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Quench rate and temperature effects on framework ordering in aluminosilicate melts

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ABSTRACT

The effect of temperature on the structure of $LiAlSiO_4$ and $NaAlSiO_4$ liquids has been studied by ^{17}O 3QMAS NMR spectroscopy using glass samples prepared with different fictive temperatures. The abundance of Al-O-Al and Si-O-Si bridging O linkages increases with increasing fictive temperature, indicating that the reaction 2 Al-O-Si ↔ Al-O-Al + Si-O-Si shifts to the right with increasing temperature in the liquid. The observed temperature dependence of Al-O-Al species abundance allows us to estimate the ΔH of this reaction to be 28.8 ± 11.3 kJ/mol for $NaAlSiO_4$ glasses and 31.7 ± 13.3 kJ/mol for $LiAlSiO_4$ glasses. Extrapolating our results to higher temperature, we estimate that 13–18% of the bridging O atoms occur as Al-O-Al in $NaAlSiO_4$ and 15–25% in $LiAlSiO_4$ at ~2000 K, as compared to 25% Al-O-Al predicted by a statistically random bridging O distribution in compositions with an Al/Si ratio of 1. Using the experimental data to estimate the contribution to configurational heat capacity from Al/Si disordering in $NaAlSiO_4$ liquid, we find that redistribution of bridging O species with increasing temperature produces a negative dC_P/dT above the glass transition and therefore cannot account for the observed positive dC_P/dT. We discuss a generalized mechanism for structural rearrangement characterized by a small initial species concentration at T_g and a large ΔH, which produces a positive dC_P/dT.

Keywords: NMR spectroscopy, ^{17}O 3QMAS NMR, alkali aluminosilicate glasses, melts, melt structure, enthalpy, configurational heat capacity, framework cation, order-disorder, Al/Si, bridging oxygen, non-bridging oxygen, network former, termperature effect, fictive temperature, quench rate

INTRODUCTION

The extent of framework cation disorder in aluminosilicate glasses and liquids is closely linked to their thermodynamic and transport properties. The ordering of framework cations such as Si^{4+} and Al^{3+} is often described in terms of Loewenstein's (1954) "Al-avoidance" principle, which postulates that Al-O-Si linkages are more favorable than a combination of Si-O-Si and Al-O-Al. Partial to nearly complete ordering of Si^{4+} and Al^{3+} via "Al-avoidance" is well-known to operate in minerals such as feldspars, zeolites, and cordierite due in part to the difficulty of charge balancing Al-O-Al oxygen, especially with large, low-charge cations (Putnis and Angel 1985; Putnis et al. 1985, 1987; Phillips et al. 1992; Phillips and Kirkpatrick 1994; Neuhoff et al. 2003). At high temperature, however, the non-infinite value of the enthalpy of rearranging framework-cation—oxygen bonds permits the formation of Al-O-Al linkages in some feldspars and in metastable disordered phases of β-eucryptite and cordierite, as demonstrated by both theoretical (Navrotsky et al. 1985; Tossell 1993; McConnell et al. 1997) and experimental studies (Putnis and Angel 1985; Phillips et al. 1992, 1997, 2000; Benna et al. 1999).

In aluminosilicate liquids at high temperature, in contrast, a largely disordered atomic-scale structure is suspected; consequently, models of aluminosilicate melts generally assume a random distribution of Si^{4+} and Al^{3+} (Weill et al. 1980; Ghiorso et al. 1983, 2002; Ghiorso and Sack 1995). In silicate and aluminosilicate glasses, considerable evidence for Al/Si ordering has been found, at least in compositions near Al/Si = 1 where ordering is most obvious, although it has been pointed out that non-negligible amounts of disordering in these glasses illustrates that "Al-avoidance" is not a rigid principle (De Jong et al. 1983; Murdoch et al. 1985). Recently, Al/Si ordering in alkali and alkaline earth aluminosilicate glasses has been inferred from ^{29}Si MAS NMR data (Lee and Stebbins 1999). It has also been observed directly and quantified using ^{17}O 3QMAS NMR, in which peaks corresponding to Al-O-Al, Al-O-Si, and Si-O-Si oxygen sites are partially to fully resolved (Lee and Stebbins 2000a, 2000b). The ordering observed in these studies represents that of the liquid structure at the glass transition temperature (T_g), implying that structural modifications must occur with increasing temperature in aluminosilicate melts if network cation distributions are to approach the statistically random values predicted by ion and molecular dynamics simulations for temperatures in excess of 4000 K (Scamehorn and Angell 1991; Stein and Spera 1995a).

Atomic-scale glass and melt structure is tied to the configurational entropy (S^{conf}), which controls the configurational heat capacity, C_P^{conf}, through the relationship $C_p^{conf} = T\left.\frac{\partial S^{conf}}{\partial T}\right|_P$. It has been suggested that changes in Al-Si ordering with temperature may contribute significantly to S^{conf} and hence to C_P^{conf} (Richet et al. 1990; Toplis et al. 1997; Scamehorn and Angell 1991; Stein and Spera 1995b). For example, the S^{conf} datum for $NaAlSiO_4$ at T_g leaves very little room for Al-Si disordering, possibly indicating that the observed increase in C_P with T in the liquid is due to

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disordering of Al and Si tetrahedra (Richet et al. 1990). Richet et al. (1986) have pointed out that in silicate liquids C_P^{conf} may be approximated as $C_P^{conf} = C_{P,liquid} - C_{P,glass}(T_g) \approx C_{P,liquid} - 3n\mathrm{R}$, where n is the number of atoms per gram formula weight, R is the gas constant and $C_{P,liquid}$ is the experimentally determined liquid heat capacity.

Available data indicate that $C_{P,liquid}$, and therefore C_P^{conf}, may or may not vary with temperature, with C_P^{conf} generally remaining constant for alkali silicate melts, increasing for aluminosilicate melts, and decreasing for alkali-titanosilicate, Al-bearing alkali-titanosilicate, alkali-ferrosilicate, and some borosilicate melts (Richet and Bottinga 1984a, 1984b, 1985, 1995; Richet et al. 1982, 1997; Lange and Navrotsky 1993; Tangeman and Lange 1998; Roskosz et al. 2004). To determine the structural modifications responsible for the variation in C_P^{conf} with temperature, direct structural measurements quantifying short- and intermediate-range order in glasses and melts are necessary.

In situ observation of atomic-scale melt structure at temperatures relevant to magmatic processes is experimentally challenging. Alternatively, a suite of glasses with identical compositions and varying thermal histories may be studied as a structural analog for a melt over a limited temperature range. This is feasible because as a liquid is cooled through the glass transition region, it passes through a temperature below which structural relaxation occurs too slowly to permit observation on the experimental timescale (Moynihan 1995). The limiting melt structure obtained upon cooling in this manner may be characterized by the limiting fictive temperature, T_f, which is dependent on the rate of cooling, q, such that $\mathrm{d}\ln|q| \propto \mathrm{d}(1/T_f)$ (Moynihan et al. 1976). Such relaxation phenomena in the geochemical context have been introduced carefully by Dingwell and Webb (1990), Dingwell (1995), and Moynihan (1995). By preparing glass samples with different quench rates (and therefore different T_f), it is possible to "sample" the structure of a melt over a range of temperatures. Such an approach has been used successfully to study a range of structural issues in glasses of both geological and technological interest, e.g.: (1) Q-species distribution in alkali silicates (Brandriss and Stebbins 1988), (2) ^{V}Si formation in alkali silicates (Stebbins 1991; Stebbins and McMillan 1993), and (3) B coordination and non-bridging oxygen (NBO) formation in alkali borosilicates and boro-aluminosilicates (Gupta et al. 1985; Stebbins and Ellsworth 1996; Sen et al. 1998; Kiczenski et al. 2005).

In this paper, we present data from the first fictive temperature study of framework cation ordering in $NaAlSiO_4$ and $LiAlSiO_4$ glasses, which may be described by a speciation reaction involving bridging O linkages:

$$2\ \text{Si-O-Al} \leftrightarrow \text{Al-O-Al} + \text{Si-O-Si} \quad (1)$$

These compositions are ideal for assessing the extent to which "Al-avoidance" operates in aluminosilicate liquids because they have an Al/Si ratio of 1, so complete "Al-avoidance" in these glasses requires the formation of only Si-O-Al. Lee and Stebbins (2000a) have used ^{17}O 3QMAS NMR to document the presence of ~9–11% each of Al-O-Al and Si-O-Si linkages in water-quenched $NaAlSiO_4$ and $LiAlSiO_4$ glasses with estimated fictive temperatures of 1170 and 1010 K, respectively (see below). By preparing $NaAlSiO_4$ and $LiAlSiO_4$ glass samples using three different quench rates and collecting ^{17}O 3QMAS NMR data for each sample, we are now able to verify the formation of additional Al-O-Al and Si-O-Si linkages with increasing fictive temperature, demonstrating that the "Al-avoidance" principle less accurately describes liquid structure with increasing temperature. Furthermore, we can use these speciation data to calculate the contribution to configurational thermodynamic quantities from Al/Si disordering in the liquid and compare our estimates with measurements of thermodynamic properties.

Experimental methods

Sample synthesis

$LiAlSiO_4$ and $NaAlSiO_4$ glasses were prepared using three different quench rates during synthesis. Glasses prepared by typical water-quenching methods represent samples with intermediate quench rates; as detailed below, these glasses were either: (1) annealed without crystallizing to produce slow-quenched samples, or (2) remelted and rapid-quenched to produce fast-quenched samples. Water-quenched samples were prepared from dried M_2CO_3 (M = Li, Na), Al_2O_3, and 45% ^{17}O-enriched SiO_2 (for $LiAlSiO_4$), or 77%^{17}O-enriched SiO_2 (for $NaAlSiO_4$). Approximately 0.1 wt% Co_3O_4 was added to each 200 mg sample to speed spin-lattice relaxation, permitting more rapid data collection during NMR experiments. Starting materials were mixed thoroughly and placed in Pt tubes that had been welded shut at one end. The other end of the tube was then crimped halfway closed, and the samples were heated under Ar at 750 °C for 4 h to allow decarbonation. The Pt capsule was then welded shut at the other end to prevent alkali loss during melting. Samples were heated at 1520–1630 °C for 1 h, and then quenched by dipping the Pt capsule in water. Glasses obtained in this manner represent the intermediate quench rate in each compositional series, and were used as starting materials for subsequent heat treatments. Experimental charges examined with an optical microscope were homogeneously isotropic and no crystalline material was observed. Several glass chips ~2–5 mm in diameter from each composition were analyzed by electron microprobe (EPMA) using silicate mineral standards and a 10 micrometer spot size. Glass chips from the $NaAlSiO_4$ sample appeared homogeneous and close to nominal composition (within less than 2%). Glass chips from the $LiAlSiO_4$ sample also appeared homogenous and close to nominal composition (within less than 1%), with Li content calculated by difference using Si and Al analyses.

To obtain samples with slow quench rates, annealing experiments using the water-quenched glasses described above were performed. Prior to annealing experiments using ^{17}O-enriched glasses, test experiments were performed using unenriched samples to determine the experimental conditions under which crystallization was avoided. For enriched glasses, several glass shards from each composition weighing ~10 mg each were selected to minimize surface area to volume ratios and decrease the likelihood of incipient crystallization. The glass shards were placed in Pt crucibles and loaded under Ar into a programmable furnace preset at ~10 °C above published T_g values ($LiAlSiO_4$: Johnson et al. 1976; $NaAlSiO_4$: Richet et al. 1990). Samples were held at temperature for 5 min to allow the structure to equilibrate, and then cooled at 0.1 K/s to several hundred degrees below T_g.

To obtain samples with high quench rates, rapid-quench experiments were performed using small amounts of each water-quenched glass. Approximately 50 mg of each starting glass was ground to a fine powder, enclosed in Pt foil envelopes to avoid alkali loss, remelted under Ar for ~30 min at 1500 °C ($LiAlSiO_4$) or 1600 °C ($NaAlSiO_4$), and fast-quenched in a newly developed, miniaturized rapid-quench apparatus (Kiczenski and Stebbins unpublished manuscript). This device consists of a vertical tube furnace fitted with two pneumatically driven pistons that collide on a small liquid sample suspended in the hot spot of the furnace. Experimental charges measured with a digital microcaliper were 200 µm thick. Quench rates were estimated for fast-quenched samples by solving a one-dimensional heat flow equation for a laterally insulated cylinder in contact with heat sinks at both ends using appropriate estimates of the boundary conditions and the sample thermal conductivities and dimensions.

Aluminum-27 MAS NMR spectra were collected at 18.8 T (method described by Allwardt et al. 2005). No peaks for octahedrally coordinated Al were observed in any spectrum, indicating that no detectable corundum or mullite crystallized in any glass regardless of thermal history. Lithium-7 MAS NMR of $LiAlSiO_4$ glasses was also used to assess alkali loss. The integrated peak area of the broad peak observed in ^{7}Li MAS NMR spectra was normalized by sample weight and compared for samples with different thermal histories. Normalized peak areas assessed in this manner were constant, indicating negligible lithium loss during either rapid-quenching or annealing experiments.

NMR spectroscopy

Oxygen-17 3QMAS NMR spectra were collected at room temperature on a Varian Infinity Plus spectrometer (9.4 T) at a Larmor frequency of 54.19 MHz, using a Varian/Chemagnetics probe with 3.2 mm zirconia rotors spinning at 20 kHz. Chemical shifts are expressed in parts per million (ppm) relative to ^{17}O-enriched H_2O at 0 ppm. Spectra were acquired using a shifted-echo pulse sequence (Massiot et al. 1996), in which optimized lengths of triple quantum excitation and reconversion pulses were about 3.2 and 0.8 μs, with an rf power of 125 kHz. A soft 180° pulse, selecting the central transition only after 1.0 ms echo time, was set to 19 μs at an rf power of 10.2 kHz. 3QMAS data processing, including a shear transformation, was performed using the software package RMN (FAT) (P.J. Grandinetti, Ohio State University). The experimental method employed in this study was very similar to that used at the same field in a previous study of these compositions (Lee and Stebbins 2000a), except that a smaller rotor diameter, faster spinning speed, and higher pulse power were used. This approach has also been described in more detail in other recent ^{17}O 3QMAS studies of borosilicate glasses (Du and Stebbins 2003a).

Fictive temperature (T_f) calculations

Fictive temperatures of glass samples were determined using the relationship described by Moynihan et al. (1976), in which T_f is dependent on the log of the quench rate:

$$\frac{(\log q_1 - \log q_2)}{\left(\frac{1}{T_{f1}} - \frac{1}{T_{f2}}\right)} = -\frac{\Delta H_A}{2.3R} \quad (2)$$

where ΔH_A is the activation enthalpy (in J/mol) associated with structural relaxation in the glass transition region, R is the gas constant, q_1 and q_2 are two different quench rates (in K/s), and T_{f1} and T_{f2} are the fictive temperatures (in K) corresponding to q_1 and q_2. If T_f and the quench rate of a sample are known, then the T_f of a sample of the same composition prepared with a different quench rate may be calculated from this relationship. In this study, T_{f1} was taken as the glass transition temperature, determined from viscosity data for $NaAlSiO_4$ (Richet et al. 1990) and by DTA experiments for $LiAlSiO_4$ (Johnson et al. 1976). The corresponding q_1 was then taken as 0.1 K/s (±0.003 K/s), the laboratory cooling rate for annealed glass samples. Quench rates for water-quenched and rapid-quenched samples were estimated as 100 ± 50 and 6 ± 4 × 10^4 K/s (Kiczenski and Stebbins in prep). Calculated fictive temperatures incorporate uncertainties in quench rate estimates, along with uncertainties in estimates of ΔH_A. Activation enthalpies were determined from viscosity data for $NaAlSiO_4$ in the glass transition region, with uncertainties in this determination reflecting the reported error in viscosity data of ±0.06 log units (Toplis et al. 1997b). Because viscosity is non-Arrhenian for these compositions, activation enthalpies may vary significantly with temperature near T_g; therefore, a mean ΔH_A value of 680 ± 15 kJ/mol was calculated for the range of T_f values estimated for $NaAlSiO_4$ samples. In the absence of viscosity data near T_g for $LiAlSiO_4$, the ΔH_A value calculated for $NaAlSiO_4$ was assumed to roughly approximate that for $LiAlSiO_4$. Recent studies of "hyperquenched" glass fibers of basaltic composition have shown that detailed measurements by differential scanning calorimetry (DSC) can provide a more direct assessment of T_f by determining the stored enthalpy of the glass and the C_p of the metastable liquid (Yue et al. 2002, 2004). However, because of high T_g values and concerns about crystallization, we have not applied this method here.

Results of fictive temperature calculations are shown in Table 1. The logarithmic dependence of fictive temperature on quench rate considerably reduces the error introduced by uncertainty in quench rate estimates such that, for example, changing the quench rate by a factor of 2 changes the calculated fictive temperature by only 5 to 10 degrees. This example highlights the already well-known need for separation of quench rates by several orders of magnitude to produce a significant spread in fictive temperature. It must also be noted that although uncertainties in estimates of individual quench rates are significant, the overall separation of quench rates is better known. Consequently, error in absolute fictive temperature calculations does not preclude constraining the *range* of fictive temperatures with some precision, which is most important for the data analysis performed here.

RESULTS

Results from ^{17}O 3QMAS NMR spectroscopy

Figure 1 shows ^{17}O 3QMAS NMR spectra for $NaAlSiO_4$ and $LiAlSiO_4$ glasses with varying quench rates. The three peaks resolved in each spectrum are assigned to unique bridging O sites based on differing quadrupolar coupling constants and studies of crystalline model compounds (Dirken et al. 1997; Stebbins et al. 1999). Mean values of quadrupolar coupling constants (C_Q) and isotropic chemical shifts were estimated from centers of gravity of each peak in two dimensions. Elongation of the Al-O-Al peak parallel to the quadrupolar-induced shift axis is consistent with its small C_Q (≈1.9 MHz), whereas elongation of the Si-O-Al and Si-O-Si peaks parallel to the MAS dimension is consistent with their larger C_Q values (≈3.3 and ≈4.5 MHz, respectively). Peaks assigned to Al-O-Al and Si-O-Si species in these spectra corroborate the observation of imperfect "Al-avoidance" documented in the ^{17}O 3QMAS NMR data of Lee and Stebbins (2000a), who collected spectra from water-quenched $NaAlSiO_4$ and $LiAlSiO_4$ glasses. Spectra from the Lee and Stebbins (2000a) study are qualitatively (and quantitatively, see below) very like those collected in this study for samples with similar compositions and thermal histories. Furthermore, the increase in Al-O-Al and Si-O-Si peak intensity with increasing fictive temperature observed in the ^{17}O 3QMAS NMR data of this study provides direct structural evidence of temperature effects on framework ordering. The overall increase in disorder with T_f described below is apparently not large enough to cause significant systematic effects on the widths of the fitted components.

In 3QMAS NMR studies, the relationship of peak area to site population generally depends in a well-studied fashion on experimental conditions and on NMR parameters, especially C_Q. (Medek et al. 1995; Lee and Stebbins 2000b). At higher fields with somewhat higher pulse powers, intensities in ^{17}O 3QMAS NMR spectra are surprisingly insensitive to the most important variable, C_Q, as documented by independent experimental assessments of populations of bridging O atoms (C_Q values typically 3–5 MHz) and non-bridging O atoms (C_Q values typically about 2 MHz) (Du and Stebbins 2003b, 2005; Allwardt and Stebbins 2004). For data acquired under the conditions described here at 9.4 T (chosen to give the best separation among bridging O peaks for alkali aluminosilicates) and for the range of observed C_Q, intensities decrease in an approximately linear fashion with C_Q (Lee and Stebbins 2000b). In the compositions studied, it is a good approximation that all O atoms are either Si-O-Al, Al-O-Al, or Si-O-Si, and, given the stoichiometry of reaction 1, that the concentrations of the latter two species must be equal. The observation (see below) that the measured intensities of the peak for the smaller C_Q site (Al-O-Al) are systematically slightly higher than those for the larger C_Q site (Si-O-Si), as also reported earlier (Lee and Stebbins 2000a), thus probably results from differences in the quantum excitation and/or reconversion efficiency of the two sites. To approximate best the effects of T_f on the extent of the Al/Si disorder reaction, we use the constraint of stoichiometry and simply average the intensity of the two peaks. Given that analyzed compositions agree well with stoichiometry, we consider that this approach does not significantly contribute to the reported uncertainty. To determine relative site populations for all bridging O sites, corresponding peaks in isotropic projections of 3QMAS data were fit with Gaussians (Fig. 2). Peak widths and isotropic dimension positions estimated from 3QMAS spectra were used as constraints in peak fitting, with an estimated error of ±5% in integrated peak areas obtained from

TABLE 1. Relative peak intensities from peak fitting of ^{17}O 3QMAS NMR isotropic projections*

T_f(K)	Estimated quench rate (K/s)	Uncorrected peak area†			Corrected peak area†		
		Al-O-Al	Al-O-Si	Si-O-Si	Al-O-Al	Al-O-Si	Si-O-Si
		$NaAlSiO_4$ glasses					
1065 ± 20	$1 \pm 0.03 \times 10^{-1}$	0.090	0.83	0.079	0.084	0.83	0.084
1170 ± 30	$1 \pm 0.5 \times 10^{2}$	0.11	0.80	0.10	0.10	0.80	0.10
1285 ± 20	$6 \pm 4 \times 10^{4}$	0.11	0.79	0.10	0.10	0.79	0.10
		$LiAlSiO_4$ glasses					
930 ± 20	$1 \pm 0.03 \times 10^{-1}$	0.11	0.82	0.080	0.093	0.82	0.09
1010 ± 30	$1 \pm 0.5 \times 10^{2}$	0.11	0.81	0.081	0.097	0.81	0.10
1095 ± 20	$6 \pm 4 \times 10^{4}$	0.13	0.76	0.11	0.12	0.76	0.12

* Shown are uncorrected data and results corrected for variation in intensity with C_Q as described in results section of text.
† Estimated error in peak fitting is ±5%.

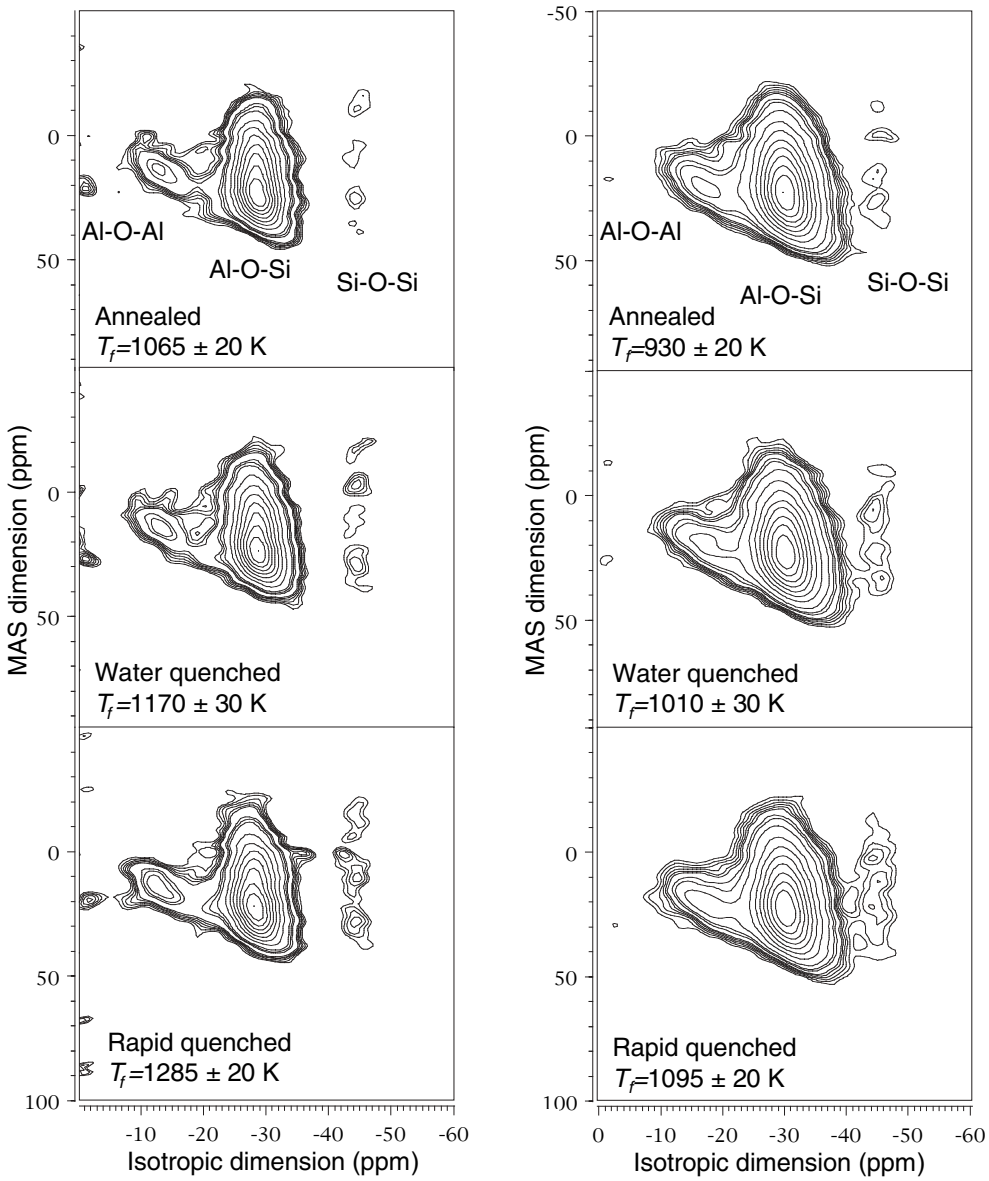

FIGURE 1. ^{17}O 3QMAS NMR spectra (9.4 T) for (**a**) $NaAlSiO_4$ glasses and (**b**) $LiAlSiO_4$ glasses. Contour lines show intensity in arbitrary units and are drawn from 5 to 100% of highest peak with spacing of 1% from 5 to 10% and spacing of 10% from 10 to 100% with contours added at 15 and 17% for $NaAlSiO_4$ and 13 and 15% for $LiAlSiO_4$, chosen to accentuate small changes in fractions of Al-O-Al and Si-O-Si species.

fitting results. Corrected and uncorrected relative peak intensities are shown in Table 1. Scaled mole fractions of Al-O-Al and Si-O-Si bridging O are estimated to increase from 0.084 ± 0.004 to 0.105 ± 0.005 with an approximate 200 degree change in T_f in $NaAlSiO_4$ glasses, and from 0.093 ± 0.005 to 0.119 ± 0.006 with an approximate 165 degree change in T_f in $LiAlSiO_4$ glasses. Because a simple linear extrapolation with temperature is likely to be unrealistic, we have chosen to analyze these data with a simple thermodynamic approach detailed below.

Thermodynamic calculations

The changes in proportions of bridging O species with changing T_f observed in the NMR data indicate that measurable structural rearrangement must occur in the liquid over a temperature interval up to two hundred degrees above T_g. To extrapolate sensibly these results up to liquidus conditions we have chosen to adopt the following approach, which also serves as a first approximation to the energetic consequences of temperature-induced framework disordering.

Energetics of Al/Si ordering. Structural rearrangement of framework cations may be expressed as the simple speciation reaction involving bridging O species described by reaction 1. For our samples, which have an Al/Si=1, increasing violation of "Al-avoidance" shifts the reaction toward the right as written. An equilibrium constant may be defined for this reaction as

$$K = \frac{[\text{Al-O-Al}][\text{Si-O-Si}]}{[\text{Al-O-Si}]^2} \tag{3}$$

where [(Al, Si)-O-(Al, Si)] are the relative concentrations of the different bridging O species quantified from peak fitting of isotropic projections of the ^{17}O 3QMAS NMR data. Assuming that the ratio of activity coefficients is temperature independent over the fictive temperature interval sampled, the equilibrium constant at different fictive temperatures may be used to estimate the enthalpy of the speciation reaction in Equation 2 from the van't Hoff equation:

$$\Delta H = -R\left[\frac{\ln K_1 - \ln K_2}{(1/T_{f1}) - (1/T_{f2})}\right] \tag{4}$$

where R is the gas constant and K_1 and K_2 reflect equilibrium configurations at fictive temperatures T_{f1} and T_{f2}, respectively. The error in estimating the reaction enthalpy in this manner was assessed by combining extreme values from errors in (1) the quantification of bridging O species from NMR data, and (2) calculation of fictive temperature. Estimates of the reaction enthalpy are 28.8 ± 11.3 kJ/mol for $NaAlSiO_4$ glasses and 31.7 ± 13.3 kJ/mol for $LiAlSiO_4$ glasses. For comparison, the reaction enthalpies determined from calorimetric data are 22.6 and 25.1 kJ/mol for glassy and crystalline $NaAlSiO_4$, respectively (Navrotsky et al. 1982), and 26 ± 3 kJ/mol for crystalline $LiAlSiO_4$ (Phillips et al. 1992).

Temperature effects on framework ordering. To use these data to assess the nature of change in framework speciation with temperature between the glass transition region and liquidus conditions, we find it useful to extend the thermodynamic considerations detailed above. In formulating a simple model, as required by the relatively large uncertainties in our experimental results, we begin by expressing mole fractions of bridging O species in our compositions as

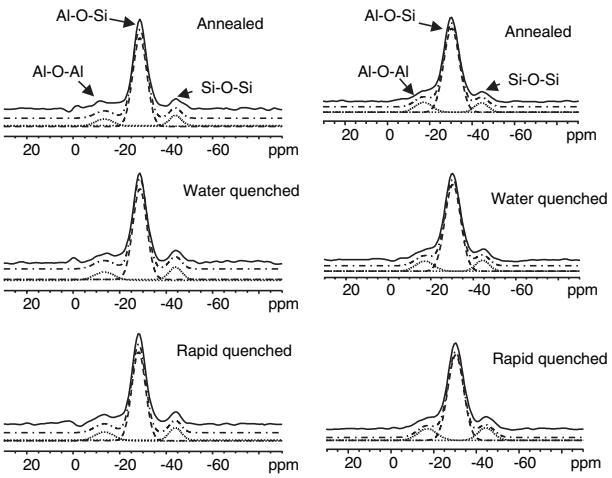

FIGURE 2. Isotropic projections of ^{17}O 3QMAS NMR spectra for (**a**) $NaAlSiO_4$ glasses and (**b**) $LiAlSiO_4$ glasses.

$$X_{\text{Al-O-Al}} = X_{\text{Si-O-Si}} = X \tag{5}$$

$$X_{\text{Al-O-Si}} = 1 - 2X \tag{6}$$

The equilibrium constant of reaction 1 may therefore be written as

$$K = \left[\frac{X^2}{(1-2X)^2}\right] \tag{7}$$

We may then use the integrated form of the van't Hoff equation to express temperature as a function of speciation, inserting the ΔH values calculated above and incrementing values of $X_{\text{Al-O-Al}}$ to solve for T.

Figure 3 shows the experimental data and the predicted relationship between temperature and proportion of Al-O-Al bridging O linkages. For comparison, we have plotted the prediction of the speciation model of Lee and Stebbins (1999) for $NaAlSiO_4$ assuming an enthalpy of speciation reaction and a proportion of Al-O-Al bridging O linkages similar to that observed in our samples. The model of Lee and Stebbins (1999) is a statistical thermodynamic treatment of framework speciation used to calculate the proportions of SiO_4 groups with varying numbers of Al neighbors with the assumption that framework speciation depends only on reaction 1. The results generated from this model are expressed in terms of Q, or "degree of Al-avoidance," which is a temperature-dependent term determined for a given Al/Si ratio by using relative lattice energy differences between different bridging O species, with $Q = 0$ representing a random distribution of Al and Si and $Q = 1$ representing perfect "Al-avoidance." The proportions of SiO_4 groups predicted by different Q values were used as constraints in fitting ^{29}Si MAS NMR spectra from a series of Na- and Ca-aluminosilicate glasses, resulting in a range of Q values for which the spectra could be fit adequately. This procedure yields an estimate of the degree of "Al-avoidance" in these glasses based on ^{29}Si MAS NMR data, from which the

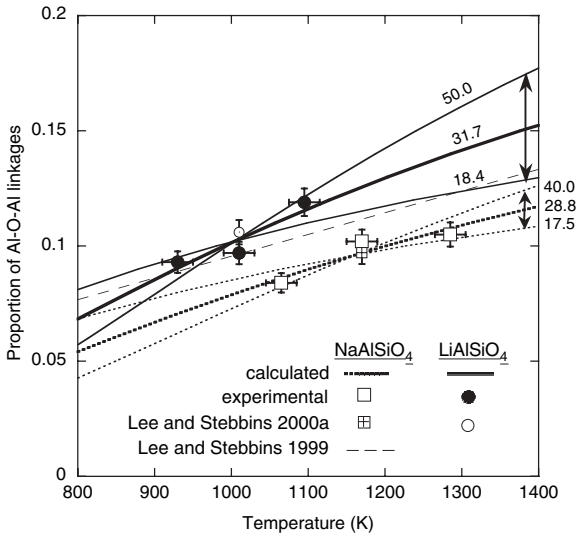

FIGURE 3. Observed and predicted proportions of Al-O-Al linkages as a function of temperature in $LiAlSiO_4$ and $NaAlSiO_4$ glasses and liquids. Solid circles and open squares show experimental data. Solid and dashed lines show predicted curves for $LiAlSiO_4$ and $NaAlSiO_4$, respectively, and are labeled with ΔH of framework speciation (in kJ/mol) for each composition determined from experimental data. Fictive temperatures of samples from Lee and Stebbins (2000a) are assumed identical to those calculated for samples prepared with the same composition and thermal history. Dashed line shows temperature dependence of speciation for $NaAlSiO_4$ liquid from model of Lee and Stebbins (1999), with a value for the "degree of Al-avoidance," Q, of 0.93.

relative proportions of bridging O species can be calculated for compositions with Al/Si = 1.

The scaled proportions of bridging O species in $NaAlSiO_4$ glasses with different T_f prepared in this study fall quite close to the values predicted by the model of Lee and Stebbins (1999). Furthermore, Lee and Stebbins (2000a) used peak fitting of isotropic projections of ^{17}O 3QMAS NMR data to quantify proportions of Al-O-Al linkages in $LiAlSiO_4$ and $NaAlSiO_4$ glasses prepared by conventional water-quenching techniques. Relative proportions of bridging O species quantified by Lee and Stebbins (2000a) are identical within error to those quantified in this study for similar compositions and thermal histories (Fig. 3). Most interestingly, the changes in proportions of Al-O-Al linkages with T_f determined in this study parallels the predicted relationship between speciation and temperature calculated by Lee and Stebbins (2000a) for $NaAlSiO_4$ using the model of Lee and Stebbins (1999).

Extrapolating up in temperature to liquidus conditions, we find that for both compositions our model does not predict a random bridging O distribution. At 2000 K, well above the $NaAlSiO_4$ and $LiAlSiO_4$ liquidii, we estimate that 13–18% of bridging O occur as Al-O-Al in $NaAlSiO_4$ and 15–25% in $LiAlSiO_4$, which is generally significantly less than the statistically random value of 25% predicted by MD simulations for $NaAlSiO_4$ liquid at temperatures in excess of 2700 K (Scamehorn and Angell 1991). A statistically random distribution is predicted in $LiAlSiO_4$ at 2000 K only when the extreme value of the reaction enthalpy (40.0 kJ/mol) is assumed. However, extrapolation of our results to 2700 K does produce speciation much closer to that produced by a fully random distribution of bridging O. These results illustrate the importance of experimental studies in reconciling structural data for glasses near T_g with results of computer simulations, which must be obtained for very high temperatures (often in excess of 4000 K) due to practical limitations of computation time.

DISCUSSION

Structure and thermodynamic properties of aluminosilicate glasses and liquids

Extensive but incomplete framework cation ordering in glasses along the joins $NaAlO_2$-SiO_2 and $CaAl_2O_4$-SiO_2 at T_g has been inferred from ^{29}Si MAS NMR linewidths and calorimetric data (Murdoch et al. 1985; Navrotsky et al. 1982). Furthermore, silica activity at liquidus temperatures may give indication of the extent of Al/Si mixing in aluminosilicate compositions (Flood and Knapp 1968). Progressive Al/Si disordering in liquids as the temperature is increased above T_g was suggested as a significant potential contribution to C_P^{conf} in $NaAlSiO_4$ liquid (Richet et al. 1990). MD simulations indicate that at very high temperatures ($T > 2000$ K) a random distribution of bridging O species occurs in aluminosilicate melts with Al/Si = 1 (Scamehorn and Angell 1991). The experimentally determined proportions of bridging O species (Table 1) are consistent with both: (1) the observation of a great degree of ordering near T_g, and (2) the prediction of increasing disorder with increasing temperature.

The data presented above may be used to estimate contributions to configurational thermodynamic quantities from framework cation disordering over a range of liquid temperatures. We have estimated the contribution to C_P from disorder due to conventional tetrahedral site mixing from framework speciation in $NaAlSiO_4$ composition liquids on a 4 O basis by approximating

$$C_p^{conf} \approx 2 \times \Delta H \times \frac{\Delta X}{\Delta T} \quad (8)$$

where ΔH is the reaction enthalpy calculated from Equation 4 (on a 2 O basis), ΔX are incremental differences in $X_{Al\text{-}O\text{-}Al}$ values used in the integrated van't Hoff approximation, and ΔT are the corresponding temperature intervals calculated for incremental differences in X. We note that our choice of tetrahedral mixing units is not arbitrary, as Toplis et al. (1997a) inferred from the variation of configurational entropy along the join SiO_2-$NaAlSiO_4$ that it is indeed tetrahedral units that are mixing. Using the ΔH value of framework speciation determined for $NaAlSiO_4$ liquid (28.8 ± 11.3 kJ/mol), we estimate that disordering of framework cations contributes approximately 13 J/(mol·K) to the heat capacity at T_g (= 1065 K), or 5 to 23 J/(mol·K) assuming the entire range of possible ΔH values. Using the data of Richet et al. (1990), we calculated a value of 23.4 J/(mol·K) for the configurational heat capacity of $NaAlSiO_4$ liquid at 1065 K [where $C_P^{conf} = C_P^{liquid} - C_P^{glass}(T_g)$; see Richet et al. (1986) for a justification of this equation]. Richet et al. (1990) also reported a significant increase in heat capacity with temperature in liquid $NaAlSiO_4$.

Our data indicate that although the temperature effect on framework disorder may account for over half of C_P^{conf} at T_g, the

contribution to configurational heat capacity from framework cation disordering decreases with increasing temperature above T_g as calculated using Equation 8 (Fig. 4). This effect was also noted in the predictions of the statistical thermodynamical model of this system developed by Lee and Stebbins (1999). We have extrapolated our results down as well as up in temperature to explore the behavior of C_P^{conf} curves modeled in this simple fashion. Intriguingly, at temperatures well below obtainable T_f values in this system, the temperature derivative of C_P^{conf} is actually strongly positive. This region is characterized by low, but rapidly increasing, proportions of the minor, energetically "costly" Al-O-Al species. This general observation may be relevant to other types of disordering processes in the real liquid at temperatures above T_g.

A negative dC_P/dT above T_g has been documented experimentally in calorimetric data for alkali titanosilicate glasses and liquids (Richet and Bottinga 1985; Lange and Navrotsky 1993). These compositions exhibit an anomalously large jump in heat capacity at T_g that is almost double that observed in Ti-free alkali silicate analogs, a behavior that has been attributed to structural changes involving major, Ti-bearing melt species (Lange and Navrotsky 1993; Farges et al. 1996a, 1996b; Tangeman and Lange 1998). Thermodynamic modeling of homogeneous equilibria involving Ti-species in K-titanosilicate melts using constraints from calorimetric data is consistent with structural

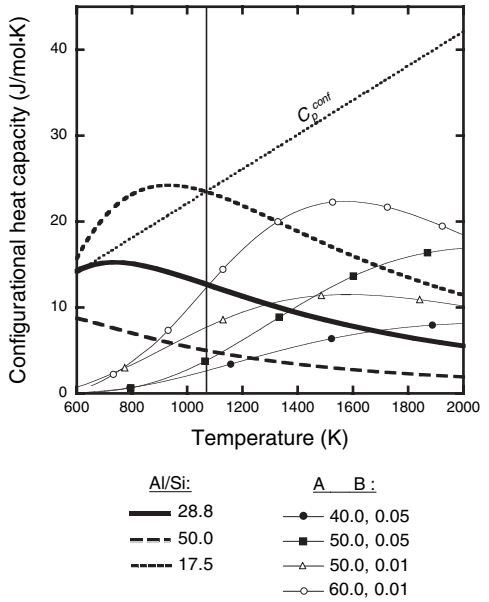

FIGURE 4. Estimated contribution to heat capacity in $NaAlSiO_4$ liquid from various structural changes as a function of temperature. Vertical line shows a typical T_g for standard laboratory cooling rates. C_P curves have been extrapolated to lower temperature for discussion purposes only; in real liquids, the configurational contribution to C_P is "frozen out" at T_g. Curves for Al/Si disordering are calculated using the ΔH values shown in kJ/mol. Curves for a reaction of the type A ↔ B are calculated using the ΔH values shown in kJ/mol and the concentration of species A assumed present at T_g. Symbols on A ↔ B reaction curves are for labeling only and do not represent experimental data. Also shown is C_P^{conf} for nepheline liquid, calculated from the data of Richet et al. (1990) using the relationship $C_P^{conf} = C_{P,liquid} - C_{P,glass}(T_g) \approx C_{P,liquid} - 3n\mathrm{R}$.

interpretations involving reorganization of network-forming species (Gan et al. 1996). Some sort of disordering of major network components may also be related to the observed negative dC_P/dT values observed in some borosilicate liquids (Richet et al. 1997). Possibly, such a negative temperature slope may be a general feature of structural disordering of the abundant, major network species in multicomponent melts, at least when considerable disorder is retained at T_g.

Implications for other structural changes

Our first-approximation approach to estimating the contribution to configurational heat capacity from framework cation/bridging O speciation in $NaAlSiO_4$ liquids suggests that this alone cannot account for large positive values of dC_P/dT observed in the liquid data. A similar conclusion was reached by Toplis et al. (1997a), who modeled configurational entropy along the join SiO_2-$NaAlSiO_4$ in terms of mixing of O sites or of tetrahedral sites. Those authors concluded that increases in chemical entropy from mixing of Al and Si in the O lattice represent only a small fraction of the configurational heat capacity, requiring that the increase in configurational heat capacity with temperature be dominated by the topological contribution to configurational entropy arising from variations in the topology of the O network. A contribution to ΔC_P from topological effects was also inferred from analysis of heat capacity data combined with liquid expansivity data for haplogranitic glasses and liquids, which yielded an estimate that ~15 ± 5% of C_P^{conf} was due to volume changes near T_g (Toplis et al. 2001). Some sort of network structural change with temperature was also evident in the ambient and high-temperature Raman data of Neuville and Mysen (1996) for Na-aluminosilicates, who attributed differences in glass and liquid spectra to the stabilization of a tetrahedral melt structural unit with a larger intertetrahedral angle.

In discussing configurational heat capacity with regard to melt viscosity, both Richet and Neuville (1992) and Toplis et al. (1997a) noted that the ability of O to participate in new configurations controls the increase in entropy and corresponding decrease in melt viscosity with increasing temperature. Furthermore, Toplis et al. (1997a) pointed out that the configurational heat capacity should therefore be proportional to the average bond strength of the melt. If this is the case, the positive correlation between heat capacity and temperature in $NaAlSiO_4$ liquid could at least in part signal an increasing concentration of a high-energy, relatively low abundance species in the melt. If the formation of such a species is considered as the general reaction A ↔ B, an equilibrium constant can be formulated as, $K = X/(1 - X)$ where X is the concentration of species A. A treatment similar to that described above for bridging O speciation may be applied to explore the contribution to configurational heat capacity from A ↔ B assuming combinations of various values of X at T_g and ΔH. The general conclusion from this simple exercise is that for small initial concentrations of species A at T_g and relatively large values of ΔH, the configurational heat capacity increases with increasing temperature, analogous to the behavior seen in the low-temperature extrapolation of the Al/Si disorder curves. To illustrate this, we have shown the results of these calculations on Figure 4 for an initial species concentration of 1% and a ΔH of 50–60 kJ/mol and also for an initial species concentration of 5%

and a ΔH of 40–50 kJ/mol. The calculated effects of initial species concentration and of ΔH on C_P^{conf} and on dC_P/dT, are highly non-linear. For example, increasing ΔH not only increases the rate of production of the minor species with increasing temperature, but each increment in species concentration contributes more to the heat capacity. The calculated C_P is thus highly sensitive to the details of a chosen structural model.

Definitive results are still lacking on the exact nature of the structural disordering that leads to a positive dC_P^{conf}/dT in aluminosilicates such as $NaAlSiO_4$, as well as $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$ (Richet and Bottinga 1984a, 1984b; Richet et al. 1990). However, both theoretical and experimental studies do provide important hints about the type of reaction that may be involved. For example, molecular dynamics simulations of aluminosilicate liquids along the join SiO_2-$NaAlSiO_4$ have estimated that ^{V}Si and ^{V}Al each comprise ~10–20% of total Si or Al species at T_f = 4000 K (Scamehorn and Angell 1991; Stein and Spera 1995). Experimental fictive temperature studies of alkali tetrasilicate glasses have used ^{29}Si MAS NMR data to demonstrate that a higher T_f produces more ^{V}Si, although the effect has not yet been seen in other compositions (Stebbins 1991; Stebbins and McMillan 1993). Additionally, fictive temperature studies of glasses along the joins CaO-Al_2O_3 and SiO_2-Al_2O_3 have used ^{27}Al NMR data to show that ^{V}Al concentration increases with T_f, a phenomenon also consistent with high-T NMR studies of Na-aluminosilicate melts (Stebbins and Farnan 1992). The available data relating increasing concentrations of high-coordinated Si^{4+} and Al^{3+} in aluminosilicate glasses to increasing T_f indicate that further consideration of the observed dC_P/dT in $NaAlSiO_4$ liquid must include, but not be limited to, investigation of structural modifications with increasing temperature involving high-coordinated Si^{4+} and Al^{3+}. Oxygen-17 NMR probably cannot directly detect small amounts of network cation change and we do not claim evidence for that phenomenon here. Ongoing studies by ^{27}Al MAS NMR and other methods may shed further light on this intriguing issue. We also note by analogy with borate and borosilicate systems that the formation of NBO in initially low-NBO compositions, accompanied by some kind of network coordination change, could contribute significantly to C_P^{conf} in aluminosilicates as well (Stebbins and Sen 1998; Sen 1999). More generally, the formation of high-energy "defect" species with increasing melt temperature could involve the hopping of cations into sites normally unoccupied at low temperature, either with or without accompanying local changes in the network structure. This may be of fundamental importance to consideration of the energetic consequences of structural changes, as has been suggested from studies of energetically dramatic premelting effects in several crystalline silicates (George et al. 1998; Courtial et al. 2000; Bouhifd et al. 2002).

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REFERENCES CITED

Allwardt, J.R. and Stebbins, J.F. (2004) Ca-Mg and K-Mg mixing around non-bridging O atoms in silicate glasses: An investigation using ^{17}O MAS and 3QMAS NMR. American Mineralogist, 89, 777–784.

Allwardt, J.R., Stebbins, J.F., Schmidt, B.C., Frost, D.J., Withers, A.C., and Hirschmann, M.M. (2005) Aluminum coordination and the densification of high-pressure aluminosilicate glasses. American Mineralogist, 90, 1218–1222.

Benna, P., Tribaudino, M., and Bruno, E. (1999) High-temperature in situ structural investigation on lead feldspar. American Mineralogist, 84, 120–129.

Bouhifd, M.A., Gruener, G., Mysen, B.O., and Richet, P. (2002) Premelting and calcium mobility in gehlenite ($Ca_2Al_2SiO_7$) and pseudowollastonite ($CaSiO_3$). Physics and Chemistry of Minerals, 29, 655–662.

Brandriss, M.E. and Stebbins, J.F. (1988) Effects of temperature on the structure of silicate liquids: ^{29}Si NMR results. Geochimica et Cosmochima Acta, 52, 2659–2670.

Courtial, P., Téqui, C., and Richet, P. (2000) Thermodynamics of diopside, anorthite, pseudowollastonite, $CaMgGeO_4$ olivine, and åkermanite up to near the melting point. Physics and Chemistry of Minerals, 27, 242–250.

De Jong, B.H.W.S., Schramm, C.M., and Parziale, V.E. (1983) Polymerization of silicate and aluminate tetrahedra in glasses, melts, and aqueous solutions. IV. Aluminum coordination in glasses and aqueous solutions and comments on the aluminum avoidance principle. Geochimica et Cosmochimica Acta, 47, 1223–1236.

Dingwell, D.B. (1995) Relaxation in silicate melts: some applications. In J.F. Stebbins, P.F. McMillan, and D.B. Dingwell, Eds., Structure, dynamics and properties of silicate melts, 32, p. 21–66. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.

Dingwell, D.B. and Webb, S.L. (1990) Relaxation in silicate melts. European Journal of Mineralogy, 2, 427–449.

Dirken, P.J., Kohn, S.C., Smith, M.E., and Vaneck, E.R.H. (1997) Complete resolution of Si-O-Si and Si-O-Al fragments in an aluminosilicate glass by ^{17}O multiple quantum magic angle spinning NMR spectroscopy. Chemical Physics Letters, 266, 568–574.

Du, L.-S. and Stebbins J.F. (2003a) Solid-state NMR study of metastable immiscibility in alkali borosilicate glasses. Journal of Non-Crystanlline Solids, 315, 239–255.

——— (2003b) Site preference and Si/B mixing in mixed-alkali borosilicate glasses: A high-resolution ^{11}B and ^{17}O NMR study. Chemistry of Materials, 15, 3913–3921.

——— (2005) Site connectivities in sodium aluminoborate glasses: multinuclear and multiple quantum NMR results. Solid State Nuclear Magnetic Resonance, 27, 37–49.

Farges, F., Brown, G.E., Jr, Navrotsky, A., Gan, H., and Rehr, J.J. (1996a) Coordination chemistry of Ti (IV) in silicate glasses and melts: II. Glasses at ambient temperature and pressure. Geochimica et Cosmochimica Acta, 60, 3039–3053.

——— (1996b) Coordination chemistry of Ti (IV) in silicate glasses and melts: III. Glasses and melts from ambient to high temperatures. Geochimica et Cosmochimica Acta, 60, 3055–3065.

Flood, H. and Knapp, W.J. (1968) Structural characteristics of liquid mixtures of feldspar and silica. Journal of the American Ceramic Society, 51, 259–263.

Gan, H., Wilding, M.C., and Navrotsky, A. (1996) Ti^{4+} in silicate melts: Energetics from high-temperature calorimetric studies and implications for melt structure. Geochimica et Cosmochimica Acta, 60, 4123–4131.

George, A.M., Richet, P., and Stebbins, J.F. (1998) Cation dynamics and premelting in lithium metasilicate (Li_2SiO_3) and sodium metasilicate (Na_2SiO_3): a high-temperature NMR study. American Mineralogist, 83, 1277–1284.

Ghiorso, M.S. and Sack, R.O. (1995) Chemical mass transfer in magmatic processes IV. A revised and internally consistent thermodynamic model for the interpolation and extrapolation of liquid-solid equilibria in magmatic systems at elevated temperatures and pressures. Contributions to Mineralogy and Petrology, 119, 197–212.

Ghiorso, M.S., Carmichael, I.S.E., Rivers, M.L., and Sack, R.O. (1983) The Gibbs Free Energy of mixing of natural silicate liquids; an expanded regular solution approximation for the calculation of magmatic intensive variables. Contributions to Mineralogy and Petrology, 84, 107–145.

Ghiorso, M.S., Hirschmann, M.M., Reiners, P.W., and Kress, V.C., III (2002) The pMELTS: A revision of MELTS for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa. Geochemistry, Geophysics, Geosystems [online computer file], 3(5), 1–36.

Gupta, P.K., Liu, M.L., and Bray, P.J. (1985) Boron coordination in rapidly cooled and in annealed aluminum borosilicate glass fibers. Journal of the American Ceramic Society, 68, C–82.

Johnson, R.T., Jr., Biefeld, R.M., Knoteck, M.L., and Morosin, B. (1976) Ionic conductivity in solid electrolytes based on lithium aluminosilicate glass and glass-ceramic. Journal of the Electrochemical Society, 123, 680–687.

Kiczenski, T.J., Du, L.-S., and Stebbins, J.F. (2005) The effect of fictive temperature on the structure of E-glass: a high-resolution, multinuclear NMR study. Journal of Non-Crystalline Solids,351, 3571–3578.

Lange, R.A. and Navrotsky, A. (1993) Heat capacities of TiO_2-bearing silicate liquids: Evidence for anomalous changes in configurational entropy with temperature. Geochimica et Cosmochimica Acta, 57, 3001–3011.

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

——— (2000a) Al-O-Al and Si-O-Si sites in framework aluminosilicate glasses

with Si/Al=1: quantification of framework disorder. Journal of Non-Crystalline Solids, 270, 260–264.
——— (2000b) 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.
Loewenstein, W. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates. American Mineralogist, 39, 92–96.
Massiot, D., Touzo, B., Trumeau, D., Coutures, J.P., Virlet, J., Florian, P., and Grandinetti, P.J. (1996) Two-dimensional magic-angle spinning isotropic reconstruction sequences for quadrupolar nuclei. Solid State Nuclear Magnetic Resonance, 6, 73–83.
McConnell, J.D.C., DeVita, A., Kenny, S.D., and Heine, V. (1997) Determination of the origin and magnitude of Al/Si ordering enthalpy in framework aluminosilicates from ab initio calculations. Physics and Chemistry of Minerals, 25, 15–23.
Medek, A., Harwood, J.S., and Frydman, L. (1995) Multiple-quantum magic-angle spinning NMR: A new method for the study of quadrupolar nuclei in solids. Journal of the American Chemical Society, 117, 12779–12787.
Moynihan, C.T. (1995) Structural relaxation and the glass transition. In J.F. Stebbins, P.F. McMillan, and D.B. Dingwell, Eds, Structure, dynamics and properties of silicate melts, 32, p. 1–19. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.
Moynihan, C.T., Easteal, A.J., DeBolt, M.A., and Tucker, J. (1976) Dependence of the fictive temperature of glass on cooling rate. Journal of the American Ceramic Society, 59, 12–16.
Murdoch, J.B., Stebbins, J.F., and Carmichael, I.S.E. (1985) High-resolution Si-29 NMR study of silicate and aluminosilicate glasses—the effect of network-modifying cations. American Mineralogist, 70, 332–343.
Navrotsky, A., Peraudeau, G., McMillan, P., and Coutures, J.P. (1982) A thermochemical study of glasses along the joins silica-calcium aluminate and silica-sodium aluminate. Geochimica et Cosmochima Acta, 46, 2039–2047.
Navrotsky, A., Geisinger, K.L., McMillan, P., and Gibbs, G.V. (1985) The tetrahedral framework in glasses and melts- inferences from molecular orbital calculations and implications for structure, thermodynamics, and physical properties. Physics and Chemistry of Minerals, 11, 284–298.
Neuhoff, P.S., Stebbins, J.F., and Bird, D.K. (2003) Si-Al disorder and solid solutions in analcime, chabazite, and wairakite. American Mineralogist, 88, 410–423.
Neuville, D.R. and Mysen, B.O. (1996) Role of aluminum in the silicate network: In situ, high-temperature study of glasses and melts on the join SiO_2-$NaAlO_2$. Geochimica et Cosmochimica Acta, 60, 1727–1737.
Phillips, B.L. and Kirkpatrick, R.J. (1994) Short-range Al-Si order in leucite and analcime: determination of the configurational entropy from ^{27}Al and variable-temperature ^{29}Si NMR spectroscopy of leucite, its Cs- and Rb-exchanged derivatives, and analcime. American Mineralogist, 79, 1025–1031.
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, 484–494.
Phillips, B.L., McGuinn, M.D., and Redfern, S.A.T (1997) Si-Al order and the *I*1–*I*2/*c* structural phase transition in synthetic $CaAl_2Si_2O_8$- $SrAl_2Si_2O_8$ feldspar: A ^{29}Si MAS-NMR spectroscopic study. American Mineralogist, 82, 1–7.
Phillips, B.L., Xu, H., Heaney, P.J., and Navrotsky, A. (2000) ^{29}Si and ^{27}Al MAS-NMR spectroscopy β-eucryptite ($LiAlSiO_4$): The enthalpy of Si, Al ordering. American Mineralogist, 85, 181–188.
Putnis, A. and Angel, R.J. (1985) Aluminum-silicon ordering in cordierite using "magic angle spinning" NMR. II: models of aluminum-silicon order from NMR data. Physics and Chemistry of Minerals, 12, 217–22.
Putnis, A., Fyfe, C.A., and Gobbi, G.C. (1985) Aluminum-silicon ordering in cordierite using "magic angle spinning" NMR. I. Silicon–29 spectra of synthetic cordierites. Physics and Chemistry of Minerals, 12, 211–16.
Putnis, A., Salje, E., Redfern, S., Fyfe, C.A., and Strobl, H. (1987) Structural states of Mg-cordierite I: order parameters from synchrotron X-ray and NMR data. Physics and Chemistry of Minerals, 14, 446–454.
Richet, P. and Bottinga,, Y. (1984a) Glass transition and thermodynamic properties of amorphous SiO_2, $NaAlSi_nO_{2n+2}$, and $KAlSi_3O_8$. Geochimica et Cosmochimica Acta, 48, 453–470.
——— (1984b) Anorthite, andesine, wollastonite, diopside, cordierite, and pyrope: thermodynamics of melting, glass transitions, and properties of the amorphous phases. Earth and Planetary Science Letters, 67, 415–432.
——— (1985) Heat capacity of aluminum-free liquid silicates. Geochimica et Cosmochimica Acta, 49, 471–486.
——— (1995) Rheology and configurational entropy of silicate melts. In J.F. Stebbins, P.F. McMillan, and D.B. Dingwell, Eds., Structure, dynamics and properties of silicate melts, 32, p. 67–93. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.
Richet, P., Bottinga, Y., Deniélou, L., Petitet, J.P., and Téqui, C. (1982) Thermodynamic properties of quartz, cristobalite, and amorphous SiO_2: drop calorimetry measurements between 1000 and 1800 K and a review from 0 to 2000 K. Geochimica et Cosmochimica Acta, 46, 2639–2658.
Richet, P., Robie, R.A., and Hemingway, B.S. (1986) Low-temperature heat capacity of diopside glass ($CaMgSi_2O_6$): A calorimetric test of the configurational-entropy theory applied to the viscosity of liquid silicates. Geochimica et Cosmochimica Acta, 50, 1521–1533.
Richet, P., Robie, R.A., Rogez, J., Hemingway, B.S., Courtial, P., and Téqui, C. (1990) Thermodynamics of open networks: ordering and entropy in $NaAlSiO_4$ glass, liquid, and polymorphs. Physics and Chemistry of Minerals, 17, 385–394.
Richet, P., Bouhifd, M.A., Courtial, P., and Tequi, C. (1997) Configurational heat capacity and entropy of borosilicate melts. Journal of Non-Crystalline Solids, 211, 271–280.
Roskosz, M., Toplis, M.J., and Richet, P. (2004) The structural role of Ti in aluminosilicate liquids in the glass transition range: Insights from heat capacity and shear viscosity measurements. Geochimica et Cosmochimica Acta, 68, 591–606.
Scamehorn, C.A. and Angell, C.A. (1991) Viscosity-temperature relations and structure in fully polymerized aluminosilicate melts from ion dynamics simulations. Geochimica et Cosmochimica Acta, 55, 721–730.
Sen, S. (1999) Temperature induced structural changes and transport mechanisms in borate, borosilicate and boroaluminate liquids: high-resolution and high-temperature NMR results. Journal of Non-Crystalline Solids, 253, 84–94.
Sen, S., Xu, Z., and Stebbins, J.F. (1998) Temperature dependent structural changes in borate, borosilicate and boroaluminate liquids: high-resolution ^{11}B, ^{29}Si and ^{27}Al NMR studies. Journal of Non-Crystalline Solids, 226, 29–40.
Stebbins, J.F. (1991) Experimental confirmation of five-coordinated silicon in a silicate glass at 1 atmosphere pressure. Nature, 351, 638–639.
Stebbins, J.F. and Ellsworth, S.E. (1996) Temperature effects on structure and dynamics in borate and borosilicate liquids: high-resolution and high-temperature NMR results. Journal of the American Ceramic Society, 79, 2247–2256.
Stebbins, J.F. and Farnan, I. (1992) Effects of high temperature on silicate liquid structure: a multinuclear NMR study. Science, 255, 586–589.
Stebbins, J.F. and McMillan, P. (1993) Compositional and temperature effects on five coordinated silicon in ambient pressure silicate glasses. Journal of Non-Crystalline Solids, 160, 116–125.
Stebbins, J.F. and Sen, S. (1998) Microscopic dynamics and viscous flow in a borosilicate glass-forming liquid. Journal of Non-crystalline Solids, 224, 80–85.
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, 983–986.
Stein, D.J. and Spera F.J. (1995a) Molecular dynamics simulations of liquids and glasses in the system $NaAlSiO_4$-SiO_2: Methodology and melt structure. American Mineralogist, 80, 417–431.
——— (1995b) Molecular dynamics simulations of liquids and glasses in the system $NaAlSiO_4$-SiO_2: Physical properties and transport mechanisms. American Mineralogist, 81, 284–302.
Tangeman, J.A. and Lange, R.A. (1998) The effect of Al^{3+}, Fe^{3+}, and Ti^{4+} on the configurational heat capacities of sodium silicate liquids. Physics and Chemistry of Minerals, 26, 83–99.
Toplis, M.J., Dingwell, D.B., Hess, K-.E., and Lenci, T. (1997a) Viscosity, fragility, and configurational entropy of melts along the join SiO_2-$NaAlSiO_4$. American Mineralogist, 82, 979–990.
Toplis, M.J., Dingwell, D.B., and Lenci, T. (1997b) 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., Gottsmann, J., Knoche, R., and Dingwell, D.B. (2001) Heat capacities of haplogranitic glasses and liquids. Geochimica et Cosmochimica Acta, 65, 1985–1994.
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.
Weill, D.F., Hon, R., and Navrotsky, A. (1980) The igneous system calcium magnesium silicate ($CaMgSi_2O_6$)-calcium aluminum silicate ($CaAl_2Si_2O_8$)-sodium aluminum silicate ($NaAlSi_3O_8$) variations on a classic theme by Bowen. In R.B. Hargraves, Ed., Physics of Magmatic Processes, p. 49–92. Princeton University Press, Princeton, New Jersey.
Yue, Y.Z., Christiansen, J.deC., and Jensen, S.L. (2002) Determination of the fictive temperature for a hyperquenched glass. Chemical Physics Letters 357, 20–24.
Yue, Y.Z., von der Ohe, R., and Jensen, S.L. (2004) Fictive temperature, cooling rate, and viscosity of glasses. Journal of Chemical Physics, 120, 8053–8059.

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