

## ISOTHERMAL TREATMENTS OF REGULARLY INTERSTRATIFIED MONTMORILLONITE-BEIDELLITE AT HYDROTHERMAL CONDITIONS

HIROHISA YAMADA AND HIROMOTO NAKAZAWA

National Institute for Research in Inorganic Materials  
Namiki 1, Tsukuba, Ibaraki 305, Japan

**Abstract**—A glass in the intermediate composition of montmorillonite and beidellite, 50/50 in mole ratio, was treated under a hydrothermal pressure of 100 MPa, in the temperature range from 250 to 500°C and durations from 2 to 129 days. The phases identified in the products were plotted in a time-temperature-transformation (TTT) diagram. The TTT diagram showed that the regularly interstratified montmorillonite-beidellite (r.i.M-B) was a metastable phase above the temperature of 350°C, and changed to the assemblage of Na-rectorite + saponite + quartz, through the intermediate assemblage of beidellite + saponite + quartz. The TTT diagram suggested also that the r.i.M-B might be a stable clay mineral below the temperature of 300°C in the middle region of montmorillonite-beidellite pseudo-binary system, although the laboratory confirmation of the mineral stability was not easy for the sluggish reaction.

**Key Words**—Hydrothermal condition, Isothermal treatments, Regularly stratified montmorillonite-beidellite.

### INTRODUCTION

It is an open question in the crystal-chemistry of clay minerals what the smectite with the intermediate composition between montmorillonite and beidellite is. It might be a two-phase mixture of montmorillonite and beidellite, or a phase of complete solid solution between them. Recently another state, the regularly interstratified montmorillonite-beidellite (r.i.M-B) has been found in the pseudo-binary system of montmorillonite-beidellite at a hydrothermal pressure of 100 MPa and below the temperature of 375°C (Yamada *et al.*, 1991b). Because of the short duration of 7 days in that synthetic experiment, the r.i.M-B and other phases that appeared might be far from their equilibrium. The confirmation of reaction sequence and the stability relations among the phases was thus necessary by a long-duration experiment.

In the present paper, a kinetic study of hydrothermal experiments at 100 MPa is performed changing the run duration and temperature.

### EXPERIMENTAL MATERIALS AND METHODS

The starting material was the same glass used in portions of the previous study (Yamada *et al.*, 1991b). The chemical composition of the glass was determined to be  $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{MgO}:\text{Na}_2\text{O} = 66.80:28.16:1.93:3.22$  wt. %, using an electron microprobe analyzer (SHIMADZU, EPMA SM-7). The composition was expressed as  $M_{48}B_{52}$ , where M and B denote the composition of ideal anhydrous Na-montmorillonite and Na-beidellite, respectively. The glass was crushed and size-fractionated to  $<10 \mu\text{m}$  by hydraulic elutriation.

The hydrothermal experiments were performed using a rapid-quench hydrothermal apparatus (Yamada

*et al.*, 1988). The mixture of glass and water in the ratio of 1:1 by weight was sealed in Au-tube, then treated at a pressure of 100 MPa and at temperatures of 250–500°C. The experimental durations ranged from 2–129 days for the kinetic study.

The run products were examined by powder X-ray diffraction (XRD) after quenching. Three samples were prepared for XRD from a run product by the same method as used in the previous study (Yamada *et al.*, 1991b): the compression-free (CF) samples, the ethylene-glycolated (EG) samples, and those treated by the so called Greene-Kelly test (GK) (Greene-Kelly, 1953; Lim and Jackson, 1986). The CF sample was prepared by crushing the quenched product and mounting on a quartz plate of an off-Bragg cut without compression to avoid the influence of preferred orientation. The EG sample was prepared as follows: The product oriented by water on a slide glass was placed in a sealed container with ethylene glycol, then heated overnight at 60°C. The GK sample was obtained in the following manner: A product was ion-exchanged by washing three times with aqueous 1 M LiCl and then three times with 80% ethanol in a test tube. An Li-exchanged sample was oriented on a silica glass slide, heated overnight at 300°C, put in a sealed glass container with glycerol, then heated overnight at 90°C.

Some products were examined by an *in situ* XRD method under various relative humidity conditions in the range of 0–100% (Watanabe and Sato, 1988).

### RESULTS

#### *Identification criteria of phases*

The phases encountered in this study were identified using the same criteria as described in Yamada *et al.* (1991b).

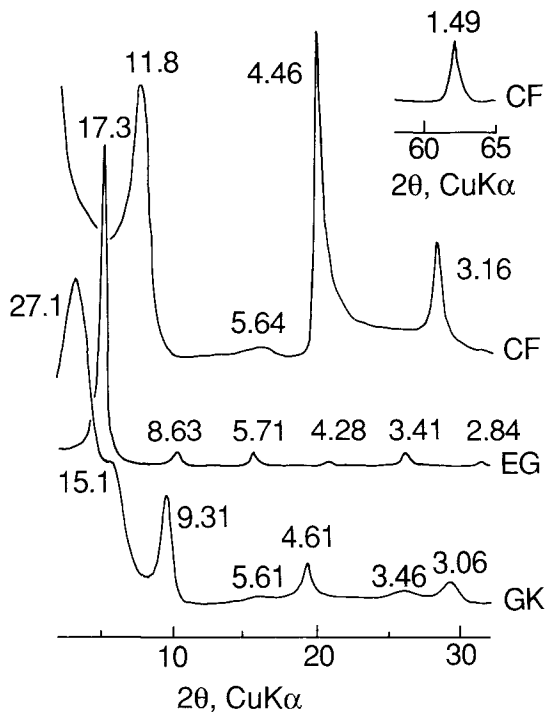


Figure 1. Powder X-ray diffraction patterns of r.i.M-B at 300°C under 100 MPa for 105 days. CF = compression-free sample for avoiding preferred orientation, EG = ethylene-glycolated sample, GK = sample after the Greene-Kelly test. The numbers indicate the observed d-spacings of peaks in Å.

*Regularly interstratified montmorillonite-beidellite (r.i. M-B).* The regular interstratification of two dioctahedral smectites, beidellite (17 Å for GK) and montmorillonite (9.6 Å for GK), is identified by a superstructure reflection (27 Å) in the GK sample (Figure 1, GK). The XRD patterns of CF and EG samples are, however, similar to those of a typical dioctahedral smectite (Figure 1, CF and EG).

*Beidellite.* Beidellite, a dioctahedral smectite with tetrahedral charge, is characteristic in that it expands to 17 Å by ethylene glycol intercalation and to 18 Å after the Greene-Kelly test. Its d(060) is 1.49 Å (Figure 2).

*Na-rectorite, regularly interstratified beidellite-paragonite.* The long spacings of 27–28 Å for the EG sample and also about 28 Å for the GK sample (Figure 3) are the basis for the identification of Na-rectorite as a regular interstratification of a beidellite layer (17 Å for EG and 18 Å for GK) and a paragonite layer (9.6 Å for EG and GK).

*Dioctahedral and trioctahedral mica-like mineral expanded with ethylene glycol, DM(EG) and TM(EG).* The phases have not been characterized in detail. The following XRD observations are attributed to the phases. The basal spacings are 9.7 Å for the CF samples and are independent of the change in the relative hu-

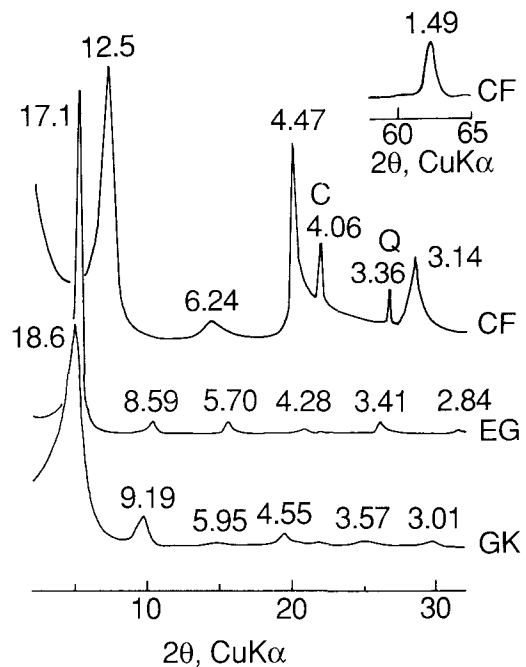


Figure 2. Powder X-ray diffraction patterns of beidellite + silica mineral at 400°C under 100 MPa for 27 days. Notations in the figure are the same as those in Figure 1. C = cristobalite, Q = quartz.

midity. The basal spacings expand, however, to 17 Å for the EG sample and shrinks to 9.5 Å for the GK sample. Two d(060) spacings are observed at 1.49 Å and 1.54 Å (Figure 4). The latter peak is overlapped with the (211) peak of quartz. A temporary interpretation of these observations is that there are two phases similar to a micaceous mineral, but having swelling characteristics with EG similar to that of montmorillonite. These phases are called here a dioctahedral and a trioctahedral mica-like mineral expanded with EG, and they are denoted by DM(EG) and TM(EG), respectively. These phases have been described in previous papers (Yamada *et al.*, 1991a, 1991b) using abbreviations DSm(M) and TSm(M), respectively. Some other interpretations may be possible for the XRD observations described above. Further inspection is surely necessary but is not in the scope of the present paper.

*Randomly interstratified paragonite-beidellite (Pa-B).* An XRD peak observed at about 14 Å for both EG and GK samples is characteristic and is attributed to the random interstratification of a paragonite layer (9.6 Å for EG and GK) and a beidellite layer (17 Å for EG and 18 Å for GK).

#### Phases appeared in the kinetic experiments

All phases identified are summarized in Table 1 for the hydrothermal products under various temperatures and durations. The observed phases and phase assem-

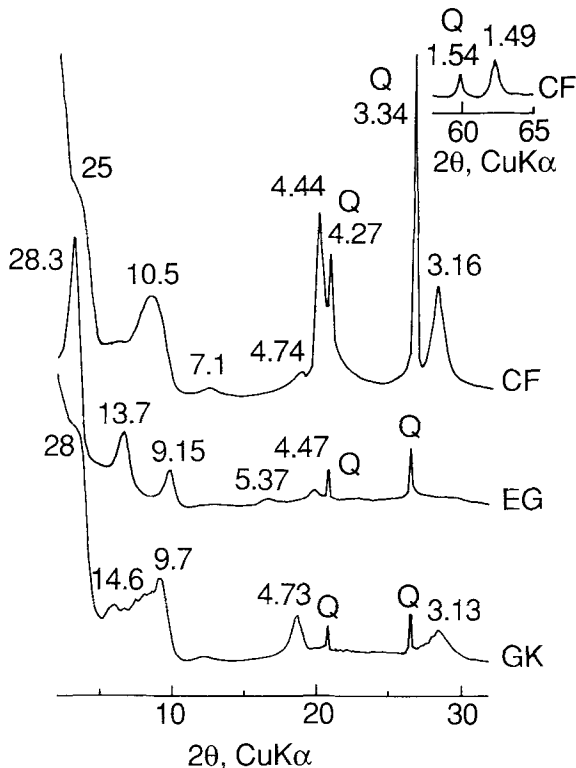


Figure 3. Powder X-ray diffraction patterns of Na-rectorite + silica mineral at 450°C under 100 MPa for 66 days. Notations in the figure are the same as those in Figure 1. Q = quartz.

blages are plotted in a diagram of temperature vs. duration (Figure 5). The diagram is called generally the time-temperature-transformation (TTT) diagram (Putnis, 1992).

The regularly interstratified montmorillonite-beidellite (r.i.M-B) appeared as a single phase at 250°C, for longer durations of 49 and 129 days, and at 300°C for the entire range of durations (solid circle). But r.i.M-B coexisted with silica mineral (cristobalite and/or quartz) at 350°C, for longer durations of 55 and 105 days (open circle), and disappeared at 400° and 450°C for a longer duration than seven days (squares and triangles). Amorphous materials coexisted with r.i.M-B at 400° and 450°C for a short duration of two days and coexisted with montmorillonite plus beidellite at 250°C for seven days.

At 400°C, beidellite was observed instead of r.i.M-B for longer duration. With increasing duration, the assemblage of beidellite and silica mineral (open square) changed to an assemblage of beidellite, a small amount of Na-rectorite, and silica mineral (solid square). At 450°C, the latter assemblage was also observed as an intermediate state; but for long duration, Na-rectorite and quartz appeared (solid triangle).

At a temperature of 500°C, DM(EG), TM(EG), and

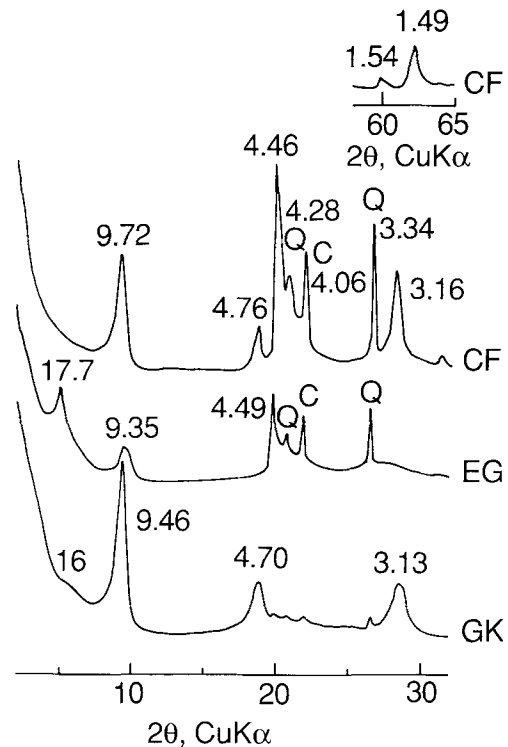


Figure 4. Powder X-ray diffraction patterns of Pa-B + DM(EG) + TM(EG) + silica mineral at 500°C under 100 MPa for 11 days. Notations in the figure are the same as those in Figure 1. C = cristobalite, Q = quartz.

a very small amount of Pa-B coexisted with the silica mineral independent from the durations (open triangle). Pa-B is not clearly detected in the present study because the amount of this phase is very small. But the presence of Pa-B was concluded by considering the previous result (Yamada *et al.*, 1991b), where Pa-B was detected more clearly in the montmorillonite-rich region.

The TTT diagram is divided into the following four regions (Figure 5): (I) r.i.M-B; (II) beidellite + saponite + quartz, (III) Na-rectorite + saponite + quartz; and (IV) Pa-B + DM(EG) + TM(EG) + quartz. In the temperature range of 350–500°C, the reaction series is as follows in increasing duration: amorphous material (glass) → (I) → (II) → (III).

The presence of saponite was not clearly confirmed in this experiment, but was inferred for the following reasons. In a previous study (Yamada *et al.*, 1991b), saponite has been clearly detected by the XRD method in the montmorillonite-rich region, but its composition was not on the montmorillonite-beidellite pseudo-binary join. To explain consistently both the mass balance of the phases that appeared and the phase relations in the intermediate composition, a Mg-rich phase, saponite, must appear, which may not be detected by the XRD method because of its small concentration.

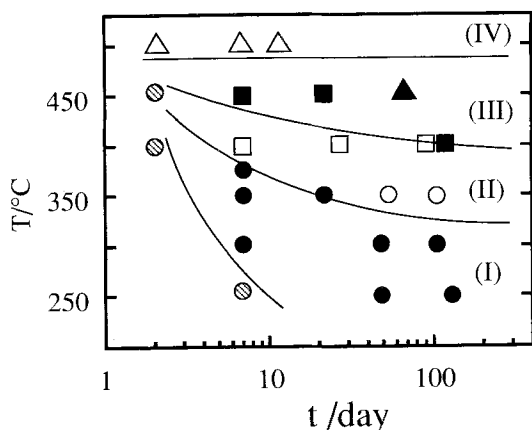


Figure 5. Duration-temperature relations of the synthesized phases. Solid circle = regularly interstratified montmorillonite-beidellite (r.i.M-B); open circle = r.i.M-B + silica mineral; circle with diagonal stripes = amorphous material + r.i.M-B or amorphous material + montmorillonite + beidellite; open square = beidellite + silica mineral; solid square = beidellite + Na-rectorite + silica mineral; solid triangle = Na-rectorite + silica mineral; open triangle = randomly interstratified paragonite-beidellite (Pa-B) + dioctahedral and trioctahedral mica expanded with ethylene glycole (DM(EG) and TM(EG)) + silica mineral. The Roman letters indicate the proposed phase assemblage: (I) r.i.M-B, (II) beidellite + saponite + quartz, (III) Na-rectorite + saponite + quartz, (IV) Pa-B + DM(EG) + TM(EG) + quartz.

Silica minerals, cristobalite and quartz, were often observed in these kinetic experiments. The amount of silica mineral, cristobalite plus quartz, increased as the duration increased at every experimental temperature. It was clearly recognized in runs at 350°C, 400°C, and 450°C, where quartz appeared for the longer duration instead of cristobalite. At 500°C, the amount of quartz increased, but that of cristobalite decreased as the duration increased. These results are consistent with the stability of quartz and metastability of cristobalite under these experimental conditions. Therefore quartz is described as a stable silica mineral in the TTT diagram.

## DISCUSSION

### Reaction sequence of r.i.M-B

In the previous study (Yamada *et al.*, 1991b), the phase relations in the montmorillonite-beidellite pseudo-binary system were tentatively proposed for a pressure of 100 MPa and temperatures of 250°–500°C using the data obtained in the synthetic experiments for a duration of seven days. Because of the short duration, the proposed phase relations were not completely reliable.

The present experiments show early that the r.i.M-B is a metastable phase above the temperature of 350°C. The assemblage (II), beidellite + saponite + quartz, is transient and the assemblage (III), Na-rectorite + saponite + quartz, may be a stable phase in the temper-

Table 1. Hydrothermal run products.

Temp. (°C)	Days	Products*
250	7**	poorly crystallized Mont., Bied, Amor
	49	r.i.M-B
	129	r.i.M-B
300	7**	r.i.M-B
	50	r.i.M-B
	105	r.i.M-B
350	7**	r.i.M-B
	21	r.i.M-B
	55	r.i.M-B, Crist
	105	r.i.M-B, Crist, Qtz
375	7**	r.i.M-B
400	2	r.i.M-B, Amor
	7**	Beid, Crist
	27	Beid, Crist, Qtz
	91	Beid, Qtz
	112	Beid, Na-rec, Qtz
	450	2
7**	Beid, Na-rec, Crist	
500	21	Beid, Na-rec, Qtz, Crist
	66	Na-rec, Qtz
	11	Pa-B, DM(EG), TM(EG), Qtz, Crist

\* r.i.M-B = regularly interstratified montmorillonite-beidellite, Beid = beidellite, Mont = montmorillonite, Na-rec = Na-rectorite (regularly interstratified paragonite-beidellite), Pa-B = randomly interstratified paragonite-beidellite, DM(EG) = dioctahedral mica-like mineral expanded with ethylene glycol, TM(EG) = trioctahedral mica-like mineral expanded with ethylene glycol, Crist = cristobalite, Qtz = quartz, Amor = amorphous material.

\*\* Results in the previous study (Yamada *et al.*, 1991b).

ature range of 350°–500°C. The TTT diagram shows a boundary curve between assemblages (I), r.i.M-B, and (II) almost parallel to the time-axis for long duration. This suggests that the r.i.M-B may be a stable phase below 300°C.

The metastability of r.i.M-B above 350°C in the present TTT diagram is consistent with the results by the hydrothermal kinetic experiments both for the reaction series of smectite and the transformation of smectite to mixed-layer mineral (Eberl and Hower, 1977; Eberl, 1978). Eberl and Hower (1977) proposed a phase diagram in the system of  $K_2O$ - $Na_2O$ - $SiO_2$ - $Al_2O_3$ , which was constructed from the kinetic experiments and from the composition and occurrence of natural clay minerals. They indicated that a beidellite-rectorite-paragonite series is observed when sodium is the interlayer cation and the temperature is above 300°C.

### Unusual expansion characteristic of DM(EG) and TM(EG)

The assemblage (IV), Pa-B + DM(EG) + TM(EG) + quartz, was not dependent on the durations and is considered to be stable at 500°C. As was shown in the previous section, DM(EG) and TM(EG) behave some-

what unusually as a mica-like mineral under ambient conditions: They do not expand with water and GK treatments, but expand with EG. Some micas—e.g., Na-taeniolite, Na-tetrasilic mica, and Na-phlogopite—are known as expandable mica (Carman, 1974; Fujita *et al.*, 1991; Kitajima and Daimon, 1975; Kitajima *et al.*, 1973; Matsuda and Henmi, 1986). These micas, however, swell with water. Therefore, DM(EG) and TM(EG) are not identified as those known expandable micas. It may be an interpretation that DM(EG) and TM(EG) are not single phase but a mixture of two or more phases. An assemblage of saponite and an interstratified paragonite/pyrophyllite may be a candidate. A three-component interstratification of paragonite/pyrophyllite/smectite may be also another candidate.

#### ACKNOWLEDGMENTS

The authors are grateful to Prof. T. Watanabe, Joetsu University of Education, for the use of a relative humidity control system for X-ray diffraction, which was designed and operated by him. We thank Dr. S. Lawson, NIRIM, for improving the English text. We also thank Mr. K. Kosuda for his help in EPMA analysis.

#### REFERENCES

- Carman, J. H. (1974) Synthetic sodium phlogopite and its two hydrates: Stabilities, properties, and mineralogic implications: *Amer. Mineral.* **59**, 261–273.
- Eberl, D. (1978) Reaction series for dioctahedral smectites: *Clays & Clay Minerals* **26**, 327–340.
- Eberl, D. and Hower, J. (1977) The hydrothermal transformation of sodium and potassium smectite into mixed-layer clay: *Clays & Clay Minerals* **25**, 215–227.
- Fujita, T., Sugimori, K., and Nakazawa, H. (1991) Conversion of fluor-phlogopite to hydroxy-phlogopite in NaOH and LiOH hydrothermal solutions: *J. Ceram. Soc. Japan* **99**, 745–750 (in Japanese with English abstract).
- Greene-Kelly, R. (1953) The identification of montmorillonoids in clays: *J. Soil Sci.* **4**, 233–237.
- Kitajima, K. and Daimon, N. (1975) Synthesis of Na-flour-tetrasilic mica  $[\text{NaMg}_{2.3}(\text{SiO}_{10})\text{F}_2]$  and its swelling characteristics: in *Nippon Kagaku Kaishi*, 1975, 991–995 (in Japanese with English abstract).
- Kitajima, K., Sugimori, K., and Daimon, N. (1973) Studies of the swelling of Na-taeniolite with water: in *Nippon Kagaku Kaishi*, 1973, 1885–1892 (in Japanese with English abstract).
- Lim, C. H. and Jackson, M. L. (1986) Expandable phyllosilicate reaction with lithium on heating: *Clays & Clay Minerals* **34**, 346–352.
- Matsuda, T. and Henmi, K. (1986) Syntheses of trioctahedral micas in the compositional join phlogopite–sodium phlogopite: *J. Min. Soc. Japan* **17**, 187–193 (in Japanese with English abstract).
- Putnis, A. (1992) *Introduction to Mineral Sciences*: Cambridge University Press, Cambridge, 351–358.
- Watanabe, T. and Sato, T. (1988) Expansion characteristics of montmorillonite and saponite under various relative humidity conditions: *Clay Science* **7**, 129–138.
- Yamada, H., Fujita, T., and Nakazawa, H. (1988) Design and calibration of a rapid quench hydrothermal apparatus: *J. Ceram. Soc. Japan* **96**, 1041–1044.
- Yamada, H., Yoshioka, K., and Nakazawa, H. (1991a) Hydrothermal synthesis of beidellite from aluminosilicate glass by varying water/solid ratio: *Mineral. J.* **15**, 300–308.
- Yamada, H., Nakazawa, H., Yoshioka, K., and Fujita, T. (1991b) Smectites in montmorillonite–beidellite series: *Clay Miner.* **26**, 359–369.

(Received 27 April 1992; accepted 12 August 1993; Ms. 2220)