The degree of aluminum avoidance in aluminosilicate glasses

SUNG KEUN LEE AND JONATHAN F. STEBBINS*

Department of Geological and Environmental Sciences, Stanford University, Stanford, Connecticut 94305–2115, U.S.A.

ABSTRACT

For two series of aluminosilicate glasses on the SiO_2-$NaAlO_2$ and SiO_2-$CaAl_2O_4$ joins, ^{29}Si magic-angle-spinning (MAS) NMR spectra were measured. Systematic variations in peak positions and widths with composition are closely related to the extent of ordering of Si and Al cations. A statistical thermodynamic model based on the quasi-chemical approximation was formulated to calculate the proportions of SiO_4 groups with varying numbers of Al neighbors and thus to quantify the extent of ordering. Multiple spectra in each compositional series were fitted simultaneously with several peaks representing each of these structural species and with area constraints generated by the model. The extent of aluminum avoidance (Q), which was defined using the relative lattice energy differences among the linkages Si-O-Si, Si-O-Al, and Al-O-Al, was optimized for each series. For the calcium aluminosilicates, the best fit is with $0.8 \leq Q \leq 0.875$, where $Q = 1$ represents perfect Al-avoidance. For the sodium series, Q was found to be larger ($0.93 \leq Q \leq 0.99$), as expected from energetic considerations and from known variations in ordering in minerals. The contributions to the overall configurational entropy and heat capacity from Si-Al disorder can be calculated, and are significant fractions of experimentally estimated values. However, major contributions must also come from other sources of disorder, such as "topological" disorder of bond angles and length.

INTRODUCTION

The ordering behavior of framework cations in aluminosilicate glasses has been studied for several decades, partly because of its fundamental interest to petrologists and geochemists and partly to its implications for macroscopic thermodynamic and transport properties of magma, such as heat capacity and viscosity. One aspect of short-range order of framework cations can be expressed as the Al avoidance or Loewenstein's rule, which postulates that the Al-O-Si linkage is more favorable than the combination of Si-O-Si and Al-O-Al (Loewenstein 1954). The extent of obedience of this principle in aluminosilicate melts and glasses still remains a major question (Cormack and Cao 1997). Based on the ^{29}Si MAS NMR line widths in aluminosilicate glasses, a tendency toward Al avoidance was inferred (Murdoch et al. 1985). Furthermore, perfect Al avoidance has usually been assumed for chemical modeling of aluminosilicate glasses (Engelhardt et al. 1985; Engelhardt and Michel 1987). Several theoretical calculations have also implied that the combination of Al-O-Al and Si-O-Si linkages is energetically less favorable than Al-O-Si (De Jong and Brown 1980).

On the other hand, calorimetric data suggest that the bond-ordering energy is about 20–40 kJ/mol, which should allow some Al-O-Al linkages (Navrotsky et al. 1982). Results of molecular dynamic simulations in fully polymerized aluminosilicate glasses also support the existence of Al-O-Al, at least at the very high temperatures typical of such calculations (Zirl

and Garofalini 1990; Stein and Spera 1995). Recently, the presence of small amounts of Si-O-Si in glasses of anorthite composition was observed with triple quantum MAS NMR spectroscopy (Stebbins and Xu 1997), which suggested some Al-O-Al linkages. Thus a certain amount of disordering is to be expected and should increase at higher temperature.

One of the major factors that can affect the ordering behavior of framework aluminosilicate glasses is the field strength of charge balancing cations such as Na^+ and Ca^{2+} (De Jong and Brown 1980; McMillan et al. 1982; Murdoch et al. 1985). Because high field strength cations favor increased negative charge concentration, the probability of finding Al-O-Al linkages should increase in Ca- over Na-containing glasses (Tossell and Sághi-Szabó 1997).

In spite of these efforts at determining the ordering of network cations in aluminosilicate glasses, the extent of Al avoidance remains uncertain, in part because NMR spectra for many compositions are entirely unresolved, making determination of populations of Si sites with varying numbers of Al neighbors very model-dependent. Most previous modeling efforts thus were forced to assume perfect Al avoidance (Murdoch et al. 1985; Engelhardt and Michel 1987; Merzbacher et al. 1991). A more sophisticated model, based on simulation analysis of higher-quality data from a range of compositions is required to go beyond these assumptions.

In this study, the extent of ordering of framework cations in aluminosilicate glasses along the 1:1 "charge compensated" joins SiO_2-$NaAlO_2$ and SiO_2-$CaAl_2O_4$, is investigated using ^{29}Si MAS NMR spectroscopy. The degree of Al avoidance is quantified using a simple statistical thermodynamic model based on the quasi-chemical approximation. The effect of cation field

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

strength on the ordering scheme is also evaluated. In addition, calculated configurational thermodynamic properties of aluminosilicate glasses are compared with experimental data.

EXPERIMENTAL METHODS

Sample preparation

Glasses were prepared from pure oxide (SiO_2, Al_2O_3) and carbonate (Na_2CO_3, $CaCO_3$) reagents with about 0.1 wt% CoO, which was added to reduce the spin lattice relaxation time. Mixtures were decarbonated at 800 °C and then fused at 1600 °C for one hour, quenched, reground, and fused again to insure the homogeneity. All glasses samples were analyzed by electron micropobe (EPMA), using oxide and silicate mineral standards and a 10 to 30 mm defocused beam. Samples on the SiO_2-$CaAl_2O_4$ join appeared to be homogeneous and close to nominal compositions (within about 0.5%). Average analyses of glasses on the SiO_2-$NaAlO_2$ join were again close to nominal (within about 1%). However, because of potential systematic errors caused by alkali migration during the analyses, we consider the nominal compositions to be more accurate and these are reported in Table 1. The two glasses in this series with the highest silica contents (R = Si/Al = 4 and 6) appeared to have minor, but real, compositional heterogeneities (about 1 to 2%). To test the sensitivity of our data analyses to this potential problem, we used the model discussed below to simulate spectra for variations in composition larger than those observed. We found that combinations of such spectra chosen to equal the average composition were indistinguishable from the simulated spectra at the average composition: for example, a 50–50 sum of spectra for R = 5 and R = 7 was essentially the same as that for R = 6. The reason for this insensitivity in this compositional range is the fact that at high silica contents, with a high degree of Al-avoidance (as deduced below), spectra are dominated by only two species. We conclude that such heterogeneities are not significant in the fitting and analysis procedure.

NMR spectroscopy

NMR spectra were obtained with a spectrometer (Varian VXR 400S, 9.4 T) operating at a Larmor frequency of 79.45 MHz for ^{29}Si. Powdered samples were packed in 7 mm zirconia rotors and spun at 6500 Hz in a Varian magic angle spinning probe. Delay times between pulses were varied for several glasses and were found not to affect the peak shape. A delay time between pulses of 1 s and a radio frequency pulse of approximately 2 ms were used. Peak positions are reported relative to external tetramethysilane (TMS). Peaks were normalized to the same height and integrals were calculated to derive a shape-independent estimation of width, as was done in a previous study (Murdoch et al. 1985). A constant Gaussian apodization was applied to increase signal-to-noise ratios but was adjusted to ensure that final peak widths did not exceed those of unapodized data by more than 0.3 ppm.

Fitting procedure

Based on extensive studies of crystalline aluminosilicates (Engelhardt and Michel 1987), each spectrum, although unresolved, was assumed to be composed of five Gaussian peaks representing the five possible Si species with zero through four Al neighbors, which are denoted $Q^4(mAl)$. For each of two compositional series (Na- and Ca-aluminosilicates), the width and position of each component peak was taken as fixed and thus independent of composition. For varying series of Q values representing different degrees of aluminum avoidance, the model described below was used to predict the relative proportions of these five species for each experimental composition in a series. Using these values to fix all component peak areas, spectra for all the glasses in the series were then fitted simultaneously by a non-linear least square algorithm, with five peak widths and five peak positions as the only adjustable parameters. Allowable ranges of these parameters were loosely constrained by ranges of chemical shifts for each species that have been previously reported for aluminosilicate minerals (Engelhardt and Michel 1987). At a specific Q value (degree of Al avoidance), the same fit was obtained independent of the initial guesses for parameters, indicating that a stable minimum in residuals was found. The Q values that gave the best overall fit were selected on the basis of maximum R^2 values (>0.99), physically most sensible peak widths (<16 ppm FWHM or 7 ppm standard deviation of Gaussian distribution function) and separations in chemical shifts from one species to the next (about 3 to 7 ppm)

SPECIATION MODEL

Several simple statistical models have described the short range ordering in framework aluminosilicates in terms of the relative population of $Q^4(mAl)$ sites. Binomial distributions of species subject to the restriction of perfect Al avoidance were applied to crystalline aluminosilicates including zeolites, and are often consistent with experimentally determined populations from NMR spectroscopy (Klinowski et al. 1982; Herrero et al. 1985; Thomas and Klinowski 1985; Murdoch et al. 1988). Few studies of the $Q^4(mAl)$ speciation in aluminosilicate glasses explored the extent of Al avoidance, primarily because of difficulties imposed by lack of spectral resolution. However, strict

TABLE 1. Peak positions and integrated areas ^{29}Si MAS NMR spectra

R = Si/Al	Composition	Peak maximum (ppm)	Normalized integral*
Calcium aluminosilicate glasses			
0.5†	CaO-Al_2O_3-SiO_2	−82.6	13.4
1	CaO-Al_2O_3-$2SiO_2$	−87.5	16.9
2†	CaO-Al_2O_3-$4SiO_2$	−95.4	21.0
3	CaO-Al_2O_3-$6SiO_2$	−101.1	21.3
4	CaO-Al_2O_3-$8SiO_2$	−103.7	21.9
6†	CaO-Al_2O_3-$12SiO_2$	−107.9	19.1
Sodium aluminosilicate glasses			
0.7‡	Na_2O-Al_2O_3-$1.4SiO_2$	−83.7	13
0.9	Na_2O-Al_2O_3-$1.8SiO_2$	−85	13.8
1	Na_2O-Al_2O_3-$2SiO_2$	-85.5	14.2
1.5‡	Na_2O-Al_2O_3-$3SiO_2$	−89.8	15.8
2	Na_2O-Al_2O_3-$4SiO_2$	−93.08	17.0
3	Na_2O-Al_2O_3-$6SiO_2$	−97.68	18.1
4	Na_2O-Al_2O_3-$8SiO_2$	-101.11	19.5
6	Na_2O-Al_2O_3-$12SiO_2$	−104.22	18.6

Notes: Areas are normalized to constant peak height, and are scaled to approximate peak width in parts per million.
* Measured in frequency range from −150 ppm to −50 ppm.
† Glasses were made by remelting of previously prepared glasses of Murdoch et al. (1985).
‡ Not included in fitting procedure.

aluminum avoidance predicts a single species $Q^4(4Al)$ at a Si-Al ratio $R = 1$ along the charge-compensated join. With the usual assumption of Gaussian peak shapes, this implies a symmetrical peak shape, not the slightly asymmetrical peaks described below for anorthite ($CaAl_2Si_2O_8$) and nepheline ($NaAlSiO_4$) glasses.

To obtain the analytical equation for the species distribution, allowing a non-zero fraction of Al-O-Al, the relative proportions of Al-O-Si, Si-O-Si, and Al-O-Al linkages were first calculated assuming that all Si and Al are in Q^4 sites ("fully polymerized" tetrahedra) and that the number of each linkage depends on their relative energy difference. The latter is the quasi-chemical approximation (Fowler and Guggenheim 1956), which has mainly been used to describe the local ordering behavior of alloys and polymers (Gogcen 1986; Gurman 1991). The $Q^4(mAl)$ species distribution function was then obtained from the expression for the probability of finding Al around Si as a next nearest neighbor and the degree of Al avoidance was also formulated. Variables used in the derivation include: N_1, N_2 = number of Si and Al cations, respectively; X_1, X_2 = mole fractions of Si and Al, respectively (relative to total Si +Al); N = total number of cations; $R = N_1/N_2$; m = number of Al first cation neighbors for a given Si; N_{ij} = number of i-O-j bonds, i and j are Si and Al respectively; z = number of tetrahedral neighbors (4 for fully polymerized aluminosilicate); λ_{ij} = lattice energy of i-j pair (in this section, it is identical to the energy of i-O-j); and k = Boltzman constant.

The ordering scheme of framework cations is assumed to depend only on the following reaction:

$$(\text{Si-O-Si}) + (\text{Al-O-Al}) = 2(\text{Al-O-Si}). \tag{1}$$

The lattice energy difference (W) of the above reaction can be expressed as:

$$W = z\left[\lambda_{12} - \frac{1}{2}(\lambda_{11} + \lambda_{22})\right]. \tag{2}$$

The relations between the number of cations and number of bonds are:

$$2N_{11} = zN_1 - N_{12} \tag{3a}$$

$$2N_{11} = zN_1 - N_{12}. \tag{3b}$$

The number of Al-O-Si linkages in framework aluminosilicates can then be calculated from energy minimization of the system:

$$N_{12} = \frac{zN_1N_2}{N}\frac{1}{\beta+1} \tag{4}$$

where

$$\beta = \sqrt{1 + 4X_1X_2(\eta^2 - 1)}$$

$$\eta = \exp(2W/zKT).$$

T is taken as 1050 K, which approximates the average glass transition temperature (T_g) in these systems, assumed to the best represent the temperature at which the Si-Al distribution

was in equilibrium. Real compositional variations in T_g of 50 to 100 K have insignificant effects on our modeling. The probability of finding each linkage can be represented as

$$P_{12} = \frac{N_{12}}{2N_{11} + N_{12}} = X_2\frac{2}{(\beta + 1)} \tag{5}$$

Therefore the proportions of each Q4(mAl) can be obtained using the binomial distribution function:

$$P(m) = {_4}C_m \frac{2^m(R\beta + R + \beta - 1)^{4-m}}{(R\beta + R + \beta + 1)^4}. \tag{6}$$

Finally for convenience, the degree of Al avoidance (Q) can be defined as follows:

$$Q = 1 - \eta^2. \tag{7}$$

A value of $Q = 1$ thus refers to perfect obedience of Al avoidance rule, and $Q = 0$ represents a fully random distribution of Si and Al. The variation of $Q^4(mAl)$ species with respect to composition and degree of Al avoidance (Q) is illustrated in Figure 1.

RESULTS

^{29}Si MAS NMR spectroscopy

Calcium aluminosilicate glasses. With increasing Si/Al ratio in this system, NMR peak positions move to lower frequency (more negative chemical shifts) primarily because of the well-known effect of replacing Al first cation neighbors with Si, each of which typically results in a shift of about 5 ppm (Engelhardt and Michel 1987). Peaks are generally asymmetric, most extremely so for compositions of $R = 0.5$ and 6 (Fig. 2). The variations of peak positions and widths in this system are consistent with previous results (Murdoch et al. 1985; Oestrike
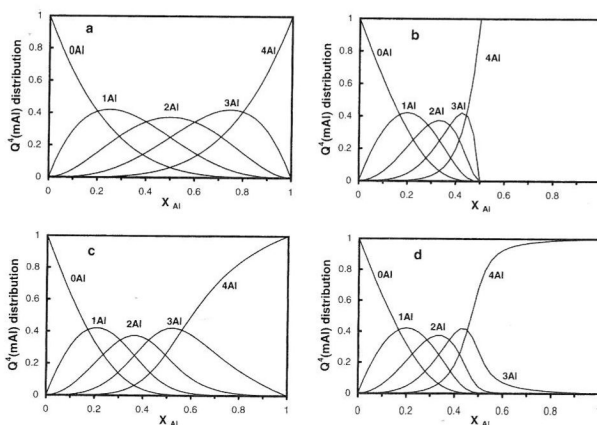

FIGURE 1. Calculated distributions of $Q^4(mAl)$ species with respect to variation of composition and degree of Al avoidance (Q). mAl refers to Q4(mAl). **(a)** random distribution of Si and Al ($Q = 0$), **(b)** Perfect Al avoidance ($Q = 1$), **(c)** $Q = 0.85$, **(d)** $Q = 0.99$
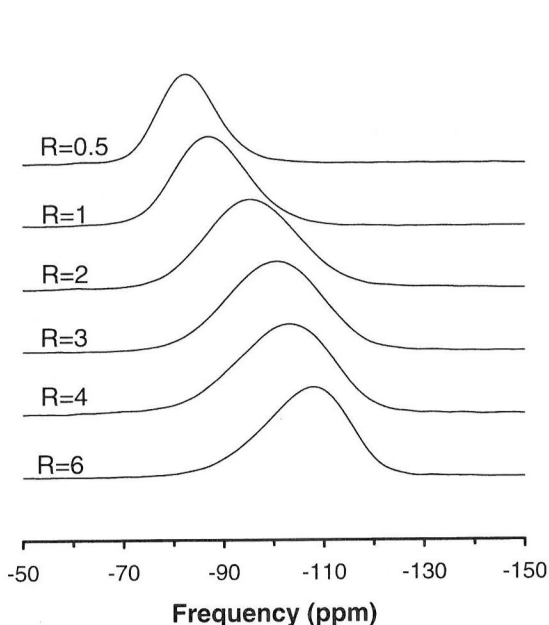
FIGURE 2. Various ^{29}Si MAS NMR spectra of calcium aluminosilicate glasses with variable ratios (R) of Si/Al.
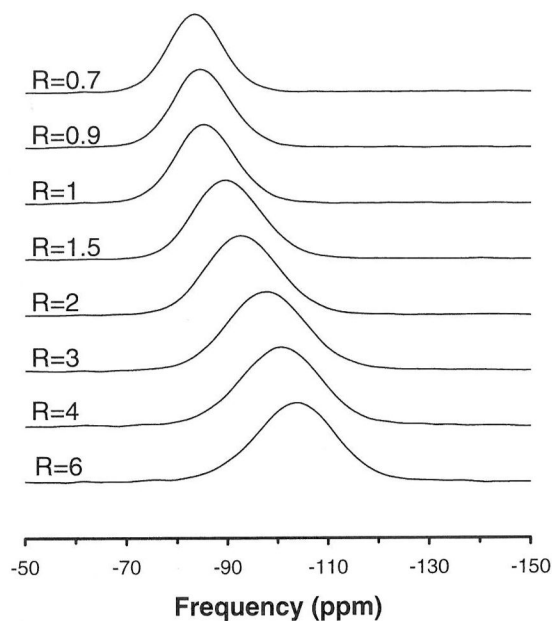

FIGURE 3. Variation of peak width (normalized) with composition.

FIGURE 4. Various ^{29}Si MAS NMR spectra of sodium aluminosilicate glasses with variable ratios of Si/Al.

and Kirkpatrick 1988; Libourel et al. 1991; Merzbacher et al. 1991) (Table 1 and Fig. 3), but these studies did not attempt quantitative peak shape modeling.

Sodium aluminosilicates. Similar variations of peak positions and asymmetry of spectra as a function of composition can be observed in this series. The asymmetries of peaks in sodium aluminosilicate glasses are less than those of the calcium aluminosilicate glasses. In addition, the normalized area (and thus peak widths) of each NMR spectrum is less than that of the corresponding calcium aluminosilicate glass (Figs. 3 and 4 and Table 1).

Fitting results based on speciation model

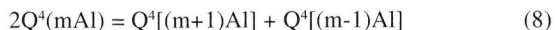The experimental spectra for the calcium aluminosilicate glasses can be fitted well with calculated $Q^4(mAl)$ distributions in which the degree of Al avoidance (Q) ranges between 0.8–0.875. The fitted results began to deviate obviously from the experimental spectra when Q exceeds 0.9 or is less than 0.8. The widths and positions of the five fitted component peaks are given in Table 2 and fits are shown in Figure 5.

Similar data are also shown for the five sodium aluminosilicates in Table 2 and Figure 6. The best fit of the NMR spectra of the sodium aluminosilicates was obtained for Q values ranging from 0.93 to 0.99. In this series, the gaps in frequency between each $Q^4(mAl)$ species are smaller than those of calcium aluminosilicate glasses. In order to test the validities of obtained peak positions and widths with degree of Al avoidance (Q), we made two other Na-aluminosilicate glasses with R (Si/Al) of 0.7 and 1.5, and compared the experimental spectra with simulated ones calculated using the previously obtained parameters. The differences between the experimental spectra for these compositions and simulated spectra are within the error range of the simulation, suggesting again that the modeling is relatively robust.

DISCUSSION

Peak positions and widths of $Q^4(mAl)$ species

Murdoch et al. (1985), suggested that wider peaks in calcium aluminosilicate glasses than in sodium aluminosilicates resulted from the fact that high field strength cation may enhance the equilibrium constant of the following type of reaction (McMillan et al. 1982), by analogy with better constrained equilibrium in binary alkali silicates (Mysen et al. 1982):

$$2Q^4(mAl) = Q^4[(m+1)Al] + Q^4[(m-1)Al] \qquad (8)$$

One of the assumptions of this argument is that the peak position for each $Q^4(mAl)$ species in calcium and sodium aluminosilicates is nearly same. In the modeling described here, we find instead that the shift in component peak positions as the number of next nearest Al changes is greater in the Ca
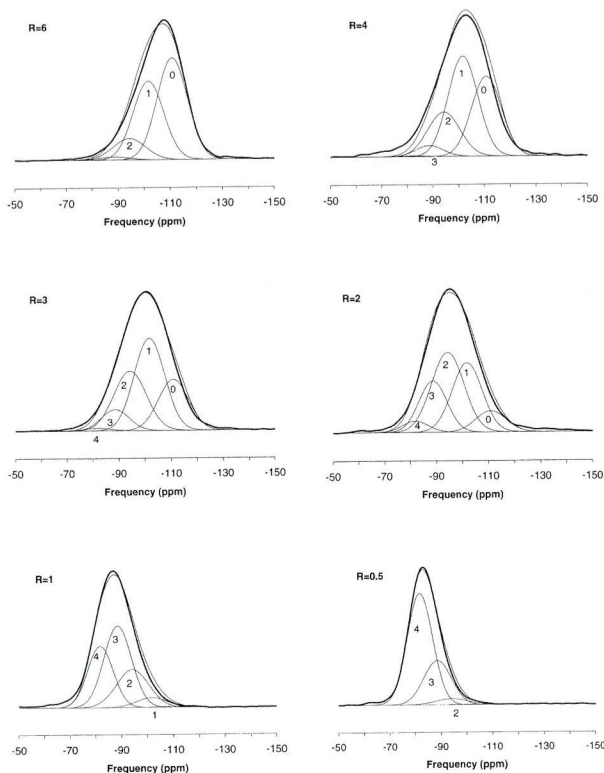
FIGURE 5. Fitting results for ^{29}Si MAS NMR spectra of calcium aluminosilicate glasses with $Q = 0.875$. Thick solids lines are the experimental spectra and thin solid lines show the fitted curves and each component.
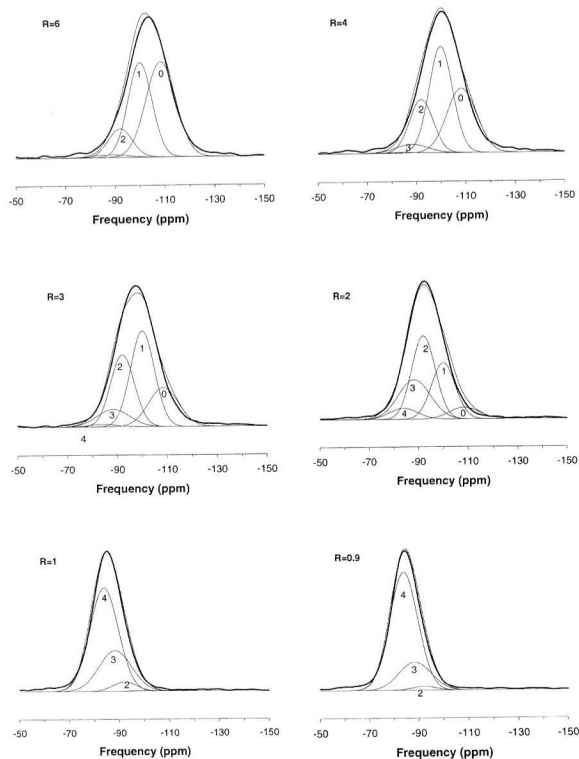
FIGURE 6. Fitting results for ^{29}Si MAS NMR spectra of sodium aluminosilicate glasses with $Q = 0.99$. Thick solids lines are the experimental spectra and thin solid lines show the fitted curves and each component.

glasses than in the Na series. This effect, combined with the reduced Si-Al order in the former, seems to dominate overall peak widths.

Although structural and chemical factors are coupled, correlations among ^{29}Si chemical shifts and structural parameters such as Si-O bond length and mean Si-O-T bond angle have been reported (Smith and Blackwell 1983; Ramdas and Klinowski 1984; Engelhardt and Michel 1987). The variation of the component peak positions of each species with the charge balancing cations may thus result from the difference in variation of bond distance and bond angle distributions in calcium and sodium aluminosilicate glasses. In particular, the stronger interaction of Ca^{2+} with Si-O-Al O atoms (when compared to Na^+) is likely to cause a greater decrease in mean Si-O-T bond

angle as each Si neighbor is replaced with an Al. Known correlations suggest that this leads to a greater increase (to less negative value) of chemical shifts.

The widths of individual component peaks in calcium aluminosilicate are also greater than those of the sodium aluminosilicate glasses, which implies some other contribution to disorder, such as ranges of bond angle. Models of ring distributions in nepheline and anorthite glasses may be consistent with this result (Taylor and Brown 1979; Seifert et al. 1982).

In our fitting procedure, we have assumed that the contribution to the spectra from each Q^4(mAl) species is a Gaussian distribution of chemical shifts whose center frequency and width are independent of composition (Si/Al). This approximation is the only appropriate one, given current limitations on our knowledge of the effects of local and intermediate range structure in glasses on NMR parameters. Future improvements in this knowledge could, of course, lead to more sophisticated modeling and refined results. The peak positions for Q^4(0Al) in our simulations of NAS glass spectra (about −108 ppm) and of CAS (about −111 ppm) are similar to those reported for pure SiO_2 glass (−108.5 to −111.5, Oestrike et al. 1987; Xue et al. 1991). However, there is some evidence from crystalline zeolites that, for a given structure, increases in Si/Al cause slight (0 to 2 ppm), systematic changes to lower frequency of ^{29}Si isotropic chemical shifts (Engelhardt and Michel 1987). We have not built such trends into our modeling both because they are not

TABLE 2. Fitted peak positions and full width at half maximum for each Q^4(mAl) species in parts per million

		Q^4(4Al)	Q^4(3Al)	Q^4(2Al)	Q^4(1Al)	Q^4(0Al)
Sodium aluminosilicate						
$Q = 0.99$	Position	−84.1	−88.5	−92.2	−100.1	−108.1
	Width(FWHM)	13.28	15.14	11.04	11.16	13.94
$Q = 0.93$	Position	−81.7	−86.1	−92.7	−100.1	−108.4
	Width(FWHM)	12.98	9.90	9.32	10.62	13.49
Calcium aluminosilicate						
$Q = 0.87$	Position	−81.9	−88.6	−94.4	−101.7	−110.8
	Width(FWHM)	11.54	12.50	14.60	13.63	13.54
$Q = 0.80$	Position	−81.3	−87.0	−93.7	−101.9	−110.9
	Width(FWHM)	11.18	11.42	11.88	12.40	13.19

systematic and well-known enough for the systems studied here (in particular the calcium aluminosilicates), and because it is possible that such trends for crystalline materials may not be accurate in glasses, depending on their structural cause. For example, the trends suggested for sodium zeolites are probably caused by slight increases in mean Si-O-T bond angles for each $Q^4(mAl)$ species as Si-Al increases. This could be caused by overall distortions in the long-range lattice structure, in which case extrapolation to glasses could be inappropriate. However, if the trend were a local effect caused by decreased interaction of charge balancing cations with bridging O atoms as the concentration of such cations decrease, then the same effect might be present in glasses. Sensitivity analyses of our fitting procedure indicate that systematic 1 ppm shifts in the isotropic chemical shifts produce changes in major species concentrations that are within the error ranges already indicated. If the postulated changes in chemical shift with composition were larger than expected, trends in overall peak shape with composition would require somewhat greater Si-Al disorder than that reported here.

Compositional effects on disorder

The finding of a significant extent of Al avoidance (Q) is consistent with the expectation that a certain amount of ordering in framework cation distribution is inherent in aluminosilicate glasses regardless of the type of network modifying cations (Murdoch et al. 1985). In addition, Ca^{2+} can apparently stabilize the Al-O-Al linkage with less energy penalty than Na^+, which is consistent with the results of molecular orbital calculations (Tossell 1993; Tossell and Sághi-Szabó 1997). The variation of $Q^4(mAl)$ species with respect to the energy penalty of the Al-O-Al linkage is illustrated in Figure 7, which shows the estimated values for the two glass series studied here.

The proportions of T-O-T linkages in the aluminosilicate glasses can be calculated from Equations 3 and 4 and are as follows (Fig. 8):

$$X_{1-O-2} = 4X_1 X_2 \frac{1}{\beta+1} \qquad (9)$$

$$X_{1-O-1} = X_1 \left(1 - \frac{2X_2}{\beta+1}\right) \qquad (10)$$

$$X_{2-O-2} = X_2 \left(1 - \frac{2X_1}{\beta+1}\right). \qquad (11)$$

The proportions of the Al-O-Al linkage in the glasses as a function of Si-Al and degree of Al avoidance are shown in Figure 9. Less than 5% of the Al-O-Al linkage is predicted in a glass of albite composition. On the other hand, in a glass of anorthite composition, about 13% of Al-O-Al linkages are expected (Table 3). These species may be detectable directly in future, high resolution NMR studies, particularly of ^{17}O (Wang and Stebbins 1998).

Effect of nonbridging O atoms

We have assumed throughout that all tetrahedral groups in SiO_2-$CaAl_2O_4$ and SiO_2-$Na_2Al_2O_4$ are connected to other tetra-

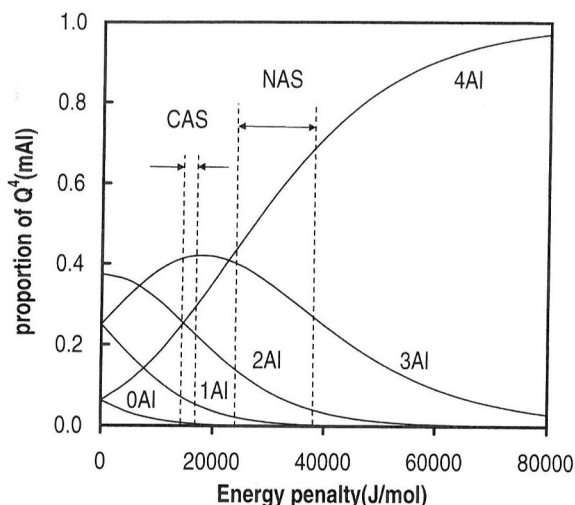**FIGURE 7.** Variation of $Q^4(mAl)$ species populations with ordering energy for $R = 1$. Dashed lines refer the derived degree of Al avoidance (Q) for calcium(CAS) and sodium(NAS) aluminosilicate glasses, which range $0.93 \leq Q \leq 0.99$ and $0.8 \leq Q \leq 0.875$, respectively. Negative energy penalty is bond ordering enthalpy of Equation 1.
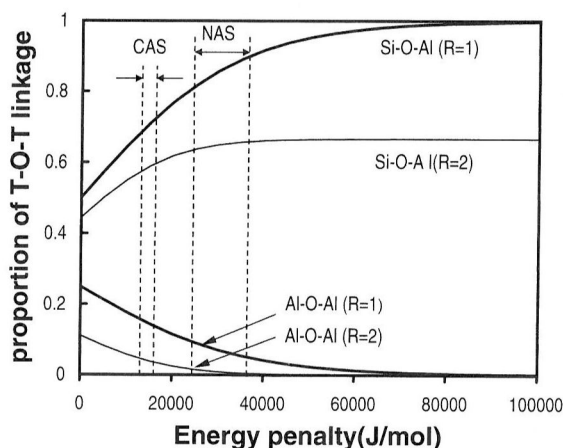

FIGURE 8. Variation of proportions of T-O-T linkages with relative lattice energy difference. Dashed lines refer the derived degree of Al avoidance (Q) for calcium (CAS) and sodium (NAS) aluminosilicate glasses, which range $0.8 \leq Q \leq 0.875$ and $0.93 \leq Q \leq 0.99$, respectively.

hedra (all Q^4), and thus that all O atoms are bridging. However, recent ^{17}O NMR has shown that in anorthite glass, 4 to 5% NBO are present (Stebbins and Xu 1997). Molecular dynamic simulation also reports such species (Zirl and Garofalini 1990). The anomalous behavior of viscosity, where the viscosity maxima deviate form SiO_2-$M_nAl_2O_4$ join, also can be related to the existence of NBO (Toplis et al. 1997). The detected fractions of NBO will not significantly affect the modeling described here: 5% of NBO would change the mean coordination number of Si by other tetrahedra from 4 to 3.9, which would have a minor effect on line shape fitting and the calculated properties in this system.
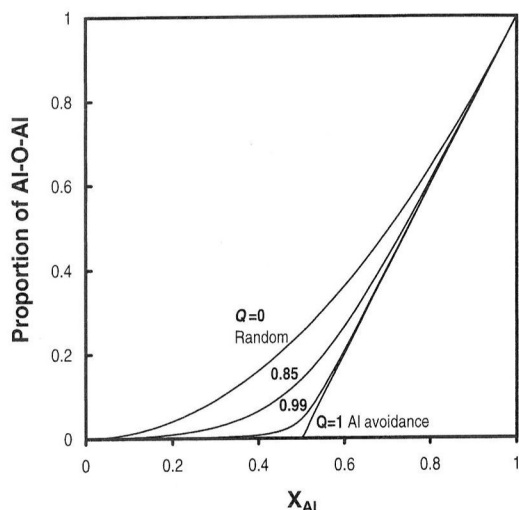
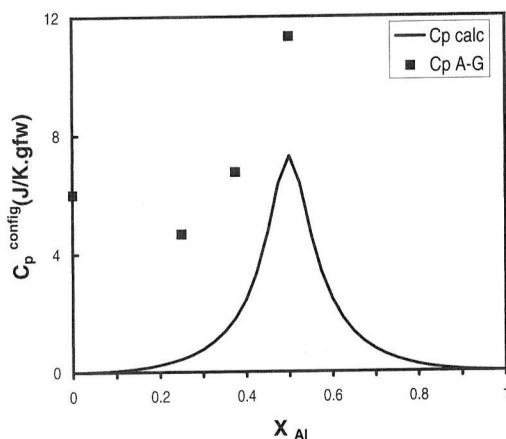**FIGURE 9.** Variation of proportions of Al-O-Al with composition.

FIGURE 11. Variation of estimated configurational heat capacity with temperature and degree of Al avoidance.

FIGURE 10. Compositional dependence of the estimated configurational heat capacity in Na-aluminosilicate glasses at $T = 1000$ K. C_p calc is the calculated configurational heat capacity and C_p A-G is the configurational heat capacity obtained from calorimetry (Richet 1984) and viscosity measurement (Toplis et al. 1997) with Adam-Gibbs formalism (Adam and Gibbs 1964).

Thermodynamic properties

The reported reaction enthalpy of rearranging the Si-Al bonds expressed as Equation 1 ranges from about –15 kJ/mol to –50 kJ/mol for crystalline aluminosilicates (Carpenter 1991; Phillips et al. 1992 and references therein) and from –20 kJ/mol to –40 kJ/mol for aluminosilicate glasses (Navrotsky et al. 1982). The enthalpy of the reaction calculated here by fitting the spectra using Q^4(mAl) species distribution function with the quasi-chemical approximation is about –16 ± 2 kJ/mol (0.8 ≤ Q ≤ 0.875). The estimated reaction enthalpy in the sodium aluminosilicate glasses is –31 ± 8 kJ/mol (0.93 ≤ Q ≤ 0.99).

In this section, configurational thermodynamic properties of aluminosilicate glasses are calculated from the degree of Al avoidance that was obtained above. Here, configurational thermodynamic properties mean the thermodynamic properties of
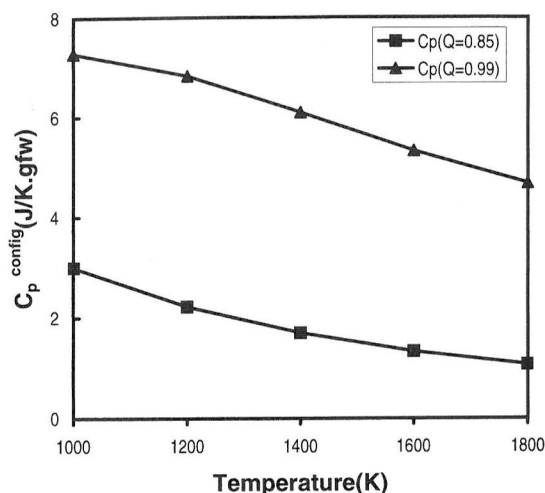
the system that originate from the rearrangement of the distribution of Si and Al that results from the interactions between them. Other configurational contributions originating from the topology and geometry of the system are not incorporated in the calculation. Configurational properties are strongly related to the relaxation behavior of melts (Adam and Gibbs 1965). Configurational enthalpy can be obtained from the configurational partition function (Gogcen 1986), which stems from the deviation of ordering of the Al and Si from random mixing and can be expressed as follows:

$$H^{\text{config}} = \frac{2X_1 X_2 W}{\beta + 1} \qquad (12)$$

As temperature increases, H^{config} decreases. The calculated configurational enthalpy is about –10 kJ/mol for anorthite glass. The magnitude and the compositional dependence of the configurational enthalpy are remarkably similar to the calorimetric heat of mixing of this composition with respect to SiO_2 and $CaAl_2O_4$ endmembers (Navrotsky et al. 1982; Navrotsky 1995), which strongly suggests that our calculated reaction enthalpy (W) of Equation 1 obtained from fitting of NMR spectra is valid. Therefore the contribution of this disordering relations to the configurational heat capacity can be obtained by differentiation of Equation 12:

$$C_p^{\text{config}} = \frac{2}{R\beta} \left[\frac{X_1 X_2 W}{(\beta + 1)T} \right]^2 \exp\left(\frac{2W}{zkT} \right) \qquad (13)$$

These values can be compared with calorimetric estimates of total configurational heat capacity (Richet 1984) and with results derived from analysis of viscosity data using the Adam-Gibbs formulation (Adam and Gibbs 1965; Richet 1984; Toplis et al. 1997). As shown in Figure 10, our estimated contributions to configurational heat capacity from Si-Al disordering can be a significant fraction of the experimental value, particularly when Si/Al approaches 1. Other contributions typically of about 5 J/gfw·K must arise from other aspects of disorder. As temperature increases, C_p^{config} also decreases (Fig.11).

TABLE 3. Calculated proportions in percent of Al-O-Al linkages in framework aluminosilicate glasses

R (Si/Al)	Q = 0.875	Q = 0.99	random	Al avoidance
6	.34	0.03	2.04	0
4	0.76	0.07	4.00	0
3	1.36	0.12	6.25	0
2	3.13	0.32	11.11	0
1	13.06	4.53	25.00	0

The excess Gibbs free energy of the system can be obtained using the Gibbs-Helmholtz Equation (Dehoff 1993) and configurational entropy was obtained by its differentiation and addition of entropy for the random distribution of linkages in the system:

$$S^{config} = \frac{2X_1 X_2 W}{(\beta+1)T} - 2\left[X_1 \ln\left(\frac{\beta-1+2X_1}{X_1(\beta+1)}\right) + X_2 \ln\left(\frac{\beta-1+2X_2}{X_2(\beta+1)}\right)\right] + S^{id} \quad (14)$$

where

$$S^{id} = -R\sum X^{id}_{i-0-j} \ln X^{id}_{i-0-j}$$

X^{id}_{i-0-j} are the mole fractions of each linkage at $\beta = 1$ (random distribution), as derived above in Equations 9–11.

Results of calculations using Equation 14 can be physically unrealistic (negative configurational entropy) when Q approaches 1. Therefore, the following simple expression can be used regardless of the magnitude of ordering:

$$S^{config} = -R\sum X_{i-0-j} \ln X_{i-0-j} \quad (15)$$

where X_{i-0-j} are the mole fractions calculated from the fitted model given in Equations 9–11. Calculated configurational entropies of the sodium aluminosilicate glasses using the quasi-chemical approximation are compared with the experimental data in Figure 12. With a simplifying assumption that all the glasses have similar "topological" contributions to entropy, which can be taken as the total configurational entropy of SiO_2 glasses, the "chemical" contribution of configurational entropy can be obtained by the subtraction of the topological contribution from the original data (Richet 1984; Toplis et al. 1997). The modeled results are close to the experimental data, which suggests that the quasi-chemical approximation can simulate the chemical contribution to the configurational entropy near the glass transition temperature. Apparently, there exists an entropy component about 5 to 6 J/gfw·K, which stems from the topological and other variations (Fig. 12).

Aluminum avoidance in aluminosilicate glasses

From the above considerations, it is evident that the distribution of framework cations in aluminosilicate glasses is not fully random, with significant ordering resulting from aluminum avoidance. However, it is also clear that such ordering is incomplete, with significant fractions of Al-O-Al linkages present, which are more prominent in calcium aluminosilicates than in the corresponding sodium-containing glasses. Because the structures of the glasses studied represent those of the liquids at the glass transition, increased disorder with increasing
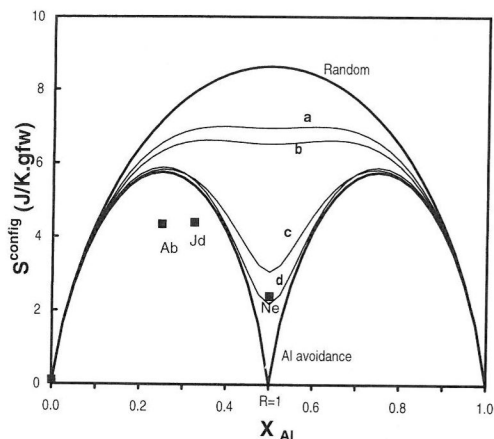

FIGURE 12. Configurational entropy of Na-aluminosilicate glasses at $T = 1000$ K. S^{config} was calculated from (**a**) Equation 15 with $Q = 0.85$; (**b**) Equation 14 with $Q = 0.85$; (**c**) Equation 14 with $Q = 0.99$ and (**d**) Equation 15 with $Q = 0.99$. Squares denote the configurational entropy obtained from calorimetric and viscosity data (Richet 1984; Toplis et al 1997), see text. Ne, Jd, and Ab refer to nepheline, jadeite, and albite composition glasses, respectively.

temperature may have an important effect on the configurational thermodynamic properties of the liquids.

REFERENCES CITED

Adam, G. and Gibbs, J.H. (1965) On the temperature dependence of cooperative relaxation properties in glass-forming liquids. Journal of Chemical Physics, 43, 139–146.
Carpenter, M. (1991) Mechanism and kinetics of Al-Si ordering in anorthite: II Energetics and a Ginzburg-Landau rate law. American Mineralogist, 76, 1120–1130.
Cormack, A.N. and Cao, Y. (1997) Molecular dynamic simulation of silicate glasses, In B. Silvi and P. D'Arco, Eds., Modelling of minerals and silicates materials, p. 341. Kluwer Academic Publisher, Dordrecht.
Dehoff, R.T. (1993) Thermodynamics in Material Science, 532 p. McGraw-Hill, New York.
De Jong, B.H.W. and Brown, G.E. Jr (1980) Polymerization of silicate and aluminate tetrahedra in glasses, melts, and aqueous solutions-I. Electronic structure of $H_6Si_2O_7$, $H_6AlSi_2O_7^{1-}$, and $H_6Al_2O_7^{2-}$. Geochimica et Cosmochimica Acta, 44, 491–511.
Engelhardt, G. and Michel, D. (1987) High-Resolution Solid-State NMR of Silicates and Zeolites, 485 p. Wiley, New York.
Engelhardt, G., Nofz, M., Forkel, K., Wihsmann, F.G., Magi, M., Samosen, 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.
Fowler, R. and Guggenheim, E.A. (1956) Statistical Thermodynamics, 701 p. Cambridge University Press, London.
Gogcen, N.A. (1986) Statistical Thermodynamics of Alloys, 326 p. Plenum Press, New York.
Gurman, S.J. (1991) Bond ordering in amorphous $Si_{1-x}N_x$. Philosophical Magazine B, 63, 1149–1157.
Herrero, C.P., Sanz, J., and Serratosa, J.M. (1985) Si, Al distribution in micas: Analysis by high-resolution ^{29}Si NMR spectroscopy. Journal of Physics C-Solid State Physics, 18, 13–22.
Klinowski, J., Ramdas, S., Thomas, J.M., Fyfe, C.A., and Hartman, J.S. (1982) A relaxation of Si and Al ordering in zeolite NaX and NaY. Journal of the Chemical Society-Faraday Transactions, 78, 1025–1050.
Libourel, G., Geiger, C., Merwin, L., and Sebald, A. (1991) High-resolution solid-state ^{29}Si and ^{27}Al MAS NMR spectroscopy of glasses in the system $CaSiO_3$-$MgSiO_3$-Al_2O_3. Chemical Geology, 96, 387–397.
Loewenstein, W. (1954) The distribution of aluminum in the tetrahedra of silicates

and aluminates. American Mineralogist, 39, 92–96.

McMillan, P.F., Piriou, B., and Navrotsky, A. (1982) A Raman spectroscopic study of glasses along the joins silica-calcium aluminate, silica-sodium aluminate, and silica-potassium aluminate. Geochimica et Cosmochimica Acta, 46, 2021–2037.

Merzbacher, C.I., McGrath, K.J., and Higby, P.L. (1991) ^{29}Si NMR and infrared reflectance spectroscopy of low silica calcium aluminosilicate. Journal of Non-Crystalline Solids, 136, 249–259.

Murdoch, J.B., Stebbins, J.F., and Carmichael, I.S.E. (1985) High-resolution ^{29}Si NMR study of silicate and aluminosilicate glasses: the effect of network-modifying cations. American Mineralogist, 70, 332–343.

Murdoch, J.B., Stebbins, J.F., Carmichael, I.S.E., and Pines, A. (1988) A silicon-29 nuclear magnetic resonance study of silicon-aluminum ordering in leucite and analcite. Physics and Chemistry of Minerals, 15, 370–382.

Mysen, B.O., Virgo, D., and Seifert, F.A. (1982) The structure of silicate melts: implications for chemical and physical properties of natural magma. Reviews of Geophysics, 20, 353–383.

Navrotsky, A. (1995) Energetics of silicate melts. In Mineralogical Society of America Reviews in Mineralogy, 32, 121–143.

Navrotsky, A., Peraudeau, G., McMillan, P., and Coutures, J.P. (1982) A thermochemical studies along the joins silica-calcium aluminate and silica sodium aluminate. Geochimica et Cosmochimica Acta, 46, 2039–2047.

Oestrike, R. and Kirkpatrick, R.J. (1988) ^{27}Al and ^{29}Si Magic angle spinning NMR spectroscopy of glasses in the system anorthite-diopside-forsterite. American Mineralogist, 73, 534–546.

Oestrike, R., Yang, W.H., Kirkpatrick, R.J., Hervig, R.L., Navrotsky, A., and Montez, B. (1987) High-resolution Na-23, Al-27, and Si-29 NMR-spectroscopy of framework aluminosilicate glasses. Geochimica et Cosmochimica Acta, 51, 2199–2209.

Phillips, B.L., Kirkpatrick, R.J., and Carpenter, M.A. (1992) Investigation of short-range Al, Si order in synthetic anorthite by ^{29}Si MAS NMR spectroscopy. American Mineralogist, 77, 484–495.

Ramdas, S. and Klinowski, J. (1984) A simple correlation between isotropic ^{29}Si-NMR chemical shifts and T-O-T angles in zeolite frameworks. Nature, 308, 525–527.

Richet, P. (1984) Viscosity and configurational entropy of silicate melts. Geochimica et Cosmochimica Acta, 48, 471–483.

Seifert, F., Mysen, B.O., and Virgo, D. (1982) Three-dimensional network structure of quenched melts (glass) in the systems SiO$_2$-NaAlO$_2$, SiO$_2$-CaAl$_2$O$_4$ and SiO$_2$-MgAl$_2$O$_4$. American Mineralogist, 67, 696–717.

Smith, J.V. and Blackwell, C.S. (1983) Nuclear magnetic resonance of silica polymorphs. Nature, 303, 223–225.

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

Stein, D. and Spera, F. (1995) Molecular dynamic simulations of liquids and glasses in the system NaAlO$_2$-SiO$_2$ methodology and melt structures. American Mineralogist, 80, 417–431.

Taylor, M. and Brown, G.E. Jr. (1979) Structure of mineral glasses-II. The SiO$_2$-NaAlSiO$_4$ join. Geochimica et Cosmochimica Acta 43, 1467–1473.

Thomas, J.M. and Klinowski, J. (1985) The study of aluminosilicate and related catalysts by high resolution solid stated NMR spectroscopy. Advances in Catalysis, 33, 199–373.

Toplis, M.J., Dingwell, D.B., Hess, K., and Lency, T. (1997) Viscosity, fragility and configurational entropy of melts along the join SiO$_2$-NaAlSiO$_4$. American Mineralogist, 82, 979–990.

Tossell, J.A. (1993) A theoretical study of the molecular basis of the Al avoidance rule and of the spectral characteristics of Al-O-Al linkages. American Mineralogist, 78, 911–920.

Tossell, J.A. and Sághi-Szabó, G. (1997) Aluminosilicate and borosilicate single 4 rings: Effect of counterions and water on structure, stability and spectra. Geochimica et Cosmochimica Acta, 61, 1171–1179.

Wang, S. and Stebbins, J.F. (1998) On the structure of borosilicate glasses : a triple quantum magic angle spinning ^{17}O nuclear magnetic study. Journal of Non-Crystalline Solids, 231, 286–290.

Xue, X.Y., Stebbins, J.F., Kanzaki, M., McMillan, P.F., and Poe, B. (1991) Pressure-induced silicon coordination and tetrahedral structural-changes in alkali oxide-silica melts up to 12 GPa: NMR, Raman, and infrared-spectroscopy. American Mineralogist, 76, 8–26.

Zirl, D.M. and Garofalini, S.H. (1990) Structure of sodium aluminosilicate glasses. Journal of the American Ceramic Society, 73, 2848–2856.