

LETTERS

Chloride ion sites in silicate and aluminosilicate glasses: A preliminary study by ^{35}Cl solid-state NMR

JONATHAN F. STEBBINS* AND LIN-SHU DU

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.

ABSTRACT

Despite the importance of the chloride ion in magmas and the fluids that separate from them, very little is known about atomic-scale structural environments for Cl^- in silicate glasses. We present here the first solid-state ^{35}Cl NMR data for Cl in silicate and aluminosilicate glasses, made possible by the availability of very high (14.1 to 18.8 Tesla) magnetic fields. We find that ^{35}Cl has a wide range in chemical shifts that correlate well with cation-Cl distance and thus contain considerable structural information. In general, Cl is coordinated primarily by network-modifying alkali or alkaline earth cations, and we see no evidence for Al-Cl bonding.

INTRODUCTION

Chlorine, largely in the form of HCl and volatile metal chlorides, is a significant minor component of fluids that form during the degassing of magmas (Carroll and Webster 1994), and in some cases is abundant enough to lead to the formation of a third liquid phase (hydrous molten salt or brine) during differentiation. The importance of the solubility of chloride in silicate melts has led to numerous studies of both natural and synthetic systems (see Webster et al. 1999 and Signorelli and Carroll 2000 for reviews). Recent work has suggested, for example, that melt composition has major effects, with alkaline earth network modifiers being particularly effective at increasing solubility, followed by alkali cations (Webster and De Vivo, unpublished manuscript). Some kind of preferential bonding interactions in the melt may thus be implied. Reduced solubility as the ratio of modifier cations to Al approaches the metaluminous join (e.g., where $\text{Na}/\text{Al} = 1$), and as silica activity increases (Webster and De Vivo, unpublished manuscript), suggest as well that Al-Cl and Si-Cl bonding is relatively unimportant. The latter may also be indicated by the low stability toward volatilization and hydration of AlCl_3 and SiCl_4 compared to NaCl, KCl, BaCl_2 , etc. Chloride is also a critical component of photochromic borosilicate glasses doped with silver and copper halides, which have seen widespread use in sunglasses and more exotic optical components (Araujo 1998).

Despite such interest, direct, atomic-scale information about Cl⁻ bonding environments in silicate glasses (which are assumed to represent the structure of the melt at the glass transition temperature) is almost non-existent. Solid-state ^{35}Cl NMR offers considerable potential for providing some of the first clues about at least the first-neighbor coordination environment, but is technically challenging (see Smith 2000 for review). Although the

nuclide comprises 75% of natural Cl, its resonant frequency is well below those of most commonly studied nuclides in silicates, such as ^{27}Al , ^{29}Si , and even ^{17}O . With a nuclear spin of 3/2 and a relatively large nuclear quadrupolar moment, this means that NMR peaks can be severely broadened, and, in the case of highly asymmetric bonding environments as found in organic compounds, may be unobservable. The exception to this difficulty has been early work on halides with cubic Cl^- sites and hence no quadrupolar broadening, which revealed a large range in isotropic chemical shift (δ_{iso}) that correlated well with cation-chloride bond distance (Weeding and Veeman 1989; Lefebvre 1992). With the development of NMR spectrometers operating at very high magnetic fields (e.g., 14.1 and 18.8 Tesla), ^{35}Cl NMR has begun to be explored in a greater range of inorganic and organic solids (Bryce et al. 2001; Skibsted et al. 2001). A recent study of perchlorates demonstrated the relationship between the quadrupolar coupling constant (C_Q) and crystal structure (Skibsted and Jakobsen 1999), and ^{35}Cl NMR on hydrocalumite [$\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$] and hydrotalcite (in both of which Cl^- is coordinated by H_2O) revealed interesting changes in dynamics with temperature (Kirkpatrick et al. 1999).

In the preliminary study reported here, we have chosen a few simple silicate glass compositions where Cl⁻ coordination environments can be directly compared to known crystalline model compounds. We find that ^{35}Cl MAS NMR spectra are readily obtainable at fields of 14.1 and 18.8 T even in samples with <1% Cl, and contain considerable structural information.

EXPERIMENTAL METHODS

Sample synthesis

The identity of a natural sample of sodalite [$\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$] was checked by X-ray diffraction. Crystalline NaCl, CsCl, and $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ reagents were dried at 300 °C, the latter transforming to orthorhombic BaCl_2 (confirmed by XRD). Cl-free base glasses NS ($\text{Na}_2\text{Si}_3\text{O}_7$), Ab ($\text{NaAlSi}_3\text{O}_8$), and NAS

* E-mail: stebbins@pangea.stanford.edu

($\text{Na}_3\text{AlSi}_6\text{O}_{15}$) were described previously (George and Stebbins 1996). BaSi_2O_5 glass (BS) was synthesized from BaCO_3 and SiO_2 by melting for about 2 h at 1510 °C. $\text{Cs}_2\text{Si}_4\text{O}_9$ (CsS) glass was made by combining dried Cs_2CO_3 and SiO_2 , decarbonating at 700 °C for 18 h, then melting at 1190 °C for 2 h. A glass containing about 4.7 wt% Al_2O_3 (CsAS) was then made by melting some of the CsS glass with alumina at 1600 °C. All glasses except NS and NAS were doped with about 0.2 wt% cobalt oxide to speed spin-lattice relaxation. Chloride was added to the base glasses by combining 5 wt% BaCl_2 with BS (at 1500 °C), 5 wt% NaCl with NS and NAS (950 °C), 1.5 wt% NaCl with Ab (1315 °C), and 5 wt% CsCl with CsS (1190 °C) and CsAS (1600 °C) in Pt tubes, followed by drying, welding, and melting with negligible weight loss (see Table 1 for sample labels). After quenching, only sample NS + Cl showed obvious inclusions of a salt phase in the glass, but other samples may have contained residual salts as vapor-deposited films on the capsule walls. Nominal sample total compositions (glass + residual salts) are given in Table 1 along with approximate Cl contents measured by electron microprobe. Difficulties in analysis of the high-alkali (and the case of CsS, quite hygroscopic) glasses, combined with the possibility of supersaturation with the salts during melting or quench (leading to mixed-phase samples), make assessment of the exact final glass compositions difficult, but the microprobe data do indicate that substantial fractions of the Cl were excluded from some of the glasses, especially in the Al-containing samples (Table 1). CsAS retained a particularly low fraction of the added Cl, possibly because of its high synthesis temperature.

NMR experiments

Solid-state ^{35}Cl NMR spectra were collected on Varian Unity/INOVA 600 (14.1 Tesla) and Varian Unity/INOVA 800 (18.8 T) spectrometers at 58.8 and 78.4 MHz, respectively. Chemical shifts are expressed relative to 1 M aqueous NaCl at 0 ppm. Chemagnetics T3-type probes with 3.2 mm ZrO_2 rotors, capable of spinning up to 24 kHz, were used at both fields. To avoid the loss of broad NMR signals in instrumental dead time, spectra were obtained using a spin echo pulse sequence optimized for quadrupolar nuclides (Kunwar et al. 1986) with

radiofrequency (rf) power of 87 and 63 kHz at 14.1 and 18.8 T, respectively. The solution $\pi/4$ and $\pi/2$ pulse lengths (1.4 and 2.8 μs for 14.1 T and 2.2 and 4.4 μs for 18.8 T) were chosen as the first and second pulses. Relaxation delays from 0.05 to 0.5 s were tested. The number of transients was 100 000 for the spectra collected at 14.1 T and 80 000 to 360 000 at 18.8 T. Central transition peak shapes of the spectrum for BaCl_2 were simulated using the Varian STARS software package. Centers of gravity of peaks for the glasses were determined by integration.

Because of the relatively low concentration of Cl in the samples, the low resonant frequency for ^{35}Cl , and the breadth of the NMR peaks for the glasses, obtaining usable signal-to-noise ratios was non-trivial even at 18.8 T. All of the glass samples (except for the Co-free NAS + Cl) showed optimal signal-to-noise ratios with very short relaxation delays of 0.05 s (0.5 s for NAS + Cl). However, the ^{35}Cl in the crystalline portions of some of the samples (which probably contained much lower levels of Co) relaxed as much as 10 to 100 times slower, making difficult the simultaneous, accurate observation of the crystalline and glassy phases; in experiments with delay times long enough to quantitatively observe the peaks for the crystalline portions of the samples, signal-to-noise ratios for the glassy components were poor.

RESULTS

As previously reported (Weeding and Veeman 1989; Lefebvre 1992; George 1997), the ^{35}Cl MAS NMR peaks for CsCl (110 ppm), NaCl (−46 ppm), and sodalite (−124 ppm) are very narrow (<1 ppm) and featureless, as expected from the cubic point symmetry of their Cl^- sites; in such cases the electric field gradients and quadrupolar coupling constants are zero ($C_Q = 0$). Their chemical shifts decrease markedly and progressively with decreasing cation-anion bond distance (0.348, 0.282, and 0.270 nm, respectively) as previously noted for alkali chlorides (Weeding and Veeman 1989). In halite, the Cl^- ion is coordinated by six Na^+ ions; in the framework aluminosilicate sodalite, Cl^- ion in the “cages” is coordinated by a perfect tetrahedron of four Na^+ ions (Hassan and Grundy 1984). The large difference between δ_{iso} for halite and sodalite thus also indicates a significant effect of bond distance and/or Cl

TABLE 1. Glass sample compositions and NMR results

Label	Starting material	wt% Cl		peak, 18.8 T* ppm ± 5	Δ c.o.g.† ppm ± 3	est. δ_{iso} ‡ ppm ± 10
		nom.	meas.§			
Glasses						
NS + Cl	$\text{Na}_2\text{Si}_2\text{O}_7$ + 5 wt% NaCl	3.0	2.7	−105	15	−77
NAS + Cl	$\text{Na}_3\text{AlSi}_6\text{O}_{15}$ + 5 wt% NaCl	3.0	1.1	−104	—	—
Ab + Cl	$\text{NaAlSi}_3\text{O}_8$ + 1.5 wt% NaCl	0.91	0.5	−135	—	—
CsS + Cl	$\text{Cs}_2\text{Si}_4\text{O}_9$ + 5 wt% CsCl	1.1	0.6	98	10	127
CsAS + Cl	$95\text{Cs}_2\text{Si}_4\text{O}_9 \cdot 5\text{Al}_2\text{O}_3$ + 5 wt% CsCl	1.1	0.05	110 ± 10	—	—
BS + Cl	BaSi_2O_5 + 5 wt% BaCl_2	1.7	1.5	113	15	143
Crystals						
NaCl						-46 ± 1
Sodalite						-124 ± 1
CsCl						110 ± 1
BaCl_2						124 ± 5
						219 ± 5

* Peak maximum at 18.8 T.

† Change in center of gravity of glass peak from 14.1 to 18.8 T.

‡ Mean isotropic chemical shift estimated from c.o.g. at 18.8 T and Δ c.o.g.

§ Electron microprobe, $\pm 20\%$ relative.

coordination number for a fixed neighbor cation, as predicted by a previous correlation of δ_{iso} with the ratio of cation electronegativity to coordination number (Weeding and Veeman 1989).

The spectrum for orthorhombic BaCl_2 is more complex, as expected from the lower symmetry of its two distinct Cl^- sites, one with four and the other with five Ba^{2+} neighbors, with mean $\text{Ba}-\text{Cl}$ distances of 0.309 and 0.337 nm respectively (Brackett et al. 1962). The spectrum is dominated by two "doublets" with distinct second-order quadrupolar line shapes, that can be simulated with equal areas and the parameters given in Figure 1. A prominent (but small-area) third component appears in the form of a narrow peak centered at about 125 ppm. This may be due to the presence of a small amount of a metastable cubic polymorph of BaCl_2 that can form during dehydration of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Haase and Brauer 1978). Because the multiplicities of the two Cl^- sites in BaCl_2 are the same, peak areas do not allow unique assignment of the spectrum, but it is likely that the higher frequency peak represents the site with higher coordination and longer bond distances.

The ^{35}Cl MAS NMR peaks for the glasses (Figs. 1, 2, and 3) are all featureless and roughly Gaussian in shape, with a suggestion of some extra intensity on the lower frequency sides as is commonly observed for quadrupolar nuclides (e.g., ^{27}Al) in glasses. In the spin-echo spectra for NS + Cl and Ab + Cl, significant amounts of crystalline NaCl were noted. In a one-pulse spectrum for CsS + Cl only (not shown), a small signal

for CsCl was observed; no peaks for crystalline phases were observed in spectra for NAS + Cl, CsAS + Cl, or BS + Cl. Full widths at half maxima for the broad, glass components of the spectra range from about 6 kHz for CsS + Cl (80 ppm at 18.8 T) to about 10 kHz for BS + Cl (130 ppm at 18.8 T). Because the contribution to these widths (in kHz) from the second-order quadrupolar coupling scales inversely with field, but that from the range of chemical shifts caused by disorder scales directly with field, the contribution from these two factors can be estimated from data at two fields (Schmidt et al. 2000). In all cases analyzed (Table 1), the latter broadening effect is about twice the former. The shift in the center of gravity of the peaks with field also allows mean C_Q values to be estimated at about 2.4 to 2.9 MHz (Table 1); similarly, mean δ_{iso} values can be estimated (Schmidt et al. 2000).

Accurate quantitation of signal intensities was made difficult by the inherently low signal-to-noise ratio of ^{35}Cl NMR spectra of samples with only a few wt% Cl, by the presence of cubic crystalline phases ($C_Q = 0$) whose response to a spin-echo NMR experiment is different than those from lower symmetry sites ($C_Q > 0$) in the glasses, and by the inconveniently slow spin-lattice relaxation of these crystalline phases. Nonetheless, it is clear from comparison of intensities among various samples that there is no large fraction of Cl that is "invisible" because of much higher C_Q values, which could lead to peak broadening severe enough to be unobservable even at 18.8 T.

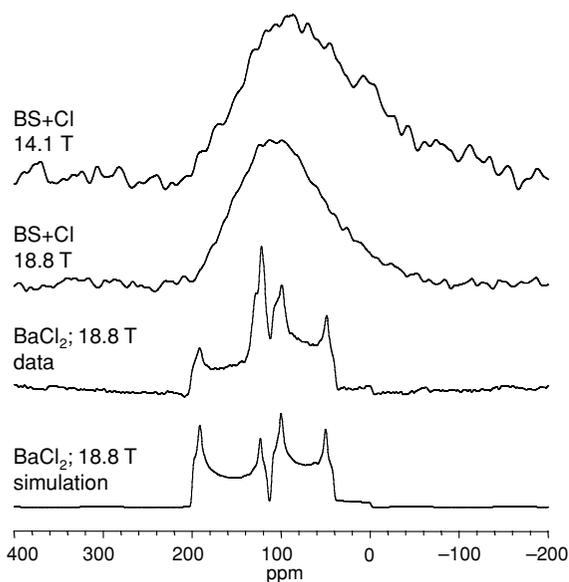


FIGURE 1. ^{35}Cl MAS NMR spectra of crystalline BaCl_2 and a Cl-containing Ba silicate glass (see Table 1). The simulation of the BaCl_2 spectrum was made with two sites (ignoring the narrow impurity peak centered at about 124 ppm), with δ_{iso} , C_Q , and η equal to 124 ± 5 ppm, 3.5 ± 0.1 MHz, and 0.15 ± 0.05 , and 219 ppm, 3.95 MHz, and 0.1 respectively.

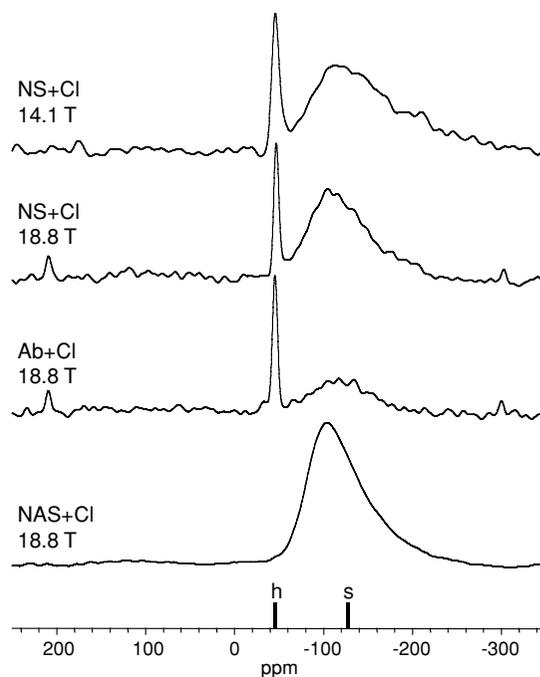


FIGURE 2. ^{35}Cl MAS NMR spectra of Cl-containing sodium silicate and aluminosilicate glasses (see Table 1). The narrow peaks at -46 ppm are from crystalline NaCl; peak positions obtained for pure samples of halite and sodalite are marked by "h" and "s".

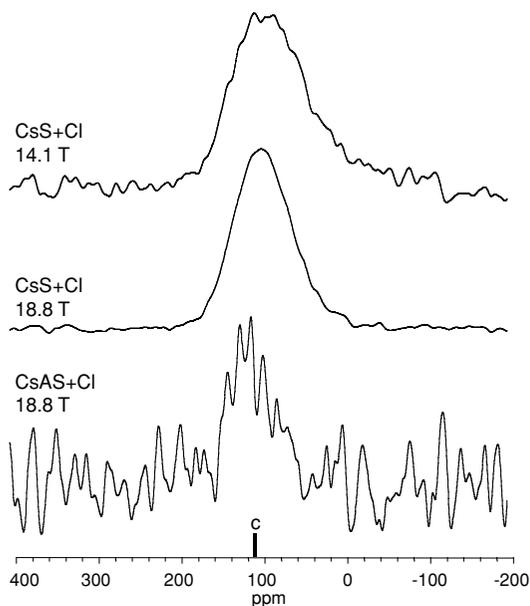


FIGURE 3. ^{35}Cl MAS NMR spectra of Cl-containing cesium silicate and aluminosilicate glasses (see Table 1). The peak position measured for pure crystalline CsCl is marked by “c.”

DISCUSSION

Chemical shift systematics

The strong dependence of ^{35}Cl chemical shift on the cation-chloride distance (i.e., on cation size), and the related trend with Cl coordination number, are qualitatively similar to those seen for other anions in inorganic materials, most notably ^{19}F in fluorides, fluorosilicates, and aluminofluorides (Stebbins and Zeng 2000; Kiczinski and Stebbins 2001), and ^{17}O in simple oxides (Turner et al. 1985) and in non-bridging oxygen sites in silicates (Florian et al. 1996; Stebbins et al. 1997). The observed *increases* in δ_{iso} with bond distance for these anions are the inverses of the *decreases* in δ_{iso} with increasing bond distance (and/or coordination number) that are well established for many cations in oxides and silicates, for example ^6Li , ^{11}B , ^{23}Na , ^{25}Mg , ^{27}Al , ^{29}Si , ^{39}K , and ^{43}Ca (Stebbins 1995; Dupree et al. 1997; George and Stebbins 1998; Stebbins 1998; Stebbins et al. 2001). The latter trends are probably related to increased ionicity, and accompanying increase in net positive charge, on the cation with increasing first-neighbor bond distance (Engelhardt and Michel 1987). For the anions, a corresponding increase in ionicity produces a *decrease* in net positive charge (i.e., an increased negative charge) and hence should contribute to the inverted chemical shift trends as observed. Much experimental and theoretical work remains to be done on δ_{iso} for ^{35}Cl , but its wide range of chemical shifts clearly can provide considerable structural information even in systems where Cl is a minor component.

Coordination of chloride ions in silicate glasses

Given that the widths of the ^{35}Cl peaks in the glasses are dominated by distributions of δ_{iso} , it is clear that there is some disorder of cation-chloride bond distances and possibly of Cl⁻ coordination numbers. However, to a first approximation, these ranges are similar to those in the corresponding crystalline phases where Cl⁻ is coordinated only by alkali or alkaline-earth cations. The relatively high symmetry of these types of environments is also reflected in the modest values estimated for C_Q for the Cl⁻ sites in the glasses (about 2 to 3 MHz), as this parameter measures the divergence from spherical symmetry in the local electric field gradient (C_Q can be greater than 70 MHz for highly asymmetrical environments such as those in carbon-chlorine bonds; Bryce et al. 2001). In more detail, mean δ_{iso} values in the Na-containing glasses seem to lie between those of crystalline NaCl (six Na neighbors) and sodalite (four Na neighbors), suggesting that the coordination of the Cl⁻ ion in the glass may be lower than that in a coexisting crystalline salt phase or NaCl-rich “brine.” This may imply a molar volume increase for NaCl on dissolution in the melt that could be related to an apparent negative dependence of solubility on pressure observed in some experiments on silicic magmas compositions (Signorelli and Carroll 2000), although these are generally complicated by the presence of H₂O.

The similarity of ^{35}Cl peak positions in the Al-free and Al-containing Na and Cs glasses suggests that most of the Cl⁻ ions in the latter are also coordinated only by the alkali cations. The lack of separate peaks that could be attributed to Cl atoms bonded to Al (or to Si) atoms supports this observation. However, as yet there are no data to allow prediction of the chemical shifts for such species, and it is also possible that such sites could have large C_Q values and could thus be difficult to observe. NMR studies of compounds such as AlCl₃ and NaAlCl₄ could answer these questions but are challenging because their extreme moisture sensitivity. Such caveats aside, the apparent lack of Al-Cl bonding in glasses is in marked contrast to what is observed for F⁻ in aluminosilicate glasses, where F sites with one Al and several alkali or alkaline earth cation neighbors are predominant (Zeng and Stebbins 2000). The apparent strong interactions between Cl⁻ and mono- and divalent network modifier cations may in turn be related to the minima in chloride solubilities observed as Na/Al approaches 1 (Webster et al. 1999). The latter effect is in turn reflected in the relatively low Cl contents of our Al-containing samples, although these experiments were not designed to measure solubilities.

Another question that may be straightforward to address in future ^{35}Cl NMR studies is the structural role of H₂O in the solubility of chloride in silicate melts, which is of obvious importance in models of the degassing of magma systems (Carroll and Webster 1994; Webster et al. 1999; Signorelli and Carroll 2000). A recent report on a variety of inorganic chloride hydrates, in which the Cl⁻ ion is coordinated only by H⁺ ions in H₂O molecules, revealed a narrow range of δ_{iso} from about 25 to 50 ppm (relative to aqueous NaCl; Skibsted et al. 2001) that is likely to be quite distinct from those for Cl⁻ coordinated to network modifier cations. Finally, the question of preferential coordination of Cl⁻ by alkaline earth vs. alkali cations, as sug-

gested by solubility data (Webster and De Vivo, unpublished manuscript), should be possible to evaluate by ^{35}Cl NMR in mixed-cation glasses.

ACKNOWLEDGMENTS

We thank J. Puglisi for access to the 18.8 T spectrometer in the Stanford Magnetic Resonance Laboratory, R. Jones for microprobe data collection, J. Webster and J. Lowenstern for helpful discussions of chloride solubility, and J. Webster and D. Bryce for useful preprints. This research was supported by NSF grant no. EAR 9803953.

REFERENCES CITED

- Araujo, R. (1998) Influence of host glass on precipitation of cuprous halides. *Journal of Non-Crystalline Solids*, 223, 53–56.
- Bryce, D.L., Gee, M., and Wasylishen, R.E. (2001) High-field chlorine NMR spectroscopy of organic hydrochloride salts: a sensitive probe of hydrogen bonding environment. *Journal of Physical Chemistry A*, 105, 10413–10421.
- Brackett, E.B., Brackett, T.E., and Sass, R.L. (1962) The crystal structures of barium chloride, barium bromide, and barium iodide. *Journal of Physical Chemistry*, 67, 2132–2135.
- Carroll, M.R. and Webster, J.D. (1994) Solubilities of sulfur, noble gases, nitrogen, chlorine, and fluorine in magmas. In M.R. Carroll and J.R. Holloway, Eds., *Volatiles in Magmas*, p. 231–280. Mineralogical Society of America, Washington, D.C.
- Dupree, R., Howes, A.P., and Kohn, S.C. (1997) Natural abundance solid state ^{43}Ca NMR. *Chemical Physics Letters*, 276, 399–404.
- Engelhardt, G. and Michel, D. (1987) *High-Resolution Solid-State NMR of Silicates and Zeolites*, Wiley, New York, 485 p.
- Florian, P., Vermillion, K.E., Grandinetti, P.J., Farnan, I., and Stebbins, J.F. (1996) Cation distribution in mixed alkali disilicate glasses. *Journal of the American Chemical Society*, 118, 3493–3497.
- George, A.M. (1997) *The Structure and Dynamics of the Non-Network Forming Elements Sodium and Magnesium in Glassy and Molten Silicates: A High Temperature NMR Study*. Ph.D. Thesis, Stanford University.
- George, A.M. and Stebbins, J.F. (1996) Dynamics of Na in sodium aluminosilicate glasses and liquids. *Physics and Chemistry of Minerals*, 23, 526–534.
- (1998) Structure and dynamics of magnesium in silicate melts: a high temperature ^{25}Mg NMR study. *American Mineralogist*, 83, 1022–1029.
- Haase, A. and Brauer, G. (1978) Hydratstufen und Kristallstrukturen von Bariumchlorid. *Zeitschrift zur Anorganische und Allgemeine Chemie*, 441, 181–195.
- Hassan, I. and Grundy, W.D. (1984) The crystal structures of sodalite-group minerals. *Acta Crystallographica*, B40, 6–13.
- Kiczanski, T.J. and Stebbins, J.F. (2001) Fluorine-19 NMR results on crystalline models for fluoride sites in silicate and alkali silicate glasses and melts. *Eos, Transaction of the American Geophysical Union*, in press.
- Kirkpatrick, R.J., Yu, P., Hou, X., and Kim, Y. (1999) Interlayer structure, anion dynamics, and phase transitions in mixed-metal layered hydroxides: Variable temperature ^{35}Cl NMR spectroscopy of hydroxalcite and Ca-aluminate hydrate (hydrocalumite). *American Mineralogist*, 84, 1186–1190.
- Kunwar, A.C., Turner, G.L., and Oldfield, E. (1986) Solid-state spin-echo Fourier transform NMR of ^{39}K and ^{67}Zn salts at high field. *Journal of Magnetic Resonance*, 69, 124–127.
- Lefebvre, F. (1992) Etude par RMN du solide du chlore 35 et du chlore 37 de chlorures minéraux. *Journal de Chimie Physique*, 89, 1767–1777.
- Schmidt, B.C., Reimer, T., Kohn, S.C., Behrens, H., and Dupree, R. (2000) Erratum to Schmidt B.C., Reimer T., Kohn S.C., Behrens H., and Dupree R. (2000) Different water solubility mechanisms in hydrous glasses along the Qz-Ab join. Evidence from NMR spectroscopy. *Geochimica et Cosmochimica Acta*, 64, 2895–2896.
- Signorelli, S. and Carroll, M.R. (2000) Solubility and fluid-melt partitioning of Cl in hydrous phonolitic melts. *Geochimica et Cosmochimica Acta*, 64, 2851–2863.
- Skibsted, J. and Jakobsen, H.J. (1999) ^{35}Cl and ^{37}Cl magic-angle spinning NMR spectroscopy in the characterization of inorganic perchlorates. *Inorganic Chemistry*, 38, 1806–1813.
- Skibsted, J., Andersen, M.D., Jensen, O.M., and Jakobsen, H.J. (2001) High-field ^{35}Cl NMR investigation of chloride ions in inorganic solids. A variable-temperature ^{27}Al and ^{35}Cl MAS NMR study of the phase transition in Friedel's salt ($\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$). 43rd Rocky Mountain Conference on Analytical Chemistry, Abstracts, 43, 120.
- Smith, M.E. (2000) Recent progress in solid-state NMR of low- γ nuclei. *Annual Reports on NMR Spectroscopy*, 43, 121–175.
- Stebbins, J.F. (1995) Nuclear magnetic resonance spectroscopy of silicates and oxides in geochemistry and geophysics. In T. J. Ahrens, Eds., *Handbook of Physical Constants*, p. 303–332. American Geophysical Union, Washington D.C.
- (1998) Cation sites in mixed-alkali oxide glasses: correlations of NMR chemical shift data with site size and bond distance. *Solid State Ionics*, 112, 137–141.
- Stebbins, J.F. and Zeng, Q. (2000) Cation ordering at fluoride sites in silicate glasses: a high-resolution ^{19}F NMR study. *Journal of Non-Crystalline Solids*, 262, 1–5.
- Stebbins, J.F., Oglesby, J.V., and Xu, Z. (1997) Disorder among network modifier cations in silicate glasses: new constraints from triple-quantum oxygen-17 NMR. *American Mineralogist*, 82, 1116–1124.
- Stebbins, J.F., Du, L.-S., Kroeker, S., Neuhoff, P., Rice, D., Frye, J., Jakobsen, H.J. (2001) New opportunities for high-resolution solid-state NMR spectroscopy of oxide materials at 21.1 and 18.8 Tesla fields. *Solid State Nuclear Magnetic Resonance*, in press.
- Turner, G.L., Chung, S.E., and Oldfield, E. (1985) Solid-state oxygen-17 nuclear magnetic resonance spectroscopic study of group II oxides. *Journal of Magnetic Resonance*, 64, 316–324.
- Webster, J.D., Kinzler, R.J., and Mathez, E.A. (1999) Chloride and water solubility in basalt and andesite melts and implications for magmatic degassing. *Geochimica et Cosmochimica Acta*, 63, 729–738.
- Weeding, T.L. and Veeman, W.S. (1989) Characterisation of the structure of inorganic chloride salts with chlorine solid state NMR. *Journal of the Chemical Society, Chemical Communications*, 1989, 946–948.
- Zeng, Q. and Stebbins, J.F. (2000) Fluoride sites in aluminosilicate glasses: high-resolution ^{19}F NMR results. *American Mineralogist*, 85, 863–867.

MANUSCRIPT RECEIVED OCTOBER 23, 2001

MANUSCRIPT ACCEPTED NOVEMBER 7, 2001

MANUSCRIPT HANDLED BY LEE A. GROAT