

Water in Silicate Glass: ^{17}O NMR of Hydrous Silica, Albite, and $\text{Na}_2\text{Si}_4\text{O}_9$ Glasses

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The mechanism of incorporation of water in silica (SiO_2), albite ($\text{NaAlSi}_3\text{O}_8$), and $\text{Na}_2\text{Si}_4\text{O}_9$ composition glass has been studied by ^1H , ^{17}O , ^{23}Na , ^{27}Al , and ^{29}Si NMR spectroscopy. Hydrated samples were prepared by quenching the melt from high pressure and high temperature with use of solid-media apparatus with a ^{17}O -enriched starting material. Water content of the hydrated glasses was estimated from ^1H NMR peak intensities compared with reference materials. For SiO_2 glass, the ^{17}O NMR spectrum has a sharp resonance line at the position corresponding to the chemical shift of molecular water. ^{17}O NMR of both dry and hydrous (50 mol % H_2O) albite glasses shows two environments with peaks for $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{O}-\text{Al}$. No significant difference was seen between dry and hydrated glasses. For the $\text{Na}_2\text{Si}_4\text{O}_9$ glass, ^1H and ^{29}Si NMR results are consistent with each other and suggest the formation of $\text{Si}-\text{OH}$ and molecular water in this glass. ^{17}O NMR of this glass shows significant differences between dry and hydrated glass. The intensity of the nonbridging oxygen peak for the hydrated sample decreased considerably with added water. The intensity change of the nonbridging oxygen peak could be quantitatively explained by a formation of a complex with equal molar amounts of Na^+ and H_2O .

Introduction

The mechanism of incorporation of hydrous species in molten and glassy silicates have long been of interest in both geochemistry and glass science.^{1,2} Water is the most important magmatic volatile, both in terms of its abundance and in its influence on melt properties and crystal–liquid phase relations. It is well-established that water dissolves in silicate glasses in at least two distinguishable forms: hydroxyl groups and H_2O molecules. The physicochemical properties of water-containing silicate melts, such as viscosity,^{3–5} melting points,⁶ and diffusivity of the cations,⁷ have been reported. Properties of water-containing silicate glasses, for example, decrease of the glass transition temperature,⁸ decrease of dc conductivity,⁹ and lowering of the chemical durabilities,¹⁰ have also been reported.

The solubility of water in silicate melts of various compositions has been investigated and its dependence on pressure has been interpreted in terms of possible hydrous species in silicate melts.^{11–19} The influence of water on the macroscopic properties of silicate melts has been studied extensively. However, direct structural information about the nature of hydrogen-bearing species and their bonding environments cannot be obtained readily from such measurements. Rather, investigation of glasses quenched from melts is often used to answer these questions.

Stolper and Silver^{20–24} extensively studied the dissolution of water in silicate melts by means of near-IR spectroscopy and demonstrated the presence of molecular water species at high water contents. At water contents < 1 wt %, formation of only hydroxyl ($-\text{OH}$) groups is a good approximation. However, for high water contents corresponding to solubilities at higher pressure, both hydroxyl and molecular H_2O groups were

found in the hydrous glasses, the ratio of molecular water to hydroxyl groups increasing rapidly with increasing water content. Recent ^1H and ^2H NMR measurements^{25–30} are consistent with the IR analysis and indicate that low levels of water (2–4 wt %) are mainly present as OH groups, whereas at higher concentrations molecular H_2O species dominate. Within binary alkali and alkaline earth silicates, there have been several IR and Raman spectroscopic studies of glasses with higher water contents, prepared by quenching hydrous liquids from high pressures and temperatures.^{31–34} The high-frequency O–H stretching region in vibrational spectra is complex, with several broad bands corresponding to a range of hydrogen-bonded OH-containing species. Kohn et al.,³⁵ using ^1H MAS NMR to investigate the hydrogen environments in alkali and alkaline earth disilicate glasses, concluded that strongly hydrogen-bonded $\text{Si}-\text{OH}$ species and molecular H_2O were present. Kummerlen et al.²⁹ measured ^{29}Si magic-angle spinning (MAS) NMR and cross-polarization (CP) MAS NMR spectra of hydrous sodium tetrasilicate glasses in which they observed a decrease of Q^4 species (where Q^n stands for a SiO_4 tetrahedron having n bridging oxygen atoms) with water incorporation. They also suggested an increase of the proportion of Q^2 species and concluded that H_2O does depolymerize the silicate network. The mechanism of water dissolution in aluminosilicate melts is even less well understood and has been the subject of some discussion.^{35–40}

Because these discussions include species associated with different oxygen environments, an analytical method that would allow quantification of different oxygen species in hydrous silicate glass could help in discussing water dissolution models in silicate melts. ^{17}O NMR measurements should be a powerful tool for investigating the water species in silicate glasses.

^{17}O ($I = 5/2$) has a relatively large nuclear quadrupole moment (eQ), which interacts with the electric field gradient (EFG) at the nucleus. This interaction is anisotropic and causes a complex line shape on the ^{17}O NMR. The line shape function

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TABLE 1: Synthesis Conditions of Hydrous Samples

sample name	temp, °C	pressure, GPa	run duration, min
SiO ₂ ·H ₂ O	1550	1.5	30
Na ₂ Si ₄ O ₉ ·H ₂ O	1200	1.0	30
NaAlSi ₃ O ₈ ·H ₂ O	1300	1.0	30

has been obtained analytically,⁴¹ and can be calculated by using a computer program.⁴² The line shape simulation yields the nuclear-quadrupole coupling constant ($\nu_Q = e^2qQ/h$) and asymmetry parameter of EFG (η) in addition to the isotropic chemical shift (δ_i), which can be related to the local structure around the oxygen atoms. Different linkage types of network structures (Si—O—Si, Si—O—Al, Al—O—P, Al—O—Al) and the terminal oxygen atoms (Si—O⁻) show distinctive ¹⁷O parameters (ν_Q and δ_i).^{43–48} In the present investigation, we present the first ¹⁷O NMR data for hydrated silicate glasses.

Experimental Section

Oxygen-17-enriched Si¹⁷O₂ was synthesized from H₂O (10–22 mol % ¹⁷O-enriched) and SiCl₄.⁴⁹ About 500 mg of oxygen-enriched Na₂Si₄O₉ and NaAlSi₃O₈ glass samples was made from high-purity Na₂CO₃, Al₂O₃, and Si¹⁷O₂. Each batch was melted at ~100 °C above its liquidus temperature and then quenched and ground to a fine powder. A relaxation reagent, 0.2 wt % Gd₂O₃, was added to each batch for NMR measurements of Na₂Si₄O₉ and albite glasses. The oxygen-enriched water was loaded into the end of the 3.8 mm (o.d.) open-ended platinum capsule with a microsyringe, after which 100 mg of the glass sample was loaded into the capsule. The capsule was then crimped, and the edge of the capsule was welded with an graphite rod arc, and the crimped platinum was folded. The seal of the capsule was checked by soaking it in a hot oil bath and noting whether there was any bubble formation from it. High-pressure runs were performed in a 1/2-in. diameter solid-media piston-cylinder apparatus. Experiments were conducted in a talc/Pyrex/graphite/Pyrex furnace assembly. Temperature was monitored by using a Pt-Pt/Rh13% thermocouple with no pressure correction on the emf output. Pressure and temperature conditions are listed in Table 1. Hydrated glasses were quenched by disconnecting the power to the furnace. The quenching rate was estimated to be 100°C/s.

NMR measurements were made with a Bruker MSL-300 spectrometer operated at 300.130, 40.700, 79.390, and 59.627 MHz for ¹H, ¹⁷O, ²³Na, and ²⁹Si, respectively. NMR measurements were also performed at higher frequency with Varian VXR-400 spectrometer operated at 54.22 MHz for ¹⁷O. External standards for chemical shift were utilized [tetramethylsilane (TMS) for ¹H, tetraethoxysilane for ²⁹Si, 1 M NaCl aqueous solution for ²³Na, and tap water for ¹⁷O]. A solid-echo pulse sequence (90°_x– τ –90°_y– τ –acquisition) was utilized for the static ¹⁷O NMR measurements with the MSL-300 spectrometer, whereas a Hahn-echo pulse sequence (90°– τ –180°– τ –acquisition) was used for the VXR-400 spectrometer. MAS NMR spectra were obtained by using a high-speed probe spinning at 14–15 kHz. MAS NMR spectra were acquired with a single-pulse sequence with short rf pulses ($<\pi/12$), in which the central transitions were equally excited regardless of the magnitude of the nuclear-quadrupole coupling constants for ¹⁷O and ²³Na. Water contents of the glass samples were determined from ¹H NMR intensities extrapolated to $t = 0$ in the static ¹H Hahn-echo NMR measurements. The ¹H NMR intensities of reference materials with known water contents—hydrated silicate and borate crystals, analcime, borax, kaolinite, pyrophyllite, and ulexite—were also measured to calibrate the water contents of

TABLE 2: ¹H NMR results

sample name	T_2 μ s ± 1.0	water contents wt %	[H ₂ O]/[OH], ± 0.5
borax, Na ₂ B ₄ O ₇ ·10H ₂ O	21.2	46.8 \pm 4.0	
ulexite, NaCaB ₅ O ₆ (OH) ₆	21.0	35.6 \pm 3.0	
kaolinite, Al ₂ Si ₂ O ₅ (OH) ₄	39.9	13.4 \pm 1.0	
analcite, NaAlSi ₃ O ₈ ·H ₂ O	61.6	12.6 \pm 1.0	
pyrophyllite, Al ₂ Si ₄ O ₁₀ (OH) ₂		6.3 \pm 0.5	
SiO ₂ glass	78.2	4.7 \pm 0.5	
Na ₂ Si ₄ O ₉ glass	50.2	6.1 \pm 0.5	1.3
NaAlSi ₃ O ₈ glass	54.4	6.5 \pm 0.5	1.0

the glasses. The water contents of the reference materials were determined by the weight loss after the samples were heated at 1000 °C for 1 h. The identities of the reference materials were confirmed by X-ray powder diffraction.

Results

Determination of the Water Contents of Glass Samples.

The spin–spin relaxation decay of the ¹H magnetization for both the reference crystalline materials and the hydrous glass samples were obtained from the ¹H NMR Hahn-echo measurements. The decay was fitted by exponential function with spin–spin relaxation time (T_2) and the initial magnitude of the ¹H NMR signal, which is proportional to the amount of ¹H in the sample. The results obtained from ¹H NMR measurements are summarized in Table 2. The relation between the water contents of the reference samples determined from the weight-loss measurement and the peak intensity of the ¹H spectra of the spin–echo experiments extrapolated to $t = 0$ was linear; we used this to determine the amount of water in the glass samples. Eckert et al.²⁷ suggested that the presence of large amounts of paramagnetic ions in glasses could cause signal loss in ¹H spectra. They estimated the effect in aluminosilicate glass samples containing 8 wt % H₂O and 0.58 or 1.27 wt % FeO and determined the observable fractions of water to be 87.4% and 73.2%, respectively. In the present investigation, we added 0.2 wt % Gd₂O₃ to the glass to shorten the spin–lattice relaxation time for ¹⁷O and ²⁹Si NMR measurements. This might result in a signal loss of <10%, which could erroneously affect our estimates of the water contents of the glass sample.

Albite Glass. Figure 1 shows ¹H static NMR spectra of hydrous glasses obtained by single-pulse NMR measurement. The spectrum is consistent with those observed in previous studies of sodium silicate glasses²⁵ and albite glass.²⁷ The spectra have the characteristics of solid-state NMR powder patterns and are not fully averaged by the isotropic molecular motion. Compared with the liquid-state ¹H NMR line width, this line width suggests that hydrogen-bearing species with isotropic mobility are not present in these glass samples. The spectra contain two distinct components: a broad line observed for molecular water units in crystalline hydrates,⁵⁰ and a narrower component that was assigned, as previously, to OH groups.^{25,27} Detailed line shape analysis must deal with the problem of isotropic and anisotropic chemical shift distributions in addition to the strong dipole–dipole interaction that affects the ¹H spectrum of the H₂O species. For a rough estimates of the H₂O and OH concentration, we assumed a Gaussian line shape for each species. For albite glass, the concentration of H₂O and OH species was estimated from the relative peak area for both H₂O and OH peaks as [H₂O]/[OH] = 1.0 \pm 0.5. This value is comparable with those obtained by previous IR and ¹H MAS NMR measurements.^{24,27} The IR measurements obtained [H₂O]/[OH] = 1.7, and ¹H MAS NMR yielded [H₂O]/[OH] = 1.2 for 5.9 and 5.59 wt % water-containing H₂O albite glass, respectively.

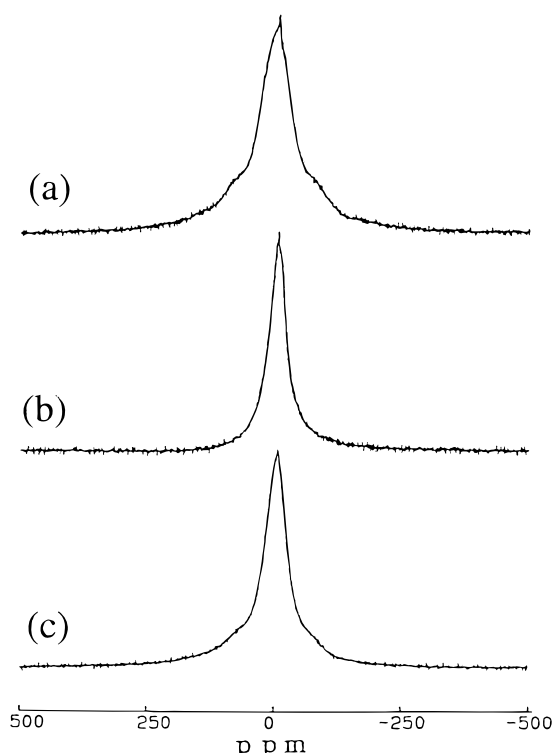


Figure 1. ^1H static NMR spectra of hydrous silicate glass samples obtained at 300.13 MHz frequency with a single pulse sequence. Wide line probe (5 mm ϕ), 90° pulse 1.5 μs , recycle delay 60 s, 16 scans. (a) $\text{Na}_2\text{Si}_4\text{O}_9$ glass (6.1 wt % H_2O), (b) SiO_2 (4.7 wt % H_2O), and (c) albite ($\text{NaAlSi}_3\text{O}_8$) glass (6.5 wt % H_2O).

Schaller and Sebald⁵¹ observed a cross-peak on two-dimensional (2-D) ^1H exchange NMR spectra for $\text{Na}_2\text{O} \cdot 4\text{SiO}_2 \cdot 0.7\text{H}_2\text{O}$ glass caused by intermolecular dipolar flip-flop processes. These authors suggested the contribution of the interaction could cause an error in estimating the $[\text{H}_2\text{O}]/[\text{OH}]$ ratio by means of a one-dimensional (1-D) ^1H NMR approach. In the present investigation, given that these exchange components would have contributed to the central part of the spectrum and would overlap with OH peak, the amount of OH estimated in the present ^1H spectrum might be overestimated and lead to a smaller $[\text{H}_2\text{O}]/[\text{OH}]$ ratio than that reported in other investigations. A 2-D NMR approach would be necessary for the detailed determination of the $[\text{H}_2\text{O}]/[\text{OH}]$ ratio of the hydrous silicate system.

Figure 2 shows static ^{17}O NMR spectra of the albite glasses obtained at two different magnetic field strengths. The spectra consist of two broad components that are strongly influenced by second-order nuclear-quadrupole interactions. Previous ^{17}O NMR measurements for zeolites^{44,45} obtained ν_Q values for oxygen atoms in different environments: 5.2 MHz for Si—O—Si oxygen and 3.8 MHz for Al—O—Si oxygen. Taking into account these ν_Q value for each oxygen environment, we used the WINFIT program⁴² to apply the line shape simulation to the spectrum of the dry glass and obtained parameters ν_Q , η , and δ_i . A comparison of the observed and the simulated spectra is shown in Figure 2(c). The two-site simulation satisfactorily reproduced the observed spectrum. The parameters used in the simulation, listed in Table 3, are in good agreement with recent 2-D NMR results.⁵² The relative intensity ratio for these two sites is almost unity, which is in good agreement with that expected from the stoichiometry if we assume there are no Al—O—Al linkages in this glass.⁵²

We observed no significant difference between the dry glasses and the water-containing glasses within the limited signal-to-

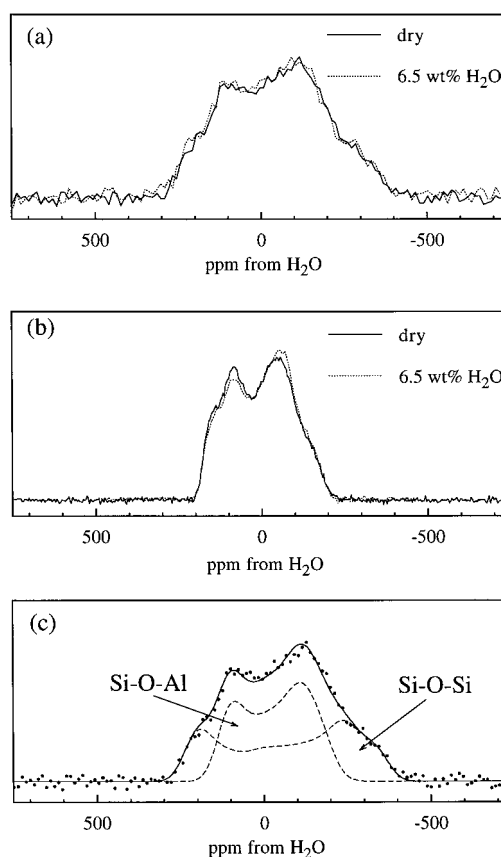


Figure 2. ^{17}O static NMR spectra of dry and hydrous albite ($\text{NaAlSi}_3\text{O}_8$) glass. Wide line probe (5 mm ϕ), solid-echo sequence ($90^\circ_x - \tau - 90^\circ_y - \tau$ -acquisition), 90° pulse 1.5 μs , refocusing delay 60 μs , recycle delay 3 s, 40 000 scans, Lorentzian line broadening 100 Hz. The intensities of each spectrum were normalized with their peak area. (a) Comparison of the spectra obtained at ^{17}O NMR frequency of 40.70 MHz. (b) Comparison of the spectra obtained at 54.22 MHz. (c) Simulation of the ^{17}O spectrum for dry sample from (a). (solid circle) data points. The solid line is a simulated spectrum. The broken lines represent each component used in the simulation. Parameters used in this simulation are listed in Table 3.

noise ratio of the present spectra obtained at lower frequency. At the higher magnetic field, however, there was a small difference between the spectra of the dry and hydrous glasses. This suggests some contribution from a new oxygen environment in hydrous glass. For further analysis of a new oxygen environment, 2-D NMR measurements are in progress.^{53,54}

$\text{Na}_2\text{Si}_4\text{O}_9$ Glass. Figure 1(a) shows ^1H static NMR spectra of 1 GPa hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glasses. The spectra consist of two components as observed for the albite glass. However, the relative intensity of the H_2O species is slightly greater than albite glass. An integration of the peak intensities of both H_2O and OH gives the ratio $[\text{H}_2\text{O}]/[\text{OH}] = 1.3 \pm 0.5$.

Figure 3 shows ^{23}Na MAS NMR spectra of 1 GPa dry and hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glasses. The line width of the spectra decreased with water incorporation, which suggests either a decrease of ν_Q or of the chemical shift distribution with water incorporation, or both. Assuming a Gaussian distribution of ν_Q in the line shape simulation, we obtained the reasonable fit shown in Figure 3. The parameters used in the simulation are shown in Table 4. The ν_Q value was suggested to decrease with water incorporation in the glass sample. This means the EFG at the ^{23}Na nucleus caused by the surrounding ions decreased with water incorporation.

Figure 4 shows ^{29}Si MAS NMR spectra of 1 GPa dry and hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glasses. The noise level of the spectrum was

TABLE 3: ^{17}O NMR Results

sample name (and conditions)	site	e^2qQ/h , MHz	η	chemical shift, ppm	intensity, % (± 2)	σ , MHz (± 0.2)
static NMR		(± 0.2)	(± 0.1)	(± 10)		
$\text{Na}_2\text{Si}_4\text{O}_9$ glass	NBO	2.6	0.15	28	24	0.3
(1 GPa, dry)	Si—O—Si	5.1	0.25	55	76	0.2
$\text{Na}_2\text{Si}_4\text{O}_9$ glass	NBO(Na^+)	2.6	0.15	25	15	0.3
(1 GPa, 6.1 wt % H_2O)	Si—O—Si	5.1	0.25	43	75	0.2
	$\text{H}_2\text{O}^?$	6.0	0.70	20	10	0.1
$\text{NaAlSi}_3\text{O}_8$ glass	Si—O—Si	5.2	0.2	40	50	-
(1 GPa, dry)	Si—O—Al	3.8	0.2	25	50	-
MAS NMR		(± 0.1)		(± 2)		
$\text{Na}_2\text{Si}_4\text{O}_9$ glass	NBO	2.4	0.25	38	28	
(1 GPa, dry)	Si—O—Si	5.1	0.0	51	72	
$\text{Na}_2\text{Si}_4\text{O}_9$ glass	NBO(Na^+)	2.7	0.25	40	14	
(1 GPa, 6.1 wt % H_2O)	Si—O—Si+ $\text{H}_2\text{O}^?$	5.2	0.22	51	86	

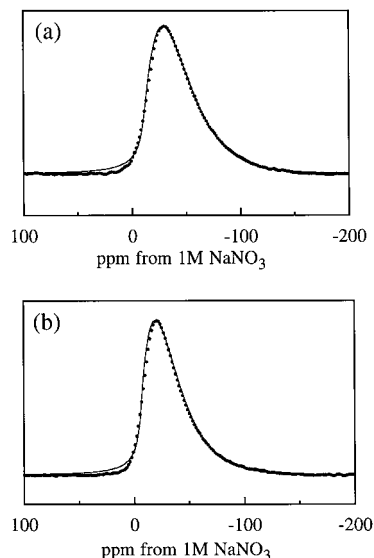


Figure 3. ^{23}Na MAS-NMR spectra of dry and hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glass obtained at 79.39 MHz. High-speed MAS probe (4 mm ϕ), spinning speed 15 kHz, excitation pulse 0.6 μs (15 $^\circ$ pulse), recycle delay 1 s, 1000 scans. (a) Dry and (b) hydrous (6.1 wt % H_2O) glass. Parameters used in this fitting are listed in Table 4.

TABLE 4: ^{23}Na NMR Results for $\text{Na}_2\text{Si}_4\text{O}_9$ Glass

conditions	e^2qQ/h , MHz, (± 0.3)	η	chemical shift, ppm, (± 3)	σ , MHz (± 0.2)
1 GPa, dry	2.4	0.5	-10.5	0.3
1 GPa, 52 mol % H_2O	2.1	0.5	-5.5	0.3

relatively high. However, an increase of the Q^n species such that n decreased with water incorporation was clearly observed. This is consistent with the previous ^{29}Si measurements on the binary sodium silicate glass of the same composition as used in the present investigation.²⁹ The relative peak intensities of Q^n species have been suggested to show different relaxation times in ^{29}Si NMR.⁵⁵ This could lead to a repetition-time dependence of the Q^n peak intensities. However, in the present condition (repetition time = 2.5 s), the difference of relaxation time does not significantly affect estimating the relative Q^n amounts within the limited signal-to-noise ratio in the present spectrum. The Gaussian line shape simulation of the ^{29}Si NMR spectrum yields the amounts of Q^n species in these glasses. The result is summarized in Table 5.

For the dry glass, almost equal amounts of Q^3 and Q^4 species were observed as expected from the stoichiometry of this glass; that is, $[\text{NBO}]/[\text{Si}] = 0.5$. On the other hand, the hydrous glass shows Q^2 species in addition to the Q^3 and Q^4 species, which is consistent with the previous ^{29}Si NMR and CP MAS NMR investigations.^{29,30} This suggests formation of silanol (Si—OH)

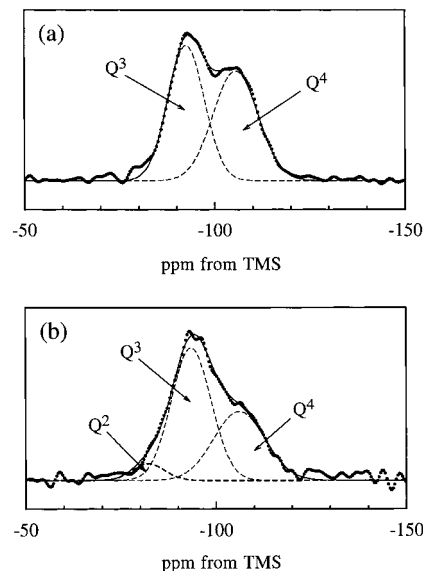


Figure 4. ^{29}Si MAS-NMR spectra of dry and hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glass obtained at 59.63 MHz. Single-pulse sequence, high-speed MAS probe (4 mm ϕ), spinning speed 15 kHz, excitation pulse 2.5 μs (90 $^\circ$ pulse), recycle delay 2.5 s, 4000–8000 scans, Lorentzian line broadening 30 Hz. The solid lines are the Gaussian fittings. The dotted lines represent each component of the fit. (a) Dry and (b) hydrous (6.1 wt % H_2O) glass. Parameters used in this simulation are listed in Table 5.

TABLE 5: ^{29}Si NMR Results for $\text{Na}_2\text{Si}_4\text{O}_9$ Glass

conditions	site	chemical shift, ppm (± 1)	line width, ppm	intensity, % (± 1)
1 GPa, dry	Q^3	-92.5	11.3	50
	Q^4	-105.5	13.9	50
1 GPa, 52 mol % H_2O	Q^2	-82.2	10.0	6
	Q^3	-93.5	12.3	56
	Q^4	-106.1	15.8	38

groups in this glass. The amount of silanol groups in this glass was estimated by using the relative peak intensities of the Q^n species and by assuming that additional nonbridging oxygens were generated by the introduction of water molecules, forming silanol groups. The estimated amount of silanol groups in this glass was $[\text{Si—OH}]/[\text{total Si}] = 0.2(\pm 0.05)$. This value is in accordance with the previous value of $[\text{NBO}]/[\text{Si}] = 0.72$ obtained by ^{29}Si measurement of glass of the same composition, with 4.8 wt % H_2O .²⁹

In contrast to the albite glass, the hydrated $\text{Na}_2\text{Si}_4\text{O}_9$ glass shows a distinct difference from the dry glass in the line shape of the ^{17}O static NMR spectra. Figure 5 shows the ^{17}O NMR spectra of dry and hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glasses. The dry glass spectrum consists of two components, narrow and broad doublet peaks. A line shape simulation of the ^{17}O NMR spectrum for

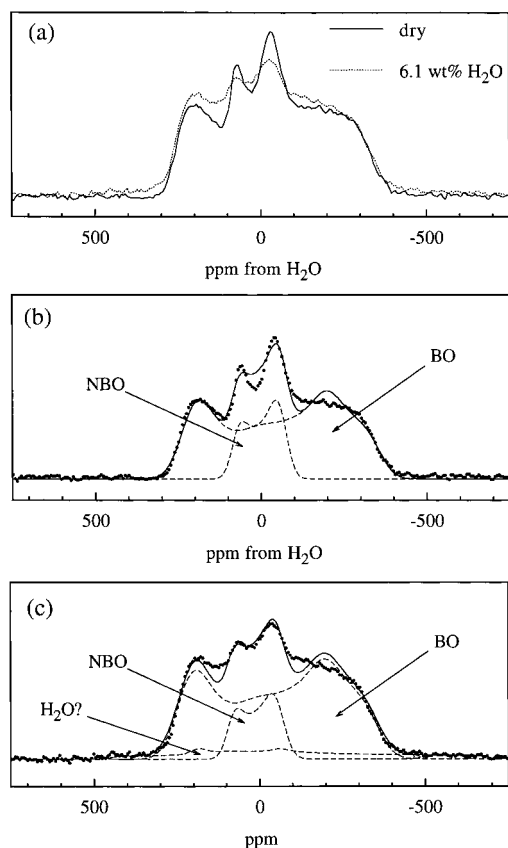


Figure 5. Static ^{17}O NMR spectra of dry and hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glass. Wide-line probe (5 mm ϕ), solid-echo sequence ($90^\circ_x - \tau - 90^\circ_y - \tau - \text{acquisition}$), 90° pulse 1.5 μs , refocusing delay 60 μs , recycle delay 3 s, 8000 scans, Lorentzian line broadening 100 Hz. The intensities of each spectrum were normalized with their peak area. (a) Comparison of the spectra obtained at ^{17}O NMR frequency of 40.70 MHz. (b) Simulation of the ^{17}O NMR spectrum for dry sample from (a). (c) Simulation of the ^{17}O NMR spectrum for hydrous sample from (a). (Solid circles) data points. The solid line is the simulated spectrum. The broken lines represent each component used in the simulation. Parameters used in this simulation are listed in Table 3.

the dry glass yielded two sites corresponding to the nonbridging oxygen (NBO) and bridging oxygen (BO) sites (Figure 5b). The ν_Q values for NBO and BO were 2.78 and 5.20 MHz, respectively, in good agreement with the previous results^{47,48} for the same glass system measured at the different magnetic field. The relative intensity ratio of NBO and BO was obtained as NBO:BO = 2:7, which is accordance with the value expected from the stoichiometry.

Introduction of water into the glass caused a significant change in the line shape of ^{17}O NMR. The central doublet peak from NBO atoms decreased, whereas both the broad components beside the tail of the BO peak and the shoulder at around 120 ppm increased. Because of the possibility of multiple sites in this glass, peak separation was quite difficult. A chemical shift dispersion as well as a change of ν_Q could strongly affect the ^{17}O NMR spectrum. Comparison of broad line spectra with ^{17}O MAS NMR spectra could thus provide information about chemical shift distribution. Figure 6 shows ^{17}O MAS NMR spectra of the same $\text{Na}_2\text{Si}_4\text{O}_9$ dry and hydrous samples. The spectrum for dry sample is the same that in the previous report.⁴⁷ In the MAS NMR spectra, a decrease of the NBO peak with incorporation of water was also observed. The broad component observed for the static ^{17}O NMR spectrum of the hydrous glass could not clearly observed in the MAS NMR spectrum. An increase of the line width for NBO peak in hydrous glass

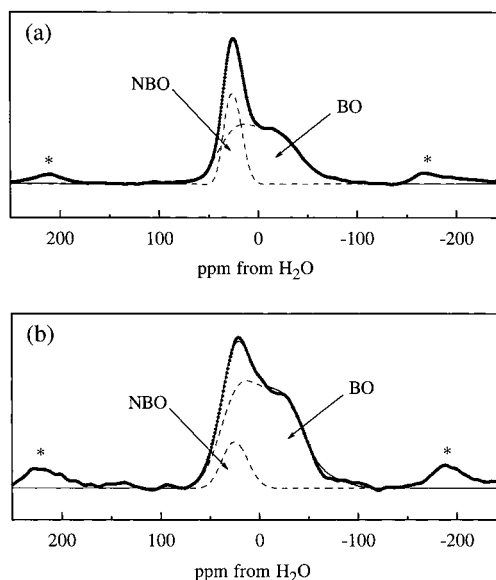


Figure 6. ^{17}O MAS-NMR spectra and their simulations of (a) dry and (b) hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glass obtained at 54.22 MHz. Single-pulse sequence, high-speed MAS probe (4 mm ϕ), spinning speed 10 kHz, excitation pulse 1 μs (15° pulse), recycle delay 30 s, 3000 scans, Lorentzian line broadening 100 Hz. The solid line is the simulated spectrum. The broken lines represent each component used in the simulation. Parameters used in this fitting are listed in Table 3.

suggests an increase of the chemical shift dispersion for NBO with water incorporation. Thus the NBO atom present in the dry glass NBO(Na^+) may also be affected by water incorporation in addition to the formation of the new hydrous species. In the present investigation, to obtain the relative intensity ratio of the NBO(Na^+) and the other sites, we assume that the NBO(Na^+) peak could be simulated by using same quadrupole parameters as for the dry glass. Other possible hydrous species were assumed to merge into BO peak such that the peak area for both the BO and hydrous species could be obtained from the peak intensity of BO peak. The simulated spectra are shown in Figure 5(c) and Figure 6, and the parameters obtained are listed in Table 2. The coupling constants for both the BO and NBO show little change with incorporation of water compared with those of dry glass, but the relative intensity ratio between BO and NBO atoms changed significantly. These results suggest that water incorporation into this glass yields a major change in the coordination environment of the NBO atoms. The origin of the broad component for broad line spectrum is not clear. In the present simulation, we assumed that the peak has a large ν_Q value corresponding to a rigid H_2O molecule, and the parameters were set on the basis of the values obtained for H_2O in ice ($\nu_Q = 6.41$ MHz, $\eta = 0.93$)⁵⁶ and $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2^{17}\text{O}$ ($\nu_Q = 6.8$ MHz, $\eta = 1.00$).⁵⁷ In the recent 2-D ^{17}O NMR investigations of hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glass, a new peak having a quadrupole coupling constant of at least 7 MHz was observed and was tentatively assigned to the oxygen in the rigid water molecule.⁵³

SiO₂ Glass. Figure 1(b) shows the ^1H NMR spectrum of hydrous SiO_2 glass. The spectrum consists of a single relatively sharp Gaussian line, in contrast to albite and $\text{Na}_2\text{Si}_4\text{O}_9$ glass. Previous ^1H MAS NMR measurements for 2.5 and 8.7 wt % H_2O containing SiO_2 glass showed at least four different environments in silica glass.⁵⁸ These were assigned to H_2O and SiOH with and without hydrogen bondings. However, the chemical shift variation for these four environments was quite small, ranging from 3.2 to 4.7 ppm. These peaks would have

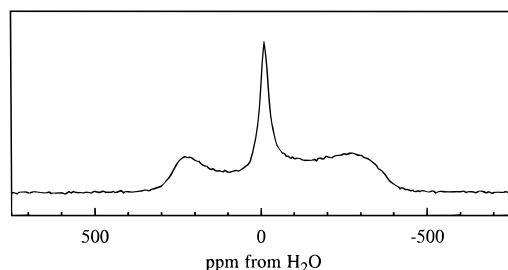


Figure 7. ^{17}O static NMR spectrum of hydrous silica (SiO_2) glass obtained at 40.70 MHz. Wide-line probe (5 mm ϕ), solid-echo sequence ($90^\circ_x - \tau - 90^\circ_y - \tau$ -acquisition), 90° pulse 1.0 μs , refocusing delay 60 μs , recycle delay 3 s, 40 000 scans, Lorentzian line broadening 100 Hz.

merged into a single peak in the broad line spectrum observed in the present investigation.

Figure 7 shows the ^{17}O NMR spectrum of hydrous SiO_2 glass. The spectrum contains a broad peak from Si—O—Si and a single sharp peak. The chemical shift, 0 ppm, of the sharp peak corresponds to that of water molecule. The signal-to-noise ratio of the ^{17}O NMR spectrum for hydrous glass is higher than that obtained for the dry sample. Because no relaxation reagent (i.e., Gd_2O_3) was introduced in this SiO_2 glass, this finding suggests that an introduction of water into the silicate network provides an effective relaxation mechanism for ^{17}O NMR. Accordingly, a dipolar coupling between oxygen and hydrogen nuclei distributed in the silicate network could operate as a major relaxation mechanism.

Discussion

The distinct difference of the ^{17}O NMR spectrum for SiO_2 glass from those for the other glasses is the sharp resonance peak at ~ 0 ppm. The sharpness of the peak suggests the presence of molecular motion. However, the half-width at half-maximum of this peak (15 ppm) suggests that the molecular motion of the water molecule is not isotropic. Thus a chemical exchange process may exist in H_2O molecules in SiO_2 glass, perhaps a formation of small clusters of H_2O molecules at voids formed in hydrous SiO_2 glass. The lack of an apparent Si—OH peak in ^{17}O NMR and the sharp ^1H spectrum for hydrous SiO_2 glass suggests the chemical exchange process is between OH and H_2O within the H_2O clusters and the silanol groups formed on the silica walls at voids. The reduction of spin—lattice relaxation time of ^{17}O NMR with incorporation of H_2O for hydrous SiO_2 glass suggests the formation of Si—OH in this glass. The dipole—dipole interaction between ^1H and ^{17}O could provide an effective relaxation mechanism on ^{17}O NMR of hydrous SiO_2 glass. For a further analysis of this spectrum, study of the temperature-dependence of the NMR spectrum would be necessary.

Combining the ^1H , ^{17}O , and ^{29}Si results allows us to consider a model of water incorporation into $\text{Na}_2\text{Si}_4\text{O}_9$ and albite glass. For the albite glass, according to the results of ^1H NMR, the introduction of water into the glass resulted in about half of the total amount of the water forming OH groups. Regarding the amount of new ^{17}O introduced from the H_2^{17}O molecule, the H_2^{17}O species should contribute to the ^{17}O NMR spectrum an intensity increase of $\sim 10\%$ over that for dry glass. No apparent change in the spectrum was observed within the limited signal-to-noise ratios of the present ^{17}O spectrum at the lower magnetic field. However, the spectrum obtained at the higher magnetic field showed a small change: a decrease of the component at ~ 100 ppm and an increase of the component at ~ -50 ppm.

This suggests the existence of new oxygen environments with water incorporation. Because these changes occur at the peak position of Al—O—Si species, the reaction of Al—O—Si species with water to form Al—OH groups or Al—O—Si protonation (or both), as suggested in previous studies,^{35–40} would be the origin of the new components. However, detailed line shape analysis is difficult because the line shapes for these new species are unknown. In the recent ^{17}O NMR study of hydrated aluminosilicate glass, a small amount (a few percent) of nonbridging oxygen peak has been suggested to appear in both the 1-D and 2-D spectra.⁵⁴ Further 2-D NMR measurements are in progress.

The broad component observed in ^{17}O NMR spectrum for hydrous $\text{Na}_2\text{Si}_4\text{O}_9$ glass is not observed in hydrous albite glass. Given that the existence of H_2O in this glass has been confirmed by ^1H NMR, a broad H_2O peak is expected in the ^{17}O spectrum of hydrous albite glass. The lack of broad peak may suggest that the quadrupole coupling constant for H_2O in albite glass is greater than that in $\text{Na}_2\text{Si}_4\text{O}_9$ glass and that the peak has become too broad to be observed in the present NMR spectrum, because of the dead-time delay problem for spectrum accumulation by the NMR spectrometer. Also, peaks from NaOH groups, which have been suggested to be present in hydrous albite glass by the previous ^{23}Na and ^{27}Al measurements,³⁵ may not be observed in the present ^{17}O NMR, because the quadrupole coupling constant for NaOH crystal is known to be very large, $\nu_Q = 7.59$ MHz.⁵⁹

On the other hand, for the $\text{Na}_2\text{Si}_4\text{O}_9$ glass, introduction of water causes a significant change in the coordination environment of both the NBO and the BO atoms. Using the value obtained for the water contents (6.1 wt % = 52 mol % H_2O) and ^1H NMR estimation of the OH and H_2O ratio ($[\text{H}_2\text{O}]/[\text{OH}] = 1.3$), we obtained a molecular formula for this glass as $\text{Na}_2\text{H}_{0.6}\text{Si}_4\text{O}_{9.3} \cdot 0.8\text{H}_2\text{O}$. This formula gives $[\text{NBO}]/[\text{Si}] = 0.65$, which is very good agreement with the value obtained from ^{29}Si NMR measurement ($[\text{NBO}]/[\text{Si}] = 0.7$). If all of the NBO atoms, including both the Si—O $^-$ Na $^+$ and Si—OH, could be observed by ^{17}O NMR, the peak intensity for NBO atoms would be 28%, while the observed intensity of NBO(Na $^+$) is ~ 14 –15%. This discrepancy suggests formation of new NBO environments, including Si—OH and hydrated Si—O $^-$ Na $^+$ in addition to the initially present NBO atoms, and suggests that this new peak would not separately observed in the present ^{17}O NMR spectra. If we assume formation of a complex constructed from an equal molar ratio of Na $^+$ and H_2O the calculated NBO(Na $^+$) value would be 13%, according to the above molecular formula for this glass. This is in good agreement with the observed value for NBO(Na $^+$) of the present ^{17}O NMR measurements (~ 14 –15%). The present multinuclear NMR results could be explained by formation of Na $^+$ ions—water molecules complexes in an equal molar ratio and by formation of new NBO atoms with different chemical bonding from that of the initial NBO atoms.

Conclusions

New ^{17}O NMR data are presented for hydrous silicate glass samples prepared at high pressures and high temperatures by using solid-media apparatus. ^{17}O NMR spectra of dry and hydrous albite glasses show no significant difference, whereas hydration of $\text{Na}_2\text{Si}_4\text{O}_9$ glass leads to significant differences, in which the intensities from nonbridging oxygen peak for the hydrated sample decrease considerably, suggesting a change of coordination environment of NBO atoms with water incorporation.

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