

## HYDRATION BEHAVIOR OF Na-SMECTITE CRYSTALS SYNTHESIZED AT HIGH PRESSURE AND HIGH TEMPERATURE

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**Abstract**—Hydration behavior of Na-smectite crystals synthesized at a pressure of 5.5 GPa and temperatures of 1400°–1500°C was examined by X-ray powder diffraction at various relative humidities (RH) in the range of 0–100%. The basal spacing of the Na-smectite crystal increased stepwise with increase in RH. The reflections observed were only normal reflections of a single or dual hydration states of smectite. No irrational, intermediate, or asymmetrical reflections were observed. The simple hydration behavior, not known for natural smectite with fine particle sizes and low crystallinity, indicates that the Na-smectite crystals are as perfect as common inorganic crystals with an ordered structure.

**Key Words**—High-pressure experiment, Hydration, Relative humidity, Smectite crystal.

### INTRODUCTION

The expansion characteristics of natural smectites have been examined in detail under various relative humidities (RH) (MacEvan and Wilson, 1984; Moore and Hower, 1986; Iwasaki and Watanabe, 1988; Watanabe and Sato, 1988; Sato *et al.*, 1992). The basal spacing is a function of H<sub>2</sub>O layers and increases gradually with increasing RH. Four hydration states of Na-montmorillonite are known to show 001 spacings of 10.0 Å, 12.4 Å, 15.6 Å, and 18.8 Å, corresponding to the intercalation state of smectite with 0, 1, 2, and 3 layers of water molecules, respectively (these are called hereafter the 0-, 1-, 2-, and 3-layer hydration state). The hydration behavior at the transition between two hydration states is complicated by scattered observations on smectite samples; irrational and asymmetrical reflections as well as rational reflections with long spacings (Moore and Hower, 1986) were observed. These observations have been interpreted as being due to various types of interstratified structures (regular, random, or segregation-type) and inhomogeneous inter- and intra-charge distribution (Iwasaki and Watanabe, 1988; Sato *et al.*, 1992).

Smectite is known as an aggregate of very fine particles usually having low crystallinity. It is, therefore, difficult to determine the structure of smectite in detail, including charge location and distribution. Recently, the layer charge of natural smectite has been estimated by several methods (Lagaly and Weiss, 1969; Taibudeen and Goulding, 1983; Howard and Roy, 1985; Nadeau and Bain, 1986), but has not been determined directly by the X-ray analytical method for single crystals. Therefore, the above interpretations have not been proven by experimental methods. Single crystals of

smectite have been examined to determine the essential expansion properties of smectite.

Smectites with high crystallinity and large grain size were experimentally synthesized by the present authors at very high pressure and temperature. The smectites were identified by XRD method using a selected-area electron diffraction method (Nakazawa *et al.*, 1992; Yamada and Nakazawa, 1992). The smectite with high crystallinity and large dimensions is hereafter denoted as smectite crystal. The purpose of this study was to examine hydration behavior under precisely controlled RH of the smectite crystals using X-ray diffraction. The results showed a simple crystal hydration process and did not require any interpretation on the structural imperfections of the smectite.

### EXPERIMENTAL METHODS

#### *Preparation of smectite crystal*

The starting material used was a fine glass powder in the composition of dehydroxylated Na-montmorillonite. The glass was obtained by fusing a mixture of Na<sub>2</sub>CO<sub>3</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> in the desired stoichiometric composition. The fusion was accomplished in an infrared focusing-image furnace, normally used for the synthesis of a single crystal by the floating-zone method, and quenched into water. The composition of the glass was determined by an electron microprobe analyzer to be Na<sub>0.70</sub>Mg<sub>0.67</sub>Al<sub>3.21</sub>Si<sub>8.08</sub>. This composition is approximately that of dehydroxylated Na-montmorillonite, although slightly richer in Na<sub>2</sub>O and SiO<sub>2</sub>. The glass was then pulverized in an alumina mortar with water, and the grain size was found to be <20 μm.

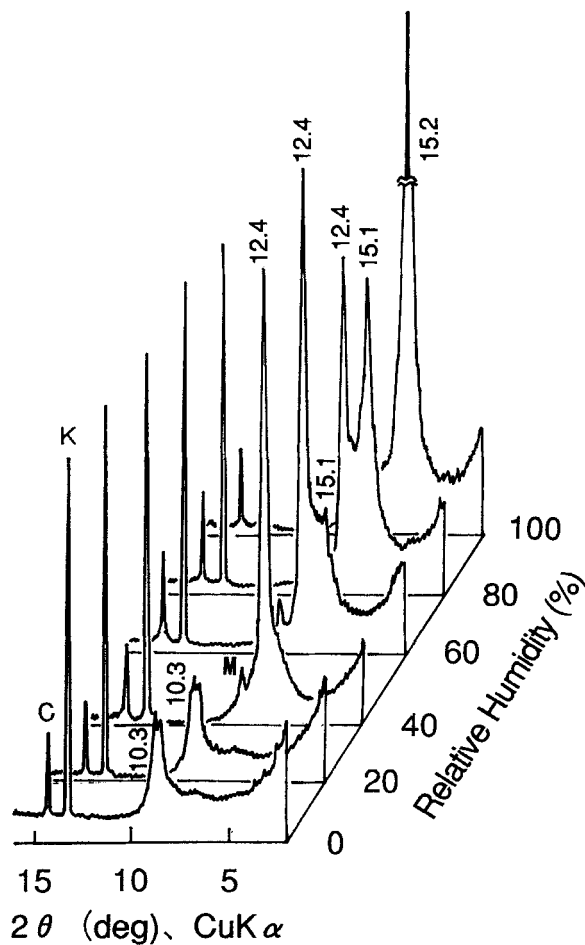


Figure 1. X-ray basal reflections of smectite crystal at 0%, 20%, 40%, 60%, 80%, and 100% relative humidity. The numbers indicate the observed d-spacing in Å. C = coesite; K = kyanite; M = mica.

The smectite crystals were synthesized with a belt-type high-pressure apparatus (Fukunaga *et al.*, 1979). The 3:1 mixture of pulverized glass and distilled water was sealed in a platinum capsule. After holding the capsule at a pressure of 5.5 GPa and at 1400°C or 1500°C for 30 minutes, the sample was quenched by shutting off the electric power supply. The pressure was then released, and the product was recovered in ambient condition.

#### Identification of smectite crystal

The run product was identified by the powder X-ray diffraction (XRD) method, as in Yamada *et al.* (1991). The run product consisted of coesite, kyanite, a small amount of jadeite, a small amount of mica, and smectite crystal. The smectite crystal was confirmed by the result that the basal spacing expanded to 16.7 Å after ethylene glycol treatment. The smectite crystal has the following characteristic: the full width at half maxi-

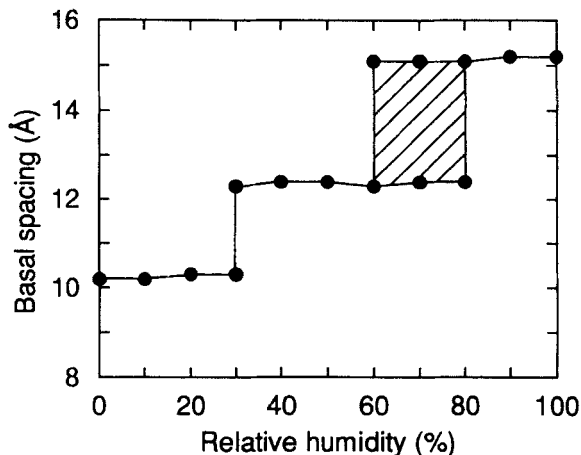


Figure 2. Basal spacing of smectite crystal at various relative humidities.

imum intensity (FWHM) of the 001 reflection is less than  $\frac{1}{3}$  of that of natural smectite, which is known to be low-crystallinity and small particle (Brindley, 1984) and is comparable to that of the other coexisting crystals (Figure 1 in Nakazawa *et al.*, 1992). This indicates that smectite crystal is supposed to be large and high in crystallinity, as compared with the usual smectite. The sizes of the smectite crystals were probably a few to 10  $\mu\text{m}$ , and the smectite crystals were recognized as a single crystal with the aid of a selected-area electron diffraction method (Figure 2 in Nakazawa *et al.*, 1992). The chemical composition of the smectite crystal was determined semiquantitatively using an energy dispersive-type of electron microanalysis (EDS, Akashi DS130C). The sample used for the EDS was a thin film of smectite crystal, dispersed by water and dried on a polished graphite disk in air. The element ratio of the smectite crystal was as follows: Na:Mg:Al:Si = 0.5:1.1:3.0:8.0. The ratio was almost equal to that of Namontmorillonite, but the Na content was poorer than the ideal layer charges calculated from the Mg, Al, and Si ratios.

#### In situ XRD observations in increasing RH

The hydration properties of the smectite crystal were examined by an *in situ* XRD method under a precisely controlled relative humidity. The apparatus and the system used have been described as ReCX (Relative humidity Control system for X-ray diffractometer) by Watanabe and Sato (1988). The principle of the apparatus is as follows: The sample holder of a powder X-ray diffractometer is surrounded by a plastic bell jar having windows for incident and diffracted X-rays covered by polyethylene terephthalate film (Mylar film). The atmosphere in the bell jar is controlled by flowing air at the desired RH. For the stabilization of RH, about 10 minutes is necessary after changing RH. Samples examined by XRD were prepared by dispersion

of the smectite crystals on a glass slide with water and air-drying. XRD measurements were carried out every 10% RH interval in the range of 0%–100%.

## RESULTS

The X-ray diffraction patterns of smectite crystals at various relative humidities are shown in Figure 1, and the basal spacings are plotted against RH in Figure 2. The basal spacing of the smectite crystals increased in distinctly stepwise fashion with the increase of RH (Figure 2). Three hydration states were observed with no intermediate state over the whole RH range. The 001 spacings were 10.0 Å, 12.4 Å, and 15.2 Å, corresponding to the 0-, 1-, and 2-layer hydration states, respectively. The 0-layer hydration state appeared at 0%–20% RH. The FWHM of this phase is about half of that of the usual smectite. The term, "usual smectite," denotes the known smectites naturally occurring and commonly synthesized (Brindley, 1984; Güven, 1988), which are aggregates of fine and low crystallinity particles. The 001 reflection of the smectite crystals at 30% RH was doubled at 10.0 and 12.4 Å, showing that the crystals of the 1-layer hydration state coexisted with those of the 0-layer hydration state in a small amount. A sharp single peak at 12.4 Å, which had an FWHM less than 1/3 of that of "usual smectite", was observed at 40%–50% RH. At 60%–80% RH, two hydration states, the 1- and 2-layer hydration states, were observed. The XRD pattern typical of the two-phase state was that at 80% RH in Figure 1, where both peaks are comparable in intensity. In that RH range, the integral intensity of the 001 peak of the 2-layer hydration state was increased and that of 1-layer hydration state decreased with the increase of RH. The single peak of the 2-layer hydration state appeared at higher humidity of 90%–100% RH. Its FWHM was the same as that of the 1-layer hydration state (Figure 2).

## DISCUSSION

As was previously known, the basal spacing of the usual smectite is a function of RH. For example, the smectites exchanged with Na ions show that the basal spacing varies gradually with increasing RH (Moore and Hower, 1986; Watanabe and Sato, 1988). The gradual increase of the basal spacing appears in irrational reflections, asymmetrical reflections, rational reflection with long spacing, and broad doublet during the transition of two hydration states. These reflections are regarded as those due to the different type of interstratified structure: regular-type (Moore and Hower, 1986) and random and segregation-type (Watanabe and Sato, 1988; Sato *et al.*, 1992). To explain such a variety in structure, any randomness of the charge distribution in the intra- or inter-layer has been supposed. The present observation shows quite simple and clear RH dependency (Figure 2). There is a first-order transition through a two-phase region having RH as a variable

parameter. The charge distribution in the intra- and inter-layer of smectite crystal may, thus, be completely ordered as a component of a crystal structure that can be described as an infinite translation of a unit structure.

The hydration state of the smectite crystal at 100% RH is the 2-layer hydration state, but that of "usual smectite" (Na-montmorillonite) is known as the 3-layer hydration state. There are two explanations for the phenomena. First, the interaction force between silicate layer and interlayer cations of the smectite crystal with three-dimensional periodicity might be stronger than that of "usual smectite" with heterogeneous charge distribution. The fact that the basal spacing of the smectite crystal was smaller (16.7 Å) after ethylene glycol intercalation than the value of "usual smectite" (17.0–17.2 Å) may support the above interpretation. In addition, the transition from the 0- to 1-layer and from the 1- to 2-layer hydration state of the smectite crystal starts at higher RH than "usual smectite" (Watanabe and Sato, 1988). Secondly, the basal spacing of the smectite is dependent on the species and amount of the interlayer cation (MacEvan and Wilson, 1984; Watanabe and Sato, 1988). As was shown in the previous section, smectite crystals do not have enough Na cations for the ideal interlayer cation estimated from the Mg/Al/Si ratio. A considerable amount of H ions may exist in the interlayer of the smectite crystal. If this is true, the maximum hydration state is different from that of Na-saturated montmorillonite and may be limited to be two water layers.

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