American Mineralogist, Volume 80, pages 861–864, 1995

LETTERS

Silicate species exchange, viscosity, and crystallization in a low-silica melt: In situ high-temperature MAS NMR spectroscopy

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Abstract

High-resolution, magic-angle-spinning (MAS), ^{29}Si NMR spectra have been obtained for a sodium silicate glass and liquid (60 mol% SiO_2) to temperatures over 600 °C. Crystallization was monitored in situ, and motional averaging of the peaks for distinct silicate anionic species (Q^2 and Q^3 species) in the liquid was observed. Modeling of the spectra yielded species exchange frequencies. The inverses of these exchange frequencies are slightly longer than shear relaxation times calculated from bulk viscosity using the Maxwell relation; viscosities calculated from the NMR data using an Eyring model are close to, but slightly less than, measured viscosities. These results are similar to those obtained for Q^3-Q^4 exchange in $K_2Si_4O_9$ liquid, indicating that local Si-O bond breaking occurs on a time scale consistent with it being the primary control on viscous flow even in lower silica liquids.

Introduction

The atomic-scale mechanism for viscous flow in silicate liquids is closely linked to diffusion of the Si cations and O anions that constitute the strongly bonded network of these materials (Dingwell and Webb, 1990; Shimizu and Kushiro, 1984). Viscosity is also fundamentally related to the configurational heat capacity and entropy of melts, and thus an understanding of transport properties may contribute to knowledge of equilibrium thermodynamic properties (Richet and Neuville, 1992). "Fragile" liquids, with highly non-Arrhenian viscosity, show large increases in heat capacity, thermal expansion, and compressibility on heating through the glass transition, whereas "strong" liquids (e.g., SiO_2) show small changes (Angell, 1991). The same kinds of molecular-scale structural processes that distinguish the equilibrium properties of a liquid from those of a glass must also be responsible for the slow relaxation that occurs when a glass is heated into the transition region during annealing. The critical role of annealing in the production of technologically useful glassy materials thus reinforces the importance of understanding the effects of temperature on structure and dynamics in oxide melts.

Using high-temperature, in situ ^{29}Si and ^{17}O NMR (including static and MAS two-dimensional NMR), we have shown for $K_2Si_4O_9$ liquid that the exchange of Si from sites with three bridging O atoms (Q^3) to sites with four bridging O atoms (Q^4), as well as the exchange between bridging and nonbridging O atoms themselves, takes place on a time scale similar to that defined by bulk viscosity (Farnan and Stebbins, 1990a, 1990b, 1994; Stebbins et al., 1992). This exchange requires breaking of the strongest bonds in the system (Si-O), and implies that such local bond breaking is the primary control on flow. Alternative mechanisms, such as the relative motion of large molecular units (e.g., chains or sheets), or of coherent domains (e.g., silica-like clusters), involving the breaking primarily of weak bonds to network-modifying cations along domain boundaries, seem to be ruled out.

This conclusion is sensible for the $K_2Si_4O_9$ composition, which has on average only 0.5 nonbridging O atoms per tetrahedral cation (NBO/T), and in which clustering is thought to be minimal. In all other silicate liquids studied, including compositions with as low as 40 mol% SiO_2, exchange among the constituent silicate species is also rapid, at least at temperatures above the liquidus (Fiske and Stebbins, 1994; Liu et al., 1988; Shimokawa et al., 1990; Stebbins and Farnan, 1992). However, the quantitative connection between exchange rates and viscosity, which on the NMR time scale is usually at least potentially observable from 50 to 200 °C above the glass transition, has not been possible because of the tendency of lower silica melts to crystallize rapidly in this temperature interval. In the study described here, rapid acquisition of high-resolution, magic-angle-spinning (MAS) ^{29}Si

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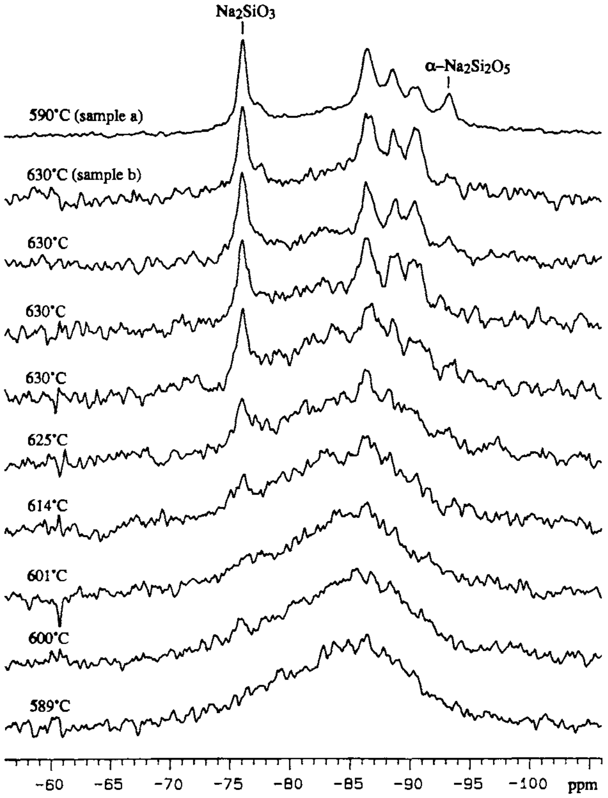

Fig. 1. The ^{29}Si MAS NMR spectra for $(Na_2O)_{0.4}(SiO_2)_{0.6}$ liquid at temperatures shown. Spectra were collected about 35 s apart. Thirty-two transients, acquired with a $\pi/6$ pulse (3 ms) and a delay time of 1 s, were used for each. The top spectrum was obtained in a previous experiment with a slower heating rate, after the sample had crystallized (200 transients).

NMR on a liquid with only 60 mol% SiO_2 has made it possible to extend to a much wider compositional range our conclusions about the fundamental dynamic control of melt viscosity.

EXPERIMENTAL METHODS

A glass with 40 mol% Na_2O and 60 mol% SiO_2 was synthesized from high-purity Na_2CO_3 and 95% ^{29}Si-enriched SiO_2 (Oak Ridge National Laboratory), with 0.2 wt% Gd_2O_3 added to enhance spin-lattice relaxation. The starting mixture was decarbonated overnight at 770 °C. The weight loss during synthesis was within 0.1% absolute of nominal. The 25 °C, ^{29}Si high-speed MAS NMR spectrum was fitted to obtain the relative proportions of Q^2 and Q^3 species, yielding 33.4% for the former (33.3% nominal).

MAS NMR spectra were collected with a modified Varian VXR-400S spectrometer at a ^{29}Si Larmor frequency of 79.5 MHz. Spectra are referenced to external tetramethyl silane at room temperature. Samples weighing about 220 mg were contained in 7 mm ZrO_2 rotors lined with BN and spun at rates of about 4 kHz in dry N_2 in a high-temperature MAS probe from Doty Scientific. Temperatures recorded by the probe's control thermocouple were carefully calibrated by non-NMR experiments in which a thermocouple was inserted into the center of a spinning rotor through a small hole in its base. This was feasible even for the rotor containing the sample because the melt flowed into a hollow cylinder lining the rotor during spinning at high temperature. The heating sequences followed during NMR data collection were then duplicated during calibration to eliminate any effects of temperature lag during rapid heating; spin-rate effects on sample temperature were also determined. A small shift of about 1 ppm to less shielded values in spectra above 500 °C was attributed, as previously (George and Stebbins, 1994), to a temperature dependence of the magnetic properties of the probe. Spectra were also obtained at ambient temperature in a 5 mm rotor spinning at a rate of over 10 kHz in a high-speed probe from Doty Scientific.

RESULTS

All spectra collected below the glass-transition temperature T_g (about 420 °C; Mazurin et al., 1983; Shelby, 1976) were typical of alkali silicate glasses, with two overlapping peaks resulting from the two predominant Si sites, Q^2 (−76.8 ppm) and Q^3 (−86.8 ppm). No differential relaxation was observed, indicating a homogeneous distribution of the sites (Sen and Stebbins, 1994). The spin-lattice relaxation time (approximated by a single exponential fit) at ambient temperature was 7.9 ± 0.9 s; at 355 °C, it had dropped slightly to 2.9 ± 0.5 s. Between 200 and 400 °C, some enhancement of resolution between the two major peaks was observed, possibly because of rapid alkali cation motion and a slight relaxation in the range of bond angles or distances. In one high-temperature experiment, in which one-half of the glass sample was heated at an average rate above T_g of about 2 °C/min, the initial stages of motional averaging were seen at about 555 °C, followed by the appearance of the narrow peaks of crystalline phases. The crystallized sample contained peaks previously reported for Na_2SiO_3 and α-$Na_2Si_2O_5$ (−77.1 and −94.4 ppm at 25 °C; Mägi et al., 1984; Murdoch et al., 1985), as well as other peaks at −86.4, −88.3, and −90.4 ppm, which are presumably due to one or more of the other, metastable polymorphs of $Na_2Si_2O_5$ (Fig. 1). (At least four phases of this composition are known; Hoffmann and Scheel, 1969; Pant, 1968). These peaks shifted to high frequency relative to those of the other phases by about 1.1 ppm at 580 °C, indicating an unusually large temperature effect on the local structure of this phase or phases. The last phase to crystallize was the high-temperature polymorph α-$Na_2Si_2O_5$. The small shoulder at −78 ppm may suggest a second crystalline metasilicate. This sample was removed from the rotor, crushed, and reanalyzed at 25 °C.

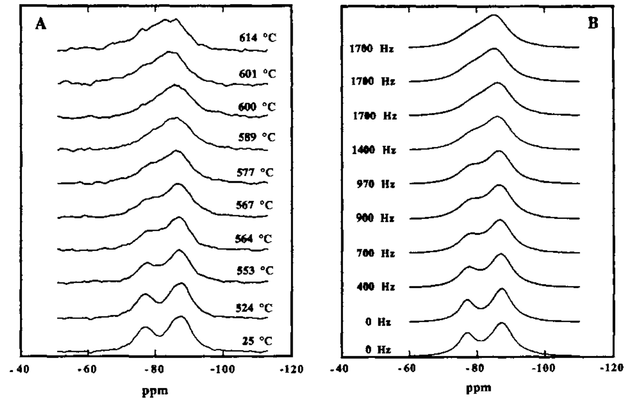

Fig. 2. (**A**) The ^{29}Si MAS NMR spectra of $(Na_2O)_{0.4}(SiO_2)_{0.6}$ liquid and glass at temperatures indicated, showing motional averaging of peaks for Q^2 and Q^3 sites. (**B**) Simulated spectra at the same temperatures, obtained from a two-site exchange model. Calculated exchange frequencies ν_{ex} are shown.

The spectrum was identical, indicating no development of preferred crystallite orientation during growth from the melt in the spinning rotor. In a second experiment, the other half of the glass batch was heated more rapidly (about 8 °C/min), with spectra collected continuously during heating. Here, a higher temperature was reached before crystallization was detected, and nearly complete motional averaging of the two peaks in the liquid was observed (Figs. 1 and 2). Spinning sidebands were reduced in intensity and somewhat broadened at the highest temperatures. At 620 °C, crystallization again became rapid (Fig. 1). The phases formed were similar to those in the first experiment, except that α-$Na_2Si_2O_5$ was low in abundance or absent.

The spectra of the supercooled liquid were simulated with a simple two-site exchange model calculated in the frequency domain (Abragam, 1961) to yield frequencies of exchange between the two sites (Fig. 2). The sidebands were not included in the calculation, and the sites were weighted according to the two (Q^2 and Q^3) center-band intensities. The two peaks in the ambient temperature spectrum were simulated with two Lorentzian lines (with the peak width at half height equal to $1/\pi T_2$) to obtain initial T_2 values for fitting spectra in the exchange regime. In a glass this is an underestimate of the actual spin-spin relaxation time T_2 because most of the line width comes from the distribution of Q^2 and Q^3 species with different chemical shifts, but the distinction is not significant in this modeling. At higher temperatures (but before exchange was obvious), T_2 was increased slightly to improve the fits of the simulated spectra. Spectra collected at 524 °C and above (where exchange was visible and as shown in Fig. 2) were fitted with a constant value of T_2.

The effect of the spinning rate (about 4 kHz) on the exchange spectra was also considered. However, this was in all cases two to three times greater than the derived exchange frequency, and broadening of the central peaks owing to the coincidence of exchange frequency and spinning frequency (Fenske et al., 1992) was not detected. In our spectra the spinning sidebands remained, and we observed the onset of Q^2 and Q^3 exchange among neighboring sidebands that resembled the center-band behavior and not exchange between the center band and sidebands of the same species. Thus, partial averaging of the chemical-shift anisotropy was negligible. This is understood because the treatment of Fenske et al. (1992) implicitly assumes an isotropic reorientation of the chemical-shift tensor, which would be unlikely for the Si species in this liquid.

A very high-quality, high-spinning-speed spectrum (signal to noise ratio >5000) obtained at 25 °C showed no peak near −150 ppm, indicating that the concentration of $^{[5]}$Si was less than about 0.01%.

DISCUSSION

The coalescence of the ^{29}Si NMR peaks corresponding to Q^2 and Q^3 silicate species within 200 °C of the glass transition indicates that local Si-O bond breaking is occurring in a liquid that contains only 60% SiO_2. The directly observed dynamics of this microscopic process of redistribution of nonbridging and bridging O atoms among Q species can be related to the macroscopic dynamics of viscous flow in several ways. The shear relaxation time for viscous flow can be calculated from the Maxwell relation $\tau_s = \eta/G_\infty$, where η is the viscosity and G_∞ is the infinite frequency shear modulus (approximated here as 10^{10} Pa·s (Dingwell and Webb, 1990). The time scale defined here by the inverse of the NMR exchange rates between Q^2 and Q^3 species in $(Na_2O)_{0.4}(SiO_2)_{0.6}$ is close to the value of τ_s derived from viscosity measurements (Mazurin et al., 1983) in this way. However, the NMR rates are approximately 0.5–1 log unit slower (Fig. 3), as observed previously for $K_2Si_4O_9$ (Farnan and Stebbins, 1994). It should be noted that the two high-temperature points in Figure 3 are fits to spectra that exhibit small contributions from the onset of crystallization. Thus, we may be detecting dynamics in a liquid slightly richer in SiO_2, apparently causing a more exaggerated deviation from the macroscopic curve for these points.

A more mechanistic approach can be taken by estimating the diffusivity D of Si from the Einstein-Smoluchowski equation, $D = d^2/6\tau$, where d is an average jump distance that we take (as previously) as 0.31 nm and τ is taken as the NMR exchange time. Here, a geometric factor of 6 is included that is more appropriate than the value of 2 used previously, because the former is probably a better measure of the number of nearby sites available for exchange. The viscosity is then estimated from an Eyring model, with $\eta = k_B T/(dD)$, where k_B is Boltzmann's constant. Again, as previously observed for $K_2Si_4O_9$, this estimate is close to the measured viscosity but falls slightly below the curve.

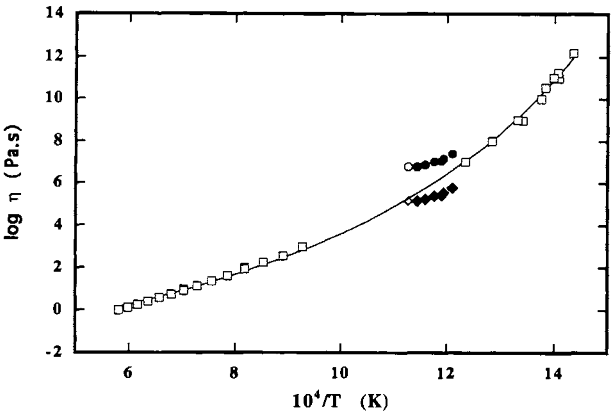

Fig. 3. Log_{10} of viscosity vs. inverse temperature (K^{-1}) for $(Na_2O)_{0.4}(SiO_2)_{0.6}$ liquid (open squares, Mazurin et al., 1983). Solid circles show viscosities calculated from NMR exchange frequencies using Maxwell relation and assuming that $1/\nu_{ex} = \tau_{ex}$ (see text); solid diamonds show data calculated using Eyring equation and assuming that the jump frequency is ν_{ex}; corresponding open symbols are at temperatures where a small amount of crystallization may have occurred, slightly changing the liquid composition.

As we concluded previously for $K_2Si_4O_9$ liquid, the fundamental control on viscosity in the 60 mol% SiO_2 liquid described here appears to be local Si-O bond breaking. Explanation of the relatively minor differences among the various approaches for estimating viscosity from microscopic exchange rates of course awaits a detailed model of the exchange and diffusion process. It is clear that our NMR observations detect only an average (characteristic of a local process) of what is undoubtedly a wide distribution of exchange and other microscopic structural relaxation rates in the liquid. Somewhat different parts of this distribution may be sampled by other measurements.

As silica content is lowered, viscosity decreases both because a smaller proportion of the bonds broken during flow are strong Si-O bonds and also because Si-O-Si linkages are weakened by increasing interactions among network modifying cations and bridging O atoms. At some SiO_2 content, for example in a liquid where the average silicate species is Q^1 (dimers, NBO/T = 3), it might be expected that the Si-O bond-breaking rate will be much less than the time scale required to control viscosity. At what composition this transition in mechanism occurs is unknown at this time. In considering the application of our conclusions to other systems it is useful to note that the range of NBO/T now covered by NMR measurements of species exchange rates (0.5–1.33) includes natural magmas from andesitic to very mafic basaltic compositions. Many O bonds in natural magmas bridge to Al and are thus weaker and even more likely to be broken during flow than Si-O bonds. Quantifying the microscopic dynamics of flow and diffusion in multicomponent liquids thus remains an important problem for future work.

ACKNOWLEDGMENTS

This project was supported by the National Science Foundation, EAR-9204458.

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MANUSCRIPT RECEIVED APRIL 10, 1995
MANUSCRIPT ACCEPTED JUNE 9, 1995