

Diffusive motion in alkali silicate melts: An NMR study at high temperature

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Abstract—Nuclear magnetic resonance (NMR) spectroscopy at high temperature is an excellent tool for studying the atomic scale diffusive processes in molten silicates which control their transport and thermodynamic properties. We present here ²³Na and ²⁹Si NMR data on lineshapes, spin-lattice, and spin-spin relaxation times in a series of alkali silicate and aluminosilicate melts from room temperature to about 1200°C.

²⁹Si lineshapes show that exchange of oxygens between bridging and non-bridging sites takes place at the microsecond to nanosecond time scale at liquidus temperatures, making the lifetimes of silicate "molecules" very short. This process is probably a fundamental step in viscous flow and configurational entropy generation. ²³Na relaxation time data suggest that the motion that causes relaxation is closely related to that of through-going diffusion, and the mixed-alkali effect is detectable in activation energies. The mechanism for ²⁹Si spin-lattice relaxation changes at or near the glass transition, showing a close link between local diffusive motion and bulk thermodynamic properties.

INTRODUCTION

MOLTEN SILICATES in nature and in industry are thermodynamically true liquids, despite their high viscosities. Their chemical and physical properties therefore depend not only on their "static", average structure as sampled by techniques such as X-ray scattering and vibrational spectroscopy, but on the longer range and intermediate time-scale dynamics. The motions of atoms and groups of atoms that are usually discussed in the context of transport properties such as diffusivity and viscous flow in melts are also fundamentally linked to equilibrium properties such as heat capacity, entropy, and thermal expansion (*e.g.* ADAM and GIBBS, 1965; RICHET, 1984; RICHET *et al.*, 1986; STEBBINS *et al.*, 1984).

The concern here is with "diffusive" motion, as distinct from vibrational motion. By this it is meant motion that is probably non-periodic, may involve cooperative motion of many atoms, has a distance scale on the order of bond lengths or greater, and a time scale many orders of magnitude longer than that of interatomic vibrations. Such motion is responsible for the on-going changes in local structure that take place in a liquid as its temperature increases, and thus for significant changes in the temperature derivatives of volume and entropy. In some cases, the distinction between diffusive and vibrational motion may become artificial, but we consider it to be a very useful one in highly structured, viscous liquids such as silicates.

The mechanistic details of diffusive motion in silicate melts are poorly known, and the specific nature of the ties to thermodynamics have been largely speculative. Recently, we have presented nuclear magnetic resonance (NMR) spectroscopic results on the structure and dynamics of molten silicates (LIU *et al.*, 1987; STEBBINS *et al.*, 1985, 1986) that have begun to

reveal the distance and time scales of motion in melts, and to suggest mechanisms connecting this motion to bulk properties.

As reviewed recently by several authors (SMITH *et al.*, 1983; BRAY, 1985; BRAY and HOLUPKA, 1985; OLDFIELD and KIRKPATRICK, 1985; KLINOWSKI and THOMAS, 1986) the use of NMR to study the local *static* structure of both crystalline and amorphous silicates has been flourishing. The number *n* of bridging oxygens coordinating silicon atoms, as symbolized by the standard notation *Qⁿ*, is particularly important in influencing the relative resonant frequency (chemical shift) of ²⁹Si in the compositions studied here.

Local atomic and molecular motions affect NMR spectra in several ways. As described in detail elsewhere (*e.g.* SPIESS, 1983; FYFE, 1983; SLICHTER, 1980; ABRAGAM, 1961) and very briefly in previous papers (LIU *et al.*, 1987), two related types of NMR data provide more-or-less direct information about low frequency (100's of MHz to Hz) motion. For example, the shapes and widths of NMR spectral "lines" often become narrower with increasing temperature as motional rates increase and averaging begins. Since NMR linewidths range from Hz to 10's or 100's of kHz in the systems studied here, the specifics of motion at these times scales can often be deduced from lineshape analysis.

A more general, but often more difficult to interpret, type of NMR data involves relaxation rates. After a nuclear spin system is excited to a high energy state by a radio frequency (rf) pulse, the only significant way that it can release energy and return to complete thermal equilibrium with its surroundings (the "lattice") is through stimulated (as opposed to spontaneous) emission. This transfer of spin energy to thermal energy is termed "spin-lattice" relaxation and the inverse of the relaxation rate is given as *T*₁. A spin-1/2 nucleus such as ²⁹Si must experience a fluctuating magnetic field at its NMR resonant (Larmor) frequency in order to undergo this relaxation. A nucleus with spin greater than 1/2 (such as ²³Na) can, in addition, couple to fluctuations in the local electric field gradient. Both types of field fluctuations at radio frequencies are often caused by the "diffusive" motion de-

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scribed above, which can include rotation, translation, jumping from one configuration to another, and less well-definable styles of motion. Measurements of T_1 can therefore reveal a great deal about structural mobility. In addition, the characteristic time for nuclear spins to reach equilibrium with one another, called the spin-spin relaxation time (T_2), is closely related to the linewidth. In some cases, independent measurements of T_2 can provide additional information about diffusive motion.

In this paper, which is an extension of our study of $\text{NaAlSi}_3\text{O}_8$ glass and liquid (LIU *et al.*, 1987), we present data on a number of other silicates and aluminosilicates (Table 1). We will show that several different types of motion in these materials can be detected and quantified by NMR, and that we can see strong hints about how these dynamics control bulk properties.

EXPERIMENTAL PROCEDURES

Sample preparation

Samples were prepared from reagent grade alkali carbonates, Al_2O_3 , and SiO_2 . Carefully mixed starting materials were decarbonated, then melted at about 300°C above the liquidus temperature. Glasses produced were ground and remelted until homogeneous. Careful weight measurements indicated that stoichiometry was maintained to within a few tenths of one percent absolute during synthesis. Glass samples

were cast in graphite molds into cylindrical slugs about 6×12 mm prior to loading into "binderless" hexagonal boron nitride (BN) capsules for the NMR data collection.

Glasses for ^{29}Si NMR were synthesized from 95% enriched SiO_2 . The oxide was repeatedly extracted from glass samples for re-use by dissolution of the samples in molten Na_2CO_3 and precipitation in acid aqueous solution.

One of the most important limits on the amount of data that could be collected on a given sample was compositional change during measurements. Run times and temperature histories were selected after many trials to minimize these effects, but some alkali loss and B_2O_3 dissolution (from the sample containers) was unavoidable. Because of the complex thermal histories of the samples, it is impossible to know the compositions at each temperature point precisely, but chemical analyses of the ^{23}Na samples indicates that effects were probably minor (Table 1). ^{29}Si enriched samples were not analyzed because of the great value of the material and need for constant "recycling", but these had thermal histories similar to the unenriched samples.

Samples made for ^{23}Na studies were also analyzed for Fe to assess the possible role of this element in nuclear spin relaxation (Table 1). Fe contents were generally less than 60 ppm, except for the two $\text{NaAlSi}_3\text{O}_8$ samples of LIU *et al.* (1987), which contained about 100 ppm Fe. Again, samples made with isotopically enriched SiO_2 were not analyzed, but probably contain even less Fe. The initial oxide was described by its producer as containing less than 5 ppm Fe, and samples were repeatedly run through a wet chemical procedure which should remove most inadvertent Fe contamination.

NMR spectroscopy

Details of the NMR spectroscopy, and of the high temperature NMR probe, are given in LIU *et al.* (1987). All NMR data were collected with a home-built Fourier transform spectrometer with a field strength of 4.2 T, corresponding to resonant (Larmor) frequencies of 35.52 MHz for ^{29}Si and 47.30 MHz for ^{23}Na . Spin-lattice relaxation times (T_1) were measured using the conventional saturation-recovery pulse sequence (*e.g.* FUKUSHIMA and ROEDER, 1981). Spin-spin relaxation times (T_2) were obtained using a Hahn spin echo sequence (HAHN, 1950). Typically, 20 to 100 free induction decay (FID) signals were averaged for each spectrum or relaxation time data point.

In the NMR probe, samples were heated in argon or Ar-3% H_2 by molybdenum resistance wires. Some of the data reported here (described in detail by SCHNEIDER, 1985) were obtained with the "shuttling" probe system (STEBBINS *et al.*, 1986), in which the sample was periodically moved from a furnace to the radio frequency (rf) NMR coil, maintained at room temperature. The majority of the results were obtained with a stationary sample in a horizontal solenoidal rf coil kept at the sample temperature. In the latter arrangement, temperatures could be easily measured with a thermocouple adjacent to the sample, and are accurate to about $\pm 5^\circ\text{C}$.

In general, agreement of the data from the two techniques is good, except for relaxation time data for T_1 values greater than 100–200 ms (unmeasurable in the "shuttling" system). Temperature stability and accuracy are considerably better with the stationary sample, and relaxation times of any reasonable length can be measured. Sensitivity can become a serious problem at very high temperatures, however, because of the increased resistance of the rf coil wire and the decreased Q of the rf tuning circuit.

RESULTS

Lineshapes: ^{29}Si

Unlike most recently published ^{29}Si NMR spectra for silicates, those presented here were collected without magic angle spinning (MAS). At relatively low temperatures where motion does not affect lineshape, these are generally termed "static" spectra. The differences in chemical shift caused by the spatial orientation of the silicon sites in the external magnetic field B_0 dominate these spectra. This chemical shift anisotropy (CSA) provides information about the local site symmetry (*e.g.*, FYFE, 1983).

Table 1. Chemical analyses of glass samples after ^{23}Na NMR data collection.

	Na_2O	K_2O	Li_2O	B_2O_3	Fe
$\text{Na}_2\text{Si}_2\text{O}_5$	31.9 34.0	-	-	0.2	50
NaKSi_2O_5	15.3 15.6	19.4 23.8	-	1.1	46
$\text{NaLiSi}_2\text{O}_5$	17.5 18.7	-	8.5 9.0	1.7	67
NaKSi_4O_9	9.1 9.7	13.1 14.8	-	1.3	37
<u>Data of Schneider, 1985</u>					
$\text{Na}_2\text{Si}_2\text{O}_5$	32.4 34.0	-	-	-	-
NaKSi_2O_5	15.0 15.6	18.9 23.8	-	-	-
$\text{Na}_2\text{Si}_4\text{O}_9$	21.2 20.2	-	-	-	-
$\text{NaAlSi}_2\text{O}_6$	13.5 15.3	-	-	-	-

Upper entry in each column is amount found, lower entry is nominal.

Upper section of table:

Alkali analyses (wt %) are by ICP, and are of relatively low precision: generally $\pm 2\%$ absolute, generally 1–2% low. Boron analyses by ICP are of high precision, but samples were heterogeneous due to small amount of BN from capsules. These results are therefore $\pm 0.5\%$ absolute, but probably represent maximum values in the bulk glass. Fe analyses (ppm) are by colorimetric methods, ± 5 ppm.

Lower section of table:

Alkali analyses (wt%) are by flame photometry, $\pm 1\%$ absolute.

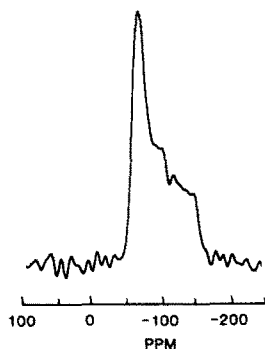


FIG. 1. ^{29}Si NMR spectrum of crystalline $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ at 700°C .

For example, the static ^{29}Si NMR spectrum of a randomly oriented powder of crystalline $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ (Fig. 1) is typical of that for a structure with a single site with nearly uniaxial symmetry of the electron distribution and therefore of shielding of the nucleus from the external field (HAEBERLEN, 1976). (A few hundred Hz, or about 10 ppm, of broadening may be caused by Si-Si and Na-Si dipolar interactions, SCHNEIDER *et al.*, 1987). The intense peak near -70 ppm is due to the statistically most common orientation with the shielding symmetry axis orthogonal to B_0 . The extreme value of the chemical shift at about -165 ppm is due to sites with this axis in the uncommon orientation parallel to B_0 . The CSA can be described by a tensor with $\sigma_{11} \approx -50$, $\sigma_{22} \approx -70$, and $\sigma_{33} \approx -165$ ppm. These results are in good agreement with the data obtained by SMITH *et al.* (1983) from "slow spinning" MAS spectra at room temperature. The spectrum is nearly identical to spectra collected recently at room temperature (STEBBINS, 1987).

Results from single-crystal studies of chemical shifts (GRIMMER *et al.*, 1981; WEIDEN and RAGER, 1985) suggest a simple relationship between this CSA tensor and local atomic structure. In a crystalline sheet silicate such as $\text{Na}_2\text{Si}_2\text{O}_5$, each silicon has three bridging oxygens with similar Si-O bond lengths, and a single non-bridging oxygen with a Si-O bond length about 4% shorter (PANT, 1968). When the latter is aligned with B_0 , the most shielded (most negative) chemical shift is seen. When longer Si-O bonds are oriented along B_0 , less negative chemical shifts are observed. Orientations in between produce the full range of the spectrum.

The top spectrum in Fig. 2 shows results for supercooled $\text{Na}_2\text{Si}_2\text{O}_5$ liquid at a temperature about 100°C above the glass transition. The shape of the spectrum resembles that of the crystal, suggesting that most of the Si in the liquid is also in Q^3 sites with nearly uniaxial symmetry. However, an obvious extra peak protrudes from the center of the pattern, which is due to the presence of 5–10% Q^4 sites. In minerals, these have small CSA values (SMITH *et al.*, 1983), and thus retain relatively narrow lines and are accentuated in static spectra. This feature is more clearly seen in spectra of the glass at room temperature (STEBBINS, 1987).

As reported previously for $\text{Na}_2\text{Si}_4\text{O}_9$ (STEBBINS *et al.*, 1986), the ^{29}Si linewidth for all liquids studied decreases with increasing temperature, until it reaches an instrumentally determined minimum. This narrowing is typical of those seen when highly viscous liquids are heated, and is the result primarily of the motional averaging of the CSA and of dipole-dipole interactions. In qualitative terms, when the reorientation rate becomes faster than the frequency width of the spectrum, a narrow line is seen.

In this and in all other compositions studied, only a single narrow line was observed at high temperature in the liquid. For compositions such as $\text{K}_2\text{Si}_4\text{O}_9$ and $\text{Na}_2\text{Si}_2\text{O}_5$ it is clear, however, that more than one type of silicate species is present in both the glass and in the supercooled liquid. As described previously for $\text{Na}_2\text{Si}_4\text{O}_9$ melt (SCHNEIDER, 1985; STEBBINS *et al.*, 1985, 1986), this indicates that the exchange rate among the different silicate species must be rapid relative to their difference in resonant frequencies. For $\text{Na}_2\text{Si}_2\text{O}_5$ liquid, the results shown in Fig. 2 suggest that by only 200°C above the glass transition, this "chemical exchange" begins to take place with a frequency on the order of a few kHz.

Lineshapes: ^{23}Na

Unlike ^{29}Si , ^{23}Na has a nuclear spin of $3/2$. In solids (particularly silicates), only the central, $-1/2$ to $+1/2$ transition is observed, because of the very large splitting between the $-1/2$ to $-3/2$ and $1/2$ to $3/2$ transitions. However, quadrupolar coupling typically increases central linewidths to 10^3 's of kHz (OLDFIELD *et al.*, 1982). In liquids, rapid motion may also average all of the transitions, and, as for ^{29}Si , a narrow line results.

As for ^{29}Si , ^{23}Na linewidths in the melts studied here are broad at low temperatures and begin to narrow as motional frequencies increase. No structure was observed in the lineshapes that would indicate distinct populations of sodium cations. Unfortunately, limited data between room temperature and $400\text{--}500^\circ\text{C}$ did not allow us to follow the possible "collapse" of the outer transitions, which could potentially provide considerable data on motion in the MHz frequency range.

^{23}Na spin relaxation times are several orders of magnitude shorter than those for ^{29}Si . It was therefore possible to observe a good agreement between high temperature ^{23}Na linewidths and the relaxation time data, as reported previously for $\text{NaAlSi}_3\text{O}_8$.

Relaxation: ^{23}Na

The effects of temperature on spin-lattice relaxation times (T_1) for ^{23}Na in glassy and molten silicates follow a general trend similar to that seen in most liquids or mobile solids for which a wide enough temperature span is accessible. At low temperatures, most diffusive motion is at frequencies much lower than the Larmor frequency, and relaxation is slow and inefficient. As temperature increases, motional frequencies increase and relaxation becomes more rapid. A minimum in T_1 is generally observed when (in simple cases) the correlation time for the motion responsible for relaxation becomes equal to the inverse of the Larmor frequency. At higher temperatures, most motion becomes too rapid, and relaxation again slows.

This pattern is well displayed in the T_1 data for NaKSi_2O_5 glass and liquid (Fig. 3). Despite gaps in the temperature coverage due to instrumental problems, a T_1 minimum is clearly implied at about

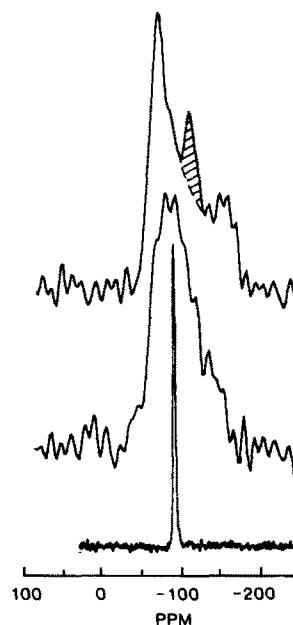


FIG. 2. ^{29}Si NMR spectra of $\text{Na}_2\text{Si}_2\text{O}_5$ liquid above the glass transition. Cross-hatched areas are due to the presence of Q^4 sites. Top: 549°C , where motion is too slow to cause significant line-narrowing. Middle: 648°C , where chemical exchange and motional averaging begin to affect lineshape. Bottom: 804°C , where structural re-arrangement takes place much more rapidly than the inverse of the static linewidth.

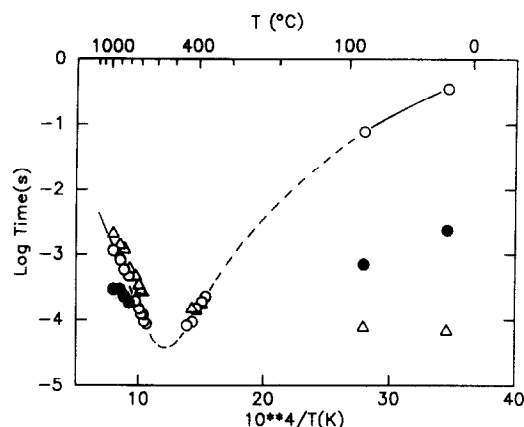


FIG. 3. ^{23}Na nuclear spin relaxation time data for NaKSi_2O_5 glass and liquid. Open circles: T_1 data. Filled circles: T_2 data. Triangles: inverse of linewidth at half intensity (FWHM).

560°C. Similar minima were observed for other disilicate compositions (Table 2).

A second feature seen in several samples is a significant increase with rising temperature in the magnitude of the slope on Arrhenius plots such as Fig. 3. At high temperatures in the liquid region however, slopes appear to be more-or-less constant.

Away from T_1 minima, such slopes can be interpreted as at least apparent activation energies through the Arrhenius equation:

$$T_1 = B \exp(-E_a/RT) \quad (1)$$

where B is a constant, E_a the activation energy, and R the gas constant. The sign before E_a is positive below the minimum. Apparent activation energies are given in Table 2. In the high temperature range, systematic effects of composition are seen. The increase in E_a caused

Table 2. Spin-lattice relaxation time results.

	Na-23 data			Si-29 data		
	temp. at $\text{Log}(T_1)$ T_1 min. at min. ± 50	E_a ± 0.2	E_a ± 5	temp. at $\text{Log}(t_1)$ T_1 min. at min. ± 10	E_a ± 0.05	E_a ± 5
$\text{Na}_2\text{Si}_2\text{O}_5$	530	-4.5	67	770 ¹ 790 ²	-0.04 -0.11	56 44
NaKSi_2O_5	560	-4.7	95	850 ³ 771 ⁴	-1.4 -0.6	98 55
$\text{NaLiSi}_2\text{O}_5$	560	-4.7	94	-	-	-
$\text{Na}_2\text{Si}_4\text{O}_9$	<695	<-3.9	66 ⁵	>920	<-0.1	-
NaKSi_4O_9	<760	<-4.2	81	-	-	-
$\text{K}_2\text{Si}_4\text{O}_9$	-	-	-	>1165	≈ -0.4	135
$\text{NaAlSi}_2\text{O}_6$ ⁵	≤ 870	≤ -3.7	61	-	-	-
$\text{NaAlSi}_3\text{O}_8$ ⁶	≈ 610 ⁷	<-4.2	71	>1140	<-0.5	130

Temperatures in °C; times in s; E_a (apparent activation energy) in kJ/mol; results for ^{23}Na are above T_1 minima; for ^{29}Si , below T_1 minima.

¹ sample 1

² sample 2

³ first run on sample

⁴ second run on same sample

⁵ data reported by Schneider, 1985

⁶ data reported by Liu *et al.* 1987

⁷ estimate based on quadrupolar relaxation mechanism, Liu *et al.* (1987)

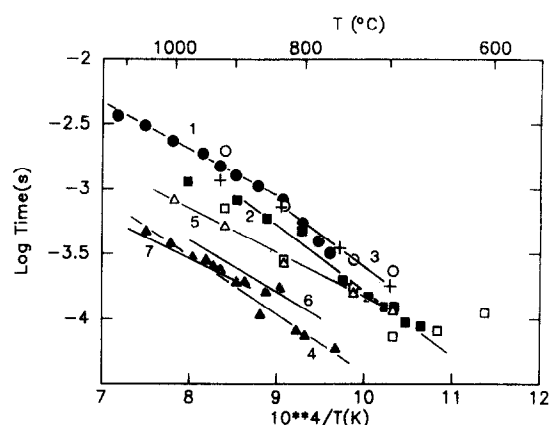


FIG. 4. ^{23}Na spin-lattice relaxation time data (T_1) for silicate liquids above the T_1 minima. Line 1 (filled circles): $\text{Na}_2\text{Si}_2\text{O}_5$. Line 2 (filled squares): NaKSi_2O_5 . Line 3 (+): $\text{NaLiSi}_2\text{O}_5$. Line 4 (filled triangles): NaKSi_4O_9 . Line 6 (fit line only): $\text{NaAlSi}_3\text{O}_8$ (LIU *et al.*, 1987). Data of SCHNEIDER (1985): Line 5 (open triangles): $\text{Na}_2\text{Si}_4\text{O}_9$. Line 7 (fit line only): $\text{NaAlSi}_2\text{O}_6$. Open circles (no fit line): $\text{Na}_2\text{Si}_2\text{O}_5$. Open squares (no fit line): NaKSi_2O_5 .

by substitution of either Li or K for half of the Na in $\text{Na}_2\text{Si}_2\text{O}_5$ melt, and of K for Na in $\text{Na}_2\text{Si}_4\text{O}_9$ (the "mixed alkali effect") is particularly clear, and is shown in Fig. 4. This figure also indicates the generally good agreement (within 10–30%) of the results of SCHNEIDER (1985) obtained with the "shuttling" probe, and the results from the stationary sample probe. However, the T_1 minima suggested by the earlier data (particularly for NaKSi_2O_5) probably actually occur at the lower temperatures illustrated by Fig. 3.

Several samples studied showed small anomalies in relaxation times at or near the macroscopic glass transition T_g . This was most clearly seen in data on $\text{NaAlSi}_3\text{O}_8$ reported earlier (LIU *et al.*, 1987), but is also apparent for ^{23}Na in $\text{Na}_2\text{Si}_2\text{O}_5$ glass (Fig. 5).

Spin-spin relaxation times (T_2) and inverse linewidths were also measured. In general both are roughly constant at about 100 μs below the T_1 minima, and follow the trend of the T_1 data above the minima. In this high temperature range, inverse linewidths are approximately twice as large as T_1 . As reported earlier for $\text{NaAlSi}_3\text{O}_8$ melt, T_2 at high temperatures is typically approximately half as large as T_1 .

Relaxation: ^{29}Si

Spin-lattice relaxation time minima for ^{29}Si in the melts studied here, where observed, are at temperatures several hundred degrees above those observed for ^{23}Na (Table 2 and Figs. 6 and 7). For the

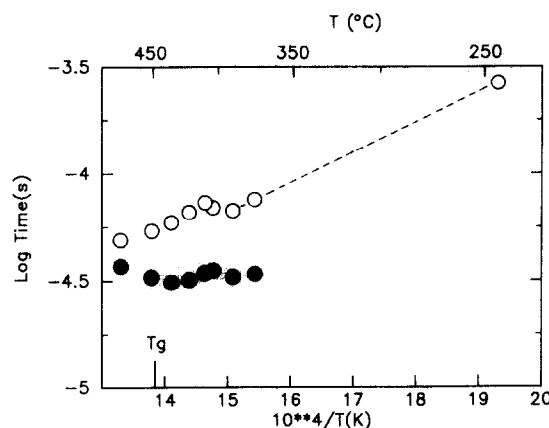


FIG. 5. ^{23}Na relaxation time data for in $\text{Na}_2\text{Si}_2\text{O}_5$ liquid near T_g . Symbols as in Fig. 3.

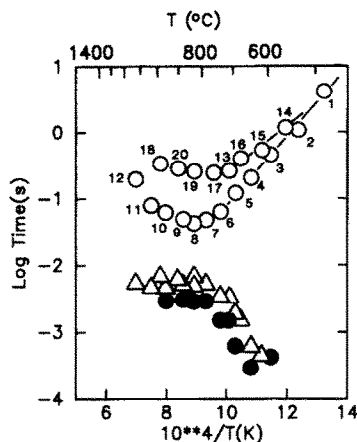


FIG. 6. ^{29}Si relaxation time data for NaKSi_2O_5 liquid. Symbols as in Fig. 3. Numerals show order in which measurements were made. Constant linewidth at high temperatures here and in Fig. 8 is caused by instrumental limitations.

more viscous melts, including $\text{K}_2\text{Si}_4\text{O}_9$ and $\text{NaAlSi}_3\text{O}_8$ (LIU *et al.*, 1987), the minima fall at temperatures above those studied and were not observed. For NaKSi_2O_5 liquid, T_1 values increased by a factor of 2–6 after initial heating (Fig. 6), presumably because of some compositional change. The release of adsorbed water in this highly hygroscopic sample is one possibility.

On the other hand, two different samples of $\text{Na}_2\text{Si}_2\text{O}_5$ had T_1 values within 5% and T_1 minima within 10–20°C, even though one began as a glass and the other began as a crystalline solid and was melted during the NMR experiment. The initially crystalline sample (Fig. 7a) had a T_1 of 15.7 s at 633°C, which decreased rapidly with increasing temperature. A clear break to an increased slope was observed as partial melting began. (The sample melted at a temperature below its nominal solidus temperature of 874°C, probably because of a slight addition of B_2O_3 from the sample container). Above about 850°C the sample was completely molten. On cooling, the sample did not crystallize and a T_1 minimum was observed. A final value of 2.0 s at 628°C was a factor of 8 lower than that for the crystal.

T_1 data for a second sample of $\text{Na}_2\text{Si}_2\text{O}_5$ which was initially glassy are shown in Fig. 7b. Phase changes can again be followed: the sample began as a supercooled liquid, then crystallized. The sample had completely re-melted at 874°C, then remained a supercooled liquid on cooling to 592°C. On reheating to 699°C, however, the crystal growth rate increased significantly. Careful measurements between this temperature and 635°C showed a relaxation which could be best fitted as a double exponential decay. The two T_1 values determined correspond well with those expected for a crystal-melt mixture.

Figure 8 shows the results for a particularly viscous liquid, $\text{K}_2\text{Si}_4\text{O}_9$, whose relaxation behavior is similar to that of $\text{NaAlSi}_3\text{O}_8$ melt (LIU *et al.*, 1987). No clear T_1 minimum is observed, only a gradual decrease in slope with increasing temperature. Both inverse linewidth and T_2 are roughly constant at low temperature, then increase until the instrumental linewidth (dictated by B_0 field inhomogeneity) is reached at high temperature. Shown also are the T_1 and T_2 data for $\text{Na}_2\text{Si}_4\text{O}_9$ collected with the "shuttling" probe and reported by SCHNEIDER (1985). The lower temperature T_1 point from this earlier report is very discrepant, because the true value was much larger than those accurately measurable at that time.

Data near and below the glass transition are incomplete for these samples, but the available T_1 data follow the pattern set by $\text{NaAlSi}_3\text{O}_8$: values near room temperature are much lower than expected from extrapolation of the data in the liquid region.

DISCUSSION

^{29}Si spectra

The dominant Q species in alkali silicate glasses are determined primarily by composition, and are well established

by data from vibrational spectroscopy (e.g. BRAWER and WHITE, 1975; MATSON *et al.*, 1983; MCMILLAN, 1984; SEIFFERT *et al.*, 1981) as well as by magic-angle spinning (MAS) NMR results (e.g. SCHRAMM *et al.*, 1984; MURDOCH *et al.*, 1985; SELVARAY *et al.*, 1985; GRIMMER and MÜLLER, 1986; GRIMMER *et al.*, 1984; DUPREE *et al.*, 1984, 1986; SCHNEIDER *et al.*, 1987). It is also now clear that small, but significant proportions of species beyond that required by composition alone are also present (STEBBINS, 1987). These may be created by disproportionation reactions such as:



Equation (2) represents both an equilibrium and a dynamic process. A second type of transformation from one local species to another is a simple exchange of a single bridging and non-bridging oxygen. The rates at which the silicate species transform from one to another can be estimated from the reduction of the ^{29}Si NMR spectral width to a single narrow

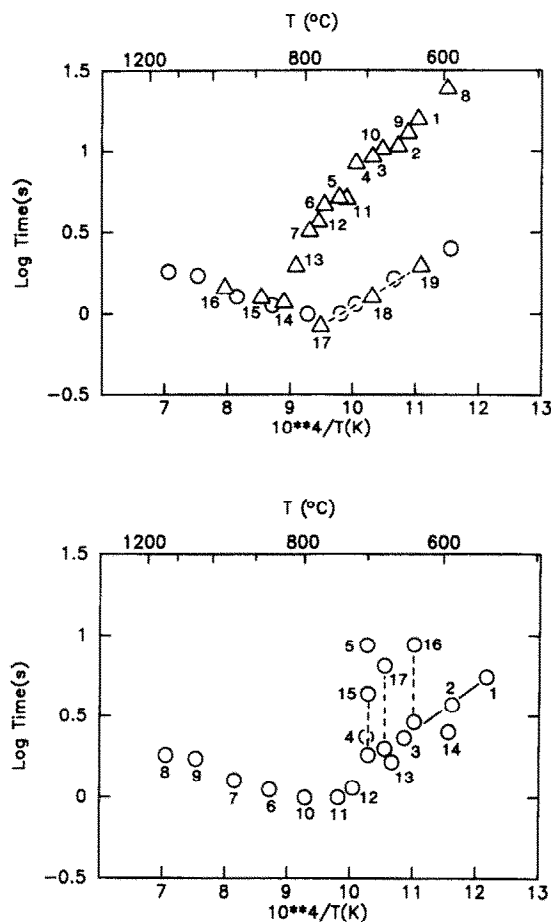


FIG. 7 (a) ^{29}Si T_1 data for initially crystalline $\text{Na}_2\text{Si}_2\text{O}_5$ sample. Numerals show order in which measurements were made. Sample became completely molten between points 13 and 14, then remained a metastable liquid on cooling. Circles show data from other sample as in Fig. 7b. (b) ^{29}Si T_1 data for initially glassy $\text{Na}_2\text{Si}_2\text{O}_5$ sample. Numerals show order in which measurements were made. Sample crystallized between points 4 and 5 after 3 hr at this temperature, remelted between points 5 and 6, then remained a metastable liquid until it was re-heated to point 15. After several hours at this point, the sample began to crystallize. Pairs of points at 15, 16, and 17 thus show T_1 for crystal and melt components.

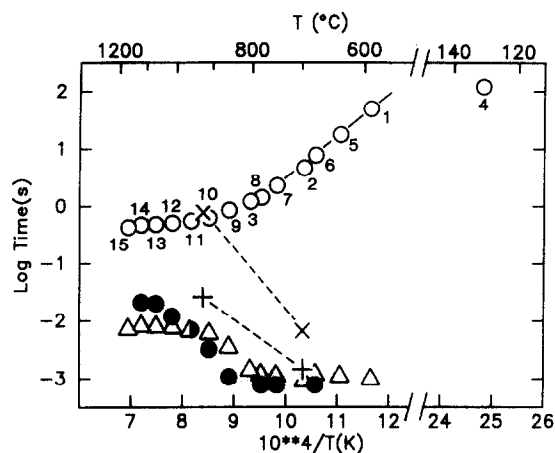


FIG. 8. ^{29}Si relaxation time data for $\text{K}_2\text{Si}_4\text{O}_9$. Symbols as in Fig. 3. Note break in axis between liquid and glass data, and the large difference between point 4 and that predicted by the liquid data. \times : T_1 data of SCHNEIDER (1985) for $\text{Na}_2\text{Si}_4\text{O}_9$. Lower temperature T_1 point is discrepant because the real T_1 value was not measurable with the "shuttling" sample technique. $+$: T_2 data of SCHNEIDER (1985) for $\text{Na}_2\text{Si}_4\text{O}_9$.

line a high temperature. A rough approximation can be made if we assume that at the temperature of the center spectrum in Fig. 2 (648°C), the resonant frequency difference between species ($\Delta\nu$) is approximately equal to the rate of exchange ($1/\tau_{\text{ex}}$), and that the effect of temperature on this rate is exponential, with

$$1/\tau_{\text{ex}} = \omega_0 \exp(-E_a/RT). \quad (3)$$

If a range of values of ω_0 typical for chemical exchange in organic liquids is chosen as 10^{13} to 10^{15} s^{-1} (GLASSTONE *et al.*, 1941), E_a can be estimated as about $200 \pm 50 \text{ kJ/mol}$. This value is of the same order as, but somewhat less than, the value of the apparent E_a for viscous flow for $\text{Na}_2\text{Si}_2\text{O}_5$ liquid at this temperature of 281 kJ/mol (RICHET, 1984), and is about half of typical values for Si-O bond energies.

This approximation can be checked by calculation of the exchange rate at several other temperatures. At 804°C , for example, the very narrow line shown in Fig. 2 requires that $\Delta\nu\tau_{\text{ex}} \ll 1$. Taking $\Delta\nu = 1800 \text{ Hz}$ (50 ppm) $\omega_0 = 10^{13}$ and the resulting E_a of 170 kJ/mol , $\Delta\nu\tau_{\text{ex}}$ is 0.03. At 549°C , the presence of the full static linewidth requires that $\Delta\nu\tau_{\text{ex}} \gg 1$. The calculated result is 11, again consistent with the data. Perhaps most intriguingly, the exchange frequency at the macroscopic glass transition of about 450°C is about 5 s, just in the range expected if the exchange process ceases to be significant at T_g . A close relationship between this exchange and the glass transition is implied.

In detail, it is unlikely that the rate of the exchange process is really "Arrhenian": viscosity for such compositions is clearly non-Arrhenian (RICHET, 1984). A more accurate picture should result from detailed simulations of the ^{29}Si line-shapes with more complete data.

This exchange process, and the reorientation of the local symmetry axis which must also occur to produce a narrow line, both must involve the conversion of bridging oxygens to non-bridging oxygens and *vice versa*. Strong Si-O bonds must therefore break and reform at a high rate in molten sili-

cates. This local rearrangement is probably also the fundamental step by which viscous flow occurs, at least in melts relatively rich in silica.

The lifetimes of silicate species in melts implied by these results are short no matter what numerical assumptions are made, being less than a few microseconds at temperatures above the liquidus for $\text{Na}_2\text{Si}_2\text{O}_5$ and approaching a nanosecond for this composition at the melting point of SiO_2 . This fact may have implications for thermodynamic modeling. Polymeric "molecules" may be present in glasses in the sense of topological connectivity, but do not persist as discrete entities in the melt at temperatures much above the glass transition. This is *not* to say that coordinated motion of small groups of silicate tetrahedra does not take place, however, only that the time scale of such coherence must be much less than the "laboratory" time scale.

Structural rearrangement of "chemical exchange" at MHz or even GHz frequencies is, of course, much less rapid than typical inter-atomic vibrational frequencies. Vibrational spectroscopy samples the structure at the 10^{-14} to 10^{-15} s timescale. The similarity of Raman spectra of alkali silicate glasses and melts (*e.g.* SEIFFERT *et al.*, 1981) thus implies that there is no fundamental change in this "snapshot" view of the local structure, although the proportions of species may not be constant. These results say little about diffusive motion, however.

Relaxation: ^{23}Na

The first step in transforming nuclear spin relaxation data into information on atomic or molecular motion must be to come to at least a general understanding of the relaxation mechanism. Spin-lattice relaxation rates depend on two types of variables which describe the fluctuations in magnetic field or electric field gradient responsible for the process. These are the size of the fluctuations, and the rate at which they occur at the Larmor frequency of the nucleus of interest. The former are generally cast in terms of interaction frequencies which describe the change in resonant frequency that can occur during the fluctuation; the latter are cast in terms of the spectral density, which describes the relative number of fluctuations that take place at the Larmor frequency. In all models of relaxation, an increase in either will increase the relaxation rate and decrease T_1 .

A common cause of relaxation in both liquids and solids is related to the presence of paramagnetic impurities such as dissolved Fe^{3+} or molecular oxygen (O_2). These are effective because of the very large gyromagnetic ratio of the electron, which when unpaired can interact strongly with nuclear spins. Although we have not yet done a systematic study of the effects of the addition of paramagnetics of ^{23}Na relaxation, we consider this mechanism to be a minor contributor for several reasons. The first is that the abundance of iron in these samples is quite low. The second is the overall consistency of the data and agreement between results on different samples of the same material which is probably too good to be fortuitous.

The simplest starting point for understanding relaxation in liquids is the work of Bloembergen, Purcell, and Pound (BLOEMBERGEN *et al.*, 1948). In this theory, the duration of

the fluctuation in local field is characterized by the correlation time τ_c . Because of the highly structured nature and high viscosity of glassy and molten silicates, a range of correlation times could be present, and the BLOEMBERGEN *et al.* theory may not be strictly applicable. However, it remains a useful starting point. In particular, a relationship holds at the point where relaxation is most efficient which allows the estimation of the correlation time (in reality some kind of average). If ω_0 is given by 2π times the Larmor frequency ν_0 , then at the T_1 minimum, $\tau_c \approx 1/\omega_0$.

As shown by LIU *et al.* (1987), the best approximation to the ^{23}Na relaxation data involves the quadrupolar coupling among the ^{23}Na nuclei. Using these results, the T_1 minimum for $\text{NaAlSi}_3\text{O}_8$ was estimated to be 610°C . The minimum is thus below T_g for the $\text{NaAlSi}_3\text{O}_8$ but above T_g for the less viscous alkali silicates (Fig. 7). This difference lies primarily in the effect of viscosity on T_g , not on the mobility of sodium.

The details of the temperature dependence of T_1 can potentially provide considerable information about the types of atomic motion involved. A relatively low apparent activation energy near room temperature in NaKSi_2O_5 glass (Fig. 3) is typical for spin-lattice relaxation in both silicate and borate glasses (HENDRICKSON and BRAY, 1974; JAIN *et al.*, 1985; BALZER *et al.*, 1984; GÖBEL *et al.*, 1979). In these studies, apparent activation energies between room temperature and T_g are only about one third of the values for tracer diffusion or electrical conductivity. This effect has been attributed to a wide distribution of correlation times for sodium motion in the glass (GÖBEL *et al.*, 1979), but JAIN *et al.* (1985) and BALZER *et al.* (1984) pointed out that the magnetic field dependence of T_1 was not appropriate for this model. They suggested that motion with a low activation energy, involving only local "rattling" of the cation in its relatively loose oxygen coordination shell, is responsible for spin relaxation in this temperature range. Higher activation barriers must be surmounted for through-going diffusion to occur.

Our results for silicate glasses and liquids probably illustrate the transition from the dominance of one type of motion to the other in the spin-lattice relaxation. Both types of motion take place at all temperatures. At low T the high-energy "jumps" from one interstitial site to another are too low in frequency to contribute greatly to relaxation. In the liquid, in contrast, the frequency of such local motion may be too high to be effective in relaxation, and the increased frequency of diffusive motions dominates.

The high activation energies of diffusion in the glass when compared to E_a for spin-lattice relaxation (JAIN *et al.*, 1985), and the increase in the latter energy with rising temperature, are thus both attributable to interactions between ions in processes involving long-range motion. These effects may be important examples of "coupling theory", which has been used to quantify a variety of transport processes in glasses (*e.g.* NGAI and JAIN, 1986).

Again, the high temperature apparent activation energies for ^{23}Na spin-lattice relaxation in all of the liquids studied here are close to measured values for tracer diffusion or electrical conductivity, unlike the situation in glasses at relatively low temperature. Typical values for sodium silicate melts and glasses are in the range from about 55–75 kJ/mol, and are not strongly dependent on composition or viscosity (*e.g.*

JAMBON, 1983; TERAJ and HAYAMI, 1975; BRAEDT and FRISCHAT, 1984; GUPTA and KING, 1967).

Our results do not show an increase in E_a with SiO_2 content, but do show a decrease in T_1 itself from $\text{Na}_2\text{Si}_2\text{O}_5$ to $\text{Na}_2\text{Si}_4\text{O}_9$ melt and from NaKSi_2O_5 to NaKSi_4O_9 melts (Fig. 4). Because these data are above the T_1 minimum, this effect must be caused by slight decreases in the frequency of sodium motion with the addition of SiO_2 . Decreases in the diffusivity of Na of the right magnitude (0.5–1.0 log units) were in fact observed in both glasses and liquids by TERAJ and HAYAMI (1975) and GUPTA and KING (1967).

Much larger increases in the apparent E_a , and comparable decreases in T_1 for ^{23}Na , are caused by replacing half of the Na in the melts with another alkali cation. These effects are examples of the well-studied "mixed alkali effect", and are apparently caused by some kind of interactions among unlike interstitial cations (*e.g.* JAIN *et al.*, 1983, 1985; DAY, 1976; TERAJ, 1971; DIETZEL, 1983). The effects seen for spin-lattice relaxation are again quite comparable to those for tracer diffusion (*e.g.* FLEMING and DAY, 1972). E_a increases in a similar way when either Li or K is substituted for Na, confirming that this is a true "mixed alkali", and not a cation-size effect.

The inflections in the T_1 curves for ^{23}Na seen for $\text{NaAlSi}_3\text{O}_8$ (LIU *et al.*, 1987) and $\text{Na}_2\text{Si}_2\text{O}_5$ at or near T_g both suggest increases in the mean correlation time on transition from glass to liquid. For $\text{NaAlSi}_3\text{O}_8$, T_1 decreases by 30–50% at T_g because T_g is above the T_1 minimum. For $\text{Na}_2\text{Si}_2\text{O}_5$, T_1 increases by about 30% near T_g because T_g is below the T_1 minimum. The most obvious mechanism that could cause this effect is the correlated motion of some sodiums with the typically much more slowly moving oxygen or silicon atoms (see below). Larger inflections at T_g might be expected for cations which interact more strongly with oxygen than does Na^+ .

Relaxation: ^{29}Si

^{29}Si relaxation in silicates at room temperature can be very slow, with T_1 's as long as hours. Relaxation mechanisms are poorly known, but both paramagnetic impurities and mobile protonated species probably are significant (GLADDEN *et al.*, 1986; SHERIFF and HARTMAN, 1985; WATANABE *et al.*, 1983; BARRON *et al.*, 1983). Coupling to alkali cations was proposed by SCHNEIDER *et al.* (1987), who also suggested a role for CSA interactions in glasses with few paramagnetic impurities or quadrupolar interactions available. In general, ^{29}Si relaxation is dominated by impurities at these temperatures because of the immobility of silicons in typical silicate crystal structures, and the weak magnetic couplings among its major element constituents.

In silicate melts, however, paramagnetic impurities probably play a minor role in ^{29}Si relaxation in the samples studied. Iron contents in these samples are not well known, but were probably below the 40–70 ppm levels determined in isotopically unenriched samples. Reproducibility among different samples and between the "shuttling" and static sample techniques was excellent, suggesting that variable, accidental contaminants were unimportant. Perhaps most significantly, it is clear that a different relaxation mechanism dominates in the liquid and glass. Extrapolations from the liquid data

to near room temperature predict T_1 values that are too high by many orders of magnitude: the estimated value at 130°C for $K_2Si_4O_9$, for example, is about 30,000 years, in contrast to the observation of 126 s. However, definite proof that paramagnetics are unimportant awaits further experiments which include systematic doping with impurities and measurements at different external magnetic field strengths.

Several other possible mechanisms were discussed for ^{29}Si relaxation in melts by LIU *et al.* (1987). We conclude there that Si-Si dipolar coupling probably plays only a minor role. The effects of Na-Si interactions are probably also small because the high mobility of the sodium cations tends to average out the dipolar couplings. The observation that $K_2Si_4O_9$ and $Na_2Si_4O_9$ liquids, and $Na_2Si_2O_5$ and $NaKSi_2O_5$ liquids (Figs. 6–8), have roughly similar ^{29}Si T_1 's is significant here: the strength of dipole-dipole couplings scales as the square of the gyromagnetic ratios (γ 's) of the nuclei involved, and the ratio of the squares of γ for ^{23}Na and ^{39}K is about 32:1. We concluded for $NaAlSi_3O_8$ melt (LIU *et al.*, 1987) that the most likely mechanism for ^{29}Si spin-lattice relaxation involves fluctuations in the orientation and magnitude of the chemical shielding at an Si site (and therefore of the resonant frequency) as silicons move with respect to their neighboring oxygens and sodiums. The total range of the CSA in a glass or liquid such as $Na_2Si_2O_5$ (Fig. 2) is about 150 ppm. The calculations presented by LIU *et al.* (1987) indicate that fluctuations with this range could result in T_1 values at the minima of about 3 s, which is 5–10 times longer than those observed in this and other samples. In this model, the relaxation rate scales as the square of the CSA, so a range that is 2–3 times greater than that observed in static spectra would be required to reproduce the data.

The range of "available" chemical shifts is actually quite likely to be much wider in melts than in glasses or crystals, although the time for which nuclei experience these shifts may be short. The line-narrowing and chemical exchange observed in ^{29}Si spectra of melts *require* the rapid breaking and re-forming of Si-O bonds. During such "events", Si-O bond distances may temporarily increase beyond their normal values, and local oxygen coordination may temporarily increase as transition states between structures form. Extreme chemical shifts are likely to be present in such sites. A temporary Si-O bond length increase of only 10 pm (about 6%) could also change the local, static chemical shift by about 100 ppm (WEIDEN and RAGER, 1985).

In order for such "transition states" to play a significant role in relaxation, their lifetimes must be on the order of the inverse of the Larmor frequency. Fast, vibrational-like transients will not be sufficient. It is not clear what the lifetimes and abundances of such states are in real melts. However, structural defects consisting of distorted and high-coordinated silicon transition states are commonly observed in molecular dynamics simulations of silicate melts, and have been given a major role in the energetic and transport properties (*e.g.* BRAUER, 1985; ANGELL *et al.*, 1983). On the basis of energy calculations, they have been suggested as the key step in viscous flow (HOCHHELLA and BROWN, 1984).

Si sites with extreme chemical shifts have not been seen in the NMR spectra of glasses (SCHNEIDER *et al.*, 1987). They may be difficult to observe because of their low abundance

or because they have a wide range of chemical shifts. If the latter is the case, however, they may (in future work) be observable indirectly as a decrease in the intensity of the NMR spectrum in the "normal" part of the spectrum. In liquids, the population of silicons in transition sites probably increases with temperature, but their lifetimes may be too short to observe.

On the other hand, "defect" bands of controversial origin are commonly observed in the Raman spectra of silica, germania, and silicate glasses (*e.g.* GALEENER, 1980; MIKKELSEN and GALEENER, 1980; SHARMA *et al.*, 1984). These increase in intensity with rising temperature. Three-membered rings are thought by many to cause one of these bands in SiO_2 glass (GALEENER *et al.*, 1983). An intriguing relationship is suggested: because of the very close oxygen-oxygen distances required to form a 3-ring, the coordination sphere of one or more of the silicons in the ring could be considered to include an extra oxygen if symmetry is not maintained. These "defects" could conceivably be the postulated transition sites.

Correlation times for the motion involved in ^{29}Si spin-lattice relaxation can be estimated as was done for ^{23}Na in the previous section. Here we simply take τ_c at the T_1 minimum for $Na_2Si_2O_5$ as $1/\omega_0 = 4.5 \times 10^{-9}$ s, and assume that at lower temperatures, τ_c is roughly proportional to T_1 . At 550°C, τ_c is therefore on the order of 2.8×10^{-8} s. This corresponds to a motional frequency in the MHz range. As shown in Fig. 2, the spectrum of the melt near this temperature still retains its full static linewidth, indicating that chemical exchange and reorientation take place with a frequency significantly less than the linewidth of about 5 kHz.

This disparity in the frequency of the motion responsible for relaxation, and that responsible for line narrowing, is not surprising. Although the two types of motion may be closely related, every "event" that leads to a site distortion and causes relaxation need not result in a long-lived rearrangement of the local structure which is necessary for motional averaging and line narrowing. The latter probably requires the cooperative motion of several oxygen atoms and possibly several silicate tetrahedra, the former may result from a single partial displacement of an oxygen or sodium and should occur much more frequently.

The difference in "style" between the motion causing ^{29}Si relaxation, and that causing chemical exchange, is also illustrated by the apparent activation energies for the former (Table 2). These are in general much lower than those observed for viscous flow. For example, the apparent E_a for viscosity at 800°C for $NaAlSi_3O_8$ liquid is about 500 kJ/mol, while that for $Na_2Si_2O_5$ is about 220 kJ/mol (RICHER, 1984). Estimates made above for the E_a of the exchange reaction itself are closer to those for viscous flow, but further studies of the ^{29}Si NMR lineshapes in melts are needed to determine the details of the temperature effects on rates of local structural change.

Despite these differences, the motion responsible for ^{29}Si spin-lattice relaxation must have close ties to the mechanism of viscous flow. This should be true regardless of the exact relaxation mechanism. The motion is much slower and more hindered than that of sodium: the T_1 minima for ^{29}Si occur at temperatures 200–300 degrees higher than those for ^{23}Na for all liquids studied here. The viscosity of the melt has a

strong effect on the size of the ^{29}Si T_1 as well: as shown in Fig. 9, the relaxation rate at 1000 K is two orders of magnitude slower in $\text{NaAlSi}_3\text{O}_8$ liquid (extrapolated slightly down in temperature from data above T_g) than in the least viscous liquid studied, NaKS_2O_5 . Although data are incomplete, it is also obvious that viscous liquids such as $\text{NaAlSi}_3\text{O}_8$ and the tetrasilicates have ^{29}Si T_1 minima at least several hundred degrees higher than the disilicate melts. These kinds of correlations are not present for the ^{23}Na relaxation data. The finding that the temperature effect on ^{29}Si T_1 changes at or near the bulk glass transition temperature also shows the link between the macroscopic and the microscopic. The data for $\text{NaAlSi}_3\text{O}_8$ liquid are most conclusive, but a similar transition is implied by the great disparities in relaxation times observed near room temperature for alkali silicate glasses and those predicted by the data for the liquids.

The macroscopic glass transition is generally considered to be the temperature at which structural relaxation becomes slower than the laboratory time scale (*i.e.* seconds to minutes or hours) and the system falls out of equilibrium with respect to local "diffusive" structural change. On heating, T_g is the point where significant local configurational change can begin. The slowness of this type of change just above the transition to the liquid is probably reflected in the persistence of the full static NMR lineshapes for 100–200°C above T_g . Apparently, however, when this slow configurational change begins, it also allows a small amount of more local, much higher frequency motion to begin as well. This latter motion rapidly lowers T_1 for ^{29}Si as temperature is raised further.

This interpretation of the meaning of nuclear relaxation data on poorly understood, structurally complex liquids is admittedly speculative, but should serve as a framework for further study. It would be particularly important to repeat some of these measurements at different field strength, and therefore a different resonant frequency. Because different coupling mechanisms may have different dependencies on frequency, this could enable more definitive choices between relaxation mechanisms to be made.

Implications for the properties of magmas

The major part of this paper has, necessarily, been devoted to the relationship between NMR results and the atomic-scale dynamics in melts. Although this is a new field not only for geochemists but for spectroscopists, we can already see several general implications for the way in which the prediction of the properties of magmas should be approached. In particular, understanding of the nature of the transition from glass to liquid is a key step in understanding the properties of liquids themselves.

Diffusion in magmas is one of the most important processes that controls crystal growth and dissolution (*e.g.* DOWTY, 1980). It may also be important in bulk differentiation, when transport across boundary layers is involved. A great many measurements have been made recently to quantify diffusion rates in melts, and to allow extrapolation to nature of the processes of both tracer and chemical diffusion (*e.g.* HOFMANN, 1980). However, even for the simplest cases of alkali cations in binary silicate compositions, the mechanism of diffusion is not completely understood.

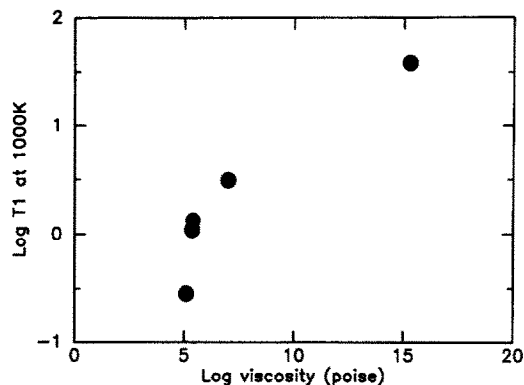


FIG. 9. ^{29}Si T_1 data at 1000 K vs. viscosity. T_1 for $\text{NaAlSi}_3\text{O}_8$ was derived from slight extrapolation from data for liquid from LIU *et al.* (1987).

The ^{23}Na NMR results at relatively low temperatures reveal the energy needed for local motion of cations in restricted, local, sites. At higher temperature, the technique samples the more energetic jumps from one site to another, and confirms that this motion is the same one responsible for bulk diffusion. The energetics of both types of motion play a role in both transport and thermodynamic processes. As for other measurements that relate to alkali diffusivity, however, there are no fundamental changes in the motion sampled by NMR at the bulk glass transition. This motion thus cannot be the direct cause of the transition.

However, NMR does show that there is some link (if rather weak) between alkali motion and the structural rearrangements that begin at T_g ; relaxation times are perturbed slightly. This implies that models of diffusion which ignore the coupling between alkali motion and Si and O motion can only be first approximations.

The interactions among the interstitial cations themselves have a more important effect on diffusion energetics. The large E_a values (relative to those for strictly local motion), and the size of the "mixed alkali effect" imply that any proposed mechanism for diffusion must include these interactions. It is probable that most motions of interstitial cations from one site to another require the displacement of another cation. This conclusion based on energies is supported by results of LIU *et al.* (1987), who showed that Na^+ cations are spaced closely enough to interact magnetically, as well as electrostatically. Models involving isolated jumps from one pre-existing "hole" to another are thus not likely to be realistic.

Diffusion of the more strongly bond tetrahedral cations (and of oxygen itself) is even less well understood, although there should be a continuum of behavior as field strength increases from, for example, Na to Mg to Al to Si. For Si, the NMR relaxation times are probably controlled by local motions only at all temperatures studied. These in turn may provide important clues as to mechanisms by which local bond-breaking and rearrangement take place.

A key question is the relative importance of the breaking and re-forming of Si-O bonds and weaker M-O bonds during viscous flow. The latter must occur much more frequently, so the question becomes whether the former is important at

all. This of course must be the case in tectosilicate melts such as SiO_2 and $\text{NaAlSi}_3\text{O}_8$, but is this a good generalization to less viscous systems?

The compositions described here and by LIU *et al.* (1987) all have between 0 and 1 non-bridging oxygens per average tetrahedral cation (NBO/T). They are thus related to natural magmas, in which NBO/T ranges from close to 0 high silica rhyolites to about 1 for mafic basalts. Up to NBO/T of about 1, flow could occur without breaking T-O bonds, but would require the alignment into planes of large anionic structures. At higher NBO/T, "cross links" would have to be broken. The NMR results show that at liquidus temperatures, local structural units are very short-lived, and Si-O bond breaking is rapid. It is difficult to see how this could not be important in flow: the activation energy estimated for this exchange process is similar to values for bulk viscosity. It is possible, of course, that anionic structures can be more persistent in systems with higher NBO/T values, and flow involving discrete silicate "molecules" could dominate.

Recently, viscous flow and the entropy and heat capacity of structured liquids have been shown to be fundamentally linked (RICHTER, 1984; RICHTER *et al.*, 1986; STEBBINS *et al.*, 1984). When the temperature of a glass is raised through its transition to a liquid, equilibrium with respect to local structural rearrangement is re-obtained, and the structure begins to change with further temperature increase. The rate at which this change occurs controls much of the thermodynamics, as well as the viscosity. The nature of this structural rearrangement is almost unknown for silicates.

NMR again provides some of the first clues. Studies of glasses with different fictive temperatures has recently quantified changes in Q species proportions with temperature, but has also suggested that this does not make a major contribution to the bulk energetics (BRANDRISS and STEBBINS, 1987). The results on the liquids, however, are among the first data that document the presumption that motion of the anionic structure is actually what is responsible for the glass transition in the first place. We see a change in relaxation mechanism at T_g , and we find that the estimated species exchange rate falls to the laboratory timescale at T_g . Finally, we may see indirect evidence for the existence of short-lived defects which perhaps are the transition states by which flow occurs as well as a major "sink" for the extra heat capacity which distinguishes a liquid from a glass.

CONCLUSIONS

NMR spectroscopy on silicate glasses and melts can provide important and possibly unique types of information about diffusive motion of both network forming and network modifying cations.

^{29}Si NMR lineshapes show that up to one or two hundred degrees above the glass transition, silicon species with clearly distinguishable numbers of bridging oxygens can be identified. At higher temperatures, rearrangement of the local structure is more rapid than the frequency widths of the spectra, indicating that Si-O bonds break and reform rapidly. A rough estimate of the activation energy of this process is similar to, but somewhat less than, apparent activation energies for viscous flow. Silicate "molecules" do not persist for times longer

than microseconds at typical liquidus temperatures. Phase changes such as melting and crystallization can be observed as they take place, both in spectra and in relaxation time data.

Nuclear spin relaxation time measurements are more difficult to interpret, but show clear relationships to bulk thermodynamic and transport properties of melts. ^{23}Na relaxation times have activation energies similar to those for tracer diffusion in melts, but not in glasses where local motion dominates. The effects of silica content and mixed alkalis on E_a are also similar to those seen for diffusion, strongly implying that through-going diffusive motion is indeed responsible for ^{23}Na spin-lattice relaxation. Anomalies in these data near T_g can be explained by some kind of cooperative motion between sodium cations and the framework structure.

^{29}Si relaxation times indicate that the responsible motion is considerably slower than for sodium, with correlation times one or two orders of magnitude longer. A fundamental change in the relaxation mechanism takes place at or near the glass transition. ^{29}Si spin-lattice relaxation may be caused by the formation of short-lived distorted sites that are intermediates in the structural rearrangements that cause line narrowing. These sites may have high coordination numbers and temporarily extreme chemical shifts, but the NMR data does not yet closely constrain their structure or abundance. The mechanism causes this relaxation is clearly more closely tied to viscous flow and the structural mobility of the melt than is the motion of interstitial cations.

These ideas about the relationship of local structural motion to NMR spectra and relaxation can be summarized in a rather speculative two-dimensional sketch shown in Fig. 10. These concepts are in part based on models presented in studies of molecular dynamics simulations (*e.g.* BRAWER, 1985; ANGELL *et al.*, 1983) and energy calculations (*e.g.* HOCELLA and BROWN, 1984). Several "styles" of motion are depicted. In the liquid, ^{23}Na relaxation is dominated by interactions among sodiums and diffusive "jumping" from one interstitial site to another. Perhaps initiated by such a "jump", a nonbridging oxygen (here, attached to a Q^1 silicon) moves close to another SiO_4 tetrahedron, forming a distorted five-coordinated site (shown with four oxygens in the figure). Most of the time, this unstable arrangement reverts to the initial structure, but the distortion causes a large enough fluctuation in the ^{29}Si chemical shift to stimulate relaxation. Occasionally, however, the high-coordinated defect breaks up in the other sense, and a relatively long-lived change in local structure occurs. When this happens, local viscous flow has occurred, and the local structural change of $Q^1 + Q^3 = 2Q^2$ has taken place.

The existence of the types of defects mentioned above has not been substantiated by direct observation, and this model serves primarily as a guide to the types of questions to be asked of these systems. As a final speculation, we offer the possibility that short-lived, distorted or odd-coordinated transition state play a major role in the thermodynamics, as well as the transport phenomena, in melts. Creation of increasing numbers of such defects with increasing temperature must require an increase in the entropy and enthalpy over and above that due to the vibrational heat capacity and thermal expansion. If the population of such states is sufficient,

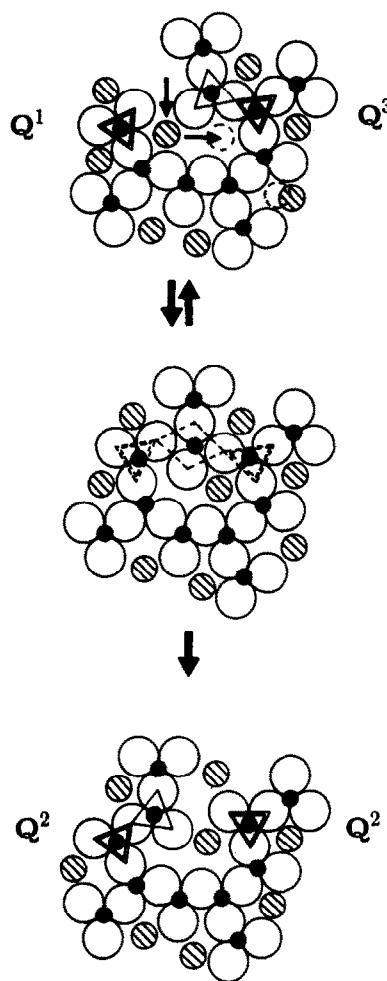


FIG. 10. Two-dimensional cartoon of hypothesized relationships of diffusive motion to NMR data for silicate melts and glasses. Open circles: oxygen atoms. Filled circles: silicon atoms. Crossed hatched circles: sodium atoms. Triangles with double lines represent Q species as labeled. See text for explanation.

they could be responsible for the fundamental energetic distinctions between glass and liquid.

Note added in proof: Further measurements of ^{29}Si spin-lattice relaxation times in $\text{K}_2\text{Si}_4\text{O}_9$ glass and liquid confirm the abrupt change in mechanism at T_g seen for $\text{NaAlSi}_3\text{O}_8$, and suggested here by Fig. 8.

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