

Proton Environments in Hydrous Aluminosilicate Glasses: A ^1H MAS, $^1\text{H}/^{27}\text{Al}$, and $^1\text{H}/^{23}\text{Na}$ TRAPDOR NMR Study

Qiang Zeng,^{*,†,‡} Hanna Nekvasil,[†] and Clare P. Grey^{*,§}

Department of Geosciences, State University of New York, Stony Brook, New York 11794-2100, and
Department of Chemistry, State University of New York, Stony Brook, New York 11794-3400

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Hydrous aluminosilicate glasses of composition $\text{NaAlSi}_8\text{O}_{18}$, $\text{NaAlSi}_3\text{O}_8$, $\text{NaAlSi}_2\text{O}_6$, and NaAlSiO_4 have been studied with ^1H MAS, and $^1\text{H}/^{27}\text{Al}$, and $^1\text{H}/^{23}\text{Na}$ TRAPDOR NMR spectroscopy. Two different environments for molecular water were identified. Three ^1H OH resonances (1.5, ca. 3.5, and 5–6 ppm) are observed in all the glasses. The resonance at 1.5 ppm shows a large ^1H – ^{27}Al dipolar coupling and is assigned an $\text{Al}(\text{Q}^3)\text{--OH}$ group; the concentration of this species increases with increasing Al content in the glass. The resonance at ca. 3.5 ppm is assigned to $\text{Si}(\text{Q}^3)\text{--OH}$ units, on the basis of its chemical shift, proximity to Na and Al, and the change in the relative intensity of the three resonances, with varying Al/Si ratio. The resonance at 5–6 ppm is assigned to a $\text{Q}^3\text{--OH}$ unit that is hydrogen bonded to another oxygen atom. These assignments imply that the aluminosilicate framework undergoes depolymerization as an outcome of water dissolution.

Introduction

Major differences in the physical and chemical properties of aluminosilicate glasses are induced by H_2O and much effort has been expended on evaluating changes in the structure of the hydrous glasses, to explain these effects. It has been generally accepted from various structural studies that hydrous silicate glasses contain both molecular water and hydroxylated species, with the latter dominating at low water contents (<30 mol %).^{1–6} However, no consensus has been achieved regarding the nature of the interaction between H_2O and the aluminosilicate network, in particular, regarding the fundamental question of whether water depolymerizes the aluminosilicate network.

Many workers have concluded, by using a variety of spectroscopic techniques, that the silicate network is ruptured upon H_2O dissolution into silica and alkali silicate glasses, thereby forming SiOH groups.^{7–11} However, based on a multinuclear NMR study of hydrous aluminosilicate glasses, it has been concluded by some previous workers^{5,12} that this water dissolution mechanism does not operate in aluminosilicate melts and glasses. Rather, in the presence of Al, H_2O dissolution only occurs through cation exchange between Na^+ and H^+ as exemplified by the reaction:



Reinterpretation of the previous NMR⁵ and Raman³ spectra, coupled with infrared spectroscopic measurements and molecular orbital calculations of the hydrous $\text{NaAlSi}_3\text{O}_8$ glasses, led to the proposal that reaction 1 was restricted to water contents above 30 mol %.⁶ Depolymerization of the framework through a reaction such as



in which H_2O preferentially breaks Al--O--Al linkages then occurs for lower total water contents.⁶

No resolution of the depolymerization question has been achieved despite further molecular orbital^{13,14} and NMR studies.^{15–18} A promising line of investigation, however, lies in the examination of the environment of the hydrogen atoms, since the key differences in the above models all pertain to the hydrogen environment. Questions regarding the H environments include the structural nature of the oxygen atoms bonded to the H atoms, and the cation associated with this OH group. Previous ^1H NMR studies of hydrous aluminosilicate glasses have not, however, yielded detailed information on hydroxyl speciation because of the severe overlap of resonances in the ^1H MAS NMR spectra.^{5,19}

^1H single-pulse and spin-echo MAS NMR experiments have been carried out, in this study, on hydrous glasses of different Al/Si ratios, in the system $\text{NaAlO}_2\text{--SiO}_2$. This compositional variation allows progressive changes in abundance of the various H-bearing species in the glasses to be tracked systematically. The proximity of the H atoms to ^{27}Al and ^{23}Na has been probed using TRAPDOR NMR, a double-resonance NMR experiment that may be used to measure the dipolar coupling between spin-half and quadrupolar nuclei.^{20,21}

In a TRAPDOR (TRANSfer of Populations in DOuble Resonance) experiment, the quadrupolar nuclei are continuously irradiated under magic angle spinning (MAS) conditions, resulting in a transfer of populations among the Zeeman states of the nuclei. This, in turn, alters the evolution of the $I = 1/2$ spins that are coupled to the quadrupolar nuclei, so that the $I = 1/2$ spins are no longer refocused at the rotor echo. The loss of signal intensity of the $I = 1/2$ spins is correlated to the strength of the dipolar coupling between the irradiated and the spin-half nuclei.^{20,21} When applied to hydrous aluminosilicate glasses, this technique detects the dipolar coupling between, and hence the proximity of ^1H and ^{27}Al or ^1H and ^{23}Na spins.

Experimental Section

Synthesis of Glass Samples. Four compositions in the system $\text{NaAlO}_2\text{--SiO}_2$ have been used in this study: NaAlSiO_4 (Ne), $\text{NaAlSi}_2\text{O}_6$ (Jd), $\text{NaAlSi}_3\text{O}_8$ (Ab), and $\text{NaAlSi}_8\text{O}_{18}$ (As). From

* Corresponding authors. E-mail: zeng@pangea.stanford.edu; cgrey@sbchem.sunysb.edu.

[†] Department of Geosciences, SUNY SB.

[‡] Current address: Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305-2115.

[§] Department of Chemistry, SUNY SB.

TABLE 1: Synthesis Conditions and Water Contents of the Samples

sample	starting material	piston–cylinder assembly	<i>P</i> (kbar)	<i>T</i> (°C)	time (h)	water content (wt %)	water content (mol %)
ab0	gel of NaAlSi ₃ O ₈		0.001	1400	4	0	0
ab1	ab0	BaCO ₃	8	1350	7	1	13
ab2	ab0	Pyrex/salt	8	1350	2	2.5	27
ab3	ab0	talc	8	1250	5	6.4 ^a	50
as0	Na ₂ CO ₃ + Al ₂ O ₃ + 16SiO ₂		0.001	1600	12	0	0
as1	as0	talc	8	1250	8	3.5 ^a	53
jd0	Na ₂ CO ₃ + Al ₂ O ₃ + 4SiO ₂		0.001	1400	11	0	0
jd1	jd0	talc	8	1250	14	2.5	22
ne0	Na ₂ CO ₃ + Al ₂ O ₃ + 2SiO ₂		0.001	1600	10	0	0
ne1	ne0	talc	8	1250	10	4	25

^a Water content is determined by weight loss upon decrepitation at 1000 °C.

stoichiometric considerations alone, anhydrous glasses with these compositions should be fully polymerized.

Anhydrous glasses were synthesized at 1 atm, using gels or Na₂CO₃–Al₂O₃–SiO₂ mixtures of desired stoichiometry as the starting materials. (No differences between the products of the two starting materials were observed in the NMR experiments for the same composition.) For each synthesis, a mixture of several grams of powdered material was placed into a Pt crucible, slowly heated to 900 °C at 5 °C per minute in air, and then held at 1400–1600 °C for 4–12 h. The charge was then quenched by removing the crucible from the furnace and immersing the bottom of the crucible in water. The products were ground and remelted until homogeneous glasses, free of crystals and bubbles, were obtained. Weight loss during heating of the carbonate–oxide mixtures could all be ascribed to the degassing of CO₂ within an error of 0.5%, indicating that the glasses are within 0.5 wt % of the nominal composition.

Hydrous glasses with various water contents were synthesized in a solid medium (piston–cylinder) pressure apparatus. For each run, anhydrous glass powder and known amounts of water were loaded into a platinum capsule with an outer diameter of 5.08 or 6.35 mm, which was then sealed by arc welding. Salt–Pyrex or BaCO₃ assemblies were employed for synthesis when using the 5.08 mm capsules, while talc assemblies were used for the synthesis with the 6.35 mm capsules. The latter has the advantage of producing larger quantities of sample, but the disadvantage of poor constraint on water content of the final products, as the vast amount of water released by talc upon heating may enter the sample through hydrogen diffusion. Talc was thus only used in synthesizing high water content samples or when a precisely known water content was not required. The runs were kept at 8 kbar of pressure, 1250–1350 °C for 2–14 h, and quenched by turning off the power supply. Synthesis conditions and water contents of the samples are given in Table 1. Unless specifically indicated, the water content of a hydrous sample is assumed to be the amount of water sealed into the capsule, as all of the water contents used were significantly below saturation.

NMR Experiments. ¹H NMR spectra were acquired on a Chemagnetics CMX-360 spectrometer and a CMX-200 spectrometer operating at 360.03 and 200.01 MHz, respectively. The reported chemical shift values for ¹H were referenced to TMS (tetramethylsilane). ¹H single-pulse MAS spectra were collected at a spinning rate of 4–8 kHz, using a $\pi/6$ pulse length of 1.9 μ s. A recycle delay of 4 s was chosen, and no differential relaxation of the different species was observed under these conditions.

Spin–echo experiments were also performed so as to remove the broad component of the ¹H probe background. Echo experiments have generally been found to be more effective than background suppression sequences at removing the majority

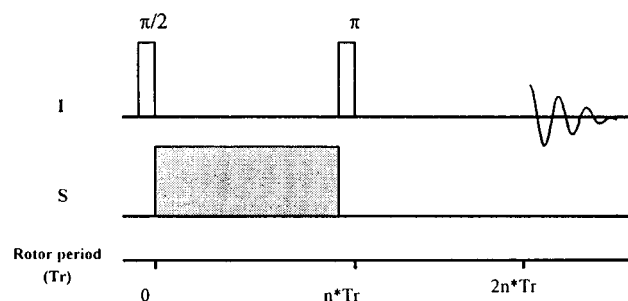


Figure 1. A schematic of the TRAPDOR pulse sequence: a spin–echo pulse sequence synchronized with the rotor cycle is applied to the $I = 1/2$ spins (I), while the quadrupolar spins (S) are continuously irradiated during the evolution period τ .

of the probe background in the probes used in these experiments.²² This method does not, however, eliminate the background signals that result from protons in the actual rotor itself, which may arise from organic contamination (e.g., finger grease), and from protons in the polymers used as “spacers” in the rotors. This source of background is usually observed as sharp resonances with chemical shifts between 0.5 and 1.2 ppm.²²

Spin–echo experiments were carried out at a spinning rate of 4–8 kHz, by using the rotor synchronized spin–echo pulse sequence $\pi/2-\tau-\pi-\tau$ –acq, with an evolution time period τ that varied from 0.125 to 1 ms. The same spin–echo pulse sequence was applied to the ¹H spins in the ¹H/²⁷Al and ¹H/²³Na TRAPDOR experiments, but the quadrupolar nuclei were also continuously irradiated at close to on-resonance conditions during the evolution period (Figure 1). A spin–echo experiment was also acquired for each TRAPDOR experiment (the control experiment). A TRAPDOR difference spectrum was obtained by subtracting the TRAPDOR spectrum from the control experiment. The TRAPDOR effect of a resonance is represented by the intensity of the resonance in the TRAPDOR difference spectrum relative to that in the control experiment. Quantitatively, this is defined by the TRAPDOR fraction $(1 - I/I_0)$, where I and I_0 are peak intensities in the spectra acquired with and without irradiation, respectively.²¹

The standard Chemagnetics VT setup was used for the variable-temperature experiments. The temperature reading in this setup is taken from a thermocouple placed near the joint of the VT stack and the probe; thus, the actual sample temperature may differ from the measured value. We have previously demonstrated that the difference in sample and thermocouple reading does not differ by more than ca. 5 °C, except at the lowest temperatures studied (–130 to –150 °C), where the real temperature is ca. 10 °C higher. Measured sample temperatures are indicated throughout. As an accurate temperature measurement was not essential for this study, no further attempt was made to calibrate the temperature.

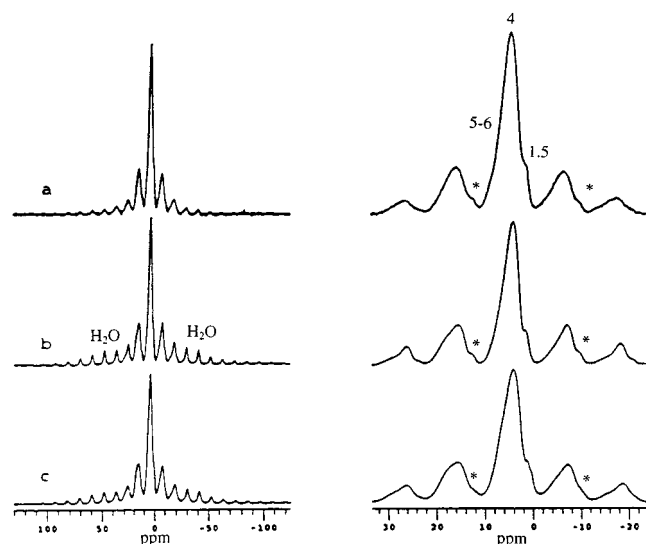


Figure 2. ^1H spin-echo MAS NMR spectra of hydrous $\text{NaAlSi}_3\text{O}_8$ glasses (a) ab1, (b) ab2, and (c) ab3 collected at a field strength of 8.45 T with a spinning speed ν_R of 4 kHz and a recycle delay of 4 s. Enlargements of the isotropic resonance and the first- and second-order spinning sidebands are shown to the right of each full spectrum.

Results

^1H MAS NMR. Figure 2 shows the spin-echo ^1H spectra of hydrous $\text{NaAlSi}_3\text{O}_8$ glasses with various water contents. Large spinning sideband manifolds are clearly visible in these spectra, spanning about 100 kHz. The width of the sideband manifolds is consistent with the size of the ^1H – ^1H dipolar coupling between the two hydrogen atoms in H_2O molecules, and thus the resonance is assigned to molecular H_2O that is structurally bound to the silicate network²³ and is not free to undergo translational motion and molecular reorientations in the time scale of the H–H dipolar coupling. A chemical shift for the molecular H_2O resonance of 4.2 ppm was calculated from the peak maximum of the higher-order spinning sidebands, e.g., from the shifts of the two fourth-order sidebands indicated in Figure 2b.

The ^1H resonances of the OH species (if any) may be expected to contribute to the isotropic resonance and the low-order spinning sidebands.²³ On this basis, the increased intensity of spinning sidebands relative to the central resonances with increasing water content is consistent with an increased $\text{H}_2\text{O}/\text{OH}$ ratio. This is in agreement with the results from infrared spectroscopy.²⁴ Analysis of the “OH” resonances is complicated by their overlap with the molecular H_2O resonance. Fortunately, the spins giving rise to the H_2O resonance possess a shorter spin–spin relaxation time owing to the stronger homonuclear dipolar coupling, and/or to any small residual motion of the H_2O species. Thus, the signal from molecular H_2O can be “filtered” out by increasing the evolution time τ in the spin-echo experiment. This is demonstrated for composition ab2 with $\tau = 0.25, 0.5, 2, 4$, and 8 ms (Figure 3). When τ is increased to 4 ms, the spinning sidebands and thus the resonance from the molecular water are barely visible (Figure 3d). The ^1H resonances in Figure 3d are, therefore, mainly due to the OH species. The spectrum shows at least three OH resonances: an intense isotropic resonance at ca. 3.5 ppm with a shoulder to higher frequency, and a smaller but distinct isotropic resonance at 1.5 ppm. The 1.5 ppm resonance is partially obscured in some spectra (e.g., Figure 2c) by a sharp resonance at 1.2 ppm that results from organic contamination (e.g., finger grease). If the rotor is baked at 250 $^\circ\text{C}$, (as was the case for the sample whose

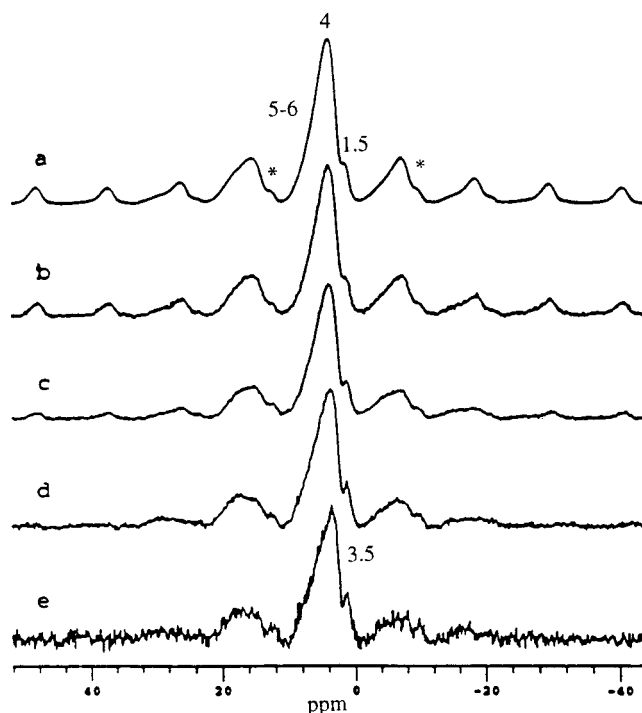


Figure 3. ^1H spin-echo MAS NMR spectra of hydrous $\text{NaAlSi}_3\text{O}_8$ glass ab2 collected with $\nu_R = 4$ kHz, a recycle delay of 4 s, and evolution/recovery times τ (the time interval between the $\pi/2$ and π pulses) of (a) $\tau = 0.25$, (b) $\tau = 0.50$, (c) $\tau = 2$, (d) $\tau = 4$, and (e) $\tau = 8$ ms.

spectrum is shown in Figure 2a) and the sample then packed without direct contact with the rotor, the signal from this source of background disappears, but the ca. 1.5 ppm resonance persists. This resonance is clearly visible in the first-order spinning sidebands (marked by *), where it is present without the superimposed ca. 1.2 ppm resonance. The shoulder on the higher frequency side of the 3.5 ppm resonance is more clearly seen in the first-order sidebands. Its chemical shift is estimated to be between 5 and 6 ppm. Note that overlap of the 3.5 ppm resonance and the H_2O resonance at 4.2 ppm results in a shift of the 3.5 ppm resonance at short τ values to approximately 4 ppm (see Figure 2).

The ^1H spin-echo spectra of the hydrous $\text{NaAlSi}_3\text{O}_8$ glasses acquired at short τ (Figure 2) and long τ (4 ms; not shown) do not show any dramatic differences in relative concentrations of the different hydroxyl species, as the water content increases. The largest change is a slight increase in the relative intensity of the 5–6 ppm resonance. This is seen most clearly by examining the changes in the intensity of the first-order sidebands to high frequency of the isotropic resonance (at approximately 17 and 15 ppm for the resonances at ≈ 4 and 5–6 ppm, respectively) in Figure 2a–c.

Variable-temperature spin-echo experiments were carried out to study proton mobility. The results for samples ab1 and ab2 are shown in Figure 4. A distinct change is observed in the resonance due to molecular H_2O with decreasing temperature; this is most clearly seen in the spinning sidebands of this resonance, the single set of sidebands that are observed at ambient temperatures gradually evolving into two separate sets. At -175 $^\circ\text{C}$ (Figure 4d, ab2; 4e, ab1), a sharp and a broader H_2O resonance are observed at 2.9 and ca. 6 ppm, respectively. The (fourth order) sidebands of these resonances are marked in Figure 4, d and e. This change in line shape may be explained by the freezing out of an exchange process. This process may involve motion (or chemical exchange) of the H_2O molecules

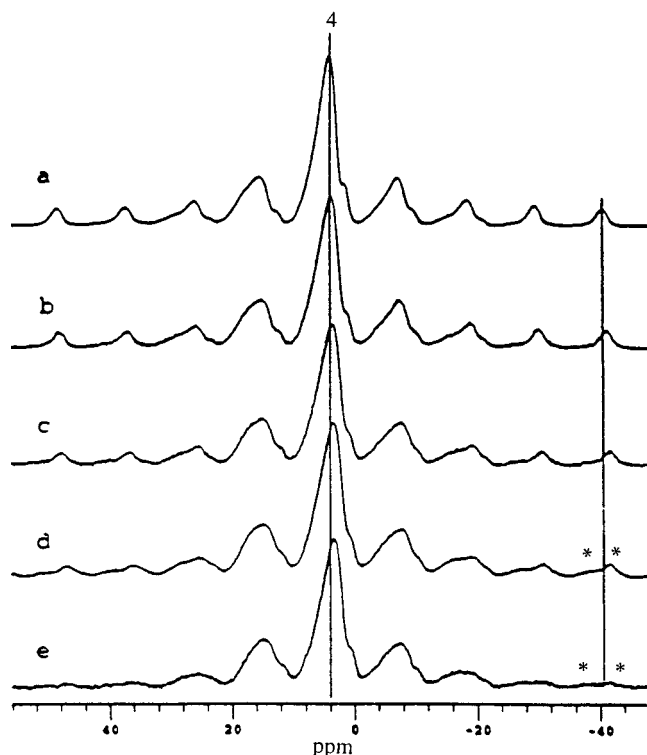


Figure 4. Variable-temperature ^1H spin-echo MAS NMR spectra of hydrous $\text{NaAlSi}_3\text{O}_8$ glass ab2 collected at (a) $T = 23$, (b) $T = -100$, (c) $T = -135$, and (d) $T = -175$ °C. Spectrum e is of sample ab1 collected at $T = -175$ °C; $\nu_R = 4$ kHz, recycle delay = 4 s, and $\tau = 0.25$ ms for all the spectra. Two vertical lines are drawn as guides for visualization at 4 ppm and through the position of the low-frequency fourth-order spinning sideband of the H_2O resonance at room temperature. Asterisks (*) mark the positions of the low-frequency fourth-order spinning sidebands of the H_2O resonance at low temperature.

between different coordination environments, but will be discussed in more detail later. The peak maximum (of the isotropic resonance) moves continuously to lower frequencies with decreasing temperature, shifting from 4.2 ppm at ambient temperature to 3.5 ppm at -175 °C. This can be explained by the change in line shape of the molecular H_2O resonance, which overlaps with the OH resonances. These spectra also indicate that the motion of the OH species is not pronounced at the NMR time scale, or is invariant (in the time scale of, for example ^1H homonuclear interactions), in this temperature range. Spin-echo ^1H MAS NMR spectra have also been collected for hydrous $\text{NaAlSi}_8\text{O}_{18}$, $\text{NaAlSi}_2\text{O}_6$, and NaAlSiO_4 glasses (Figure 5) at ambient temperatures. In addition to the resonance ascribable to the molecular H_2O species, with its large associated sideband manifolds, all three of the OH resonances observed in the ^1H spectra of hydrous $\text{NaAlSi}_3\text{O}_8$ glasses are also present. However, some systematic changes in the position and intensity of these resonances with increasing Al/Si ratio are also observed. The first one is the increase in chemical shift values of the molecular H_2O resonance, ranging from 2.7, 4.2, 4.5, to 4.8 ppm for hydrous $\text{NaAlSi}_8\text{O}_{18}$, $\text{NaAlSi}_3\text{O}_8$, $\text{NaAlSi}_2\text{O}_6$, and NaAlSiO_4 glass, respectively. As before, these chemical shifts were calculated from the positions of the spinning sidebands within the large spinning sideband manifolds. The increase in ^1H chemical shift value likely represents an increase in hydrogen-bonding strength¹⁹ of the hydrogen atoms of the H_2O molecule to the Si/Al–O framework, which presumably results from the increase in the abundance of negatively charged oxygens due to substitution of Si with Al in the Si/Al–O framework. The increase in Al/Si ratio also results in an increase in the intensity

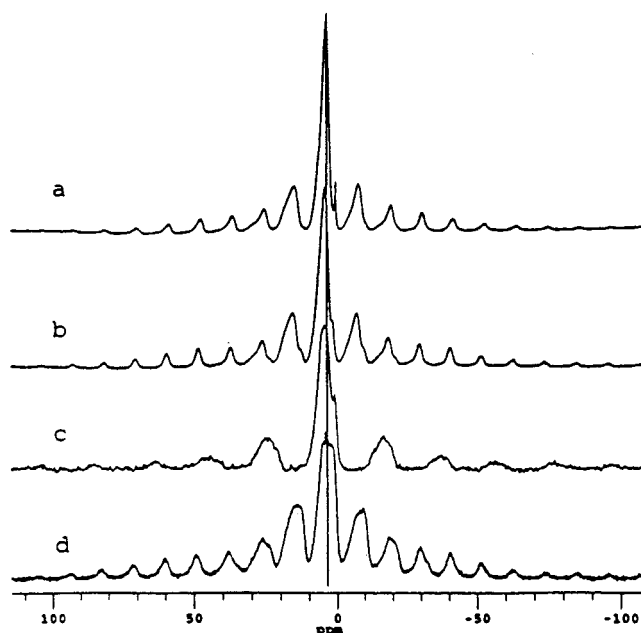


Figure 5. ^1H spin-echo MAS NMR spectra of the hydrous glasses (a) $\text{NaAlSi}_8\text{O}_{18}$, (b) $\text{NaAlSi}_3\text{O}_8$, (c) $\text{NaAlSi}_2\text{O}_6$, and (d) NaAlSiO_4 collected at 8.45 T (except (c) collected at 4.7 T). $\nu_R = 4$ kHz, recycle delay = 4 s, $\tau = 0.25$ ms. The vertical line is drawn at 3.5 ppm.

of the spinning sidebands of the OH resonances, due to larger ^1H – ^{27}Al (and/or ^1H – ^{23}Na) dipolar couplings. For instance, in the spectra of hydrous NaAlSiO_4 glass shown in Figure 5d (the composition with the highest Al/Si ratio among the glasses studied), the first- and second-order spinning sidebands are very intense, in comparison to the sidebands in Figure 5a ($\text{NaAlSi}_8\text{O}_{18}$).

The most significant differences between the spectra shown in Figure 5 occur in the relative intensity of the different OH resonances, the resonances at ≈ 1.5 and 5–6 ppm increasing in intensity in comparison to the resonance at ≈ 3.5 ppm as the aluminum content increases. This trend is seen much more clearly in the spin-echo spectra of hydrous $\text{NaAlSi}_8\text{O}_{18}$, $\text{NaAlSi}_3\text{O}_8$, and NaAlSiO_4 glasses, after filtering out most of the molecular H_2O resonance (by using a long τ) (Figure 6). The ≈ 1.5 ppm shoulder is barely visible in the spectrum of hydrous $\text{NaAlSi}_8\text{O}_{18}$ glass. Its relative intensity increases with increasing Al/Si ratio and becomes the most intense OH resonance in the hydrous NaAlSiO_4 glass. (Note: the sharp resonance at 0.5 ppm is due to proton background in the rotors.) This resonance also shifts slightly to higher frequencies with increased aluminum content. The intensity of the ca. 3.5 ppm resonance, in contrast, decreases with increasing Al/Si ratio. In hydrous NaAlSiO_4 glass, this resonance is no longer the most intense OH resonance and is hidden between the pronounced 5–6 and 1.5 ppm resonances (Figure 6c). The 5–6 ppm resonance is present throughout as a broad shoulder at higher frequency in the spectra of the hydrous $\text{NaAlSi}_8\text{O}_{18}$, $\text{NaAlSi}_3\text{O}_8$, and $\text{NaAlSi}_2\text{O}_6$ glasses. When the intensity of the ca. 3.5 ppm resonance is reduced (as is the case in the spectrum of NaAlSiO_4 glass), this shoulder is resolved as a distinct peak at 5.6 ppm (Figure 6c). The fwhms of the three OH resonances were estimated by assuming that the line width is independent of the Al/Si ratio. Spectra in which these three resonances are at least partially resolved (e.g., Figure 6a,c) can be deconvoluted, yielding an estimated fwhm of 2.25 ± 0.25 ppm for the resonances at 1.5 and ca. 3.5 ppm, and of 4 ± 0.5 ppm for the resonance at 5–6 ppm. Note, that we have not attempted to extract accurate values for the relative intensities from experi-

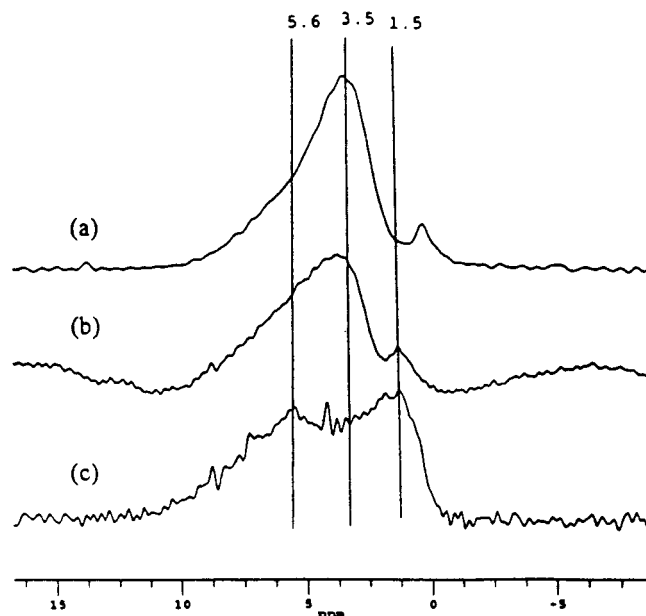


Figure 6. ^1H spin-echo MAS NMR spectra of the hydrous glasses $\text{NaAlSi}_8\text{O}_{18}$, $\text{NaAlSi}_3\text{O}_8$, and NaAlSiO_4 acquired with a long recovery delay: (a) as1, acquired at 4.7 T, $\nu_R = 4$ kHz, $\tau = 1$ ms; (b) ab2, acquired at 8.45 T, $\nu_R = 8$ kHz, $\tau = 2$ ms; (c) ne1 acquired at 8.45 T, $\nu_R = 8$ kHz, $\tau = 2$ ms.

ments performed with long τ values because of possible errors arising from differences in the T_2 values associated with these resonances.

$^1\text{H}/^{27}\text{Al}$ and $^1\text{H}/^{23}\text{Na}$ TRAPDOR NMR. TRAPDOR experiments were carried out for the hydrous samples at different spinning speeds and irradiation times. The spectra collected at ambient temperature are shown in Figure 7. The control (spin-echo) experiment is shown along with the $^1\text{H}/^{27}\text{Al}$ and $^1\text{H}/^{23}\text{Na}$ TRAPDOR difference spectra obtained by subtracting the control spectrum from the double resonance spectra. All the proton resonances described above show both $^1\text{H}/^{27}\text{Al}$ and $^1\text{H}/^{23}\text{Na}$ TRAPDOR effects to some extent, as all of the resonances appear in the TRAPDOR difference spectra. For each resonance, the TRAPDOR fraction increases with increasing Al/Si ratio, probably indicating an increase in the number of Na or Al neighbors. No significant differences in the TRAPDOR fractions are observed for hydrous $\text{NaAlSi}_3\text{O}_8$ glasses with different water contents (not shown).

Any differences between the TRAPDOR fractions of the three OH resonances will be visible as a change in line shape of the TRAPDOR difference spectrum, compared with the original spin-echo spectrum. The relative intensity of the ca. 1.5 ppm resonance is significantly more pronounced in the $^1\text{H}/^{27}\text{Al}$ TRAPDOR difference spectra than in the original spin-echo spectra, indicating that it has the largest $^1\text{H}/^{27}\text{Al}$ TRAPDOR effect. This is most clearly seen by comparing the $^1\text{H}/^{27}\text{Al}$ TRAPDOR effect of the ca. 1.5 and the 5–6 ppm resonances in the spectra of hydrous NaAlSiO_4 glass (Figure 7d). The ca. 3.5 ppm and molecular water resonances overlap in most cases, forming a single broad peak with a maximum between 3 and 5 ppm. Separation of the contribution to the TRAPDOR effect from the 3.5, H_2O , and 5–6 ppm resonances is difficult. However, the shoulder of the isotropic resonance (at 5–6 ppm) and its associated first-order spinning sidebands are larger in the $^1\text{H}/^{27}\text{Al}$ TRAPDOR difference spectra than in the ^1H spin-echo spectra (Figure 7), implying that the 5–6 ppm resonance has a larger $^1\text{H}/^{27}\text{Al}$ TRAPDOR effect. Thus, at ambient temperature the $^1\text{H}/^{27}\text{Al}$ TRAPDOR effect increases in the order

of ca. 3.5 ppm, 5–6 ppm, and ca. 1.5 ppm. A similar line-shape analysis of the $^1\text{H}/^{23}\text{Na}$ TRAPDOR spectra shows that ca. 1.5 ppm has a slightly larger $^1\text{H}/^{23}\text{Na}$ TRAPDOR effect than the other two (which show similar behavior).

$^1\text{H}/^{23}\text{Na}$ and $^1\text{H}/^{27}\text{Al}$ TRAPDOR spectra acquired at -175 °C for the sample ab2 are shown in Figure 8. Compared with those acquired at ambient temperature, the low-temperature TRAPDOR experiments show an increase in the $^1\text{H}/^{23}\text{Na}$ TRAPDOR effect, as can be seen from the increase in the intensity of the high-frequency shoulder in the first-order spinning sidebands in the $^1\text{H}/^{23}\text{Na}$ TRAPDOR difference spectrum. The increase in $^1\text{H}/^{27}\text{Al}$ TRAPDOR effects with decreasing temperature is much less pronounced. Figure 8 also provides a basis for the comparison of the TRAPDOR effects of the two H_2O resonances that are resolved at -175 °C. While both resonances are present in the $^1\text{H}/^{27}\text{Al}$ TRAPDOR difference spectrum, only the broad resonance at ca. 6 ppm appears to possess a significant $^1\text{H}/^{23}\text{Na}$ TRAPDOR effect.

In principle, the TRAPDOR fraction decreases as a function of the irradiation frequency offset, reaching zero when the offset frequency is no longer within frequency range of the first-order quadrupolar spectrum,²¹ which for $I = 5/2$ nuclei (^{27}Al) extends from $-2\nu_Q$ to $+2\nu_Q$, and for $I = 3/2$ nuclei (^{23}Na) from $-\nu_Q$ to $+\nu_Q$, where ν_Q is the quadrupole frequency. As a result, the TRAPDOR-effect cutoff ν_C (i.e., the offset frequency at which the TRAPDOR fraction drops to zero) can be used to determine the quadrupole coupling constants (QCCs) of ^{27}Al and ^{23}Na nuclei that are coupled to ^1H (given by $2\nu_C$ for ^{23}Na , and $3.33\nu_C$ for ^{27}Al). TRAPDOR experiments with varying irradiation offsets were, therefore, performed, and the TRAPDOR fractions as a function of irradiation-frequency offset are plotted in Figure 9. TRAPDOR fractions were determined for the 1.5 and 5.6 ppm resonance for hydrous NaAlSiO_2 glass, and the 1.5 and 3.5–4.5 ppm resonances for the $\text{NaAlSi}_3\text{O}_8$ glass, by measuring the peak heights of these resonances in the difference and control experiments. Errors will be introduced into the absolute values of the TRAPDOR fractions due to the overlap of these resonances with (a) background signal (for the 1.5 ppm resonance), (b) the H_2O resonances (for the 3.5 ppm resonance), and (c) each other. Nonetheless, the changes in the TRAPDOR fractions with offset frequency can still be used to provide an estimate of the ν_C . As can be seen in Figure 9, $\nu_C = 0.9$ – 1.2 MHz (^{23}Na), and $\nu_C = 1.2$ – 2.0 MHz (^{27}Al), for all these resonances. Therefore, the QCC of ^{23}Na nuclei coupled to the ^1H spins ranges from 1.8 to 2.4 MHz, while the QCC of ^{27}Al nuclei ranges from 4.0 to 6.6 MHz. Close to ν_C , the peak intensities in the TRAPDOR difference spectra are of the same order of magnitude as the noise level thereby resulting in fairly large errors in the estimation of the QCC; in addition, a range of QCCs is to be expected in these disordered materials.²⁵ The QCCs determined from the TRAPDOR experiments are similar to those determined from the ^{23}Na and ^{27}Al spectra of the bulk glass.²⁵

Discussion

Molecular Water. Two molecular H_2O resonances (ca. 6 and 2.9 ppm) have been identified for hydrous albite glasses. The relative proportion of the two different H_2O sites does not appear to be affected significantly by bulk water content, as their presence and relative intensity in the spectra collected at -175 °C does not seem to vary between the 1 and 2.5 wt % $\text{NaAlSi}_3\text{O}_8$ samples (Figure 5). Both species show $^1\text{H}/^{27}\text{Al}$ dipolar coupling to the aluminosilicate structure. An important difference between the two species is their respective proximity to ^{23}Na . The H_2O

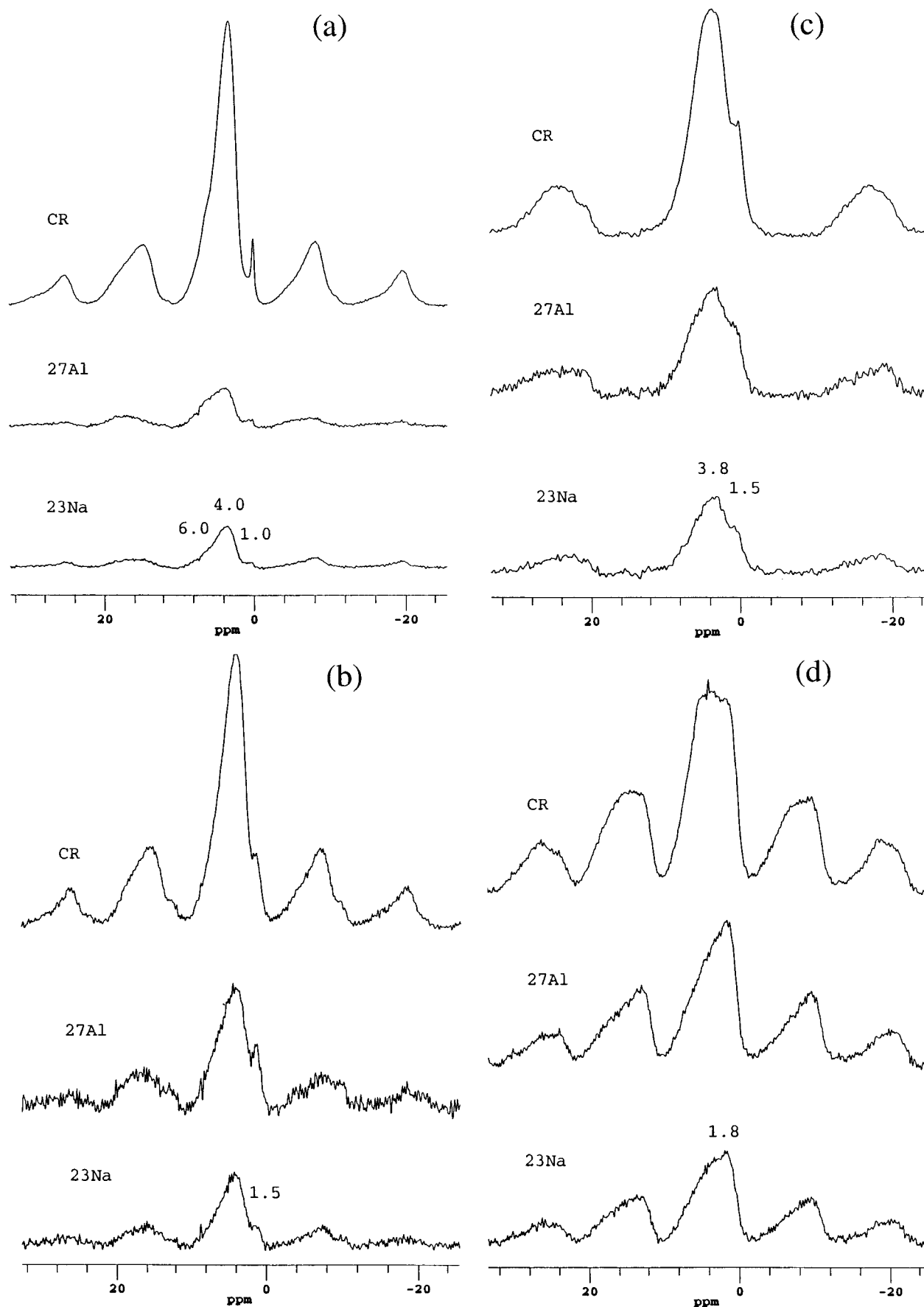


Figure 7. $^1\text{H}/^{27}\text{Al}$ and $^1\text{H}/^{23}\text{Na}$ TRAPDOR NMR spectra of the hydrous glasses (a) $\text{NaAlSi}_8\text{O}_{18}$, (b) $\text{NaAlSi}_3\text{O}_8$ [ab2], (c) $\text{NaAlSi}_2\text{O}_6$, and (d) NaAlSiO_4 . The spin-echo spectra are plotted on the top, and in the middle and bottom are the $^1\text{H}/^{27}\text{Al}$ and $^1\text{H}/^{23}\text{Na}$ difference spectra, respectively, where each of these spectra has been plotted using the same scaling factor. Spectra (a), (b), and (d) were collected at 8.45 T, while (c) was collected at 4.7 T. The parameters $\nu_R = 4$ kHz, recycle delay = 4 s, $\tau = 0.25$ ms, and r.f. field strengths ν_1 of 82 kHz, for both ^{27}Al and ^{23}Na , were used for all the spectra; $^{27}\text{Al}/^{23}\text{Na}$ irradiation was applied at close to on-resonance conditions (i.e., close (≤ 0.5 kHz) to the $^{27}\text{Al}/^{23}\text{Na}$ central transition resonance).

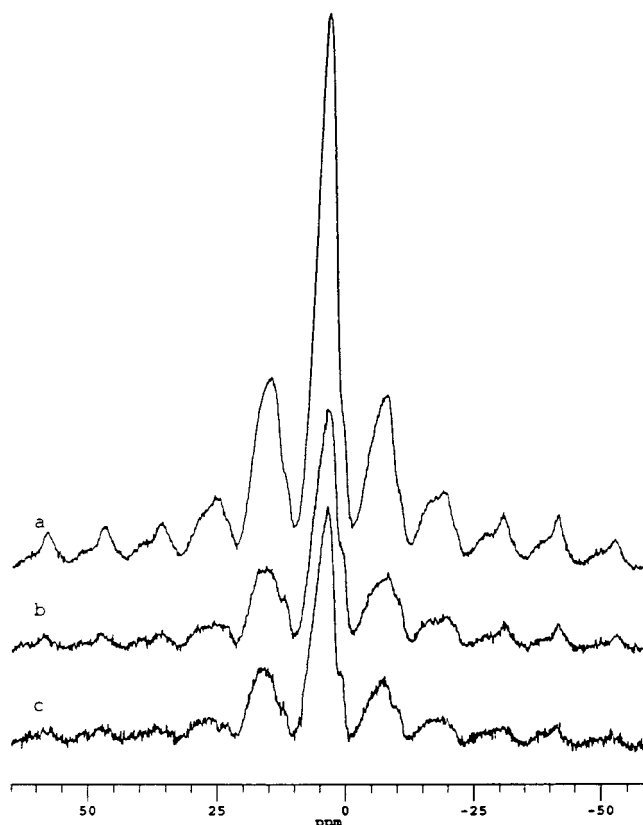


Figure 8. $^1\text{H}/^{27}\text{Al}$ and $^1\text{H}/^{23}\text{Na}$ TRAPDOR NMR spectra (at 8.45 T) of the hydrous $\text{NaAlSi}_3\text{O}_8$ glass ab2, acquired at $-175\text{ }^\circ\text{C}$: (a) spin-echo spectrum, (b) $^1\text{H}/^{27}\text{Al}$ TRAPDOR difference spectrum, and (c) $^1\text{H}/^{23}\text{Na}$ TRAPDOR difference spectrum. $\nu_R = 4\text{ kHz}$, recycle delay = 4 s, and $\tau = 0.25\text{ ms}$. Spectra are plotted on the same scale.

molecules giving rise to the 2.9 ppm resonance seem to be more distant from ^{23}Na , as indicated by their negligible $^1\text{H}/^{23}\text{Na}$ TRAPDOR fraction.

The presence of two distinct structural H_2O species is not unique to hydrous $\text{NaAlSi}_3\text{O}_8$ glasses. ^1H NMR data have revealed two molecular H_2O resonances for hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glass at 3.4 and 4.6 ppm.²⁶ Infrared spectroscopy²⁷ and differential thermal analysis²⁸ have also indicated the presence of two molecular H_2O species with different hydrogen bonding environments. For hydrous $\text{NaAlSi}_3\text{O}_8$ glass, one of the possible structural arrangements of the two species is that the molecular H_2O species represented by the 2.9 ppm resonance is hydrogen-bonded to the framework only (Figure 10A) and that represented by the broad ca. 6 ppm resonance is also coordinated to Na^+ (Figure 10B). This latter species must also be hydrogen-bonded to the framework, since both species show a $^1\text{H}/^{27}\text{Al}$ TRAPDOR fraction.

One explanation for the presence of only one H_2O resonance at ambient temperature is that chemical exchange between the two different species, or between different sites on the framework (with and without nearby Na^+), occurs. This exchange must occur at a time scale of less than 1 ms (i.e., the inverse of the frequency separation of the two resonances) at ambient temperatures, but cannot occur at significantly faster time scales, as the large sideband manifolds are still observed. The H_2O ^1H resonances are readily broken up into a series of spinning sidebands even at relatively modest MAS speeds, and at low temperatures, indicating that the ^1H – ^1H dipolar interaction is inhomogeneous. Thus, the ^1H spectra indicate that the H_2O molecules are isolated rather than clustered, with little intermolecular homonuclear dipolar coupling. This suggests inter-

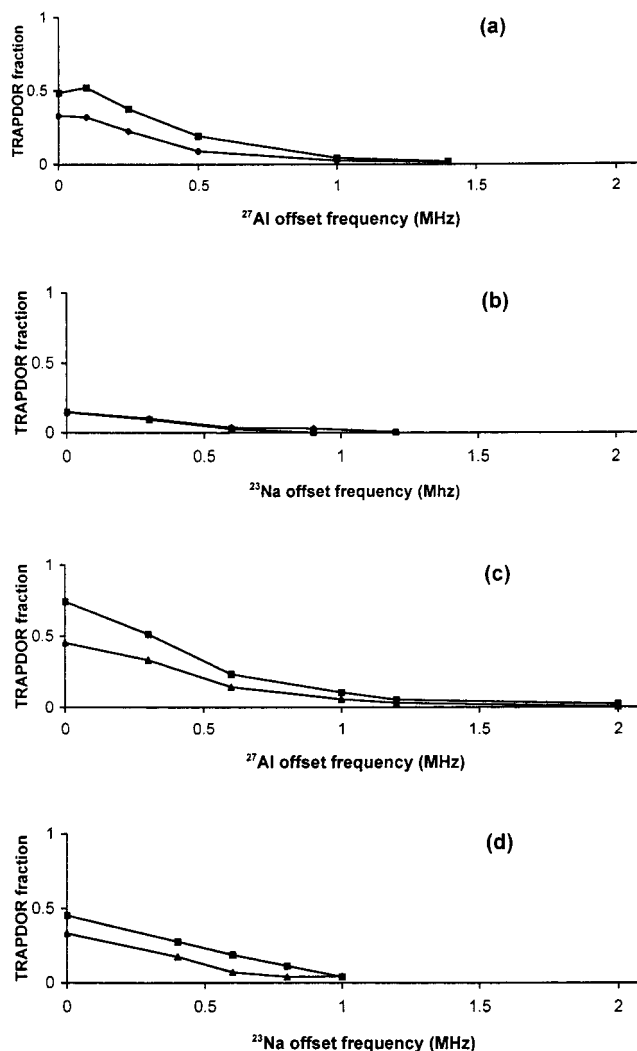


Figure 9. $^1\text{H}/^{27}\text{Al}$ and $^1\text{H}/^{23}\text{Na}$ TRAPDOR fractions as a function of irradiation frequency offset: (a) $^1\text{H}/^{27}\text{Al}$; hydrous $\text{NaAlSi}_3\text{O}_8$ glass ab2, (b) $^1\text{H}/^{23}\text{Na}$; hydrous $\text{NaAlSi}_3\text{O}_8$ glass ab2, (c) $^1\text{H}/^{27}\text{Al}$; hydrous NaAlSiO_4 glass, and (d) $^1\text{H}/^{23}\text{Na}$; hydrous NaAlSiO_4 glass. Symbols: squares, 1.5 ppm resonance; diamonds, the ca. 3.5 ppm resonance; triangles, the 5–6 ppm resonance.

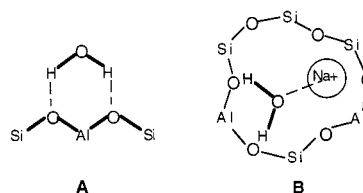


Figure 10. Molecular water bonding environment for a Si/Al–O six-membered ring (hydrogen bonding to the framework is not shown for clarity): (A) molecular H_2O (species A) bound to the Si–O–Al framework; (B) additional coordination to a sodium cation (species B) (see text).

molecular H-exchange is unlikely to be rapid, and thus the exchange process most probably occurs between different framework sites. A second explanation for the observation of only one resonance at room temperature is that some of the sodium cations coordinated to the water molecules are themselves mobile, so that only one water environment is observed at ambient temperatures. High to moderate mobility of sodium cations in glasses, at close to ambient conditions, has been reported from other studies.²⁹

Hydroxyl Species. Assignments of the three “OH” resonances may be proposed from a combination of their chemical shift

values, the change of their relative intensities with Al/Si ratio, and their respective $^1\text{H}/^{23}\text{Na}$ and $^1\text{H}/^{27}\text{Al}$ TRAPDOR effects. The size of the TRAPDOR function is a function of the dipolar coupling constant and the adiabaticity parameter α . α depends of the QCC, the spinning speed (ω_R) and the r.f. field strength (ω_1) ($\alpha = \omega_1^2/\omega_R\omega_Q$)³⁰ and is greater than 1 (as determined from the QCCs extracted from the data of Figure 9), for both the ^{23}Na and ^{27}Al spins, indicating that the experiments are performed under adiabatic conditions, and small changes in the QCCs between different sites will not affect the TRAPDOR fractions, significantly. The TRAPDOR fraction will also be affected by the relative orientation of the dipolar coupling and electric field gradient tensors at the site of the quadrupolar nucleus.²¹ This will most likely vary from OH site to site, and may result in different TRAPDOR fractions, even for spin systems with similar dipolar couplings. In a disordered sample, however, there is likely a distribution of relative orientations for each type of site, and this parameter may not be as critical as for a crystalline material. Nonetheless, we recognize that any comparisons made between the relative TRAPDOR fractions of the different sites may be, at least in part, a result of this parameter, and not just a result of changes in the dipolar couplings.

The $^1\text{H}/^{27}\text{Al}$ TRAPDOR fractions for the 1.5 ppm resonance, for close to on-resonance ^{27}Al irradiation, are similar to those observed for tetrahedral AlOH groups and Brønsted acid sites in zeolites (obtained for similar spinning speeds and ^{27}Al r.f. fields²²) in which protons are coordinated to aluminum atoms (via oxygens). At least two Al–OH species have been observed in the ^1H MAS NMR of acidic zeolites at ca. 0.9 and 2.7 ppm,^{22,31} which were tentatively assigned to octahedral and tetrahedral terminal Al–OH groups, respectively. At least nine resonances have been observed between -0.3 and 7.3 ppm for $\gamma\text{-Al}_2\text{O}_3$ and those in the range $0.2\text{--}2.4$ ppm were assigned to protons coordinated to basic oxygen atoms.³² The shift from -0.2 to 2.4 ppm for the Al–OH species was ascribed to the decreased basicity of the oxygen atoms, the higher frequency resonances being assigned to protons coordinated to bridging Al–O–Al groups.³¹ We, therefore, assign the ≈ 1.5 ppm resonance to an Al(Q³)–OH species consistent with these previous results. (No 6-coordinate aluminum species are seen in the ^{27}Al MAS NMR of these samples.) This assignment is further consistent with the increase in intensity of this resonance with increasing Al/Si ratio. The proton on the Al–OH group is relatively rigid (in the time scale of the ^{27}Al – ^1H dipolar coupling) and does not undergo exchange with molecular water or any other framework sites. The observation of this resonance provides definitive evidence that there is some breakage of the Al/Si–O framework in the hydrous samples.

The two higher frequency resonances at 3.5–6 ppm are associated with much smaller $^1\text{H}/^{23}\text{Na}$ and $^1\text{H}/^{27}\text{Al}$ TRAPDOR fractions. On this basis, these resonances cannot be assigned to isolated and rigid Na^+OH^- and Si-O(H)-Al species, i.e., the species proposed by reaction 1, since large $^1\text{H}/^{23}\text{Na}$ and $^1\text{H}/^{27}\text{Al}$ TRAPDOR fractions are expected for these complexes, respectively. There are three possible causes of the small TRAPDOR fractions. The first is that these resonances are associated with long $^1\text{H}\cdots^{23}\text{Na}$ and $^1\text{H}\cdots^{27}\text{Al}$ internuclear distances. Second, proton mobility between different nearby sites will reduce both TRAPDOR fractions considerably. This motion may not necessarily be frozen out in the temperature range accessible by our MAS system, since it will involve some proton tunneling. Finally, proton exchange of a proton in an OH group with molecular water, or rapid exchange between hydrogen-

bonded molecular water molecules will also result in reduced dipolar couplings to the aluminum atoms in the framework. This exchange must involve a number of hydrogen-bonded water molecules in the cluster, as large sideband manifolds are expected for isolated $\text{H}^+\cdots\text{O}_2\text{H}$ clusters. The molecular water is still, however, bound to the framework, since liquidlike ^1H line widths are not observed for these resonances. The last proposal of the cause of the small TRAPDOR fractions appears the least likely for four reasons: (a) the OH resonances predominate at low water contents, while the intensity of the resonances assigned to *isolated* water molecules increases at higher water contents; (b) the line widths, chemical shift positions, and intensity of the spinning sidebands of the two high-frequency resonances do not change significantly with increased water content, which may be expected if larger networks of water molecules become involved in the exchange processes; (c) an increase in the intensities of the sidebands may be expected, as the temperature of the system is decreased, particularly if the exchange process only involves molecular water (e.g., the tetrahedral reorientation of water molecules in ice, which result in reduced homonuclear dipolar coupling, is frozen out, in the time scale of the ^2H QCC (216 kHz) and ^1H CSA (6 kHz) of the hydrogen atom in H_2O , by ≈ 220 and 163 K, respectively³³); (d) the OH resonances show longer ^1H T_2 s than the isolated H_2O resonances, even at low temperatures, inconsistent with the presence of residual homonuclear coupling. Thus, our spectra do not appear to suggest the presence of extended H-bonded networks of molecular water in these systems. A similar conclusion was reached by Eckert et al. for these and similar glasses.¹⁹

The 3.5 ppm resonance is the most intense resonance in hydrous $\text{NaAlSi}_8\text{O}_{18}$ and $\text{NaAlSi}_3\text{O}_8$ glasses but decreases in intensity with increased Al concentration. It is almost concealed by the other two resonances in the hydrous NaAlSiO_4 glass. The 3.5 ppm resonance possesses the smallest $^1\text{H}/^{27}\text{Al}$ TRAPDOR effect among all three OH resonances. These two observations suggest that it is associated with silicon (and not aluminum). The similarity in chemical shift value of this resonance with that of the non-hydrogen-bonded SiOH resonance in hydrous silica glass (at 3.1 ppm⁵) and in hydrous $\text{Na}_2\text{-Si}_4\text{O}_9$ glass (at 3.0 ppm²⁶), as well as its small ^1H – ^{27}Al TRAPDOR fraction, suggests that this resonance may be due to a SiOH species. Given the low frequency of this resonance, this SiOH group cannot be strongly hydrogen bonded to another oxygen atom (e.g., an atom in the Si–O–Al linkage). This is consistent with its small $^1\text{H}/^{27}\text{Al}$ TRAPDOR effect.

The intensity of the 5–6 ppm resonance is significant in samples with widely varying Al/Si ratios and its relative intensity increases slightly with water content. The $^1\text{H}/^{23}\text{Na}$ TRAPDOR effect of this resonance increases with decreasing temperature, probably indicating some motion of either or both the ^1H or ^{23}Na spins. At least part of this motion can be ascribed to a change of the motion of the sodium cations, relative to the network, because there is no change in the ^1H – ^{27}Al TRAPDOR fractions with decreasing temperature. A change in the sodium motion was also proposed as an explanation for the temperature dependence of the $^1\text{H}/^{23}\text{Na}$ TRAPDOR fraction of the molecular H_2O resonance.

An interesting feature of the 5–6 ppm resonance is its significantly larger fwhm (3.5–4.5 ppm vs 2–2.5 ppm) compared with that of the other resonances and this resonance, most likely, consists of a number of overlapping resonances, resulting from a distribution of local environments. If this is the case, the distributions do not seem to change significantly

with varying Al/Si ratios, as the line shape of the shoulder remains approximately the same. The assignment of this resonance is not straightforward. At least two scenarios may be proposed, where we favor the first for the following reasons: (i) An Si—OH or Al—OH resonance that is hydrogen bonded to the Si/Al—O framework: $Q^3-OH\cdots O(-Al)(-Si)$ with a nearby sodium cation; again exchange between (similar) proton sites is required to explain the small TRAPDOR fractions. H_2O coordination, as discussed above, to the species proposed in this assignment is difficult to exclude completely. (ii) The species giving rise to the 5–6 ppm resonance is due to a Si—O(H)—Al species in exchange with different Si—O—Al sites. The shift to higher frequency, in comparison to the other two OH resonances is consistent with stronger hydrogen bonding; the large line width of this resonance may be ascribed to a wide distribution of the $O-H\cdots O$ distances. Each Si—O(H)—Al unit must, however, be associated with one NaOH group (from reaction 1). The “NaOH” resonance cannot be assigned to the 3.5 ppm (or 1.5 ppm) resonance due to the mass-balance constraints, and thus should also be assigned to the broad 5–6 ppm resonance(s). Again, both species *must* be undergoing chemical exchange either between different sites or with each other, or they are coordinated to water molecules, so as to reduce the $^1H/^{27}Al$ and $^1H/^{23}Na$ TRAPDOR fractions at room temperature. The formation of a hydroxide and a bridging (acidic) hydrogen atom does not appear to be thermodynamically favorable, and this assignment appears less plausible. In addition, the hydrogen atoms in NaOH groups are not expected to be involved in strong hydrogen-bonding and are expected to resonate at lower frequencies.

Implications for the Water Dissolution Mechanism

The experimental data obtained in this study do not fully support either of the currently competing water dissolution models.^{5,6,12} In one of these models,^{5,12} the presence of H_2O does not result in the depolymerization of the aluminosilicate framework; rather, the dissolution mechanism involves only cation exchange between Na^+ and H^+ (reaction 1). If reaction 1 were the only reaction between water and glass, only two H-bearing species other than molecular H_2O would be produced: NaOH and $HAISi_3O_8$. From the data presented above, however, there is strong evidence for at least three distinct OH species in hydrous $NaAlSi_3O_8$ and the other aluminosilicate glasses investigated. Certainly caution must be exercised in correlating the number of species directly with the number of resonances observed since one species may give rise to more than one 1H resonance if it is involved in more than one hydrogen-bonding environment. There is no way, however, that the three resonances at 1.5–6 ppm, observed in varying intensities in the samples with different Si/Al ratios, can be assigned to NaOH or $HAISi_3O_8$ species while maintaining the important constraint of the 1:1 ratio of the two species. Thus, reaction 1 cannot be the only water dissolution mechanism, if it is one at all. Reaction 1 was also questioned above for thermodynamic reasons.

In an alternate model,⁶ at water contents below 30 mol %, water preferentially breaks down Al—O—Al linkages, forming mainly Al—OH species (reaction 2). If this were the case, the main OH resonance at ca. 3.5 ppm observed for a low water content sample, e.g., ab1 (13 mol % water), would have to be assigned to an AlOH group whose protons are rapidly jumping between different binding sites, so as to result in a small $^1H/^{27}Al$ TRAPDOR fraction. The minor resonance at 1.5 ppm is then assigned to isolated Al—OH groups. This assignment does

not hold for the samples with increased aluminum contents: the resonance at 3.5 ppm decreases in intensity in these samples while the resonance at higher frequencies increases, although this may be due to a consequence of increased sites with additional H-bonding in the higher Al-content materials. Nonetheless, the assignment of the 3.5 ppm resonance to a Si—OH group appears more plausible.

Independent of the assignment of the 3.5 ppm resonance, the presence of isolated AlOH groups (which resonate at ≈ 1.5 ppm) (i.e., AlOH groups with rigid proton atoms that do not undergo chemical exchange with other sites) indicates that water does indeed depolymerize the aluminosilicate network. The concentration of isolated AlOH groups is significant at low Si/Al ratios. The assignment of the resonance at 3.5 ppm to SiOH groups is consistent with Si—O—Al or Si—O—Si bond breakages. That the equilibrium rate constants favor a small amount of cation exchange (reaction 1) cannot be totally excluded. If the 5–6 ppm resonance is assigned to NaOH and $HAISi_3O_8$ species, then reaction 1 must occur in combination with the dissolution mechanism.

Conclusion

Two molecular H_2O species have been identified for hydrous $NaAlSi_3O_8$ glasses, one with a closer proximity to Na than the other. Three 1H resonances (at ca. 1.5, 3.5, and 5–6 ppm) from OH groups are present in the 1H NMR spectra of hydrous glasses of composition $NaAlSi_8O_{18}$, $NaAlSi_3O_8$, $NaAlSi_2O_6$, and $NaAlSiO_4$. The resonance at 1.5 ppm is assigned to a $Al(Q^3)-OH$ group. A number of assignments for the two higher frequency resonances may be proposed. However, the assignment of the 3.5 and 5–6 ppm resonances to $Si(Q^3)-OH$ and $Si(Q^3)-OH/Al(Q^3)-OH$ groups which are also H-bonded to the framework, respectively, is the most consistent with our experimental data (i.e., their chemical shift values, the change of their relative abundances with varying Al/Si ratio, and their $^1H/^{23}Na$ and $^1H/^{27}Al$ TRAPDOR fractions). The assignments are consistent with a water dissolution mechanism that involves depolymerization of the aluminosilicate network.

There is considerable proton motion in the system, which results in reduced $^1H-^{23}Na$ and $^1H-^{27}Al$ dipolar coupling. There may also be some sodium cation motion, which will also complicate the analysis of the spectra. Further experiments are planned to examine the dynamics in this system in greater detail.

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