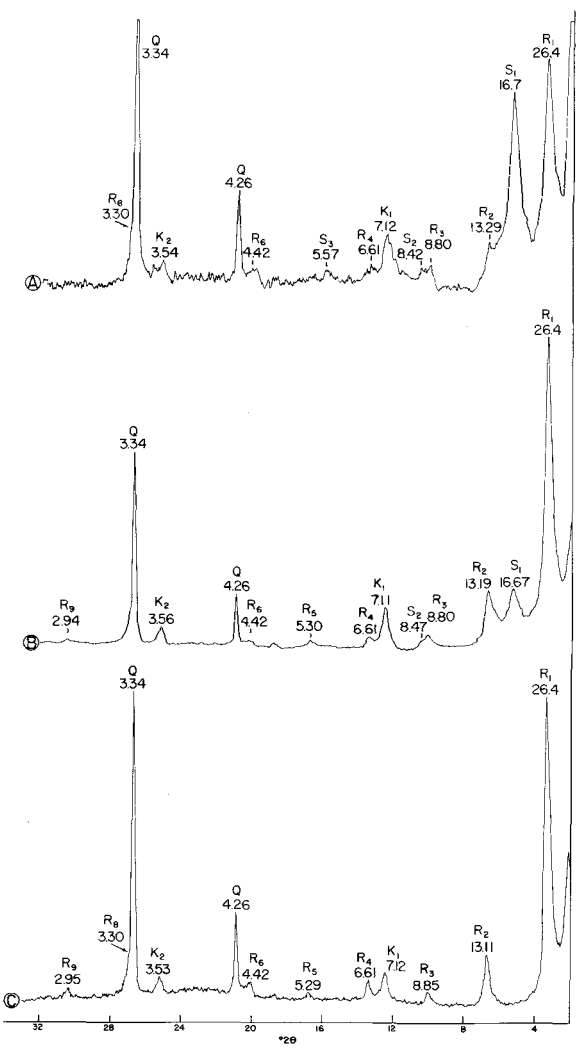


Fig. 10. Ca-montmorillonite series saturated with ethylene glycol. *K* is kaolinite. *Q* is quartz. *R* is Ca-rectorite. *S* is unreacted smectite. *Pattern A* shows Ca-rectorite formed in run 31. *Pattern B* is Ca-rectorite from run 32. *Pattern C* is Ca-rectorite from run 33.

discussed in Eberl et al. (1978). Raising the temperature to 600°C with autoclave pressures led to the development of anthophyllitelike and micalike phases, chlorite (cookeite?), quartz, and mullite (Figure 8D, run 23). Adding LiCl to the run solution led to the formation of rectorite as well as Li-tosudite (Figure 8E, run 24). A natural sample studied by Nishiyama et al. (1975) that has a mineralogy similar to run 24 is shown in Figure 8F. The main difference between Figures 8E and 8F is in the relative amounts of kaolinite and unreacted smectite in the samples.

Mg-montmorillonite series

Montmorillonite saturated with Mg reacted as follows:

Mg-montmorillonite → Mg-rectorite;
Mg-montmorillonite + Mg^{2+} → tosudite.

At 400°C Mg-montmorillonite formed Mg-rectorite plus a 7 Å phase and quartz (Figure 9A, run 26). The addition of $MgCl_2$ or $Mg(OH)_2$ to the experimental system led to the development of tosudite as well as rectorite (Figure 9B, runs 27 and 28). The chlorite layers in the tosudite were identified with the techniques mentioned previously. After 30 days at 400°C in a $MgCl_2$ solution, all of the rectorite disappeared and the products were tosudite, a 7.14 Å phase and quartz (run 29). It is interesting that the addition of $MgCl_2$ led to the formation of chlorite/smectite and the disappearance of rectorite for the Mg-montmorillonite, whereas the addition of LiCl to the Li-montmorillonite runs produced the opposite effect. A sample of natural tosudite was not available, but a diffractogram of a natural corrensite from New Mexico (Figure 9C) is shown for comparison.

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Ca-montmorillonite series

Reaction for Ca-montmorillonite was as follows:

Ca-montmorillonite → Ca-rectorite.

Reaction began at 400°C where the rectorite structure was formed along with kaolinite and quartz (Figures 10A and B, runs 31 and 32). The addition of a chloride or hydroxide of the interlayer cation to the run solution did not, as was the case with Mg-montmorillonite, lead to the development of a tosudite since Ca^{2+} does not enter into octahedral coordination in clays. An anion effect was seen in runs 33 and 34: the presence of $CaCl_2$ led to complete reaction of the montmorillonite to Ca-rectorite, kaolinite, and quartz at 400°C after 30 days (Figure 10C), whereas clay treated in the $Ca(OH)_2$ solution reacted more slowly and formed anorthite in addition to the other products. Velde (1971) also has noted that the formation of anorthite is favored by high pH.

Al-montmorillonite series

In the Al-montmorillonite series reaction was as follows:

Ca-montmorillonite + Ca^{2+} + Al^{3+}
→ pyrophyllite/smectite → pyrophyllite.

In order to form this series the Si/Al ratio of the system was varied. This ratio was held constant for the other series. Aluminum, in the form of $AlCl_3 \cdot 6H_2O$, was added to the run solution of a Ca-smectite in addition to $CaCl_2$. Under the proper conditions, this type of run led to the development of a random mixed-layer pyrophyllite/smectite plus kaolinite, quartz, and anorthite (Figure 11, run 36). Subsequent experiments have shown that Ca^{2+} in solution is not always necessary and that Na-montmorillonite will also work (Eberl, in preparation). Runs of similar composition made at 150°C by Środoń (personal communication) led to the development of a mixed-layer kaolinite/smectite.

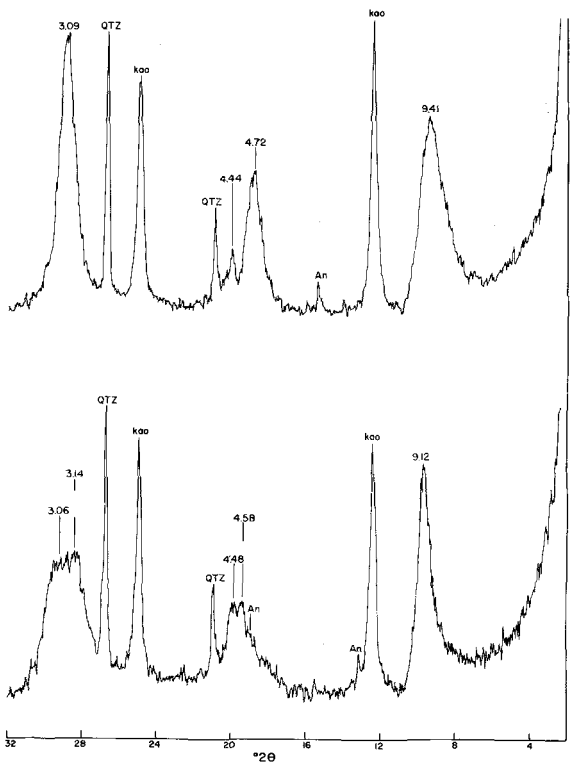


Fig. 11. Al-montmorillonite series. The products are from run 36. Air-dried sample is at top, ethylene glycol-treated at bottom. *An* is anorthite. *Kao* is kaolinite. *Qtz* is quartz. The other peaks are attributed to 25% expandable random pyrophyllite/smectite.

DISCUSSION

As was mentioned previously, the general direction in a reaction series is towards the development of a collapsed structure with increasing run time and temperature. The formation of this structure for the mica and chlorite trends probably results from the development of a highly negative charge on the 2:1 layers which leads either to a dehydration of the interlayer cation to form a micalike interlayer, or to a loss of protons from the hydrated interlayer cation to form a hydroxide interlayer. Al^{3+} also must enter into the hydroxide interlayer to produce the net positive charge necessary for electrical neutrality. The negative charge on the 2:1 layers arises most likely from the substitution of Al^{3+} for Si^{4+} in the tetrahedral sheets, with charge balance by an increase in interlayer cations. Al^{3+} and the interlayer cations for this reaction come from the breakdown of some of the montmorillonite, a reaction which also leads to the formation of quartz and kaolinite (or pyrophyllite). Infrared studies are currently underway to study this mechanism.

K-smectite series

As was mentioned previously, two potassium subseries are recognized in these experiments, one formed from K-beidellite gel, and the other from K-montmorillonite. They are distinguished from each other on the basis of the first appearance of layer ordering and the speed of reaction. The K-montmorillonite probably develops ordering at a higher expandability and reacts faster because the precursor montmorillonite already has an ordered structure. A relatively high tetrahedral charge may already be developed around every other interlayer. These alternate high-charged interlayers would collapse faster than beidellite layers formed from the gel because they would require less $Al^{3+} \rightarrow Si^{4+}$ substitution to form illite. Illite/smectite so formed from the montmorillonite would be ordered at 50% expandable. Evidence for a mixed-layer charge distribution in Wyoming montmorillonite has been given by Lagaly and Weiss (1975).

A third potassium subseries also has been recognized: the glauconite/smectite series. Velde and Odin

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(1975) showed that this series can be distinguished from the illite/smectites on the basis of iron and alkali contents. The glauconite/smectites are also crystallographically different from the illite/smectites. In glauconite/smectites ordering is evident only below about 25% expandable layers, and the alkali content of a glauconite layer in glauconite/smectite is less than that of an illite layer in illite/smectite, indicating that a lower layer charge is required for the collapse of smectite to glauconite (Thompson and Hower, 1975).

Natural examples of the K-smectite reaction series have been reported to form under burial diagenesis (Perry and Hower, 1970; Weaver and Beck, 1971; Hower et al., 1976), under regional metamorphism (Frey, 1970, 1974), in hydrothermal deposits (Nemecz et al., 1963; Rodriques and Perez, 1965; Eslinger and Savin, 1973), and in thick bentonite beds (Środoń, 1972; Parachoniak and Środoń, 1973).

Illite/smectite can also form during weathering. An illite/vermiculite series can develop in a soil profile, resulting from, for example, the weathering of mica (MacEwan and Ruiz-Amil, 1975): an increasing number of mica layers will open up as potassium is progressively leached from the interlayer position and replaced with cations of greater hydration energy such as H_3O^+ or Ca^{2+}. The charge on the vermiculite layers could then be decreased by the substitution of Si^{4+} for tetrahedral Al^{3+} and Fe^{3+} (Sridhar and Jackson, 1974), or by the oxidation of Fe^{2+}, thereby leading to the formation of smectite layers. This origin for illite/smectite by degradation reveals an alternate mechanism for producing mixed-layer clays other than by the reaction of smectite.

Na-smectite series

The sodium series, consisting of Na-smectite, Na-rectorite, and paragonite, has been studied in some detail by Eberl and Hower (1977). It was discovered that Na-rectorite could be formed hydrothermally from a Na-beidellite gel after the reaction had proceeded through a beidellite phase, thereby ending the predilection that rectorite most likely forms from the leaching of alternate layers in a precursor mica (Sudo et al., 1962; Brindley et al., 1963; Henderson, 1971). A leaching mechanism is possible provided it is accompanied by a decrease in charge on the opened layers; otherwise the clay would be a mixed-layer mica/vermiculite rather than a mica/smectite. Natural Na-rectorites have been reported from regionally metamorphosed rocks (Henderson, 1971; Frey, 1970, 1974) and from hydrothermal deposits (Brackett and Williams, 1891; Miser and Milton, 1964).

Li-montmorillonite series

Members of the Li-montmorillonite series include Li-tosudite, Li-rectorite, and possibly the completely non-expanded end-members cookeite and Li-mica. A micalike structure, labeled "L" in Figure 8D, was synthesized in run 23, but its presumed 001 spacing of 8.45 Å, which lies between pyrophyllite and kaolinite, is difficult to rationalize with any known phyllosilicate structure and therefore may be misidentified. However, it does give integral reflections to at least the seventh order which do not shift upon glycollation. As was mentioned, a chlorite phase also developed in this run, but could not be positively identified as cookeite.

Li-tosudite has been reported only in hydrothermal deposits. Li-rectorite may also occur in nature, as is discussed below. Nishiyama et al. (1975) list 13 occurrences of tosudite in Japan, and describe a Li-tosudite associated with rectorite found in veinlets in the Tooho "Roseki" deposit. A diffractogram of this sample is given in Figure 8F. Their chemical analysis for this Li-tosudite yielded a higher Li-content than that found for other occurrences. In order to determine the composition of this mineral, they subtracted out the contribution to the chemical analysis of the associated rectorite, assuming that the associated rectorite in the veinlets had the same chemical composition as Li-deficient rectorite found in the surrounding rock. It may be that the rectorite in the veinlets is actually a Li-rectorite similar to that formed in run 24 (Figure 8E) when Li-montmorillonite was run in a LiCl solution. The presence of this Li-rectorite would then explain the high lithium content of the sample. Details of the structure of Li-rectorite are not known, but if the Tooho sample does contain Li-rectorite, then the Li is fixed in the structure since Nishiyama et al. (1975) report that there was no exchangeable Li in the natural sample.

Ichikawa and Shimoda (1976) have synthesized Li-tosudite starting with a natural sample of <2 μm illite/smectite (Li-rectorite?), kaolinite, and minor montmorillonite that was associated with natural Li-tosudite at the Hokuno Mine. They observed the following reaction sequence at 400 atm:

$$\text{I/S} \xrightarrow[2\text{ days}]{400^\circ\text{C}} \text{smectite} \xrightarrow[5\text{ days}]{450^\circ\text{C}} \text{tosudite}.$$

The second step in this reaction duplicates results found in the present experiments. The association of Li-tosudite, montmorillonite, and illite/smectite (Li-rectorite?) in the deposit may represent a natural occurrence of three members of the Li-montmorillonite reaction series.

Mg-montmorillonite series

The Mg-series includes Mg-rectorite, tosudite, and presumably sudoite. Although the latter was not synthesized in these experiments, it can probably be included in the series. Wyart and Sabatier (1966) produced a montmorillonite → ordered chlorite/smectite → chlorite series by increasing the $MgCO_3$/montmorillonite ratio of a hydrothermal system at about 450°C. Their diagram indicates that our failure to form a chlo-

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ritelike clay probably resulted from insufficient Mg^{2+}. Their reaction products were, however, trioctahedral. A natural tosudite–chlorite association has been reported in Montana by Blatter et al. (1973) in a metasomatic occurrence associated with a dike intruding chloritic shales. Tosudite was found next to the dike, grading into chlorite with increasing distance from the dike. Natural Mg-rectorite has not been reported.

Ca-montmorillonite series

The completely collapsed end-member in this series should be margarite, but it was not formed in our experiments. Velde (1971) showed that the conditions for margarite formation are very restricted. It may be that margarite can be formed from montmorillonite, but that the proper P, T, and Ca^{2+} concentrations were not found. It is also possible that the Si/Al ratio of the system must be adjusted. The inclusion of margarite in the Ca-series is therefore tentative. Natural Ca-rectorite has not been reported.

Al-montmorillonite series

As was mentioned previously, Środoń (pers. comm.) formed kaolinite/smectites at 150°C with run chemistries similar to those tried in runs 35–37. Our attempts to form it at 250°C failed (run 35), and pyrophyllite/smectite was formed at 320°C. The existence of natural kaolinite/smectite has been confirmed by Sakharov and Drits (1973) who compared calculated diffraction curves with those of the natural mineral. Kaolinite/smectite forms during weathering (Altschuler et al., 1963; Schultz et al., 1970) and hydrothermally (Wiewiora, 1971, 1972). It has also been reported in underclays beneath coal seams in Illinois (White et al., 1977). Natural mixed-layer pyrophyllite/smectite has not been reported, except possibly by Kodama (1958).

Trioctahedral smectite reaction series

Analogous reaction series do not exist for saponite and hectorite. These minerals resist reaction to mixed-layer clay because they contain little aluminum. Without aluminum, a charge cannot be built on the 2:1 layers to yield a micalike or chloritelike structure (Eberl et al., 1978). For starting materials which are closer in composition to talc or to phlogopite than is saponite, however, mixed-layer talc/saponite and phlogopite/saponite have been synthesized (Whitney, pers. comm.).

PARAGENESIS IN A REACTION SERIES

The concept of a reaction series makes no statement concerning mineral stability. It says only that by starting with a montmorillonite or an analogous gel composition (constant Si/Al ratio for the system, except for the Al-series), and by making changes in the interlayer cation and in its salt concentration in solution, a certain series of phases will be realized on hydrothermal treatment.

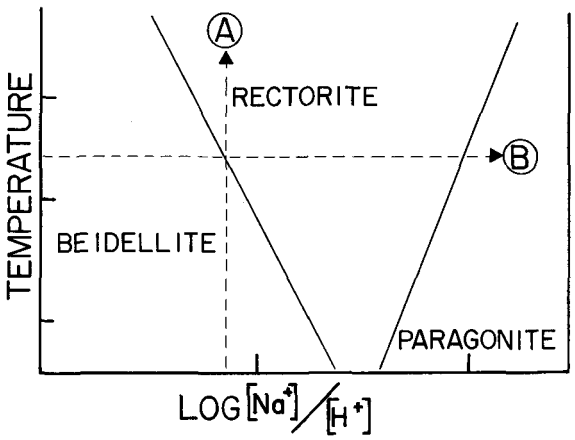


Fig. 12. Theoretical activity-temperature diagram for a Na-beidellite series. The pressure is one bar. Each stability field contains H_2O and quartz in addition to the phase shown.

If the reaction products are thermodynamically stable under the run conditions, then the structure of the starting material should not be important: it could be a montmorillonite, a gel or a mixture of other minerals which give the required run composition, although the smectite precursor may lead to a faster reaction. A possible example of this situation is Na-rectorite which forms both from the gel and from Na-montmorillonite, with reaction from Na-montmorillonite going faster. A crystalline smectite starting material may or may not be necessary to synthesize a metastable mixed-layer clay. If the run product is metastable, however, then given enough time at an appropriate temperature reaction would completely eliminate the mixed-layer phase. An example of this situation is illite/smectite which reacts towards forming illite at the experimental temperatures (Eberl and Hower, 1976). The speed of this reaction is a function, for example, of temperature and K^+ content of the system. The path of this reaction for a gel starting composition appears to be related to the Al/Si ratio of the system: Velde (1969) has shown that K-mica starting gel, in contrast to K-beidellite gel, will react directly to a micalike phase without passing through intermediate illite/smectites. The illite/smectites may have stability fields at temperatures below 200°C (Eberl and Hower, 1977).

In the following discussion on paragenesis it is assumed that the reaction products, particularly those in the Na-series, have stability fields. This assumption may be valid for Na-rectorite since: 1) it occurs in nature in deposits that have had a long time to react; 2) it can be formed from both smectite and gel starting material; 3) it appears to be very unreactive under the proper hydrothermal conditions. Its stability in our hydrothermal systems has not been demonstrated with any certainty, however, since the reactions smectite → rectorite and rectorite → paragonite have not been reversed.

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Assuming rectorite stability, an activity/temperature diagram (Figure 12) has been calculated after the method of actual and average heat capacities of Helgeson (1969) based on reactions such as the following:

beidellite
$1.09(Al_{2.02})(Si_{3.49}Al_{0.51})O_{10}(OH)_2Na_{0.46} + 0.135Na^+ + 1.02H_2O$
rectorite
$Al_{2.03}(Si_{3.28}Al_{0.72})O_{10}(OH)_2Na_{0.63} + 0.52H_4SiO_4 + 0.135H^+$

The formula for beidellite is simplified from the Black Jack beidellite (Weir and Greene-Kelley, 1962) and that for rectorite from the Baluchistan rectorite (Brown and Weir, 1963b). The reaction as written ignores the effects of interlayer water. Standard Gibbs free energies of formation at 25°C for beidellite and rectorite, quantities necessary for the calculation, were calculated according to the thermochemical approximations of Tardy and Garrels (1974). The details of the calculation will be presented in a later paper, but it can be seen that the relative stabilities of rectorite, beidellite and, for the unwritten reaction, paragonite, will depend on the $[Na^+]/[H^+]$ ratio of the solution, assuming that the silica concentration is a function of quartz saturation.

Actual activities and temperatures are not included in Figure 12 due to the approximate nature of the thermodynamic values. The figure is schematic and shows how the interplay of solution composition and temperature can affect paragenesis in the Na-smectite series, and, by analogy, in the other series. For example, assuming constant $[Na^+]/[H^+]$ in solution (path A), a Na-smectite → rectorite series would be realized with increasing temperature, and paragonite would not form. Keeping temperature constant (path B), a Na-smectite → rectorite → paragonite series would form with increasing $[Na^+]/[H^+]$. The effect of increasing pressure is probably to increase the size of the smectite stability field, as has been discussed by Eberl et al. (1978).

SUMMARY

Some dioctahedral clay minerals are related genetically as well as structurally. Dioctahedral smectite will react under the proper hydrothermal conditions to yield one of four structural trends: the mica, chlorite, pyrophyllite or kaolinite trend. The trend that evolves depends on the interlayer cation and on the concentration of its salt in the run solution. Generally, all of the alkali and alkaline earth interlayer cations yield the mica trend: smectite → mica/smectite → mica. The exception is Li-montmorillonite which follows the chlorite trend: montmorillonite → chlorite/smectite → chlorite. Li-montmorillonite will follow the mica trend in a run solution containing Li^+. Mg-montmorillonite will follow the chlorite trend if the run solution contains Mg^{2+}. The pyrophyllite and kaolinite trends are produced from Ca-montmorillonite at 320 and 150°C respectively if the run solution contains Al^{3+}.

The family of clays that forms from the association of smectite with a particular cation in a hydrothermal system is known as a reaction series and is named for the cation. The K-smectite series includes K-rectorite and illite. Three subseries have been recognized: the K-beidellite gel, the K-montmorillonite, and the glauconite/smectite. The Na-smectite series includes Na-rectorite and paragonite; the Li-montmorillonite series includes Li-tosudite, Li-rectorite, and cookeite(?); the Ca- series includes Ca-rectorite and margarite(?); the Mg- series includes Mg-rectorite, tosudite and sudoite(?); and the Al- series includes pyrophyllite/smectite, pyrophyllite, kaolinite/smectite, and kaolinite.

If stability can be assumed for the mixed-layer phases, paragenesis in a reaction series is a function of P, T, and X conditions and stability fields can be represented on a simple activity-temperature diagram, assuming constant pressure. If the mixed-layer phases are metastable, however, paragenesis is a function of the speed of the reaction and its path.

Minerals in the reaction series can develop from processes other than by the reaction of dioctahedral smectite. For example, illite/smectite can form from illite during weathering. The concept of a reaction series, however, does represent one way of relating the origins of several geologically diverse clay minerals to a common mechanism.

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Резюме- Несколько диоктаэдрических глинистых минералов связываются посредством реакционных серий. Эти серии могут быть получены гидротермически из бейделлитового геля и монтмориллонита в результате простых изменений в межслойных промежутках и в химии раствора. Этими сериями являются :

гель--К-бейделлит --любой иллит/смектит--К-ректорит--иллит
К-монтмориллонит--К-ректорит--иллит
Na- монтмориллонит или бейделлит--Na-ректорит--парагонит
Li-монтмориллонит--Li-тосудит--Li-ректорит--кукеит(?)
Mg-монтмориллонит--Mg-ректорит--тосудит--судоит(?)
Ca-монтмориллонит--Ca-ректорит--маргарит(?)
Al-Ca-монтмориллонит--каолинит/смектит--каолинит(150°C)
Al-Ca-монтмориллонит--пирофиллит/смектит--пирофиллит(320°C)

Если предположить стабильность смешанно-слойных фаз,парагенезис является функцией условий P,T,X. Если фазы рассматривать как неустойчивые,парагенезис является функцией скорости и пути реакции.

Kurzreferat- Mehrere dioktahedrische Tonmineralien gehören zu denselben Reaktionsserien. Diese Serien können aus Beidellitgel und Montmorillonit hydrothermisch hergestellt werden, indem einfache Änderungen in der Zwischenschicht-und Lösungschemie gemacht werden. Die Serien sind die folgenden:

Gel--K-Beidellit--nicht geordnetes Illit/Smektit--K-Rektorit--Illit
K-Montmorillonit--K-Rektorit--Illit
Na-Montmorillonit oder Beidellit--Na-Rektorit--Paragonit
Li-Montmorillonit--Li-Tosudit--Li-Rektorit--Cookeit (?)
Mg-Montmorillonit--Mg-Rektorit--Tosudit--Sudoit (?)
Ca-Montmorillonit--Ca-Rektorit--Margarit (?)
Al-Ca-Montmorillonit--Kaolinit/Smektit--Kaolinit (150°C)
Al-Ca-Montmorillonit--Pyrophyllit/Smektit--Pyrophyllit (320°C)

Wenn man annimmt, daß die gemischt-Schicht Phasen stabil sind, dann ist die Paragenesis eine Funktion der P,T,X Konditionen.Falls die Phasen für metastabil gehalten werden,dann ist die Paragenesis eine Funktion der Geschwindigkeit der Reaktion und des Reaktionsweges.

Résumé-Plusieurs minéraux argileux dioctaèdraux sont apparentés par des suites de réaction.Ces suites peuvent être produites de manière hydrothermale à partir de gels de beidellite et de montmorillonite en faisant de simples changements dans la chimie interfeuillet et de solution.Ces suites sont:

gel--K-beidellite--illite/smectite--K-rectorite--illite
K-montmorillonite--K-rectorite--illite
Na-montmorillonite , beidellite--Na-rectorite--paragonite
Li-montmorillonite--Li-tosudite--Li-rectorite--cookeite(?)
Mg-montmorillonite--Mg-rectorite--tosudite--sudoite(?)
Ca-montmorillonite--Ca-rectorite--margarite(?)
Al-Ca-montmorillonite--kaolinite/smectite--kaolinite(150°C)
Al-Ca-montmorillonite--pyrophyllite/smectite--pyrophyllite(320°C)

Présumant un état de stabilité pour les phases à feuillets mélangés, la paragénèse est une fonction des conditions P,T,X.Si les phases sont considérées comme étant métastables,la paragénèse est une fonction de la vitesse et de la direction de réaction.

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