Clays and Clay Minerals, Vol. 48, No. 3, 400–404, 2000.

STEPWISE HYDRATION OF HIGH-QUALITY SYNTHETIC SMECTITE WITH VARIOUS CATIONS

KENJI TAMURA,[1] HIROHISA YAMADA,[2] AND HIROMOTO NAKAZAWA[2]

[1]Central Research Laboratory, Kawasaki, Showa Denko K.K., 3-2 Chidori-cho, Kawasaki-ku, Kawasaki, Kanagawa, 210-0865 Japan

[2]National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044 Japan

Abstract—Smectites synthesized from experiments at 5.5 GPa and 1500°C are of high quality, crystals are large at >10 μm, and the 2:1 layers may have a homogeneous charge distribution. Smectite was exchanged with various cations (Na^+, Li^+, K^+, Ca^{2+}, and Mg^{2+}) and the hydration behavior of each sample was observed by an *in situ* powder X-ray diffraction method under precisely controlled relative humidity (RH). The smectite showed distinct stepwise (discontinuous) hydration versus RH. During the transition between two hydration states, the coexistence of the two states was observed. Randomly interstratified structures with one and two planes of H_2O are time-dependent phenomena and relate to hydration and dehydration processes.

Key Words—Crystalline Swelling, Hydration, Interlayer Cation, Smectite.

INTRODUCTION

The interlayer hydration of smectites as a function of interlayer cation species and relative humidity (RH) has been studied extensively (Norrish, 1954; Sposito and Prost, 1982; Bérend *et al.*, 1995; Laird, 1996). The variation in basal spacings of hydrated smectites is caused primarily by the number of H_2O molecules between the layers after equilibration at varying RH. Interlayer H_2O molecules may be arranged as layers, ranging from zero to three. However, the number of H_2O layers (*i.e.*, hydration states) is not always defined clearly, because X-ray data at a given RH may show broad, irrational, and asymmetrical (00*l*) reflections. These observations were interpreted as relating to a small particle size, a high number of defects, and an inhomogeneous charge distribution in the 2:1 layers (Watanabe and Sato, 1988; Sato *et al.*, 1992).

Smectites formed metastably during the quench of a high-pressure and high-temperature hydrous silicate melt have a large particle size and are of high quality, based on the peak sharpness of *d*(00l) (Nakazawa *et al.*, 1992), and may have a homogenous charge distribution (Yamada *et al.*, 1994a, 1995). These smectite samples were used to obtain X-ray data to study the interlamellar hydration of smectite. The smectite was saturated with various cations (Na^+, Li^+, K^+, Ca^{2+}, and Mg^{2+}) and the hydration behavior of each sample was observed using an *in situ* powder X-ray diffraction (XRD) method under precisely controlled RH.

EXPERIMENTAL

Sample preparation

The smectite was prepared in experiments at 5.5 GPa and 1500°C using a modified belt-type high-pressure apparatus (Nakazawa *et al.*, 1992; Yamada *et al.*, 1994b, 1995). The smectite forms in back reactions during the quench process of the hydrous silicate (Bai *et al.*, 1993; Yamada *et al.*, 1995). The 3:1 mixture of pulverized glass and distilled water, which was sealed in a platinum capsule, was used as starting material. The composition of the glass, $Na_{0.70}Mg_{0.67}Al_{3.21}Si_{8.08}$, was determined by electron microprobe analysis. Coesite, kyanite, jadeite, and a micaceous phase were minor impurities in the products. The smectite obtained expanded to *d*(001) of 16.7 Å after ethylene-glycol treatment. The energy dispersive X-ray analysis in a scanning electron microscope (SEM) indicated that the smectite contains Na, Mg, Al, and Si in the ratio of 0.5:1.1:3.0:8.0, which is consistent with montmorillonite (Nakazawa *et al.*, 1992). The smectite is of "high quality" judging from the sharpness of XRD *d*(001) peak and the large particle size (see below). The full-width at half-maximum (FWHM) of the (001) reflection for a random mounted aggregate sample is ~0.3 of that of natural smectite and is comparable in sharpness to peaks of the coexisting phases. Transmission electron microscopy showed that the particle size of the smectite is >10 μm and selected electron diffraction patterns indicated that the smectite crystals were single crystals (Nakazawa *et al.*, 1992). This smectite is hereafter denoted as HQSm.

Ion-exchange experiments were performed at 23 ± 2°C with 1 mol L^{-1} aqueous solutions of alkali metal and alkaline-earth metal chlorides and with HQSm in 50-mL polyethylene tubes (solid-to-solution ratio: 1.2 g L^{-1}). The tubes were agitated on a mechanical shaker at 200 strokes per min for 5 d. Free alkali metal and alkaline-earth metal ions were removed by washing with distilled water five times. Smectite was separated from suspension by centrifugation for 20 min at 15,000 rpm. Finally, the solid phase was lyophilized under vacuum (<10^{-2} torr).

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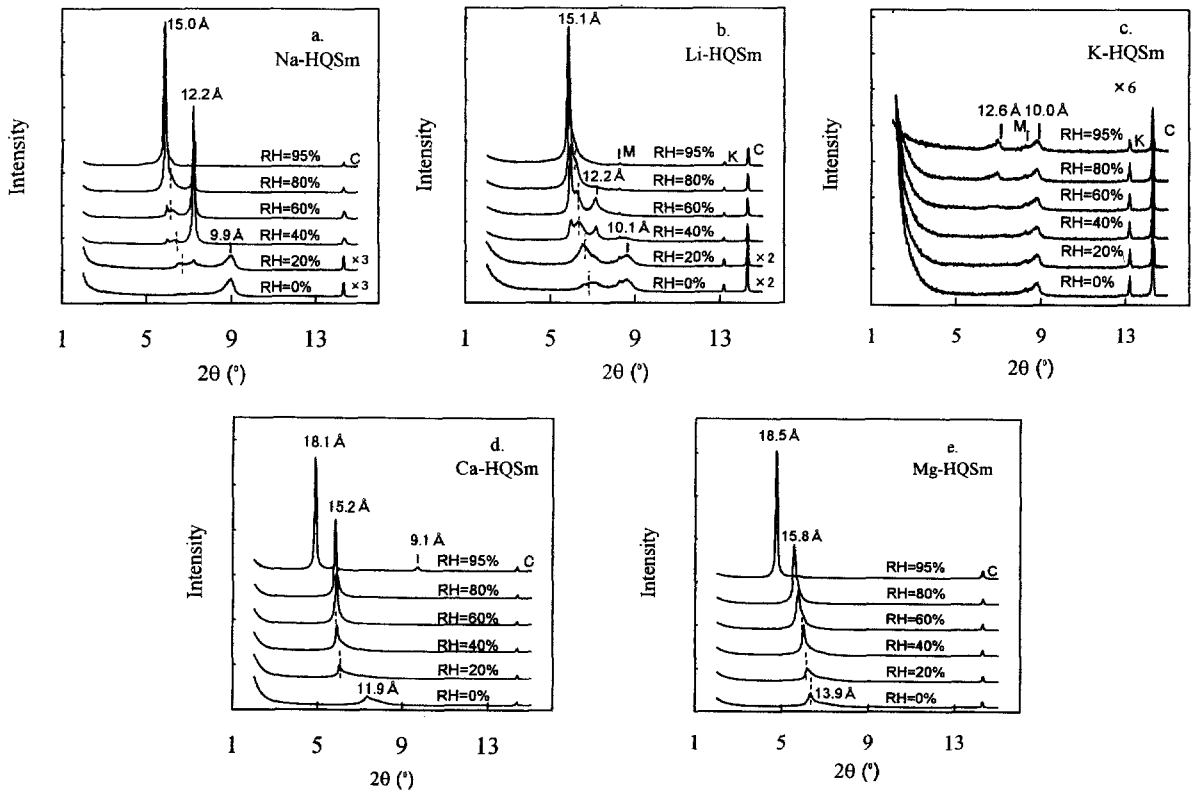


Figure 1. X-ray basal reflections of HQSm with various exchangeable cations at 0, 20, 40, 60, 80, and 95% relative humidity. (a) Na-, (b) Li-, (c) K-, (d) Ca-, and (e) Mg-HQSm. The numbers indicate the observed *d* value. M = micaceous phase. K = kyanite. C = coesite.

For comparison to HQSm, montmorillonite from pyroclastic rocks from Tsukinuno mine, Yamagata Prefecture, Japan was used. This montmorillonite coexists with a small amount of quartz, and the exchange cations are Na^+ (87%), Ca^{2+} (10%), and K^+ (3%). There is also a small amount (2 wt. %) of Fe^{2+} (Kunimine Industries, 1978).

XRD observations under controlled RH

The swelling properties of HQSm were examined by an *in situ* XRD method under precisely controlled RH (see Hashizume *et al.*, 1996). In brief, the sample holder of the powder X-ray diffractometer (Rigaku, Tokyo) was covered by a stainless steel chamber with windows of polyimide film (Kapton film) for the incident and diffracted X-ray beams. The RH in the sample chamber was controlled by mixing wet and dry nitrogen gas. RH and temperature stabilization occurred within ~60 min; the RH fluctuation was ±0.2% and temperature was ±0.1°C. The ion-exchanged samples were dried on a glass slide. The XRD data were collected at a scan rate of 1.0 °2θ min^{-1} using Ni-filtered CuKα radiation. The RH in the sample chamber was controlled every 10% RH interval in the range of 0–90% and at 95% RH, and the temperature was fixed at 30°C. Because HQSm with divalent exchangeable cations produced a shoulder peak at lower RH, the dehydration process was also monitored at RH = 0% for an extended period of 1–100 h for additional characterization of the smectite.

RESULTS

XRD patterns are presented for the homoionic Na-, Li-, K-, Ca- and Mg-exchanged HQSms at intervals of 20% RH in the range 0–95% RH (Figure 1), and *d*(001) peaks are plotted against RH in Figure 2. Three faint XRD peaks of micaceous phase, kyanite, and coesite are observed at 2θ values of ~8.5°, ~13.3°, and ~14.3°, respectively.

The *d*(001) values of Na-HQSm varied from 9.9 to 12.2 Å at 0–80% RH, and to 15.0 Å at 40–95% RH (Figures 1a and 2a). These values correspond to zero-, one-, and two-layer hydration states (0W, 1W, and 2W), respectively. A (001)-reflection doublet was observed during the hydration-state transition. An extremely weak reflection, marked (Figure 1a) by the broken line between the two peaks at 12.2 and 15.0 Å, appeared in the range of 10–90% RH (Figure 2a). The peak shifted towards the 15.0-Å peak with increasing RH. The gradual change in the *d* value indi-

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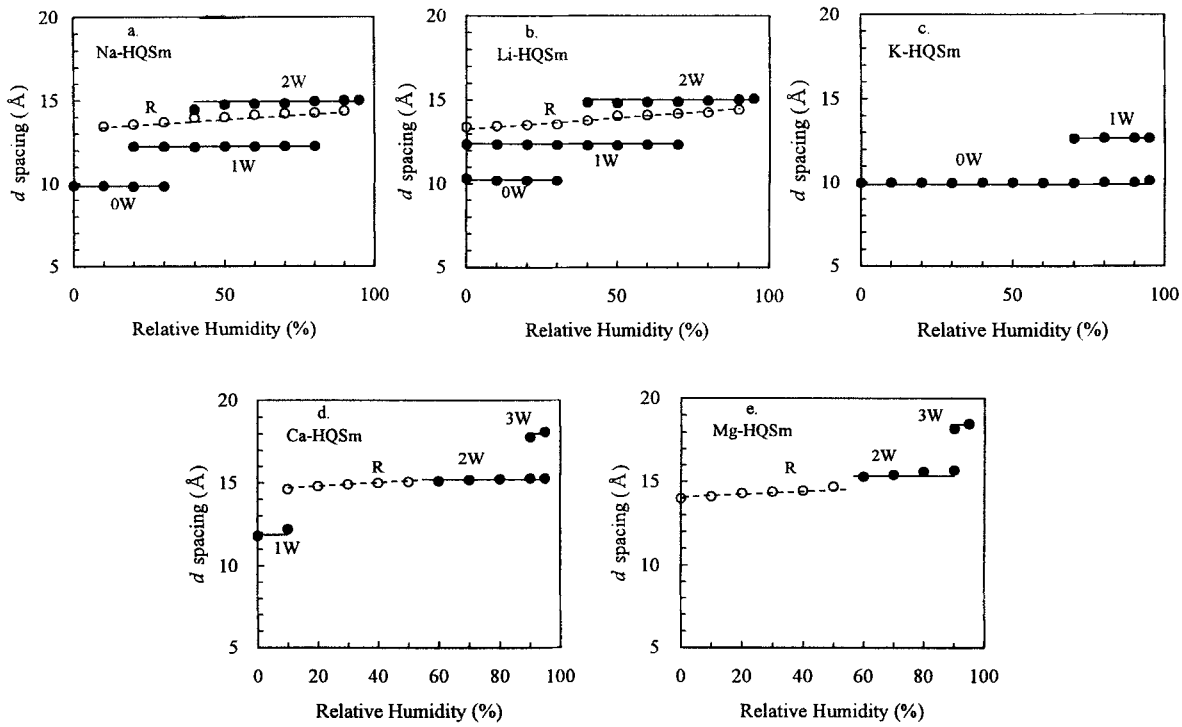


Figure 2. Basal spacing of HQSm at various relative humidities. (a) Na-, (b) Li-, (c) K-, (d) Ca-, and (e) Mg-HQSm. The symbols 0W, 1W, and 2W show the 0-, 1-, and 2-layer hydration states and R indicates a random mixture of the hydration states. A solid circle represents the basal spacing of the normal peak and an open circle is that of the random mixture.

cates that hydration occurs by an increase in the number of two-layer forms, which is randomly interstratified with one-layer forms. The random mixture of two hydration states is denoted by R (Figure 2a).

For Li-HQSm, three hydration states, 0W, 1W, and 2W, occur in the 0–95% RH range (Figures 1b and 2b). Asymmetric and weak reflections (broken lines, Figure 1b) occur between the 12.2 and 15.1-Å peaks in the range 0–90% RH. Coexistence of the 0W and 1W hydration states occurred in the range of 0–30% RH and the 1W and 2W states at 40–70% RH. The R state was observed from 0 to 90% RH (Figure 2b).

K-HQSm displayed broad, irrational, and asymmetrical reflections over the entire RH range measured (Figure 1c). Only two peaks, at 10.0 and 12.6 Å, occurred. The 10.0-Å spacing, corresponding to 0W, predominated in the range 0–95% RH. The 0W and 1W hydration state was observed only at RH of 70% and higher. The hydration curve plotted against RH shows distinct stepwise behavior (Figure 2c).

XRD profiles for Ca-HQSm (Figure 1d) show sharper reflections than those obtained from monovalent cations. The *d* values of the three reflections were 11.9, 15.2, and 18.1 Å, corresponding to the one-, two-, and three-layer hydration states. A doublet involving the basal spacings of 15.2 Å (2W) and 18.1 Å (3W) occurs above 90% RH. The plot of observed *d* value *vs.* RH forms a slightly inclined line below 50% RH (Figure 2d). The gradual change in the *d* value indicates a randomly interstratified structure of 1W and 2W units.

The swelling behavior of Mg-HQSm was similar to that of the Ca-exchanged form. The hydration curve of Mg-HQSm indicated the presence of an R state below 50% RH, and hydration states of 2W–3W above 90% RH. A single state of 3W occurred at 95% RH (Figures 1e and 2e).

To analyze the relation between the R state and the hydration (W) phases at 0% RH, XRD patterns of Mg-HQSm, prepared by allowing paste mounts to dry for 1–100 h, were inspected. The Mg-HQSm sample showed an asymmetric (001)-reflection profile (Figure 3, inset). The asymmetry is related to the coexistence of many hydration states, but with two dominating states at 13.9 Å (R state) and at 12.5 Å (1W), the latter represented by a shoulder peak. The relative intensity of the two peaks, the ratio of I_R/I_{1W}, defines the asymmetry, which decreases with an increase in sample drying time (Figure 3).

DISCUSSION

Stepwise hydration is generally characteristic for each HQSm with a different interlayer cation (Figures 1 and 2). Coexistence of two states during hydration occurs as shown by the intensity of the two (001) re-

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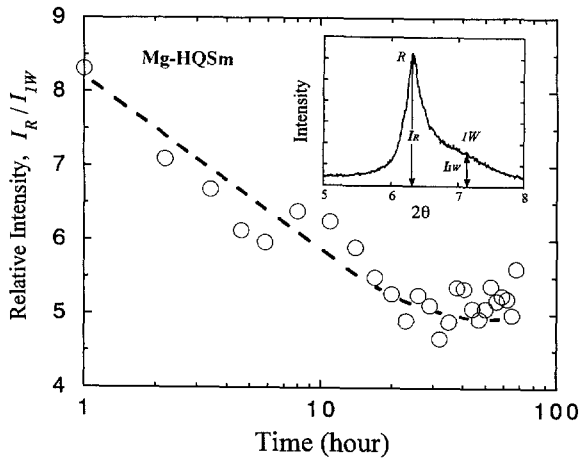


Figure 3. Data summaries of the ratio of I_R/I_{1W} *vs.* drying time at 0% RH and temperature of 30°C. The inset shows a typical diffraction peak after drying for 1 h.

flections changing with increasing RH (*e.g.*, Figure 1a and 1b). We suggest that the swelling of the synthetic smectite must be essentially a series of discontinuous phase transitions rather than a continuous transition.

A weak and broad XRD reflection was observed from 12.2 to 15.0 Å for Na^+ and Li^+-rich smectites (Figure 1a and 1b). R states occurred clearly in Na-HQSm, but they were not observed by Yamada *et al.* (1994a). The *d* value approaches 15.0 Å as RH increases. This change is related to the randomly interstratified structures of 1W (12.2 Å) and 2W (15.0 Å) units. The structure is produced when HQSm is dispersed in alkaline metal solution for ion exchange and dried for XRD sample preparation. For HQSm intercalates with divalent cations, the peak of the R state dominates even those of the end-member 1W and 2W phases (Figure 1d and 1e). The existence of the R state is supported by the following observations: (1) the *d* value of the R state increases continuously with increasing RH (Figure 2), (2) the peak has a shoulder at 12.5 Å corresponding to the *d* value of the 1W phase (Figure 3, inset), and (3) the intensity of the R state relative to that of the 1W phase decreases with increasing sample drying time after ion exchange (Figure 3).

The drying experiment indicates that the R state is an intermediate and metastable form between 1W and 2W. Drying process is apparently too rapid for the segregation and growth of an end-member state. Given sufficient time, the crystal of Mg-HQSm may convert to the 1W state entirely at RH = 0%. The R state, once formed in sample preparation, maintains the random structure and increases its interlayer spacing continuously with increasing RH. The hydration force of the exchangeable cation may greatly affect the occurrence of the R state. The amount of the R state relative

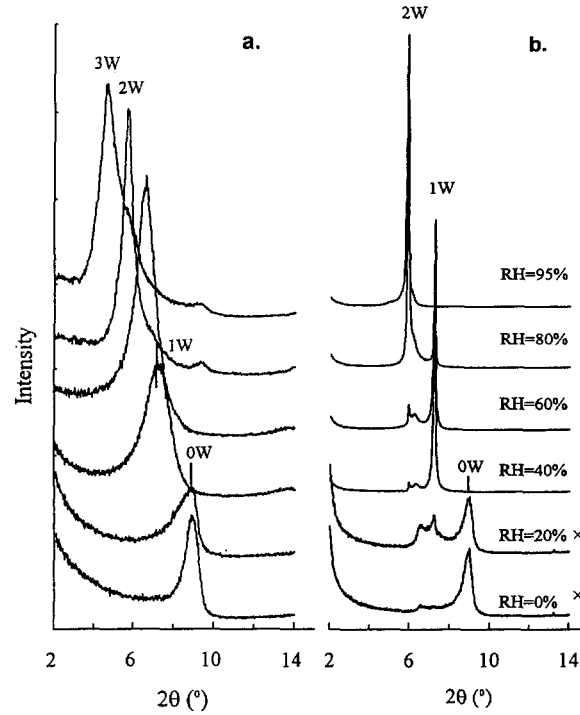


Figure 4. X-ray basal reflections of (a) Na-rich montmorillonite (Tsukinuno mine, Yamagata Pref., Japan) and (b) Na-HQSm at 0, 20, 40, 60, 80, and 95% relative humidity.

to the end-member 1W and 2W phases increases in the order of K < Na < Li < Ca < Mg. This order is consistent with the magnitude of hydration force of the interlayer cation (Parker, 1986; Güven, 1992).

The continuous hydration behavior in the sample from the Tsukinuno mine is quite similar to that of the R state of HQSm. Natural smectite does not show a stepwise hydration against RH, but continuous hydration (Figure 4a), although the origin of the randomness in layer-stacking is probably different. In natural smectites (*e.g.*, Tsukinuno sample), layer-stacking characteristics are probably related to a heterogeneous charge distribution in the 2:1 layers and small particle size (Watanabe and Sato, 1988; Sato *et al.*, 1992; Sato, 1996), whereas in HQSm it is related to the time-dependent phenomenon described here. The difference in the structure is also shown by the FWHM of the (001) reflections. For Na-HQSm, these peaks are narrower than that of Na-rich montmorillonite at each RH (Figure 4a and 4b).

ACKNOWLEDGMENTS

The authors are indebted to H. Hashizume, NIRIM, for his cooperation for the *in situ* XRD measurement. Thanks are also due to J.R. Hester, NIRIM, for critical reading of manuscript and correction of English. We also thank S. Guggenheim, D. Laird, L. Burras, and an anonymous reviewer for their constructive, helpful reviews.

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E-mail of corresponding author: tamurak2@kpl.sdk.co.jp

(Received 27 August 1999; accepted 3 March 2000; Ms. 375; A.E. David A. Laird)

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