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^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy of Al-substituted tobermorites

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Solid-state ^{27}Al and ^{29}Si NMR spectroscopy with magic angle spinning (MAS) of samples was used to study several 1.13 nm tobermorites, most of which were deliberately substituted with aluminium. ^{27}Al MASNMR clearly showed that aluminium is tetrahedrally co-ordinated in tobermorite structures. In addition two different aluminium environments resonating at ~57 and 64 ppm from $[Al(H_2O)_6]^{3+}$ were detected. ^{29}Si MASNMR of pure, anomalous tobermorites showed resonances at −85.7 and −95.7 ppm from tetramethylsilane representing chain middle groups (Q^2) and branching sites (Q^3), respectively. Anomalous Al-substituted tobermorites, on the other hand, showed two to four resonances representing different silicon environments. One Al-substituted tobermorite showed two resonances at −84.6 and −91.5 ppm which were assigned to Q^2 (0 Al) and Q^3 (1 Al), respectively. In the above tobermorite aluminium appeared to have substituted into branching sites only. Two other Al-substituted tobermorites, however, showed four distinct resonances at ~ −82.0, −85.2, −92.0 and −96.0 and these were assigned to Q^2 (1 Al), Q^2 (0 Al), Q^3 (1 Al) and Q^3 (0 Al), respectively. Thus these two tobermorites showed substitution of aluminium in the chain middle groups as well as branching sites. Another Al-substituted tobermorite which showed a normal thermal behaviour exhibited, as expected, only Q^2 (0 Al) and Q^2 (1 Al) sites resonating at −84.7 and ~ −80.2 ppm, respectively. No Q^3 sites were detected because few or no branching sites are present in this normal tobermorite. The results reported here clearly demonstrate the usefulness of solid-state ^{27}Al and ^{29}Si MASNMR spectroscopy for the investigation of short-range order in alumino-silicate materials.

1. Introduction

Tobermorite, a rare hydrous calcium silicate mineral ($Ca_5Si_6H_2O_{18} \cdot 4H_2O$) was described first by Heddle in 1880 and it has been found to be the principal binding agent in autoclaved concrete which is of considerable technical importance. A poorly organized phase, CSH, which is the principal product of ordinary

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cement hydration is also thought to belong to this structural family. The senior author's recent discovery of substituted and unsubstituted tobermorites as a new family of cation exchangers [1–4] has generated new interest in the study of tobermorites. The ion exchange and ion sieve processes in tobermorite cation exchangers are of relevance to myriad applications in catalysis, nuclear and hazardous waste disposal and waste water treatment.

An understanding of the crystal chemistry of tobermorites is essential in interpreting the cation exchange phenomenon in these calcium silicate hydrates. The crystalline calcium silicate hydrates of the tobermorite group give characteristic basal reflections between 0.9 and 1.4 nm which represent the thickness of the elementary layers. Tobermorites were classified [5] on the basis of their basal reflections. The crystal structure of 1.1 nm tobermorite was first determined by Megaw and Kelsey [6]. According to their structure determination, the basic unit consists of a central sheet comprising a double layer of calcium and oxygen ions, connected with rows of silicon tetrahedra that are linked into chains running parallel to the *b*-axis direction [7]. Tobermorites have layer structures similar to those of 2 : 1 clay minerals [8] but rather different in their swelling and shrinkage behaviour. Tobermorite minerals vary in some properties, notably in whether or not unidimensional lattice shrinkage occurs by about 300° C to give a 0.93 nm form; specimens that do this are called normal and the ones that do not are called anomalous [9]. The term "mixed tobermorite" is used for tobermorites showing various kinds of intermediate behaviour, of which the most usual was a change in the basal reflection to a broad peak at about 1.05 nm at 300° C [9]. The structure of tobermorite varies with the chemical composition, ionic substitutions, and synthesis conditions [10]. The existence of Si–O–Si bridges in tobermorites had been first proposed by Taylor [7]. Tobermorites with a few or no Si–O–Si bridges collapse upon heat treatment just as in the case of swelling clay minerals while the tobermorites with numerous Si–O–Si bridges have non-shrinking layers even after heat treatment at 300° C for 24 h and in this respect resemble the zeolites. These non-shrinking tobermorites are potentially capable of functioning as cation sieves with proper substitutions just like the zeolites do [11]. In fact, our recent results [1–3] show that partial substitution of aluminium for silicon in the tobermorite structure along with sodium incorporation resulted in high selectivity of caesium and rubidium because of an ion sieving effect while unsubstituted tobermorites exhibited selective exchange of heavy metals [4].

The existence of Si–O–Si bridges as proposed by Taylor [7] in non-shrinking 1.1 nm tobermorites has been recently demonstrated by solid-state ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy [12]. The substitution of aluminium for silicon in the tetrahedral co-ordination has been demonstrated with solid-state ^{27}Al MASNMR [13]. The objective of the present study is to probe the environment of silicon and aluminium in unsubstitued and Al-substituted tobermorites by high-resolution ^{29}Si and ^{27}Al MASNMR.

Lippmaa *et al.* [14, 15] were the first to probe the structures of silicates, aluminosilicates and calcium silicates by solid-state MASNMR. The range of isotropic ^{29}Si chemical shifts in silicates and aluminosilicates were shown to be related to polymerization of the SiO_4 tetrahedra (Q^0, Q^1, Q^2, Q^3 and Q^4) and their linkage to AlO_4 tetrahedra [15]. Here Q represents the SiO_4 tetrahedron while the superscript refers to the number of other tetrahedra to which it is linked. The total range of ^{29}Si chemical shifts is from -60 to -120 ppm in the samples studied by the above authors. The shift ranges of aluminosilicates are designated as Q(n Al) where n may vary from 0 to 4. Recent studies have shown that chemical shifts correlated with Si–O–Si bond angles and Si–Si bond lengths [16]. Based on the chemical shifts, the co-ordination of silicon can be determined by ^{29}Si MASNMR [16] while the co-ordination of aluminium can be determined by ^{27}Al MASNMR [17, 18]. Thus it is possible to probe the nearest neighbour environment by MASNMR and the above cited studies form the basis for the interpretation of results reported here.

2. Experimental details

2.1. Synthesis of tobermorites

Several synthetic tobermorites were prepared using different starting materials and widely varying conditions as shown in Table I. Both unsubstituted and aluminium and alkali

TABLE I Reaction mixtures, synthesis conditions* and XRD analyses of synthetic tobermorites

Sample	Initial reactant mixture	Temperature (° C), and treatment time (days)	Phases detected by XRD after treatment
1	Quartz + CaO	175° C; 18 h	Tobermorite, (A)†
2	Na_2SiO_3 + $FeCl_3$ + CaO	175° C; 14 day	Tobermorite (A); calcite; goethite
3	Amorphous SiO_2 + kaolinite + KOH	175° C; 7 day	Tobermorite (A); calcite
4	Na_2SiO_3 + $AlCl_3$ + CaO	180° C; 7 day	Tobermorite (A); calcite
5	Amorphous SiO_2 + kaolinite + CaO + NaOH	175° C; 7 day	Tobermorite (A); calcite
6	Amorphous SiO_2 + zeolite Linde 3A + CaO + NaOH	80° C; 22 day	Tobermorite (N); calcite
7	Na_2SiO_3 + $AlCl_3$ + CaO	85° C; 4 day	Tobermorite (N); calcite
8	Na_2SiO_3 + $AlCl_3$ + CaO	180° C; 1 day	Tobermorite (A); calcite
9	Amorphous SiO_2 + kaolinite + CaO + KCl	175° C; 7 day	Tobermorite (A); trace xonotlite
10	Clinoptilolite + CaO	175° C; 7 day	Tobermorite (A); calcite
11	Phillipsite + CaO	225° C; 5 day	Tobermorite (A); calcite
12	Amorphous SiO_2 + zeolite	85° C; 120 day	Tobermorite (A); calcite
13	Fumed silica + γ-Al_2O_3 + CaO	80° C; 120 day	Tobermorite (N)

*Saturated steam pressure in all cases.
†A = Anomalous; N = Normal.

substituted tobermorites were synthesized in Parr bombs. A Ca/[Si + Al] atom ratio of ~ 0.83 was used in all the tobermorite syntheses.

2.2. Characterization of tobermorites

Powder X-ray diffraction (XRD) was used to identify the phases in the synthetic preparations. XRD was carried out with a Philips X-ray diffractometer using graphite monochromated Cu*Kα* radiation. The normal or anomalous nature of the tobermorites was determined by heat treatment of samples at 300° C for 20 h [9].

Solid-state ^{27}Al MASNMR spectra were obtained for all the samples while ^{29}Si MASNMR spectra were obtained for six of the samples. A high-resolution Bruker WH-400 narrow-bore commercial spectrometer with a home-built MAS broad-banded probe fitted with a standard Andrew-Beams spinning assembly [19] was used for recording the ^{27}Al and ^{29}Si MASNMR spectra. ^{27}Al MASNMR spectra at ambient temperature were obtained at 104.22 MHz while ^{29}Si MASNMR spectra were recorded at 79.5 MHz using the above spectrometer. Some high-resolution ^{27}Al MASNMR spectra were obtained at 156.3 MHz using the 14.1 T (600 MHz for protons) spectrometer of the NMR Facility for Biomedical Studies located at Carnegie-Mellon University. Spinners made of Delrin have an internal volume of ~ 450 μl and were spun at ~ 3.5 to 4.0. kHz with compressed air as the driving gas. ^{27}Al chemical shifts were recorded with respect to $[Al(H_2O)_6]^{3+}$ as an external reference and ^{29}Si chemical shifts were recorded with respect to tetramethylsilane (TMS). No resolution enhancement was undertaken and the ^{29}Si spectra were presented with the appropriate line broadening.

3. Results and discussion

3.1. ^{27}Al MASNMR

All the synthetic tobermorites show ^{27}Al chemical shifts between 56.3 and 65.9 ppm from $[Al(H_2O)_6]^{3+}$ (Table II; Fig. 1) which indicates that the aluminium is tetrahedrally co-ordinated. Only tobermorite Sample 5 (Table II) exhibits a small resonance at 9.5 ppm which is attributed to octahedrally co-ordinated aluminium probably due to the presence of an impurity such as boehmite. However, XRD did not show the presence of boehmite in this synthetic preparation (Table I). The assignment of ^{27}Al chemical shifts to tetrahedral and octahedral co-ordination is based on previous studies [17, 18] which showed that tetrahedrally coordinated aluminium resonates at ca. 50 $\pm$ 20 while octahedrally co-ordinated aluminium resonates at about 0 $\pm$ 10 ppm from $[Al(H_2O)_6]^{3+}$. All the tobermorites excepting two show two different resonances (Table II; Fig. 1) suggesting the presence of aluminium in two distinct local environments. This result further substantiates

TABLE II ^{27}Al and ^{29}Si chemical shifts of 1.1 nm tobermorites

Synthetic tobermorite sample*	^{27}Al chemical shifts, ppm from $[Al(H_2O)_6]^{3+}$ Tetrahedral Al co-ordination, two environments	Si/Al atom ratio	^{29}Si chemical shifts ppm from tetramethylsilane			
			Q^2		Q^3	
			1 Al	0 Al	1 Al	0 Al
1	60.0, 64.1	No added Al		−85.7		−95.7
2	58.8, 64.5	No added Al		−85.7		−96.3
3	59.1, 64.5	20		−84.6	−91.5	
4	57.5, 65.6	9	−82.0	−84.6	−92.0	−95.9
5†	57.3, 64.2	20	−82.0	−85.2	−92.0	−96.0
6	56.7, 64.5	5.7	nd‡		nd	
7	57.6, 65.9	9	nd		nd	
8	56.3, 64.8	9	nd		nd	
9	64.9	20	nd		nd	
10	57.8, 64.7	3.7	nd		nd	
11	58.1	3	nd		nd	
12	56.8, 64.4	7.7	nd		nd	
13	62.0	5	~ −80.2	−84.7		

*Ca/[Si + Al] atom ratio is ~0.83 in all samples.

†This sample showed a small resonance at 9.5 ppm due to the presence of octahedrally co-ordinated Al (see text for reason).

‡nd = not determined.

our earlier findings [13] of two different tetrahedral environments for aluminium in Al-substituted tobermorites. Tobermorites (1 and 2 in Table II) prepared without the deliberate addition of aluminium reactant also showed ^{27}Al resonances which are attributed to the trace amounts of aluminium present as an impurity in the reactants. Thus it is obvious that ^{27}Al MASNMR is a highly sensitive probe owing to the 100% isotopic abundance of this quadrupolar nucleus.

One disadvantage with ^{27}Al MASNMR is that often it is difficult to get well resolved spectra at low magnetic fields because of unaveraged

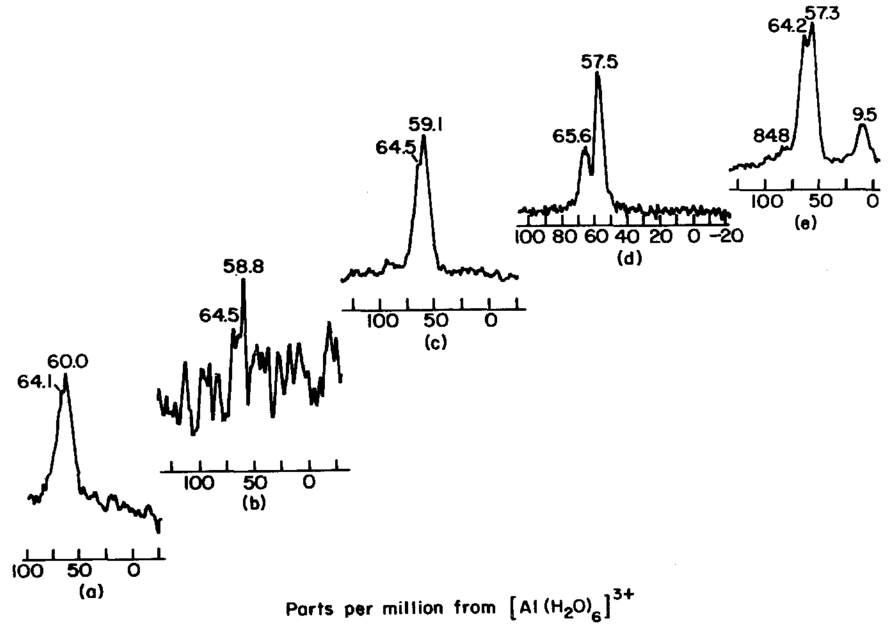

Figure 1 ^{27}Al MASNMR spectra of synthetic tobermorites. Spectra (a) to (e) represent samples 1–5, respectively, in Tables I and II. Spectra (a) and (b) represent tobermorites without deliberate addition of aluminium while (c) to (e) represent Al-substituted tobermorites.

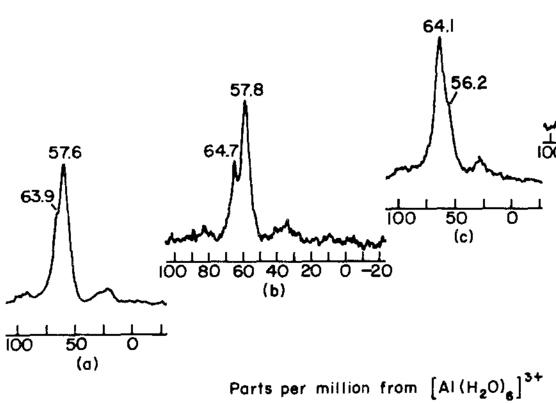

Figure 2 ^{27}Al MASNMR spectra of Al-substituted tobermorites (Tables I and II, Samples 12 and 8). (a) Spectrum of Sample 12 recorded at 104.22 MHz; (b) same sample as (a) but shows better resolution at 156.3 MHz; (c) spectrum of Sample 8 recorded at 104.22 MHz; (d) same sample as (c) but shows better resolution at 156.3 MHz.

second order quadrupolar interactions. It is possible to circumvent this problem by using very high magnetic fields since these second order quadrupolar interactions are inversely proportional to the magnetic field strength. Here we show spectra for two Al-substituted tobermorites at two different magnetic fields in Fig. 2. It is clear from Fig. 2 that the spectra obtained at 156.3 MHz are well resolved compared to the spectra obtained at 104.22 MHz. These ^{27}Al MASNMR results unequivocally show the presence of aluminium in the tetrahedral co-ordination (i.e., aluminium for silicon substitution) confirming the earlier findings by infrared and X-ray emission techniques [20].

3.2. ^{29}Si MASNMR

The ^{29}Si chemical shifts of several different tobermorites are given in Table II and Fig. 3. The interpretation of ^{29}Si chemical shifts is based on Wieker *et al.* [12], who first studied pure tobermorites. Tobermorites (Table II, Samples 1 and 2; Figs. 3a and b) without added aluminium exhibit two resonances at -85.7 and -95.7. These two resonances arise from chain middle groups (Q^2) and branching sites (Q^3), respectively, as has been suggested by Wieker *et al.* [12]. Since these two tobermorites exhibit anomalous thermal behaviour [9], they are expected to have Si–O–Si branching sites and NMR results clearly showed their presence. The

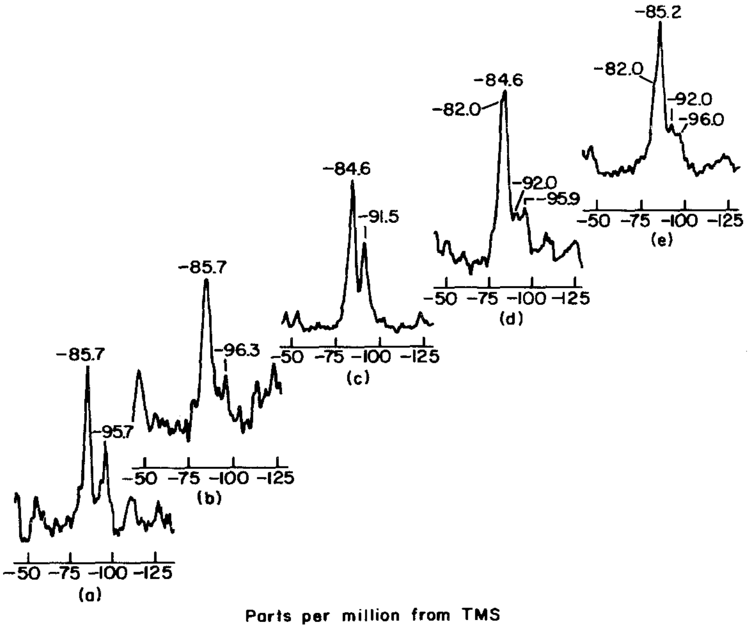

Figure 3 ^{29}Si MASNMR spectra of tobermorites synthesized with and without the addition of aluminium. Spectra (a) to (e) represent Samples 1–5, respectively, in Tables I and II. Spectra (a) and (b) represent tobermorites without deliberate addition of aluminium while (c) to (e) represent Al-substituted tobermorites.

ratio of Q^2/Q^3 resonances is approximately 2 as can be anticipated for tobermorites with a Ca/Si ratio of 0.83 [12]. The effect of partial substitution of aluminium for silicon on the ^{29}Si chemical shifts is shown (Table II; Figs. 3c, d and e). The substitution of aluminium in tobermorite Sample 3 (Table II; Fig. 3c) caused a low field shift of the Q^3 resonance from −95.7 to −91.5 ppm. However, there is little or no effect on the Q^2 resonance. A 4.2 ppm low field shift is typical for Q^3(1 Al) in layered silicates [21, 22] and the resonance can be assigned to Q^3(1 Al) in tobermorites which have layer type of structures. This assignment is also consistent with an Si/Al atom ratio of 20 for the above tobermorite (Si/Al for Q^3 sites is ~ 7) and the tetrahedral co-ordination of aluminium [Table II]. Thus, it appears that a regular ordering of Si_3Al_1 has taken place in this synthetic Al-substituted tobermorite.

Spectra for two other anomalous Al-substituted tobermorites (Table II, Samples 4 and 5; Figs. 3d and e) show four different resonances at ~ −82, −85, −92 and −96 ppm. These results show that the substitution of aluminium is occurring in both Q^3 and Q^2 units because of the 4 and 3 ppm low field shift of the Q^3 and Q^2 resonances, respectively. Therefore, the observed resonances can be assigned as follows: Q^2(1 Al) = −82 ppm; Q^2(0 Al) = −85 ppm; Q^3(1 Al) = −92 ppm and Q^3(0 Al) = −96 ppm.

The spectrum for a normal Al-substituted tobermorite (Table II, Sample 13) shows the presence of only Q^2(0 Al) sites at ~ −84.7 and Q^2(1 Al) at ~80.2 ppm. This assignment is consistent with that of the above. Since this is a normal tobermorite, there are no Q^3 branching sites. These ^{29}Si and ^{27}Al MASNMR results clearly show the immediate environment of the silicon and aluminium atoms in the layered tobermorite structures and this information will be very useful in their X-ray crystallographic studies.

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