

## COOLING RATE DEPENDENCY OF THE FORMATION OF SMECTITE CRYSTALS FROM A HIGH-PRESSURE AND HIGH-TEMPERATURE HYDROUS MELT

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**Abstract**—The effect of cooling rate on the formation of smectite crystals with high crystallinity was investigated using two different types of high-pressure and high-temperature apparatus, a modified belt type and a uniaxial split-sphere type. The cooling rate was changed after a treatment of the sample at 5.5 GPa and 1500°C. Smectite crystals were obtained at faster cooling rate, coexisting with coesite, kyanite, jadeite, corundum and/or glass. In the slowly cooled process, no smectite crystals were obtained but coesite, kyanite, jadeite and clinoenstatite were formed. These results indicate that smectite crystals are formed metastably during the quenching of the high-pressure and high-temperature hydrous silicate melt.

**Key Words**—High pressure experiment, Quenching rate, Smectite crystals.

### INTRODUCTION

Smectite is recognized to be a very fine and low-crystallinity material. A single crystal of smectite has been demanded to understand the essential properties of smectite. Smectites with high crystallinity were synthesized by the hydrothermal treatment of glass with the composition of Na-montmorillonite at the high-pressure and high-temperature of 5.5 GPa and 1500°C (Nakazawa *et al* 1992), and were observed with high-pressure minerals such as coesite, kyanite and jadeite. The smectites were identified by the powder X-ray diffraction method and confirmed by an expansion with ethylene glycol. Transmission electron microscopy showed that the smectite occurred as single crystals in the forms of thin ribbons, lathes and plates, which had dimensions of a few tens of microns. The chemical composition of the smectites was similar to that of Na-montmorillonite. The smectites with high crystallinity and large dimension are denoted as smectite crystals hereafter.

Recently the formation conditions of smectite crystals were investigated by the quenching method in the range of pressure and temperature from 2 to 5.5 GPa and from 700 to 1800°C, respectively (Yamada *et al* 1994). They indicated that the conditions of above 3 GPa and 1000°C were essential for the formation of smectite crystals. These physical conditions are rather similar to those of a hydrous silicate melt. The smectite crystals may be formed as a metastable phase by quenching of a hydrous silicate melt.

In order to examine the metastable formation of the smectite crystals, the syntheses of smectite crystals are carried out in two types of high-pressure and high-temperature apparatus by changing the cooling rate

after the treatment at 5.5 GPa and 1500°C in the present study.

### EXPERIMENTAL

The starting material used was synthetic Na-montmorillonite. It was obtained by the hydrothermal treatment of glass with the composition of the dehydrated Na-montmorillonite,  $\text{Na}_{0.70}\text{Mg}_{0.67}\text{Al}_{3.21}\text{Si}_{8.08}\text{O}_{22.0}$  at 100 MPa and 325°C for 10 days.

Two types of high-pressure and high-temperature apparatus were used in this study. One of them was a modified belt-type high-pressure apparatus with a bore diameter of 32 mm (Yamaoka *et al* 1992). The pressure was calibrated at room temperature from the known pressure induced phase transitions of Bi, T and Ba metals. Temperature was calibrated before experiment from the relation between the input power and the temperature in the heating process, using a Pt-6%Rh/Pt-30%Rh thermocouple without correction for the pressure effect on emf.

The starting materials were sealed with distilled water in Pt capsules, 6.0 mm in outer diameter, 0.25 mm in thickness and about 10 mm in length. The water content was fixed to be 30% by weight. The capsule was then embedded in the sample assembly (Figure 1). The sample was kept at 5.5 GPa and 1500°C for 30 minutes, and then cooled by three different processes as shown in Figure 2: (A) the sample was quenched by shutting off the electric power supply, (B) the input power was decreased at the desired rate by a programmable controller, and (C) the power was decreased at a constant rate to the desired value, and then shut down for quenching. After allowing the sample to reach room

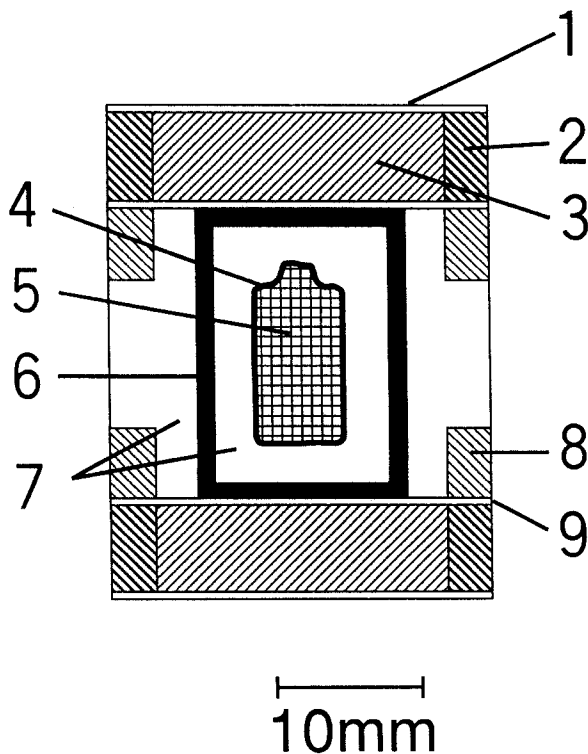


Figure 1. Sample assembly for the high-pressure and high-temperature experiment using a modified belt-type apparatus. 1: stainless steel plate, 2: current ring, 3:  $ZrO_2$  thermal insulator, 4: platinum capsule, 5: sample, 6: graphite heater, 7: NaCl-10% $ZrO_2$  by weight pressure medium, 8: steel ring, 9: molybdenum plate.

temperature, the pressure was released and the run product was recovered under ambient conditions.

The other apparatus used was a uniaxial split-sphere type (USSA-5000) at the Institute for Study of the Earth's Interior, in which the cubic assembly of eight tungsten carbide anvils is compressed with the aid of a 5000-ton hydraulic press (Ito *et al* 1984). The generated pressure was calibrated at room temperature using the relation of the applied load and the known transitions of Bi, I-II and III-V, and at high temperature using the relation between the applied load and known transformations of  $\alpha$ - $\beta$  of  $Fe_2SiO_4$  (Akimoto *et al* 1977),  $\alpha$ - $\beta$  of  $Co_2SiO_4$ , and  $\beta$ - $\gamma$  of  $Co_2SiO_4$  (Akimoto and Sato 1968) at 1300°C.

In this apparatus, the starting materials were sealed with distilled water of 30 wt% in Pt-capsules (3.0 mm in outer diameter, 0.15 mm in thickness and about 5 mm in length). The capsule was then placed in the sample assembly (Figure 3). Run temperatures were monitored by a Pt/Pt-13%Rh thermocouple with terminals at ambient conditions and no correction was made for the pressure effect on emf. After the pressure and temperature had been held at 5.5 GPa and 1500°C for 15–20 minutes, the sample was treated in two ways:

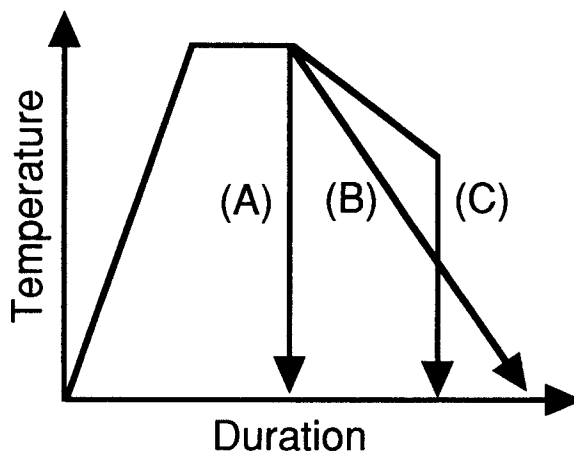


Figure 2. Schematic illustration for cooling processes: (A) quenched, (B) cooled at constant rate, and (C) cooled at constant rate and then quenched processes.

(A) the sample was quenched by shutting off the electric power, and (B) the sample was cooled at a desired rate by decreasing the input power manually while monitoring the temperature with a thermocouple. After the sample was cooled to room temperature, the pressure was released and the product was recovered.

The products were examined by X-ray diffraction in order to identify the phases.

## RESULTS

### *Products obtained using a modified belt type high-pressure apparatus*

In the quench process (A), a large amount of smectite crystals, whose basal spacing expanded to 16.7 Å after glycolation, were obtained together with a large amount of coesite and small amounts of kyanite and jadeite (Figure 4). In the cooled process (B) with an estimated cooling rate of "1500 °C/min," a small amount of smectite crystals coexisted with coesite, kyanite and jadeite. In the cooled process (B) with an estimated cooling rate of "150 °C/min," no smectite crystals were observed in the products, but the high-pressure minerals, coesite as a main phase and kyanite, jadeite, and clinoenstatite as minor phases were obtained (Figure 5). The estimated cooling rate of the sample, which was denoted with quotes, was evaluated from the linear relation between the input power and the temperature calibrated in the heating process. Therefore it is difficult to estimate the cooling rate of the sample from the relation in the heating process because of the large volume of the heat insulations. These values are probably high but are used hereafter as a scale of comparison. In the process (C), sample was cooled at a rate of "100 °C/min" to 1000°C and then quenched to room temperature from 1000°C. The phases obtained were coesite, kyanite, jadeite and a small amount of smectite crystals. Those were the same as the quenched products

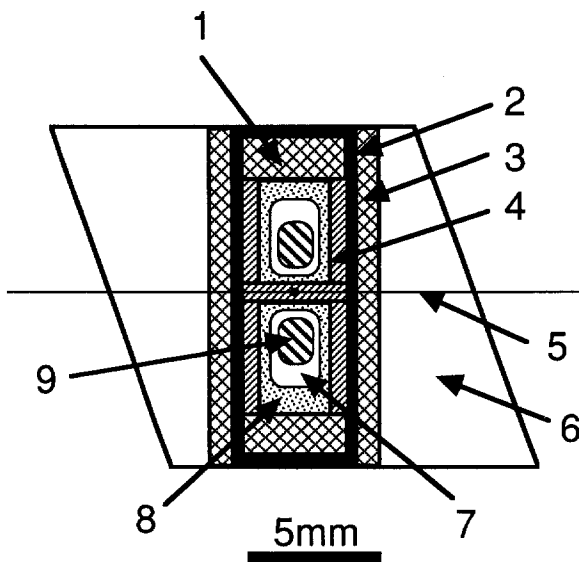


Figure 3. Sample assembly for the high-pressure and high-temperature experiment using a uniaxial split-sphere type apparatus. 1: zirconia rod, 2: graphite heater, 3: zirconia sleeve, 4: BN sleeve, 5: thermocouple, 6: MgO pressure medium, 7: Pt-capsule, 8: NaCl-10%ZrO<sub>2</sub> by weight pressure medium, 9: sample.

after the treatment at 5.5 GPa and 1000°C (Yamada *et al* 1994). In the sample, which was cooled at the rate of "100 °C/min" to 800°C and then quenched from 800°C, there were no smectite crystals, but coesite as a main phase coexisted with kyanite, jadeite, clinostatite and chlorite. The phase assemblages were the same as the quenched product after the treatment at 5.5 GPa and 800°C (Yamada *et al* 1994).

#### Products obtained using a uniaxial split-sphere type high-pressure apparatus

In the quenched process (A), a large quantity of smectite crystals were obtained. It coexisted with a very small amount of coesite, kyanite and/or glass (Figure 6). In the cooled processes (B), with a cooling rate between 1500°C/min and 500°C/min, smectite crystals were obtained as a single phase or an assemblage with a small amount of coesite, kyanite and/or corundum. The cooling rate was monitored by a thermocouple directly. The quantity of smectite crystals were similar to those obtained in the quench process (A). In a slowly cooled process with the rate of 200°C/min, the smectite crystals appeared as a minor phase coexisting with major phases of coesite, kyanite and/or corundum.

#### DISCUSSION

The formation of the smectite crystals was highly dependent on the cooling rate and the cooling process. It is generally not easy to compare in detail the cooling processes of the samples placed in two different types of high pressure apparatus. Only qualitative compar-

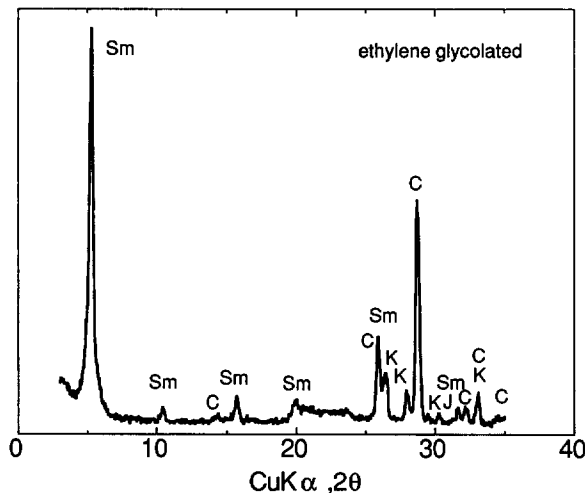


Figure 4. X-ray powder diffraction patterns of a quenched product formed in a modified belt-type apparatus (treated with ethylene glycol). Sm: smectite crystal. C: coesite. K: kyanite. J: jadeite.

ison of the cooling rates can be made for the two types of apparatus.

For the modified belt-type apparatus, the sample was surrounded by a large volume of thermally insulating medium (pyrophyllite, NaCl-10%ZrO<sub>2</sub> and ZrO<sub>2</sub> disk), and the volume of the sample and the size of the graphite heater were larger than those in a uniaxial split-sphere apparatus (Figures 1 and 3). The temperature gradient in the sample space was very small (less than 10°C/mm, Yoshikawa *et al* 1988; Kanda *et al* 1990). Therefore it is easily supposed that the sample was not cooled at the desired cooling rate estimated from the

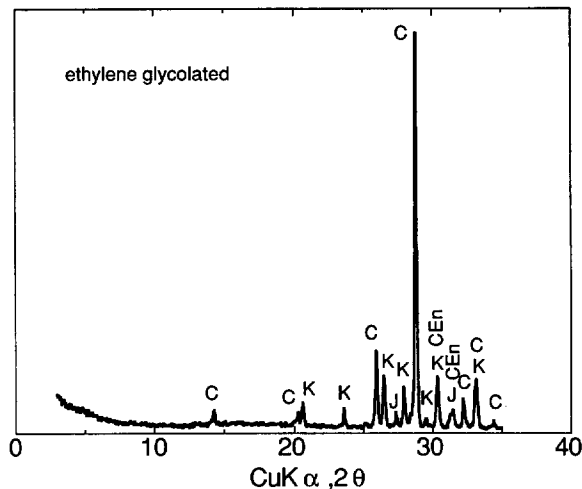


Figure 5. X-ray powder diffraction patterns of a product formed in a slowly cooled process ("150 °C/min") using a modified belt type apparatus (treated with ethylene glycol). C: coesite. K: kyanite. J: jadeite. CEN: clinoenstatite.

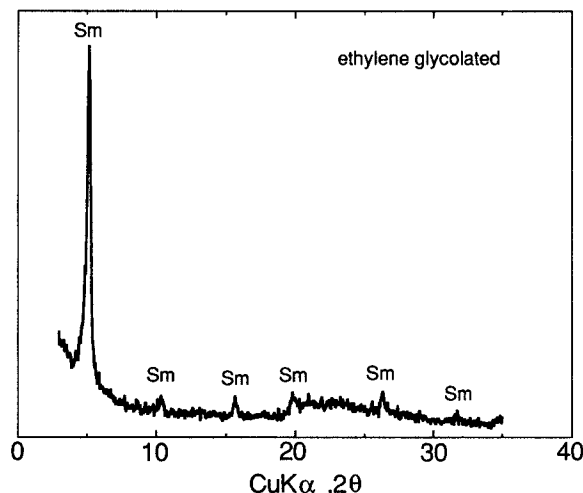


Figure 6. X-ray powder diffraction patterns of a quenched product formed in a uniaxial split-sphere apparatus (treated with ethylene glycol). Sm: smectite crystal. A broad peak around 20–30 degrees with originates from quenched glass was observed.

input power-temperature relation. The cooling rate of the sample is smaller than the estimated value.

For a uniaxial split-sphere apparatus, the sample was surrounded by a small volume of pressure medium, which was in contact directly with tungsten carbide anvils. The temperature gradient along the length of the furnace assembly was very large and was more than 200°C/mm (Takahashi *et al* 1982; Ito and Takahashi 1989). Therefore the heat dispersion of the sample in the uniaxial split-sphere apparatus must be larger than that in the modified belt-type apparatus. The quenching rate of the sample in the uniaxial split-sphere apparatus is much faster than that in the modified belt type apparatus. The similar behavior is also expected for the cooling process (B). The above discussion is supported by the result that some silicate glass could be quenched from an anhydrous melt by the uniaxial split-sphere apparatus, but not by the modified belt-type apparatus (Kanzaki, June 1993, personal communication).

Taking these comparisons of cooling rate into consideration, the experimental results for both the quench process (A) and the cooling process (B) are reasonably explained as follows. The smectite crystals were dominantly formed during the faster cooling process higher than 500°C/min using the uniaxial split-sphere apparatus. For the belt-type apparatus, similar results were obtained by shutting off the electric power. These results provide evidence that the smectite crystals are formed during the faster cooling process. The results for cooling process (C) indicate that the rapid cooling of the sample from the temperature above the liquidus is essential for obtaining the smectite crystals, but the cooling rate above liquidus is not effective. The liqui-

duis temperature was not determined precisely for this study, but the temperature of 1000°C is comparable to the liquidus temperature of silicate with similar composition under hydrous condition (Wyllie 1979). These results provide evidence that the smectite crystals are formed as a metastable phase during the rapid cooling of a hydrous silicate melt of montmorillonite composition.

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