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COMPOSITIONAL GAP IN DIOCTAHEDRAL-TRIOCTAHEDRAL SMECTITE SYSTEM: BEIDELLITE-SAPONITE PSEUDO-BINARY JOIN

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Abstract—A series of hydrothermal experiments were performed to determine the phase relations on the beidellite-saponite pseudo-binary join. Quenched glasses with stoichiometric dehydrated compositions of an Na-rich smectite on the join were heated at 250–500°C for durations of 1–151 d at 100 MPa. Time-temperature diagrams showed that immiscibility occurs between dioctahedral smectite (beidellite) and trioctahedral smectite (saponite) below 400°C. Thus, smectite with intermediate chemical composition was considered as metastable in this system. Above 400°C, the assemblage of regularly interstratified saponite-chlorite, quartz, and feldspar was recognized in the intermediate chemical compositional region of this join. On the beidellite side of this join, beidellite and mixed-layer phases of smectite and a regular interstratification of montmorillonite-beidellite, are possible phases that occur at <300°C. They readily reacted to form a mixture of dioctahedral rectorite plus quartz at 300°C. This assemblage then reacted to a dioctahedral "mica", which can expand with glycol and quartz. On the saponite side of this join, a single phase, saponite, existed at <400°C, and transformed to saponite plus trioctahedral rectorite with aging and increasing temperature of synthesis. The alteration was affected strongly by the chemical composition of the binary system.

Key Words—Beidellite-Saponite Join, Compositional Gap, Hydrothermal Experiment, Mixed-Layer Phases.

INTRODUCTION

Smectites are classified as either dioctahedral or trioctahedral by the isomorphous substitution of trivalent and divalent cations in the octahedral sheets (Brindley and Brown, 1980). Statistical analysis of chemical data of natural smectites showed large compositional gaps between the two groups (Güven, 1988; Weaver and Polland, 1975). Smectites of intermediate composition are believed to be mixtures of dioctahedral and trioctahedral end-members. Theoretical treatments of unit-cell dimensions of layer silicates also suggested that a discontinuity between dioctahedral and trioctahedral clay minerals exists and that minerals with intermediate chemical composition are metastable (Radoslovich, 1962, 1963a, 1963b; Radoslovich and Norrish, 1962; Veitch and Radoslovich, 1963). In some clays, however, smectite with intermediate chemical compositions were reported (Curtin and Smile, 1981; Kodama *et al.*, 1988; Nahon *et al.*, 1982).

To characterize "intermediate" smectite between trioctahedral and dioctahedral end-members, the synthesis of smectite containing Al^{3+} and Mg^{2+} as octahedral cations was performed at 200°C for 30 and 60 d, and at 250°C for 15 and 30 d under equilibrium water pressure (Decarreau *et al.*, 1992). They used the superposed (060) and (330) X-ray diffraction peaks [hereafter referred to as (060)] to determine the presence of dioctahedral or trioctahedral character (Brindley and Brown, 1980). With longer synthesis time and higher temperature, the product obtained from starting material with composition between beidellite and saponite showed two distinct peaks at 1.49 and 1.53 Å. From these results, Decarreau *et al.* (1992) suggested that an immiscibility exists between beidellite and saponite. Another experimental study of the beidellite-saponite series was performed at 200–250°C for 15–60 d by Grauby *et al.* (1993). Their study by X-ray diffraction (XRD) and analytical transmission electron microscopy showed that the beidellite-saponite series involved different structures at a fine scale. Thus the series was discontinuous and showed a large immiscibility gap. Leger *et al.* (1995) studied the Al^{3+}-Fe^{3+}-Mg^{2+} (octahedral) solid solution in smectites. These experiments were performed at 200°C for 30 d under autogeneous water pressure, but the chemical gap was not observed.

In this paper, smectites in the beidellite-saponite series were synthesized systematically above 250°C at 100 MPa for 1–151 d. Synthesis products were examined by the powder XRD method for randomly oriented mineral aggregates and glycolated samples. The Greene-Kelly test (Greene-Kelly, 1953; Lim and Jackson, 1986) was also performed. The stability of smectite and the transformation of smectite to interstratified minerals are discussed. Based on the experimental results, the compositional gap between beidellite and saponite is confirmed.

EXPERIMENTAL

Starting materials were quenched glasses made from a mixture of Na_2CO_3, Al_2O_3, MgO, and SiO_2 with stoi-

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Table 1. Criteria for X-ray identification of phases.

	d(001) (Å)		*d*(060) (Å)
	EG[1]	GK[1]	CF[1]
Beidellite	17	17	1.49
Saponite	17	17	1.53
Dioctahedral rectorite (di-rectorite)	27	28	1.49
Trioctahedral rectorite (tri-rectorite)	27	28	1.53
Mixed-layer phase of smectite and the 1:1 regular interstratification of montmorillonite and beidellite (S/r.i.M-B)	17[2]	20–27	1.49
Regularly interstratified saponite-chlorite	30–33	31–35	ND[3]
Dioctahedral mica-like phase expanded with ethylene glycol [DM(EG)][4]	17	9.5	1.49
Randomly interstratified paragonite-beidellite (Pa-B)	14	14	1.49
Randomly interstratified chlorite-smectite	15	15	ND[3]

[1] EG: ethyelene-glycolated sample; GK: sample treated by the Greene-Kelly test; CF: compression-free sample for avoiding preferred orientation.
[2] This value is *d*(002).
[3] Not determined.
[4] Yamada *et al.* (1991a), Yamada and Nakazawa (1993).

chiometric dehydrated Na-rich smectite compositions on the beidellite-saponite pseudo-binary join: $Na_{0.6}(Mg_{6-2x}Al_{1.3x})(Al_{0.6}Si_{7.4})O_{22}$, where x = 3, 2.7, 2.2, 1.2, and 0. When x is 3, the chemical composition is that of ideal Na-rich beidellite. When x is 0, the composition is that of Na-rich saponite. The oxide mixtures were fused by an infrared focusing-image furnace, and quenched in water. The furnace was described originally to synthesize single crystals of rare-earth garnets by the floating-zone method (Kimura *et al.*, 1983), and was operated to make starting glasses without a crucible. The glass was crushed and fractionated at <10 μm by hydraulic elutriation, and used as starting material.

Hydrothermal experiments were performed using a rapid-quench type hydrothermal apparatus (Yamada *et al.*, 1988). One hundred mg of pulverized glass and 100 mg of distilled water were sealed in a gold tube. The mix of glass and water was heated at 250–500°C and at 100 MPa. The experiments ranged from 1 to 151 d.

Synthesis products were examined by powder XRD after quenching. Three samples were prepared following the method used by Yamada *et al.* (1991a): compression-free (CF) samples, ethylene-glycolated (EG) samples, and samples treated by the Greene-Kelly test (GK) (Greene-Kelly, 1953; Lim and Jackson, 1986). The CF sample was obtained by crushing and mounting the sample on a "backgroundless" quartz plate without compression to reduce the influence of preferred orientation. The EG sample was prepared as follows: the product was oriented by sedimentation in water onto a glass slide, dried at room temperature, placed in a sealed container with ethylene glycol, and then heated overnight at 60°C. For the GK test, the product was dispersed in 1 M LiCl solution. The sample was isolated from the suspension by centrifugation and the process repeated four times to fully exchange Li for Na. The Li-exchanged sample was washed three times with 90% ethanol to remove excess cations and chloride. This material was oriented on a pure silica glass slide by sedimentation, heated overnight at 300°C, placed in a sealed container with glycerol and then heated overnight at 90°C.

RESULTS

Phase identification criteria

The phases encountered in this study were identified using the same criteria as described previously (Yamada *et al.*, 1991a) and are summarized in Table 1. The typical XRD patterns of the products are shown in Figure 1. The (060) reflection of the CF sample (Figure 1) determined the dioctahedral (*e.g.*, beidellite) or trioctahedral (*e.g.*, saponite) phase. A *d*(060) of 1.48–1.50 Å indicates a dioctahedral phase, and a spacing of 1.53–1.55 Å indicates a trioctahedral phase (Brindley and Brown, 1980). The EG sample is used for the identification of smectite which expands to 17 Å. The GK sample was used to confirm smectite with a tetrahedral negative layer-charge, either beidellite or saponite. After the GK test, a smectite with tetrahedral charge has a spacing of 18 Å, whereas, a smectite with octahedral charge, montmorillonite, has a spacing of 9.6 Å. Beidellite (17 Å for EG, 18 Å for GK, and *d*(060) = 1.49 Å, Figure 1a) and saponite (17 Å for EG, 18 Å for GK, and *d*(060) = 1.53 Å, Figure 1b) were easily identified. The coexistence of beidellite and saponite was characterized by two (060) peaks (Figure 1c).

Two types of rectorite occurred, one involving beidellite and paragonite (di-rectorite) and the other saponite and phlogopite (tri-rectorite). Both rectorite samples have long spacings, 27–28 Å for EG and 28–29 Å for GK. The *d*(060) = 1.49 Å (Figure 1d) of beidellite-paragonite indicated dioctahedral character, whereas saponite-phlogopite was trioctahedral with *d*(060) = 1.53 Å (Figure 1e).

A new interstratification of smectites was observed. The phase has a broad peak near 20–27 Å for GK, but a typical dioctahedral character of smectite for CF and EG (Figure 1f). Thus, the phase consists of a random interstratification of smectite and a rectorite-like material. The rectorite-like material involves the regular (r) interstratification (i) of montmorillonite (M) and

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Table 2. Hydrothermal run products.

T (°C)	t (d)	Product
$Na_{0.6}Al_4(Al_{0.6}Si_{7.4})O_{22}$ (x = 3, beidellite)		
250	7	beid, kaol
	19	beid, kaol
	49	beid, kaol
	129	beid, kaol
300	7	beid
	21	beid
	49	beid
	105	beid
350	7	beid
	21	beid
	49	beid
	55	beid
	105	beid, di-rect
400	7	beid
	27	beid
	55	di-rect
	91	di-rect
	112	di-rect, Qz
450	7	di-rect, DM(EG)
	21	di-rect, DM(EG)
	66	di-rect, DM(EG), Qz
500	7	Pa-B, DM(EG), Crist
	11	DM(EG), Crist
	29	DM(EG), Qz
$Na_{0.6}(Mg_{0.7}Al_{3.5})(Al_{0.6}Si_{7.4})O_{22}$ (x = 2.7)		
250	19	S/r.i.M-B
	50	S/r.i.M-B, Qz
	151	S/r.i.M-B
300	7	S/r.i.M-B, Qz
	21	S/r.i.M-B
	50	S/r.i.M-B, Qz
	105	S/r.i.M-B, Qz
350	7	S/r.i.M-B, Qz
	21	S/r.i.M-B
	51	S/r.i.M-B, Qz
	105	beid, Az
400	7	beid
	31	beid, Qz
	55	beid, Qz
	91	beid, di-rect, Qz, lizar, feld
450	7	di-rect, DM(EG), Qz
	21	di-rect, DM(EG), Qz
	66	di-rect, Qz
500	1	beid, Qz
	11	DM(EG), lizar, Qz
	29	DM(EG), lizar, Qz
$Na_{0.6}(Mg_{1.7}Al_{2.8})(Al_{0.6}Si_{7.4})O_{22}$ (x = 2.2)		
250	19	poorly crystallized S/r.i.M-B
	50	poorly crystallized S/r.i.M-B, Qz
	151	poorly crystallized S/r.i.M-B, Qz
300	7	S/r.i.M-B, Qz
	21	S/r.i.M-B
	50	S/r.i.M-B, Qz
	105	S/r.i.M-B, Qz
350	7	beid, sap, S/r.i.M-B
	21	beid, sap, S/r.i.M-B, Qz
	51	beid, sap, Qz
	105	beid, sap, Qz
400	7	beid, sap, S/r.i.M-B, Qz
	31	beid, sap, Qz
	55	beid, sap, Qz
	91	r.Ch-Sm, Qz
450	7	beid, sap, r.Ch-Sm, Qz
	21	r.Ch-Sm, Qz
	66	r.Ch-Sm, Qz
500	1	beid, sap, Qz
	11	r.Ch-Sm, Qz
	29	Ch-Sm, Qz
$Na_{0.6}(Mg_{3.7}Al_{1.5})(Al_{0.6}Si_{7.4})O_{22}$ (x = 1.2)		
250	19	poorly crystallized sap
	50	poorly crystallized sap
	151	sap, beid
300	7	sap, beid, Qz
	21	sap, beid
	50	sap, beid, Qz
	105	sap, beid, Qz
350	7	sap, beid
	21	sap, beid
	51	sap, beid, Qz, Crist
	105	sap, beid, Qz
400	7	sap, beid, Qz
	31	sap, beid, Qz
	55	sap
	91	r.Ch-Sm, Qz, feld
450	7	sap, r.Ch-Sm, Qz
	21	sap, r.Ch-Sm, Qz
	66	r.Ch-Sm, Qz, feld
500	1	sap, Qz, Crist
	11	sap, r.Ch-Sm, Qz
	29	sap, r.Ch-Sm, Qz
$Na_{0.6}Mg_6(Al_{0.6}Si_{7.4})O_{22}$ (x = 0, saponite)		
250	19	sap
	49	sap
	129	sap
300	7	sap
	21	sap
	49	sap
	105	sap
350	7	sap
	21	sap
	49	sap
	105	sap
400	2	sap
	7	sap
	31	sap
	91	sap
	112	sap, tri-rect
450	2	sap, tri-rect
	7	sap, tri-rect
	21	sap, tri-rect
	66	sap, tri-rect
500	1	sap
	2	sap, tri-rect
	7	sap, tri-rect
	29	sap, tri-rect

beid = beidellite. sap = saponite. di-rect = dioctahedral rectorite. tri-rect = trioctahedral rectorite. S/r.i.M-B = mixed-layered phase of smectite and the 1:1 regularly interstratified montmorillonite-beidellite. r.Ch-Sm = regularly interstratified chlorite-smectite. Ch-Sm = randomly interstratified chlorite-smectite. DM(EG) = dioctahedral mica expanded with ethylene glycol. Pa-B = randomly interstratified paragonite-beidellite. kaol = kaolinite. Qz = quartz. Crist = cristobalite. feld = feldspar. lizar = lizardite.

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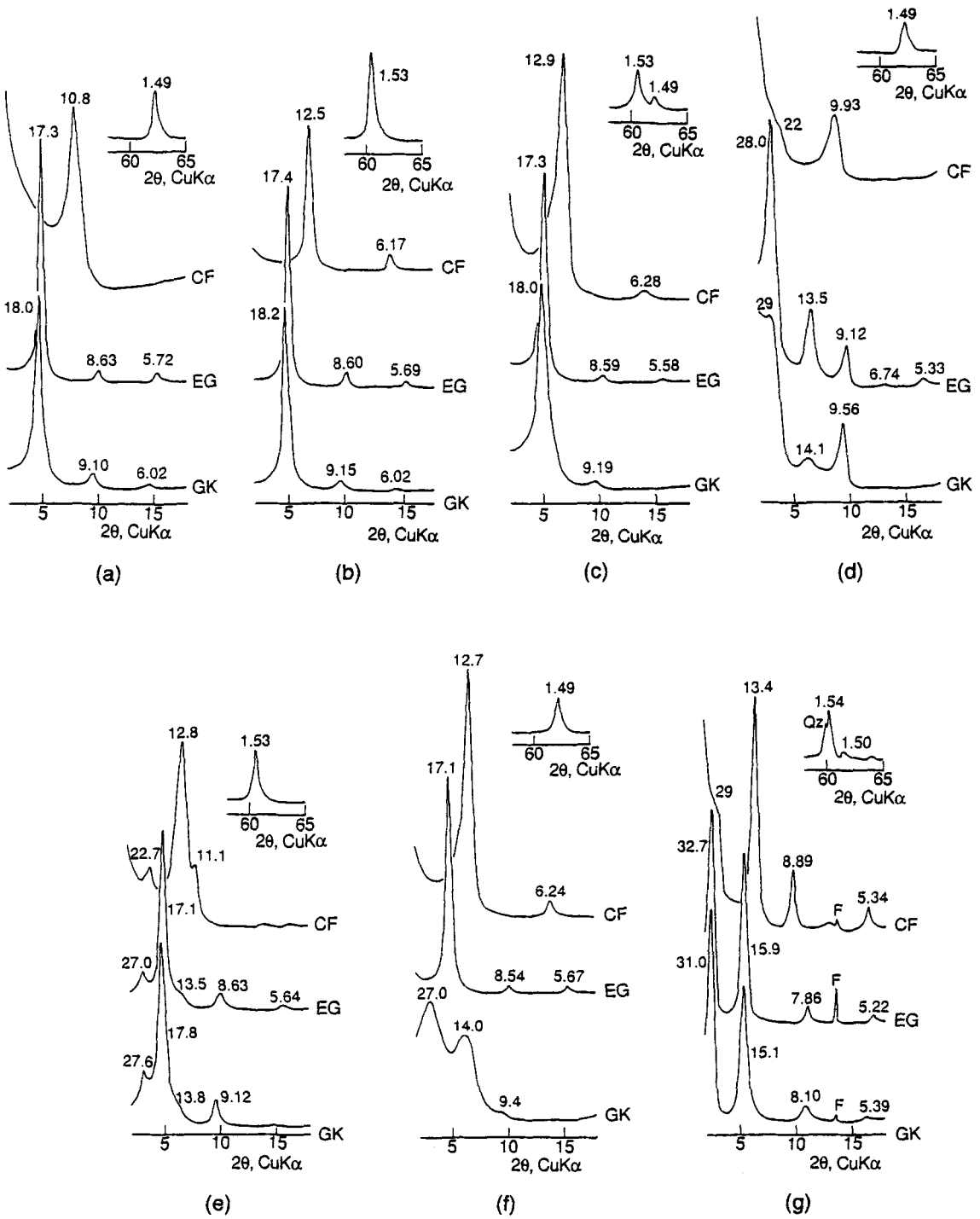


Figure 1. XRD patterns of hydrothermal products from synthetic glass. CF = compression-free sample to reduce preferred orientation. EG = ethylene-glycolated sample. GK = sample after the Greene-Kelly test. (a) Beidellite from $Na_{0.6}Al_4(Al_{0.6}Si_{7.4})O_{22}$ (x = 3) glass at 350°C for 55 d. (b) Saponite from $Na_{0.6}Mg_6(Al_{0.6}Si_{7.4})O_{22}$ (x = 0) glass at 400°C for 31 d. (c) Beidellite and saponite from $Na_{0.6}(Mg_{3.7}Al_{1.5})(Al_{0.6}Si_{7.4})O_{22}$ (x = 1.2) glass at 350°C for 7 d. (d) di-rectorite and quartz from $Na_{0.6}Al_4(Al_{0.6}Si_{7.4})O_{22}$ (x = 3) glass at 400°C for 112 d. (e) Saponite and tri-rectorite from $Na_{0.6}Mg_6(Al_{0.6}Si_{7.4})O_{22}$ (x = 0) glass at 500°C for 2 d. (f) S/r.i.M-B and quartz from $Na_{0.6}(Mg_{0.7}Al_{3.5})(Al_{0.6}Si_{7.4})O_{22}$ (x = 2.7) glass at 350°C for 7 d. (g) r.Ch-Sm, quartz and feldspar from $Na_{0.6}(Mg_{3.7}Al_{1.5})(Al_{0.6}Si_{7.4})O_{22}$ (x = 1.2) glass at 450°C for 66 d. The numbers indicate the observed *d*-values in Å. Qz = quartz. F = feldspar.

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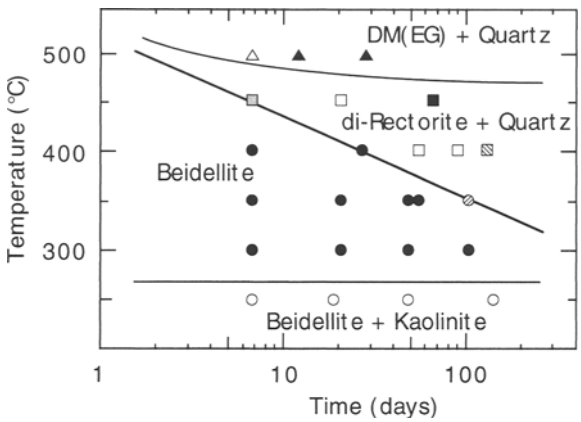


Figure 2. Time-temperature relations of products from $Na_{0.6}Al_4(Al_{0.6}Si_{7.4})O_{22}$ (x = 3) glass. ○ = beidellite + kaolinite. ● = beidellite. ⊘ = beidellite + di-rectorite. □ = di-rectorite. ▨ = di-rectorite + quartz. ▦ = di-rectorite + DM(EG). ■ = di-rectorite + DM(EG) + quartz. △ = Pa-B + DM(EG) + cristobalite. ▲ = DM(EG) + silica mineral (quartz or cristobalite).

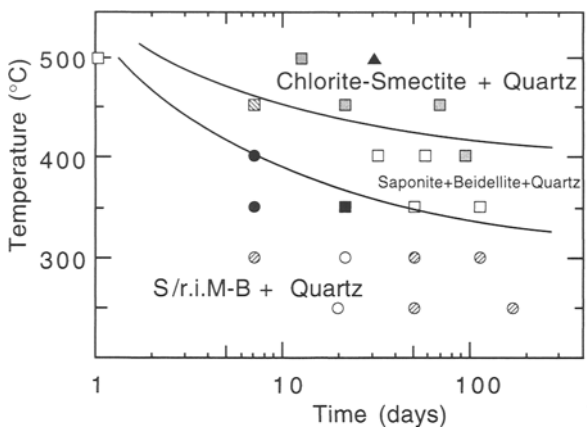


Figure 4. Time-temperature relations of products from $Na_{0.6}(Mg_{1.7}Al_{2.8})(Al_{0.6}Si_{7.4})O_{22}$ (x = 2.2) glass. ○ = S/r.i.M-B. ⊘ = S/r.i.M-B + quartz. ● = beidellite + saponite + S/r.i.M-B. ■ = beidellite + saponite + S/r.i.M-B + quartz. □ = beidellite + saponite + quartz. ▨ = beidellite + saponite + r.Ch-Sm + quartz. ▦ = r.Ch-Sm + quartz. ▲ = Ch-Sm + quartz.

beidellite (B) in a 1:1 ratio. Yamada *et al.* (1991a) referred to the rectorite-like material as "r.i.M-B". Here, because of the presence of an additional smectite component, we refer to the phase as "S/r.i.M-B" for convenience.

There are two chlorite-bearing interstratified minerals. One is a regular interstratified saponite-chlorite with spacings of 30–33 Å for EG and 31–35 Å for GK (Figure 1g). The other was randomly interstratified saponite-chlorite (14 Å for both EG and GK).

Reaction series in beidellite-saponite pseudo-binary system

Experimental results are summarized in Table 2 and plotted in diagrams of temperature *vs.* time (Figures 2–6). In most cases, smectite was the initial phase crystallized from glass, which then reacted to form other phases. The product mineral assemblage was a function of synthesis temperature, synthesis time, and the chemical composition of the starting glass.

For beidellite-like compositions, a poorly crystallized beidellite coexists with kaolinite, and S/r.i.M-B with quartz were initial phases from the glass of x = 3 and x = 2.7, respectively (Figures 2 and 3). With increasing temperature and time, a single phase of beidellite was obtained, which then changed to an assemblage of di-rectorite plus quartz. Above 450°C, DM(EG) [dioctahedral mica-like phase (expanded

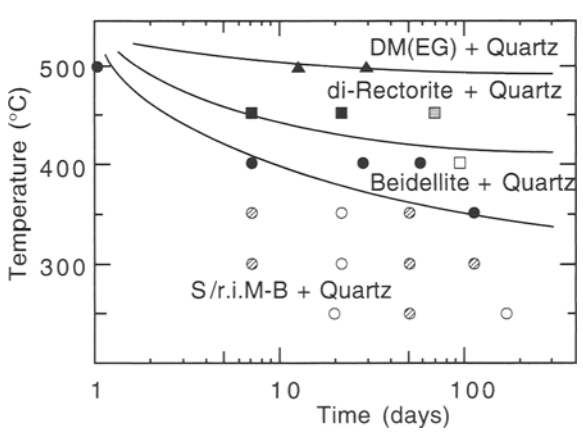


Figure 3. Time-temperature relations of products from $Na_{0.6}(Mg_{0.7}Al_{3.5})(Al_{0.6}Si_{7.4})O_{22}$ (x = 2.7) glass. ○ = S/r.i.M-B. ⊘ = S/r.i.M-B + quartz. ● = beidellite + quartz. □ = beidellite + di-rectorite + lizardite + feldspar. ▦ = di-rectorite + quartz. ■ = di-rectorite + DM(EG) + quartz. ▲ = DM(EG) + quartz + lizardite.

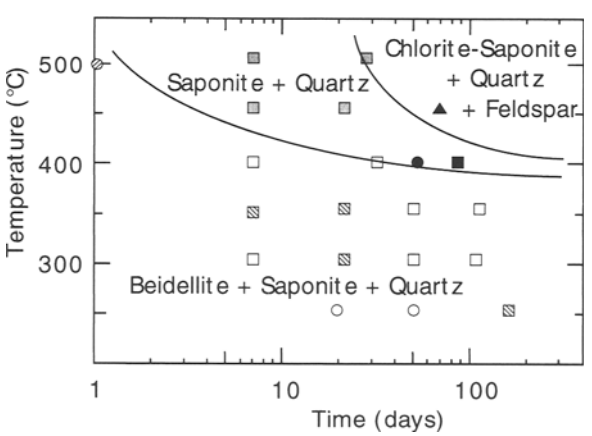


Figure 5. Time-temperature relations of products from $Na_{0.6}(Mg_{3.7}Al_{1.5})(Al_{0.6}Si_{7.4})O_{22}$ (x = 1.2) glass. ○ = poorly crystallized saponite. □ = beidellite + saponite + quartz. ▨ = beidellite + saponite. ● = saponite. ■ = r.Ch-Sm + quartz + feldspar. ▦ = saponite + r.Ch-Sm + quartz. ▲ = r.Ch-Sm + quartz + feldspar.

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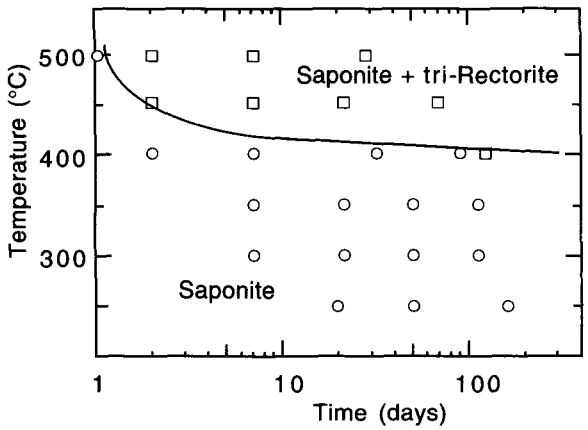


Figure 6. Time-temperature relations of products from $Na_{0.6}Mg_6(Al_{0.6}Si_{7.4})O_{22}$ (x = 0) glass. ○ = saponite. □ = saponite + tri-rectorite.

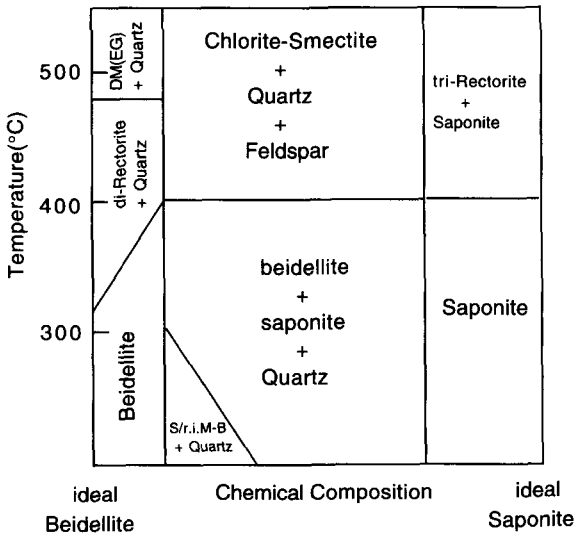


Figure 7. Schematic phase relation in the beidellite-saponite pseudo-binary system. S/r.i.M-B = mixed-layer phase of smectite and the 1:1 regularly interstratified montmorillonite-beidellite. di-rectorite = dioctahedral rectorite. tri-rectorite = trioctahedral rectorite. DM(EG) = dioctahedral mica-like phase expanded with ethylene glycol. Chlorite-smectite = interstratified chlorite and smectite.

with ethylene glycol); Yamada *et al.*, 1991a; Yamada and Nakazawa, 1993] occurred with quartz and/or lizardite.

From glass of x = 2.2, S/r.i.M-B and quartz were identified below 350°C (Figure 4). With increasing synthesis temperature and time, the assemblage changed from S/r.i.M-B + quartz to saponite + beidellite + quartz, and then to interstratified chlorite-smectite + quartz. For the assemblage of saponite + beidellite, the ratio of the integral intensity of the (060) peaks (1.49-Å and 1.53-Å peaks) was 2:1. The integrated intensity of the (060) peaks was measured planimetrically. No attempt was made to either calculate the absolute value of the structure factor for each phase or to make comparisons to a standard for quantitative analysis. Thus, the two peaks at 1.49 and 1.53 Å were used to characterize octahedral components and the ratio was used to estimate qualitatively the amount of coexisting saponite and beidellite (see below).

At x = 1.2, the assemblage of beidellite + saponite + quartz was observed at lower temperature (Figure 5). The ratios of the (060) reflection of beidellite and saponite at 300 and 350°C was 5:1 and 8:1, respectively. With increasing synthesis temperature and time, beidellite was not observed, but saponite of high crystallinity (the full width at half maximum intensity of the (001) reflection was ~0.5°) was observed coexisting with quartz and regularly interstratified saponite-chlorite. After long duration, regularly interstratified saponite-chlorite was obtained with quartz and feldspar.

From glass of saponite composition (x = 0), saponite was obtained in the entire range of the temperature-time diagram (Figure 6). With increasing temperature and duration, the amount of the regularly interstratified saponite-mica (tri-rectorite), which coexisted with saponite, increased.

DISCUSSION

A summary of the probable phase relations in this pseudo-binary system is shown schematically in Figure 7. The diagram is based on the present results and some speculation. The temperatures of the phase boundaries given are probably slightly higher than those found in nature owing to the short duration and chemical purity of the synthetic system.

Immiscibility between dioctahedral and trioctahedral smectites

In natural samples of smectite, large compositional gaps occur in the temary diagram (Al^{3+}-Fe^{3+}-Mg^{2+}) of dioctahedral and trioctahedral smectites (Güven, 1988; Weaver and Polland, 1975). For the beidellite-saponite system (Decarreau *et al.*, 1992; Legar *et al.*, 1995), a smectite with intermediate dioctahedral-trioctahedral structure occurred at 200°C for experiments of 30 d. At higher temperatures and longer time, two phases, saponite and beidellite, crystallized at 250°C (Decarreau *et al.*, 1992). Thus, the smectite with intermediate chemical compositions between dioctahedral and trioctahedral end-members was assumed to be metastable; an immiscibility was postulated between dioctahedral and trioctahedral phases. A similar study, but using chemical microanalysis and careful XRD analyses showed also a large chemical gap (Grauby *et al.*, 1993).

The present study, using temperature-time relations supports the earlier work (Decarreau *et al.*, 1992; Grauby *et al.*, 1993). If the ratio of the intensity of the

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(060) reflection for dioctahedral (beidellite) *vs.* trioctahedral (saponite) components may be applied quantitatively, the estimated range for the compositional gap for x = 2.2 and 1.2 is $B_{85}S_{15}$-$B_{35}S_{65}$, where B and S are the compositions of ideal beidellite and that of saponite, respectively (Figure 7). This compositional gap is comparable to those obtained from *d*(060)-values for (Mg-Al)-smectite in Decarreau *et al.* (1992).

Phase changes in beidellite-saponite pseudo-binary system

In the intermediate region of this pseudo-binary system, the assemblage of beidellite, saponite, and quartz, and the assemblage of S/r.i.M-B and quartz were considered as low-temperature phases. The former assemblage was observed in nearly the entire range of this system, but the latter appeared only in a limited compositional range below 300°C. The regularly interstratified chlorite-smectite was obtained at high temperature. Thus the results show that smectite is transformed to the mixed-layer phase of chlorite-smectite, which is consistent with occurrences of the trioctahedral chlorite-smectite, tosudite. Tosudite is rare and limited to hydrothermal alteration of acidic igneous rocks (Reynolds, 1988).

In the Al-rich region of this system, beidellite is obtained below 300°C, but transforms to di-rectorite at higher temperatures. The beidellite region in the temperature-time diagram is consistent with that obtained in previous studies. Beidellite was synthesized below 400°C in 7 d (Yamada *et al.,* 1991a, 1991b), and at 350°C for 20 d (Kloprogge *et al.,* 1990). The hydrothermal synthesis of $Na_{0.7}$-beidellite occurred also at 250–450°C (Kloprogge *et al.,* 1993). The reaction sequence from beidellite to rectorite is the same as that observed in previous studies (Carman, 1974; Eberl and Hower, 1977; Eberl, 1978; Yamada *et al.,* 1991a, 1991b; Kloprogge *et al.,* 1993). Above 450°C, the assemblage of DM(EG) + quartz was independent of time and was considered to be a high-temperature phase of di-rectorite. DM(EG) expands with EG intercalation, but does not expand with water and GK treatment. Therefore, it is not an expandable mica, such as Na-rich taeniolite, Na-rich tetrasilicic mica, and Na-rich phlogopite (Kitajima *et al.,* 1973; Kitajima and Daimon, 1975; Matsuda and Henmi, 1986; Fujita *et al.,* 1991). Yamada and Nakazawa (1993) proposed a mixture of two or more phases for DM(EG). They suggested an assemblage of smectite + interstratified paragonite-pyrophyllite or a three-component interstratification of paragonite-pyrophyllite-smectite. Another possible candidate for DM(EG) is a high-charge beidellite, which was synthesized by Kloprogge *et al.* (1993). A more detailed characterization of DM(EG) is necessary to understand the unusual expansion behavior.

The trioctahedral smectite, saponite, occurs in a wide compositional range below 400°C, which is consistent with Eberl *et al.* (1978) and Whitney (1983). They showed that trioctahedral smectites are more thermally stable than dioctahedral smectites at high temperatures. With increasing temperature and time, the appearance of tri-rectorite with saponite in the Mg-rich region is explained by analogy to the reaction sequence from dioctahedral smectite to di-rectorite (*e.g.,* Eberl, 1978).

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