

# Oxygen Speciation in Hydrous Silicate Glasses: An Oxygen-17 NMR Study

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**Abstract:** The structural roles of H<sub>2</sub>O and OH in hydrous Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> (sodium tetrasilicate, NTS) and NaAlSi<sub>3</sub>O<sub>8</sub> (“albite”) glasses have been investigated with <sup>17</sup>O, one-dimensional fast magic-angle spinning (MAS), static, and cross-polarization (CP), and two-dimensional triple quantum MAS (3QMAS) NMR techniques. Silica gel and crystalline analcime (NaAlSi<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O) were also studied as model compounds. Peaks for molecular H<sub>2</sub>O are clearly identified in the analcime and in the hydrous glasses in one-dimensional, partial saturation experiments. Bridging and nonbridging oxygen sites are clearly resolvable in the 3QMAS spectra, as is a feature related to SiOH in hydrous NTS glass. This feature may also be present in the hydrous albite glass, although, lacking further characterization of other site types (e.g., NaOH, AlOH, Si–OH–Al), this assignment remains tentative. <sup>1</sup>H–<sup>17</sup>O CP experiments with short contact times reveal a peak that is similar in both hydrous glasses and silica gel, again possibly related to SiOH groups.

## Introduction

The dissolution of water in molten silicates has profound effects on physical properties such as viscosity, conductivity, and melting points. A full understanding of the water dissolution process continues to be of major importance in geochemistry and glass science. However, due to experimental difficulties, in situ spectroscopic measurements of hydrous molten silicates, which can provide microscopic information on melt structure, are at present limited to infrared and Raman techniques.<sup>1–5</sup> As a starting point for studying the structure of the melt, quenched hydrous glasses have been used to represent the quenched-in structure of the melt at the glass transition temperature in many spectroscopic studies, e.g., infrared, Raman, and nuclear magnetic resonance (NMR). Numerous spectroscopic studies of hydrous silicate and aluminosilicate glasses have been made to clarify the structural role of water in these systems.<sup>3,6–18</sup> Infrared studies showed that both hydroxyl groups and molecular water exist in hydrous silicate and

aluminosilicate glasses with >0.5 wt % total water. At low total water contents, hydroxyl groups are the dominant hydrogen-bearing species. At total water contents >4%, more than half of the water is dissolved as molecular H<sub>2</sub>O.<sup>15–19</sup>

However, the key question of how the OH species is incorporated into the structure of multicomponent glasses and melts is not fully understood. In alkali silicate glasses, <sup>1</sup>H magic angle spinning (MAS) NMR studies confirmed the presence of both molecular H<sub>2</sub>O and strongly hydrogen bonded SiOH species.<sup>11,19</sup> NMR results on <sup>29</sup>Si, <sup>1</sup>H–<sup>29</sup>Si cross-polarization (CP) and <sup>1</sup>H combined rotation and multiple pulse sequence (CRAMPS) further showed that the proportion of the Q<sup>4</sup> species (tetrahedral SiO<sub>4</sub> groups connected to four other SiO<sub>4</sub> or AlO<sub>4</sub> groups) decreases with the addition of water in sodium tetrasilicate (NTS) glass and the fraction of Q<sup>2</sup> and Q<sup>3</sup> species increases.<sup>6,11,12,20</sup> These data indicate that water attacks the bridging oxygen bonds between tetrahedra (BO) and forms SiOH when added into anhydrous NTS glass. A quantitative relationship between the decrease in BO, as sampled by Q<sup>n</sup> speciation, and the OH content has recently been demonstrated for NTS glass in several reports, one of which was made on a sample studied here.<sup>6,18,20</sup>

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For hydrous aluminosilicate glasses the mechanism of water dissolution is more controversial. On the basis of thermodynamic data and Raman spectra, it was suggested that H<sub>2</sub>O attacks the framework as in the binary system, and tetrahedral oxygen bonds break to form SiOH or AlOH groups.<sup>14,21</sup> Such a “depolymerization” of the hydrous melt structure qualitatively agrees with the well-known large decrease in viscosity, and has proven useful for modeling of phase equilibria.<sup>22</sup> A different dissolution model based on NMR (<sup>1</sup>H, <sup>27</sup>Na, <sup>27</sup>Al, <sup>29</sup>Si) was later introduced, proposing the exchange of H<sup>+</sup> ions in the water with the Na<sup>+</sup> ions in the aluminosilicate glasses as the main mechanism.<sup>7,9,10,23</sup> In the latter model, no network oxygen bonds (T–O–T) are broken and there are no AlOH or SiOH species, although oxygens in Al–O–Si and Si–O–Si sites may be protonated. However, on the basis of ab initio calculations and infrared measurements, NMR results were reinterpreted and it was argued that T–O–T bonds are broken when water is added, forming terminal AlOH species.<sup>17,24</sup> It thus appears that there is not yet enough spectroscopic evidence about OH and H<sub>2</sub>O groups and their bonding environments to unambiguously support or to rule out either model.

<sup>17</sup>O NMR is sensitive to the bonding environments of oxygen in silicate materials and has successfully been applied to identify and quantify bridging oxygens and nonbridging oxygens (NBO) in silicate glasses.<sup>25,26</sup> However, the low Larmor frequency and large quadrupolar interaction severely limit the resolution of conventional 1D <sup>17</sup>O NMR. Recently, two-dimensional, high-resolution NMR experiments that eliminate second-order quadrupolar broadening have shown great potential for increasing the information content of <sup>17</sup>O spectra for oxide glasses. These include “dynamic angle spinning” (DAS) NMR<sup>27,28</sup> and, more recently, triple quantum magic angle spinning (3QMAS).<sup>29,30</sup> For example, the latter method can clearly separate oxygens in Al–O–Si and Si–O–Si sites in aluminosilicate crystals<sup>31</sup> and in anhydrous<sup>32</sup> and hydrous glasses.<sup>33–35</sup>

In this study, we have applied fast magic-angle spinning (MAS), static, MAS with saturation, <sup>1</sup>H–<sup>17</sup>O static cross polarization, and 3QMAS NMR techniques to study <sup>17</sup>O-enriched hydrous and anhydrous Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> (NTS) and NaAlSi<sub>3</sub>O<sub>8</sub> (“albite”) glasses, silica gel, and crystalline analcime (NaAlSi<sub>3</sub>O<sub>8</sub>·H<sub>2</sub>O). We have observed and assigned the contribution to the spectra from molecular H<sub>2</sub>O in hydrous NTS and albite glasses, based on the model compound analcime. We have also detected

the <sup>17</sup>O signal of the SiOH species in the NTS glass. Together with the <sup>1</sup>H–<sup>17</sup>O static CP results, we were able to examine the proton-bearing species in hydrous albite glass. These results extend previous work on these samples using <sup>29</sup>Si MAS, <sup>1</sup>H, and 1D <sup>17</sup>O NMR at a lower magnetic field.<sup>18</sup>

## Experimental Section

**Samples.** Analcime was chosen as the model compound for studying water in aluminosilicate glasses because the bulk oxygen isotope exchange kinetics have been studied in detail,<sup>36,37</sup> and large crystals are easy to obtain. High-quality crystals (Table Mountain, CO) were hand picked, ground to powder, and sieved to a size ranging between 44 and 75 μm. The <sup>17</sup>O isotope enrichment was achieved by mixing the powder with an equal weight of 46 atom % <sup>17</sup>O-enriched water and sealing the mixture in a gold tube, which was then held in a cold seal pressure vessel at 400 °C and 0.1 GPa for 10 days. The material was then dried in air at ambient temperature. The analcime sample was characterized with X-ray powder diffraction and <sup>29</sup>Si MAS NMR before and after the enrichment process. These methods confirmed that the enriched analcime had the same crystal structure as that of the starting material, as expected from previous studies.<sup>36,37</sup>

<sup>17</sup>O-enriched anhydrous Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> (NTS) and NaAlSi<sub>3</sub>O<sub>8</sub> (“albite”) glass samples were synthesized from high-purity Na<sub>2</sub>CO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, the latter enriched to about 45% <sup>17</sup>O. Gd<sub>2</sub>O<sub>3</sub> (0.2%) was added to speed spin–lattice relaxation. Each batch was melted at about 100 °C above its liquidus temperature and then quenched and ground to a powder. <sup>17</sup>O-enriched hydrous NTS (10 wt % water) and hydrous albite glasses (5 wt % and 10 wt % water) were made by mixing the <sup>17</sup>O-enriched anhydrous silicate glass powder with an appropriate amount of 46 atom % <sup>17</sup>O-enriched water and sealing the mixture in a platinum capsule. The capsules were then held at 1.5 GPa and 1200 °C (hydrous NTS glass) and 1300 °C (hydrous albite glasses) for 0.5 h in a 1/2 in. solid-media piston-cylinder apparatus. The quenching rate was about 100 °C/s. The detailed synthesis procedure was published elsewhere.<sup>18</sup> <sup>1</sup>H NMR was used to confirm water contents and OH/H<sub>2</sub>O ratios, and samples were characterized with <sup>29</sup>Si MAS NMR.<sup>18</sup>

Silica gel was synthesized by hydrolysis of SiCl<sub>4</sub> with 46 atom % <sup>17</sup>O-enriched water. The typical amount of water present as OH groups in the resulting silica gel was about 5%.

**<sup>17</sup>O NMR Spectroscopy.** <sup>17</sup>O NMR spectra were obtained at 54.2 MHz with a modified Varian VXR-400S NMR spectrometer (9.4 T) with a 5-mm Doty Scientific “supersonic” MAS probe. Static (nonspinning sample) CP spectra were obtained with a 5 mm CPMAS probe from the same manufacturer. Static one-pulse, CP, magic-angle spinning (MAS), MAS with saturation, and triple quantum magic-angle spinning NMR techniques were applied to analyze <sup>17</sup>O NMR spectral intensities and peak shapes. Spin–lattice relaxation times (*T*<sub>1</sub>) were measured with the saturation-recovery method, and the delay times in all except the saturation MAS experiments were chosen to be at least three times *T*<sub>1</sub> to ensure nearly complete relaxation, typically 0.7 to 1.0 s. The rotor spinning speed was about 14.5 kHz in the MAS experiments on glasses and 16.0 kHz for analcime. 1D spin–echo experiments were also performed to acquire undistorted static spectra for all the samples. The pulse lengths for the selective 90° and 180° pulses used in the latter were 10 and 20 μs, respectively. The external reference for <sup>17</sup>O chemical shifts is tap water.

The recently developed 3QMAS NMR technique not only expands the quadrupolar interactions into a second dimension but also averages the anisotropy of quadrupolar interactions to the second order in the isotropic dimension.<sup>38–41</sup> Therefore, each of the Gaussian-like peaks

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in the isotropic dimension represents a different type of oxygen site and the line width of each peak is only about 10% of the line width for the corresponding site in the 1D MAS experiment. The other dimension in the 3QMAS spectrum is the MAS dimension, where a typical quadrupolar line shape for each individual site is present. It has been shown that from the peak positions in both MAS and isotropic dimensions the isotropic chemical shift and quadrupolar product ( $P_Q$ ) for each site can be calculated.<sup>42</sup> The latter is defined as  $C_Q(1 + \eta^2/3)^{1/2}$ , where  $C_Q$  is the quadrupolar coupling constant and  $\eta$  the asymmetry parameter. With typical values of  $\eta$  ranging from 0 to 0.5 for  $^{17}\text{O}$ ,  $P_Q$  exceeds  $C_Q$  by at most 4%.

A three-pulse version of 3QMAS was used with an echo time of two rotor periods.<sup>38,39,42</sup> The first and second pulses of this sequence are hard (ideally nonselective)  $540^\circ$  and  $180^\circ$  pulses with pulse lengths of 9.0 and 3.4  $\mu\text{s}$ , respectively. The advantage of such a choice is described elsewhere.<sup>41</sup> The third pulse was a soft (central transition selective) pulse of  $180^\circ$  with a length of 14.5  $\mu\text{s}$ . The 2D data were processed with the program RMN (P. J. Grandinetti, Ohio State University) and only the echo part of the spectrum was used. The low efficiency of the triple quantum excitation and the limited amount of  $^{17}\text{O}$ -enriched hydrous silicate glasses (about 40 mg for NTS) resulted in typical total acquisition times for the 3QMAS spectra shown here of 3 days to 1 week. Typically, 250 Hz exponential apodization was applied to 1D and 2D spectra, which did not significantly affect peak shapes.

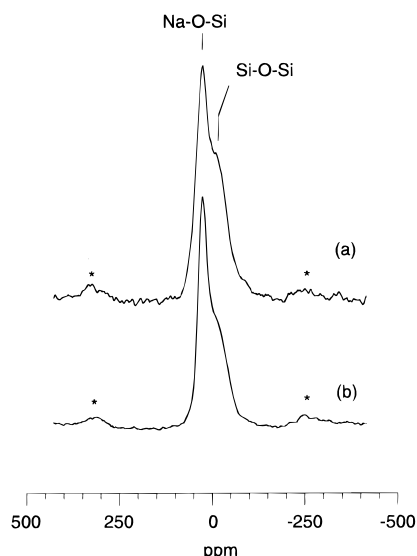
A MAS experiment with saturation pulses (16 pulses) was used to accentuate the molecular  $\text{H}_2\text{O}$  species in the hydrous glasses and to extract the well-defined quadrupolar line shape for  $\text{H}_2\text{O}$  in analcime. The pulse sequence was similar to the saturation-recovery measurement of  $T_1$ , except that the final observe pulse was given immediately after saturation. The delay times between the saturation pulses were systematically varied and were at least as long as the duration of the free induction decay (FID) time. The  $^{17}\text{O}$  MAS quadrupolar line shape was fitted with the program WINFIT (D. Massiot, CNRS, Orléans, France).

Static CP ( $^1\text{H}$  to  $^{17}\text{O}$ ) spectra were obtained by using the single contact spin-lock method,<sup>43</sup> with high-power  $^1\text{H}$  decoupling during acquisition. The Hartman–Hahn matching condition was reached by adjusting the  $^1\text{H}$  power level to observe the maximum  $^{17}\text{O}$  signal intensity in  $^{17}\text{O}$ -enriched silica gel.  $^1\text{H}$  and  $^{17}\text{O}$  radio frequency (RF) field strengths during cross polarization were typically 31.3 and 10.4 kHz, respectively. Contact times varying from 50 to 2000  $\mu\text{s}$  were applied to selectively accentuate the oxygen sites closest to  $^1\text{H}$  in the hydrous glasses.

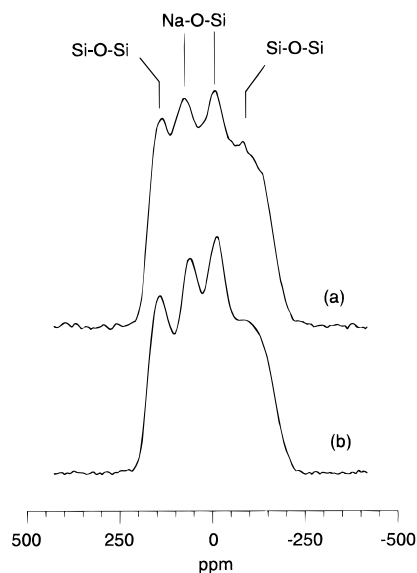
## Results

MAS  $^{17}\text{O}$  NMR spectra of hydrous and anhydrous NTS glasses are shown in Figure 1. Both spectra are made up of two overlapping components as seen before: a narrower peak centered around 20 ppm and a broader one around 0 ppm.<sup>26</sup> As in previous studies, the narrow peak is assigned to the nonbridging oxygen (NBO, Na–O–Si) sites and the broad one is assigned to the bridging oxygen (BO, Si–O–Si) sites.

Figure 2 shows the  $^{17}\text{O}$  static spin–echo NMR spectra for hydrous and anhydrous NTS glasses. The two main components are better seen than in the MAS spectra and the peak shapes are well-known: the narrower doublet is from the NBO sites and the broader doublet is from the BO sites.<sup>25,26</sup> The peak widths and shapes are dominated by the second-order quadrupolar interaction, with additional broadening caused by distributions of isotropic chemical shifts and quadrupolar parameters. In both the MAS and static  $^{17}\text{O}$  NMR spectra for hydrous and anhydrous NTS glasses, the NBO peak height seems to decrease with added water, as noted previously in studies of this sample



**Figure 1.**  $^{17}\text{O}$  MAS spectra for the hydrous (a) and anhydrous (b) NTS glasses. Asterisks in this and other spectra indicate the positions of spinning sidebands.



**Figure 2.**  $^{17}\text{O}$  static spin–echo spectra for the hydrous (a) and anhydrous (b) NTS glasses.

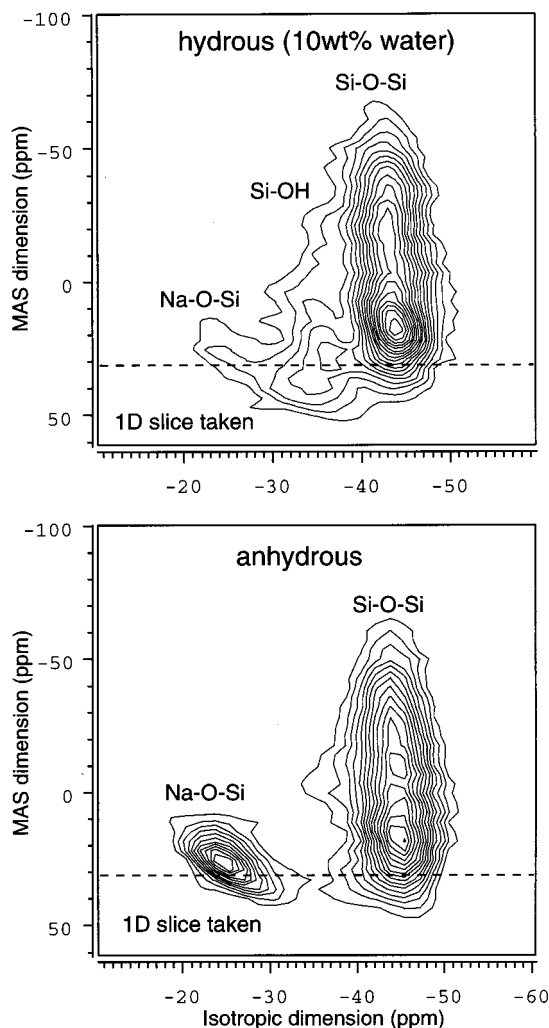
at lower magnetic field.<sup>18</sup> This observation apparently contradicts the finding that the fraction of NBO increases with the addition of water, and suggests that an additional peak or peaks are generated that are unresolvable in 1D spectra. Other experiments are thus required to better characterize even such a relatively simple system.

One obvious approach to improving resolution is 3QMAS. The results are shown in Figure 3. For the anhydrous NTS glass, the NBO and BO peaks are clearly separated, as seen before in other silicate glass samples studied by this technique.<sup>29</sup> The positions of both peaks along the isotropic and MAS dimensions agree well with those calculated from the known chemical shifts and quadrupolar parameters.<sup>26,28</sup> For the hydrous NTS glass, the NBO peak has a wider distribution than in the anhydrous sample, ranging from  $-23$  to  $-38$  ppm along the isotropic dimension. A broad new feature was observed centered at about  $-33$  to  $-38$  ppm in the isotropic dimension. This peak is seen more clearly by comparing 1D slices of the isotropic dimension of the 3QMAS spectra of the hydrous and anhydrous NTS glasses (Figure 4). The center of gravity for

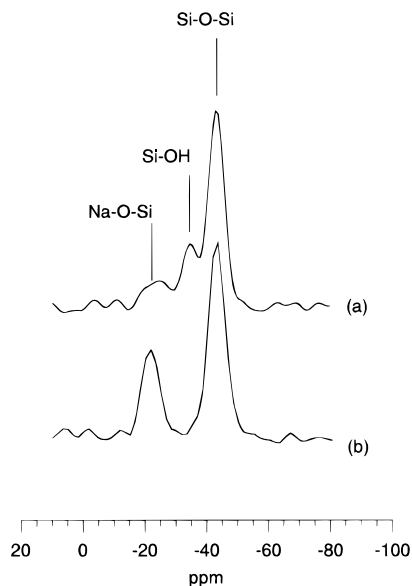
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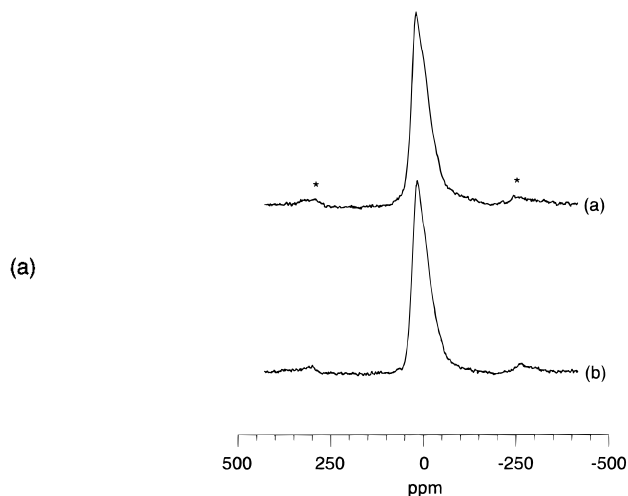


**Figure 3.**  $^{17}\text{O}$  3QMAS spectra of hydrous (a) and anhydrous (b) NTS glasses.



**Figure 4.** 1D slices of the isotropic dimension of  $^{17}\text{O}$  3QMAS spectra of the hydrous (a) and anhydrous (b) NTS glasses in Figure 3, at positions shown by dashed lines in that figure.

this extra peak along the MAS dimension is about 20 to 30 ppm. We have not attempted to fit its MAS dimension because of its breadth and relatively low intensity. The position



**Figure 5.**  $^{17}\text{O}$  MAS spectra for the hydrous (a) and anhydrous (b) albite glasses.

of this feature is such that it completely overlaps the more intense BO peak in the MAS dimension and hence is unresolvable in standard 1D spectra, as suggested in a previous 1D NMR study of this sample.<sup>18</sup>

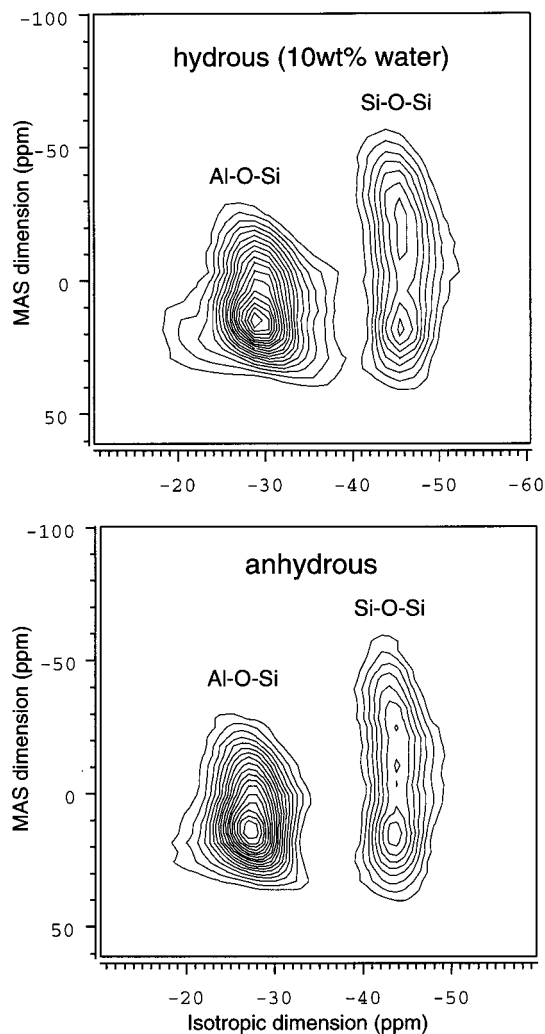
Conventional MAS  $^{17}\text{O}$  NMR spectra of hydrous and anhydrous albite glasses are relatively unresolved (Figure 5). The MAS spectra, as well as static spectra (not shown), are very similar for the two samples, as previously reported.<sup>33</sup> In contrast, 3QMAS spectra (Figure 6) show clearly separated peaks for Si-O-Al and Si-O-Si sites, as also recently reported by others.<sup>32</sup> The ratio of the area of the Al-O-Si peak to that of the Si-O-Si peak is close to 1:1 for both samples, which is expected from stoichiometry if Al-O-Al linkages are uncommon. Unlike another recent comparison,<sup>33</sup> we see subtle differences between hydrous and anhydrous albite glasses, as best seen in the 1D total projection along the isotropic dimension (Figure 7): in the hydrous glass, the Al-O-Si peak is broadened, with intensity in the same region as the new peak in the 3QMAS NMR spectrum of hydrous NTS glass.

Static  $^1\text{H}$ - $^{17}\text{O}$  CP experiments were performed on hydrous NTS glass, hydrous albite glass, and silica gel to better constrain peak assignments. For the hydrous NTS glass (Figure 8), the NBO doublet is accentuated at moderate contact time. At a very short contact time (50  $\mu\text{s}$ ), however, an additional broad, overlapping peak is observed. The NBO peak is also seen at reduced intensity, probably because protons are close to at least some NBO's. For the hydrous albite glass (Figure 9), the Si-O-Al and Si-O-Si peaks are clear in the one-pulse static NMR spectra. At medium contact times, the Al-O-Si peak is enhanced. At very short contact times, a featureless, asymmetrical peak was observed, with a center of gravity at about  $60 \pm 10$  ppm.

Figure 10 compares the CP spectra of the hydrous glasses and silica gel, again at a 50  $\mu\text{s}$  contact time. The similarity of the short contact time peaks in all three spectra is clear, suggesting that a common component might be present.

Analcime was chosen as a model compound for molecular  $\text{H}_2\text{O}$ . Three components are clearly resolved in the  $^{17}\text{O}$  MAS spectra of this mineral (Figure 11). Overlapping quadrupolar doublets for Al-O-Si and Si-O-Si sites are centered around 25 and 0 ppm, respectively, as previously seen in other framework silicates.<sup>31,44</sup> A third, broad, component that we

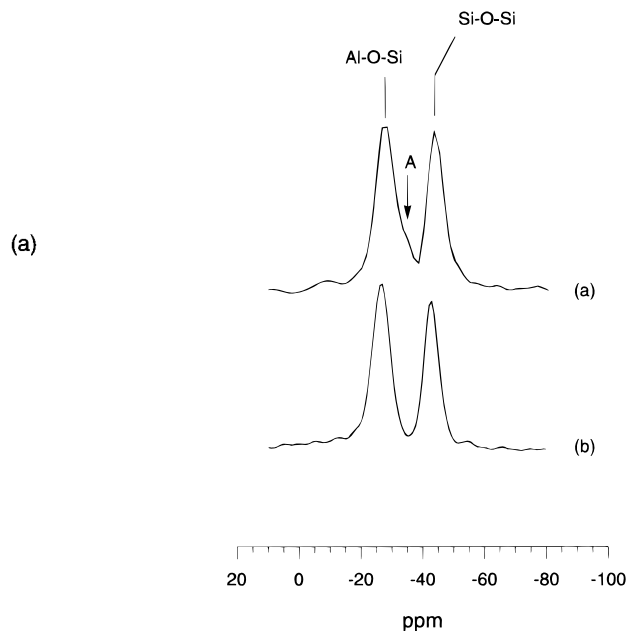
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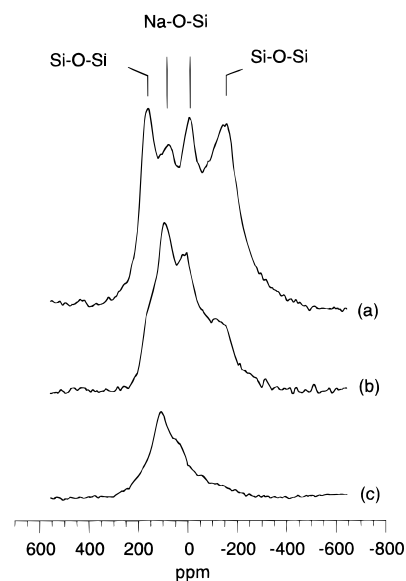
**Figure 6.**  $^{17}\text{O}$  3QMAS spectra of hydrous (a) and anhydrous (b) albite glasses.

assign to  $\text{H}_2\text{O}$  is centered around  $-100$  ppm with the line width of about 9 kHz. The relative area of the  $\text{H}_2\text{O}$  peak is about 15% of the total area of the center band. The  $\text{H}_2\text{O}$  peak is more clearly seen in the partially saturated spectrum, where its rapid spin-lattice relaxation causes it to be accentuated:  $T_1$  for this peak is much shorter ( $<0.1$  s) than the  $T_1$ 's for the framework oxygens (about 2.0 s). Computer simulation of the partially saturated spectrum is shown in Figure 11b, with the derived  $C_Q = 7.6 \pm 0.2$  MHz,  $\eta = 0.0 \pm 0.2$ , and isotropic chemical shift =  $18 \pm 2$  ppm.

MAS  $^{17}\text{O}$  NMR spectra of the hydrous NTS glass with partial saturation are shown in Figure 12. In addition to the BO and NBO peaks, an additional broad component was detected, and was accentuated with the shorter delay times. The position and line width for this component is comparable to the broad peak observed in analcime (Figure 11), although the line shape is different. This broad component was not observed in the anhydrous NTS glass spectrum under the same saturation conditions (Figure 13). Spectra of hydrous albite glass with partial saturation are shown in Figure 14. A broad component, absent from the anhydrous glass (Figure 15), was again detected under saturation conditions. The broad component resembles the one observed in hydrous NTS glass in terms of position, line shape, and line width (Figure 12). As for the hydrous NTS glass, this broad component in hydrous albite glass has a  $T_1$  less than 20 ms, much shorter than the  $T_1$ 's for the framework oxygens (about 200 ms). The broad component was observed



**Figure 7.** Total projections of the isotropic dimension of hydrous (a) and anhydrous (b) albite glasses in Figure 6. The shoulder at "A" is at the same position as the SiOH peak in hydrous NTS glass (Figure 4).

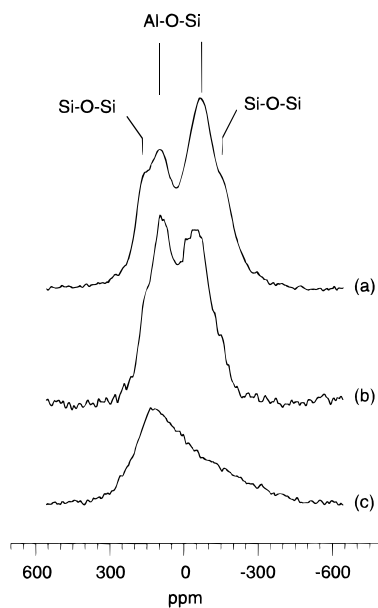


**Figure 8.** Comparisons of the  $^{17}\text{O}$  static one pulse spectrum with CP experiments for hydrous NTS glass: (a) one pulse; (b) CP, contact time = 0.8 ms; and (c) CP, contact time = 0.05 ms.

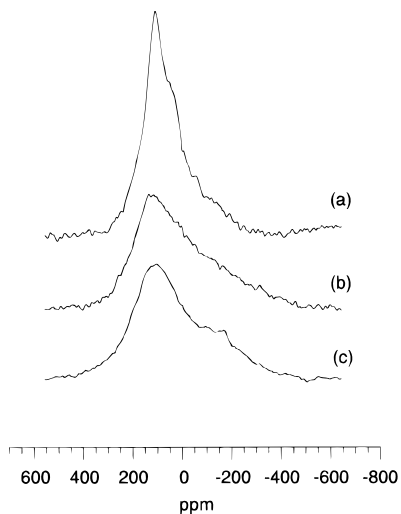
in hydrous albite glasses with both 5 and 10 wt % of water, and is significantly larger in the latter.

## Discussion

**SiOH in Hydrous NTS Glasses.** Previous  $^1\text{H}$  MAS and CRAMPS NMR,  $^{29}\text{Si}$  and  $^1\text{H}$ - $^{29}\text{Si}$  CP-MAS,  $^2\text{H}$  static NMR, infrared, and Raman spectroscopic studies of alkali and alkaline earth silicate glasses (containing high water contents) concluded that strong hydrogen-bonded SiOH species and molecular  $\text{H}_2\text{O}$  were present.<sup>6,8,11,14,19,20,45</sup> However,  $^{17}\text{O}$  NMR spectra for the SiOH peak in these glasses have not been reported. The  $^{17}\text{O}$  NMR peak for SiOH sites in silica gel was observed with static  $^1\text{H}$ - $^{17}\text{O}$  CP experiments on silica gel at short contact times,<sup>43</sup> with a reported  $C_Q$  of about 4.1 MHz. A probably more accurate observation was made by using standard MAS NMR on silica



**Figure 9.** Comparisons of the  $^{17}\text{O}$  static one pulse spectrum with CP experiments for hydrous albite glass with 10 wt % water: (a) one pulse; (b) CP, contact time = 2 ms; and (c) CP, contact time = 0.05 ms.



**Figure 10.** Comparison of the  $^{17}\text{O}$  static CP experiments with short contact times for (a) hydrous NTS glass, (b) hydrous albite glass, and (c) silica gel.

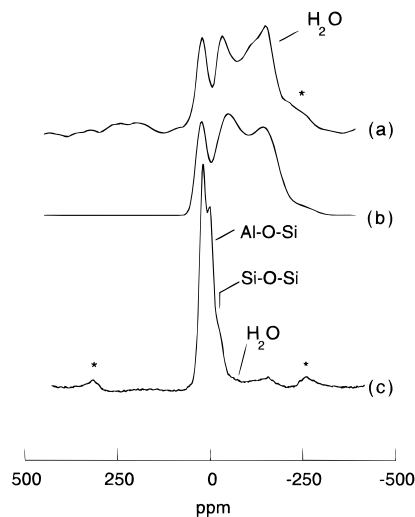
gel with selective  $^{17}\text{O}$  enrichment.<sup>46</sup> Fitting of spectra resulted in estimates of  $\delta_{\text{iso}} \approx 37$  ppm and  $C_Q \approx 4.4$  MHz. A corresponding peak in a 3QMAS spectrum would be centered at  $(-2, -33)$  ppm in the MAS and isotropic dimensions, respectively, and would be roughly similar in shape to the BO peaks shown in Figures 3 and 6.  $^{17}\text{O}$  peaks for “SiOH” sites in several hydrous Ca-silicates were also derived from fitting of complex spectra.<sup>46,47</sup> A typical peak had  $\delta_{\text{iso}} \approx -4$  ppm and  $C_Q \approx 5.0$  MHz. In a 3QMAS spectrum, this would be centered at  $(-55, -14)$  ppm. The large offsets of such peaks suggest an as-yet poorly understood effect of partial coordination of the oxygen site by other cations such as  $\text{Ca}^{2+}$ .

In the 3QMAS spectrum for hydrous NTS glass (Figure 3b), the extra peak around  $-36$  ppm along the isotropic dimension

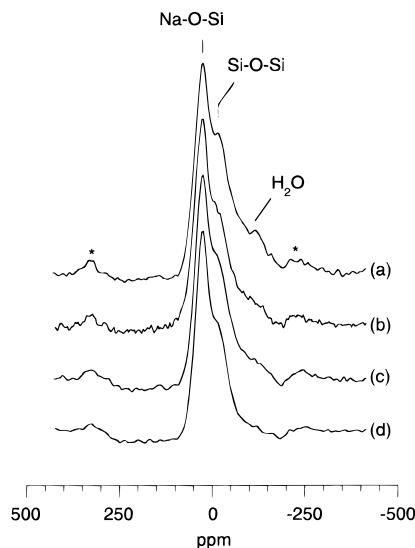
(45) McMillan, P. F.; Holloway, J. R. *Contrib. Mineral. Petrol.* **1987**, *97*, 320–332.

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**Figure 11.**  $^{17}\text{O}$  MAS NMR spectra of  $^{17}\text{O}$ -enriched analcime: (a) one pulse with saturation; (b) the fitted result for the spectrum in (a); and (c) the fully relaxed one-pulse spectrum.

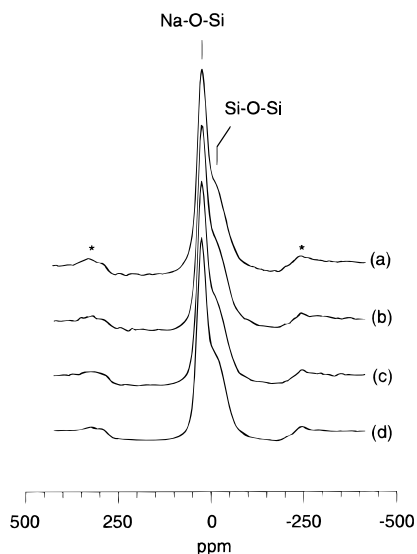


**Figure 12.**  $^{17}\text{O}$  MAS saturation spectra for hydrous NTS glasses with various delay times: (a) 10 ms; (b) 20 ms; (c) 50 ms; and (d) 200 ms.

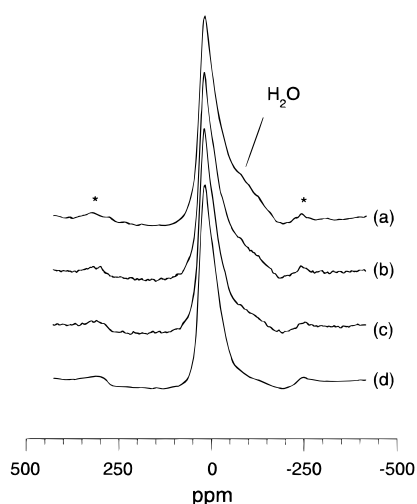
cannot be due to Na–O–Si or Si–O–Si because neither the chemical shift nor the quadrupolar coupling constant matches the known values.<sup>26,28,29</sup> This peak cannot be assigned as molecular  $\text{H}_2\text{O}$  either (see below). Models of water dissolution in alkali silicate glasses generally do not suggest the presence of NaOH groups (in which the O is not bonded to Si), and it is not clear where the spectral signature of such sites would appear: the large  $C_Q$  for  $^{17}\text{O}$  in crystalline NaOH ( $C_Q = 7.59$  MHz,  $\eta = 0$ ) suggests that such sites might be difficult to observe.<sup>48</sup> The large  $C_Q$  values (6.5 to 7.6 MHz) reported for CaOH sites in hydrous Ca silicates tend to corroborate this problem,<sup>46,47</sup> although “NaOH” sites (and their NMR parameters) in hydrous glasses may of course be quite different from those in previously studied materials.

We thus conclude that the most likely assignment for the new peak in the hydrous NTS glass is SiOH. The mean quadrupolar product  $P_Q$  for this peak, estimated from the peak centers of gravity along both MAS (about 21 ppm) and isotropic dimensions ( $-36$  ppm) as was done previously,<sup>42</sup> is about  $3.7 \pm 0.5$  MHz, somewhat less than the reported value for SiOH in silica

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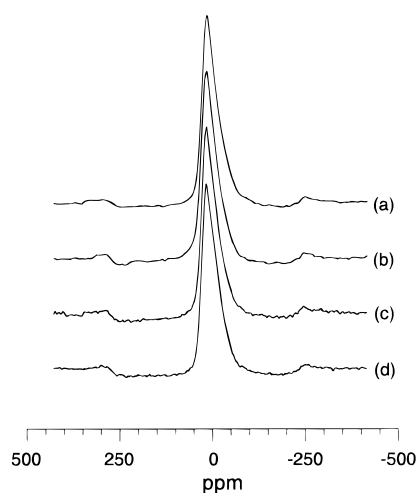
**Figure 13.**  $^{17}\text{O}$  MAS saturation spectra for anhydrous NTS glasses with various delay times: (a) 10 ms; (b) 20 ms; (c) 50 ms; and (d) 200 ms.



**Figure 14.**  $^{17}\text{O}$  MAS saturation spectra for hydrous albite glasses (10 wt % water) with various delay times: (a) 10 ms; (b) 20 ms; (c) 50 ms; and (d) 200 ms.

gel, and the mean isotropic chemical shift of about  $48 \pm 10$  ppm is somewhat higher. These differences may be due to a broad distribution of parameters for sites of this type in our sample, or to a more systematic effect caused by interactions with other ligands (e.g.,  $\text{Na}^+$  or H-bonded  $\text{H}_2\text{O}$ ). The latter is likely, as oxygens in SiOH groups in multicomponent glasses are probably coordinated by network modifier cations as well as by  $\text{H}^+$ , as is almost universally found for silanol groups in silicate minerals.<sup>49</sup> We see no MAS or 3QMAS peaks in this or other samples that correspond in position to any of the other SiOH or CaOH peaks reported previously in hydrous calcium silicates.<sup>46,47</sup>

As in our previous  $^{17}\text{O}$  3QMAS NMR study of Ba–Ca binary silicate glasses,<sup>29</sup> the enlarged width of the NBO peak in the 2D contour plot (Figure 3a) corresponds to a wide distribution of chemical shifts for the NBO site. Such a wide range could be the reason that the NBO peak in 1D MAS and static NMR spectra of hydrous NTS is slightly broader than the corresponding NBO peak in anhydrous NTS glass (Figures 1 and 2). This wide chemical shift distribution is probably related to a range



**Figure 15.**  $^{17}\text{O}$  MAS saturation spectra for anhydrous albite glasses with various delay times: (a) 10 ms; (b) 20 ms; (c) 50 ms; and (d) 200 ms.

in the number and distances of protons and  $\text{Na}^+$  cations close to the NBO's. Such an argument could also explain the fact that at short contact time some intensity of the NBO peak was observed in the static CP experiment of the hydrous NTS glass (Figure 8c).

The apparent decrease in NBO peak intensity in 1D spectra for hydrous NTS glass is thus explained by the wider distribution of NBO sites and the overlapping between the SiOH peak and BO peaks. "Simple" NBO sites, coordinated only by Si and Na, are probably actually lower in concentration than in the anhydrous glass, having been partially replaced by oxygens with both  $\text{Na}^+$  and  $\text{H}^+$  neighbors.

**Albite Glasses.** Unambiguous peaks for NaOH, AlOH, or SiOH are not resolved in our 3QMAS spectrum of hydrous albite glass. However, careful comparison between the spectra of the hydrous and anhydrous albite glasses (Figures 6 and 7) shows that the Si–O–Si peaks are similar for both, but the Al–O–Si peak for the hydrous glass is broader in the isotropic dimension than that in the anhydrous sample. The extra contours of the Al–O–Si peak for the hydrous glass are right at the location of the assigned SiOH peak in the 3QMAS spectrum of hydrous NTS glass (Figures 3 and 4). This shoulder ("A" in Figure 7) could thus be due to SiOH. The strong overlap of this peak with the Al–O–Si peak makes its confirmation somewhat problematical. In addition, because we do not know the peak positions and quadrupolar parameters for either AlOH or protonated Al–O–Si sites, we cannot rule out the possibility that this feature is due to one or both of these two species, or even to some other broadening mechanism, such as a slight increase in overall disorder in the hydrous sample. Further experiment, such as five-quantum MAS NMR and studies of other compositions, might resolve this assignment.

The isotropic dimension projections shown in Figure 7 suggest furthermore that regardless of the mechanism of water solution in this composition, the relative ratios of Si–O–Al and Si–O–Si sites are not strongly perturbed. If bonds between tetrahedra are indeed broken by the reaction, this implies a surprisingly nonselective attack by  $\text{H}_2\text{O}$ . On the other hand, if such bonds are not broken, the perturbation of the spectra by the accompanying formation of protonated bridging oxygens is surprisingly minimal.

**Cross-Polarization Spectra.** The static  $^1\text{H}$ – $^{17}\text{O}$  CP NMR experiment on the hydrous albite glass at a medium contact time (2 ms) accentuates the Al–O–Si peak relative to the Si–O–

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Si peak, compared with the one-pulse  $^{17}\text{O}$  NMR spectrum collected under similar conditions (Figure 9), as has been reported previously.<sup>33</sup> This observation suggests that, on average, Al–O–Si sites are closer to protons than Si–O–Si sites, as expected from charge balance considerations.<sup>33</sup> These data do not reveal, however, whether such protons are directly bonded to the bridging oxygens or are part of  $\text{H}_2\text{O}$  groups.

At the short contact time (50  $\mu\text{s}$ ), the asymmetric broad peak with a maximum at 140 ppm does not resemble either the Al–O–Si or the Si–O–Si peak. Such a peak cannot be due to molecular  $\text{H}_2\text{O}$  because its line width (fwhm) is about 320 ppm while the line width for the  $\text{H}_2\text{O}$  peak of  $^{17}\text{O}$ -enriched analcime is about 650 ppm (see below). On the other hand, this peak is similar to the static  $^1\text{H}$ – $^{17}\text{O}$  CP NMR result for silica gel collected under the same conditions (Figure 10). Therefore, we tentatively assigned this peak as SiOH, supporting our early suggestion about the 3QMAS NMR results. Again, we cannot exclude the possibility of this peak being either AlOH or protonated Al–O–Si, although of course these cannot be present in silica gel or NTS glass. This peak is broader and is offset to somewhat higher frequency than either the “SiOH” peak observed by 3QMAS in our hydrous NTS sample or what is expected from previous studies of other silica gel samples with different experimental conditions.<sup>43,46</sup> Because of the nonquantitative nature of the CP experiment, it may be sampling a somewhat different population of sites than is observed by other methods. In addition, the fraction of total oxygen present in such sites is difficult to estimate.

For the CP NMR spectrum of hydrous NTS glass with short contact time, a spectrum with two components was observed. Spectral fitting showed that the central, narrow component resembles the NBO peak obtained with long contact times. The remaining broad component is surprisingly similar to the CP peaks observed in both hydrous albite glass and silica gel with the same contact time, suggesting a common structural feature in all three samples (Figure 10). Again, because this broad component in hydrous NTS glass is too narrow to be molecular  $\text{H}_2\text{O}$  and too wide to be Na–O–Si, the only likely assignment is SiOH.

**Molecular  $\text{H}_2\text{O}$  in Hydrous Silicate Glasses.** Analcime is a useful model compound for the  $^{17}\text{O}$  NMR signal of the molecular  $\text{H}_2\text{O}$  in glasses. This framework aluminosilicate mineral has 4- and 6-membered tetrahedral rings forming channels that are partially occupied by  $\text{H}_2\text{O}$ . Previous  $^1\text{H}$  NMR studies showed that  $\text{H}_2\text{O}$  molecules are static within the channels.<sup>19</sup>

In hydrous silicate glasses, previous infrared, Raman, and  $^1\text{H}$  NMR studies showed that molecular  $\text{H}_2\text{O}$  is dissolved in the structure, and is not merely present as sub-microscopic bubbles of trapped fluid.<sup>13</sup>  $^1\text{H}$  and  $^2\text{D}$  NMR studies indicated that except for a 2-fold flipping,  $\text{H}_2\text{O}$  molecules are immobile on the NMR time scale.<sup>19,50</sup>

We assigned the broad peak centered around  $-100$  ppm in the  $^{17}\text{O}$  spectrum of analcime to molecular  $\text{H}_2\text{O}$ . When accentuated in a partially saturated spectrum (Figure 11a), the typical quadrupolar line shape of this peak is clearly visible. The fitted  $C_Q$  for this species (7.6 MHz) is similar to that of ice ( $C_Q = 6.41$  MHz,  $\eta = 0.93$ ), and  $\text{H}_2\text{O}$  in the hydrate  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  ( $C_Q = 6.8$  MHz,  $\eta = 1.0$ ),<sup>51,52</sup> supporting our assignment,

although our observed value for  $\eta$  ( $\approx 0$ ) is quite different. A peak with this coupling constant is too large to be detected with conditions used in our 3Q MAS experiments.

During the initial  $^{17}\text{O}$  exchange procedure (400  $^\circ\text{C}$ , 0.1 GPa, 10 days) more than 98% of all the oxygens in analcime should have been exchanged with the enriched water.<sup>36</sup> For ideal stoichiometry,  $1/7$  or 14.3% of the total oxygen in analcime is in  $\text{H}_2\text{O}$ , which compares well with our estimate of a 15% relative area for the  $\text{H}_2\text{O}$  peak in our fully relaxed  $^{17}\text{O}$  spectrum.

The  $^{17}\text{O}$  NMR peak for  $\text{H}_2\text{O}$  in hydrous silicate glasses has not been previously reported. In Figure 12, the partially resolved broad peak, absent from the anhydrous NTS glass, cannot be due to oxygens in SiOH sites because of its much too large quadrupolar interaction and peak position (see below). The only other sensible assignment for this peak is thus molecular  $\text{H}_2\text{O}$ . The peak width, peak position, and  $T_1$  for this broad peak are similar to those of the  $\text{H}_2\text{O}$  peak observed in analcime (Figure 11). The triangular shape for this broad water peak could result from a broad distribution of chemical shifts and/or  $C_Q$  values, or to relatively large values of  $\eta$ . If the molecular  $\text{H}_2\text{O}$  peak width is dominated by quadrupolar interaction, the quadrupolar product can be estimated to be between 6 and 7 MHz, somewhat smaller than for analcime. This could be due to the 2-fold flipping motion of water molecules, which was observed with  $^2\text{H}$  NMR.<sup>50</sup> Similarly, the partially resolved broad peak in hydrous albite glasses (Figure 14), which is again absent in the anhydrous glass, could be assigned to molecular  $\text{H}_2\text{O}$ .

Quantifying the contribution of the  $\text{H}_2\text{O}$  peak to a fully relaxed MAS spectrum is made difficult by its breadth and low intensity. However, if the  $\text{H}_2\text{O}$  peak is approximated by a Gaussian shape with a width corresponding to the  $\text{H}_2\text{O}$  peak in analcime, its relative intensity in the  $\text{NaAlSi}_3\text{O}_8$  glass spectrum is about  $10 \pm 4\%$ . This corresponds approximately to the estimate of the fraction of the total oxygen present as  $\text{H}_2\text{O}$  of about 10%, based on previous infrared spectroscopy.<sup>16</sup>

$^{17}\text{O}$  NMR is potentially one of the key experiments to resolve the controversy of the mechanism of water dissolution in aluminosilicate glasses, e.g., to identify hydroxyl species including possible molecular water, AlOH, SiOH, or protonated Al–O–Si. Our observation and identification of molecular  $\text{H}_2\text{O}$  in silicate glasses is one step toward this goal. It is interesting to note that the  $\text{H}_2\text{O}$  peak is similar in terms of peak positions and spin–lattice relaxation times for all three hydrous silicate glasses we studied. This preliminary result could be used to constrain the bonding and structural environments for this species. Although the saturation experiments on both hydrous and anhydrous silicate glasses are informative, the experimental results are difficult to quantify and the peak resolution is low. Further experiments are necessary to extract more detailed information.

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