

## CHARACTERIZATION OF SILANOL GROUPS IN PROTONATED MAGADIITE BY $^1\text{H}$ AND $^2\text{H}$ SOLID-STATE NUCLEAR MAGNETIC RESONANCE

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**Abstract**—Silanol groups in protonated magadiite (H-magadiite) were characterized by  $^1\text{H}$  and  $^2\text{H}$  solid-state nuclear magnetic resonance (NMR). H-magadiite and deuterated (D) magadiite were synthesized by the treatment of Na-rich magadiite with 0.2 N HCl and 0.2 N DCl, respectively. In the  $^1\text{H}$  NMR spectrum measured at room temperature, silanol groups of H-magadiite showed two signals at 3.75 and 5.70 ppm, indicating that two types of silanol groups were present. The ratio of silanol groups associated with strong hydrogen bonding (5.70 ppm) to those with weaker hydrogen bonding (3.75 ppm) was 2 to 1. The  $^2\text{H}$  NMR spectra of deuterated magadiite were measured in the temperature range from 150 to 440 K. In the spectra measured at temperatures below 294 K, silanol groups showed Pake doublet patterns. These patterns were composed of two components corresponding to the two types of silanol groups shown in the  $^1\text{H}$  NMR analysis. Both silanol groups produced wobbling motions with increasing temperature. Above 294 K, the profile of the Pake doublet pattern was transformed gradually to a near triangular pattern, indicating that the silanol groups underwent other motions also, such as a two-site jump.

**Key Words**— $^1\text{H}$  NMR,  $^2\text{H}$  NMR, Hydrogen Bonding, Magadiite, Silanol Group.

### INTRODUCTION

Na-rich magadiite is a layered polysilicate consisting of  $\text{SiO}_4$  tetrahedra and protonated magadiite (H-magadiite,  $\text{H}_4\text{Si}_{14}\text{O}_{30}\cdot x\text{H}_2\text{O}$ ) derived from Na-rich magadiite by an acid treatment to produce abundant silanol groups in the interlayer (Lagaly *et al.*, 1975a, 1975b). Because magadiite has poor crystallinity and large single crystals are not available (Brindley, 1969), its structure has not been refined. Although many structural models have been proposed on the basis of the chemical composition, infrared (IR) analysis, and the ratio of  $\text{Q}^3$  [ $\text{HOSi}(\text{OSi})_3$ ] to  $\text{Q}^4$  [ $\text{Si}(\text{OSi})_4$ ] environments obtained by  $^{29}\text{Si}$  magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) (Almond *et al.*, 1996, 1997; Brandt *et al.*, 1987, 1988; Garcés *et al.*, 1988; Huang *et al.*, 1999; Pinnavaia *et al.*, 1986; Scholzen *et al.*, 1991; Schwieger *et al.*, 1985), the structure of magadiite is still obscure. On the other hand, intercalation reactions and further silylation reactions involving magadiite (Mercier *et al.*, 1994; Ogawa *et al.*, 1998a; Okutomo *et al.*, 1999; Ruiz-Hitzky and Rojo, 1980; Ruiz-Hitzky *et al.*, 1985; Yanagisawa *et al.*, 1990, 1988a, 1988b) have attracted considerable attention for many applications, such as in adsorbents (Hadjar *et al.*, 1995; Ogawa *et al.*, 1998b) and microporous materials (Dailey and Pinnavaia, 1992; Landis *et al.*, 1991; Sprung *et al.*, 1990; Wong and Cheng, 1993; Yanagisawa *et al.*, 1991). Thus, it is important to investigate the interlayer silanol

groups, which are intimately related to the structure and surface properties of magadiite.

Solid-state NMR techniques offer powerful approaches to investigate a local structure with short-range order and a unique chemical environment.  $^1\text{H}$  NMR techniques have been applied to investigate various kinds of hydroxyl groups to reveal such characteristics as hydrogen bonding and acidity (Pfeifer, 1994; Xie and Hayashi, 1999a). For magadiite, Rojo *et al.* (1983, 1988) utilized  $^1\text{H}$  NMR and IR measurements and identified two types of silanol groups with different thermal properties. One type of silanol group involves strong hydrogen bonds which are lost below 500°C, and the other type consists of nearly free silanol groups which are lost above 500°C. Furthermore, Almond *et al.* (1994) measured  $^1\text{H}$  MAS NMR spectra of layered polysilicates and suggested that the signal from the silanol groups in H-magadiite was quite different from that in Na-rich magadiite. The  $^2\text{H}$  nucleus has a spin quantum number of 1, and its quadrupole interaction is very sensitive to hydrogen bonding and dynamic properties (Hoatson and Vold, 1994). Application of  $^2\text{H}$  NMR techniques for hydroxyl groups has revealed the strength of hydrogen bondings and motions (Eckert *et al.*, 1989; Gluszak *et al.*, 1992; Hayashi *et al.*, 1994; Kobe *et al.*, 1995; Xie and Hayashi, 1999b).

In the present paper, we describe further characteristics of silanol groups in H-magadiite by solid-state

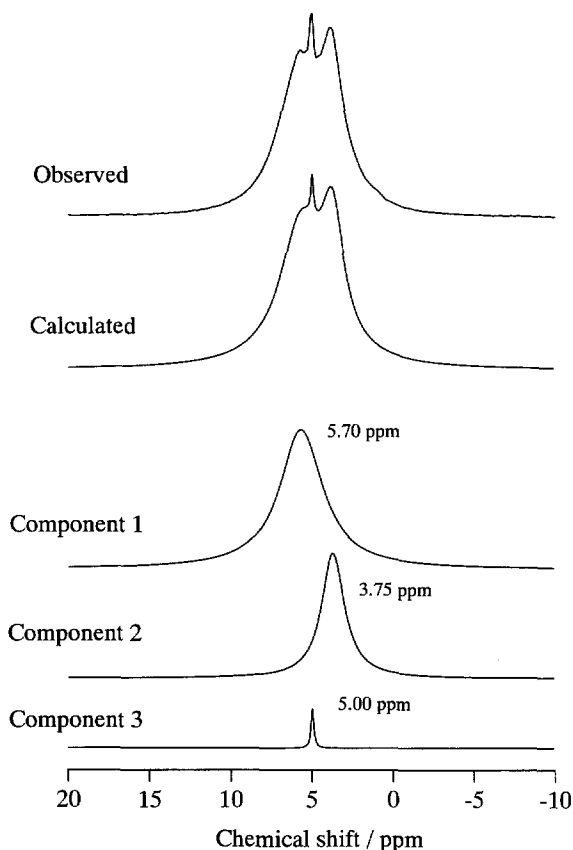


Figure 1.  $^1\text{H}$  MAS NMR spectrum of H-magadiite and its simulation. Calculated spectra were obtained assuming the presence of three components.

$^1\text{H}$  MAS NMR and  $^2\text{H}$  NMR spectroscopies. A combination of these techniques is suitable for characterizing silanol groups. We analyzed these spectra by using line-shape simulation. Chemical environments, motions, and interatomic distances in the silanol groups are discussed quantitatively.

#### EXPERIMENTAL

##### Preparation of H- and D-magadiite

Na-rich magadiite was prepared hydrothermally according to the method reported by Kosuge *et al.* (1992). The Na-rich magadiite (2.5 g) was ion-exchanged to H-magadiite or deuterated magadiite (D-magadiite) by using 15 mL of 0.2 N HCl in water or 0.2 N DCl in deuterated water, respectively. To remove molecular  $\text{H}_2\text{O}$  adsorbed on the external surface, the products were dried at  $200^\circ\text{C}$  under a reduced pressure for 1 h. For the preparation of D-magadiite, the treatment with DCl and the drying procedure were repeated three times under a nitrogen atmosphere to increase the amount of deuterium atoms. The obtained magadiites were identified by X-ray powder diffraction and  $^{29}\text{Si}$  MAS NMR measurements (Dailey and Pinnavaia,

Table 1.  $^1\text{H}$  NMR results of H-magadiite.<sup>1</sup>

Component	Shift (ppm)	<sup>2</sup> fwhm (ppm)	<sup>3</sup> f (%)
1	5.70	3.20	66
2	3.75	1.70	33
3	5.00	0.20	1

<sup>1</sup> Lorentzian line shapes are assumed.

<sup>2</sup> Full width at half-maximum.

<sup>3</sup> Fraction of the component.

1992; Kosuge *et al.*, 1992; Rojo *et al.*, 1983, 1988). For the D-magadiite, the displacement of sodium ions and protons with deuterons was confirmed by IR spectra, where the O-D stretching bands were observed in the region  $2400\text{--}2800\text{ cm}^{-1}$  which replaced the O-H stretching bands ( $3300\text{--}3700\text{ cm}^{-1}$ ).

##### Analyses

The  $^1\text{H}$  MAS NMR spectrum of H-magadiite was recorded at room temperature by a Bruker MSL400 pulsed spectrometer with a MAS rate of 10 kHz. The  $^1\text{H}$  Larmor frequency was 400.13 MHz and the recycle delay was 6 s. The  $^2\text{H}$  NMR spectra of D-magadiite were recorded for a static sample by the MSL400 spectrometer in the temperature range from 150 to 440 K. The  $^2\text{H}$  Larmor frequency was 61.42 MHz. The quadrupole echo-pulse sequence was used with the  $90^\circ$  pulse width of  $2.5\ \mu\text{s}$  and the pulse interval between the two pulses was  $15\ \mu\text{s}$ . The recycle delay was carefully determined to be 4 s so that the polarization was fully relaxed during the recycle time. The frequency scales of the  $^1\text{H}$  and  $^2\text{H}$  spectra were expressed with respect to pure tetramethylsilane and  $\text{D}_2\text{O}$ , respectively.

#### RESULTS AND DISCUSSION

The  $^1\text{H}$  NMR spectrum of H-magadiite and its simulation are shown in Figure 1. The spectrum is deconvoluted into three components at 5.70, 3.75, and 5.00 ppm. The parameters extracted from the simulation are listed in Table 1. The small signal at 5.00 ppm had a sharp profile and no spinning sidebands. Thus, this signal was assigned to significantly mobile  $\text{H}_2\text{O}$  molecules adsorbed on the external surface. The other two components were assigned to the silanol groups of magadiite. Because signals of strong acids or hydrogen-bonded protons appear at higher frequencies (Pfeifer, 1994), the silanol group showing the signal at 5.70 ppm has stronger hydrogen bonding or acidity than the silanol group producing the signal at 3.75 ppm. The fractions of the components at 5.70 and 3.75 ppm were 66 and 33%, respectively. In conclusion, two types of silanol groups are present in H-magadiite and the ratio of silanol groups with the stronger hydrogen bonding to those with the weaker bonding is 2 to 1.

The chemical-shift values of silanol groups in H-magadiite are much smaller than that of Na-rich ma-

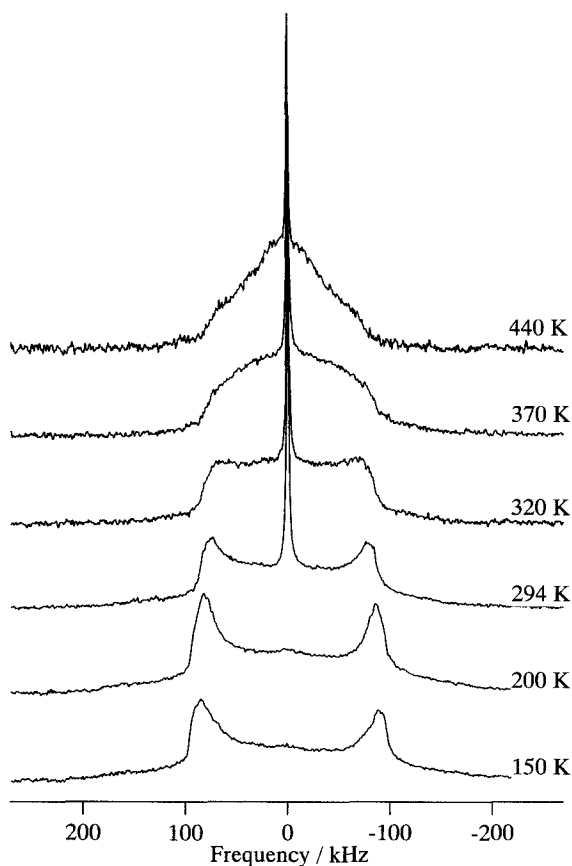


Figure 2.  $^2\text{H}$  NMR spectra of deuterated magadiite at various temperatures.

gadiite (14.9 ppm) (Almond *et al.*, 1994). However, the chemical shifts are similar to those of silicate glasses (4.3–5.2 ppm) (Eckert *et al.*, 1989; Pfeifer, 1994), indicating that the hydrogen bonding of the silanol groups in H-magadiite is similar to that of silicate glasses. The correlation between the  $^1\text{H}$  chemical shift and the interatomic distance between oxygen atoms in O-H-O hydrogen bonding has been reported (Hayashi *et al.*, 1994; Yesinowski and Eckert, 1987). The chemical shift of 5.70–3.75 ppm leads to the O-O interatomic distance of  $\sim 0.28$ – $0.29$  nm.

Density distributions of the two types of silanol groups were estimated by the second moment, which was calculated from the intensity of the spinning sidebands in the  $^1\text{H}$  NMR spectrum (Satozawa *et al.*, 1997). On both sides of the central peaks at 5.70 and 3.75 ppm, spinning sidebands for each component were observed (not shown). The obtained values of the second moment for the components at 5.70 and 3.75 ppm were 33 and 30  $\text{kHz}^2$ , respectively. The second moment reflects the strength of the dipole-dipole interaction between protons. Because the second moments of the two types of silanol groups were very

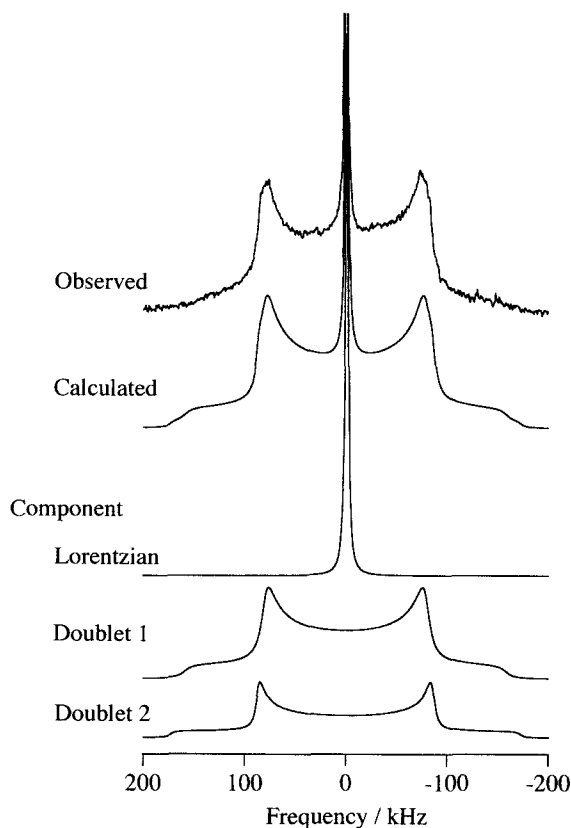


Figure 3. Simulation of the  $^2\text{H}$  NMR spectrum of deuterated magadiite measured at 294 K. The calculated spectrum was obtained assuming the presence of two doublet components with asymmetry factors of 0 and one Lorentzian component.

similar, the two groups have similar spatial distributions. They probably interact with each other through the dipole-dipole interaction; in other words, they are dispersed homogeneously. Furthermore, the values of the second moment were smaller than that of kaolinite ( $67 \text{ kHz}^2$ ) (Hayashi *et al.*, 1992) and larger than that of talc ( $5.7 \text{ kHz}^2$ ) (Hayashi, 1994), indicating that the spatial distribution of protons was less dense than in kaolinite and more dense than in talc.

The  $^2\text{H}$  NMR spectra of D-magadiite at various temperatures are shown in Figure 2. In the temperature range from 150 to 294 K, Pake doublet patterns were observed. Based on the presence of two types of silanol groups as described above, the doublet patterns were simulated by two components. Figure 3 shows the results of deconvolution of the spectrum measured at 294 K. The spectrum consists of three components: two Pake doublet patterns with asymmetric factors of 0 and a central sharp signal. The central signal was simulated by a Lorentzian line shape and assigned to adsorbed  $\text{H}_2\text{O}$  on the external surface (Kobe *et al.*, 1995). Two components of the doublet patterns were ascribed to immobilized silanol groups. Quadrupole-

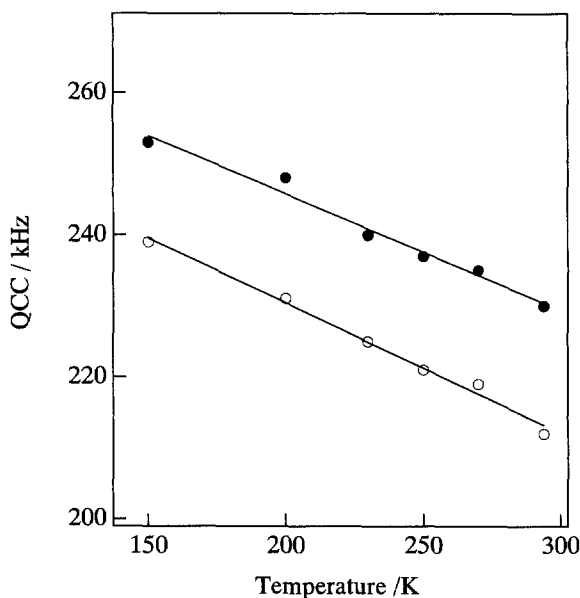


Figure 4. Temperature dependence of the quadrupole coupling constant for the doublet components. The open and solid circles indicate the doublet 1 and the doublet 2 in Figure 3, respectively. The straight line is drawn with a *least-squares* fit.

coupling constants (QCCs) extracted from the simulations were 212 (doublet 1) and 230 kHz (doublet 2), whereas the fractions of intensities were 58 and 30% for doublet 1 and doublet 2, respectively. Because the smaller QCC corresponds to the stronger hydrogen bonding or greater mobility (Butler and Brown, 1981; Hayashi *et al.*, 1994), the doublet 1 with the smaller QCC was ascribed to the silanol group with the stronger hydrogen bonding. Based on the strength of the hydrogen bonding, doublet 1 and doublet 2 corresponded to signals at 5.70 and 3.75 ppm in the  $^1\text{H}$  NMR spectrum, respectively. The ratio for doublet 1 (58%) to doublet 2 (30%) was nearly 2 to 1, which is consistent with the  $^1\text{H}$  MAS NMR result.

The temperature dependence of the QCCs is plotted in Figure 4. Each QCC decreased linearly with temperature, being expressed as  $\text{QCC (doublet 1)} = 267 - 0.183 T$  and  $\text{QCC (doublet 2)} = 279 - 0.164 T$ , where QCC and  $T$  are in units of kHz and K, respectively. The temperature dependence of the QCC is related to the motions of the silanol groups. With increasing temperature, the QCC for each component decreased linearly whereas the asymmetry factor did not change from zero. Thus, the most likely motion involves wobbling. Where the O-D group rotates around an axis which is inclined at angle  $\theta$ , the effective asymmetry factor remains zero whereas the effective QCC is reduced by a factor of  $(3 \cos^2 \theta - 1)/2$  (Barnes, 1974). If the QCC extrapolated to 0 K (279 kHz, 267 kHz) corresponds to the value in the rigid

state ( $\theta = 0$ ) (Hayashi *et al.*, 1994), the QCC at 230 and 212 kHz at 294 K leads to  $\theta = 20^\circ$  and  $\theta = 22^\circ$ , respectively. The temperature dependence of the QCC is larger than that of the hydroxyl groups in kaolinite ( $\text{QCC} = 286.7 - 0.10 T$ ) (Hayashi *et al.*, 1994), and this is indicative of the greater mobility of the silanol groups in D-magadiite.

The QCCs in D-magadiite were similar to those of silicate glasses and zeolites ( $\text{QCC} = \sim 200\text{--}250$  kHz at room temperature) (Eckert *et al.*, 1989; Kobe *et al.*, 1995), indicating that the property of the silanol groups in magadiite is similar to that in silicate glasses and zeolites. The QCC is correlated with the interatomic distance between oxygen atoms in O-D-O hydrogen bonding (Hayashi *et al.*, 1994; Butler and Brown, 1981). The QCCs at 212 and 230 kHz indicate the distances between two oxygen atoms of 0.276 and 0.284 nm, respectively, which are consistent with the  $^1\text{H}$  NMR results.

As the temperature increases above 294 K, the profile of the spectra transformed gradually from the Pake doublet pattern to a nearly triangular pattern (Figure 2). This transformation indicates that the effective asymmetry factor increased from 0. The silanol groups may undergo other motions, such as a two-site jump (Barnes, 1974). However, it is difficult to simulate these patterns, because the observed spectra were relatively featureless and two types of silanol groups were present.

We have demonstrated that combination of  $^1\text{H}$  and  $^2\text{H}$  NMR measurements revealed the presence of two types of silanol groups in protonated magadiite. The ratio of silanol groups with the stronger hydrogen bonding to those with the weaker one was 2 to 1. The similar second moments for the two silanol groups suggested that the two groups are dispersed homogeneously. Furthermore,  $^2\text{H}$  NMR showed that two types of silanol groups underwent similar wobbling motions.

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(Received 28 February 2000; accepted 17 June 2000; Ms. 431; A.E. William F. Bleam)