

## EFFECTS OF TEMPERATURE AND COMPOSITION ON SILICATE GLASS STRUCTURE AND DYNAMICS: SI-29 NMR RESULTS

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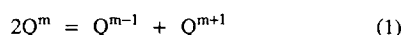
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The distribution of bridging and non-bridging oxygens is a fundamental aspect of the intermediate range order of silicate glasses and liquids. Disorder in this distribution can be characterized by the relative abundances of  $Q^n$  species, which can be quantified by  $^{29}\text{Si}$  NMR on both spinning and static samples. We emphasize the latter here, and show that increasing the field strength of the network modifying cation and increasing temperature have similar randomizing effects on this distribution. These changes have a major influence on thermodynamic activities. In the liquid, exchange between sites is rapid, but the exchange rate may become slow enough with decreasing temperature to actually define  $T_g$ . In silicate liquids, some kind of high energy, low abundance, defects probably are present to allow this structural change to occur, to account for the bulk of the configurational heat capacity, and to explain the observed spin-lattice relaxation times.

### 1. INTRODUCTION

Many glass-forming liquids are described as "highly structured", meaning that energetically significant order extends beyond the first coordination sphere. In molten and glassy silicates (as in their crystalline counterparts), the short range order is usually dominated by the formation of tightly bound, regular  $\text{SiO}_4$  (and  $\text{AlO}_4$ ) tetrahedra. The first aspect of intermediate range order is thus the type of coordination of each of the four oxygen atoms. A continuous range of bond types is possible, of course, but the distinction between relatively weak, highly ionic bonds to large low-charge cations (e.g.  $\text{Na}^+$ ) and relatively strong, more covalent bonds to small, high-charge cations (e.g.  $\text{B}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ ) remains useful. Counting the number of these non-bridging (4-n) and bridging (n) oxygens leads to the description of a given tetrahedral ("Quaternary") silicon site as  $Q^n$ . The distribution of  $Q^n$  species in a glass or liquid thus becomes a key part of the description of intermediate range order.

Variation in the physical and chemical properties of silicate liquids and glasses have often been attributed to changes in  $Q^n$  speciation (or equivalent descriptions such as " $\text{Si}_2\text{O}_5$ " for  $Q^3$ ) with composition. Reactions of the form:



( $4 > m > 0$ ) have often been written<sup>1-4</sup>, and it has been qualitatively demonstrated that smaller, higher charge network modifying cations systematically favor greater disproportionation (right-hand side). However, quantifying such results has been

controversial. Raman spectroscopic data often indicate a wide variety of species<sup>2,3,5</sup>, while x-ray scattering results have often been interpreted in terms of the minimum of 1 or 2 species required by stoichiometry<sup>6,7</sup>.  $^{29}\text{Si}$  Magic Angle Spinning (MAS) NMR spectra have been interpreted as indicating simple or complex species distributions, depending on assumptions of parsimony and/or style of curve fitting.<sup>1,8-14</sup>

The effect of temperature, as well as composition, on intermediate range order has obvious importance in understanding the effects of annealing on glass, but has a more fundamental role in controlling the thermodynamic and transport properties of the liquid itself. It is clear in most cases that liquids at high temperature have structures qualitatively similar to their quenched equivalents<sup>15-21</sup>. However, quantitative differences may be important, as liquidus temperatures are usually many hundreds of degrees higher than transition temperatures ( $T_g$ ). Thermodynamic models ignoring temperature effects may therefore not be accurate in predicting high temperature behavior.

The common assumption that high temperature liquid and low temperature glass structures are the same also apparently contradicts the theoretical viewpoint that the distinction between the two phases lies in the ability of the liquid to undergo configurational *change* with temperature. Constant volume heat capacities for silicate liquids are usually considerably larger than 3 times the gas constant  $R$  per gram atom<sup>21,22</sup>, requiring (as for water) that the configurational

contribution is substantial: the structure must become more random at higher temperature. The microscopic nature of this configurational change with temperature in silicates is poorly known, however. Such effects are, of course, small for liquids (such as  $\text{SiO}_2$ ) which are dominated by network formers, but can be quite large in less interconnected systems. The entropy of fusion for  $\text{CaMgSi}_2\text{O}_6$ , for example, is underestimated by almost a factor of 2 if the distinction between glass and liquid heat capacity is neglected<sup>22</sup>. Intriguingly, there are good empirical correlations between the extent of reactions such as (1) and configurational heat capacities and entropies<sup>22</sup>.

Configurational change with temperature in silicate liquids can be directly linked to the commonly-observed non-Arrhenian viscosity behavior through theory based originally on organic polymers<sup>23-25</sup>. The mechanism of structural change with temperature is therefore fundamental to transport, as well as to thermodynamic properties. Again, however, very little information is available about how such changes take place.

One tool that has recently been successfully applied to all of these interrelated problems is NMR spectroscopy. Most prominent among relatively early studies on stationary glass samples are those which concentrated on boron speciation<sup>26</sup>, and relied on the differences in quadrupolar coupling caused by varying site symmetry. More recently, Magic Angle Spinning (MAS) techniques have given considerable insight into Q species abundances, ranges of Si-O-Si bond angles, and aluminum and oxygen coordination<sup>27,28</sup>, although quantifying interpretations has sometimes been controversial. In some cases,  $^{29}\text{Si}$  NMR on static samples can more easily quantify species populations<sup>29</sup>, particularly for  $\text{Q}^4$ . In these studies, the distinctions among sites is made through the effects of local site symmetry rather than the isotropic, averaged chemical shift that is observed in MAS work.

Dynamics can also be studied by NMR, although this approach is just beginning for silicates<sup>44</sup>. Observable static NMR spectral linewidths for commonly observed nuclei in silicates may vary from a few Hz to 10's or even 100's of kHz. In some cases (e.g.  $^{29}\text{Si}$  in  $\text{SiO}_2$  glass) static line shapes are dominated by a distribution of some structural variable such as bond angle or distance. In other cases (e.g.  $^{29}\text{Si}$  in most other glasses and most spin  $> 1/2$  nuclei such as

$^{11}\text{B}$ ,  $^{23}\text{Na}$ , and  $^{27}\text{Al}$ ) lineshapes are mostly controlled by orientation dependent effects such as chemical shift anisotropy or quadrupolar coupling. In both situations, however, exchange of atoms from one site to another, or rotation with respect to the external magnetic field, can cause line narrowing in a more-or-less predictable fashion if the motion has a frequency greater than the line width. In addition, spin-lattice relaxation is controlled by the intensity of interatomic motion at the Larmor frequency (the resonant NMR frequency observed), which for modern spectrometers typically ranges from 10's to 100's of MHz. Together, lineshape analysis and measurement of relaxation times can help define the types, rates, and mechanisms of atomic or molecular motion at time scales ranging from seconds to nanoseconds. This range is an important complement to the much shorter time scale of dynamics sampled by vibrational spectroscopy. More importantly here, NMR studies of glass-forming liquids have the potential to reveal the details of the atomic-scale dynamics which actually cause the glass transition. Almost by definition, this is the point at which structural rearrangement becomes slower than laboratory cooling times, which are in s to  $\mu\text{s}$  region. This is just the range where NMR is most sensitive to molecular and atomic motion.

## 2. EXPERIMENTAL

Details of experimental procedure are the same as reported previously<sup>29,34,41,42</sup>, but data for the Li, Ca, and K glasses and liquids are reported here for the first time. Briefly, all samples were synthesized from high purity carbonates and  $^{29}\text{Si}$  enriched  $\text{SiO}_2$  obtained from Oak Ridge National Laboratory. We have found that this material is necessary for the high temperature experiments to minimize run times and accompanying composition changes. Usable static  $^{29}\text{Si}$  spectra can be obtained with natural isotopic abundance material if relaxation times are reduced by doping with a small amount of paramagnetic Mn or Fe, but the subtle effects of fictive temperature on speciation do require extremely high signal to noise ratios.

All data on the glasses were collected at field strengths of either 9.4 T (Varian VXR-400S, Stanford University Center for Materials Research) or 8.5 T (Bruker HX-360, Stanford Magnetic Resonance Laboratory), with 30°C pulse lengths of 3-6  $\mu\text{s}$ , and either an MAS probe from Doty Scientific or a

static solenoid probe from Varian. High temperature data were collected with a home built spectrometer with 4.2 T field strength (laboratory of A. Pines at the University of California, Berkeley) using a static sample probe. All data were collected with sufficient time between rf pulses to ensure that all observed spins were fully, or at least equally, relaxed, to allow accurate quantification.

### 3. STATIC $^{29}\text{Si}$ NMR SPECTRA

Because almost all published  $^{29}\text{Si}$  NMR spectra were collected with the MAS technique, a few comments are needed concerning the interpretation of static spectra. We have presented more details earlier<sup>29,34</sup>

The chemical shift for  $^{29}\text{Si}$  in a site with lower than cubic local symmetry varies as much as 150 ppm depending on the orientation of the site in the external magnetic field. In a powdered crystal or in a glass, it is often observed that this chemical shift anisotropy (CSA) causes sufficient line broadening to eliminate the resolution among sites with similar geometry. The CSA is averaged away in an MAS NMR experiment, or in a sufficiently mobile liquid, usually improving resolution.

In highly disordered materials, however, MAS peaks may be sufficiently broad and overlapping to make species quantification difficult, or at least dependent on sometimes *ad hoc* assumptions about lineshape<sup>43</sup>. In some cases, better resolution can be obtained in static spectra, relying on differences in CSA rather than in isotropic chemical shift. A highly symmetrical site, for example, can be greatly accentuated in a static spectrum because its peak is not broadened as much as a low symmetry site. (In both MAS and static spectra, of course, peak areas are strictly proportional to species abundance if complete relaxation is allowed during the experiment and no signal is lost due to paramagnetic broadening.)

We are concerned here primarily with determining the abundance of the highly symmetrical  $Q^4$  species. As shown in figure 1, the  $Q^4$  peak is generally well enough resolved to roughly determine its abundance simply by interpolating a baseline beneath it. For a more complete picture, however, we have simulated the spectra with CSA patterns for a total of two or three species. Four parameters are required for each pattern: the three principal elements of the CSA tensor

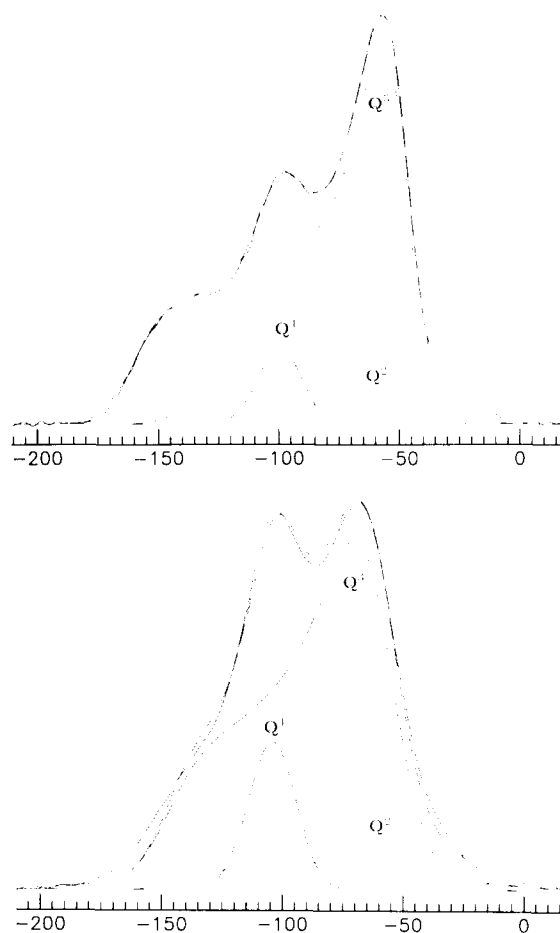


FIGURE 1

(Top) Static  $^{29}\text{Si}$  spectrum of annealed 34%  $\text{Na}_2\text{O}$  glass (close to  $\text{Na}_2\text{Si}_2\text{O}_5$  in composition). Solid curve shows data, dashed curves simulations for each of three species, and their sum. Scale in ppm relative to tetramethylsilane (TMS).

(Bottom) Static spectrum for  $\text{Li}_2\text{Si}_2\text{O}_5$  glass.

( $\sigma_{11}$ ,  $\sigma_{22}$ , and  $\sigma_{33}$ ), and a Gaussian broadening function which approximates the effects of disorder. In all cases, the  $Q^4$  peak was assumed to have a Gaussian shape, as has been seen for most spectra on  $Q^4$  glasses. Constraints used include data from crystals of known structure and mass balance among species as well as the glass spectra themselves.  $Q^2$  peak shapes were chosen to be the same as in the crystalline  $Q^2$  phase  $\text{Na}_2\text{SiO}_3$ <sup>44</sup>, and their areas were fixed by assuming that all Si is in either  $Q^4$ ,  $Q^3$ , or  $Q^2$  sites. The technique is

described in more detail elsewhere<sup>34</sup>, but it should be emphasized that our general conclusions about the effects of composition and temperature on speciation do not depend on this curve-fitting.

#### 4. EFFECTS OF COMPOSITION ON DISORDER

The distribution of Q species in a glass (and presumably in the liquid at its temperature of transition to the glass) reflects the degree of ordering of bridging and non-bridging oxygens. Since oxygen is the volumetrically dominant ion in glass forming silicates, this distribution is probably of fundamental importance.

Speciation reactions such as (1) for  $m=3,2$ , or 1 can be discussed in terms of idealized equilibrium constants defined in terms of mole fractions as:

$$K_m = \frac{X_{m+1}X_{m-1}}{X_m^2} \quad (2)$$

$K_m=0$  implies a highly ordered distribution. For example, a disilicate glass (e.g.  $\text{Na}_2\text{Si}_2\text{O}_5$ ) with  $K_3=0$  would have a single non-bridging oxygen at each Si site just as in the crystal. There would therefore be no contribution to the configurational entropy from this aspect of the structure, although of course other types of positional disorder would be present. For a non-stoichiometric composition, at most a binary species distribution would be present.  $K_m>0$  implies the presence of a greater configurational entropy resulting from the mixing of at least 3 Q species in any composition.

We have recently confirmed conclusions from Raman spectroscopy that  $K_3$  is indeed greater than 0 in alkali and alkaline earth silicate glasses<sup>29</sup>. As shown in figures 1 and 2, small amounts of the  $Q^4$  species are accentuated in static <sup>29</sup>Si spectra, because the symmetry of the sites leads to a much smaller chemical shift anisotropy (CSA) than for  $Q^3$  and  $Q^2$  species. In contrast, for these compositions the  $Q^4$  species is apparent only as small shoulders or asymmetries in MAS spectra (figure 3), leading to the disagreements in interpretation mentioned above.

Although a disordered Q species distribution is qualitatively similar to results from Raman spectra<sup>2,3</sup>, our measured abundances of  $Q^4$  species are in general much lower. The relationship between peak area and site population in a properly performed NMR experiment is inherently simple and therefore quantitative. Raman absorption cross sections

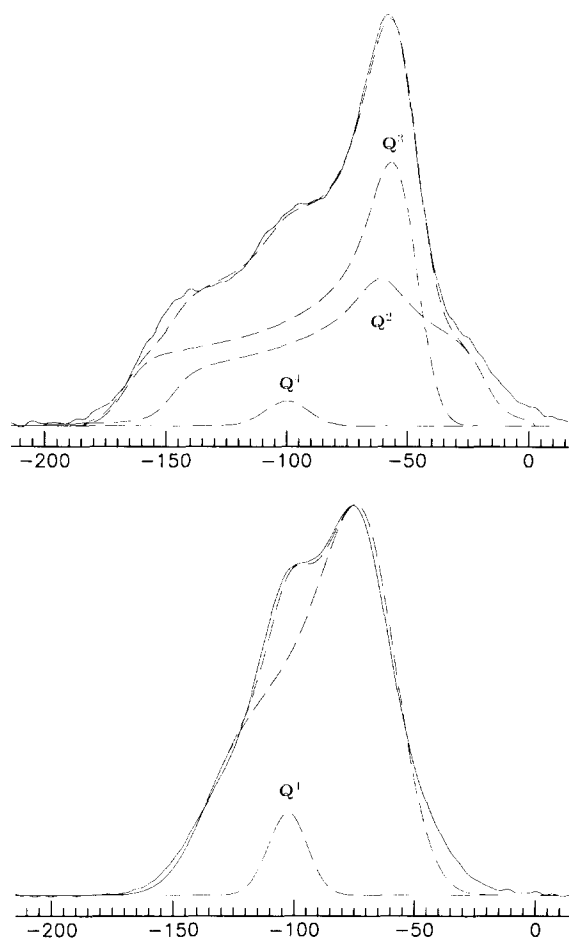


FIGURE 2

(Top) Static spectrum for  $(\text{Na}_2\text{O})_{0.41}(\text{SiO}_2)_{0.59}$  glass. Scale and simulations as in figure 1.  
(Bottom) Static spectrum for  $(\text{CaO})_{0.40}(\text{SiO}_2)_{0.60}$  glass. Note that the major CSA pattern is probably a mixture of at least two unresolved species.

depend on molecular polarizabilities which are difficult to calculate and in general must be calibrated, causing potential inaccuracies in quantifying abundances of sites whose bonding environment is poorly known<sup>52</sup>. We therefore consider that these new NMR results have greater absolute accuracy when contributions from different species are clearly resolved. (Resolution is often better in the vibrational spectra, however.)

Silicate species distributions are thus far from ordered: the

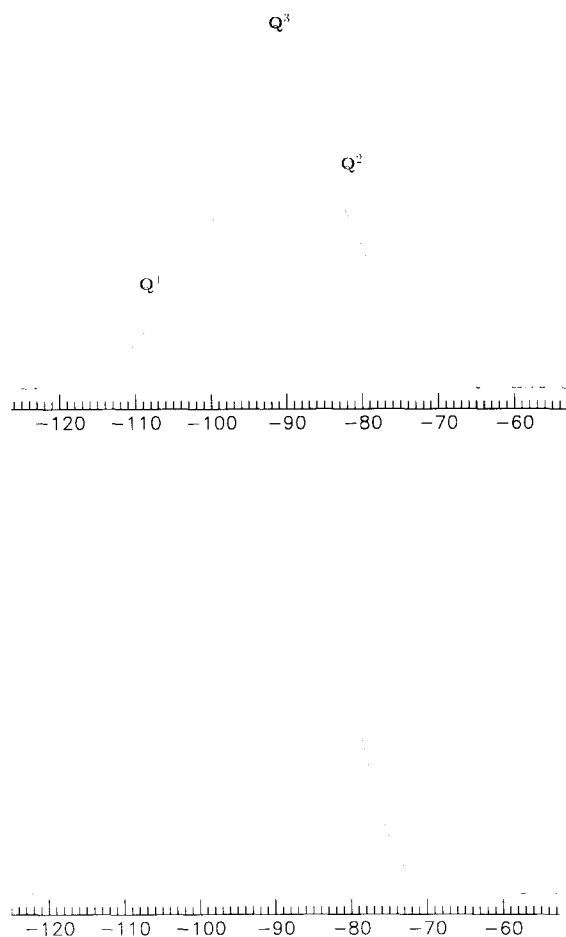


FIGURE 3

(Top) MAS spectrum for  $\text{Li}_2\text{Si}_2\text{O}_5$  glass.(Bottom) MAS spectrum for  $(\text{CaO})_{0.40}(\text{SiO}_2)_{0.60}$  glass.

simplest possible estimate of their contribution to the total configurational entropy of a glass indicates that as much as half of the difference between glass and crystal could be the result of their mixing<sup>29</sup>. On the other hand, the disorder in bridging and non-bridging oxygens is far from complete. Calculations of speciation with a random oxygen distribution, for example, give a very large value for  $K_3$  (0.375), and a  $Q^4$  abundance in a disilicate glass of 32% (vs. observed value of about 6-8% in  $\text{Na}_2\text{Si}_2\text{O}_5$ )<sup>30</sup>.

It has often been suggested, again primarily from vibrational spectra, that smaller, more highly charged (higher field

strength) network modifying cations increase one or more of the  $K$  values in reaction (1), leading to increased randomness<sup>4,5</sup>. This is caused by the same effects that eventually cause liquid-liquid phase separation: the tendency for high field strength cations to cause local concentrations of non-bridging oxygens in order to better maintain local charge balance. We have previously qualitatively confirmed this through MAS NMR linewidth data<sup>1</sup>, and can now present static NMR spectra which allow at least rough quantification.

As shown in figures 1 and 2 and table 1, the  $Q^4$  abundance in  $\text{Na}_2\text{Si}_2\text{O}_5$  glass is much lower than in  $\text{Li}_2\text{Si}_2\text{O}_5$  glass, and that in  $(\text{Na}_2\text{O})_{0.4}(\text{SiO}_2)_{0.6}$  glass is much lower than the corresponding Ca sample. Even in the latter composition, however, the disorder in bridging and non-bridging oxygens is still less than that predicted by a random model (18%)<sup>30</sup>. For the two disilicate compositions, it is possible to estimate  $K_3$  by neglecting the undetected populations of  $Q^1$  and  $Q^0$  sites, and calculating  $Q^2$  abundances from the observed  $Q^4$  contents and mass balance. The value for anneal for annealed  $\text{Na}_2\text{Si}_2\text{O}_5$  is about 0.008, whereas that for  $\text{Li}_2\text{Si}_2\text{O}_5$  is about 0.022. The parameters used to fit these spectra are also revealing. For the sodium glass, the main  $Q^3$  peak was simulated by a CSA tensor with  $\sigma_{11} = -48$  ppm,  $\sigma_{22} = -55$  ppm,  $\sigma_{33} = -162$  ppm, convoluted with a Gaussian broadening function with full width at half maximum of 19 ppm. For the lithium glass, the values used were  $\sigma_{11} = -53$  ppm,  $\sigma_{22} = -70$  ppm,  $\sigma_{33} = -148$  ppm, with a broadening of 25

Table 1.  
 $Q^4$  abundances in glasses

sample	$Q^4$ (% , $\pm 0.5$ )
$\text{Na}_2\text{Si}_2\text{O}_5$ , $T_g \approx 530^\circ\text{C}$	7.9
$\text{Na}_2\text{Si}_2\text{O}_5$ , $T_g \approx 450^\circ\text{C}$	6.4
$\text{Li}_2\text{Si}_2\text{O}_5$	11.5
37% $\text{Na}_2\text{O}$	4.2
41% $\text{Na}_2\text{O}$	1.9
40% $\text{CaO}$	6.4

ppm. The broadening function is thus considerably greater for the Li sample than for the Na sample, implying a greater disorder in bond lengths and distances as well as a wider distribution of Q species. In addition, the function  $\Delta\sigma = \sigma_{33} - 1/2(\sigma_{11} + \sigma_{22})$  can be used to characterize the total range is CSA, and has a value of -111 for the sodium glass and -87 for the lithium glass. This results from a smaller distortion of the  $Q^3$   $SiO_4$  tetrahedron by the higher field strength cation: the Si-O-Li bond resembles the Si-O-Si bond more closely than does the Si-O-Na bond. Both of these effects can also be seen qualitatively when comparing the 41%  $Na_2O$  and 40%  $CaO$  glass spectra.

##### 5. TEMPERATURE EFFECTS ON SPECIATION

The increase in disorder in silicate liquid structures has been observed previously both by spectroscopy at high temperature and on glass samples with varying fictive (glass transition) temperatures<sup>19,31-33</sup>. However, these effects have been difficult to quantify and have perforce been neglected in most treatments of the thermodynamics of these systems.

Again,  $^{29}Si$  NMR on static samples of carefully selected compositions has enabled us to begin to quantify the effect of temperature on  $K_3$  for reaction (1)<sup>34,35</sup>. For several carefully selected compositions, we prepared rapidly and slowly cooled samples which had significantly different fictive temperatures, and thus sampled the liquid structure at different real temperatures. Examples of these changes are shown in table 1, where there is a clear increase in  $Q^4$  (and presumably  $Q^2$ ) abundance as fictive temperature increases. From the change in  $K_3$  with temperature, we estimated the enthalpy change for reaction 1 ( $m=3$ ) to be  $30 \pm 15$  kJ/mol. A gross extrapolation from the glass transition to liquidus temperatures suggests as much as a doubling of  $Q^4$  contents. The size of this relative effect is in surprisingly good agreement with high temperature Raman data<sup>19</sup>, although again, absolute abundances determined by NMR are substantially lower.

We will show below that a temperature effect of this magnitude may have major consequences for thermodynamic activities. However, it is unlikely that this kind of structural change is a major part of the total configurational entropy change of the liquid with temperature: the enthalpy of reaction (1) is simply too small<sup>34</sup>. We have suggested that some kind of low abundance, high energy defect structure may play

a major role in overall energetics. As will be seen below, this is also indicated by relaxation time studies at high temperature, and by molecular dynamics simulations.

Both increasing temperature and increasing network modifier cation field strength promote a greater variety of Q speciation and increased randomness in the distribution of bridging and non-bridging oxygens. The thermodynamic consequences of the temperature effect can therefore be explored by examining the much better known effects of composition.

It is a well known observation that the constant temperature molar  $SiO_2$  content (X) of binary silicate liquids in equilibrium with crystalline silica decreases as the cation field strength increases<sup>36</sup>. Because the activity (a) of  $SiO_2$  is fixed by the crystalline phase, the activity coefficient  $\gamma = a/X$  must increase in the series  $Rb < K < Na < Li \approx Ba < Sr < Ca < Mg$ . Substitution of one alkali cation for another thus causes major changes in the solid-liquid phase diagrams. For example,  $SiO_2$  liquidus temperatures in the  $Li_2O$ - $SiO_2$  system can be 100 or more degrees higher than in the sodium system at the same value of  $X_{SiO_2}$ ; at a given temperature in equilibrium with silica,  $X_{SiO_2}$  in a liquid in the former system can be 10% or more lower than in the latter.

Although a complete model relating silicate speciation to activities is not available, it is reasonable to suppose that  $a_{SiO_2}$  is more-or-less directly related to the abundance of the  $Q^4$  species, which has the same local structure as crystalline silica. Certainly there is a systematic, if not linear, correlation between  $X_{Q^4}$  and  $\gamma_{SiO_2}$ . There is about a 70-90% increase in observed  $Q^4$  contents from  $Na_2Si_2O_5$  to  $Li_2Si_2O_5$  glass. (This difference may be somewhat underestimated, because the latter actually has a *lower* fictive temperature.) Extrapolating our results on fictive temperature dependence of speciation, a temperature increase of 400-600°C from  $T_g$  has a similar effect on the  $Q^4$  abundance. A large change in temperature might therefore change  $a_{SiO_2}$  in a way that is similar to that of the substitution of Li for Na, and thus clearly cannot be neglected in thermodynamic modeling.

This reasoning is born out by comparison with the isocompositional effect of temperature on  $a_{SiO_2}$  calculated from empirical models of the phase equilibria of multicomponent liquids. For example, liquids of basaltic lava composition typically have an average of about one non-bridging oxygen

per tetrahedral cation, as does  $\text{Na}_2\text{Si}_2\text{O}_5$ . Raising the temperature of such a liquid from 1100 to 1540°C increases  $a_{\text{SiO}_2}$  by about 20-25%<sup>37</sup>. Remarkably, a gross extrapolation of our results for  $\text{Na}_2\text{Si}_2\text{O}_5$  predicts a change of 25% over the same interval<sup>34</sup>. This agreement is undoubtedly partially fortuitous, but does suggest a real chemical significance to these spectroscopic observations.

A second kind of confirmation of the relationship of temperature dependent speciation to thermodynamics comes from enthalpy measurements on liquid silicates. Heat capacity data in the system  $\text{CaMgSi}_2\text{O}_6 - \text{NaAlSi}_3\text{O}_8$  suggests that heats of mixing *increase* with rising temperature<sup>22</sup>. This is contrary to the usual expectations of a closer approach to ideal solution behavior with increasing temperature, but has recently been confirmed by a more direct type of calorimetry<sup>38</sup>. The enthalpic drive for liquid-liquid unmixing is therefore *reduced* as temperature decreases, although it remains sufficiently great to permit metastable unmixing in the sub-liquidus region<sup>39</sup>.

Reaction (1) can symbolize the atomic-scale initiation of phase separation, as a homogeneous composition splits into liquids of higher and lower  $X_{\text{SiO}_2}$ . The spectroscopically observed temperature effect on (at least) the  $m=3$  reaction therefore also reduces the tendency to unmix as temperature is lowered. This is qualitatively the same as the rather unexpected thermodynamic results. Quantitative correlation awaits more data on both speciation and on excess heat capacities.

In crystalline materials, pressure effects on structure are generally opposite to those of temperature<sup>53</sup>. There are very few data available on the pressure dependence of Q speciation in simple alkali silicate liquids or glasses. One intriguing preliminary result from experiments to 26 kbar on  $\text{K}_2\text{Si}_4\text{O}_9$  liquid<sup>40</sup> suggests that pressure effects may be *similar* to those of temperature, instead of the opposite. Here the cause must be volumetric, not entropic. It is not obvious that a more random distribution of bridging and non-bridging oxygens should be denser. However, most bond compression in this type of silicate takes place in the weak, long, alkali-oxygen bonds<sup>53</sup>, effectively reducing the size of the network modifying cation at high pressure. Perhaps, then, the response of the structure to a compressed alkali site at high pressure is similar to that for the substitution of a smaller cation at low pressure. A greater abundance of  $\text{Q}^4$  sites, and

corresponding greater amount of  $\text{Q}^2$  and smaller amount of  $\text{Q}^3$  sites could be the result.

## 6. DYNAMICS

Spectroscopy on glass has begun to give a quantitative view of some aspects of the static, quenched-in disorder of silicate liquids at the glass transition, and has provided some clues as to the effects of raising temperature above  $T_g$ . Available data do not, however, reveal the "sink" for most of the excess heat capacity that distinguishes a liquid from a glass. Furthermore, there is not yet much direct structural information to constrain the mechanism of this structural change with temperature, or of the closely related viscous flow. NMR on liquids at high temperature can potentially help resolve these issues.

We have recently shown<sup>41,42</sup> that static  $^{29}\text{Si}$  lineshapes of silicate glasses are retained in the liquid to temperatures of roughly 100°C above  $T_g$ . This confirms that there is no *qualitative* change in the major (i.e. easily observable) structural speciation on transformation from glass to liquid, despite the *quantitative* changes in the liquid noted above. At higher temperatures, each NMR spectrum decreases in width until a single narrow line is present by 200-300°C above  $T_g$ . A good example of this process is  $\text{K}_2\text{Si}_4\text{O}_9$ . The static glass spectrum at room temperature (figure 4) shows two distinct components. The first can clearly be attributed to a nearly uniaxially symmetric site with a large chemical shift anisotropy ( $\text{Q}^3$ ), the second to a much more symmetrical site ( $\text{Q}^4$ ). Not far above  $T_g$ , the shape of the spectrum is similar (figure 5), with the signal to noise ratio reduced by all of the technical difficulties of this experiment. As temperature is increased further, both components become more narrow and merge together. Motional averaging of orientational effects and line narrowing are expected for any molecular species in a liquid as its frequency of reorientation becomes greater than the static linewidth. However, the observation of only a single peak, instead of the two expected for the two major species, has great importance to the dynamics. The only interpretation of this surprising result is that silicate species at high temperature have lifetimes much shorter than the NMR timescale, but longer than the vibrational timescale: in some way, silicon atoms are continuously exchanged among various sites, resulting in an average spectrum. These results can

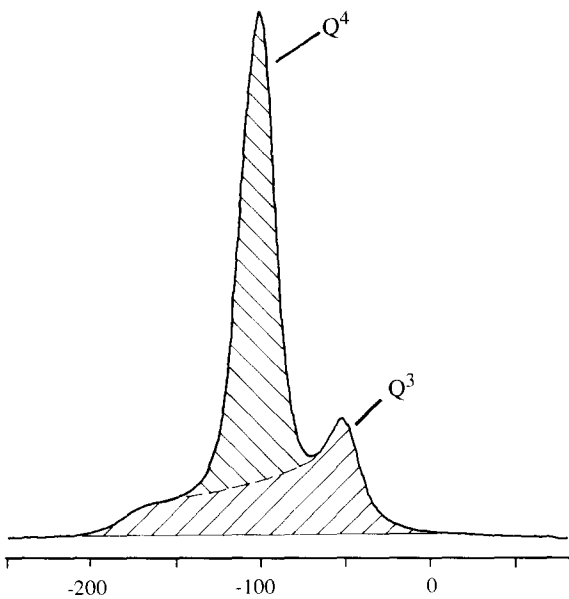


Figure 4  
Static spectrum for  $K_2Si_4O_9$  glass, with areas due to the two major species shown. Scale as in figure 1.

be roughly quantified, and indicate lifetimes of  $\mu s$  to ns at liquidus temperatures. Because exchange among Q species can take place only through the breaking and re-forming of strong Si-O bonds, this exchange must have major energetic significance.

Extrapolations of exchange frequency down in temperature to  $T_g$  gives estimates on the order of Hz<sup>41</sup>. At this rate, species exchange rates may become too slow to allow the structure to adjust to decreasing temperature at typical laboratory cooling rates. The observed exchange process may therefore be fundamental to the glass transition itself.

Nuclear spin relaxation time data also can be very sensitive indicators of diffusive time scale motion. Spin lattice relaxation (characterized by the time  $T_1$ ) for  $^{29}Si$  is caused by fluctuations in local magnetic field at the Larmor resonant frequency, which is about 35 MHz for the liquid data presented here. These fluctuations are in turn the result of relative motion of the Si atoms and surrounding nuclear and electronic spins. A key observation is that in all samples studied at appropriate temperatures, an abrupt change in the effect of temperature on  $T_1$  is observed close to the bulk, thermodynamic glass transition (figure 6). Although it is

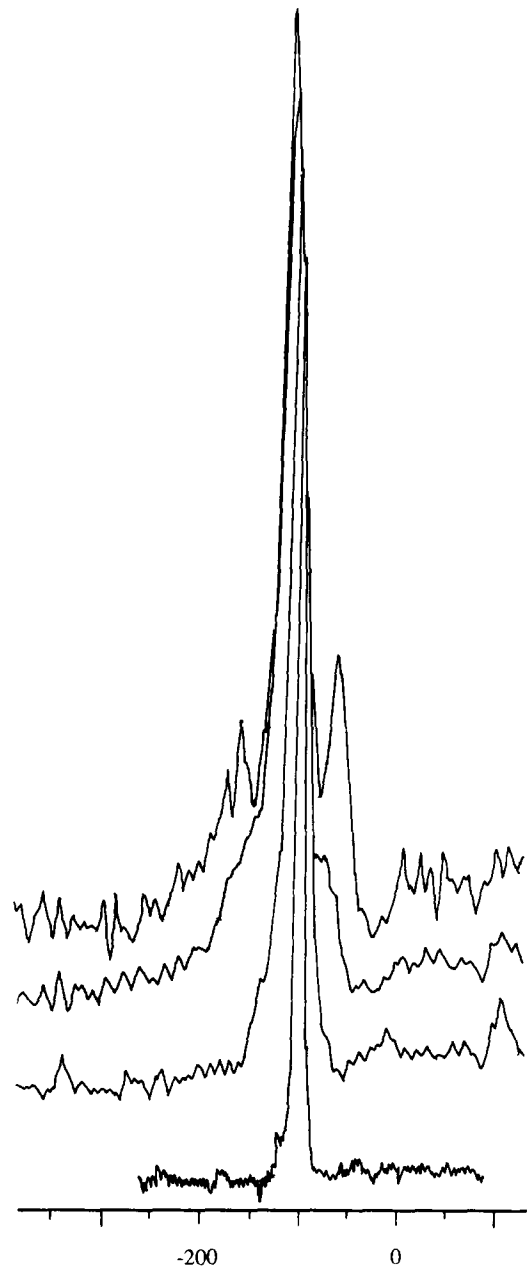


FIGURE 5  
Static spectra for  $K_2Si_4O_9$  liquid at high temperature at 35.5 MHz Larmor frequency. From top to bottom, temperatures are 705, 726, 779, and 857°C. Note decrease in linewidths and coalescence of  $Q^3$  and  $Q^4$  due to motional and exchange narrowing. Scale as in figure 1.



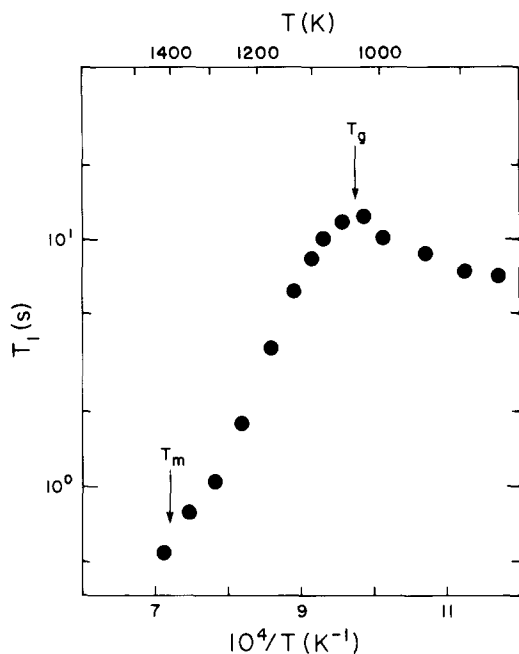


FIGURE 6

Spin-lattice relaxation time ( $T_1$ ) for  $\text{NaAlSi}_3\text{O}_8$  glass and liquid at 35.5 MHz.  $T_g$  is glass transition temperature from bulk thermal expansion data,  $T_m$  is the melting point of the crystal.

difficult to precisely characterize the motion responsible for the relaxation, it is clear that on heating through  $T_g$ , a rather abrupt change in mechanism begins which involves the network forming silicon atoms. Thus again we are "seeing" hints of the atomic-scale process that actually causes the glass transition. This result confirms the general perception that the dynamics which become "frozen in" at  $T_g$  do indeed involve the network structure.

The magnitudes of observed  $^{29}\text{Si}$   $T_1$ 's has suggested that relaxation in the liquid involves the formation of short lived structures with extremes in bond angles and distances and therefore extremes of chemical shifts<sup>42</sup>. We have suggested that these may, in fact, be the transition states that must be present during exchange of a silicon from one site to another.

## 7. CONCLUSIONS

The distribution of bridging and non-bridging oxygens around tetrahedral cations in silicate liquids and glasses is an

important part of the description of intermediate range order in these systems. It is now clear that this distribution is neither fully ordered nor completely disordered, but increases with increased network modifying cation field strength, with temperature, and possibly with pressure. Compositional and temperature effects are similar in magnitude, strongly suggesting that the latter should not be neglected in thermodynamic modeling. This is particularly true in calculating thermodynamic activities of components such as  $\text{SiO}_2$  that may depend rather directly on the abundance of a particular species.

On the other hand, the enthalpy change of this kind of speciation reaction is not enough to explain the often large configurational heat capacities of liquid silicates. It is likely that some type of high energy defect sites are important. For example, if a given defect site has an enthalpy of a few hundred kJ/mol as suggested by recent theoretical calculations<sup>45,47</sup>, a change in its abundance from near zero at  $T_g$  to a few percent at liquidus temperatures would be sufficient. Such abundances may be difficult to detect directly, but the recent progress among glass scientists in this area is encouraging. It is clear at least that some defects easily detectable by vibrational spectroscopy increase dramatically in abundance with increasing temperature in silicate and related liquids<sup>19</sup>.

The fundamental role of minor, high energy structures in silicate liquids is also suggested by high temperature NMR data. We have shown that Q species exchange rapidly at high temperature. Such exchange must involve the formation of some kind of highly strained transition state, which might also be responsible for spin-lattice relaxation. A logical candidate for this transition state is Si with a temporarily increased coordination number, as often reported in molecular dynamics simulations<sup>47-49,51</sup>. This kind of site has been previously suggested as a key part of the mechanism for viscous flow<sup>47,50</sup>. If such sites are abundant enough, and have long enough lifetimes, they may also be fundamental to the bulk energetics. It is likely that direct spectroscopic observation, and hopefully quantification, of these hypothesized species will have to be done at high temperature on actual liquids.

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