Structure of Cl-containing silicate and aluminosilicate glasses: A ^{35}Cl MAS-NMR study

Travis O. Sandland,[1] Lin-Shu Du,[1] Jonathan F. Stebbins,[1,]* and James D. Webster[2]

[1]Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA
[2]Department of Earth and Planetary Science, American Museum of Natural History, Central Park West at 79th Street,
New York, NY 10024-5192, USA

Abstract—Chlorine-35 magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were collected at 14.1 and 18.8 Tesla fields to determine the atomic scale structural environments of the chloride ions in anhydrous and hydrous silicate and aluminosilicate glasses containing 0.2 to 0.7 wt% Cl. NMR peaks are broad and featureless, but are much narrower than the total chemical shift range for the nuclide in inorganic chlorides. Peak widths are primarily due to quadrupole interactions and to a lesser extent to chemical shift distributions. Peak positions are quite different for the Na- and Ca-containing glasses, suggesting that most Cl$^-$ coordination environments contain network modifier cations. Comparison of peak positions and shapes for silicate and aluminosilicate glasses containing either Na or Ca suggests that there is no obvious contribution from Cl$^-$ bonded to Al, and relative quantitation of peak areas indicates that there is no systematic undercounting of ^{35}Cl spins in the aluminous vs. the Al-free samples. In Ca-Na silicate glasses with varying Ca/(Ca + Na), the mixed-cation glasses have intermediate chemical shifts between those of the end members, implying that there is not a strong preference of either Ca^{2+} or of Na$^+$ around Cl$^-$. Hydrous Na-aluminosilicate glasses with H$_2$O contents up to 5.9 wt% show a shift to higher frequency NMR signal with increasing H$_2$O content, while the quadrupole coupling constant (C_Q) remains constant at ~3.3 MHz. However, the change in frequency is much smaller than that expected if H$_2$O systematically replaced Na$^+$ in the first-neighbor coordination shell around Cl$^-$. A series of hydrous Ca-aluminosilicate glasses with H$_2$O contents up to 5.5 wt% show no shift in NMR signal with increasing H$_2$O content. The C_Q remains constant at ~4.4 MHz, again suggesting no direct interaction between Cl$^-$ and H$_2$O in these samples.   *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

In oxide melts and glasses, halogens and other volatile constituents such as H$_2$O can greatly affect physical properties and thus the dynamic processes in these systems. Evidence for the participation of volatiles in magmatic processes is widespread (e.g., fluid inclusions, hydrous minerals, etc.) and in some cases quite dramatic, as in explosive volcanism, which is generally driven by volatile exsolution (Carroll and Webster, 1994). The evolution of an immiscible Cl-rich hydrous phase ("brine") is important in the concentration, transport, and deposition of ore metals, especially in porphyry-type deposits (Barnes, 1997). These processes are affected by the solubility and exsolution of Cl$^-$ in magmas and their variation with composition, temperature, and pressure, which, in turn, are controlled by the speciation or interaction of Cl$^-$ with other components in the melts. In addition to its geologic significance, Cl$^-$ is also an important component of many Ag- or Cu-containing photochromic silicate glasses (Armistead and Stookey, 1964), and it is an important component of some fast-ionic-conducting glasses (Vogel et al., 2002). Increasingly, Cl$^-$ is also being recognized for its role in ultra-low-loss glasses for optical data transmission (Saito and Ikushima, 1998).

In several studies, a strong tendency for Cl$^-$ to associate with alkaline and alkaline earth cations has been inferred to account for effects on solubility or other properties (e.g., Dotsenko et al., 1998; Webster and De Vivo, 2002). While there is

considerable interest in the behavior and properties of dissolved chloride in silicate magmas and glasses, few direct data are available concerning the atomic-scale bonding of chloride in these systems. X-ray absorption and Raman spectroscopic studies by Ponader and Brown (1989) and Marr et al. (1999) have indirectly examined the interaction of Cl$^-$ with high field strength cations in some silicate glasses. ^{35}Cl MAS NMR, which provides a more direct view of the Cl$^-$ environment, is proving to be a promising technique for addressing this type of question. The method is generally regarded as technically difficult (see Smith, 2000, for a full review), and as such its use has generally been limited to cases where Cl$^-$ is in a highly symmetric environment (i.e., some crystalline chlorides and perchlorates). Recently, however, the technique has provided useful new structural information about Cl-containing silicate glasses (Stebbins and Du, 2002). ^{35}Cl, with a natural abundance of 75%, has a large chemical shift range (Fig. 1) with systematic effects of bond distance and coordination number for groups of chlorides of the same valence (LiCl being a notable exception) (Weeding and Veeman, 1989). However, acquisition of high-resolution ^{35}Cl MAS NMR spectra can be difficult. ^{35}Cl is a spin 3/2 quadrupolar nuclide with a large quadrupole moment and a relatively low resonance frequency, meaning that observed peaks can be very broad. As a consequence, in highly asymmetric bonding environments (e.g., C-Cl bonding in organic compounds) peak broadening can be severe enough to make peaks indiscernible from background. In addition, the solubilities of chlorides in most naturally occurring silicate melts are low (e.g., Carroll and Webster, 1994), further reducing the measured signal intensity from a given sample.

* Author to whom correspondence should be addressed (stebbins@stanford.edu).
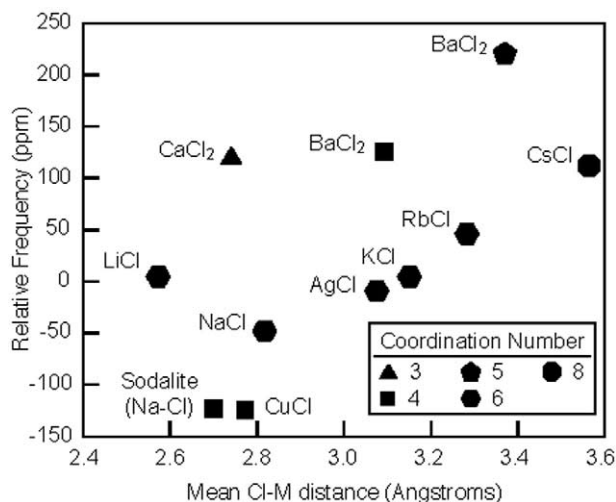
Fig. 1. ^{35}Cl NMR chemical shifts of anhydrous crystalline materials. Data for NaCl, Sodalite, CsCl, and BaCl$_2$ are from Stebbins and Du (2002). Data for LiCl, KCl, and RbCl are from Hayashi and Hayamizu (1990). Data for AgCl and CuCl are from Hayashi and Hayamizu (1992). Data for CaCl$_2$ are from this study.

Several previous solid-state ^{35}Cl NMR studies have focused on crystalline compounds with cubic sites, for which quadrupolar broadening is absent (Weeding and Veeman, 1989; Hayashi and Hayamizu, 1990, 1992; Lefebvre, 1992). This has shown that the isotropic chemical shift (δ_{iso}) varies widely and is well often correlated with cation-chloride bond distance (Fig. 1). High-speed magic angle spinning (MAS) and the use of higher magnetic fields, both of which decrease peak width, have recently facilitated the acquisition of ^{35}Cl spectra of solids, including hydrocalumite and hydrotalcite (Kirkpatrick et al., 1999), perchlorates (Skibsted and Jakobsen, 1999), organic hydrochloride salts (Bryce et al., 2001), and Friedel's salt (Skibsted et al., 2001). The technique has also been used to detect small amounts of Cl$^-$ in fluid inclusions (Sherriff et al., 1987) and even in coal (Saito et al., 2001). The mechanisms of chloride sorption in Portland cement (Yu and Kirkpatrick, 2001), and the solid solution behavior of mixed-halide sodalite systems (Trill et al., 2003) have also been investigated using ^{35}Cl NMR. A preliminary study on silicate and aluminosilicate glasses by Stebbins and Du (2002) has shown that with the use of very high magnetic fields (14.1 to 18.8 T), ^{35}Cl NMR spectra can be acquired and that considerable structural information can be obtained. That study analyzed several sodium silicate and aluminosilicate, cesium silicate and aluminosilicate and barium silicate glasses, and showed that there is a distribution of δ_{iso}, clearly indicating some disorder in cation-chloride bond distances and possibly Cl coordination numbers. Also, the results noted a close similarity of ^{35}Cl peak positions and shapes in the Al-free and Al-containing Na- and Cs-silicate glasses, suggesting that most Cl$^-$ ions are coordinated only by the alkali cations, in marked contrast to what is observed for F$^-$ in aluminosilicate glasses (Zeng and Stebbins, 2000).

Here we apply ^{35}Cl MAS NMR to further constrain the structure of silicate and aluminosilicate glasses, which we take as approximating the structure of the corresponding melt at the temperature of its transition to a glass. Specifically, we address

whether or not Cl$^-$ is coordinated by network (i.e., Al^{3+} or Si^{4+}) or network modifier cations (e.g., Na$^+$ or Ca^{2+}). In glasses containing both Ca^{2+} and Na$^+$, we investigate the potential ordering of cations around Cl$^-$, and we compare spectra of hydrous and anhydrous Cl-containing aluminosilicate glasses to provide spectroscopic data relevant to models of Cl$^-$ coordination and dissolution in these melts.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation

Crystalline AlCl$_3$ and CaCl$_2$ were obtained commercially as anhydrous powders in sealed ampoules from Sigma-Aldrich Co. To avoid hydration of the extremely hygroscopic AlCl$_3$, it was sealed into glass tubing with epoxy under a dry nitrogen atmosphere. This approach allowed only "static" (non-MAS) spectra to be collected (see below). The CaCl$_2$ sample was loaded into a normal (not air-tight) MAS rotor under dry nitrogen. Spectra were collected rapidly, before hydration affected the bulk of the sample.

A series of Na- and Ca-silicate glasses with end member compositions of Na$_2$Si$_3$O$_7$ and CaSi$_2$O$_5$ were synthesized from dried, decarbonated, reagent grade Na$_2$CO$_3$, CaCO$_3$, Al$_2$O$_3$, and SiO$_2$. Components were melted in open Pt crucibles, water quenched, and found to be crystal free when examined with a petrographic microscope. These base glasses were then reground, mixed, melted, and quenched to form intermediate compositions with molar Na:Ca ratios of ~1:1, 1:2, and 2:1. ~1 wt% Cl$^-$, added as NaCl (because of the difficulty of handling anhydrous CaCl$_2$), was then mixed with the powdered glasses. Samples were sealed in Pt tubes, melted at ambient pressure, quenched in water, and reexamined with a petrographic microscope. A glass with a composition of Ca$_4$Al$_2$Si$_4$O$_{15}$ was made in a similar fashion. An additional Cl-bearing CaSi$_2$O$_5$ sample was synthesized using BaCl$_2$ as a source of Cl$^-$. All glasses contain ~0.1 wt% cobalt oxide to speed the spin-lattice relaxation rate. Sample compositions were measured by electron microprobe with mineral standards (Table 1).

Hydrous, Cl-bearing Na-aluminosilicate samples were synthesized from NaAlSi$_3$O$_8$ gel, silica gel, NaCl, and water. These samples all have similar compositions (78 wt% SiO$_2$, 13% Al$_2$O$_3$, 9% Na$_2$O, 0.5% Cl) with varying amounts of H$_2$O added via silica gel or distilled water. Samples were fused at 1085°C and 2.8 kbar in sealed Pt capsules for 90 h in an internally heated pressure vessel at the American Museum of Natural History and quenched isobarically. Glasses were analyzed using microprobe and IR spectroscopy to confirm sample composition (Table 1).

Hydrous, Cl-bearing Ca-aluminosilicate samples were made in the Magma Dynamics Laboratory at the U. S. Geological Survey in Menlo Park, CA. Samples were prepared by adding measured amounts of H$_2$O and NaCl to a base glass with an approximate composition of Ca$_{1.5}$AlSi$_3$O$_9$, synthesized as described above, with total sample weights of ~ 150 mg. The 5 mm Pt capsules were arc welded in an ice-water bath to prevent H$_2$O loss, then melted in a piston-cylinder apparatus using 2.54 cm talc-graphite furnace assemblies at 8 kbar and 1175 to 1250 °C, with boron nitride pressure media. Glasses were quenched by turning off the power to the furnace. Samples quickly cooled (first 100° in ~ 2 s) below the glass transition temperature and there was no obvious formation of an immiscible phase in any of the samples. Cooling reduced the pressure by ~1/2. Once the samples reached room temperature, the remaining pressure was continuously released over 5 s. Water concentrations were measured by FTIR (Table 1), using extinction coefficients for glasses of similar bulk composition (Silver et al. 1990).

2.2. NMR Spectroscopy

^{35}Cl MAS NMR spectra of the glasses were collected with Varian Unity/INOVA spectrometers at 14.1 and 18.8 Tesla (T) using 3.2 mm Varian/Chemagnetics T3-type probes, with spinning rates of 20 kHz and referenced to 1 M aqueous NaCl. An echo pulse sequence, optimized for quadrupolar nuclides, was used (Kunwar et al., 1986). Full-echo spectra were collected at 14.1 T with radiofrequency power (ω_1) of 86 kHz, echo time of 200 μs, and pulse lengths of 1.6 and 3.3

Table 1. Glass sample compositions. Cations were analyzed as oxides by electron microprobe using mineral standards; mol % O was calculated and corrected for measured Cl. H$_2$O and OH$^-$ were measured by FTIR.

	mol%								wt%	
Sample	Na	Ca	Ba	Al	Si	O	H	Cl	Cl	H$_2$O + OH$^-$
NS	12.0	0.0			27.2	60.1		0.6	1.0	
N2CS	10.7	5.6			24.1	59.0		0.6	1.0	
CNS	7.2	9.1			23.5	59.6		0.5	0.8	
C2NS	5.7	9.9			23.8	60.1		0.5	0.8	
CS	0.7	15.1			22.8	60.8		0.6	0.9	
CS + BaCl$_2$		15.1	0.4		22.9	60.9		0.7	1.1	
NAS1	5.5			5.1	25.9	62.6	0.7	0.2	0.4	0.3
NAS2	5.4			5.2	25.4	62.0	1.7	0.3	0.5	0.8
NAS3	4.7			4.6	23.2	59.4	7.8	0.3	0.5	3.9
NAS4	4.7			4.3	21.7	57.7	11.3	0.3	0.5	5.9
CAS1	0.6	14.5		8.6	16.1	59.7		0.5	0.9	
CAS2	0.3	6.7		6.7	22.9	62.7	0.4	0.3	0.5	0.3
CAS3	0.3	6.3		6.2	21.2	60.6	5.1	0.3	0.5	3.3
CAS4	0.3	5.9		5.7	19.7	58.7	9.3	0.3	0.5	5.5

μs, which correspond to the solid $\pi/2$ and π radiofrequency (rf) tip angles respectively. Spectra were collected at 18.8 T with ω_1 of 66 kHz, echo time of 200 μs, and pulse lengths of 1.9 and 3.8 μs. Most experiments lasted between 10 and 48 h with delay times as short as 0.05 s between pulses. Longer relaxation delays (up to 10 s) were used to collect fully relaxed spectra and show no differential relaxation. Due to the challenges of acquiring ^{35}Cl spectra mentioned above, signal-to-noise ratios in the spectra can be low. To compare total signal intensities, peak areas for relaxed spectra were integrated, including the first set of (central transition) spinning sidebands.

^{35}Cl static spin-echo spectra for AlCl$_3$ were collected at 14.1 T using a Varian/Chemagnetics static (non-MAS) probe with a 10 mm horizontal coil, and checked by independently collecting data with a 5 mm sample coil. First and second pulse lengths of 1 and 2 μs were used with ω_1 of 63 kHz. A pulse delay of 10 s and echo time of 50 μs were used. Roughly 44,000 transients were collected during a typical experiment. ^{35}Cl MAS NMR spectra for CaCl$_2$ were collected at 14.1 T using the same procedure used for the glasses. A pulse delay of 0.5 s was used to collect a relaxed spectrum, with 28,000 transients.

2.3. Calculations of NMR Parameters

Mean values of the quadrupolar coupling constant (C_Q), which is related to the electric field gradient at the observed nucleus, were estimated from the spectra using the following equation (Schmidt et al., 2000a):

$$\delta_{cg} = \delta_{iso} - \frac{10^6}{40} \cdot \frac{C_Q^2 \cdot (3 + \eta^2)}{v_0^2 \cdot I^2 \cdot (2I - 1)^2} \cdot (I(I + 1) - 3/4) \qquad (1)$$

where I is the nuclear spin, v_o is the resonance frequency of the nuclei, δ_{cg} the center of gravity of the peak, and δ_{iso} the isotropic chemical shift (center of gravity at infinite magnetic field). The quadrupolar asymmetry parameter η was chosen rather arbitrarily as 0.7 in all calculations, but variation of η over its full range (from 0 to 1) would result in only ~15% variations in the derived C_Q values. The observed value of δ_{cg} was determined graphically for each sample at two magnetic fields (14.1 and 18.8 T) and plotted against $1/v_0^2$. This yields a straight line, allowing estimation of δ_{cg} at $1/v_0^2 = 0$ (i.e., infinite magnetic field), which is by definition δ_{iso}, and the derivation of a mean value for C_Q. Multiple measurements of δ_{cg} were made at each field, and uncertainties propagated into those tabulated for δ_{iso} and C_Q (Table 2).

Contributions to peak widths from the distributions of chemical shift (W_{csd}) and from second order quadrupolar effects (W_q) were calculated based on the full widths at half maxima (FWHM) using the following corrected equations from Schmidt et al. (2000b).

$$FWHM_1^2 = W_q^2 + W_{csd}^2$$
$$FWHM_2^2 = (B_1/B_2)^2 \cdot W_q^2 + (B_2/B_1)^2 \cdot W_{csd}^2 \qquad (2)$$

B_1 and B_2 are the strengths of the magnetic fields and $FWHM_1$ and $FWHM_2$ are the peak widths at the lower and higher fields, respectively. FWHM was determined graphically and measured multiple times at both fields to estimate uncertainties.

NMR parameters for AlCl$_3$ and CaCl$_2$ were obtained from simulations of the central transition spectra using the STARS simulation package (Varian, Inc.) to calculate quadrupolar line shapes.

3. RESULTS

3.1. Crystalline Chlorides

To better understand ^{35}Cl MAS NMR spectra of Cl-containing aluminosilicate glasses in which Cl$^-$ might be coordinated by Al^{3+}, static ^{35}Cl NMR spectra were collected for anhydrous AlCl$_3$ at 14.1 T (Fig. 2). In AlCl$_3$, Cl$^-$ ions are in deformed cubic close-packing, with Al ions in some of the octahedral holes, yielding highly asymmetrical Cl$^-$ environments. The observed peak is extremely broad (>4000 ppm). The spectrum, while not ideal because of the difficulties of exciting such a broad line with the maximum power level allowed by the NMR probe, does show the discontinuities expected for a quadrupolar line shape. Simulations of the spectra allowed estimation of δ_{iso} as 2880 ± 40 ppm, C_Q as 9.4 ± 0.2 MHz and η as 0.4 ± 0.05. Note that Cl$^-$ in a site with a C_Q this large would not be detectable in the MAS spectra collected for the glass samples, but the presence of significant fractions of such species would be recognized as "missing signal" in relative peak area quantification (see below). The extreme chemical shift is somewhat surprising, but was checked by repeating the measurements with a second sample and a different probe configuration.

^{35}Cl MAS NMR spectra were also collected for anhydrous CaCl$_2$ at 14.1 T (Fig. 3). The Cl$^-$ site in this crystal is trigonal planar, and as such the C_Q of the site might be expected to be relatively high. However, simulation of the peak shape allows estimations of C_Q as 2.1 ± 0.1 MHz, δ_{iso} as 122 ± 5 ppm, and η as 0.7 ± 0.1. ^{35}Cl sites with C_Q values like those observed for CaCl$_2$ should be readily observable using MAS NMR at 14.1 and 18.8 T. The peak shape is similar to that reported by Saito

Table 2. Peak positions, widths, and quadrupolar parameters for ^{35}Cl in glasses, and quadrupolar parameters for crystalline materials.[a]

Sample	δ_{cg} (ppm)		FWHM (Hz)		Mean δ_{ISO} (ppm)	Mean C_Q[b] (MHz)	W_q (ppm) 14.1 T	W_{esd} (ppm) 14.1 T
	18.8 T	14.1 T	18.8 T	14.1 T				
Glasses								
NS	−116	−155	5680	6200	−65 ± 5	3.3 ± 0.1	93 ± 3	50 ± 2
N2CS	−107	−141	9820	10230	−67 ± 10	3.0 ± 0.2	145 ± 30	95 ± 16
CNS	−84	−123	9970	11750	−35 ± 15	3.2 ± 0.4	186 ± 3	72 ± 6
C2NS	−72	−114	9910	12490	−20 ± 15	3.3 ± 0.3	209 ± 15	40 ± 30
CS	10	−61	9820	11250	102 ± 22	4.4 ± 0.4	175 ± 25	78 ± 35
NAS1	−130	−163	5710	6190	−89 ± 11	3.0 ± 0.3	97 ± 15	54 ± 8
NAS4	−106	−138	6020	6550	−65 ± 7	2.9 ± 0.2	92 ± 3	51 ± 3
CAS1	−7	−53	9940	13180	52 ± 38	3.5 ± 0.9	218 ± 20	33 ± 30
CAS3	−1	−50	101380	11380	62 ± 45	3.6 ± 1.0	175 ± 35	85 ± 45
CAS4	3	−56	11220	11870	79 ± 42	4.0 ± 0.9	170 ± 50	105 ± 50
Crystals								
AlCl$_3$					2880 ± 40	9.4 ± 0.2		
CaCl$_2$					122 ± 5	2.1 ± 0.1		
NaCl					−46 ± 1	0		

[a] Uncertainties in measurements of δ_{cg} and FWHM differ for each sample due to varying signal to noise levels, leading to maximum errors in calculated values as reported above.

[b] C_Q was calculated with η arbitrarily set at 0.7. Variation over its full allowed range (0 to 1) would affect the estimated mean C_Q values by at most 15%.

et al. (2001), although derived NMR parameters were not reported.

3.2. Silicate and Aluminosilicate Glasses

^{35}Cl MAS NMR spectra were collected for Cl-containing Ca- and Na-silicate and aluminosilicate glasses with the compositions described in Table 1. In the Ca-containing glasses (Fig. 4), there is a broad peak (FWHM = 167 and 191 ppm at 18.8 and 14.1 T respectively) with a center of gravity at ~ 2 and −57 ppm at 18.8 and 14.1 T. Fully relaxed spectra were collected with a relaxation delay of 5 s. Higher signal-to-noise spectra were collected with shorter (0.05 s) delay times. Comparison of spectra for the Al-containing and Al-free samples shows the peak shapes to be the same within the noise level,

indicating very similar Cl⁻ environments. Spectra were also collected for a similar Ca-silicate glass with Cl⁻ added as BaCl$_2$ instead of NaCl. The spectra for the two samples are identical, indicating that the observed peak represents Cl⁻ coordinated almost entirely by Ca^{2+}, as expected simply from the high Ca^{2+}/Na$^+$ and Ca^{2+}/Ba^{2+} ratios in these samples. (^{35}Cl NMR peak positions for Na and Ba silicate glasses differ by >200 ppm, Stebbins and Du, 2002.)

In the Na-containing glasses, the observed peak is narrower (FWHM = 72 and 105 ppm at 18.8 and 14.1 T respectively) and is centered at −116 and −155 ppm at 18.8 and 14.1 T (Fig. 5), similar to that previously reported (Stebbins and Du, 2002). The large shift in position from the Ca-containing glasses indicates again that the Cl⁻ environments are dominated by the network modifier cations. Experiments with different relaxation delays between pulses showed that 0.05 s resulted in fully
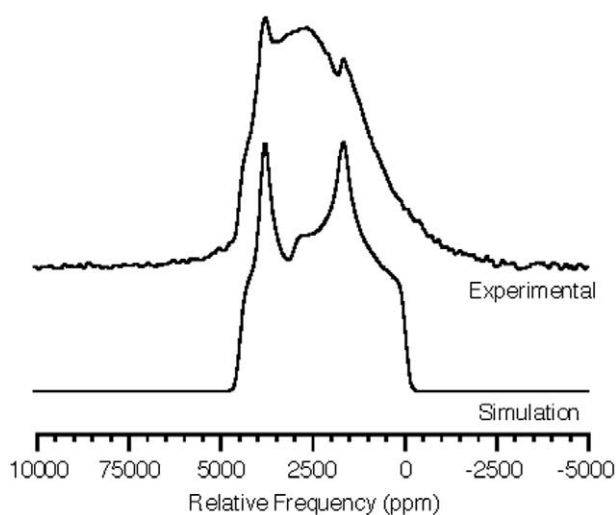

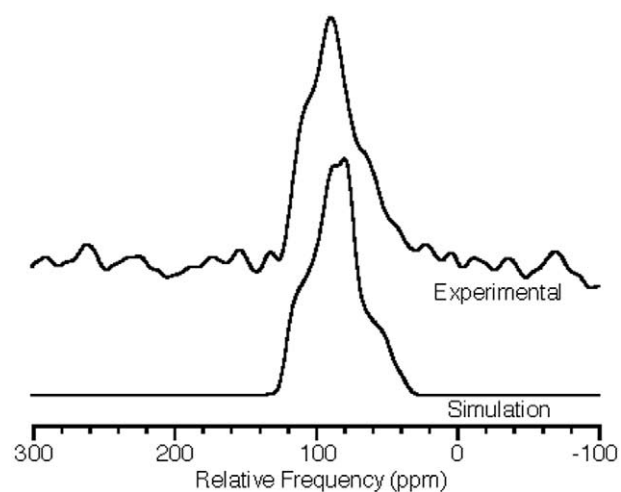Fig. 2. Static spin-echo ^{35}Cl NMR spectrum and simulation of AlCl$_3$ (14.1 T).

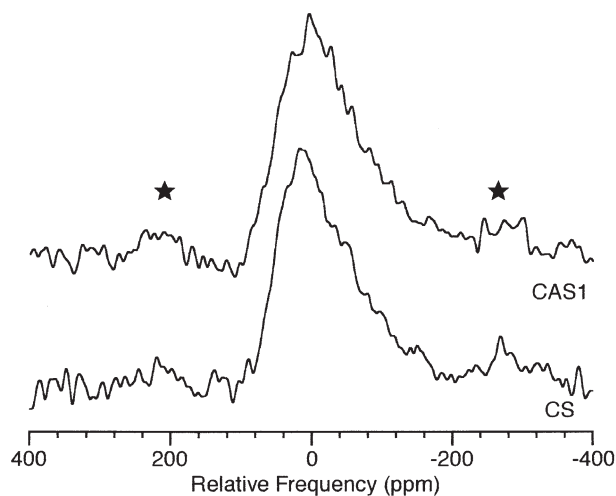Fig. 3. ^{35}Cl MAS NMR spectrum and simulation of crystalline CaCl$_2$ (14.1 T).

Fig. 4. Comparison of ^{35}Cl MAS NMR spectra for Cl-bearing aluminous (CAS1) and Al-free (CS) Ca-silicate glasses (18.8 T). Spinning sidebands here and elsewhere are marked with stars. When overlain, the spectra are identical within the noise level.

relaxed spectra, indicating very fast spin-lattice relaxation of Cl. The spectra from the Al-containing sample contains crystalline NaCl with a sharp peak located at −46 ppm. This signal was subtracted out from integrated peak areas wherever it was observed. As for the Ca-containing glasses, spectra for the Na silicate and Na aluminosilicate glasses are identical within the noise level. This peak is thus assumed to represent Cl^{-} coordinated primarily by Na^{+}.

The lack of any noticeable changes in the spectra between Al-free and Al-rich glasses, for both the Na and Ca systems (and similar, if much noisier, results for the Cs system, Stebbins and Du, 2002), coupled with the large differences in peak positions caused by the various modifier cations, strongly in-
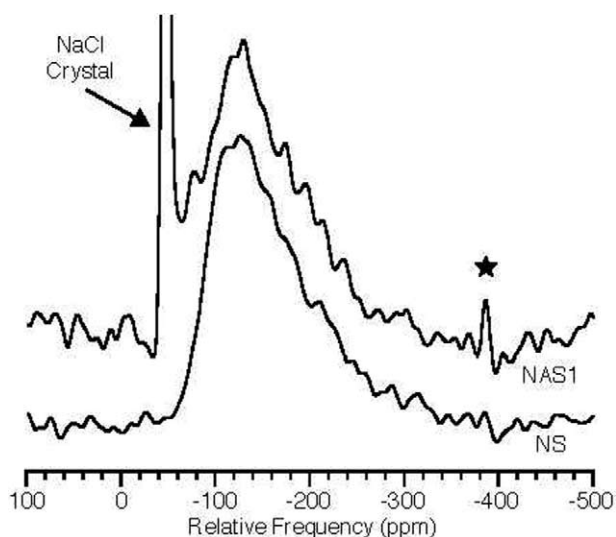

Fig. 5. Comparison of ^{35}Cl MAS NMR spectra for Cl-bearing Al-containing (NAS1) and Al-free (NS) Na-silicate glasses (14.1 T). When overlaid, the spectra are identical within the noise level, except for the signal from the crystalline NaCl impurity.
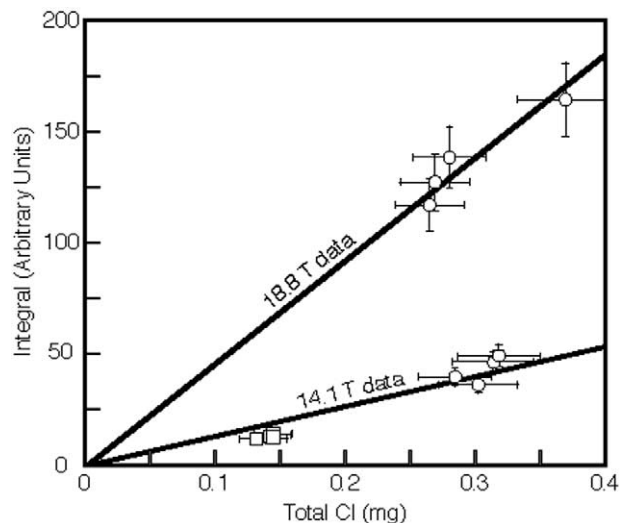

Fig. 6. Comparison of total, central-transition ^{35}Cl MAS NMR signal with the total Cl in glass samples as determined by sample weight and microprobe analysis. Squares indicate hydrous Na-aluminosilicate glasses. Circles indicate anhydrous Na-, Ca-, and mixed-cation-silicate and -aluminosilicate glasses.

dicate that Cl^{-} bonded to Al does not contribute significantly to the spectra: such sites, if "visible" in the spectra, should produce a noticeable change in peak shape in at least one of the ranges of chemical shifts sampled by the different compositions, or to add signal in another part of the frequency range observed. However, it is possible that bonds to Al^{3+} could lead to large asymmetry in the local electric field gradient for Cl^{-}, resulting in a high C_Q for such sites, as was observed for anhydrous AlCl$_3$. The corresponding NMR signal might thus be broadened enough to be unobservable. We have tested for this effect by plotting integrated ^{35}Cl NMR peak areas for relaxed spectra vs. the analyzed Cl content of each sample at 14.1 and 18.8 T (Fig. 6). Within uncertainties, both data sets fall on straight lines through the origins, indicating that there is not a significant systematic undercounting of the ^{35}Cl spins in the Al-containing glasses relative to the Al-free samples (i.e., at least ~90% of the ^{35}Cl that is detectable in the Al-free samples is detected in the aluminous glasses). This approach does not rule out the possibility that some fraction of the NMR signal is "invisible" in *all* samples studied, although for that proportion to be large and to remain constant over such a wide compositional range seems highly unlikely. The lack of such an effect could, in principle, be confirmed by comparing intensities to those of a pure standard, the most likely ones being a crystalline alkali halide or aqueous solution. However, because the spectral intensities resulting from typical NMR echo pulse sequences for nuclei in sites with $C_Q = 0$ (as in such standards) are very different from those with moderate C_Q values as in the glass samples, we did not make this comparison (in effect, the Al-free glasses serve as relative intensity standards for the aluminous glasses). The most likely cause of additional high-C_Q sites for Cl^{-} would be Si-Cl bonding (e.g., frozen SiCl$_4$ has C_Q reported to be 40.8 MHz, Johnson et al., 1969). However, for chemical reasons discussed below, it is unlikely that such species account for a high percentage of the total Cl^{-} in the glasses described here.
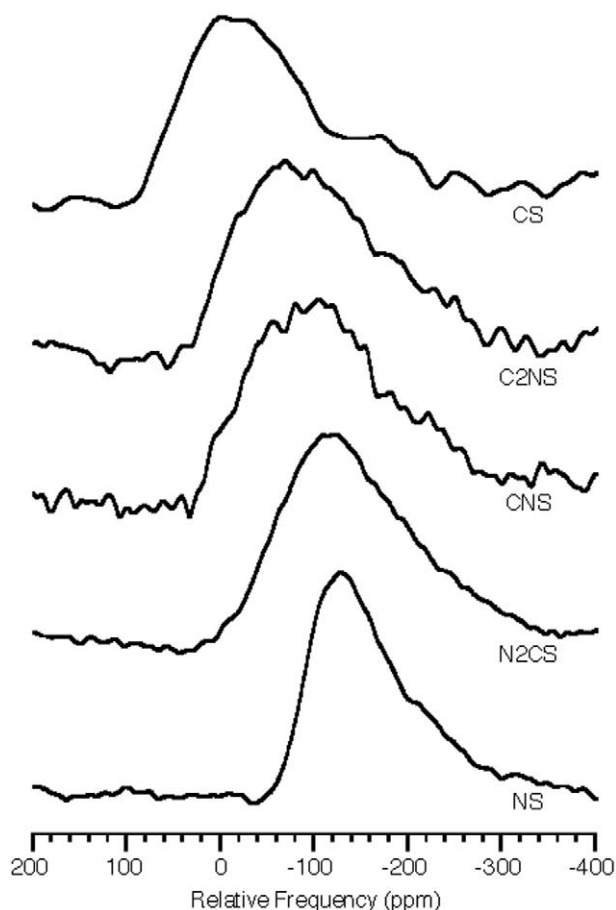
Fig. 7. ^{35}Cl MAS NMR spectra of Cl-containing mixed-cation Ca- and Na-silicate glasses (14.1 T).
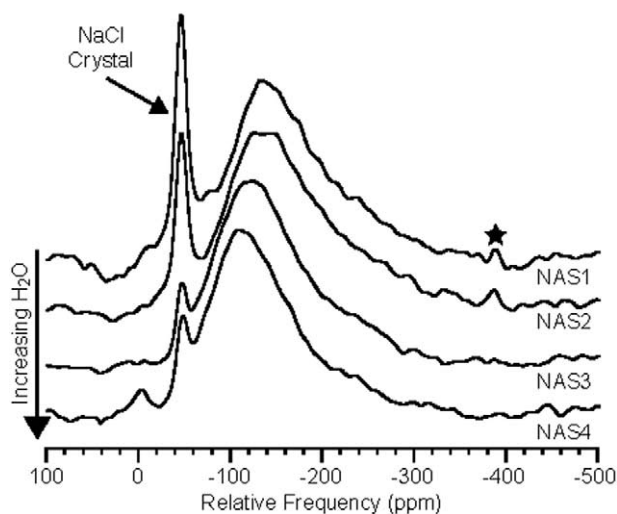

Fig. 8. ^{35}Cl MAS NMR spectra of hydrous, Cl-containing Na-aluminosilicate glasses (14.1 T). A small peak at 0 ppm in the most hydrous sample (NAS4) likely represents small fluid inclusions (see text). The widths of this and NaCl peaks are exaggerated by the apodization used in the data processing.

3.3. Mixed-Cation Ca- and Na-Silicate Glasses

A series of mixed Ca/Na silicate glasses (Table 1) was also analyzed using ^{35}Cl MAS NMR at 18.8 and 14.1 T (Fig. 7) to investigate the possibility of cation charge effects on the preference for Cl$^-$ coordination. As the Ca^{2+} content of the glasses increases, the peaks are broadened considerably, mostly due to increases in C_Q (Table 2). The pulse delays required to obtain fully relaxed spectra increase from 0.05 s for Na$_2$Si$_3$O$_7$ to 5 s for CaSi$_2$O$_5$, suggesting a possible role for residual ^{23}Na-^{35}Cl dipolar coupling in spin-lattice relaxation. The mixed-cation glasses have chemical shifts between those of the end members, with peaks shifting to higher frequency with increasing Ca^{2+} content. Again, relative quantification of the peak areas suggests that little or no Cl$^-$ (< 10%) is present in sites with C_Q high enough to render their signal "invisible" (Fig. 6), barring an unexpected systematic "undercounting" as mentioned above. A more detailed analysis of the spectra is discussed below.

3.4. Hydrous Na- and Ca-Aluminosilicate Glasses

Spectra for the hydrous, Cl-bearing Na-aluminosilicate glasses (Table 1) all show similar features (Fig. 8). There is a broad glass peak (peak maximum located at about −105 to −140 ppm at 14.1 T) with δ_{cg} ranging from −163 to −138 ppm (Table 2) as the water contents of the glasses increase. This shift to higher NMR frequency is also seen at 18.8 T. C_Q remains constant with increasing H$_2$O content at ∼3.3 MHz (Table 2). These spectra show the presence of a minor crystalline NaCl impurity as a sharp peak at −46 ppm. We do not know the significance of the apparent increase in this component with water content: neither the synthesis nor the NMR experiments were designed to account for total Cl$^-$ in all phases (glass, brine, fluid) in the system, and the analyzed Cl$^-$ contents of the hydrous glasses are all similar (Table 1). An additional small peak at 0 ppm was observed in the spectrum for the sample with the highest water content. Changes in the intensity of this peak with varying pulse widths indicate that this feature, like the crystalline NaCl peak, has a lower rf nutation frequency than the glass peak, indicating a very low C_Q (∼0 MHz), and thus that it most likely is due to small inclusions of aqueous NaCl.

Spectra for the Cl-bearing hydrous Ca-aluminosilicate glasses collected at each field are similar to each other, and with increasing water content there is no detectable change in the chemical shift or peak shape (Fig. 9). The estimated mean C_Q remains constant with increasing H$_2$O content at ∼ 4.4 MHz (Table 2).

4. DISCUSSION

4.1. Silicate and Aluminosilicate Glasses

The lack of noticeable effects of added alumina on the ^{35}Cl spectra of Na and Ca silicate glasses indicates that Al-Cl bonding is not common in these systems, as was also suggested by earlier experiments in the Na and Cs systems (Stebbins and Du, 2002). In addition, the relative quantitation of the peak areas, barring a systematic "undercounting" of the ^{35}Cl spins, suggests that at least ∼90% of the Cl$^-$ in these glasses is
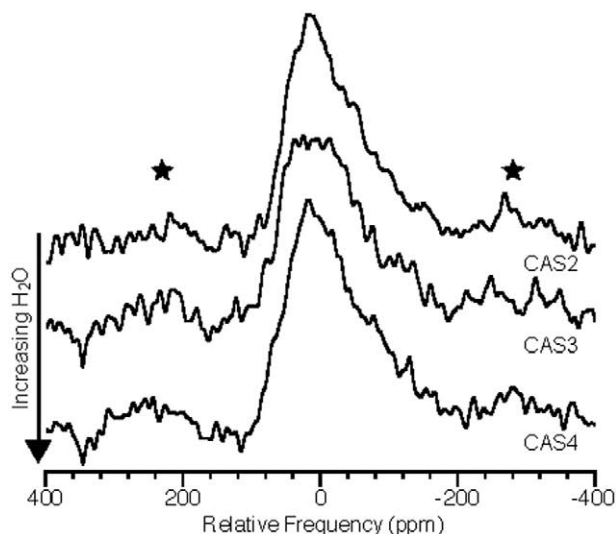
Fig. 9. ^{35}Cl MAS NMR spectra of hydrous, Cl-containing Ca-aluminosilicate glasses (18.8 T). When overlain, spectra are identical within the noise level.

coordinated solely by alkali or alkaline earth cations. A remaining uncertainty is the extent of Si-Cl bonding, which could conceivably render a fraction of the ^{35}Cl signal "invisible" by the formation of sites with very large C_Q's. It is unlikely that such bonding is common in these systems: the instability of such linkages relative to Si-O bonds is indicated by the lack of solid compounds with such structures that are stable in O-rich compositions. In addition, where Si-F bonding has been unambiguously detected by ^{19}F NMR on multicomponent silicate glasses, it is always much less common than linkages to alkali, alkaline earth, or aluminum cations, involving at most a few % of the total F (Stebbins and Zeng, 2000; Kiczenski and Stebbins 2002). We cannot rule out the presence of small amounts of Al-Cl or Si-Cl bonding in the glasses studied here (perhaps up to ~10%), and such minor species could be interesting in their potential affects on dynamical properties such as viscosity, as been suggested for Si-F groups (Stebbins and Zeng, 2000). Such bonding could well be important in very different compositions, e.g., pure silica glass. However, chloride solubility, the property of probably greatest petrological interest, is likely to be most strongly controlled by the thermodynamic activity established by the most common chemical environments for the chloride ion.

Domination of chloride speciation by alkali, alkaline earth, or other network modifier cations has also been suggested by previous phase equilibrium studies. For example, Kravchuck and Kepler (1994) calculated partition coefficients between melt and brine in systems containing various proportions of $NaAlSi_3O_8$, $KAlSi_3O_8$, SiO_2, HCl, KCl, NaCl, and H_2O components. The results suggested that chloride solubility and speciation are primarily dependent on the network-modifying cations, not the network formers Al and Si, but seems to be a complex function of the composition. (Cl^- solubility as used is those studies and here refers to the concentration of Cl^- in a melt in equilibrium with a vapor and/or hydrous chloride melt and thus is a relative term.) Various cations affect Cl^- solubility, but solubility generally increases with increasing con-

centrations of modifier cations in the melt phase (Webster and De Vivo, 2002.) Molten silica and molten NaCl are almost entirely immiscible, suggesting that the solubility of Cl^- in pure SiO_2 is low (Kotlova et al., 1960), although dynamically interesting concentrations of Cl have been introduced into SiO_2 by direct Cl for O substitution (Saito and Ikushima, 1998).

The apparent low amount of Al-Cl bonding in the systems studied here differs from the observations of the coordination environment of F^- in silicate and aluminosilicate melts and is sensible in terms of known effects on melt properties. For example, the viscosities of silicate and aluminosilicate melts decrease dramatically with the substitution of F^- for O^{2--} (Dingwell et al., 1985), suggesting that F^- depolymerizes the melt by forming bonds with at least some of the network-forming cations. This has been supported spectroscopically in several studies (e.g., Takusaga, 1980; Kohn et al., 1991; Schaller et al., 1992; Zeng and Stebbins, 2000; Kiczenski and Stebbins, 2002), indicating that Al-F bonding is predominant and that minor Si-F bonding is sometimes detectable. The addition of Cl^-, however, seems to have a relatively small effects on melt viscosities. In a recent study by Dingwell and Hess (1998), shear viscosities were determined in the system $Na_2Si_2O_5$ + Fe_2O_3 or $FeCl_3$. Substitution of two Cl^- for one O^{2--} causes a small increase in viscosity (relative to that observed for substitution of two F^- for each O^{2--} in the same system) in the high viscosity range and a slight decrease in the low viscosity range. Early work on the influence of Cl^- on the viscosities of low silica slags indicated a slight increase in viscosity (Hirayama and Camp, 1969), and measurements on an NaCl-saturated $NaAlSi_3O_8$ melt at 1.5 GPa indicated as well a higher viscosity than the Cl-free composition (Baker and Vaillancourt, 1995). Regardless, Cl^- generally seems to have a much smaller effect on viscosity than does F^-, which is sensible in light of our conclusion that Al-Cl or Si-Cl bonding is not common in these glasses. We note however, that in Al-free glasses, Cl^-, like F^-, is primarily coordinated by network modifier cations, and in that sense the two halides are analogous.

4.2. Mixed-Cation Ca- and Na-Silicate Glasses

In mixed Ca/Na, Na/K, and La/Na silicate glasses, a strong tendency for F^- to be preferentially coordinated by the higher field strength modifier cation was recently observed by ^{19}F NMR (Stebbins and Zeng, 2000). In Mg/K silicate glasses, a strong ordering of Mg^{2+} around the nonbridging oxygens has been detected by ^{17}O NMR (Allwardt and Stebbins, 2004), while in contrast a preference for mixed Ca + Na environments over a random distribution has been reported (Lee and Stebbins, 2003). Chloride solubility studies have suggested that divalent modifier cations are even more effective than alkalis in dissolving chloride in multicomponent melts (Webster and De Vivo, 2002). These results prompted the experiments reported here on ^{35}Cl NMR of mixed Na/Ca glasses.

An initial look at the spectra of these samples shows that the mixed-cation glasses have intermediate chemical shifts between the end member glasses (Fig. 7), suggesting that most Cl^- is in a mixed-cation environment, as opposed to having only exclusively Ca- or Na-coordination and indicating that deviation from random cation mixing around Cl^- is not ex-
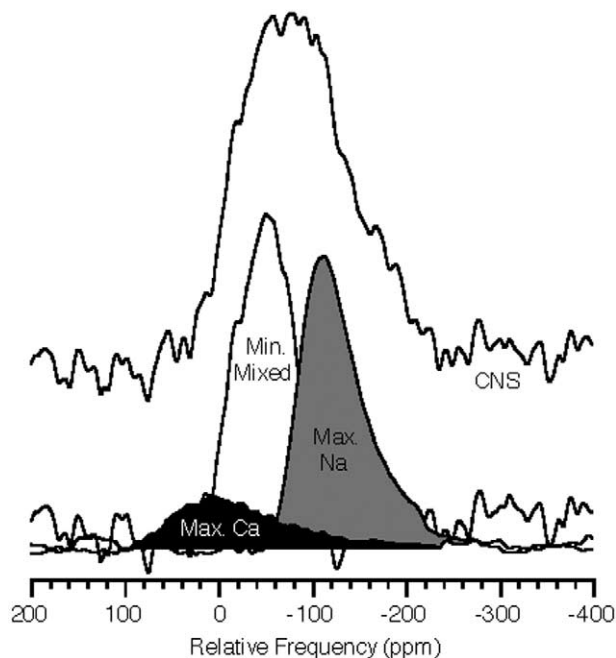
Fig. 10. Method used to estimate Cl⁻ speciation in glasses containing both Ca^{2+} and Na^+ as described in the text, for 18.1 T data. The original spectrum (sample CNS) has been offset for clarity.
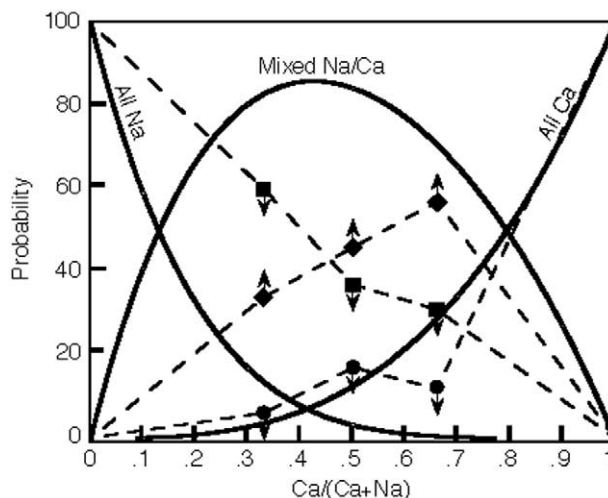

Fig. 11. Model of random mixing of Na^+ and Ca^{2+} around Cl⁻ sites in Na/Ca silicate glasses and comparison to experimentally estimated limits on species concentrations. Data points show speciation data estimated as described in the text and as illustrated in Figure 10. Circles mark maximum experimental fraction of Cl⁻ sites with "all Ca" coordination, squares mark maximum fraction of Cl⁻ sites with "all Na" coordination, and diamonds mark minimum fraction of Cl⁻ sites with mixed Na/Ca coordination. Arrows indicate the direction of allowed variation from these estimates. Dashed lines are guides to the eye only. Solid lines show theoretical fractions of various types of Cl⁻ sites.

treme. A more quantitative analysis of the set of spectra is inherently model-dependent and thus nonunique, but may still provide some useful guidelines for future experimental studies. Because the NMR peaks shapes even for the end member glasses are nongaussian due to distributions of structural parameters and to quadrupolar broadening, rather than fitting the data in a conventional way we take the following simple approach. We first assume that the spectra for the end members represent the contributions from the "all-Na" or "all-Ca" environments for the mixed compositions. This is a reasonable, if rough approximation, as for many better-studied nuclides, the identity and number of first neighbors has the largest effect on the chemical shift and C_Q, generally outweighing longer-range effects such as those of the second atom neighbor, bond angles, etc. As shown in Figure 10, the end member spectra (labeled "Max. Ca" and "Max. Na"), were scaled such that when subtracted from the intermediate composition spectra (e.g., CNS) the difference spectrum (labeled "Min. Mixed") remained positive within the noise level. These peak intensities thus estimate the maximum fractions of such "end-member" Cl⁻ sites in the mixed cation glasses. The resulting difference spectrum is then assumed to represent the Cl⁻ in "mixed coordination" environments, that is, Cl⁻ coordinated by both Na^+ and Ca^{2+}. The calculated "Min. Mixed" peak area thus represents the *minimum* amount of Cl⁻ in such environments. Following this procedure for the spectra of glasses of intermediate composition collected at both 14.1 and 18.8 T (Fig. 11) makes it clear that a large portion of the Cl⁻ in these samples must be in mixed coordination environments. This again suggests no strong preference for Cl⁻ groups with either all-Na or all-Ca neighbors.

A theoretical mixing model assuming that the probability of Cl⁻ being coordinated by Ca^{2+} or by Na^+ is random was

devised for comparison with the experimental data (Fig. 11). The model assumes that Cl⁻ is coordinated by 3 Ca^{2+}, 6 Na^+, or an intermediate mixture of Ca^{2+} and Na^+. The "all Na" and "all Ca" coordination numbers are based on the crystalline NaCl and CaCl₂. Mixed coordination environments of 1 Ca^{2+} 4 Na^+ and 2 Ca^{2+} 2 Na^+ were assumed for the intermediate compositions. A alternate model could be generated in which Cl⁻ is always coordinated by 6 cations (e.g., 6 Ca^{2+} or 3 Ca^{2+} 3 Na^+) but would result in locally excess positive charge, which seems unrealistic. Comparison of this model with the estimated ranges of speciation (Fig. 11) suggests the possibility of some preference for Cl⁻ to coordinate with Na^+ over Ca^{2+}, as in the highest Ca sample the allowable "all-Ca" intensity falls below the theoretical curve. However, this somewhat tentative finding is difficult to relate in detail to previous solubility studies, as the compositional ranges explored are generally distinct. This approach does hold promise for both future spectroscopic and phase equilibrium studies on identical compositions.

4.3. Hydrous Aluminosilicate Glasses

It has been suggested that the addition of Cl⁻ lowers the solubility of H₂O in granitic melts (Webster, 1992; Hedenquist et al., 1998), and that the addition of H₂O lowers the solubility of Cl⁻ in similar systems (Webster et al., 1999). The later could happen simply because of dilution of Cl⁻ in the volatile phase in equilibrium with the silicate melt, or because of effects of H₂O in the melt on the activity of cations that coordinate Cl⁻ (e.g., Na^+ and Ca^{2+}). It has also been suggested that silicate melt phase Cl⁻ may be coordinated primarily by H^+ in the systems albite-quartz-H₂O-HCl and orthoclase-quartz-H₂O-

HCl because Cl$^-$ solubility seems to be relatively independent of the presence of K$^+$ or Na$^+$ (Kravchuck and Kepler, 1994), and also by comparisons drawn to the speciation of F$^-$ in comparable melts (e.g., Burnham, 1979). In hydrated crystalline phases, Cl$^-$ is primarily coordinated by molecular H$_2$O. These observations, which indirectly hint at Cl$^-$ speciation, lead to our investigation of the effects of H$_2$O on Cl$^-$ speciation.

Recent data on a series of hydrated crystalline chlorides of Al^{3+}, Mg^{2+}, and Ca^{2+} give ^{35}Cl chemical shifts within a narrow range from ~25 to 50 ppm with respect to aqueous Cl$^-$ (Skibsted et al., 2001). In these phases, Cl$^-$ is coordinated primarily by molecular H$_2$O. This relatively tight cluster of ^{35}Cl chemical shifts suggests that if a large fraction of the Cl$^-$ in the hydrous glasses studied here was coordinated directly by H$_2$O we should see added intensity in the spectra in this general chemical shift range. However, that is not observed.

In the Na-aluminosilicate glasses, with increasing H$_2$O content there is a moderate shift to higher frequency NMR signal (Fig. 8). This change (~35 ppm) is much less than would be expected if Cl$^-$ coordination was changing from primarily Na$^+$ to primarily H$_2$O. The observed shift suggests instead that Cl$^-$ is not predominantly directly associated with H$_2$O, and rather undergoes a relatively minor change in its local coordination environment (e.g., coordination number by Na$^+$) due to perturbation of the network structure by the H$_2$O or as an indirect consequence of known H$_2$O-Na$^+$ interactions (Kohn et al., 1989). The ^{35}Cl MAS NMR spectra of the Ca-aluminosilicate glasses show no observable change in chemical shift or line shape (Fig. 9) with increasing H$_2$O content, again suggesting no significant change in the Cl$^-$ coordination environment and little to no direct interaction between Cl$^-$ and H$_2$O. For both the Na-aluminosilicate and the Ca-aluminosilicate compositions, the most water-rich samples contain more than enough H$_2$O to coordinate all Cl$^-$ by H$^+$ or H$_2$O if there were a strong energetic preference for such bonding.

Mean C_Q values for the hydrous glasses are constant within error for samples of comparable compositions, independent of the amount of H$_2$O present (Table 2), again suggesting that Cl$^-$ is not directly associated with H$_2$O. Quantification of the total ^{35}Cl NMR signal in these spectra as described above also indicates that there are not large populations of Cl$^-$ with anomalously large C_Q's in the hydrous glasses, at least when compared to their anhydrous equivalents.

Based on the present data, the presence of H$_2$O probably does not directly affect the dissolution mechanisms of Cl$^-$ in Ca- or Na-aluminosilicate melts, at least not by causing radical changes in its average local chemical environment. It has been shown that in aluminosilicate melts (basalt, andesite, latite) in equilibrium with a vapor, hydrosaline liquid, or both, the maximum concentration or solubility of Cl$^-$ present in the melt phase decreases with increasing H$_2$O content of fluid saturated melt (e.g., Webster et al., 1999). The NMR results suggest that the effects of water (H$_2$O or OH$^-$) on Cl$^-$ solubilities in these glasses may be indirect, and any changes in Cl$^-$ speciation or solubility are mainly a result of the overall structure of the glass changing or a decrease in the activity of Cl$^-$ in the melt through dilution of Cl$^-$ by H$_2$O in the coexisting second phase. This result does seem to potentially simplify the problem of predicting the behavior of volatiles (chlorides and H$_2$O) in these

systems. The main factor affecting Cl$^-$ coordination in these melts is probably the identity and concentration of the network modifier cations, e.g., Na$^+$ and Ca^{2+} in this study. Other elements in the melt (e.g., Al^{3+} or H$_2$O) seem to have minor direct effects on the dissolution mechanisms of Cl$^-$ in these melts and glasses. Other modifier cations common in natural magmas (e.g., Mg^{2+}, K$^+$, etc.) are likely to play roles similar to Na$^+$ and Ca^{2+}, and this is consistent with interpretations of prior volatile solubility experiments (Webster and De Vivo, 2002).

4.4. Intermediate Range Structure

In this paper, we have focused on the local coordination environments of chloride ions in a variety of silicate and aluminosilicate melts, as this information is most apparent in the NMR spectra and is probably most relevant to changes with melt composition in the activity coefficient for Cl$^-$ in these systems, and hence to solubility. However, longer-range aspects of the structure may have fundamental importance for some melt properties, such as viscosity and diffusivities. For example, Cl$^-$ could be primarily concentrated in Cl-rich domains (presumably too small to behave as a separate "phase"), with the coordinating modifier cations predominantly surrounded by other Cl$^-$. Given the low total Cl$^-$ contents of most silicate glasses, documenting such intermediate-range structure may be difficult. In such a case, however, dissolved alkali or alkaline-earth chlorides might be expected to behave primarily as neutral "space fillers" and to not strongly affect bulk melt properties. In contrast, chloride ions could be dispersed throughout the melt network, such that their coordinating cations are themselves primarily coordinated by bridging or nonbridging oxygens linked in turn to Si or Al. Such a scenario would of course have a major affect on the mixing entropy of the Cl$^-$, but could also lead to significant effects in bulk properties as well, albeit limited by low total Cl$^-$ contents. In this case, each Cl$^-$ ion would effectively be replacing one half of an oxide ion. Because the Cl$^-$ is primarily not bonded to Si or Al, to maintain charge balance one nonbridging oxygen (NBO) would have to be converted to a bridging oxygen, or, in the case of melts with very few NBO (e.g., "tectosilicate" compositions), "triclusters" of three tetrahedra could form (Baker, 1995). In either case, an actual increase in viscosity could result, as has been measured in a few systems and explained by a similar structural mechanism (Baker, 1995). Very recent studies of fluoride-containing silicate glasses, where F-F interactions can be detected by NMR, suggest that fluoride-rich, intermediate-scale aggregations occur only in glasses with the highest field strength modifying cations (e.g., La^{3+}). In these Al-free systems, as in the chloride-containing glasses described here, most of the F$^-$ bonding is to network modifier cations. However, whether or not fluoride and chloride behave analogously with respect to intermediate-range structure remains to be seen in future studies.

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