Bonding preferences of non-bridging O atoms: Evidence from ^{17}O MAS and 3QMAS NMR on calcium aluminate and low-silica Ca-aluminosilicate glasses

JEFFREY R. ALLWARDT,* SUNG KEUN LEE,† AND JONATHAN F. STEBBINS

Department of Geological and Environmental Sciences, Building 320, Stanford University, Stanford, California, 94305-2115, U.S.A.

ABSTRACT

The fraction of O atoms as non-bridging O atoms (NBO) can be well approximated based on composition alone in many silicate glasses, but the NBO preference for specific network forming cations is much less well known. Using oxygen-17 (^{17}O) NMR on low-silica calcium aluminosilicate (CAS) glasses, this study shows that Al-NBO (155 ppm) can be readily distinguished from Si-NBO (110-120 ppm), and that there is a strong preference for the latter. This study also presents a consistent equilibrium constant formulation that indicates that for thermodynamic modeling of most CAS melts with Si > Al, Al-NBO are of minor importance, although they could be significant in some models of diffusion and viscosity. Al-27 one pulse NMR and analyses of spinning side bands show that AlO_5 and AlO_6 species are below detection limits (<0.5%) in the low-silica ($SiO_2 \leq 20$ mol%) glasses of this study (NBO/T = 0.6 to 0.8). In addition, ^{17}O MAS NMR does not detect any obvious (<2%?) Al_3O triclusters; hence calculations of NBO assignments can be assigned unambiguously.

INTRODUCTION

Discussion of oxide glass structure relies heavily upon the principle that there are network formers (i.e., Si, Al, B) and network modifiers (i.e., Ca, Na, K etc.). The network formers provide the framework and rigidity of the glass while the network modifier oxides break apart this structure through the formation of non-bridging O atoms (NBO). An NBO is an O atom bonded to only one network former leaving the network modifiers to balance the remaining valence charge.

Network connectivity plays a significant role in the thermodynamic (Navrotsky 1995; Hess 1995) and transport properties (Hess et al. 1995, 1996) of magmas and glasses. For instance, the orthosilicate composition (33 mol% SiO_2) of the binary compositions of SiO_2-alkali or alkaline earth glasses is thought to contain the most NBO of any composition (Hess 1980). In binary silicate glasses, as the amount of silica is increased from the orthosilicate composition (increasing the network connectivity and reducing the number of NBO), enthalpies, free energies, component activities, and viscosity are all strongly affected (Hess 1995; Navrotsky 1995; Hess et al. 1995, 1996). This is the result of increasing the network connectivity as Q^0 species are being converted to Q^1, Q^2, and even more connected species, where 0, 1, and 2 represent the number of bridging O atoms (BO) bonded to the Si tetrahedron. Similar effects are expected for other network forming cations. The average degree of network connectivity is relatively well known for silicate and aluminosilicate glasses, but

the distribution of NBO on different network cations is much less well understood. Certain combinations of framework cations in some composition ranges show no preference in competing for NBO, such as B and Si in the Ba-borosilicates (Zhao et al. 2000). In contrast, there is much indirect evidence that suggests that Si has a strong preference over Al for NBO in the alkali and alkaline earth aluminosilicate systems (Mysen 1988 and references therein).

Most previous studies of NBO preferences in aluminosilicates have used relatively indirect methods for NBO detection such as Raman spectroscopy (Mysen et al. 1981, 1985; Domine and Pirou 1986), X-ray and/or neutron scattering (Petkov et al. 1998, 2000; Cormier et al. 2000), and ^{27}Al and ^{29}Si magic-angle spinning (MAS) NMR (Engelhardt et al. 1985). For example, Engelhardt et al. (1985) used the observed ^{29}Si chemical shifts to estimate the average Q speciation for Si and Al in "low silica" (<10% SiO_2) glass as Q^0 and Q^4, respectively. However, the uniqueness of such conclusions is uncertain because of the lack of resolution among ^{29}Si peaks for different network species and the dependence of ^{29}Si MAS chemical shift on both the average Q speciation and next nearest neighbor effects (Si vs. Al).

Oxygen-17 NMR can provide a much more direct evaluation of this issue. Previous ^{17}O NMR spectra have shown the presence of NBO in several calcium aluminosilicate (CAS) glasses on the $CaAl_2O_4$-SiO_2 join (Stebbins and Xu 1997; Stebbins et al. 1999; Oglesby et al. 2002; Lee and Stebbins 2002). The observed ^{17}O MAS chemical shifts for NBO in these glasses are similar to those found in calcium silicate glasses in which all NBO are bonded to Si (Stebbins 1995; Stebbins et al. 1997). In addition, a recent ^{17}O MAS study of an NBO-containing impurity phase in crystalline $CaAl_2O_4$ showed that the Al-NBO peak is shifted to a higher frequency by 30 to 40 ppm

* E-mail: allwardt@pangea.stanford.edu
† Present address: Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, Washington, D.C. 20015, U.S.A.

from that of the NBO peak observed for the CAS and Ca-silicate glass spectra (Stebbins et al. 2001). These findings further suggested that Si is the preferred network cation of NBO in aluminosilicate glasses and thus in melts at the glass transition temperature.

An intriguing complication to the conventional network picture of the melt structure is the possible presence of minor concentrations of "triclusters" containing three tetrahedral network formers linked to a single O atom (Lacy 1963). These have been suggested by Toplis et al. (1997) and others on the basis of viscosity anomalies in Na-aluminosilicate liquids near the charge-balanced ($NaAlO_2$-SiO_2) join, and could increase the predicted fraction of NBO. Although ^{17}O NMR data on crystalline $CaAl_4O_7$ indicated a distinct set of NMR parameters for at least Al_3O triclusters, overlap with bridging O atom peak intensity in the Ca-aluminosilicate glasses has not yet allowed unambiguous detection of this species (Stebbins et al. 2000). Low-silica glasses provide an opportunity to more clearly resolve such groups.

The observation of small amounts of high-coordinated Al ([5]Al and [6]Al) in some alkaline earth aluminosilicates of glasses (Toplis et al. 2000; Stebbins et al. 2001) and in the calcium aluminate glasses (Shelby et al. 1989) can also complicate the calculation of average Q speciation and the NBO to tetrahedra ratio (NBO/T). For instance, are O atoms bonded to [5]Al and [6]Al considered bridging (BO) or non-bridging (NBO) in aluminosilicate glass structure? If the higher coordinated Al atoms are considered as network forming, should they be counted in the number of tetrahedra? To make an unambiguous assignment of NBO/T, it must be shown that concentrations of high-coordinated Al atoms in the glass structure are negligible. Aluminum-27 MAS NMR data are thus a useful complement to ^{17}O spectra.

By investigating Si-poor Ca-aluminosilicates with ^{17}O NMR, it is thus possible to observe to what extent NBO "prefer" Si as a framework host compared to Al, because Al-NBO can be directly observed and quantified. Here we describe results for Al-NBO and Si-NBO in calcium aluminate and low-silica (10, 20, and 33 mol%) calcium aluminosilicate glasses utilizing ^{17}O MAS and ^{17}O triple-quantum MAS (3QMAS) NMR, where for the first time both species can be directly quantified, and the "preference" for Si-NBO rigorously defined.

EXPERIMENTAL PROCEDURE

The eutectic composition of calcium aluminate (62 CaO·38 Al_2O_3) was chosen due to its low liquidus temperature (1360 °C) and relatively good glass-forming ability; calcium aluminosilicate (CAS) compositions were selected to keep the ratio of NBO/T (0.62) and the percentage of total O atoms as NBO (27%) near constant to aid in the direct comparison of spectra.

Glass samples were made using CaO, ~45% ^{17}O-enriched SiO_2 (Stebbins et al. 1997), and ~20% ^{17}O-enriched Al_2O_3. Some of the latter was made by hydrothermal exchange between ^{17}O-enriched water and $Al(OH)_3$, as in Stebbins et al. (2001). The remainder of the enriched Al_2O_3 was made using a new method, by slowly injecting 1 mL of 40% ^{17}O-enriched H_2O (Icon Stable Isotopes) into a water-cooled flask containing the stoichiometric amount (4.6 g) of Al-tri-*sec*-butoxide. The reactants were stored in a sealed flask for a week to allow ample time for the reaction to occur. The resulting $Al(OH)_3$ was then rinsed with isopropanol, dried at 120 °C, and slowly heated to 1000 °C in Ar to form Al_2O_3. Calcium oxide was used in place of $CaCO_3$ to avoid loss of ^{17}O during decarbonation. Due to the hygroscopic behavior of CaO, it was dried overnight at 1000 °C and was used immediately. No significant weight gain occurred during the weighing of this reagent.

To speed spin-lattice relaxation, 0.2 wt% cobalt oxide was added to the oxide powders. The 200 mg samples were then melted in Ar (Table 1) and quenched by dipping the bottom of the Pt crucible in water. Samples were found to be entirely amorphous when examined with a 400× petrographic microscope. Compositions were measured by electron microprobe using mineral standards (Table 1). This analysis showed small amounts of unexpected MgO (< 0.5 mol%), which when compared to the amount of CaO in the sample will cause errors in data analysis much less significant than some of the other uncertainties. Additionally, the microprobe data of the CA glass showed 0.6 mol% SiO_2 from an unknown source.

The ^{17}O and ^{27}Al MAS NMR spectra were collected on a Varian Unity/Inova 600 spectrometer (14.1 Tesla) using a Chemagnetics "T3" probe with 3.2 mm zirconia rotors spinning at 18 kHz. The ^{17}O and ^{27}Al frequencies are reported relative to tap water and 0.1 M acidified $Al(NO_3)_3$, respectively. Single pulse acquisition was used with pulse widths corresponding to approximately 30° rf tip angles for the solid (about 0.3 and 0.2 μs for ^{17}O and ^{27}Al, respectively); one second delays between pulses were used to optimize the signal to noise ratio and to ensure a nearly fully relaxed sample. The 3QMAS NMR spectra were collected with a modified Varian VXR/Unity 400S spectrometer (9.4 Tesla), using a Doty Scientific Inc. "Supersonic" probe with 5 mm silicon nitride rotors spinning at 15 kHz. The 3QMAS spectra used a shifted echo pulse sequence consisting of two hard pulses (5.0 μs and 1.5 μs, respectively) followed by a soft pulse (26 μs) similar to that used by Lee and Stebbins (2000). Delay times of 2 s and 37 μs were used. Processing of the 3QMAS data was done with the software package RMN (FAT) (P.J. Grandinetti, Ohio State University). The resulting 3QMAS spectra are two-dimensional plots in which the isotropic dimension is free of second order quadrupolar broadening and the MAS dimension portrays a somewhat distorted view of the 1-D MAS spectrum.

For nuclides with nuclear spin I = 5/2, such as ^{27}Al and ^{17}O, the spinning side-bands for the "inner satellite" ($\pm 1/2 - \pm 3/2$) transition are much less affected by quadrupolar broadening than the central transition ($-1/2 - +1/2$) (Jäger 1994), often providing enhanced resolution. For each of the ^{27}Al spectra of this study, six inner satellite sidebands were stacked to enhance the signal to noise ratio and compared to the main peak to investigate the presence of higher coordinated Al, as in Stebbins et al. (2000). The largest noise "peak" in the summed spectrum was integrated and compared to the integral of the main peak to obtain a minimum detection limit for [5]Al and [6]Al sites of about 0.5 atomic percent.

RESULTS

The ^{17}O MAS spectra for the calcium aluminate (CA) and aluminosilicate (CAS) glasses are shown in Figure 1. For the calcium aluminate, there are two main peaks: a large Al-O-Al peak at 72 ppm (Stebbins et al. 1999) and a smaller peak at 155 ppm. This smaller peak can be uniquely assigned to Al-NBO because this is the only other major O atom species present. There is also a small shoulder at about 120 ppm, which can be assigned to Si-NBO (Stebbins 1995; Stebbins et al. 1997). This peak was not expected but was later shown to be due to a small amount of silica contamination of the CA glass. From the CA glass data and the previously mentioned work, the peak assignments of the other CAS glasses are straightforward, as both Si-NBO and Al-NBO peaks at these same positions are clearly, if only partially, resolved. As silica is added, the peak assigned to Si-NBO increases in intensity and the peak assigned to Al-NBO decreases in intensity. The BO peak in the CA glass spectrum shifts to lower relative frequencies as more SiO_2 is added and more Si-O-Al sites are formed (Lee and Stebbins 1999, 2000). The spectrum of the CAS33 glass may also contain a small, broad shoulder, possibly due to Al-NBO, but its relative area is difficult to assess accurately.

Several recent reports (Xu and Stebbins 1998; Lee and Stebbins 2000) describe the interpretation of ^{17}O 3QMAS NMR spectra of aluminosilicates in detail. Here such data serve to extend the conclusions drawn from the MAS spectra. For ex-

TABLE 1. Composition, synthesis temperatures, and MAS fitting results for the three samples of this study

Sample	Mole percent				Nominal		(Measured from MAS fit)				
	CaO	Al_2O_3	SiO_2	T(°C)	%NBO	NBO/T	%NBO*	%Si-NBO*	%Al-NBO*	NBO/Al	NBO/Si
CA	61.5	37.9	0.6	1470	26.8	0.62	28.4	~0.9	27.6	0.6	2.5
CAS10	58.5	29.4	11.8	1606	34.2	0.82	36.0	17.0	19.0	0.5	2.3
CAS20	52.0	28.0	20.3	1542	27.2	0.63	32.4	21.6	10.8	0.3	1.6

Notes: "Nominal" values are based on stoichiometry only.
* The estimated uncertainties in the measured component peak areas are about 1% absolute, based on sensitivity to fitting and baseline corrections.
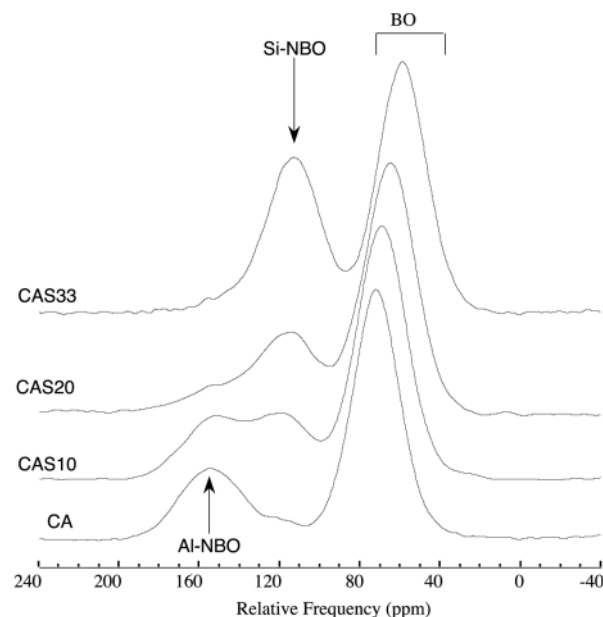
FIGURE 1. ^{17}O MAS NMR spectra for calcium aluminate and low-silica calcium aluminosilicates glasses collected at 14.1 T. Sample compositions are given in Table 1, except for CAS33 (nominal composition: 50 mol% CaO, 17% Al_2O_3, 33% SiO_2, CAS312 in Lee and Stebbins, in preparation).

ample, the BO peak in the MAS spectrum for CAS20 contains no discernible components, but the 3QMAS (Fig. 2) data partially resolves the Al-O-Si and Al-O-Al peaks that are expected from the MAS data and also from previous work in this ternary system (Lee and Stebbins 1999, 2000; Cormier et al. 2000). In the ^{17}O 3QMAS spectra of the CAS10 and CAS20 glasses, no Si-O-Si peak is seen, indicating that less than a few percent of the total O atoms are Si-O-Si. The peak assigned to Al-NBO is slightly offset from the Si-NBO peak, which further lends support to the presence of two distinct types of NBO.

The quantitative nature of MAS NMR allows the percentage of each type of O atom to be determined from the relative area of each peak. For ^{17}O spectra at 14.1 T, for sites with relatively low values of quadrupolar coupling constant (C_q), quadrupolar peak shapes are not obvious and are often well approximated by Gaussians, which were used to fit the spectra (Fig. 3). The average network connectivity of each framework cation can then be obtained from the fitted areas, because the total number of Al and Si atoms are known from electron microprobe analysis (Table 1). As silica is added, the network con-

nectivity of the Al increases markedly (decreasing Al-NBO/Al).

An equilibrium constant formulation with species concentrations measured from MAS NMR can be used to predict percentages of Al-NBO and Si-NBO for glasses based on composition. In determining the relevant equilibrium expression, Si-O-Si was neglected because of its low abundance in the systems of this study:

$$Si-O-Al + Al-NBO \leftrightarrow Al-O-Al + Si-NBO \qquad (1)$$

The resulting idealized equilibrium constant, K_1, (ignoring activity coefficients) is [Al-O-Al][Si-NBO]/[Si-O-Al][Al-NBO], where brackets denote the fraction of O atoms at each site type. Atomic percentages of Al and Si-NBO were measured by fitting ^{17}O MAS NMR spectra. Atomic percentages of Si-O-Al and Al-O-Al were then calculated from composition using the approximation that [Si-O-Si] = 0. For the CAS10 glass, in which the two large NBO peaks made peak fitting relatively straightforward, the calculated value of K_1 is 4.1 ± 1.1, where the uncertainty reflects the propagated fitting errors (Table1). By assuming K_1 is constant, predictions of the percentages of Si-NBO and Al-NBO can be made for CA (+ 0.6 mol% SiO_2), CAS20, and CAS33 and compared to the measured values (Table 2). These predictions show good agreement with those measured from fitting ^{17}O MAS NMR spectra. The equilibrium constant formulation can then be used to predict the amount of Al-NBO in compositions where there are no suitable data (Fig. 4). An apparent slight, systematic excess of total NBO (Table 1) may result from a small difference in the spin-lattice relaxation rate of the NBO vs. the BO.

Of all BO, Al-O-Al groups have the highest frequency chemical shifts in ^{17}O spectra (Stebbins et al. 1999), allowing a more definitive look for Al_3O triclusters than has previously been possible in higher silica glasses (Stebbins et al. 2000). Such groups should produce a peak with a maximum at about 35 ppm at a magnetic field of 14.1 T (Stebbins et al. 2001). The absence of an obvious feature (other than the "tail" of the Al-O-Al peak) in this region of the spectrum for CA glass indicated that at least in this composition range, triclusters concentrations are below the detection limit of about 2%. This finding does not, however, constrain the concentrations of the other triclusters species such as $(Si_2Al)O$, or their concentrations in glasses with higher Al/Ca ratios, or their possible effects on producing a slight excess of NBO above that estimated from composition (Toplis et al. 1997).

As is typical for glasses, the ^{27}Al MAS spectrum for the CA glass (Fig. 5) is broad and unresolved and shows only one peak centered at 74 ppm, which suggests that most Al are Q^3 and Q^4 species (Stebbins 1995). The peak maximum of the CAS20
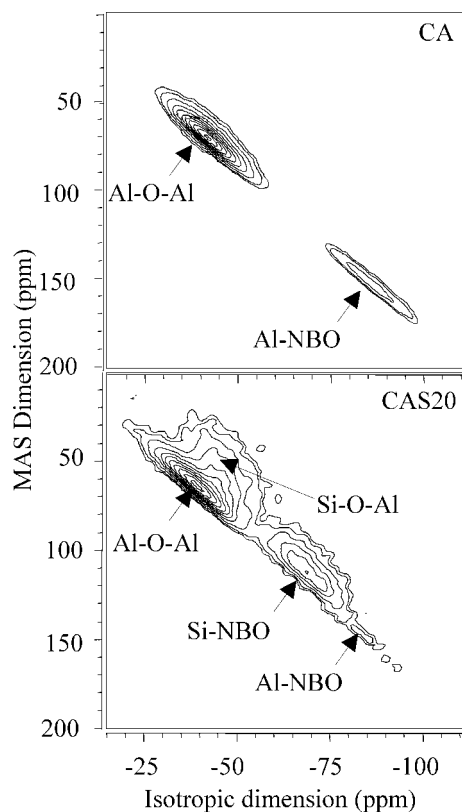
FIGURE 2. [17]O 3QMAS spectra for CA and CAS20 glasses where the contour lines are from 7 to 97% spaced at intervals of 10% with an extra interval placed at 10% to emphasize the peak maximum of Al-NBO.
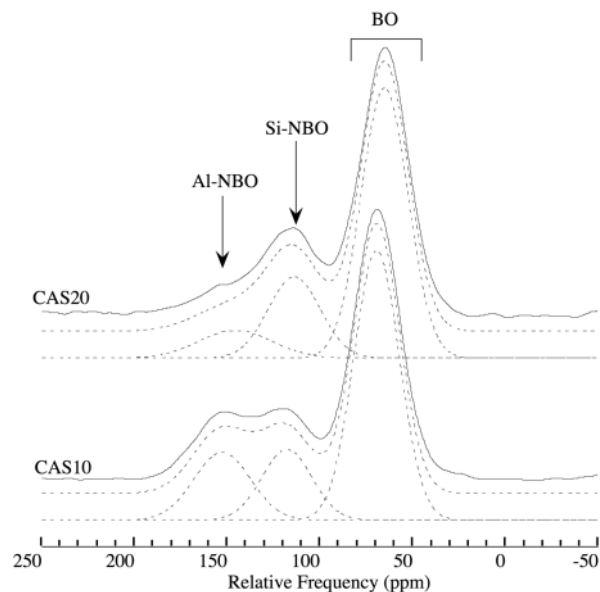

FIGURE 3. Peak fits for the ^{17}O MAS NMR spectra for calcium aluminosilicate glasses (CAS10 and CAS20), in which peak shapes are assumed to be Gaussian.

spectrum is shifted about 10 ppm to a lower frequency, which suggests that most Al is present as Q^4 species and is consistent with the [17]O results. Within detection limits (~0.5 atomic percent), only [4]Al was detected in the [27]Al MAS stacked sideband spectra of the CA, CAS10, and CAS20 glasses (Fig. 5), because there was no obvious signal in the regions expected for [5]Al (30 to 45 ppm) or [6]Al (0 to 16 ppm) (Poe et al. 1994; Stebbins 1995).

DISCUSSION

Both the qualitative changes in the proportions of the Al-NBO and Si-NBO peaks with silica content (Fig. 1), and the calculated value of K_1, support and quantify previous conclusions that there is a strong preference for NBO to be localized on Si (Engelhardt et al. 1985; Mysen et al. 1981,1985; Domine and Pirou 1986; Petkov et al. 1998, 2000; Stebbins et al. 2001), presumably because there is less tendency for O atom "underbonding" (insufficient charge compensation) to occur with the higher charge network forming cations.

To further extend the equilibrium constant formulation and make it applicable to more silica-rich, and hence, more geologically relevant systems, the interaction of all three BO species should be considered with the reaction:

$$2\text{Si-O-Al} \leftrightarrow \text{Al-O-Al} + \text{Si-O-Si} \qquad (2)$$
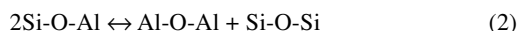
The work of Lee and Stebbins (1999, 2000), which models the results of detailed ^{29}Si and ^{17}O NMR studies, has shown that there is a significant disproportionation in reaction 2. This leads to, for example, about 14% of the total O atoms as Al-O-Al in CaAl$_2$Si$_2$O$_8$ (anorthite) glass (Lee and Stebbins 1999). If Si-O-Si linkages are formed by reaction 2, additional Al-O-Al is also formed and the fraction of Si-O-Al decreases, resulting in an increased estimated value for K, as calculated above. However, the model for network speciation developed by Lee and Stebbins (1999, 2000) predicts that there will be only about 0.5 atomic% of Si-O-Si for the CAS10 composition, which would lead to a small correction in K_1, which makes $K_1 = 4.6 \pm$

TABLE 2. Comparison of measured and predicted NBO percentages based on fits of ^{17}O NMR data for CAS10. R_{NBO} = [Si-NBO]/[Al-NBO]

	Measured*	Calculated
CA		
R_{NBO}	0.03	0.03
% Si-NBO	~0.9	0.9†
% Al-NBO	27.6	27.5†
CAS20		
R_{NBO}	1.9	2.4
% Si-NBO	21.6	23.0†
% Al-NBO	10.8	9.6†
CAS33		
R_{NBO}	9 − ∞	10.6
% Si-NBO	36 − 40	36.6
% Al-NBO	0 − 4	3.4

* The estimated uncertainties in the measured component peak areas are about 1% absolute, based on sensitivity to fitting and baseline corrections.
† The sum of the percentages for NBO species has been normalized to the total NBO measured from peak fitting (Table 1) to aid in comparison.
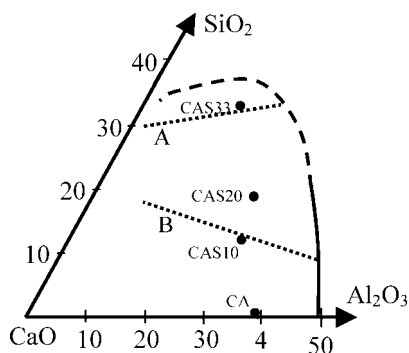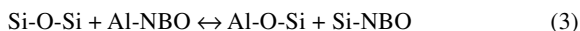
FIGURE 4. Ca-rich portion of the CAS ternary showing predictions for the fraction of total O atoms as Al-NBO, assuming $K_1 = 4.1$. The dotted lines "A" and "B" reflect the (Si-NBO)/(Al-NBO) ratios (R_{NBO}) of 1 and 10, respectively. The solid, curved line shows compositions where Al-NBO are ~2% of the total O atoms and where the "lack of Si-O-Si" assumption is relatively accurate. This model neglects the NBO that have been measured in the CAS charge balanced join compositions so the "2% Al-NBO" predictions will likely be pushed to more Al-rich compositions. The extrapolated, dashed line, is the prediction of Al-NBO in the region where the Si-O-Si species become more significant.

FIGURE 5. ^{27}Al MAS spectrum at 14.1T of the calcium aluminate glass showing the central transition (ct), and the sum of the six consecutive ($\pm 1/2$-$\pm 3/2$) satellite spinning sidebands (ssb), shifted to their central frequency for comparison.

1.1 and the predicted Al-NBO = 18.6 instead of 19.0 atomic%. In contrast, for a K_1 value based on low silica glasses, as is derived here, neglecting Si-O-Si in higher silica compositions will lead to an underestimation of the predicted fraction of Al-NBO.

In Figure 1, the CAS33 ^{17}O MAS spectrum has a small shoulder at about 150 ppm that might be due to the presence of a small fraction of Al-NBO, although the presence of this species is not clearly required by the data. Our estimated equilibrium constant (K_1) predicts that this composition could contain about 3% Al-NBO (Table 2). However, the accuracy of this prediction from very low silica glasses is probably reduced by the increase in the Si-O-Si fraction at higher silica contents.

By subtracting Equation 2 from Equation 1, one obtains:

$$\text{Si-O-Si} + \text{Al-NBO} \leftrightarrow \text{Al-O-Si} + \text{Si-NBO} \qquad (3)$$

Although Equation 3 is more directly applicable to natural systems, its "equilibrium constant" cannot be calculated directly from the present data set due to difficulties in measuring very small concentrations of Si-O-Si and Al-NBO with high accuracies. As more data become available on the thermodynamics of such reactions, especially the effects of temperature, a consistent, predictive formulation of their free energies should become feasible.

The contour line in Figure 4, denoting regions where the fraction of O atoms as Al-NBO is less than a few percent, indicates that for most or all geologically "interesting" Ca-aluminosilicate compositions, these species are probably of low enough concentration to be excluded from thermodynamic models of overall free energies and chemical potentials. However, small fractions could remain important in models of dy-
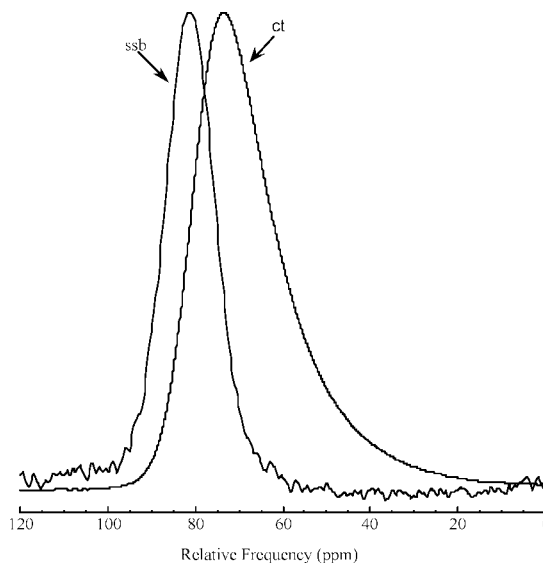
namics. This conclusion also has important implications for the way thermodynamic models of melts are formulated. If, for example, mixing of estimated "Q^n" species populations enter into the formulation of configurational entropy, the distribution of such species over Si and Al will be quite different (most Al will be in Q^4 groups). Similarly, if silica activity is related to the fraction of SiO$_4$ groups with 4 Si neighbors (Stebbins and Farnan 1989), then it will be overestimated if NBO are assumed to be equally distributed over Si and Al.

Even with the enhanced resolution provided by the "inner satellite" spinning side bands (Fig. 5), we see no evidence for [5]Al and [6]Al in the calcium aluminate glass. This agrees with the ^{27}Al MAS NMR study of McMillan et al. (1996) at 7.4 T, but contradicts the study of Shelby et al. (1989), which was also done at the relatively high frequency of 14.1 T. The latter showed a small shoulder (~1%) at 9 ppm, which we did not detect. It is possible that this peak may have resulted from octahedral Al in a crystalline phase due to the difficulty in quenching large batches of calcium aluminate glasses.

The lack of measurable concentrations of high-coordinated Al and triclusters supports our study's assignment of Al-NBO/Al and Si-NBO/Si ratios (Table 1) because there is no ambiguity in the assignment of NBO and tetrahedral species. However, the observation that higher-coordinated Al is undetectable in the glass (which represents the melt at T_g) does not necessarily mean that such groups are not present in the melts at higher T. Ion dynamics has shown that as the temperature of the melt increases, the Al-coordination increases slightly (Poe et al. 1994). However, probably a more important factor in the average Al coordination of aluminosilicate melts is the effect of the percentage of Al$_2$O$_3$. Poe et al. (1993, 1994) have utilized ion dynamics and in situ high-temperature ^{27}Al MAS NMR of cal-

cium aluminates to show that the average aluminum coordination increases with an increasing percentage of Al_2O_3. For instance, ion dynamics predicts that there would be an increase in the average coordination of Al by 0.2 when the percentage of Al_2O_3 increases from 38% (this study) to 50% (charge-balanced join) (Poe et al. 1994). This is the same trend as that seen when these samples are compared to the amount of higher-coordinated Al measured in samples along the CAS "charge balanced" join (Toplis et al. 2000; Stebbins et al. 2000). In general, temperature effects on all aspects of melt structure should be carefully considered before extrapolating results from glasses to liquidus temperatures.

REFERENCES CITED

Cormier, L., Neuville, D.R., and Calas, G. (2000) Structure and properties of low-silica calcium aluminosilicate glasses. Journal of Non-Crystalline Solids, 274, 110–114.

Domine, F. and Pirou, B. (1986) Raman spectroscopic study of the SiO_2-Al_2O_3-K_2O vitreous system: distribution of silicon second neighbors. American Mineralogist, 71, 38–50.

Engelhardt, G., Nofz, M., Forkel, K., Wihsmann, F.G., Mägi, M., Samoson, A., and Lippmaa, E. (1985) Structural studies of calcium aluminosilicate glasses by high resolution solid state ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance. Physics and Chemistry of Glasses, 26, 157–165.

Hess, P.C. (1980) Polymerization model for silicate melts. In Hargrves, Ed. Physics of magmatic processes, p. 3–48. Princeton University Press, Princeton, New Jersey.

Hess, P.C. (1995) Thermodynamic mixing properties and structure of silicate melts. In J.F. Stebbins, P.F. McMillan, and D.B. Dingwell, Eds., Structure, Dynamics and Properties of Silicate Melts, p. 121–144. Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C.

Hess, K.-U., Dingwell, D.B., and Webb, S.L. (1995) The influence of excess alkalis on the viscosity of a haplogranitic melt. American Mineralogist, 80, 297–304.

——— (1996) The influence of alkaline-earth oxides (BeO, MgO, CaO, SrO, BaO) on the viscosity of a haplogranitic melt: systematics of non-Arrhenian behaviour. European Journal of Mineralogy, 8, 371–381.

Jäger, C. (1994) Satellite transition spectroscopy of quadrupolar nuclei. In P. Diehl, E. Fluck, H. Günther, R. Kosfeld, and J. Seelig, Ed., Solid State NMR III: Inorganic Matter, p. 135–170. Springer-Verlag, Berlin.

Lacy, E.D. (1963) Aluminum in glasses and melts. Physics and Chemistry of Glasses, 4, 234–238.

Lee, S.K. and Stebbins, J.F. (1999) The degree of aluminum avoidance in aluminosilicate glasses. American Mineralogist, 84, 937–945.

——— (2000) The structure of aluminosilicate glasses: High-resolution ^{17}O and ^{27}Al MAS and 3QMAS NMR study. Journal of Physical Chemistry B, 104, 4091–4100.

——— (2002) Extent of intermixing among framework units in silicate glasses and melts. Geochimica et Cosmochimica Acta, 66, 303–309.

McMillan, P.F., Petuskey, W.T., Coté, B., Massiot, D., Landron, C., and Coutures, J.P. (1996) A structural investigation of CaO-Al_2O_3 glasses via ^{27}Al MAS-NMR. Journal of Non-Crystalline Solids, 195, 261–271.

Mysen, B.O. (1988) Structure and properties of silicate melts. Elsevier, Amsterdam.

Mysen, B.O., Virgo, D., and Kushiro, I. (1981) The structural role of aluminum in silicate melts—a Raman spectroscopic study at 1 atmosphere. American Mineralogist, 66, 678–701.

Mysen, B.O., Virgo, D., and Seifert, F.A. (1985) Relationship between properties and structure of aluminosilicate melts. American Mineralogist, 70, 88–105.

Navrotsky, A. (1995) Energetics of silicate melts. In J.F. Stebbins, P.F. McMillan, and D.B. Dingwell, Eds., Structure, Dynamics and properties of silicate melts, p. 121–144. Reviewes in Mineralogy, Mineralogical Society of America, Washington, D.C.

Oglesby, J.V., Zhao, P., and Stebbins, J.F. (2002) Oxygen sites in hydrous aluminosilicate glasses: The role of Al-O-Al and H_2O. Geochimica et Cosmochimica Acta, 66, 291–301.

Petkov, V., Gerber, Th., and Himmel, B. (1998) Atomic ordering in $Ca_{x/2}Al_xSi_{1-x}O_2$ glasses (x=0,0.34,0.5,0.68) by energy-dispersive x-ray diffraction. Physical Review B, 58, 11982–11989.

Petkov, V. Billinge, S.J.L., Shastri, S.D., and Himmel, B. (2000) Polyhedral units and network connectivity in calcium aluminosilicate glasses from high-energy x-ray diffraction. Physical Review Letters, 85, 3436–3439.

Poe, B.T., McMillan, P.F., Coté, B., Massiot, D., and Coutures, J.P. (1993) Magnesium and calcium aluminate liquids: In situ high-temperature ^{27}Al NMR spectroscopy. Science, 259, 786–788.

——— (1994) Structure and dynamics in calcium aluminate liquids: high-temperature ^{27}Al NMR and Raman spectroscopy. Journal of the American Ceramic Society, 77, 1832–1838.

Shelby, J.E., Shaw, C.A., and Spess, M.S. (1989) Calcium fluoroaluminate glasses. Journal of Applied Physics, 66, 1149–1154.

Stebbins, J.F. (1995) Nuclear magnetic resonance spectroscopy of silicates and oxides in geochemistry and geophysics. In T.J. Ahrens, Ed., Handbook of Physical Constants, p. 303–332. American Geophysical Union, Washington D.C.

Stebbins, J.F. and Farnan, I. (1989) NMR spectroscopy in the earth sciences: structure and dynamics. Science, 245, 257–262.

Stebbins, J.F. and Xu, Z. (1997) NMR evidence for excess non-bridging oxygens in an aluminosilicate glass. Nature, 390, 60–62.

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., Lee, S.K., and Oglesby, J.V. (1999) Al-O-Al oxygen sites in crystalline aluminates and aluminosilicate glasses: high resolution oxygen-17 NMR results. American Mineralogist, 84, 1116–1124.

Stebbins, J.F., Kroeker, S., Lee, S.K., and Kiczenski, T.J. (2000) Quantification of five-and six-coordinated aluminum in aluminosilicate and fluoride-containing glasses by high field, high resolution ^{27}Al-NMR. Journal of Non-Crystalline Solids, 275, 1–6.

Stebbins, J.F., Oglesby, J.V., and Kroeker, S. (2001) Oxygen triclusters in crystalline $CaAl_4O_7$ (grossite) and in calcium aluminosilicate glasses: ^{17}O NMR. American Mineralogist, 86, 1307–1311.

Toplis, M.J., Dingwell, D.B., and Lenci, T. (1997) Peraluminous viscosity maxima in Na_2O-Al_2O_3-SiO_2 liquids: The role of triclusters in tectosilicate melts. Geochimica et Cosmochimica Acta, 61, 2605–2612.

Toplis, M.J., Kohn, S.C., Smith, M.E., and Poplett, I.J.F. (2000) Fivefold-coordinated aluminum in tectosilicate glasses observed by triple quantum MAS NMR. American Mineralogist, 85, 1556–1560.

Xu, Z. and Stebbins, J.F. (1998) Oxygen sites in the zeolite stilbite: a comparison of static, MAS, VAS, DAS and triple quantum MAS NMR techniques. Solid State Nuclear Magnetic Resonance, 11, 243–251.

Zhao, P., Kroeker, S., and Stebbins, J.F. (2000) Non-bridging oxygen sites in barium borosilicate glasses: results from ^{11}B and ^{17}O NMR. Journal of Non-Crystalline Solids, 276, 122–131.