# Disorder among network-modifier cations in silicate glasses: New constraints from triple-quantum $^{17}$O NMR

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## Abstract

The state of ordering among network-modifier cations in molten silicates has a potentially large effect on their overall configurational entropy, on free energies of mixing, and on viscosity and diffusivity. Most models of thermodynamic and transport properties assume random mixing, but there is relatively little direct microstructural information to constrain the real extent of this disorder. Two-dimensional $^{17}$O NMR can produce spectra that are free of quadrupolar broadening and thus in which peak widths for non-bridging oxygen sites directly reflect the extent of disorder in the local structural environment. In this report, we describe new data from triple-quantum magic-angle-spinning (3QMAS) NMR for a series of barium and calcium silicate glasses. Results are best explained by completely random mixing of Ba and Ca, confirming conventional modeling assumptions. Other recent data show, however, that significant ordering may be present (at least at the temperature of the glass transition) for modifier cations with greater differences in size or charge, and among network-forming cations.

## Introduction

The extent of disorder among metal cations has been a first-order question in the thermodynamics of molten silicates since the earliest attempts at modeling phase diagrams and activities (e.g., Bowen 1913; Flood and Knapp 1968). It is generally thought that large differences in cation size and charge cause major structural ordering in melts as in crystals. In particular, small, high-charge "network formers" ($Si^{4+}$, $Al^{3+}$, $B^{3+}$, $P^{5+}$), which at low pressure are primarily threefold or fourfold coordinated by oxygen, are not mixed with lower-charged, larger "network modifiers" (e.g., $Na^+$, $Ca^{2+}$) in models of configurational entropy. This separation of role is either maintained implicitly by the choice of components or explicitly by division of the system into two or more "sublattices" (Weill et al. 1980). The distinction between network modifier and former cations is reasonably well supported by direct, microscopic information: X-ray and neutron scattering, and spectroscopic data in general confirm that ranges of coordination number and bond distances for these two categories are non-overlapping (Brown et al. 1995). This division has recently become blurred, however, with the finding that $Fe^{3+}$ and even $Fe^{2+}$ and $Mg^{2+}$ may sometimes be fourfold coordinated in melts and glasses (Mysen 1988; Brown et al. 1995), and that even at ambient pressure significant proportions of fivefold-coordinated Si and Al may occur (Risbud et al. 1987; Sato et al. 1991; Stebbins 1991; McMillan and Kirkpatrick 1992). The consequences of these findings for entropy models have not been quantified.

Within the two divisions of network formers and modifiers, random mixing among different cations is almost universally assumed in models of thermodynamics, in which at least the mixing entropy (if not the enthalpy) is taken as the ideal value (e.g., Ghiorso et al. 1983; Ghiorso and Sack 1994). The importance of disorder among network modifiers in transport properties has recently been highlighted by calculations relating configurational entropy to viscosity by means of the Adam-Gibbs formulation (Richet 1984; Richet and Neuville 1992). For the binary systems $CaSiO_3$-$MgSiO_3$ and $Ca_3Al_2Si_3O_{12}$-$Mg_3Al_2Si_3O_{12}$, random mixing of Mg and Ca gives remarkably accurate predictions of the changes in viscosity with composition, over a wide range of temperatures (Neuville and Richet 1991). Disorder among modifier cations also has major consequences in models of their diffusivity and cationic conductivity (Greaves and Ngai 1994; Sen et al. 1995). However, despite the major consequences of cation order-disorder in such a wide range of models, there is surprisingly little direct microscopic information to evaluate independently the true extent of this randomness.

Some insight into ordering among modifier cations in melts may perhaps be gained from crystalline silicates. For example, the extensive substitution of $Fe^{2+}$ and $Mg^{2+}$ in octahedral sites in many silicates, the fairly wide range of substitution of $Ca^{2+}$ and $Mg^{2+}$ in pyroxenes and garnets at high temperature, and extensive solid solution of $Na^+$, $K^+$, and $Ca^{2+}$ in feldspars at high temperature suggest that these geologically common groups of cations might indeed mix randomly in melts. In ternary systems of alkali and alkaline earth oxides with silica, extensive solid solution is often noted for neighboring pairs in the periodic

table with the same charge, for example Li-Na, Na-K, Mg-Ca, Ca-Sr, and Sr-Ba. However, systems with cation pairs with larger size differences, or size plus charge differences, usually have intermediate, ordered ternary phases, especially at silica contents of 50 mol% and higher (Levin et al. 1964, 1969; Roth et al. 1987). An example is the leucite analog $K_2MgSi_5O_{12}$, in which $Mg^{2+}$ forms part of the tetrahedral network (Kohn et al. 1991).

One view of modifier cation ordering in melts can be obtained from the range of local environments around non-bridging oxygens (NBO). In crystalline alkali and alkaline earth silicates, NBO are generally coordinated by Si and three or four +1 or +2 cations. If the same is true in glasses (which are generally presumed to represent the structure of the liquid at the glass transition temperature), then extensive disordering of the modifier cations should be reflected in a wide range of NBO coordination environments; the converse is expected if the structure is more ordered. The technique of $^{17}O$ NMR is especially sensitive to the extent of ordering because chemical shifts for NBO peaks vary over a wide range depending on the identity of the neighboring cations (Timken et al. 1986; Stebbins 1995). For example, an early study (Kirkpatrick et al. 1986) reported $^{17}O$ MAS spectra of glasses on the $CaSiO_3$-$MgSiO_3$ join that seemed to indicate substantial mixing of Ca and Mg. To obtain much higher resolution, reduce overlap of NBO and BO peaks, and eliminate quadrupolar broadening, later work used two-dimensional (2-D) dynamic angle spinning (DAS) NMR to obtain $^{17}O$ spectra for $K_2Si_4O_9$ and $KMg_{0.5}Si_4O_9$ glasses (Farnan et al. 1992). NBO and bridging oxygen peaks were well-resolved and free of the quadrupolar broadening that complicates standard 1-D MAS spectra. In the mixed-cation glass, the NBO peak was similar in width to that in the K end-member, with very little intensity at the position of the peak with all K neighbors. It was therefore concluded that $K^+$ and $Mg^{2+}$ had a highly ordered distribution, probably with most NBO coordinated by two $K^+$ and one $Mg^{2+}$.

A second study of this type examined what was expected to be a disordered system, the $K_2Si_2O_5$-$Na_2Si_2O_5$ binary (Florian et al. 1996). Here, spectra of the end-member glasses and three intermediate compositions showed clearly that the NBO peak shapes, broadened by disorder, were very well fitted by a model with random mixing of K and Na on four adjacent sites. This is consistent with expectations from extensive (if incomplete) solid solution in the crystalline phases (Kracek 1932).

In the study described here we extend this work to a mixed alkaline-earth system, the barium-calcium silicate ternary. In this system, extensive solid solution appears to be present only for crystalline $(Ba,Ca)_2SiO_4$, whereas ordered ternary compounds (e.g., $Ca_2BaSiO_3$) appear at higher silica contents (Brisi and Appendino 1967; Levin and McMurdie 1975). Some degree of ordering thus appears to be caused by the large size difference of the cations [0.11 vs. 0.14 nm in eightfold coordination (Shannon and Prewitt 1969)]. We have again examined the

NBO to determine if this ordering is reflected in the glasses and to seek more general constraints on the correctness of the common assumption of full disorder in thermodynamic and transport models.

## TRIPLE-QUANTUM MAS NMR

For this study, we used the recently developed technique of triple-quantum magic-angle spinning (3QMAS) NMR, which, like DAS, produces spectra free of second-order quadrupolar broadening for nuclides with spin $\frac{3}{2}$, $\frac{5}{2}$, etc. (Frydman and Harwood 1995; Samoson 1995; Amoureux et al. 1996; Massiot et al. 1996). Because of the relative simplicity of this method, which can be done with any high radiofrequency power, high-speed MAS probe (instead of a mechanically complex DAS probe), 3QMAS has received widespread attention since its announcement in 1995. A useful comparison of 3QMAS, DAS, and other techniques has been presented by Youngman et al. (1996). Tests of 3QMAS have included studies of $^{27}Al$ in zeolites, in glasses, and in crystalline aluminosilicates and phosphates (Fernandez and Amoureux 1995; Frydman and Harwood 1995; Baltisberger et al. 1996; Fernandez et al. 1996; Sarv et al. 1996), and of $^{23}Na$ in a variety of oxysalts (Medek et al. 1995). The technique of 3QMAS has also recently been applied to $^{17}O$ in zeolites and $NaAlSi_3O_8$ glass (Xu and Stebbins 1996, 1997; Dirken et al. 1997). The relatively esoteric theory upon which this approach is based has been discussed in the references cited above. In brief, the anisotropic effects on peak position that are not averaged away by conventional MAS (the second-order quadrupolar broadening) are refocused and eliminated by excitation and manipulation of the triple-quantum transition, i.e., the $+\frac{3}{2}$ to $-\frac{3}{2}$ instead of the usual $+\frac{1}{2}$ to $-\frac{1}{2}$ transition. The resulting 2-D spectrum displays the normal MAS spectrum along one direction and an isotropic spectrum along the other. As in DAS NMR, the peak positions in the isotropic dimension are not those of the isotropic chemical shift but are the sum of this term and a term including the isotropic average of the second-order quadrupolar coupling. A disadvantage of either technique is that the NMR signal is spread out in two dimensions, reducing the signal-to-noise ratio and often making data collection rather time consuming (sometimes several days per spectrum). This is particularly a problem for 3QMAS because of the inherent inefficiency of triple-quantum excitation. The latter is also complicated by the dependence of this excitation on the quadrupolar coupling constant ($C_q$) of the site under observation, resulting in systematically reduced spectral intensities when $C_q$ is large (Baltisberger et al. 1996). This is not expected to be a problem in the current study, however, because $C_q$ values for NBO sites in silicates are relatively small and vary over a relatively narrow range, usually between about 2 and 3 MHz (Timken et al. 1986; Mueller et al. 1990, 1992; Stebbins 1995).

The widths of the peaks in 3QMAS (and DAS) spectra

therefore reflect in a somewhat complex fashion the real distribution of local structural environments. This is particularly important for $^{17}O$ in glasses: In standard 1-D MAS spectra peak widths are strongly affected by quadrupolar broadening. Ranges of local coordination environments that are the source of the entropy differences between glasses and crystals are thus difficult to quantify from 1-D data. For this reason, $^{17}O$ DAS on glasses was a major step forward in characterizing the disorder around both BO and NBO (Farnan et al. 1992; Florian et al. 1996). Here we use both 1-D MAS and 2-D 3QMAS to search for relative changes in NBO peak widths as a function of composition (Oglesby et al. 1996).

## SAMPLE PREPARATION AND NMR METHODS

The compositional join with 55 mol% $SiO_2$ was chosen to minimize liquidus temperatures and improve glass-forming ability. Two end-member glass compositions [$(BaO)_{0.45}(SiO_2)_{0.55}$ and $(CaO)_{0.45}(SiO_2)_{0.55}$] were prepared by melting mixtures of reagent-grade BaO, CaO, and $^{17}O$-enriched $SiO_2$ at 1540–1615 °C in Pt tubes in pure Ar. The enriched silica was made as previously described by reacting $H_2O$ with about 45 atom% $^{17}O$ (Cambridge Isotope Laboratories, Inc.) with $SiCl_4$ (Geissberger and Bray 1983). BaO and CaO (natural isotopic abundance) were used instead of carbonates to minimize the loss of $^{17}O$ due to exchange with volatilizing $CO_2$; $H_2O$ contents were carefully assessed by weight-loss studies during trial syntheses with isotopically normal $SiO_2$; 0.1 wt% CoO was added to speed spin-lattice relaxation. A 50:50 molar mixture of the two end-members was re-melted at 1400 °C.

The 1-D MAS and 3QMAS spectra were collected with a modified Varian VXR-400S spectrometer (9.4 Tesla field), using a high-speed MAS probe from Doty Scientific, 5 mm sample rotors, and spinning rates of 10–12 kHz. All spectra are referenced to $^{17}O$ in tap water. Relaxation times ($T_1$) were determined and experimental delay times were adjusted accordingly to ensure that there was no differential relaxation (3.5 s for the Ca glass, 130 ms for the Ba glass, 415 ms for the BaCa glass). DAS spectra were acquired as previously reported, using a probe constructed by P.J. Grandinetti (Florian et al. 1996). The single-hop DAS method was used, with rapid flipping of the sample spinning angle back and forth from 37.4 to 79.2° with respect to the external field and spectra acquired at the latter angle. The hypercomplex shifted-echo NMR pulse sequence was used as described previously (Grandinetti et al. 1993; Grandinetti 1995). The resulting 2-D data display an isotropic spectrum along one dimension (free of quadrupolar broadening) and the 79.2° ("VAS") spectrum along the other. In the Ba glass sample, the $T_1$ value was too short for DAS spectra to be collected. The 3QMAS spectra were collected as previously described (Baltisberger et al. 1996; Massiot et al. 1996). The spectral widths in the $t_1$ and $t_2$ dimensions were 20 kHz and 30 kHz, and about 600 transients were averaged per each of about 20 $t_1$ points, with delay times
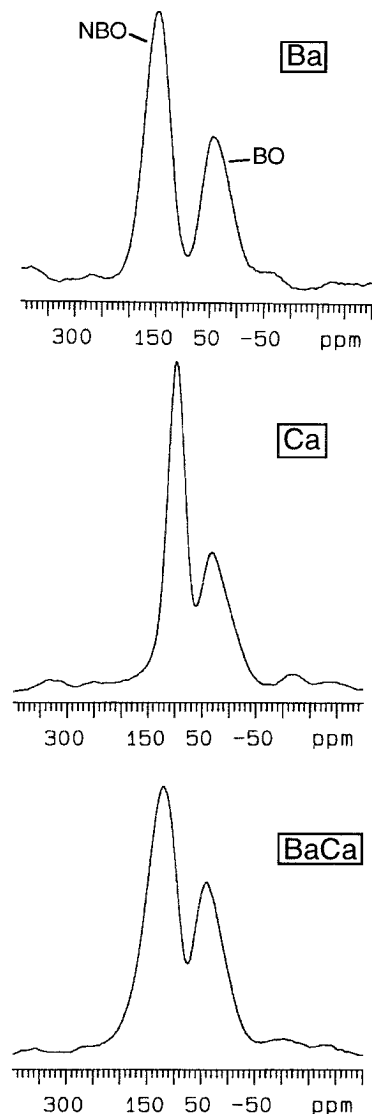


**FIGURE 1.** The $^{17}O$ MAS NMR spectra for $(Ba_xCa_{1-x}O)_{0.45}(SiO_2)_{0.55}$ glasses. Bridging oxygen (BO) and non-bridging oxygen (NBO) peaks are labeled.

of about three times $T_1$. The first and second rf pulses were 18 μs long, the third "soft" pulse was 27 μs. An echo time of only two rotor periods (169 μs) was required by the short $T_2$ values (broad peaks) of the samples, allowing only the echo portion of the data to be used (not the "anti-echo").

## RESULTS

The 1-D $^{17}O$ MAS spectra for the three glasses are shown in Figure 1. As reported previously for $CaSiO_3$ glass, the spectra contain two roughly Gaussian peaks. Their area ratios are close to that expected from stoichiometry (NBO/BO ≈ 1.38). The lower frequency (~35 ppm) peak can be unambiguously attributed to BO by comparison with data on crystalline silicates (Timken et

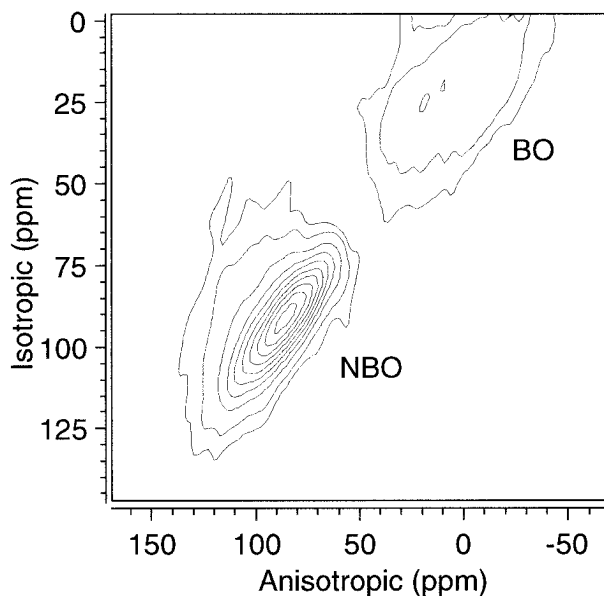**FIGURE 2.** Contour plot of $^{17}$O dynamic angle spinning (DAS) NMR spectrum for $(CaO)_{0.45}(SiO_2)_{0.55}$ glass. To match previous publications (Farnan et al. 1992; Florian et al. 1996), the anisotropic (79° spinning angle) dimension is plotted horizontally, the isotropic dimension vertically. Contours are evenly spaced.



**FIGURE 3.** Total isotropic projection of spectrum in Figure 2.

al. 1987; Mueller et al. 1992; Stebbins 1995). The position of the higher frequency peak (NBO) varies strongly with change in the network modifier, from 150 ppm in the Ba glass to 100 ppm in the Ca glass; that of the BO varies over a much narrower range, from 40 to 30 ppm. This is expected from previous studies of silicate and oxide crystals (Timken et al. 1987) and glasses (Kirkpatrick et al. 1986): Shorter M-O bonds or greater electronegativity of first cation neighbors leads to more covalent bonding and to more electronic shielding. This effect is analogous to well-known effects of bonding on chemical shifts for cations (e.g., for $^{29}$Si, $^{27}$Al, $^{11}$B, $^{23}$Na, $^{25}$Mg, and $^{6}$Li), but is necessarily in the opposite direction for the oxide anion. The Gaussian or even triangular shapes of the BO peaks indicate that the quadrupolar asymmetry parameter $\eta_q$ is relatively large (probably >0.3), as expected from the relatively strong interactions between divalent modifier cations and bridging oxygens, which leads to relatively narrow Si-O-Si angles (Farnan et al. 1992; Grandinetti et al. 1995).

The NBO peak in the BaCa glass MAS spectrum is particularly broad and contains significant intensity at the positions seen in the end-member glasses, which are due to NBO with all Ca or all Ba neighbors. Substantial cation disorder in the BaCa glass is thus suggested, but this conclusion is not definitive because of the possibility of an unexpected increase in $C_q$ and thus in quadrupolar broadening in the mixed composition.

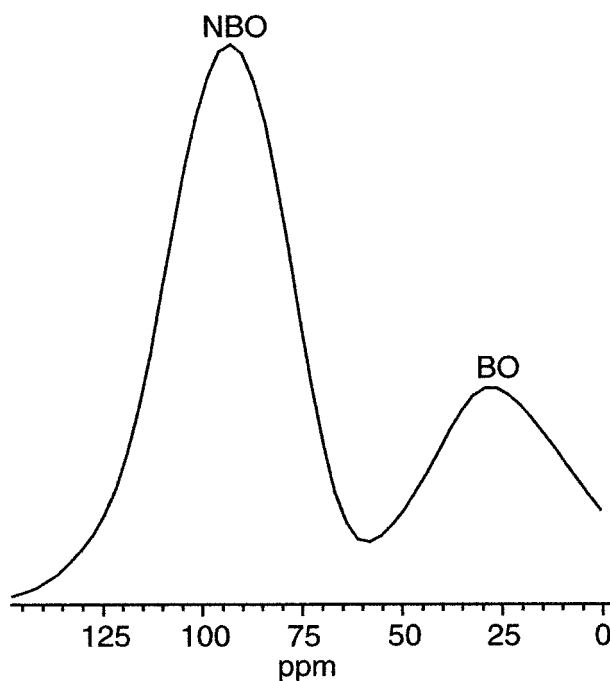The 2-D DAS spectrum for the Ca glass (Fig. 2) resembles those previously published for potassium silicate glasses, with excellent separation of the BO and NBO peaks (Farnan et al. 1992; Florian et al. 1996). The isotropic projection is shown in Figure 3 for comparison. The width (in the isotropic dimension) of the NBO peak for the Ca glass is about twice that for $K_2Si_2O_5$ or $K_2Si_4O_9$ glasses, indicating a greater disorder in the local structural environment, perhaps related to the similar trends reported for silicate anionic species from Raman (McMillan 1984) and $^{29}$Si NMR studies (Murdoch et al. 1985; Stebbins 1988). For the BO peak, the lack of a long "tail" in the anisotropic dimension (as seen previously for the potassium silicates) is expected if, as suspected from the 1-D MAS data, $\eta_q$ has a value of about 0.3 or higher. Because of difficulties in acquiring a DAS spectrum for the Ba end-member, however, we will not analyze the DAS data in detail.

Contour plots of the 3QMAS spectra for the three glasses are shown in Figure 4. They each contain two well-separated peaks, which again can be unambiguously attributed to NBO and BO sites. As in the 1-D spectra, the BO peak is spread over a relatively narrow range in $\delta_{3QMAS}$ (the position in the isotropic dimension). As in a previous 3QMAS study (Baltisberger et al. 1996), we have analyzed the positions of the peak maxima in the two dimensions to estimate means in the isotropic chemical shift ($\delta_{CS}$) and $C_q$. These values for the Ca glass are 59 ± 2 ppm and 4.7 ± 0.4 MHz, for the CaBa glass 68 ppm and 4.1 MHz, and for the Ba glass 78 ppm and 4.0 MHz. Estimates of $C_q$ were made assuming $\eta_q = 0.3$; ranges in this parameter over values reasonable for BO (0 to 0.5) contribute only about ± 0.2 MHz to the uncertainty.
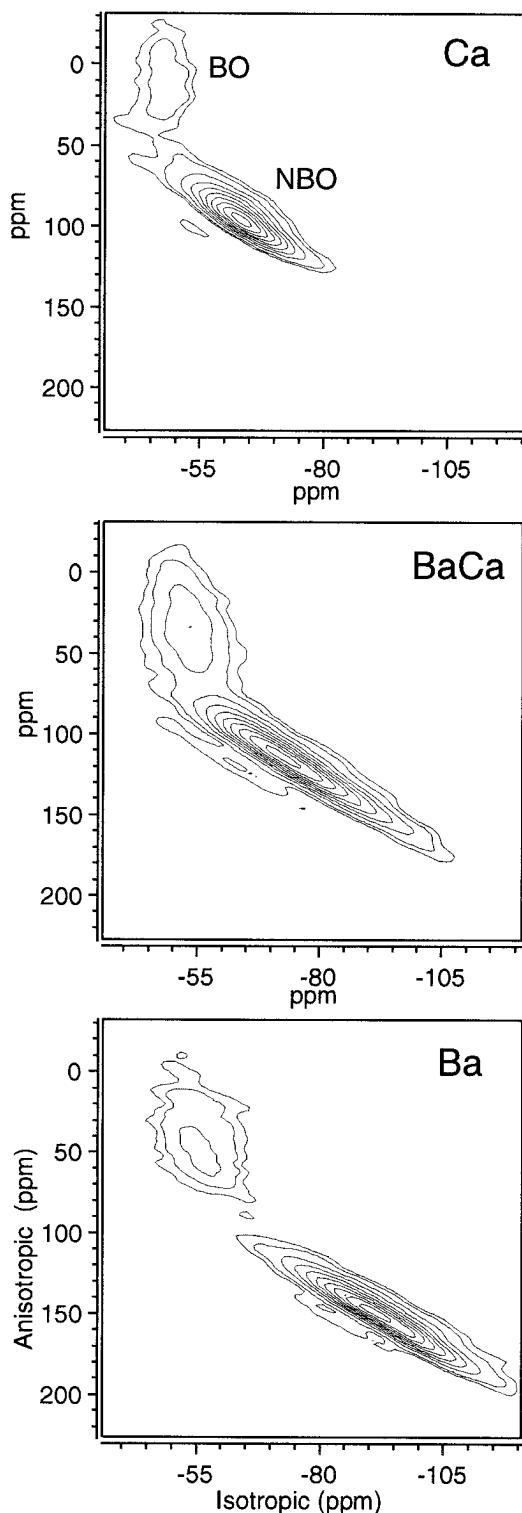
**FIGURE 4.** Contour plots of $^{17}O$ triple-quantum (3Q) MAS NMR spectra for $(Ba_xCa_{1-x}O)_{0.45}(SiO_2)_{0.55}$ glasses. To match earlier work (Baltisberger et al. 1996), the anisotropic (MAS) dimension is plotted vertically, the isotropic dimension horizontally. Contours are evenly spaced.

In contrast to the BO peaks, the NBO peaks are spread over a wide range in $\delta_{3QMAS}$, indicating a corresponding dispersion of either $\delta_{CS}$ or of $C_q$. The narrow, almost linear shape of the NBO peaks in the 2-D plot indicates, however, that $C_q$ has only a narrow range for each glass. This is also the simplest explanation for the near constancy in width of slices in the MAS dimension taken at various positions. Again using the positions in the two dimensions of the high points along the NBO "ridges" (as for the BO peaks), we estimate $C_q$ values to be between about 1.8 and 2.0 MHz. The widths of the NBO peaks in the isotropic dimension are therefore controlled primarily by distributions in $\delta_{CS}$ and are probably thus related in a fairly simple fashion to real distributions of local structural parameters, such as number and identity of cation neighbors, bond distances, and so forth. The near constancy in $C_q$ also means that relative peak areas should not be significantly distorted by variation in triple-quantum excitation and thus are close to quantitative.

As in the 1-D MAS spectrum, the NBO peak in the 3QMAS spectrum for the BaCa glass covers the full range from one end-member to the other, but with no ambiguity in the nature of this broadening: It clearly is the result of disorder. The widths and shapes of the peaks are shown in projections in the isotropic dimension in Figure 5. For the Ca and BaCa glasses, there is a slight overlap of the BO and NBO peaks that introduces a small extra intensity in the high frequency ends of the projections (toward 0 ppm). Given the relatively low total intensities of the BO peaks, this is only a minor influence on the NBO peak shapes and does not affect the conclusions drawn below.

To explore the extent of disorder more quantitatively, we have made forward simulations (not fits) of the isotropic projection of the NBO peak for the BaCa glass. To do this, we first fitted the NBO peaks for the end-members with Gaussians to measure their widths better. We assumed that each NBO has three modifier cation neighbors. The NBO can then be divided into four populations, with either 3Ca, 2Ca and 1Ba, 1Ca and 2Ba, or 3Ba neighbors. We generated peaks for each by taking the appropriately weighted average of the positions and widths for the end-member peaks, and areas appropriate to various ordering schemes. The only simple pattern that closely approximated the observed peak was that expected from a random (binomial) distribution, with area ratios of 1:3:3:1 (Fig. 5). The slight extra width on both sides of the experimental peak for the BaCa glass is most likely the result of the peaks not being perfectly Gaussian in character; this can also be seen in the fits to the peaks for the end-members. Models with four modifier neighbors give similar results.

## DISCUSSION

Along the Ba-Ca and Na-K (Florian et al. 1996) joins that were explored with 2-D $^{17}O$ NMR, random mixing of modifier cations on sites adjacent to NBO seems to be the best approximation, supporting the assumption gen-

erally made in thermodynamic models of melts. Greater differences in cation radius, or the combination of differences in charge and radius, may still lead to significant ordering, as suggested by the previous study of K-Mg mixing (Farnan et al. 1992). Particularly in compositions in which $Mg^{2+}$ may be partly or entirely in fourfold coordination (e.g., high-alkali liquids at low temperature) (Fiske and Stebbins 1994; Brown et al. 1995), mixing of this cation with larger or lower charged modifiers may be limited.

These results have important implications for understanding the origins of the configurational heat capacity of melts. If modifier cations are fully disordered at temperatures as low as the glass transition, then additional classical site mixing at higher temperature cannot contribute to the increased configurational entropy, unless mixing begins with energetically unfavorable sites that are unoccupied at low temperature (Fiske and Stebbins 1994; George and Stebbins 1996). This conclusion is consistent with the linearity in composition commonly seen in models of heat capacity (Richet 1984; Stebbins et al. 1984; Richet and Neuville 1992): At least as detected by multiple regressions of complex data sets, no extra heat capacity is generated by mixing of unlike cations. On the other hand, if partial ordering were present at low temperature, disordering with increasing temperature will add to the configurational heat capacity. The high configurational heat capacities of Mg-rich melts (Stebbins et al. 1984) may conceivably be related to such an effect.

In the BaCa glass, the lack of extra (non-random) intensity in the 3QMAS NBO peaks for 3Ca and 3Ba neighbors indicates that there is not an obvious tendency for modifier cations to segregate into clusters of one type. Other recently developed multinuclear NMR techniques have the potential for examining this question more directly. For example, spin echo double resonance (SEDOR) has recently been applied to constrain the distribution of distances among $Na^+$ and $Li^+$ cations in silicate glasses and thus search for segregation (Gee and Eckert 1996; van Wüllen et al. 1996a). Models of the results were not unique, but implied random Na-Li mixing if the cations were uniformly dispersed. However, some like-cation segregation was suggested if alkali-rich regions were present. The $^{23}Na$ and $^7Li$ NMR peak widths and positions change uniformly as Na/Li varies in disilicate glasses, also suggesting random cation mixing (Ali et al. 1995). In some cases, X-ray absorption spectroscopy can also characterize first cation neighbors for cations, providing real potential for detecting like-like clustering or avoidance (Farges et al. 1991; Houde-Walter et al. 1993; Farges et al. 1994; Brown et al. 1995).

Another important aspect of intermediate range ordering is the extent of dispersion of modifiers within the silicate network. Our and other $^{17}O$ NMR data do not quantitatively constrain the extent of segregation into modifier-rich and modifier-poor regions, but they do require that extensive interactions exist between modifier cations and bridging O atoms. If this were not the case,
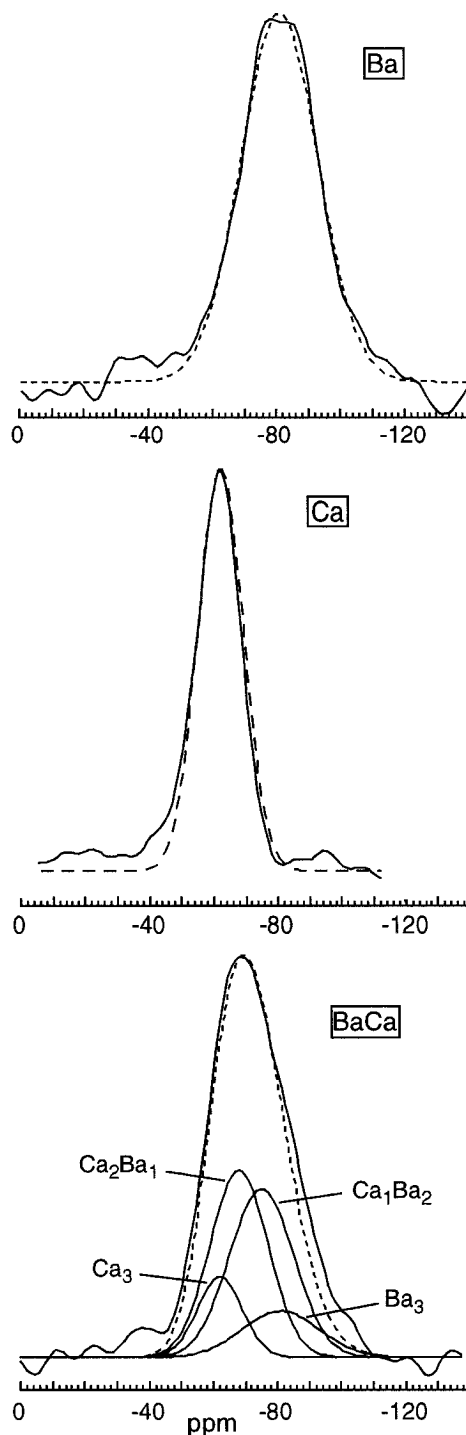


**FIGURE 5.** Isotropic projections of the NBO peaks of the 3QMAS spectra. In the pure Ba and Ca glasses, Gaussian fits are shown, which were used to specify peak positions and widths in simulations of the spectrum for the BaCa glass. For the latter, results of a forward simulation (not a fit) are shown, which assumes a random mixing of Ba and Ca on three sites adjacent to each NBO. The corresponding peaks for the various site occupancies are shown with solid lines; their sum is shown by the dashed line.

the differences in BO isotropic chemical shifts between Ba and Ca glasses would not be observed; nor would the differences in BO MAS peak shapes between the Ba and Ca glasses and Na and K glasses (suggestive of differences in $\eta_q$) be present. These findings in turn imply that most bridging O atoms are not in "silica-like" regions with low local concentrations of modifier cations. This may place limits on the scale of Ca-rich segregation in a glass near CaSiO$_3$ in composition that was detected by neutron scattering experiments (Gaskell et al. 1991; Gaskell 1992).

Other NMR data suggest the presence of some intermediate-range ordering among network-forming cations in melts. For sodium and calcium aluminosilicate glasses, $^{29}$Si NMR spectra have reduced peak widths as the Al/Si ratio approaches 1, suggesting that Al avoidance causes some degree of Si-Al ordering (Murdoch et al. 1985). In contrast, thermodynamic modeling has generally assumed random mixing of Si and Al on tetrahedral sites (Weill et al. 1980; Ghiorso and Sack 1994). Double-resonance techniques for the $^{11}$B-$^{27}$Al pair have been applied to boroaluminate glasses and indicate that most or all Al have B neighbors (van Wüllen et al. 1996b). In both types of glasses, there may thus be some possibility of increased disorder among network formers with increasing temperature.

The complement to cation ordering is ordering in the anionic network itself. Here, it has been known from the first high-resolution $^{29}$Si studies of glasses that the distribution of anionic species Q$^n$ (where $n$ counts the number of bridging O atoms on a Si tetrahedron) is more ordered than predicted by a random distribution of BO and NBO (Dupree et al. 1984, 1986; Stebbins 1987; Stebbins et al. 1992). Recently developed 2-D NMR techniques have made Q$^n$ species quantitation much more precise even for systems (such as CaSiO$_3$) where peaks are unresolved in 1-D spectra (Grandinetti 1996; Zhang et al. 1996, 1997). These confirm non-random Q-species distributions, demonstrate the greater disorder in alkaline earth silicate glasses when compared to alkali silicates, and support the likelihood that increase in anionic disorder with increasing temperature makes some contribution to the configurational heat capacity as previously suggested (Brandriss and Stebbins 1988; Stebbins 1988).

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