

Oxygen sites in silicate glasses: a new view from oxygen-17 NMR

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Abstract

Nuclear Magnetic Resonance (NMR) studies of ¹⁷O in silicate glasses is beginning to provide new information on structure from an “anionic” viewpoint, which is an important complement to more traditional discussions of cation coordination and connectivities. A variety of techniques are discussed here, but the most important recent advances have used the new, two-dimensional, high resolution techniques of Dynamic Angle Spinning (DAS) and Triple Quantum Magic Angle Spinning (3QMAS), which have resolved and distinguished peaks for bridging oxygens linking Si, Al and B cations, as well as non-bridging oxygens. These approaches have provided some of the first quantitative constraints on the extent of ordering, both among network modifier cations and among network former cations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Traditionally, most of our thinking about the structure of oxide glasses has been based on a “cation centric” view, in that the types of cation polyhedra and their interconnections are at least the starting, if not the ending point. While obviously useful (and taken for good historic and experimental reasons), this approach needs to be complemented by one that tells us about the structure in terms of the volumetrically and numerically most abundant ions in nearly all oxide glasses, i.e., oxygen itself. For example, the extent of Si–Al disorder in framework silicate glasses (and crystals) is most commonly

discussed in terms of pairs of cation tetrahedra, but perhaps more naturally can be viewed by “counting” Si–O–Si, Si–O–Al, and Al–O–Al sites directly.

In the last few years, ¹⁷O nuclear magnetic resonance (NMR) spectroscopy has begun to provide this viewpoint, giving detailed and, at times, highly quantitative information about oxygen coordination environments, and hence, going well beyond early attempts by other oxygen-specific methods such as X-ray photoelectron spectroscopy (XPS) (Hochella, 1988). The purpose of this contribution is to briefly summarize this work in for the geochemical community. We will not attempt a complete review, but rather will highlight a few interesting applications, point out a number of problems remaining to be solved, and present several new data sets.

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2. NMR techniques for ^{17}O in glasses

Readers are referred to original papers and to in-depth books and chapters for a detailed technical introduction to NMR spectroscopy (Chmelka and Zwanziger, 1994; Eckert, 1994; Engelhardt and Michel, 1987; Kirkpatrick, 1988; Popov and Hallenga, 1991; Stebbins, 1995). It is possible, however, to readily appreciate the different types of information that can be obtained on structure.

The natural isotopic abundance of ^{17}O (0.035%), as well as the relatively low NMR resonant (Larmor) frequency, mean that solid-state NMR studies of anything other than the most symmetrical of oxide sites requires isotopic enrichment, which places some limits on experimental possibilities. A few relatively early studies at low magnetic fields on stationary (“static”) samples showed that useful ^{17}O spectra could be obtained for SiO_2 and B_2O_3 glasses (Geissberger and Bray, 1983; Jellison et al., 1977), but most work has been done since about 1985, when high field magnets (8.4 to 11.3 T and above) and magic angle spinning (MAS) probes became routinely available. Both greatly reduce the broadening that results from the second order quadrupolar interaction, and enhance sensitivity and resolution.

Empirical calibrations of observed NMR parameters are generally required, through the study of crystalline phases of known structure. For example, the isotropic chemical shift (δ_{iso}), which for many nuclides has the clearest correlation with short-range structure, is well correlated for non-bridging oxygens (NBO) with the size and electronegativity of the first cation neighbors (Bastow and Stuart, 1990; Maekawa et al., 1996; Timken et al., 1987; Turner et al., 1985), as well as with the oxygen coordination number (Dirken et al., 1995; Xue et al., 1994). For more commonly observed nuclides with nuclear spin = 1/2, such as ^{29}Si , δ_{iso} directly controls the observed NMR peak position. However, for quadrupolar nuclides such as ^{17}O (spin = 5/2), peak positions and shapes are also affected by the interaction between the nucleus and the local electric field gradient. The quadrupolar coupling constant (C_Q), which measures the principle component of the tensor that describes this gradient at the site, and hence, scales with site distortion from spherical symmetry, is known from studies of bridging oxygens (BO) to be strongly

affected by the type of cation neighbor (B, Al, Si) (Dirken et al., 1997; Stebbins et al., 1999a; Timken et al., 1986; Wang and Stebbins, 1998; Wang and Stebbins, 1999; Xu et al., 1998) as well as the Si–O–Si bond angle (Farnan et al., 1992; Grandinetti et al., 1995; Maekawa et al., 1996; Xue and Kanzaki, 1998). Theoretical calculations have also proven to be very useful in interpreting spectra, particularly the relative effects of structure (coordination number, bond angle, etc.) on chemical shift and C_Q (Tossell, 1990; Tossell and Saghi-Szabo, 1997; Vermillion et al., 1998). NMR spectra can be highly quantitative, but for sites with large site asymmetries and large C_Q values (such as those predicted for Si–OH sites (Xue and Kanzaki, 1998), detection, let alone quantitation, can be difficult.

Both “static” and MAS spectra may be useful. The former approach is most applicable when large C_Q differences are present among sites, which is often the case for BO and NBO in alkali and alkaline earth silicates (Timken et al., 1987; Xue et al., 1994). As shown in Fig. 1, static ^{17}O spectra at

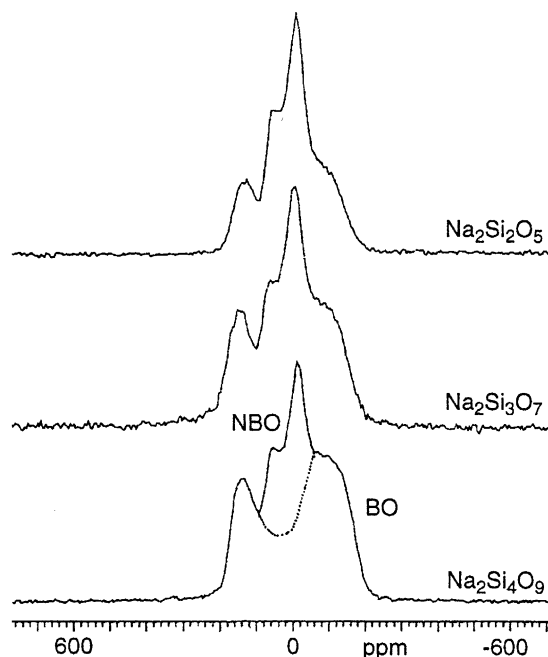


Fig. 1. Static ^{17}O NMR spectra of sodium silicate glasses, acquired using a “solid echo” technique (Xue et al., 1994). Narrow quadrupolar doublet is from non-bridging oxygens (NBO), broad doublet is from bridging oxygens (BO), which characteristically have a much higher C_Q .

intermediate magnetic fields (e.g., 9.4 T) may be dominated by quadrupolar line shapes, which are often characteristic of C_Q (and hence the identity of the site) but which obscure the distributions of parameters that provide clues about the extent of disorder. This approach also proved useful in the detection of changes in oxygen sites that accompanied the formation of five- and six-coordinated silicon in alkali silicate glasses quenched from melts at very high pressures (Xue et al., 1994), and in searching for the effects on NBO/BO ratios of adding water to silicate and aluminosilicate glasses (Maekawa et al., 1998; Xu et al., 1998). Detailed simulations of static (and MAS) ^{17}O NMR peak shapes have led to new information about distributions of oxygen sites in germanate glasses (Hussin et al., 1999; Hussin et al., 1998). In contrast, MAS will be most helpful when there are significant differences in δ_{iso} among site types, as is the case for BO vs. NBO in glasses with relatively large modifier cations, such as Ca^{2+} , Ba^{2+} , La^{3+} , etc. (Kirkpatrick et al., 1986; Schaller and Stebbins, 1998; Stebbins et al., 1997; Stebbins and Xu, 1997). Fig. 2 shows this resolution in Ba, Ca silicate glasses. Here, the peak shapes are close to Gaussian, but are still somewhat affected by the second-order quadrupolar broadening that cannot be removed by MAS. This figure also illustrates the relatively large effect of modifier cation on peak position for NBO (150 ppm in the Ba-silicate, 100 ppm in the Ca-silicate) and the small but measurable effect on that for BO (40 vs. 30 ppm). The latter indicates at least some interaction between BO and modifier cations, perhaps manifested as Si–O–Si bond angle changes.

Recently, several methods have been developed that have greatly enhanced the information content of ^{17}O NMR (as well as other quadrupolar nuclides such as ^{11}B , ^{27}Al and ^{23}Na). The most commonly used of these (Dynamic Angle Spinning or “DAS” and triple quantum MAS or “3QMAS”) produce two-dimensional spectra where one dimension contains peaks that are not broadened by the second order quadrupolar interaction (Amoureux et al., 1996; Baltisberger et al., 1996; Chmelka and Zwanziger, 1994; Fernandez and Amoureux, 1995; Frydman and Harwood, 1995; Grandinetti, 1995; Massiot et al., 1996; Samoson, 1995; Youngman et al., 1996). These “isotropic shifts” contain terms for both C_Q and δ_{iso} ,

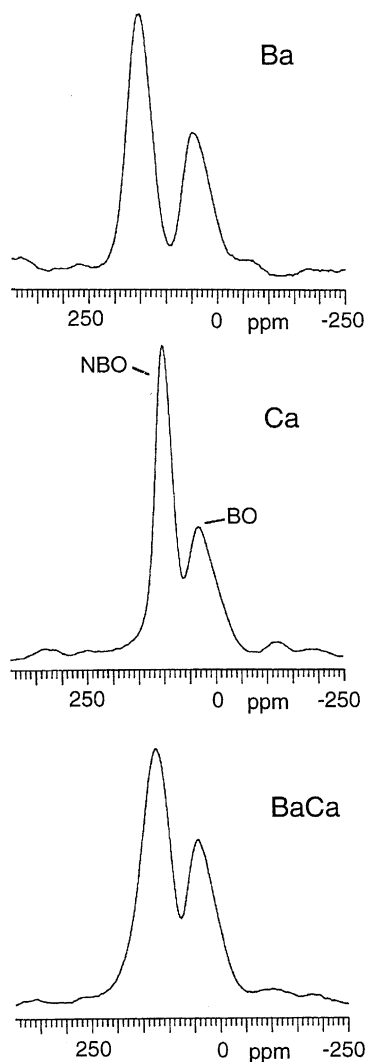


Fig. 2. ^{17}O MAS NMR spectra for $\text{Ca}_{0.45}(\text{SiO}_2)_{0.55}$ glass (“Ca”), $\text{Ba}_{0.45}(\text{SiO}_2)_{0.55}$ glass (“Ba”), and the composition half way between them (“BaCa”) (Stebbins et al., 1997).

and can be somewhat complex to interpret, but are correlated with data in the “anisotropic” dimension that help in extracting parameters. Resolution may be greatly enhanced, and isotropic peak widths are more directly related to distributions of NMR parameters and hence at least in a relative sense to the extent of structural disorder. DAS involves rapidly flipping the sample spinning angle back and forth between two or three orientations, and thus can be somewhat difficult to implement. It is however, relatively quantitative and useful results on ^{17}O in silicate glasses

have been obtained (Farnan et al., 1992; Stebbins et al., 1997; Florian et al., 1996). For example, Fig. 3 shows two-dimensional DAS spectra for a series of $(\text{K,Na})_2\text{Si}_2\text{O}_5$ glasses. In the pure-Na endmember, the BO and NBO peaks are partially overlapped, but, nonetheless, projections of the data in the isotropic dimension (Fig. 4) allow clear separation of the two types of sites, whose component peaks are close to

Gaussian in shape and reflect the degree of disorder (see below).

Triple-quantum MAS NMR is undergoing rapid development and has become popular because it does not require a special NMR probe. The somewhat daunting theory behind this approach is discussed in the references cited above. To summarize, the resolution-limiting, anisotropic effects that are

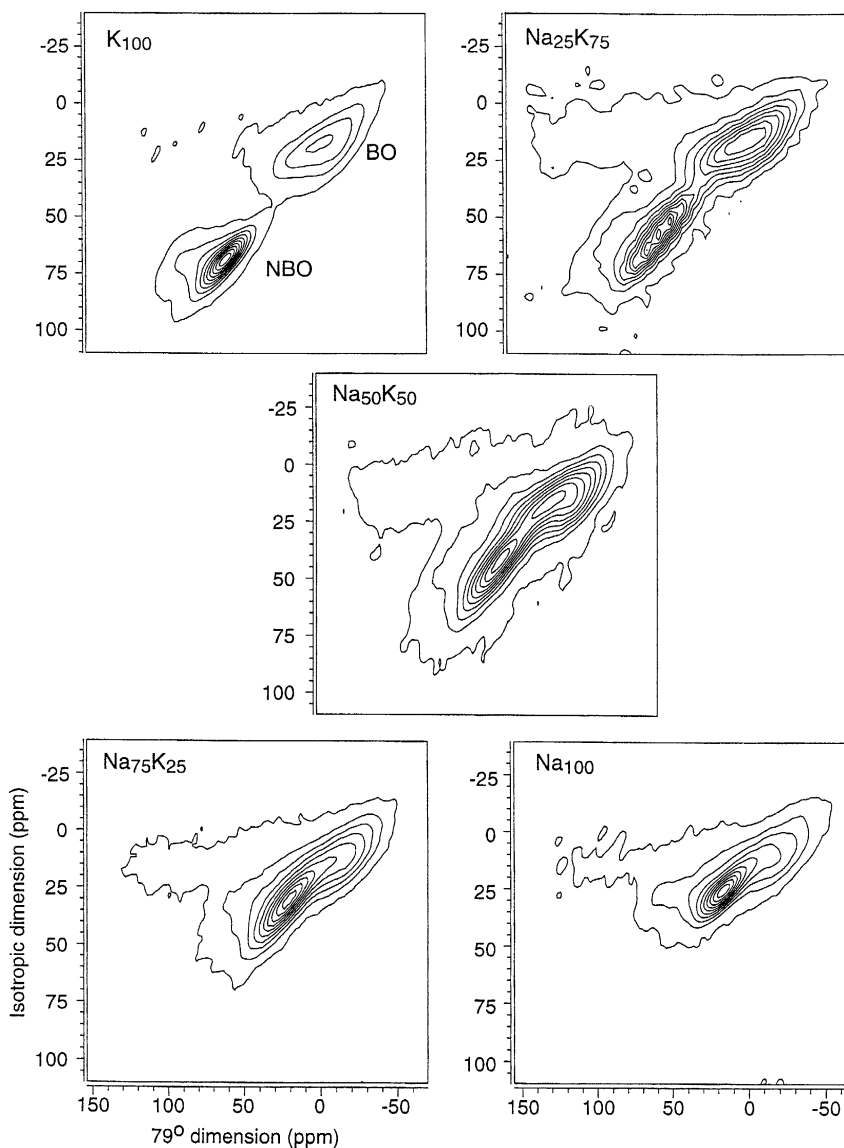


Fig. 3. ^{17}O dynamic angle spinning (DAS) spectra for $(\text{Na,K})_2\text{Si}_2\text{O}_5$ glasses. Scales in all spectra are the same, with “isotropic dimension” vertical (Florian et al., 1996).

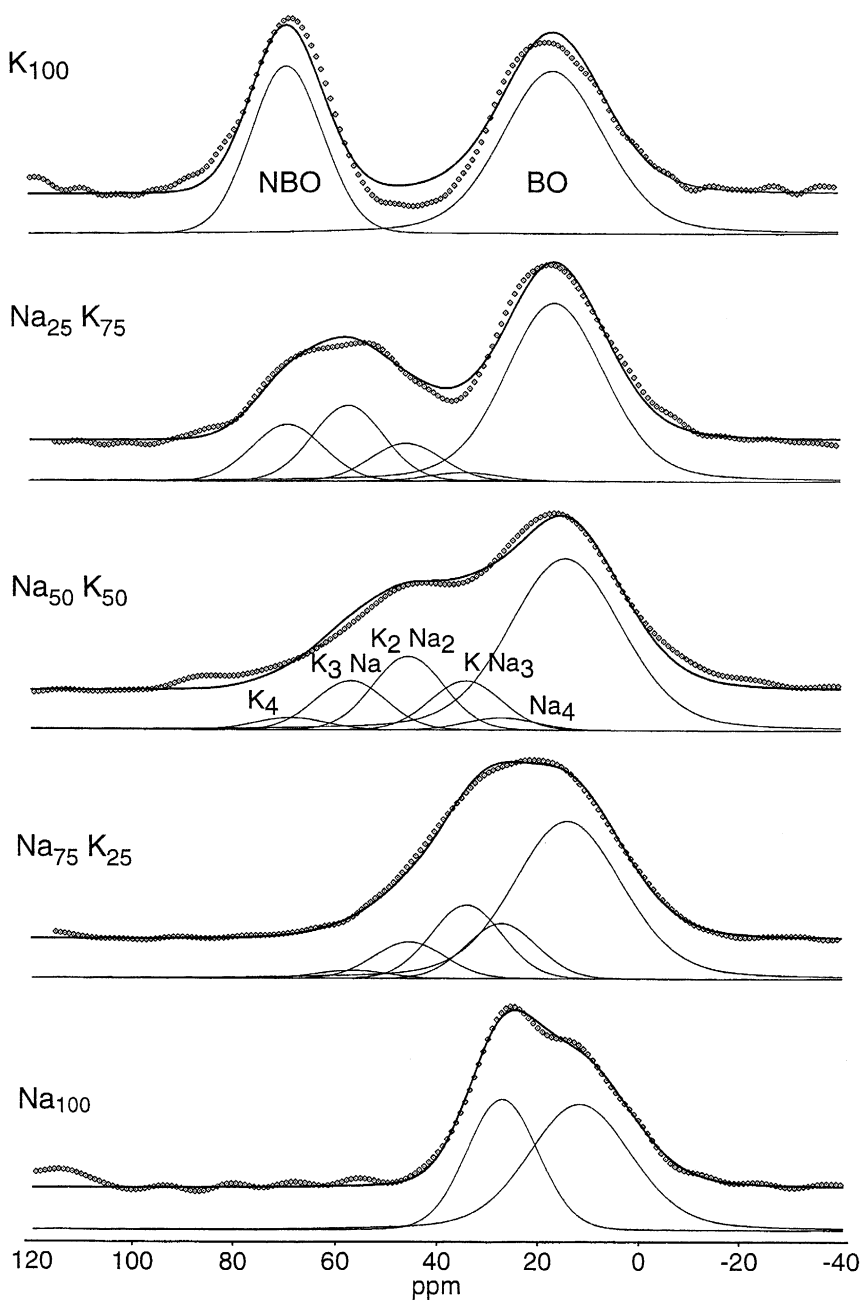


Fig. 4. Total isotropic dimension projections for spectra shown in Fig. 3 (Florian et al., 1996). Projections are simply the sum of all intensities along a line of constant isotropic shift, i.e., along horizontal lines in Fig. 3, and are free of second-order quadrupolar broadening. Dotted lines are experimental data; thin lines show Gaussian peaks for NBO with various Na, K neighbors as labeled, derived as discussed in text. Heavy lines show their sums for each composition.

not averaged away by conventional MAS (i.e., the second-order quadrupolar broadening) are eliminated

by excitation and manipulation of the triple-quantum nuclear spin transition ($+3/2$ to $-3/2$) instead of

the usual $+1/2$ to $-1/2$ transition. The resulting two-dimensional spectrum displays a “normal” (if often somewhat distorted) MAS spectra when projected in one direction, and an “isotropic” spectrum when projected in the other dimension, which is often much better resolved. An important limitation of 3QMAS is that peak intensities are affected by C_Q and hence may not be strictly quantitative, although systematic efforts at deriving correction factors have been made (Medek et al., 1995). However, a variety of important, at least semi-quantitative findings have been made for ^{17}O in silicate glasses including characterization of bridging oxygen sites in hydrous aluminosilicate glasses (Dirken et al., 1997; Xu et al., 1998), detection of non-bridging oxygens (NBO) in a nominally “fully polymerized” glass of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) composition (Stebbins and Xu, 1997), estimation of the degree of randomness of modifier cations around NBOs in alkaline-earth silicate glasses (Stebbins et al., 1997), the first direct detection of Al–O–Al sites in aluminosilicate glasses (Stebbins et al., 1999a), oxygen sites in Y- and La-aluminosilicates (Schaller and Stebbins, 1998), framework disorder in borosilicates (Wang and Stebbins, 1998; Wang and Stebbins, 1999), and NBO sites in borates (Stebbins et al., 2000). Several of these examples are discussed below. An even newer approach, involving “rotationally induced excitation of triple quantum coherence” (RIACT) holds promise as an inherently more quantitative technique, and has been demonstrated for ^{17}O in silica gel (Mildner et al., 1999).

3. Experimental section

Because some of the data presented below have not been previously published, we will summarize here the synthesis and NMR techniques used. The NaAlSiO_4 glass was produced as previously described (Lee and Stebbins, 1999), from SiO_2 prepared from 45% ^{17}O H_2O , Na_2CO_3 and Al_2O_3 , with melting at 1600 °C in an Ar atmosphere. The anhydrous glass of nominal $\text{Ca}_{0.5}\text{AlSi}_3\text{O}_8$ was produced in a similar manner, with initial melting at 1370°C. A portion of this was then combined with 10 wt.% of ^{17}O -enriched H_2O and melted for 5 h at 1150°C and 20.5 kb in a sealed Pt tube in a piston cylinder apparatus.

The new 3QMAS spectra presented here for sodium aluminosilicate glasses were collected as recently described (Stebbins et al., 1999a) with a modified Varian VXR 400S spectrometer at a field of 9.4 T, using a Doty Scientific, 5 mm “supersonic” probe, and a spinning rate of about 12 kHz. A standard 2-pulse 3QMAS sequence was used (Stebbins et al., 1999a), with a delay time chosen to avoid saturation. Data were processed with apodization chosen to not significantly broaden peaks and were plotted after a shear transformation. Axes follow conventions previously described (Baltisberger et al., 1996; Schaller and Stebbins, 1998). The new MAS spectra shown for the hydrous calcium aluminosilicate were collected with a Varian Inova 600 spectrometer at a field of 14.1 T, using a Chemagnetics/Varian 3.2 mm probe and a spinning rate of about 13 kHz. A radiofrequency tip angle of 30° was selected, and the delay time of 1 s was chosen to ensure that there was no differential relaxation among different components of the spectrum. Frequency shifts in ppm are reported relative to external H_2O .

4. Studies of non-bridging oxygen sites

Standard models of glass structure assume that in pseudobinary systems such as $\text{SiO}_2\text{--Na}_2\text{Al}_2\text{O}_4$ and $\text{SiO}_2\text{--CaAl}_2\text{O}_4$, all Si and Al are in four-coordinated sites and all oxygens are BO's connecting these tetrahedra. In the corresponding ternary systems, viscosity maxima at $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ or $\text{CaO}/\text{Al}_2\text{O}_3 = 1$ were taken as evidence for this “fully polymerized” structure (Riebling, 1966). The recent finding that viscosity maxima are actually displaced to Na/Al slightly less than 1 thus required a refinement of this approximation (Toplis et al., 1997b), and, coupled with the lack of NMR evidence for five- or six-coordinated Al in glasses of feldspar stoichiometry (Baltisberger et al., 1996), lead to a model calling for a significant fraction of non-bridging oxygens and “tri-clusters” of three corner-shared tetrahedra. This possibility was at least qualitatively confirmed by ^{17}O MAS and 3QMAS spectra on $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass that clearly showed the presence of a few %NBO (Stebbins and Xu, 1997). Such sites, whose chemical shifts are nearly identical to those in binary CaO--SiO_2 glasses (Stebbins et al., 1997), have also been seen in several glasses on the $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--SiO}_2$

join (new spectra shown in Fig. 5), but intriguingly, seem to disappear when H₂O is added. Previous work on ¹⁷O spectra of Na-silicate glasses suggests, however, that this does not necessarily mean that the NBO content decreases, but simply that the peak could be broadened considerably by partial substitution of H⁺ or H₂O for Na⁺ or Ca²⁺ in the first shell of the NBO (Xu et al., 1998). This may occur because C_Q increases with H coordination (Xue and Kanzaki, 1998) or because of an increased range in chemical shift values caused by disorder in NBO environments. The loss of intensity in the 60–70 ppm region of the main, BO peak with the addition of water (leading to an overall narrower peak) may be related to reaction with Al–O–Al sites, which occur in this region in an Al-rich Ca-aluminosilicate glass (Stebbins et al., 1999a). The broad component on the low frequency (right) side for the hydrous glass is probably from rigidly bonded H₂O (Xu et al., 1998), possibly combined with incompletely observed signal from OH groups. NBO were not observed in an ¹⁷O 3QMAS NMR study of NaAlSi₃O₈ glass (Dirken et al., 1997; Xu et al., 1998), but in this composition, NBO and Si–O–Al peaks are substantially overlapped, making the former difficult to detect even if present.

The extent of ordering of the number of NBO per SiO₄ tetrahedra (and the distributions of the resulting anionic species) has been extensively studied by

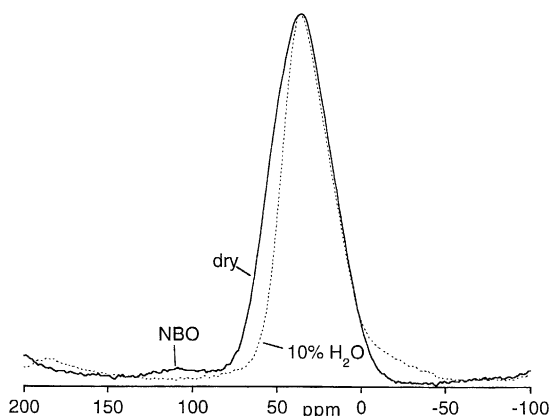


Fig. 5. ¹⁷O MAS spectra for Ca_{0.5}AlSi₃O₈ glass, anhydrous (solid line) and with about 10 wt.% H₂O (dotted line). Note the similarity in position between the NBO peak and that for the Ca-silicate glass in Fig. 2 (Oglesby and Stebbins, in preparation).

vibrational spectroscopy (Mysen, 1988) and by ²⁹Si MAS NMR (Stebbins, 1995), and is clearly related to thermodynamic properties such as configurational entropy and immiscibility. For the local structure around oxygen ions, such effects involve the second neighbor oxygens, and hence are indirect. Nonetheless, the greater disorder seen among the anionic units in alkaline earth silicate glasses as opposed to alkaline silicates (Murdoch et al., 1985; Stebbins, 1995) is probably the cause of the greater isotropic ¹⁷O peak widths seen in the former (Stebbins et al., 1997).

In ternary and more complex systems, disorder of differing modifier cations around NBO's is itself an important issue for models of thermodynamic and transport properties, which generally assume the random mixing of different modifiers or of the components that represent them (Ghiorso and Sack, 1994; Stebbins et al., 1997; Weill et al., 1980). In some cases, this assumption can be shown to be consistent with configurational entropy models of viscosity, as for Ca–Mg mixing in glasses of pyroxene and garnet stoichiometry (Neuvill and Richet, 1991). In most cases, however, a lack of suitable structural techniques has left this hypothesis untested. ¹⁷O NMR in a number of cases has provided important constraints on this issue. For example, MAS spectra of glasses on the CaSiO₃–MgSiO₃ join seem to show discrete peaks, with distinct chemical shifts, for NBO coordinated with Mg²⁺ and with Ca²⁺ (Kirkpatrick et al., 1986). This suggests a significant degree of cation ordering that seems incompatible with purely random models. In DAS spectra of K₂Si₄O₉ and KMg_{0.5}Si₄O₉ glasses, BO and NBO peaks were well separated (Farnan et al., 1992). In the mixed cation glass, the NBO peak was similar in width to that in the pure-K endmember, but shifted by the presence of Mg²⁺, again suggesting cation ordering, for example with most NBO having two K⁺ and one Mg²⁺ neighbors. Perhaps ordering is to be expected in such a system, given the charge and size difference of the cations, which can lead to ordered crystal structures with very different coordination environments, e.g., the leucite analog K₂MgSi₅O₁₂ (Bell et al., 1994). In this case, the order in the crystal structure is reflected in that of the glass.

Disordered models of modifier cations have been further tested by ¹⁷O DAS NMR on (Na,K)₂Si₂O₅

glasses (Florian et al., 1996) and 3QMAS and DAS on $(\text{Ba,Ca})_{0.45}(\text{SiO}_2)_{0.55}$ glasses (Stebbins et al., 1997). Projections in the isotropic dimensions for the mixed cation glasses were modeled by assuming that the NBO peaks for the endmembers were Gaussian in shape. Spectra for intermediate compositions (e.g., Fig. 4) were calculated (not fitted) by assuming that the peak widths and positions for each combination of modifier neighbors were simply linear combinations of the endmembers, with intensities derived from the random binomial distribution at the nominal composition. Agreement with this model was good in both systems. In the (Ba,Ca) glasses, this is particularly interesting because this system contains intermediate ordered crystalline compounds (e.g., $\text{Ca}_2\text{BaSiO}_3$), which apparently do not reflect the ordering state of their precursor liquids.

5. Studies of bridging oxygen sites

Order/disorder among network forming cations is another key issue in thermodynamic models of silicate melts, and is particularly important in calculations of configurational entropy and its consequences for viscosity and diffusion (Richet, 1984; Richet and Neuville, 1992). Out of necessity of lack of data, most quantitative solution models for multi-component melts assume random mixing of Si and Al, or, as for modifiers, of components that stand in for these cations (Ghiorso and Sack, 1994; Weill et al., 1980). On the other hand, the unusual progressive increases in configurational heat capacity between the glass transition and the melting point for liquids such as $\text{NaAlSi}_3\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Richet and Neuville, 1992) suggest the possibility of a change in ordering state and hence incomplete disorder at lower temperatures, and significant differences in heats of mixing on the $\text{NaAlO}_2\text{-SiO}_2$ and $\text{CaAl}_2\text{O}_4\text{-SiO}_2$ joins (Navrotsky, 1995; Navrotsky et al., 1982) may suggest compositional effects on the ordering state. An obvious question is to what extent “aluminum avoidance”, which is thought to greatly limit the formation of Al–O–Al tetrahedral pairs in crystalline aluminosilicates with $\text{Si}/\text{Al} \geq 1$, applies to glasses and melts.

^{29}Si MAS spectra for aluminosilicate glasses have recently been analyzed with a model based on a

single order parameter that translates into the an energetic penalty for formation of Al–O–Al linkages (Lee and Stebbins, 1999). Because spectra are completely unresolved, results are model-dependent, but do indicate significant ordering, i.e., less Al–O–Al than would be present in a random model with no energy differences among different pairs of tetrahedral cations, a result consistent with a previous qualitative study (Murdoch et al., 1985). Na-aluminosilicates appear to be somewhat more ordered than Ca-aluminosilicates, and estimated energies are consistent with calorimetric studies of heats of mixing (Navrotsky, 1995; Navrotsky et al., 1982).

^{17}O NMR can potentially provide a more direct view of this problem. Static spectra have been known from studies of zeolites to partially resolve Si–O–Al and Si–O–Si sites (Timken et al., 1986; Xu and Stebbins, 1998), although MAS spectra are less useful. DAS and 3QMAS spectra, in contrast, give excellent resolution between these two types of sites in both glasses and crystals (Dirken et al., 1997; Xu et al., 1998; Xu and Stebbins, 1998) (Fig. 6). In some cases, it has been possible to simulate one-dimensional MAS spectra for individual component peaks in 3QMAS spectra, producing relatively accurate data on chemical shifts and C_Q values, which can carry important structural information (Dirken et al., 1997). The ^{17}O NMR parameters for the critical

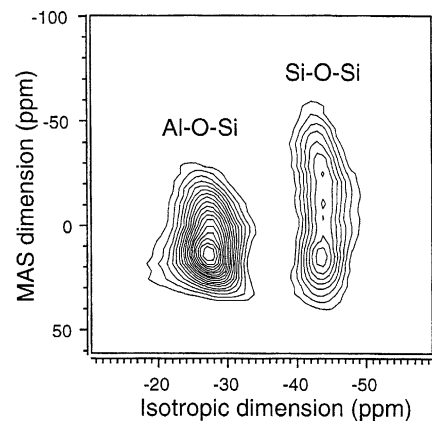


Fig. 6. ^{17}O 3QMAS spectrum for $\text{NaAlSi}_3\text{O}_8$ glass, showing Si–O–Al and Si–O–Si peaks (Xu et al., 1998). Here and in Figs. 7 and 8, the isotropic dimension is plotted horizontally. Note that if the data are projected in the MAS dimension, the two peaks overlap completely, consistent with their poor resolution in normal MAS spectra.

Al–O–Al sites were recently determined from studies of crystalline NaAlO_2 and CaAl_2O_4 , which contain only these linkages (Stebbins et al., 1999a), and allowed such sites to be unequivocally detected in sodium and calcium aluminosilicate glasses with $\text{Si}/\text{Al} < 1$ (Stebbins et al., 1999a) and then in a glass of NaAlSiO_4 stoichiometry (Fig. 7). The presence of any such sites at the latter composition confirms that “aluminum avoidance” is not perfect, but their concentration is clearly well below that for a fully random model. The quantitative test of the ordering state should be possible with further analysis of the effects of C_Q on peak intensities in 3QMAS spectra. In the spectra shown in Fig. 7, broad, low

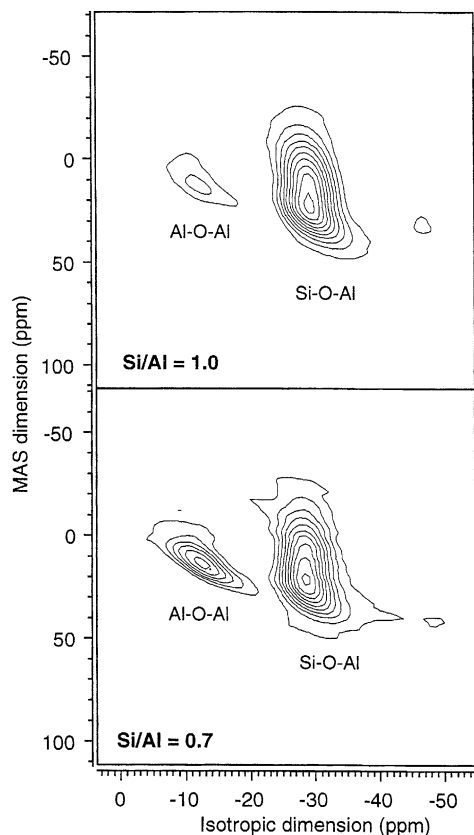


Fig. 7. ^{17}O 3QMAS spectra for two relatively aluminous glasses on the $\text{NaAlO}_2\text{--SiO}_2$ join, with Si/Al values as labeled. Small features to the right of Si-O-Al peaks are probably the highest points of broad Si-O-Si peaks that are almost lost at this signal-to-noise level. Lower data set is from (Stebbins et al., 1999a), upper is from Lee and Stebbins, 2000.

intensity peaks (centered at about -45 ppm in the isotropic dimension) are probably also present for small concentrations of Si-O-Si sites, but these may be underrepresented because of their larger C_Q values (Lee and Stebbins, in preparation). Unfortunately, severe peak overlap between the Al-O-Al and Si-O-Al peaks in calcium aluminosilicates (caused by the effects on chemical shift of the charge balancing cation) makes quantitation of spectra for such glasses difficult, although features of previously published spectra for $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass do indicate the presence of a significant fraction of Al-O-Al (Stebbins and Xu, 1997). Al-O-Al sites have not yet been detected in $\text{NaAlSi}_3\text{O}_8$ glass (Dirken et al., 1997; Xu et al., 1998) (Fig. 6), but their concentration is expected to be only a few percent at this relatively high Si/Al ratio (Lee and Stebbins, 1999).

Boron is a relatively minor component of natural silicate melts, but plays a central role in technological borosilicate and borosilicate glasses. Again, ^{17}O 3QMAS NMR has begun to have a major impact on structural models of these materials, which have been primarily based on a long series of ^{11}B studies of the distribution of trigonal and tetrahedral boron sites (Bray and Liu, 1986; Dell et al., 1983). So far, many of the possible bridging oxygen sites (B-O-B , B-O-Si , Si-O-Si) have been resolved, as have NBO sites (Wang and Stebbins, 1998; Wang and Stebbins, 1999). One of the most important results of these first studies is that the borate and silicate components are much more intimately mixed than anticipated from previous models. For example, in a simple, binary $\text{B}_2\text{O}_3\text{--SiO}_2$ glass, B-O-B , Si-O-B , and Si-O-Si sites are all of roughly similar concentration (volume integrals of the three peaks are similar, as are C_Q values), suggesting a nearly random model for their mixing (Fig. 8). We note that in contrast to Al-Si mixing, B-Si mixing in this composition involves almost entirely three-coordinated B, which may behave quite differently from four-coordinated Al.

All of the above examples of cation disorder can be considered as “chemical” contributions to the configurational entropy, meaning those that can be simply attributed to mixing of cations on equivalent sites (Richet and Neuville, 1992). The contributions to the entropy of “topological” disorder, such as ranges of bond distances and angles, are more diffi-

cult to quantify, but are nonetheless significant (Lee and Stebbins, 1999; Richet and Neuville, 1992; Toplis et al., 1997a). In pure SiO_2 , ^{29}Si NMR as well as a variety of other techniques have been applied to estimate ranges of mean Si–O–Si angles around SiO_4 groups (Gladden et al., 1986). In more complex compositions, a technique is needed that can isolate BO from NBO, which again is feasible in some systems by ^{17}O NMR. The most complete example so far of this approach was an analysis of a DAS spectrum of $\text{K}_2\text{Si}_4\text{O}_9$ glass (Farnan et al., 1992), which took advantage of the two-dimensional correlations obtained between the isotropic spectra and anisotropic “slices”. The latter, which have peak shapes equivalent to those obtainable by sample spinning at 79° to the external field axis, could be fitted to yield estimates of C_Q , which has been shown to be well-correlated with Si–O–Si angle. Integrated relative intensities for each slice thus yielded the relative fraction of BO’s with each C_Q and thus with each angle (Fig. 9). The distribution appeared to be narrower than that derived from X-ray scattering data for SiO_2 glass. Although it can be risky to compare such different methods on different materials, this result would make sense if the presence of network modifiers allows more of the

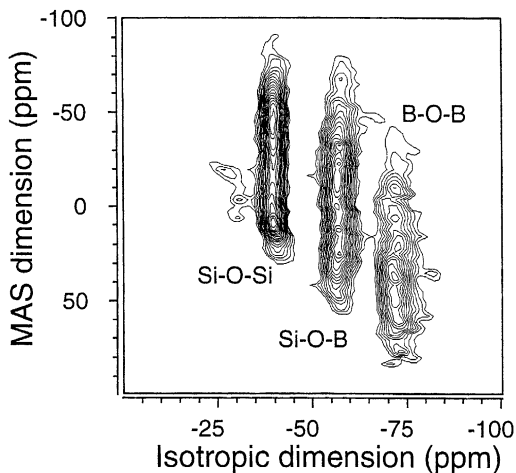


Fig. 8. ^{17}O 3QMAS spectrum for a glass containing 40 mole% B_2O_3 and 60 mole% SiO_2 (Wang and Stebbins, 1998). Peaks for bridging oxygens between SiO_4 and BO_3 groups are labeled.

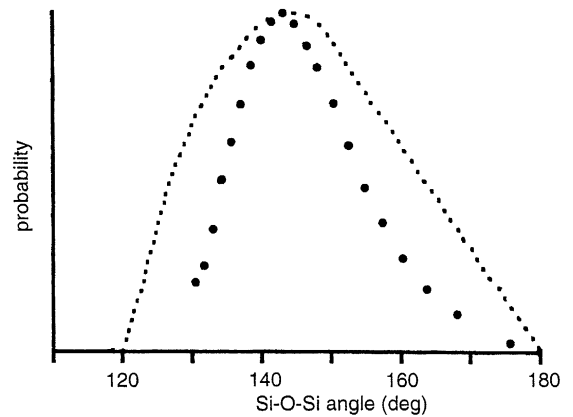


Fig. 9. Distributions of Si–O–Si bond angles derived from ^{17}O DAS NMR spectrum of $\text{K}_2\text{Si}_4\text{O}_9$ glass (large dots) and from X-ray scattering study of SiO_2 glass (small dots) (Farnan et al., 1992).

structure to relax to an energetically more optimal angle.

6. Prospects for future studies

^{17}O NMR, particularly spectra collected with new, high-resolution techniques, is beginning to provide a new view of oxide glass structure. As technology continues to advance, particularly with higher field magnets and high spinning speed probes with small sample volumes, sensitivity will improve and studies of small, high-pressure samples should be more feasible. There is much that remains to be learned about interpretation of spectra, some of which will come from further systematic studies of crystalline model compounds and of compositional series of glasses where at least the relative variation in oxygen species concentrations can be predicted from other techniques, e.g., ^{29}Si and ^{27}Al NMR, Raman, and X-ray spectroscopy. More work on the theory of NMR, especially 3QMAS, the application of existing theory to studies of glasses, and as always, the development of new NMR techniques, should help resolve issues of quantitation. Ab initio studies will continue to be helpful, not only in predicting the NMR parameters for newly sought sites, but guiding the development of correlations between NMR observable and local structures. It is likely that ^{17}O solid-state NMR of glasses will continue to require isotopically enriched materials, which may keep it from becoming as

routine as studies of more abundant nuclides, but synthesis techniques continue to improve as more systems are studied. High quality two-dimensional spectra can now routinely be obtained on samples of 20–30 mg, reducing costs and opening many new research opportunities. Finally, future studies of the effects of quench rate, and hence of fictive temperature, should provide clues to how disorder increases with temperature in the melt.

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