

Table 1 Acid dissolution of Nakhla

BM 1913,26 (43.17 mg)			BM 1911,370 (152.61 mg)		
Extraction time (h)	p.p.m. C	$\delta^{13}\text{C}$ (% PDB)	Extraction time (h)	p.p.m. C	$\delta^{13}\text{C}$ (% PDB)
18	21	+8	18	15	+6
24*	8	+12	48*	7	+46†
			24*	4	+49†
42	29	+9	90	26	+24

*Supplementary to original extraction time.

†Mass scans of these samples indicated the presence of organic species, which may have interfered with the isotope ratio measurements of the CO_2 . Hence, the determined $\delta^{13}\text{C}$ values may show an apparent enrichment in ^{13}C above the true value.

recognized during H_3PO_4 treatment of a sample of a second stone from the Nakhla meteorite shower (BM1911, 360) suggests that the species is not calcite but more probably dolomite or an iron-containing carbonate. Neither of the other nakhlites show any evidence of a ^{13}C -rich component decomposing at between 300 and 500 °C, although this may be because of the release of relatively large amounts of organic material from these contaminated samples. During the stepped combustions of one sample of Shergotty and the Chassigny specimen, $\delta^{13}\text{C}$ values did increase to -12% and -18% respectively¹⁰, but more work would be necessary to demonstrate the presence of carbonate.

A petrological investigation to confirm the presence of carbonate in Nakhla is required, but assuming that its existence is verified, the question which must be answered concerns its origin—terrestrial or martian? Terrestrial carbonates with $\delta^{13}\text{C}$ values higher than +10% are rare¹². Terrestrially produced carbonates are a common feature of Antarctic weathering; all appear to have normal $\delta^{13}\text{C}$ values but such features are less conspicuous in non-Antarctic meteorites⁵. For martian carbonate to survive in Nakhla, the shock events involved in its ejection from the planet surface would presumably need to be such that temperatures did not rise to greater than 500 °C.

We have speculated that carbon dioxide in the martian atmosphere is enriched in ^{13}C relative to carbon of presumed igneous origin as present in the SNC meteorites. It may be coincidence, but recognition of enrichments of the same order for the carbonate may be circumstantial evidence for an origin by weathering in the martian environment, particularly as dolomite would be an expected product of gas-solid reaction of martian pyroxenes¹³. We note, too, that Nakhla contains iddingsite, an aqueous alteration product of olivine, which is believed to be preterrestrial in origin¹⁴. Unfortunately, the pyrolysis gas chromatograph-mass spectrometer experiment¹⁵ carried out by Viking Landers, which might have been able to detect the decomposition products of carbonate and provide some isotope information was performed in such a way as to preclude such identification. It does not seem possible that the carbon dioxide trapped in EETA79001 is the relict of carbonate decomposed during shock heating, as such a route would be extremely unlikely to preserve the observed relative abundance to other atmospheric gases.

The existence of a trapped component of carbon dioxide in the correct abundance relative to noble gases and nitrogen and of an appropriate isotope composition to be of martian atmospheric origin strengthens the case that EETA79001 originated from our sister planet. The relationship between the martian atmospheric composition and data from EETA79001, other shergottites, and the nakhlites (inset in Fig. 1b) demonstrates that all these meteorites are related and presumably also derived from Mars. Likewise, demonstration of the existence of a carbonate mineral with a martian atmospheric composition would be direct evidence of the origin of Nakhla and its consorts from the planet.

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A high-temperature high-resolution NMR study of ^{23}Na , ^{27}Al and ^{29}Si in molten silicates

J. F. Stebbins*†, J. B. Murdoch*†, E. Schneider‡§, I. S. E. Carmichael* & A. Pines‡§

* Earth Sciences Division, Lawrence Berkeley Laboratory, ‡ Department of Chemistry, University of California and § Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, USA

Molecular and atomic motions over longer distances, and with much lower frequencies than interatomic vibrations, have a major role in the energetic and dynamic properties of highly structured liquids such as molten aluminosilicates. Rearrangement with increasing temperature of the polymerized anionic network (composed of linked SiO_4^{4-} and AlO_4^{5-} tetrahedra) controls viscosity and influences thermal expansion and configurational heat capacity^{1,2}. Diffusive motion of network modifying cations (such as Na^+) through the structure allows electrical conductivity and probably also affects entropy. To study such motion directly and to compare liquid and glass structure, we have developed a novel high-temperature high-resolution NMR apparatus. We report here the first data on ^{23}Na , ^{27}Al , and ^{29}Si in liquids in the system $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$ at temperatures to about 1,300 °C. Observed changes in NMR resonant frequencies (chemical shifts) give information on the effects of composition on local structure. Line shapes and widths, and relaxation time measurements, reveal details of the dynamics and of the transition from liquid to glass.

The apparatus developed for high-temperature liquid-state NMR will be described in detail elsewhere. A sample in a 1-cm diameter boron nitride capsule is rapidly shuttled 15 cm between a furnace and a room-temperature radio frequency NMR coil, spending 10 s in the former and ~0.5 s in the latter during each cycle, during which data from a single free-induction decay (FID) is recorded. Both the probe and the furnace are mounted in a 4.2 T superconducting magnet. Sample temperatures could not be measured during actual NMR experiments, but calibration runs indicate that reported values are accurate to within about 30 °C.

Samples were prepared from reagent grade oxides and carbonates. For all ^{29}Si NMR, 95% enriched $^{29}\text{SiO}_2$ was used. Analyses of unenriched samples after the NMR runs showed that by the end of runs of 6-12 h, Na_2O contents were reduced by 5-20% of the amount present. B_2O_3 contents became as high as 4 wt%.

Measurements were made with a home-built Fourier-transform NMR spectrometer, with 90° pulse lengths of 39 μs for ^{23}Na and ^{27}Al and 45 μs for ^{29}Si . Data from 40 FIDs were averaged per spectrum for ^{23}Na , and up to 400 for ^{27}Al and ^{29}Si .

†Present addresses: Department of Geology, Stanford University, Stanford, California 94305, USA (J.F.S.); Technicare Corporation, PO Box 5130, Cleveland, Ohio 44101, USA (J.B.M.).

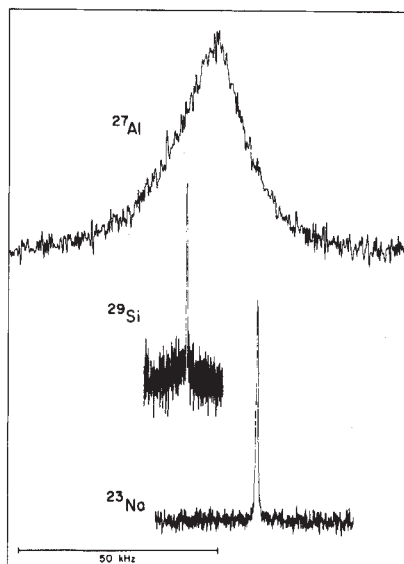


Fig. 1 Typical NMR spectra for molten silicates. Data are for $\text{NaAlSi}_2\text{O}_6$ at about $1,300^\circ\text{C}$. Relative location of the spectra is arbitrary, but all have the same frequency scale.

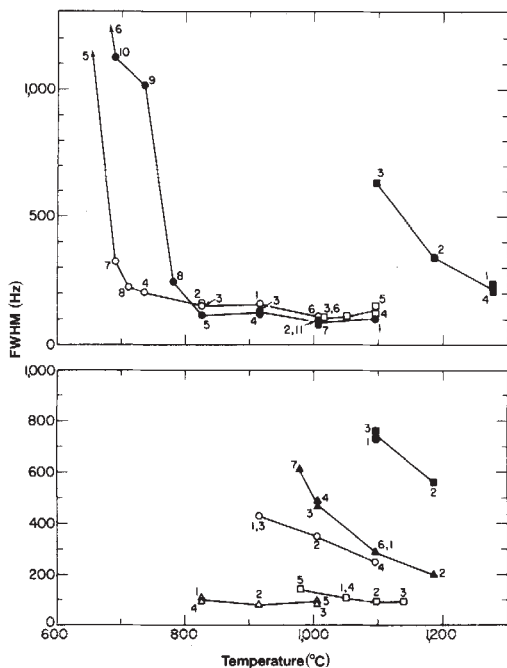


Fig. 2 Linewidths for ^{29}Si (top) and ^{23}Na (bottom) liquid spectra, as a function of temperature. Symbols indicate nominal composition: ●, $\text{Na}_2\text{Si}_4\text{O}_9$; ○, $\text{Na}_2\text{Si}_2\text{O}_5$; ■, $\text{NaAlSi}_2\text{O}_6$; □, Na_2SiO_3 ; ▲, 'R15' (see text); △, NaCl. Numbers show the order in which measurements were made and indicate reproducibility.

Relaxation time measurements were made by standard pulse techniques, using compensated π pulse sequences³. Chemical shifts are referenced to saturated aqueous NaCl (about 6.5 M), $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, and TMS, all at room temperature.

Typical spectra are shown in Fig. 1, linewidths in Fig. 2 and chemical shifts in Fig. 3. The chemical shift measurements were made at the beginning of runs when compositions were presumed to be close to nominal.

As shown in Fig. 3, ^{29}Si chemical shifts (δ) change systematically with composition, as expected from data on glassy and crystalline solids⁴⁻⁷. Liquids that are more polymerized (higher mean Q^n number, where n is the number of other AlO_4 or SiO_4 units bound to a given SiO_4 tetrahedron) have more negative δ

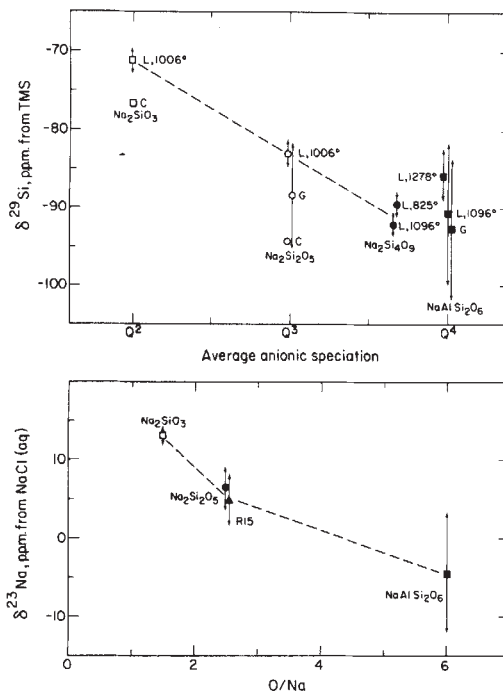


Fig. 3 Chemical shifts in silicates. Symbols as in Fig. 2, with L indicating liquid (at temperatures shown), C, crystalline solid, and G, glass (the latter two at room temperature). Arrows indicate linewidth, not errors. Q^n is the average speciation of the liquid, indicating n other (Si, Al) O_4 tetrahedral structural groups attached to a given group.

values, showing that ^{29}Si nuclei in tetrahedral sites with greater numbers of surrounding SiO_4 tetrahedra are more chemically shielded. Substitution of Al for some of the Si reduces this shielding, as shown for $\text{NaAlSi}_2\text{O}_6$ liquid and glass. Silicon chemical shifts in the liquids are systematically less negative (less shielding) than in the corresponding glasses and crystals.

Sodium chemical shifts in liquid silicates seem to have a simpler variation with composition. In all four silicate samples studied, $\delta(^{23}\text{Na})$ is well correlated with the ratio of the number of oxygen to sodium atoms, independent of polymerization state or the Al/Si ratio. Crystalline $\text{NaAlSi}_3\text{O}_8$ (-7.7 p.p.m.)⁸ falls very close to the trend for the liquids, when referenced to the same standard⁹. Our value of 6.8 p.p.m. for $\delta(^{23}\text{Na})$ in molten NaCl agrees well with data for the solid (6.7 p.p.m.)⁸.

Spectra for ^{27}Al in samples $\text{NaAlSi}_2\text{O}_6$ and R15 (Na_2O : 35, Al_2O_3 : 15, SiO_2 : 50 mol%) each contain only a single very broad feature (about 20 kHz wide), centred at $\sim 29 \pm 20$ p.p.m. The breadth of the peaks makes it difficult to draw conclusions about Al coordination in the liquids¹⁰.

Observed linewidths (FWHM) at the highest temperatures studied for both ^{23}Na and ^{29}Si are quite narrow (100–200 Hz, or 2–5 p.p.m.), with symmetrical lorentzian line shapes. Direct measurements of T_2 for ^{23}Na and ^{29}Si indicate that, for linewidths greater than about 200 Hz, the 'intrinsic' contribution from relaxation of spins dominates, and that, therefore, $\text{FWHM} \approx 1/(\pi T_2)$, where T_2 is the spin-spin relaxation time¹¹. Smaller linewidths are dominated by instrumental effects. A few T_1 (spin-lattice) relaxation times for ^{23}Na show that $T_1 \approx T_2$ in $\text{Na}_2\text{O}/\text{SiO}_2$ liquids, but that $T_1 > T_2$ in the more viscous aluminosilicate liquids. Narrow high-temperature linewidths for ^{29}Si indicate that silicate species move rapidly enough to average out the effects of chemical shielding anisotropy (at least 3.5 kHz)⁶, while ^{23}Na motion in the binary liquids is probably at least as fast as the NMR resonant frequency of the nucleus (or, the Larmor frequency, 47.3 MHz). For both nuclei, the FWHM increases (T_2 decreases) dramatically with decreasing temperature, as the motion that induces relaxation is 'frozen out'. For ^{29}Si , the lowest temperature at which data were

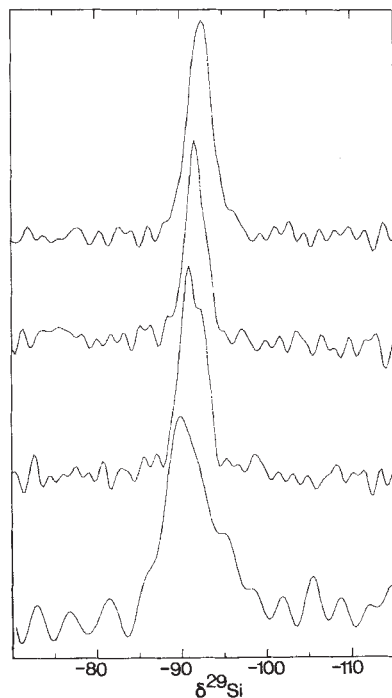


Fig. 4 ^{29}Si spectra for $\text{Na}_2\text{Si}_4\text{O}_9$ liquid at 1,096 °C (top), 1,006 °C, 915 °C, and 779 °C (bottom), normalized to the same peak height. $\delta(^{29}\text{Si})$ is in p.p.m. Note the development of a shoulder on the central peak as the temperature is lowered.

collected was that at which the spectrum became extremely broad and 'solid-like'. In $\text{Na}_2\text{Si}_2\text{O}_5$, this was probably the result of crystallization. The $\text{NaAlSi}_2\text{O}_6$ sample, however, was recovered as a glass, indicating that the 'glass transition' with respect to molecular motion faster than 3.5 kHz was observed. Not surprisingly, more-polymerized more-viscous liquids have wider NMR lines (shorter T_2 values) at a given temperature (Fig. 2).

The very broad bands observed for ^{27}Al indicate that even though these samples were liquid, quadrupole coupling was strong enough to cause the nuclei to relax very rapidly ($T_2 \approx 20 \mu\text{s}$).

For Na and Si in a series of silicate liquids at high temperatures, molecular motion has a significant component at or above the kHz frequency range. At lower temperatures, the loss of this motion can be observed. The nature of this motion remains a key problem. In a discussion of liquid heat capacities, Stebbins *et al.*² emphasized the possibilities of rotational and translational motion of anionic molecular groups, but pointed out that mechanisms involving the breaking of strong Si-O or Al-O bonds must become important in more polymerized liquids.

Raman and magic-angle spinning NMR spectra of glasses^{7,12} show that a range of silicate (Q^n) species, with a different range of chemical shifts for each value of n , make up the anionic structure of these materials. Observation of only one narrow ^{29}Si NMR line in the liquid suggests that these species chemically-exchange rapidly with respect to the typical separation in resonant frequency between the species (10–15 p.p.m. or 300–500 Hz). Only a time-averaged spectrum is observed. In aqueous silicate solutions, similar effects are seen, until temperature is lowered enough and exchange rates become slow enough to allow peak splitting to occur¹³. The development of shoulders on ^{29}Si peaks in some silicate melt spectra may suggest a similar slowing of reaction rates (Fig. 4). Structural rearrangement that includes the exchange of Q^n species involves breaking and reforming of Si-O bonds and apparently occurs even in a rather depolymerized liquid such as Na_2SiO_3 . The relative contribution of this type of motion to the overall energetics of the liquid remains unknown.

The preliminary results presented here thus show that NMR spectroscopy on silicate liquids can help to identify what types

of molecular motion occur, can begin to quantify the rates of such motions, and demonstrates the effects of composition. These and further data should prove useful in the understanding of both the thermodynamic properties of melts and the closely related processes of flow and diffusion.

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Alteration of basalt glasses: implications for modelling the long-term stability of nuclear waste glasses

W. Lutze*, G. Malow*, R. C. Ewing†, M. J. Jercinovic† & K. Keil†

* Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Glienicke Strasse 100, 1000 Berlin 39, FRG

† Department of Geology and Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131, USA

The long-term stability of nuclear waste form borosilicate glasses must be predicted from extrapolations of short-term laboratory data and then verified, which is only possible by comparing the glasses with their natural analogues of geological age. Here, we suggest that basalt glasses are useful analogues for predicting the long-term behaviour of nuclear waste form borosilicate glasses. Previous workers^{1–11} have considered the possibility of using natural glasses as analogues, but our study is a direct comparison of the experimentally studied corrosion products of basalt glasses, their natural long-term corrosion products and those of borosilicate glasses. Observations on the alteration processes for natural basalt glasses are combined with the experimental data on the alteration of basalt glasses and borosilicate glasses and are used to generate radioactivity release curves for nuclear waste form borosilicate glasses using the QTERM computer code^{12–15}. Our data on natural glasses place significant constraints on the anticipated fraction of activity released; major differences between our two release curves do not occur until after 1,000 years.

Hydrothermal leaching experiments were completed on three glasses: two basalt glasses (KL 9 and 11) from Kilauea, Hawaii ($\text{SiO}_2 = 50 \text{ wt}\%$, 24 kyr old) and a simulated borosilicate nuclear waste glass, C-31-3EC-SPF-Na ($\text{SiO}_2 = 35 \text{ wt}\%$). We report here the results of experiments at 200 °C in saturated synthetic NaCl solution for 30 days. The basalt glasses were melted before leaching and their chemical composition determined by electron probe analysis (EPA) (Table 1). The compositions of the surface layers and solutions were determined by optical emission spectroscopy (ICP) and the surfaces examined by scanning electron microscopy. The compositions of a basalt glass and its palagonite surface layer (deep-sea dredge sample, USNM 113715, from