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A ^{29}Si MAS NMR Study of Tetrahedral Site Distributions in the Layered Silicic Acid H^+-Magadiite ($H_2Si_{14}O_{29} \cdot nH_2O$) and in Na^+-Magadiite ($Na_2Si_{14}O_{29} \cdot nH_2O$)

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The structural compositions of the layered silicic acid H^+-magadiite ($H_2Si_{14}O_{29} \cdot 5.4H_2O$) and the corresponding Na^+ salt ($Na_2Si_{14}O_{29} \cdot 9\text{–}11H_2O$) have been investigated by ^{29}Si MAS NMR. Both compounds exhibit resonances characteristic of Q^3 and Q^4 environments in which three and four oxygen atoms of the silicate tetrahedra are bridging adjacent silicons, respectively. The Q^3 and Q^4 chemical shifts assignments for Na^+-magadiite (−102 and −113 ppm) and H^+-magadiite (−105, −115 ppm) were supported by the chemical-shift position (−101 ppm) for kanemite, $NaHSi_2O_5 \cdot 3H_2O$, a layered silicate with only Q^3 environments. The $Q^3 : Q^4$ site ratios are approximately 1 : 3 for both H^+- and Na^+-magadiite. A previously reported value of 1 : 1 based on estimates of the surface density of OH groups (cf., Ref. (*6*)) is not confirmed. Some interlayer cross-linking involving the condensation of silanol groups occurs in H^+-magadiite upon dehydration at 230°C, a temperature considerably lower than that previously estimated from thermal analysis data for the onset of interlayer siloxane bond formation (cf., Ref. (*3*)).

Introduction

The intercalation chemistry of 2 : 1 phyllosilicate clays has provided an important basis for the rational design of several new classes of microporous adsorbents and shape selective catalysts (*1*). A related class of solids, namely, the layered silicic acids and their alkali metal salts, also exhibit a rich intercalation chemistry (*2–5*). It is likely that many of the general concepts (*1a*) developed for the transformation of smectite clays into microporous systems will be extendable to the layered silicic acids.

The structures of the simplest layered silicic acids and their corresponding salts consist exclusively of Q^3 tetrahedra of the type $HOSiO_3$ or $M^+[^-OSiO_3]$, wherein three of the four oxygens are bridging adjacent silicons. However, the more highly condensed layered structures are made up of a combination of Q^3 and Q^4 tetrahedra, the latter type having all four oxygens bridging adjacent silicons. One such derivative, synthetic H^+-magadiite, with an em-

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pirical composition normally expressed as $H_2Si_{14}O_{29} \cdot nH_2O$ ($n = 1.8\text{–}5.4$), represents one of the best characterized layered silicic acids from the standpoint of intercalation chemistry (*2, 5*). However, the structure of magadiite is unknown.

The ratio of Q^3 to Q^4 tetrahedra present in silicic acids is important in understanding their intercalation properties and in assisting in their design as microporous catalysts. Efforts have been made to determine the $Q^3 : Q^4$ site ratio for H^+-magadiite from studies of the surface OH group density (*2, 6*) and ^1H NMR relaxation measurements (*7*), but the values range from approximately 1 : 1 to 1 : 3. ^{29}Si magic angle spinning (MAS) NMR spectroscopy recently has been shown to be a quantitative tool for the study of silicate structures (*8–10*), including layered silicates (*11–15*). In the present work we make use of ^{29}Si MAS NMR to determine the $Q^3 : Q^4$ site ratio in synthetic H^+-magadiite. Also, we have included in our study the sodium form $Na_2Si_{14}O_{29} \cdot nH_2O$, and the related layered sodium silicate kanemite, $NaHSi_2O_5$ $3H_2O$.

Experimental

Na^+-magadiite was prepared by reaction of silica gel with aqueous NaOH according to previously described methods (*15*). The Na^+ salt then was converted to H^+-magadiite by exchange with aqueous HCl[3], and the final product wsa air-dried. The X-ray powder diffraction patterns and basal spacings (15.5 Å for Na^+-magadiite, 13.2 Å for H^+-magadiite) were in agreement with those previously reported for the compositions $Na_2Si_{14}O_{29} \cdot nH_2O$ ($n = 9, 11$ (*15, 16*)) and $H_2Si_{14}O_{29} \cdot 5.4H_2O$[3]. To assist with the ^{29}Si MAS NMR assignments, we also prepared a sample of synthetic kanemite according to the method of Lagaly (*17*). The X-ray powder diffraction pattern (d_{001} = 10.3 Å) for this latter synthetic product was in agreement with that reported previously for natural kanemite with the composition $NaHSi_2O_5 \cdot 3H_2O$[18]. ^{29}Si MAS NMR spectra were recorded on Bruker AM-400 and WH-180 spectrometers operated at 75.5 and 35.8 MHz, respectively. The reported chemical shifts are relative to tetramethylsilane. Relative intensities were determined by planimetry.

Results and Discussion

Figure 1A illustrates the ^{29}Si MAS NMR spectra for Na^+-magadiite and kanemite. Na^+-magadiite exhibits two resonances at −102 and −113 ppm with an intensity ratio of 0.25 : 0.75. On the basis of chemical shift positions, the −102 and −113 ppm lines are assigned to Si in Q^3 and Q^4 tetrahedral environments, respectively. Support for the Q^3 assignment is provided by the spectrum for the kanemite sample which contains a

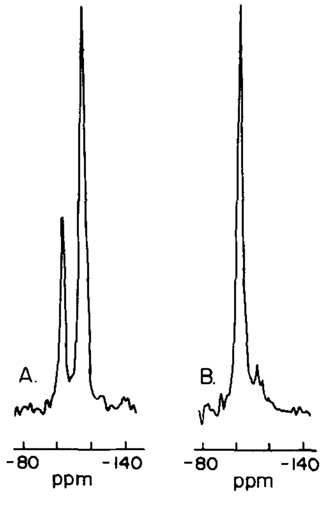


FIG. 1. ^{29}Si MAS NMR spectra (79.50 MHz) for (A) synthetic Na^+-magadiite, $Na_2Si_{14}O_{28} \cdot nH_2O$ ($n = 9\text{–}11$) and (B) synthetic kanemite, $NaHSi_2O_5 \cdot 3H_2O$. The weak peak at −113 ppm for sample B is attributed to silicon in a Q^4 tetrahedral site arising from in impurity phase. Spectroscopic parameters: pulse width 2.0 μsec; delay time, 4.0 sec; line broadening, 50 Hz; number of scans, 1230 for sample A and 2450 for sample B; spinning frequency, 4.5 kHz.

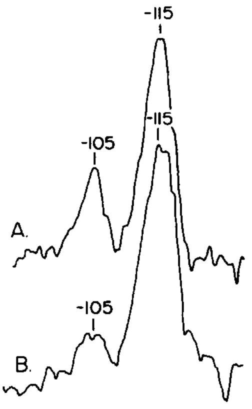


FIG. 2. ^{29}Si MAS NMR spectra (35.8 MHz) for H^+-magadiite (A) dried at 25°, (B) dried at 230°, 3 hr. Spectroscopic parameters: pulse width, 0.25 μsec; delay time, 0.20 sec; number of scans, 12,000 and 5000 for samples A and B, respectively; spinning frequency, 2.5 kHz.

TABLE I

^{29}Si MAS NMR CHEMICAL SHIFTS AND $Q^3:Q^4$ RATIOS

Compound	Chemical shifts (ppm)		$Q^3:Q^4$ site ratio
	Q^3	Q^4	
Na^+-magadiite ($Na_2Si_{14}O_{29} \cdot 9\text{-}10H_2O$)	−102	−113	0.25:0.75
Kanemite ($NaHSi_2O_5 \cdot 3H_2O$)	−101	—	1.0 :0.0
H^+-magadiite[a] ($H_2Si_{14}O_{29} \cdot 5.4H_2O$)	−105	−115	0.26:0.74
H^+-magadiite[b] ($H_2Si_{14}O_{29} \cdot 4H_2O$)	−105	−115	0.18:0.82

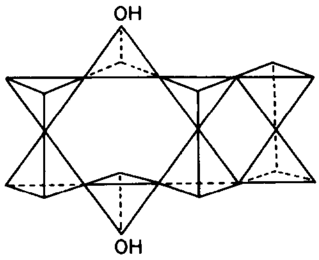
[a] Dried in air at 25°.

[b] Dried at 230°C for 3 hr.

strong resonance at −101 ppm along with a much weaker resonance (<10%) at −113 ppm. Since pure kanemite consists exclusively of Q^3 silicate tetrahedra (*17*), the strong resonance at −113 ppm is attributed to the Q^3 site. The weak resonance at −113 ppm for kanemite may be due to a Q^4 tetrahedral site of an impurity phase originating from the hydrolysis of kanemite itself. Kanemite is known to be much more sensitive to hydrolysis than magadiite (*17*). Because <10% of the more reactive kanemite has undergone condensation of Q^3 units, it is unlikely that the relative Q^3 and Q^4 intensities of magadiite have been affected by hydrolysis. It is noteworthy that both Na^+-magadiite and kanemite exhibit single Q^3 resonances; that is, Q^3 sites of the type $HOSiO_3$ and $Na^+[^-OSiO_3]$ are not distinguished.

Figure 2 provides the ^{29}Si MAS NMR spectra at 35.8 MHz for H^+-magadiite after drying at room temperature and at 230°C for 3 hr. Under the latter conditions the basal spacing is 11.2 Å and the composition is near $H_2Si_{14}O_{29} \cdot 4H_2O^3$. The ^{29}Si chemical shifts and $Q^3:Q^4$ site ratios as obtained from integral intensities are provided in Table I along with those for kanemite. Within experimental uncertainty the $Q^3:Q^4$ site ratio is unchanged upon conversion of Na^+-magadiite to H^+-magadiite. However, the dehydration of H^+-magadiite does lead to a decrease in the relative number of silicon atoms in Q^3 sites.

On the basis of the above ^{29}Si MAS NMR results, we conclude that the relative $Q^3:Q^4$ ratio of silica tetrahedra in Na^+- and H^+-magadiite is approximately 1:3. One plausible arrangement of Q^3 and Q^4 tetrahedra leading to a layered structure is shown in scheme I.



In this scheme the layers would consist of five planes of atomic oxygen, in reasonable agreement with the observed basal spacing for Na^+-magadiite (11.5 Å) and H^+-magadiite (11.2 Å) in the absence of interlayer water. The layers could be imagined as arising from double sheets of Q^4 tetrahedra with 25% of the tetrahedra "inverted" to form Q^3 units. The positions of the protonated Q^3 tetrahedra in the layers and their interactions across interlayers cannot be deduced from the NMR data. Previously reported IR and ^1H NMR studies[6] of dehydrated H^+-magadiite show the presence of two kinds of silanol protons associated with Q^3 tetrahedra. One type exhibits hydroxyl stretching frequencies $\nu_{OH} \leq 3440\ cm^{-1}$. These protons are separated from neighboring ones by 2.2–2.9 Å. The second type of silanol protons has $\nu_{OH} \simeq 3600\ cm^{-1}$, and the near-neighbor proton distance is 4.3–5.2 Å. The silanol groups of the first type are attributed to those involved in strong interlayer hydrogen bonding, because the intensity of the 3440-cm^{-1} band decreases upon dehydroxylation and cross-linking of the layers through formation of SiOSi bonds at elevated temperatures.

It is particularly noteworthy that previous reported thermal analyses (*3*) would lead one to conclude that interlayer siloxane bond formation (*3*) in H^+-magadiite does not occur until about 400°C. However, our ^{29}Si NMR results suggest that *some* layer cross-linking occurs upon dehydration even at 230°C, as evidenced by the substantial decrease in $Q^3:Q^4$ site ratio (cf., Fig. 2, Table I). Differences in the layer cross-linking reactivity of H-bonded silanols may be reflecting differences in their positions in the interlayers. Finally, we note that the approximately 1 : 3 $Q^3:Q^4$ site ratio found in the present work for air-dried H^+-magadiite is significantly different from the 1 : 1 ratio deduced from estimates of the OH surface density (*6*). However, the values derived from thermogravimetric analysis (*2*) (~1 : 2) and proton T_2 relaxation measurements (*7*) (~1 : 3) are in accord with our findings.

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