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## Oxygen sites in hydrous aluminosilicate glasses: The role of Al-O-Al and H<sub>2</sub>O

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**Abstract**—We describe here high-field <sup>17</sup>O magic-angle-spinning (MAS) and triple-quantum MAS (3QMAS) NMR spectra for several alkali silicate and Na, K, and Ca aluminosilicate glasses containing up to 10 wt.% water. The H<sub>2</sub>O site appears to have a large quadrupolar coupling constant, and its chemical shift increases from Na- to K- glasses, suggesting significant cation-H<sub>2</sub>O interactions. In <sup>17</sup>O one-pulse MAS and 3QMAS and <sup>27</sup>Al one-pulse NMR experiments, major differences were seen between spectra for anhydrous and hydrous calcium aluminosilicate glasses. The changes in the <sup>17</sup>O MAS spectra can be explained by the addition of an H<sub>2</sub>O peak and to the disappearance of an Al-O-Al peak from the <sup>17</sup>O NMR spectrum for the hydrous glass. The <sup>27</sup>Al results are consistent with this interpretation. Copyright © 2002 Elsevier Science Ltd

### 1. INTRODUCTION

The effect of water on the physical properties of aluminosilicate melt is well known (for review, see Lange, 1994; Watson, 1994), but a number of unresolved questions about structure remain (for review, see McMillan, 1994; Kohn, 2000). For example, it is clear from IR and <sup>1</sup>H-NMR studies that H<sub>2</sub>O and OH sites are present (Stolper, 1982; Eckert et al., 1988; Kohn et al., 1989a; Mysen, 1990; Nowak and Behrens, 1995; Schaller and Sebald, 1995; Robert et al., 2001; Schmidt et al., 2001a; ), but the precise structural role of the H<sub>2</sub>O group is poorly known. H<sub>2</sub>O is unlikely to be chemically inert, because it is a strongly polar molecule that may interact with the interstitial and the network cations or anions, as is commonly the case in hydrous minerals such as zeolites (Mazzi and Galli, 1978). Here we demonstrate that H<sub>2</sub>O sites can be observed using <sup>17</sup>O NMR, and that quantitative information about these sites can be obtained. There is clearly a cation effect on H<sub>2</sub>O oxygen, suggesting interactions with the glass structure.

A second major question is: To what are the OH groups bonded? One early theory supporting network oxygen bond breaking to form Si-OH (and/or Al-OH) groups was developed in part to explain the changes in viscosity with the addition of water (Burnham, 1975). However, NMR-based studies (Kohn et al., 1989b, 1998; Schmidt et al., 2000a) have not supported this view. Kohn et al. (1989b) showed that the major changes were seen in the <sup>23</sup>Na spectra (as opposed to those for <sup>29</sup>Si or <sup>27</sup>Al spectra), and thus concluded that water only exchanged cations with the melt and did not break network oxygen bonds. Only minor perturbations in the <sup>17</sup>O NMR signal for Na-aluminosilicate glasses have been found (Kohn et al., 1997; Xu et al., 1998), and the effects of water on the <sup>17</sup>O spectra of K-aluminosilicate glasses is even less (Oglesby et al., 2001). In fact, the most likely type of nonbridging oxygen site, based on the crystalline analog KHSi<sub>2</sub>O<sub>5</sub> (Oglesby et al., 2001), is not observed, further supporting Kohn et al. (1989b). However, we could speculate that these findings do not necessarily contradict the Burnham model, since network bond breaking may still be

important at temperatures greater than the glass transition temperature, T<sub>g</sub>. There is not yet any direct NMR data on this question, however.

Another outstanding question is whether H<sub>2</sub>O breaks higher energy network bonds, specifically Al-O-Al linkages. These groups have been directly observed by <sup>17</sup>O NMR in Na and Ca aluminosilicate glasses (Stebbins et al., 1999; Lee and Stebbins, 2000a, 2000b) and related to a model previously developed by Lee and Stebbins (1999); they used the relationship of systematic variations in <sup>29</sup>Si peak positions and widths with composition for aluminosilicate glasses to the ordering of Al and Si cations to develop a statistical thermodynamic model to quantify the extent of ordering. Al-O-Al was found to be energetically unfavorable but some is present, and more sites are present in the Ca than in the Na system (Tossel, 1993; Lee and Stebbins, 1999), because the high charge on Ca stabilizes the highly charged oxygen on Al-O-Al. However, the concentrations of Al-O-Al sites remain well below those of a fully random distribution, at least at the temperatures at which the melts transformed to the glasses studied. Further studies by <sup>17</sup>O 3QMAS NMR allowed direct quantitation of the fraction of Al-O-Al sites and confirmed the major conclusions of this model (Lee and Stebbins, 2000a, 2000b; Lee et al. in press). Previous <sup>27</sup>Al NMR work on water-containing glasses in these systems (Kohn et al., 1992) showed that a calcium aluminosilicate glass exhibited effects of hydration different from those in NaAlSi<sub>3</sub>O<sub>8</sub> glasses (Kohn et al., 1989b), suggesting that a decrease in the number of structurally different Al sites might occur instead of solely an increase in the symmetry of the Al site. Here we show that unlike in the Na and K systems, there is an effect of H<sub>2</sub>O on the network in the Ca system, probably related to its greater concentration of Al-O-Al sites. The role of this interaction is thus more likely to be important for the properties of mafic rather than alkali-rich felsic magmas.

<sup>17</sup>O NMR would seem to be an ideal tool for investigating silicate glass structure, as oxygen is the most abundant element in most geologic materials. However, this approach has not been fully exploited because of the low natural abundance (0.037%) of this nuclide, and because it has a nuclear spin of 5/2. Thus, the observed <sup>17</sup>O NMR peaks are often broadened due to the interaction of the nuclear quadrupolar moment with

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the local electric field gradient. This interaction is characterized by the quadrupolar coupling constant,  $C_Q$ , which provides a measure of the distortion from spherical symmetry of the site, and an asymmetry parameter,  $\eta$ , which measures deviation from uniaxial symmetry.  $^{27}\text{Al}$  is also a 5/2-spin nuclide but is 100% abundant and thus has been used more frequently for NMR spectroscopy (Ghose and Tsang, 1973; Kirkpatrick et al., 1985).

Magic-angle spinning (MAS) is typically used to narrow the broad NMR peaks often present in solids but is only partially effective for quadrupolar nuclides with half integer spins such as  $^{17}\text{O}$  and  $^{27}\text{Al}$ . Nonetheless, the quadrupolar parameters and the isotropic chemical shifts,  $\delta_{\text{iso}}$ , obtained from  $^{17}\text{O}$  and  $^{27}\text{Al}$  NMR, have been useful for studying geologic materials (Kirkpatrick et al., 1985; Turner et al., 1985; Engelhardt and Michel, 1987; Walter et al., 1988; Mueller et al., 1990; Stebbins et al., 2001). The relatively new 3QMAS technique produces two-dimensional spectra. Projection (integration) in one dimension gives a somewhat distorted version of the normal MAS spectrum. In the other dimension, the anisotropy of the quadrupolar interaction is averaged to the second order, yielding an isotropic spectrum that often shows much higher resolution (Frydman and Harwood, 1995). 3QMAS often allows for the separation of the Al-O-Al, Al-O-Si, Si-O-Si, and nonbridging oxygen peaks in aluminosilicate glasses, which are usually overlapped in the normal MAS spectra (Dirken et al., 1997; Stebbins and Xu, 1997; Lee and Stebbins, 2000a; Oglesby et al., 2001).

Here we present  $^{17}\text{O}$  and  $^{27}\text{Al}$  MAS and  $^{17}\text{O}$  3QMAS NMR data on hydrous calcium aluminosilicate glasses as well as  $^{17}\text{O}$  MAS spectra on hydrous alkali silicate and aluminosilicate glasses collected with a pulse sequence designed to accentuate the signal from  $\text{H}_2\text{O}$  groups (Xu et al., 1998). We use known  $^{17}\text{O}$  NMR peak parameters for Al-O-Al (Stebbins et al., 1999) and newly derived parameters for the  $\text{H}_2\text{O}$  peak to interpret the spectra for the calcium aluminosilicate glasses.

## 2. EXPERIMENTAL METHODS

### 2.1. Sample Preparation

The anhydrous silicate glasses were synthesized from decarbonated mixtures of reagent-grade  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $^{17}\text{O}$ -enriched (~45%)  $\text{SiO}_2$  to form glasses with these compositions: sodium tetrasilicate ( $\text{Na}_2\text{Si}_4\text{O}_9$ ), albite ( $\text{NaAlSi}_3\text{O}_8$ ), sanidine ( $\text{KAlSi}_3\text{O}_8$ ), and anorthite-quartz ( $\text{Ca}_{0.5}\text{AlSi}_3\text{O}_8$ ) as described previously (Xu et al., 1998; Oglesby et al., 2001; Stebbins et al., 2001). The hydrous glasses were formed by sealing a measured quantity of  $^{17}\text{O}$ -enriched water with the crushed (10–100  $\mu\text{m}$ ) anhydrous glass in a platinum or gold capsule. The samples were then loaded into a piston-cylinder assembly at 15 to 20 kbar (for the Na-containing glasses). The run temperatures were 1500°C for the K- composition glass, 1350°C for the Ca-composition glass, 1300°C for the albitic glass, and 1200°C for the sodium tetrasilicate glass. After 2 to 5 h, the runs were isobarically quenched in < 1 min and were found to be bubble free using an optical microscope. Total H contents were checked using  $^1\text{H}$ -NMR and were found to agree with the nominal values to within 5% relative.

### 2.2. NMR Spectroscopy

NMR spectra were recorded using a modified Varian VXR-400S spectrometer with a 9.4 Tesla magnet (54.2 MHz for  $^{17}\text{O}$ ) and a Doty Scientific MAS probe with a 5-mm rotor as well as a Varian Inova 600 spectrometer with a 14.1 Tesla magnet (81.3 MHz for  $^{17}\text{O}$  and 156 MHz for  $^{27}\text{Al}$ ) using a Varian/Chemagnetics 3.2-mm MAS probe. The

peak positions were referenced to an external  $\text{H}_2\text{O}$  standard for  $^{17}\text{O}$  and an external 1M  $\text{Al}(\text{NO}_3)_3$  standard for  $^{27}\text{Al}$ . One-pulse MAS  $^{17}\text{O}$  and  $^{27}\text{Al}$  NMR spectra were collected with radio frequency pulse lengths of 0.2  $\mu\text{s}$ , which corresponds to a radio frequency tip angle of  $\sim 20^\circ$  for the  $^{17}\text{O}$  central transition. Relaxation delay times ranged from 0.5 to 5 s to collect fully relaxed spectra (no intensity increases or peak shape changes at longer delay times). Rotor spinning rates were between 14 and 16 kHz.

An MAS experiment with 16 closely spaced saturation pulses, followed by a short delay and observation pulse (Xu et al., 1998) was used to accentuate the fast-relaxing  $\text{H}_2\text{O}$  species. With a short delay time between the applied pulses, some nuclei with relatively slow spin-lattice relaxation may not have enough time to return to their equilibrium energy levels before the next pulse is applied. Signal from such sites will thus have a reduced relative intensity. Sites with faster relaxation rates relax more fully, and thus the peaks for these sites will have enhanced relative intensity in the saturation spectrum. The difference spectra for the hydrous alkali silicate glasses were found by subtracting the maximum amount of the saturation spectrum with a longer delay (200 ms) from the saturation spectrum with a shorter delay (10 ms) that would allow a positive difference spectrum.

A three-pulse, shifted echo version of 3QMAS was used, with two hard pulses ( $540^\circ$  and  $180^\circ$ ) and a third, lower-power pulse ( $180^\circ$ ), which is selective of the central transition (Baltisberger et al., 1996; Xu et al., 1998). The delay times for the experiments on the hydrous glass were chosen to be three times the measured relaxation time, except for the anhydrous glass whose long relaxation time of several seconds necessitated a time delay of 1 s to maximize signal to noise. In the data processing, only the echo part of the data was used to produce the 2D spectra. This approach has been applied successfully in obtaining high-resolution  $^{17}\text{O}$  NMR spectra of glassy silicates (Dirken et al., 1997; Stebbins and Xu, 1997; Lee and Stebbins, 2000a; Oglesby et al., 2001).

## 3. RESULTS

### 3.1. Alkali Silicate and Aluminosilicate Glasses

Two  $^{17}\text{O}$  MAS saturation spectra for a  $\text{KAlSi}_3\text{O}_8$  glass with 10 wt.% water are shown in Figure 1. Signal from sites with faster spin-lattice relaxation rates are accentuated in both of these spectra relative to relaxed MAS spectra, but more so in the shorter delay time (10 ms) spectra. From previous studies (Kohn et al., 1997; Xu et al., 1998; Oglesby et al., 2001), it is clear that the major peak in both represents the predominant bridging oxygen (BO) sites. A broad, low frequency shoulder in the more relaxed spectra (with a 200-ms delay) appears as a partially resolved peak in the more saturated spectrum. In previous work at a lower magnetic field we assigned a similar, but less well-resolved peak to  $\text{H}_2\text{O}$  oxygens based on its similarity in position and width to the  $\text{H}_2\text{O}$  peak in analcime (Xu et al., 1998). The partially saturated MAS spectra also show a peak at a higher frequency, representing a fraction of a percent of the oxygen sites, which is in the same position as nonbridging oxygen (NBO) sites in anhydrous potassium tetrasilicate glasses (Xue et al., 1994). (This minor feature was not detected in our recent report on fully relaxed MAS spectra (Oglesby et al., 2001). The difference spectrum between the longer and shorter delay time-saturation experiments allows the shape and position of the fast-relaxing component to be better defined. The difference spectrum also contains residual intensity, which was best fit with a quadrupolar line shape consistent with bridging oxygen (Si-O-Si) in potassium tetrasilicate

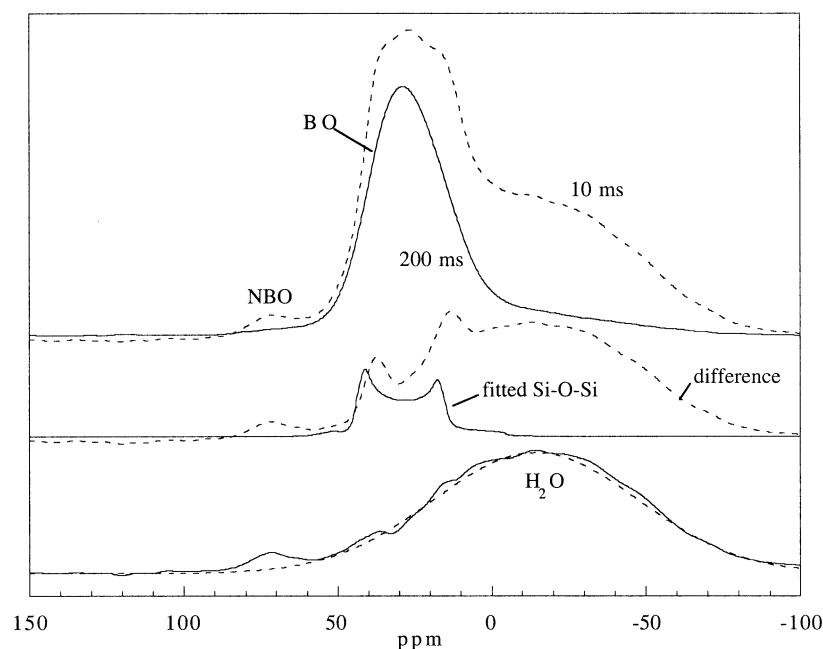


Fig. 1.  $^{17}\text{O}$  MAS saturation spectra collected at 14.1 T for  $\text{KAlSi}_3\text{O}_8$  glass with 10 wt.% water (upper spectra, saturation delays as labeled). BO denotes the signal for bridging oxygens. The difference spectrum and the fitted residual Si-O-Si peak are plotted in the middle, and the broad component and its gaussian fit (dashed line) are shown at the bottom of the figure.

glasses ( $\delta = 52$  ppm,  $C_Q = 4.9$  MHz,  $\eta = 0$ ; Xue et al., 1994). After the residual bridging oxygen intensity is subtracted out, the peak that remains can be fit with a gaussian shape that has a center of gravity at  $-14.3$  ppm and a width at half height of 80.6 ppm (Table 1).

The MAS saturation spectra for the  $\text{NaAlSi}_3\text{O}_8$  glass with 10 wt.% water are shown in Figure 2, and again, the broad, low-frequency component is emphasized in the most saturated spectrum. The difference spectrum also has a minor Si-O-Si intensity (similar to Si-O-Si in sodium tetrasilicate; Maekawa et al., 1998) and a predominant broad peak, which was fit with a gaussian peak centered at  $-23$  ppm with a width at half height of 85.2 ppm. The broad peak in the difference spectrum for  $\text{NaAlSi}_3\text{O}_8$  glass with 5 wt.% water can be fit with the same parameters, as shown in Figure 3.

Figure 4 shows the MAS saturation spectra for the sodium tetrasilicate (NTS) glass with 10 wt.% water. The broad component for this silicate glass has the same width as for the

sodium aluminosilicate glasses, but its position is shifted by 10 ppm to a lower frequency. As expected in this Al-free composition, a significant NBO peak is observed in the difference spectrum at a position that is well known from previous NMR studies of alkali silicates (Xue et al., 1994; Maekawa et al., 1998; Xu et al., 1998).

To gain an idea of the fraction of oxygens represented by this broad component, its maximum contribution in the fully relaxed one-pulse MAS experiments was estimated by subtracting out a simulated peak of the appropriate width and position with the maximum intensity possible (Fig. 5). Only the maximum can be estimated because of the possibility of other unresolved contributions to the low-frequency shoulders on the main BO peaks. The results of this estimate and results for the Na-glasses can be seen in Table 1 and are compared with OH and molecular  $\text{H}_2\text{O}$  concentrations estimated from the composition and from previous studies by infrared spectroscopy and  $^1\text{H}$ -NMR.

Table 1. Hydrous alkali silicate and aluminosilicate glass compositions, water speciation, and  $^{17}\text{O}$  NMR data at 14.1 T.

Composition	Total water content	Mole % $\text{H}_2\text{O}^d$	Mole % OH <sup>d</sup>	Broad component		Maximum contribution of broad component, %
				Position	Width	
$\text{KAlSi}_3\text{O}_8$	10 wt. %	13	6 <sup>a</sup>	$-14.3$ ppm	80.6 ppm	12
$\text{NaAlSi}_3\text{O}_8$	10 wt. %	13	6 <sup>b</sup>	$-23$ ppm	85.2 ppm	13
$\text{NaAlSi}_3\text{O}_8$	5 wt. %	6	6 <sup>b</sup>			5
$\text{Na}_2\text{Si}_4\text{O}_9$	10 wt. %	10	13 <sup>c</sup>	$-33$ ppm	85.2 ppm	11

<sup>a</sup> Silver et al. (1990)

<sup>b</sup> Schmidt et al. (2001a)

<sup>c</sup> Zotov and Keppler (1998)

<sup>d</sup> mol% based on total moles of oxygen in the glass.

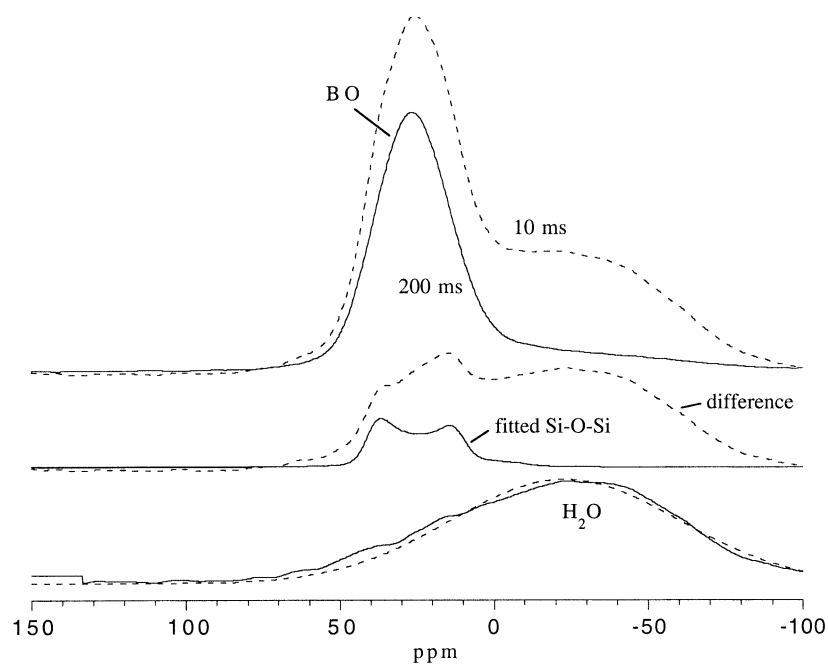


Fig. 2.  $^{17}\text{O}$  MAS saturation spectra collected at 14.1 T for  $\text{NaAlSi}_3\text{O}_8$  glass with 10 wt.% water (upper spectra, saturation delays as labeled). BO denotes the signal for bridging oxygens. The difference spectrum and the fitted residual Si-O-Si peak are plotted in the middle, and the broad component and its gaussian fit (dashed line) are shown at the bottom of the figure.

### 3.2. Calcium Aluminosilicate Glasses

#### 3.2.1. $^{17}\text{O}$ NMR spectroscopy

When the one-pulse MAS spectra collected at 14.1 T for the hydrous and anhydrous  $\text{Ca}_{0.5}\text{AlSi}_3\text{O}_8$  glasses are compared

(Fig. 6), some major differences exist that were not seen in previous work on alkali aluminosilicates (Kohn et al., 1997; Maekawa et al., 1998; Xu et al., 1998; Oglesby et al., 2001). A small peak, accounting for  $\sim 1\%$  of the oxygen sites, is seen at 100 ppm at the same position reported for NBO sites in calcium

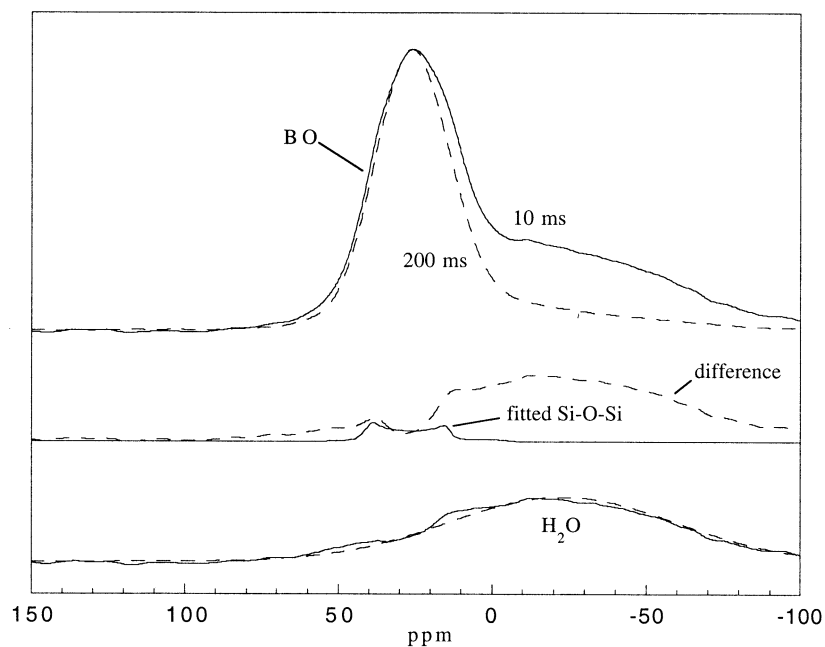


Fig. 3.  $^{17}\text{O}$  MAS saturation spectra collected at 14.1 T for  $\text{NaAlSi}_3\text{O}_8$  glass with 5 wt.% water (upper spectra, saturation delays as labeled). BO denotes the signal for bridging oxygens. The difference spectrum and the fitted residual Si-O-Si peak are plotted in the middle, and the broad component and its gaussian fit (dashed line) are shown at the bottom of the figure.

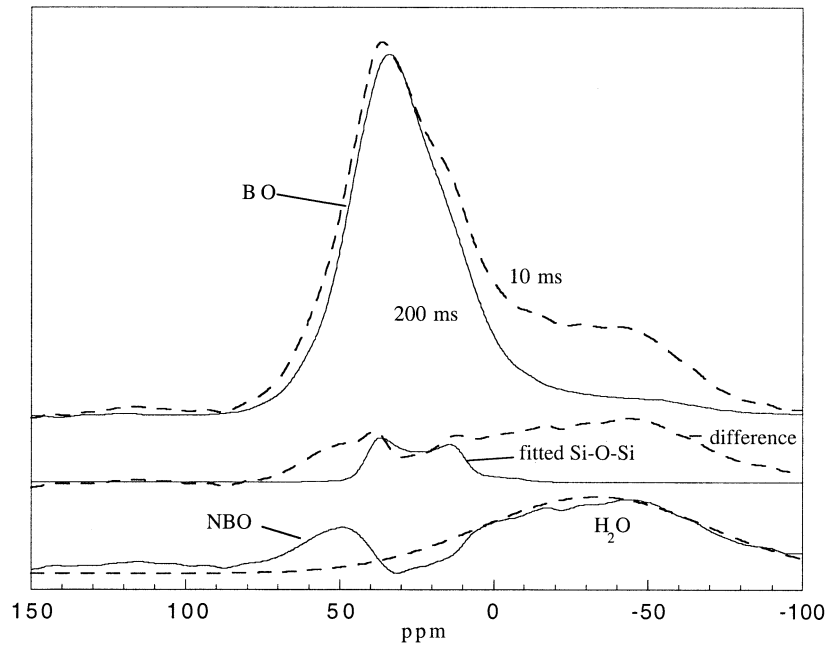


Fig. 4.  $^{17}\text{O}$  MAS saturation spectra collected at 14.1 T for  $\text{Na}_2\text{Si}_4\text{O}_9$  glass with 10 wt.% water (upper spectra, saturation delays as labeled). BO denotes the signal for bridging oxygens. The difference spectrum and the fitted residual Si-O-Si peak are plotted in the middle, and the broad component and its gaussian fit (dashed line) are shown at the bottom of the figure. NBO denotes the residual nonbridging oxygen peak.

silicate and calcium aluminosilicate glasses (Stebbins and Xu, 1997; Stebbins et al., 1997, 1999). This feature disappears with the addition of water due to shifting or broadening of the NBO peak as seen for sodium and potassium silicates (Xu et al.,

1998; Oglesby et al., 2001). The main bridging oxygen peak loses intensity on its high frequency side with the addition of water, as previously noted in preliminary results (Stebbins et al., 2001). There is also the addition of a broad component to

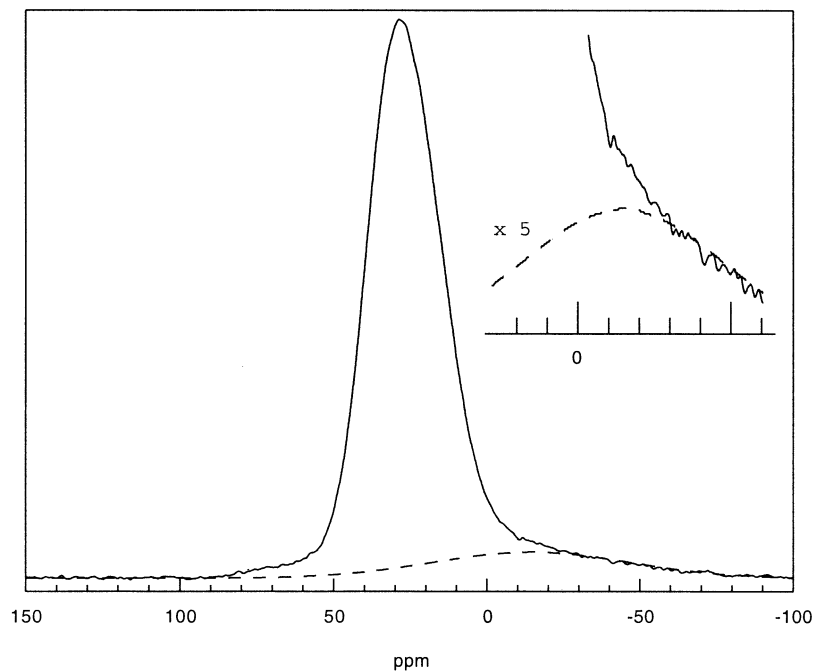


Fig. 5.  $^{17}\text{O}$  one-pulse MAS spectrum collected at 14.1 T for hydrous  $\text{KAlSi}_3\text{O}_8$  glass with the maximum allowed contribution of the broad  $\text{H}_2\text{O}$  component shown (dashed line). The upper right shows a portion of the spectrum at five times the vertical scale.

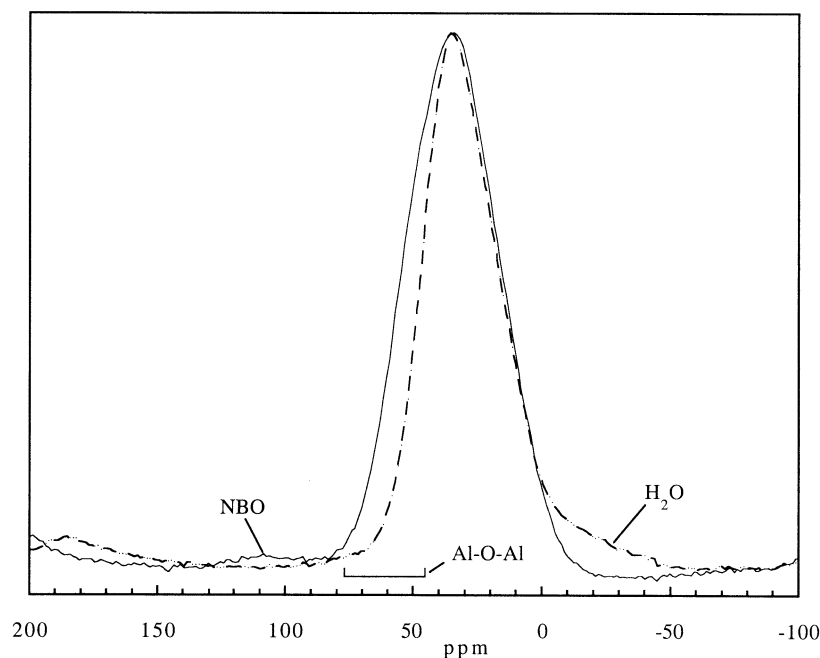


Fig. 6.  $^{17}\text{O}$  one-pulse MAS spectra collected at 14.1 T for hydrous (10 wt.% water; dashed line) and anhydrous (solid line)  $\text{Ca}_{0.5}\text{AlSi}_3\text{O}_8$  glasses. Expected region for Al-O-Al oxygens in Ca-aluminosilicates is shown.

the low-frequency side of the peak, which is similar to the fast-relaxing component described above for alkali silicates.

The observed narrowing of the main bridging oxygen peak on addition of water could be related to a number of different effects, such as the simultaneous reduction in the mean quadrupolar coupling constant and mean chemical shift for all oxygens or a change in the relative populations of the different bridging oxygens (i.e., of Si-O-Si-, Si-O-Al, Al-O-Al). The 3QMAS spectra collected at 9.4 T (Fig. 7) help to resolve this ambiguity, although the signal-to-noise ratio for the anhydrous sample is degraded by its relatively long relaxation time ( $\sim 5$  s). Here the two predominant types of bridging oxygen sites (Si-O-Si and Al-O-Si) are slightly overlapped but still resolved and are assigned based on previous  $^{17}\text{O}$  NMR studies of glasses and crystalline framework silicates (Dirken et al., 1997; Stebbins and Xu, 1997; Xu and Stebbins, 1998; Lee and Stebbins, 1999). The most obvious change from the anhydrous to the hydrous glass is a decrease in intensity in the area where Al-O-Al sites are expected (Stebbins et al., 1999), which is consistent with the MAS spectra. Intensity changes are observed neither in the regions where silanol (Si-OH) sites have been reported for Ca-cement phases, nor in the area of peaks seen in crystalline  $\text{Ca}(\text{OH})_2$  (Cong and Kirkpatrick, 1996). The broad shoulder observed in the one-pulse spectrum is not observed in the 3QMAS spectrum, probably because of larger  $C_Q$  values for the corresponding oxygen sites, which make them less efficient for excitation using 3QMAS (Lee and Stebbins, 2000a). The small NBO signal is also not observed, simply because of its low intensity.

The 3QMAS spectra collected at the higher field (14.1 T) show less separation between the Al-O-Si and Si-O-Si peaks (Fig. 8), but the Al-O-Al shoulder is again clearly visible. (The best resolution for an individual spectrum is not always found

at higher field, because the separation of the peaks is dependant in part on differences in  $C_Q$ .) It is again obvious that oxygen sites are lost in this region of the spectrum with the addition of water to the glass, and that no new peaks are formed.

### 3.2.2. Al-27 NMR spectroscopy

In Figure 9, the  $^{27}\text{Al}$  one-pulse MAS spectra for the calcium aluminosilicate glasses are shown. Addition of water to the anhydrous glass seems to progressively narrow the spectrum, as previously noted for a slightly more silica-rich Ca-aluminosilicate glass with several water contents (Kohn et al., 1992). In alkali aluminosilicate composition glasses that also displayed a narrowing of the  $^{27}\text{Al}$  MAS spectra on hydration (Kohn et al., 1989b; Schmidt et al., 2001b), the changes in the spectra were attributed primarily to quadrupolar effects, since the reduction in  $C_Q$  would result in intensity loss at low frequency. However, in Ca aluminosilicates, Kohn et al. (1992) suggested that the change in the width of the spectra might be dominated by a reduction in the range of chemical shifts and thus in the range of local chemical environments (bond distance, next nearest neighbor populations, etc.). Using a technique suggested by, and data from, Schmidt et al. (2001b) and the Kohn et al. (1992) study, the full widths at half maximum (FWHM) of the  $^{27}\text{Al}$  spectra were analyzed at two external magnetic fields ( $B_1$  and  $B_2$ ) to give two constants: the width contribution due to quadrupolar coupling,  $W_q$ , and the width due to chemical shift dispersion,  $W_{\text{csd}}$  (Table 2). The constants are related to the spectral widths at the two fields by:  $\text{FWHM}_1^2 = W_q^2 + W_{\text{csd}}^2$  and  $\text{FWHM}_2^2 = (B_1/B_2)^2 * W_q^2 + (B_2/B_1)^2 * W_{\text{csd}}^2$ . The widths and peak positions for our spectra and that collected at 14.1 T by Kohn et al. (1992) were very similar and show that the contribution due to chemical shift dispersion decreases significantly

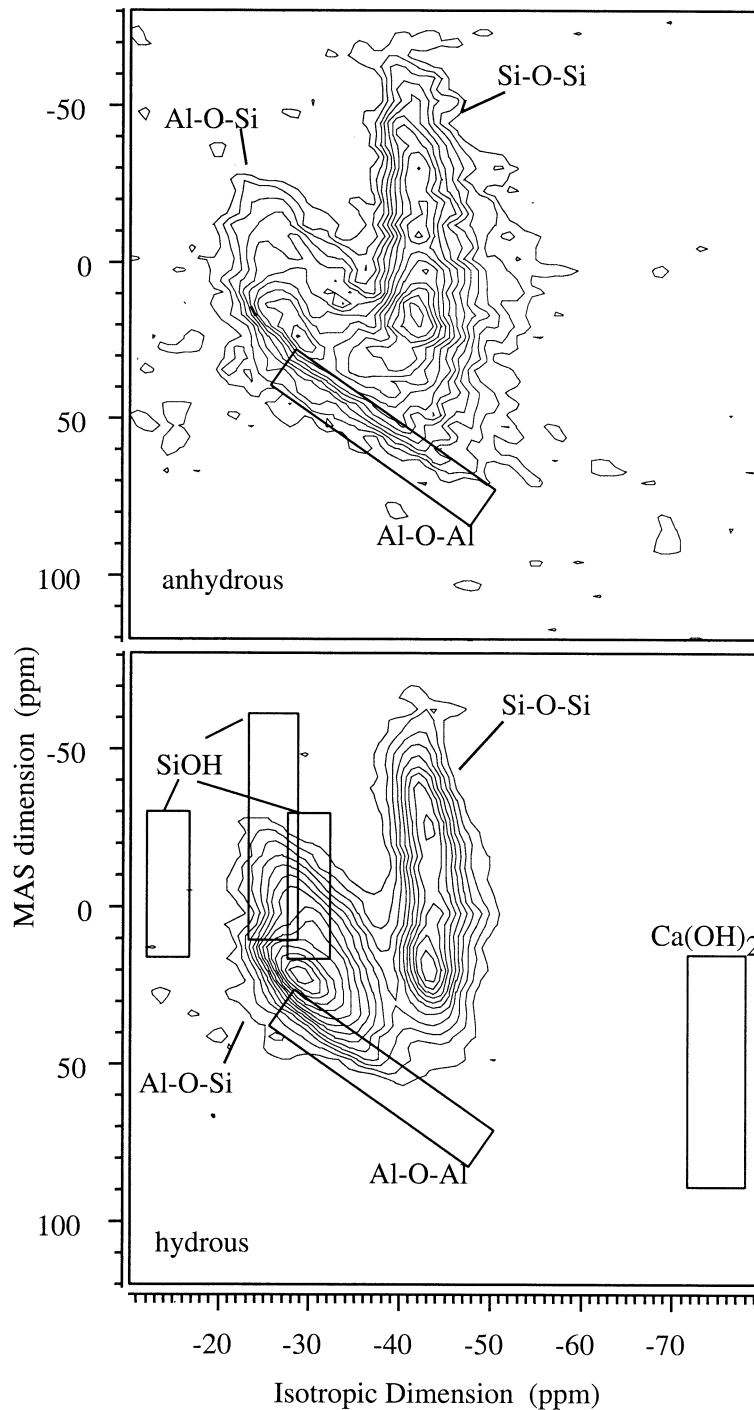


Fig. 7.  $^{17}\text{O}$  3QMAS spectra collected at 9.4 T for the  $\text{Ca}_{0.5}\text{AlSi}_3\text{O}_8$  glasses. The solid boxes represent the expected positions of the Al-O-Al oxygen sites based on data for crystalline  $\text{CaAl}_2\text{O}_4$  (Stebbins et al., 1999) and potential Si-OH positions as observed in hydrous Ca-silicates and in crystalline  $\text{Ca}(\text{OH})_2$  (Cong and Kirkpatrick, 1996).

with the addition of water to the glass, and there is only a slight contribution to the decrease in width due to a decrease in mean  $C_Q$ . This is in contrast to haplogranitic glasses, which show a decrease in the quadrupolar width with the addition of water and not a decrease in the width due to the range of chemical shifts (Schmidt et al., 2001b), indicating an increase in the local symmetry around Al sites.

#### 4. DISCUSSION

##### 4.1. Alkali Silicate and Aluminosilicate Glasses

The saturation NMR experiments accentuate a broad peak similar to that reported by Xu et al. (1998) at 9.4 T and attributed to  $\text{H}_2\text{O}$  oxygens. Here, the better resolution provided

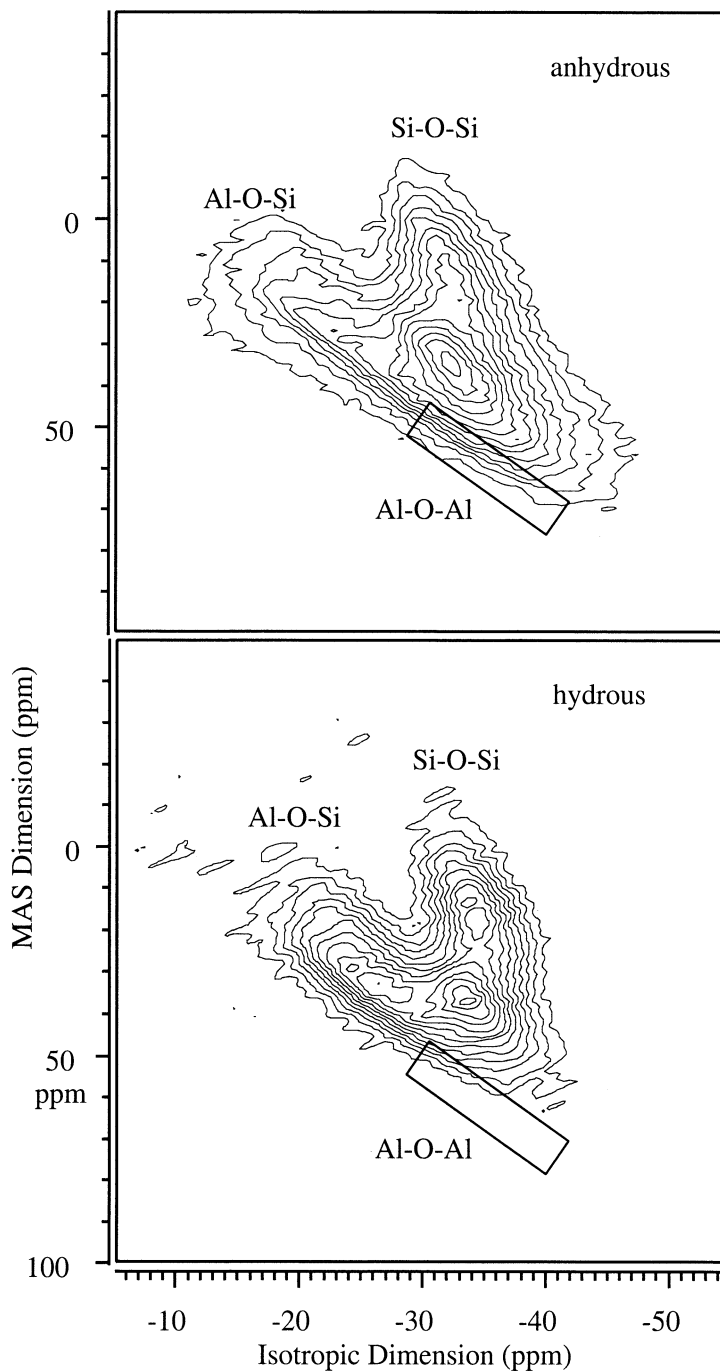


Fig. 8.  $^{17}\text{O}$  3QMAS spectra collected at 14.1 T for the  $\text{Ca}_{0.5}\text{AlSi}_3\text{O}_8$  glasses. The solid boxes represent the expected positions of the Al-O-Al oxygen sites based on data for crystalline  $\text{CaAl}_2\text{O}_4$  (Stebbins et al., 1999).

by the 14.1 T field allows more accurate description of the positions and widths of this component and estimation of its maximum contribution to the total peak area. Such estimates match the expected concentrations of oxygen in molecular  $\text{H}_2\text{O}$  sites (Silver et al., 1990; Zotov and Keppler, 1998; Schmidt et al., 2001a) and are not consistent with representing only the OH sites or the sum of OH and  $\text{H}_2\text{O}$ . The study by Kohn et al. (1997) on water solubility mechanisms in alkali aluminosilicates using  $^{23}\text{Na}$  NMR suggested that there is an interaction

between water groups and the alkali cations. Schmidt et al. (2001b) showed an influence of  $\text{H}_2\text{O}$  concentration on  $^{23}\text{Na}$  NMR spectra for haplogranitic glasses. With the assignment of this peak to molecular  $\text{H}_2\text{O}$ , there is more evidence to support significant interactions of the alkali cations with the  $\text{H}_2\text{O}$  oxygen, as the  $^{17}\text{O}$  NMR peak position for  $\text{H}_2\text{O}$  depends on the coordinating cations. The peak shifts to a higher frequency for  $\text{K}^+$  compared to  $\text{Na}^+$  for the same Al/Si ratio and could thus be expected to shift to an even higher frequency for  $\text{Ca}^+$ . The



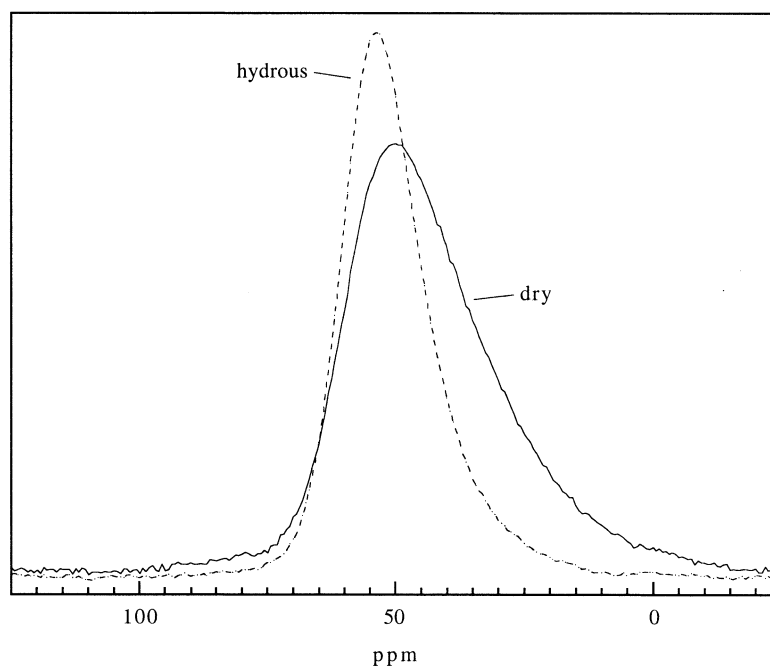


Fig. 9.  $^{27}\text{Al}$  one-pulse MAS spectra collected at 14.1 T for hydrous and anhydrous  $\text{Ca}_{0.5}\text{AlSi}_3\text{O}_8$  glasses.

direction of this shift is the same as that which is well known for alkali cation effects on  $^{17}\text{O}$  chemical shifts for NBO, although its magnitude is less (Kirkpatrick, 1988; Xue et al., 1994; Xu and Stebbins, 1998) and probably implies the presence of one or more alkali cations in the first shell of the  $\text{H}_2\text{O}$  oxygen, as is common in zeolites. The larger negative shift for the  $\text{H}_2\text{O}$  peak in the  $\text{Na}_2\text{Si}_4\text{O}_9$  glass is probably also consistent with its higher alkali activity. The similarity of the  $\text{NaAlSi}_3\text{O}_8$  composition glasses with 5 and 10 wt.% water and the differences with the hydrous sodium tetrasilicate glass also suggest that the alkali activity in the host glass, not the  $\text{Na}/\text{H}_2\text{O}$  ratio, is most important; and this also suggests a different structural role for  $\text{H}_2\text{O}$  in the Al-containing and the Al-free glasses. The breadth of the  $\text{H}_2\text{O}$  peak is likely due, at least in part, to a large  $C_Q$ , as for the  $\text{H}_2\text{O}$  site in analcime (Kroeker et al., 2001); the position of the  $\text{H}_2\text{O}$  peak in  $\text{NaAlSi}_3\text{O}_8$  glass is similar to that for analcime.

#### 4.2. Calcium Aluminosilicate Glasses

For the  $\text{Ca}_{0.5}\text{AlSi}_3\text{O}_8$  glass spectra, the intensity lost on the high-frequency side of the BO peak on hydration corresponds

to ~2% of the total, and the decrease is seen in the same position as that expected for Al-O-Al sites. These sites account for 1.4% of the total oxygen sites, according to the model of Lee and Stebbins (1999), and thus the decrease is consistent with the destruction of Al-O-Al sites by reactive  $\text{H}_2\text{O}$ . The infrared spectra predict that, for this composition, OH groups should account for ~6% of the total oxygen (McMillan et al., 1986; Silver et al., 1990). Thus, given a reaction  $\text{Al-O-Al} + \text{H}_2\text{O} \rightarrow 2\text{AlOH}$ , it is possible that half of the OH groups could be formed by such a mechanism. Thus, bridging oxygen bonds could be broken without perturbation of Si-O-Si or Si-O-Al bonds. In addition, the 3QMAS spectra have the same decrease in intensity in the Al-O-Al region and no increase in intensity in the areas that SiOH might be expected, based on a study of calcium silicates by Cong and Kirkpatrick (1996). If Al-O-Al sites are lost on hydration, then a decrease in intensity on the higher frequency side of the  $^{27}\text{Al}$  spectrum would be expected (Kirkpatrick et al., 1985; Skibsted et al., 1993), but the creation of Al-OH sites might increase the intensity in the same region and/or the peak for the network Al might also change in width, as seen for Na aluminosilicate glasses (Kohn, 1989b). The  $^{27}\text{Al}$

Table 2. The  $^{27}\text{Al}$  MAS peak width data and analysis for the calcium aluminosilicate glasses.

Composition	FWHM (kHz) at		$W_q$ (MHz)	$W_{\text{csd}}$ (Hz)
	8.45 T	14.1 T		
10 wt. % water		2.8		
7.0 wt. % water	3.3 <sup>a</sup>	3.1 <sup>a</sup>	2922	1535
5.0 wt. % water	3.8 <sup>a</sup>	3.4 <sup>a</sup>	3440	1620
Anhydrous		4.8		
	4.3 <sup>a</sup>	4.8 <sup>a</sup>	3424	2600

<sup>a</sup> Data taken from Kohn et al. (1992).

data thus seem to support the suggestion from  $^{17}\text{O}$  data: Al-O-Al sites are being preferentially destroyed by the addition of water to the glass.

As has been true in our previous  $^{17}\text{O}$  NMR studies of hydrous aluminosilicate glasses (Xu et al., 1998; Oglesby et al., 2001) and those of others (Kohn et al., 1997; Maekawa et al., 1998), we see no direct signature of either Al-OH sites or any other OH sites, which should be of roughly comparable concentrations to  $\text{H}_2\text{O}$  groups. As discussed previously, this may be because OH sites are highly disordered, leading to large ranges in chemical shifts that could overlap with signals from more abundant sites and/or are highly distorted, leading to large  $C_Q$  values and again, to broad peaks. In addition, some types of OH groups, such as those in silica gel (Van Eck et al., 1999) but not  $\text{KHSi}_2\text{O}_5$  (Oglesby et al., 2001), have very short spin-spin relaxation times and can thus disappear in spin echo experiments, including standard 3QMAS spectra. We have also recently observed this phenomenon for the Al-OH sites in gibbsite (Oglesby, 2001).

The interpretation of the results described here for calcium aluminosilicate glasses is not unique, as it is conceivable that the Al-O-Al component of the bridging oxygen shifts in position or is broadened by the substitution of  $\text{H}^+$  for  $\text{Ca}^{2+}$  among the charge-balancing cations, as is known to occur for NBO sites in alkali silicate glasses (Oglesby et al., 2001). If this occurred, however, we might expect a corresponding shift in Al-O-Si peaks in Na- and K- aluminosilicate systems, which is not observed. At the lower glass transition temperature of the hydrous glass, the proportion of Al-O-Al may be lowered by the reaction  $\text{Al-O-Al} + \text{Si-O-Si} \rightarrow 2\text{Al-O-Si}$ , but this effect should not be big enough to account for the differences seen (Lee and Stebbins, 2000b). Also, peak intensity in the region expected for Si-O-Si is not lost in MAS or 3QMAS spectra. However, it is reassuring that in at least some aluminosilicate glasses, significant changes in oxygen speciation can be detected by  $^{17}\text{O}$  NMR, including the reduction of the Al-O-Al peak from the high-frequency side and the addition of an  $\text{H}_2\text{O}$  peak to the low-frequency side of the MAS spectrum. This gives hope for future insight into the complex problem of water dissolution in magmas.

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