

Oxygen self-diffusion in $\text{Na}_2\text{Si}_4\text{O}_9$ liquid up to 10 GPa and estimation of high-pressure melt viscosities

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ABSTRACT

The self-diffusivity of O has been measured in $\text{Na}_2\text{Si}_4\text{O}_9$ liquid at 1625 and 1825 °C and pressures in the range 2.5–10 GPa using a 1200-ton multianvil apparatus. Diffusion couples were prepared from glass starting materials with one-half of the sample enriched in ^{18}O and the other half containing the natural abundance (~ 0.2 wt%). Following exchange of O across this diffusion couple at high temperature and pressure, ^{18}O concentration profiles were analyzed using an ion microprobe. O diffusivities were obtained by fitting the equation for diffusion between two semi-infinite bodies to the concentration profiles. At 1825 °C, O diffusivity increases continuously from 1×10^{-10} m²/s at 2.5 GPa to 4×10^{-10} m²/s at 10 GPa, yielding an activation volume of -3.3 ± 0.4 cm³/mol. This trend is consistent with the results of molecular dynamics calculations and may be related to an increase in fivefold-coordinated Si with increasing pressure. The viscosity of $\text{Na}_2\text{Si}_4\text{O}_9$ liquid at high pressure is estimated from the O diffusivity data using the Eyring relationship, which has been shown to be applicable to polymerized silicate liquids up to at least 2 GPa. Estimated viscosities at 1825 °C and high pressure are consistent with an extrapolation of viscosity data obtained at 1 bar by other techniques and suggest a viscosity decrease of ~ 0.8 log units from 1 bar to 10 GPa. The results also suggest that the activation energies for viscous flow and O diffusivity decrease significantly in the pressure range 1 bar to 4 GPa. Provided the validity of the Eyring relationship can be established, these results demonstrate that melt viscosities can be estimated from O-diffusion experiments up to at least 10 GPa. In contrast, measurements using falling-sphere viscometry are extremely difficult at such conditions because of low viscosities and small sample size.

INTRODUCTION

Knowledge of the transport properties of silicate liquids at high pressure is crucial for understanding magmatic processes within the Earth. Experimental and theoretical studies of silicate liquids have demonstrated that pressure can have a major effect on both diffusivity and viscosity (Watson, 1979; Angell et al., 1982; Shimizu and Kushiro, 1984; Scarfe et al., 1987). Such pressure effects will be important in controlling processes such as melt segregation and chemical equilibration of migrating melts in the Earth's mantle. A knowledge of transport properties at high pressure is also necessary for understanding the dynamics, evolution, and crystallization of a magma ocean that may have formed during the early history of the Earth (e.g., Wetherill, 1990).

It has been demonstrated that significant changes in the structure of silicate liquids occur with increasing pressure (Stebbins and McMillan, 1989; Xue et al., 1989, 1991).

For this reason, the effects of pressure on transport properties are more difficult to predict from simple kinetic theory for silicate liquids than for crystalline phases, and in general direct measurements are required. Although viscosity and O diffusivity have been studied experimentally for a range of compositions, the maximum pressures reached in these studies have been low (≤ 2.5 GPa) compared with pressures in the Earth's mantle. The development of the multianvil high-pressure apparatus now makes it possible to greatly extend the pressure range of such studies.

We present results of an experimental study of O self-diffusion in $\text{Na}_2\text{Si}_4\text{O}_9$ liquid in the pressure range 2.5–10 GPa. This composition was chosen primarily because changes in the structure of $\text{Na}_2\text{Si}_4\text{O}_9$ glasses quenched at pressures up to 12 GPa are well documented (Xue et al., 1991). Therefore, for this composition, a direct correlation between O diffusivity and structural changes should be possible. Our results are also used to show that the

Eyring relationship may be useful for estimating melt viscosities at conditions where falling-sphere viscosity measurements (Kushiro, 1976) are not feasible.

EXPERIMENTAL PROCEDURE

Starting material

Experiments were performed using diffusion couples in which one-half of the $\text{Na}_2\text{Si}_4\text{O}_6$ melt sample was enriched in ^{18}O and the other half contained the natural abundance (0.2 wt%). The ^{18}O -enriched $\text{Na}_2\text{Si}_4\text{O}_6$ glass starting material was prepared following the method of Shimizu and Kushiro (1984). SiO_2 enriched in ^{18}O was produced by reacting Si metal with H_2^{18}O (99% enriched) in sealed Au capsules. Synthesis conditions were 800–850 °C at 1.5–2.8 kbar for 24–72 h. The products of these syntheses were examined in grain mounts for completeness of reaction, and no unreacted Si metal was found. An equimolar mixture of ^{18}O -enriched SiO_2 and isotopically normal SiO_2 (Aldrich, 99.995% SiO_2) was mixed with an appropriate amount of reagent grade Na_2CO_3 , ground under acetone for 30 min, and then melted for 30 min at 1200 °C in a covered Pt crucible. The sample was quenched by removing the crucible from the furnace and placing it in a small Pt dish containing H_2O (<1 cm deep). No H_2O got into the crucible, which was 2.5 cm high, during quenching. This procedure resulted in a clear crystal-free glass that was crushed, ground under alcohol, and stored in a desiccator. The unenriched sample was made from an appropriate mixture of reagent grade Na_2CO_3 and SiO_2 using the same procedure as for the ^{18}O -enriched $\text{Na}_2\text{Si}_4\text{O}_6$ glass. The compositions of the two glasses were checked using an electron microprobe and were statistically indistinguishable in Na_2O and SiO_2 contents. The grain size of the powdered samples was mostly $\leq 5 \mu\text{m}$, but a small proportion of grains had diameters up to $\sim 40 \mu\text{m}$.

High-pressure experiments

High-pressure experiments were performed using a 1200-ton uniaxial split-sphere multianvil apparatus. The sample assembly consisted of an octahedron of MgO (5 wt% Cr_2O_3) with an edge length of 18 mm containing a cylindrical graphite heater with a variable wall thickness to reduce temperature gradients (for details see Canil, 1991). Toshiba F-grade WC anvils with edge lengths of 11 mm and preformed pyrophyllite gaskets (cross section $5 \times 3 \text{ mm}^2$) were used for pressure generation (for details see Remsburg et al., 1988). Pressure was calibrated at room temperature using transitions in Bi and at 1000 and 1450 °C by reversing the equilibria quartz = coesite (Bohlen, 1984), coesite = stishovite (Yagi and Akimoto, 1976), and olivine = spinel for Fe_2SiO_4 composition (Yagi et al., 1987) (Fig. 1). There was no detectable difference between the calibrations at 1000 and 1450 °C (Fig. 1), and quoted pressures are considered accurate to within $\pm 5\%$. The hydraulic oil pressure was computer controlled and varied by less than ± 1 bar from the set point. Temper-

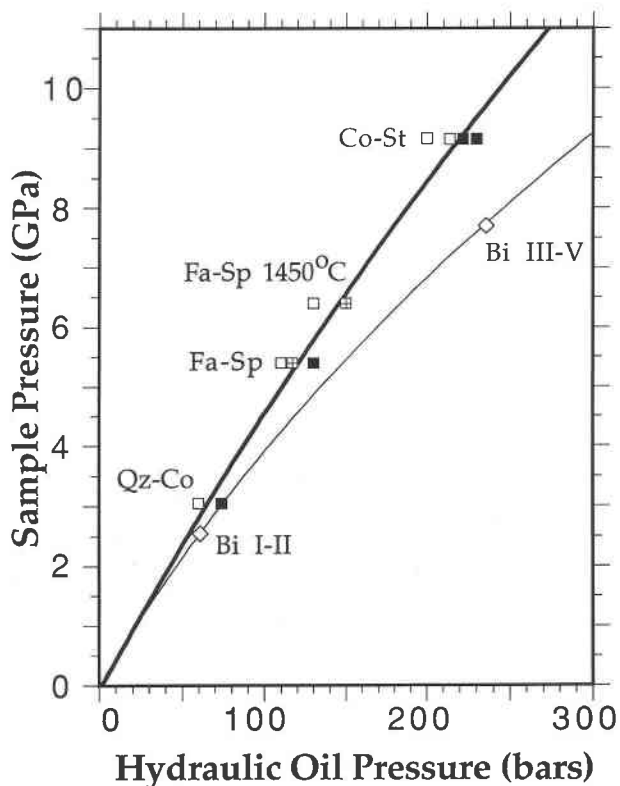


Fig. 1. Multi-anvil calibration curves for an MgO octahedron with 18-mm edge length and WC anvils with a truncation edge length of 11 mm. Details of the sample assembly are given by Canil (1991, his Fig. 1). A hydraulic oil pressure of 100 bars corresponds to a uniaxial load of 171 tons. The room temperature calibration (thin line) is based on Bi transitions. The high-temperature curve (thick line) is based on reversals of quartz = coesite (Qz-Co), coesite = stishovite (Co-St), and Fe_2SiO_4 fayalite = spinel (Fa-Sp) equilibria at 1000 °C. A Fe_2SiO_4 calibration at 1450 °C is consistent with the 1000 °C curve. Filled squares: high-pressure phase stable; open squares: low-pressure phase stable; crossed squares: both phases present.

atures were measured using W3%Re-W25%Re thermocouples and were controlled to ± 5 °C. No correction was made for the effect of pressure on thermocouple emf; this effect is probably small for W3%Re-W25%Re thermocouples relative to Pt-Rh thermocouples (Kato and Kumazawa, 1985; Tsuzaki and Takahashi, 1992). The heater geometry (Fig. 1 of Canil, 1991) results in a maximum temperature variation along the 3-mm capsule length of ~ 20 °C at 1500 °C (Kanzaki, 1987; Yasuda et al., 1990). At the higher temperatures of this study this variation will be larger, but it should still be < 40 °C. Recorded thermocouple temperatures have been corrected by +20 °C to account for the temperature gradient, and the temperature uncertainty is estimated to be ± 30 °C.

Diffusion couples were prepared by loading the powdered glass samples into Pt capsules 2 mm in diameter and 3–3.5 mm long after sealing. One end of the capsule was sealed by welding. The ^{18}O -enriched sample was first packed into the capsule using a tightly fitting metal rod

TABLE 1. Summary of experimental conditions and calculated O diffusivities

Expt.	T (°C)	P (GPa)	t (min)	t _{800-T} (min)	Diffusivity (m ² /s)
NS4-6	1630	4.0	1.25	2.25	1.00(6) × 10 ⁻¹⁰
NS4-9	1620	4.0	5.0	1.25	1.15(4) × 10 ⁻¹⁰
NS4-16	1825	2.5	3.0	1.25	1.00(10) × 10 ⁻¹⁰
NS4-12	1825	4.0	3.0	2.0	1.56(19) × 10 ⁻¹⁰
NS4-11	1825	6.0	3.0	1.5	1.97(7) × 10 ⁻¹⁰
NS4-13	1825	8.0	3.0	0.9	3.80(30) × 10 ⁻¹⁰
NS4-14a	1830	10.0	0.8	0.9	3.90(30) × 10 ^{-10*}
NS4-14b	1830	10.0	0.8	0.9	4.20(60) × 10 ^{-10*}

Note: t_{800-T} = duration of heating period from 800 °C to the temperature of the experiment. Estimated standard deviations (1σ) for O diffusivities are listed in parentheses.

* Results derived from parallel traverses on the same sample.

with a polished end surface to compress the powder and to produce a flat, smooth surface. The isotopically normal glass was then loaded on top of the ¹⁸O-enriched sample to form the diffusion couple. Two Pt disks (each 25 μm thick) were placed in the capsule on top of the sample, and the end of the capsule was folded over and was then sealed by cold-welding by hammering in a cylindrical die. Conventional welding of the second end of the capsule was unsatisfactory because it resulted in a geometrical irregularity in the diffusion couple after pressurization.

A number of precautions were taken to minimize the H₂O content of the melts during the diffusion experiments, particularly as Na₂Si₄O₉ glass is hygroscopic. All the ceramic components of the sample assembly were fired at 1000 °C for >1 h and were then stored at 230 °C in a vacuum oven until ready for use. The capsule containing the diffusion couple was heated at 230 °C under vacuum for 30 min immediately prior to sealing by cold welding. Finally the complete sample assembly was heated at 230 °C under vacuum for 20 min immediately before starting the experiment. The use of a vacuum oven at 230 °C has been found to be very effective in producing anhydrous experimental products in other studies (Rubie et al., 1993). The standard procedure in multianvil experiments, of firing the sample assembly at 1000 °C prior to the experiment (e.g., Xue et al., 1991), obviously cannot be used in diffusion studies.

To inhibit convection in the liquid diffusion couple during the experiments, the sample capsule was always arranged vertically with the slightly denser ¹⁸O-enriched glass situated in the lower part of the capsule. Experiments were carried out by first compressing the sample at room temperature to the desired pressure. The temperature was then increased to 800 °C over a period of 4–5 min and from 800 °C to the desired temperature (1625 or 1825 °C) in ~1.5 (±0.6) min (see Table 1). This final stage of heating was rapid to avoid significant diffusion of O prior to reaching the final temperature. After being held at the desired temperature for a period of time (0.8–5 min), the samples were isobarically quenched by switching off the electrical power. During quenching the

temperature dropped to <400 °C in 1–2 s. The experimental conditions (2.5–10 GPa and 1625–1825 °C) are listed in Table 1 and were selected on the basis of the results of a recent study of the equilibrium melting relationships of Na₂Si₄O₉ (Kanzaki et al., in preparation), which shows that the liquidus varies from 1500–1600 °C at 6 GPa to ~1800 °C at 12 GPa.

Analytical procedure

Following the high-pressure diffusion experiments, the cylindrical samples were cut parallel to the long axis (i.e., perpendicular to the original interface in the diffusion couple), and the exposed surface was polished. The samples were analyzed for distribution of ¹⁶O and ¹⁸O isotopes at the University of Edinburgh using a Cameca IMS-4f ion microprobe (Slodzian, 1980) equipped with a Charles Evans and Associates control system. The primary beam was 1–3 nA of ¹³³Cs⁺ accelerated through 10 kV in the primary column onto the polished section of the diffusion couple. The secondary beam of sputtered negative ions was accelerated through 4.5 kV into the mass analyzer. In order to avoid a charge build-up on the sample, the polished surface had to be Au coated using a vacuum sputter unit and the sample surface illuminated during analysis with a normal-incident low-energy electron flood gun.

At each analysis point the primary beam was defocused to give a spot of 30–60 μm diameter. The secondary beam current was limited by inserting a small field aperture in the secondary beam so that only the central area of the spot (8 μm in diameter) was sampled. At the start of each measurement, the sample was sputtered for ~2 min while the instrument was calibrated, followed typically by 100 s of count accumulation, giving ~10⁵–10⁶ total counts for O. Excluding the initial counts from each analysis point avoided sampling of the cold-worked surface, with its possible contaminants, such as ¹⁶O derived from absorbed H₂O (see below).

Concentration profiles for ¹⁶O and ¹⁸O were obtained over the full length of the sample capsule along traverses perpendicular to the original interface of the diffusion profile. In addition, ²⁸Si was also usually measured to monitor instrument stability. In some cases, two parallel traverses were made on the same sample (e.g., Table 1, NS4-14).

The errors on ion microprobe measurements made on conducting materials can be predicted from counting statistics. However, we have found that errors associated with measurements made on insulating materials are considerably larger than those expected from counting statistics. Possible factors contributing to these errors include the use of electron flood gun charge compensation, electron gun alignment stability, and irregularities of the polished sample surface. It must be emphasized that without a knowledge of the errors, and particularly the relation of the error to concentration, the diffusion coefficients and associated standard deviations derived from such measurements must be judged carefully.

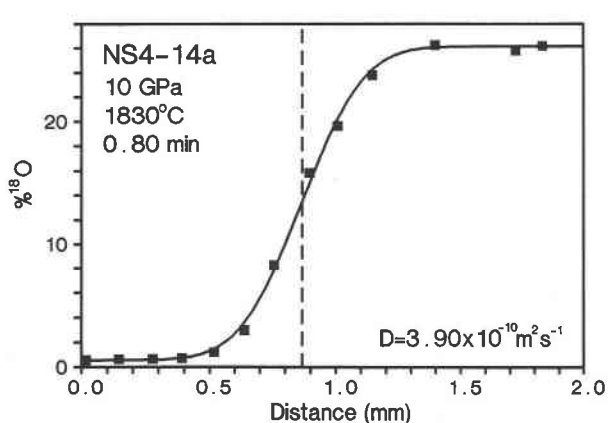
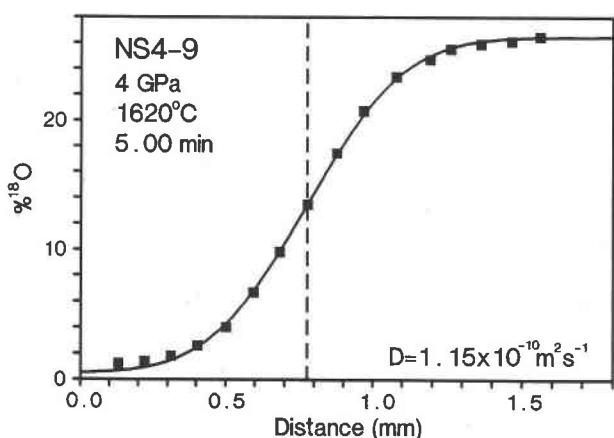
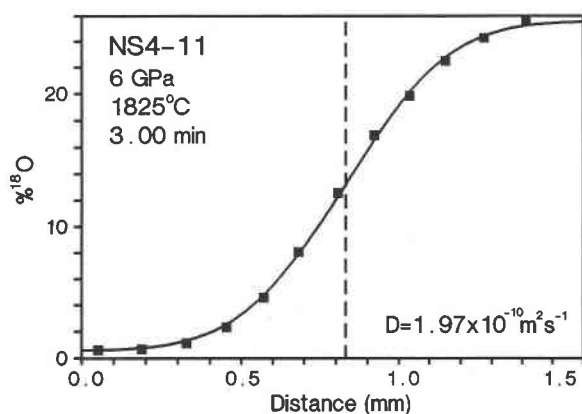
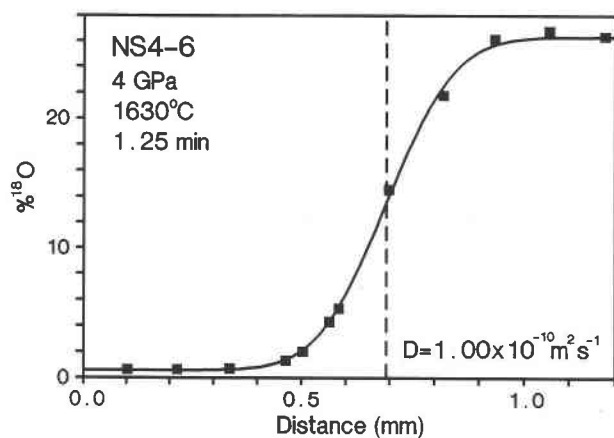


Fig. 2. The ¹⁸O concentration profiles across Na₂Si₄O₉ diffusion couples after 1.25 (NS4-6) and 5.0 (NS4-9) min at 4 GPa and 1625 ± 30 °C. The data points are ion microprobe analyses, and the curve is a least-squares fit of Eq. 1 to the data in which the O diffusivity (*D*) and the interface position (dashed line) were refined.

Fig. 3. The ¹⁸O concentration profiles across Na₂Si₄O₉ diffusion couples after 3.0 min at 6 GPa and 1825 °C (NS4-11) and 0.8 min at 10 GPa and 1830 °C (NS4-14a). The data points are ion microprobe analyses, and the line is a least-squares fit of Eq. 1 to the data in which the O diffusivity (*D*) and the interface position (dashed line) were refined.

After ion microprobe analysis, the position of each analyzed point was measured to an accuracy of ±5 μm using a microscope with a vernier X-Y stage. The position of each analyzed point was identified in reflected light by the absence of the Au coating.

RESULTS

In experiments performed at 2.5 and 4 GPa, the Na₂Si₄O₉ melts quenched to a glass free of quench crystals. In samples quenched at higher pressures (6–10 GPa), the glasses contain quench crystals 10–20 μm across and up to 400 μm long, which are probably stishovite. The presence of these crystals appears to have no effect on the estimates of O diffusivity, as discussed below.

Representative ¹⁸O concentration profiles [wt% ¹⁸O/(¹⁸O + ¹⁶O)] from the high-pressure diffusion experiments are shown in Figures 2 and 3. Estimates of O self-diffusivity were obtained from nonlinear least-squares fits of the equation for self-diffusion between two semi-infinite bodies (Crank, 1975)

$$C(x, t) = \frac{C_1 + C_2}{2} + \frac{C_1 - C_2}{2} \operatorname{erf} \left[\frac{(x - x_0)}{2\sqrt{Dt}} \right] \quad (1)$$

to the measured concentration profiles. In Equation 1, *C* = ¹⁸O/(¹⁸O + ¹⁶O), *C*₁ and *C*₂ are the limiting ¹⁸O concentrations at *x* = ±∞, *x* is the position of the analysis, *x*₀ is the position of the original interface (both measured from an arbitrary origin), *D* is the diffusion coefficient, and *t* is the duration of the experiment. Because of the problems in determining the appropriate variances for the measurements, unit weights were used during the refinement. If the true standard deviations of measurement are constant, then replacing the unit weights by the appropriate statistical weights has no effect on the estimated diffusivities and their standard deviations. If, however, the true standard deviations of measurement are not constant but vary, for example, with concentration, then some effect on the diffusivities and their standard deviations is to be expected.

Three refinement models were examined when fitting

Equation 1 to the data by nonlinear least-squares regression. In all models D was refined, but in alternative models the interface position (x_0) and the limiting concentrations (C_1 and C_2) were also refined. The results reported in Table 1 are based on a model in which only D and x_0 were refined. Refinement of the limiting concentrations yielded results statistically indistinguishable from simply estimating the limiting compositions from the extreme values shown by the data.

The estimated diffusion coefficients and associated standard deviations are listed in Table 1. Representative results shown in Figures 2 and 3 document the good agreement between the calculated and measured concentration profiles. Although not all results are shown, in no case considered was the fit sufficiently poor as to suggest that an alternative model (in particular diffusion between noninfinite bodies) was warranted. Several data sets were used to refine models of diffusion between noninfinite bodies, but no significant improvement in fit was found.

Several factors indicate that the transport of O in the high-pressure experiments occurred by diffusion rather than by some other mechanism, such as convection. First, the fits of Equation 1 to the concentration profiles are in all cases good. Second, fits to different concentration profiles from the same sample yield diffusion coefficients that are identical within error (e.g., NS4-14, Table 1). Third, in two experiments at 1625 °C and 4 GPa, for 1.25 and 5.0 min, respectively, the estimated diffusion coefficients are almost identical within error and are therefore independent of time (NS4-6 and NS4-9, Table 1). Finally, the geometry of an interface in $\text{Na}_2\text{Si}_4\text{O}_9$ liquid at 9.5 GPa and 1825 °C (for 3 min) was observed directly in a quenched sample in which the interface had been marked with fine-grained Pt powder. There was no evidence to suggest that this interface was unstable when the sample was liquid.

Sources of error

In addition to the analytical errors discussed above, there are a number of additional sources of error that may affect the estimates of O diffusivity in these experiments. These include: (1) the presence of quench crystals in some samples, (2) temperature gradients across the sample, (3) the time required to heat the sample to the desired temperature, and (4) deviation of the angle between the interface and the analyzed concentration profile from 90°.

As stated above, samples quenched at pressures of 6 GPa and above contain quench crystals, which probably consist of stishovite. At the experimental conditions, fractionation of ^{18}O between the crystals and glass should be insignificant, and the presence of quench crystals should therefore have no effect on the analyzed $^{18}\text{O}/^{16}\text{O}$ ratios. The analytical results are consistent with this conclusion. Irregularities in the ^{18}O concentration profiles, which would result if the quench crystals were significantly enriched in either isotope, are not apparent in any profiles; the smoothness of the profiles is similar both for samples with quench crystals (Fig. 3) and for those without (Fig. 2). In contrast to these conclusions, however, ion micro-

probe imaging of the sample surface suggests that the quench crystals are significantly enriched in ^{18}O relative to the adjacent glass. An explanation for this result is that, because $\text{Na}_2\text{Si}_4\text{O}_9$ glass is hygroscopic, H_2O becomes absorbed onto the glass at the sample surface during and after sample preparation, thus diluting the ^{18}O content as measured by the imaging technique. A drift in the $^{18}\text{O}/^{16}\text{O}$ ratio during the initial period of sputtering is consistent with this hypothesis.

The presence of a significant temperature gradient along the axis of the sample would result in a diffusion coefficient that varies along the analyzed concentration profile. The goodness of fit of Equation 1 (in which D is constant) to the data suggests that any spatial variation of D due to temperature gradients is small. In addition, with the assumption that the temperature variation along the sample length is ~ 40 °C, on the basis of the small activation energy estimated below, the variation in diffusivity along the sample is expected to be within the quoted standard deviations (Table 1).

A further potential source of error in the estimated diffusion coefficients arises because the time taken to heat the sample was significant compared with the time spent at the nominal temperature of the experiment (Table 1). However, the time spent heating at high temperature is relatively small (e.g., 1400–1825 °C in ~ 20 s), so the amount of diffusion occurring during the heating period should be limited; this conclusion is supported by the result of a preliminary zero-time experiment. In addition, the two experiments performed at 1620–1630 °C and 4 GPa, for 1.25 and 5.0 min, respectively (NS4-6 and NS4-9), give almost identical best fit values for the diffusion coefficient (Table 1). The smaller D value comes from the 1.25-min experiment (which also took longer to achieve the desired conditions), whereas if the error caused by the heating time were significant, this experiment should have yielded the larger estimate of D . On the basis of the results of these two experiments, the error caused by the length of the heating period can be regarded as small. Although this error will lead to a slight overestimate of the diffusion coefficients, it is of negligible importance when comparing diffusivities obtained at different pressures. Ideally a more thorough time study should be performed to test further the effect of the heating period, but in practice that is difficult because the semi-infinite reservoir condition will not be fulfilled when diffusion times significantly exceed 5 min (cf. Fig. 2). Furthermore, if the activation energy is known accurately it should be possible to incorporate the effect of the heating time in the model used to refine the diffusion coefficients. We have not attempted to do this because the activation energy estimated below is based on very limited data and has a large uncertainty.

Finally, the determination of the diffusion coefficient requires the accurate determination of both the composition of a particular point in the sample and the normal distance from that point to the interface. If the polished surface of the sample is not perpendicular to the plane of the interface, or the interface itself is not planar, then

errors are introduced. In the case when the surface of the sample and the interface are not perpendicular, then the normal distance from the sample point to the interface is less than that measured in the plane of the sample. This introduces a systematic error, the effect of which is to increase the diffusion coefficients, i.e., the rate of diffusion appears to be higher than it really is. The actual angle between the interface and the analyzed concentration profile is difficult to estimate, but it is unlikely to deviate from 90° by more than 5–10°; the maximum effect on D , therefore, is ~4%.

H₂O content of quenched samples

Because the presence of dissolved H₂O in the silicate liquid could influence the transport mechanism by which O diffusion occurs, the products of the diffusion experiments were examined for H₂O content using Fourier-transform infrared spectroscopy (FTIR). The measurements were made on doubly polished cross sections through the sample capsules, with thicknesses of 40–250 μm. FTIR spectra were collected using a Nicolet model 800 FTIR spectrometer equipped with a Spectra-Tech IR microscope and a liquid N₂-cooled MCT detector. Spectra were recorded from 400–7500 cm⁻¹, with a resolution of 4 cm⁻¹, using a 100-μm aperture to limit the area from which the spectrum was taken. Between 100 and 500 scans were averaged for each spectrum, and the height above the background of the absorption band at ~3500 cm⁻¹ (which is proportional to the total H₂O content) was measured from a plot of the spectrum. Absorbances were converted to wt% H₂O using a glass density of 2300 g/L and the absorption coefficient for albite glass from Newman et al. (1986).

Examples of H₂O contents determined by FTIR are as follows: NS4-16 (2.5 GPa, 1825 °C), 0.092–0.118 wt%; NS4-12 (4.0 GPa, 1825 °C), ~0.16 wt%; and NS4-6 (4.0 GPa, 1630 °C), 0.12–0.15 wt%. In the experiments analyzed, the H₂O contents lie in the range 0.1–0.2 wt%. There is no obvious systematic variation of measured H₂O content with P , T , or t . Also, measurements of multiple spots in a single sample show no significant spatial variation (<±10%). It should be emphasized that, because H₂O adsorbed onto the sample surface could contribute to these measured values, the actual H₂O contents of the melts at high P and T could be considerably less than 0.2 wt%.

The possibility that the small amounts of H₂O dissolved in the Na₂Si₄O₉ melt have a significant effect on O diffusivity cannot be excluded. There is however no obvious correlation between measured H₂O contents and estimated O diffusivities. A comparison of estimated viscosities at 1 bar and high pressure also argues against a significant effect, as discussed below.

DISCUSSION

Effect of pressure on O self-diffusivity

The results shown in Figure 4 demonstrate that O self-diffusivity in Na₂Si₄O₉ liquid at 1825 °C increases by ~0.6

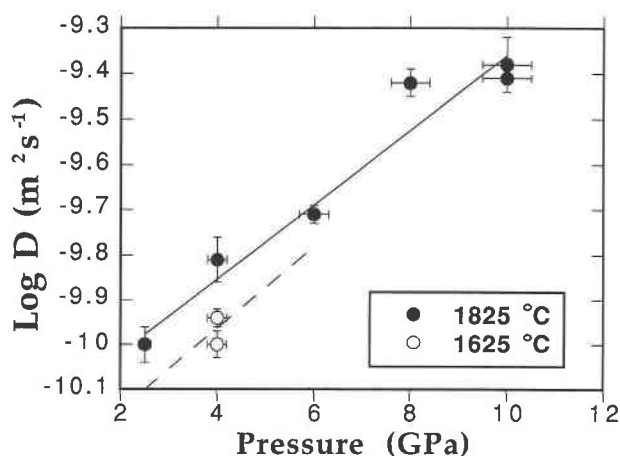


Fig. 4. O diffusivity (D) in Na₂Si₄O₉ liquid at 1825 ± 30 and 1625 ± 30 °C as a function of pressure. Fits of Eq. 2 to the data are shown for 1825 (solid line) and 1625 °C (broken line) with $V^* = -3.3$ cm³/mol and $Q = 55$ kJ/mol. These fits do not take into account possible changes in activation volume and activation energy with temperature and pressure, respectively, as discussed in the text. Deviations of the data at 1825 °C from the fitted line may indicate that the activation volume is pressure dependent (i.e., the trend is not linear) or could be the result of slight variations in H₂O content among different samples.

log units as pressure increases from 2.5 to 10 GPa. This trend is similar to that observed for jadeite liquid in the pressure range 0.5–2 GPa at 1400 °C (Shimizu and Kushiro, 1984). With the assumption that the pressure and temperature dependence of O self-diffusivity can be described by

$$D = D_0 \exp[-(Q + PV^*)/RT] \quad (2)$$

where D_0 is a constant, Q is the activation energy, V^* is the activation volume, P is pressure, T is temperature, and R is the gas constant, a linear least-squares regression of the data (Table 1) gives $D_0 = 1.5 (\pm 1.6) \times 10^{-9}$ m²/s, $V^* = -3.3 \pm 0.4$ cm³/mol (at 1825 °C), and $Q = 55 \pm 17$ kJ/mol (at 4 GPa). There is a high correlation between the values of D_0 and Q in this regression, so these parameters are not well constrained. In comparison, for O diffusion in jadeite liquid, Shimizu and Kushiro (1984) determined $V^* = -6.3 \pm 1.2$ cm³/mol at 1400 °C, and $Q = 255 \pm 8$ kJ/mol at 1.5 GPa. The difference between the values of V^* determined for O diffusion in Na₂Si₄O₉ and in jadeite liquids could be a result of the difference in composition, or it may be due to the activation volume increasing as a function of temperature (Watson, 1979; Shimizu and Kushiro, 1984). As discussed below, Equation 2 may not be an adequate description of the dependence of D on P and T , but a more complex relationship (e.g., Watson, 1979) is not justified by the present data set.

An increase in the diffusivity of O, Si, and Al with increasing pressure in polymerized silicate liquids has been predicted by Angell et al. (1982) on the basis of molecular dynamics calculations. The results of their calculations

for 6000 K suggest that diffusivities should increase to a maximum value at ~30–40 GPa and then subsequently decrease as the pressure is increased further. Angell et al. (1982) related the increase in the diffusivity of the network-forming species to an increase in fivefold-coordinated Si (⁵Si) with increasing pressure. They further argued that the diffusivity maximum corresponds to a prevalence of fivefold-coordinated Si.

Changes in the structure of Na₂Si₄O₉ liquid with pressure have been identified by Xue et al. (1991) in a study of quenched glasses. Concentrations of both ⁵Si and ⁶Si increase systematically with pressure up to at least 12 GPa, where the abundance of these species is estimated to be ~9 and ~6%, respectively. Thus, in agreement with Angell et al. (1982), Xue et al. (1991, their Fig. 14) also proposed that the dominant process of diffusion and viscous flow in network liquids involves the transient formation of ⁵Si as an intermediate structural state. According to this model, the negative activation volume obtained in this study is due to a local densification of the structure that accompanies this transient coordination change. Because the concentration, as well as the ease of formation, of ⁵Si increases at high pressure, diffusion of O and Si becomes faster and the viscosity becomes lower with increasing pressure, until the structural conversion is complete and the diffusivity maximum (viscosity minimum) is reached. The results of this experimental study are consistent with this model.

The diffusivity of nonnetwork-forming species in polymerized silicate liquids has been found to decrease with increasing pressure (Watson, 1979), and such a trend is also predicted from molecular dynamics calculations (Angell et al., 1982). Thus, with increasing pressure, the diffusivities of O and the network-forming species Si and Al are found or are predicted to increase, whereas the diffusivities of network-modifying species decrease. The increase in density and the associated increase in five- and sixfold-coordinated Si with increasing pressure may affect the mobility of network-modifying species by reducing the space available for such cations to migrate. This proposal is consistent with the observation that the activation energy for diffusion of network-modifying species increases with pressure (Watson, 1979).

The effect of temperature on O self-diffusivity at high pressure is discussed below.

Viscosity of Na₂Si₄O₉ liquid at high pressure

The viscosities of silicate liquids at high pressure have mostly been measured by falling-sphere viscometry (e.g., Kushiro, 1976; Scarfe et al., 1987). Because of various experimental limitations, this technique is unsuitable for determining very low viscosities (e.g., <1 Pa·s) (Kanzaki et al., 1987). Thus, the possibility of measuring viscosities by falling-sphere viscometry at very high pressures (e.g., >5 GPa), where very high temperatures are also required, is limited. One elegant solution to this problem was found by Kanzaki et al. (1987), who made in-situ measurements of the settling velocity of Pt spheres in

silicate melts at high pressure using synchrotron radiation to produce X-ray shadowgraphs. Although viscosities as low as 10⁻³ Pa·s at pressures up to 10 GPa are in principle measurable using this technique, problems with large temperature gradients and possible reaction between the silicate liquid and volatiles derived from the pressure medium have yet to be overcome (Kanzaki et al., 1987).

In the case of liquids in which the units involved in diffusion and viscous flow are the same, diffusivity and viscosity are inversely correlated (Cohen and Turnbull, 1959). Thus, an alternative approach for estimating the viscosities of silicate liquids at high pressure when O diffusivity data are available is to use the Eyring relationship

$$D = kT/\eta\lambda \quad (3)$$

where D is O diffusivity, k is the Boltzmann constant, T is absolute temperature, η is viscosity, and λ is the diffusive jump distance. The approximate validity of this relation for a polymerized liquid (jadeite) at pressures up to 2 GPa has been demonstrated by Shimizu and Kushiro (1984, their Fig. 2). It is also well known that melts with a highly polymerized structure show an isothermal decrease in viscosity with increasing pressure (e.g., Scarfe et al., 1987), which, on the basis of the Eyring relation, is consistent with the increases in O diffusivity observed in this study and by Shimizu and Kushiro (1984). It should be noted, however, that data for diopside, a more depolymerized liquid, are not well approximated by Equation 3 (Shimizu and Kushiro, 1984). Molecular dynamics simulations of MgSiO₃ liquid also suggest that Equation 3 is not valid for depolymerized liquids at very high pressures (Wasserman et al., 1993). These observations suggest that the breaking of Si-O (or Al-O) bonds is a fundamental feature of both viscous flow and O diffusion in polymerized silicate liquids; this conclusion is also supported by the observation from NMR studies that the time scale for Si-O bond breaking is similar to the time scale for viscous flow (Liu et al., 1988; Dingwell and Webb, 1989). In contrast, the diffusivity of network-modifying species is inconsistent with the Eyring relationship (Hofmann, 1980), thus indicating that the mechanisms of diffusion of network modifiers are decoupled from the bond-breaking processes that accompany viscous flow, except at very low viscosities (Dingwell, 1990).

Viscosities of Na₂Si₄O₉ liquid at 1625 and 1825 °C at 1 bar have been estimated by extrapolating the data of Bansal and Doremus (1986) and Dingwell (unpublished data) (Fig. 5). We have estimated viscosities at 1625 and 1825 °C and pressures up to 10 GPa by substituting our data into Equation 3, taking λ equal to the diameter of an O anion (2.8 Å). The results, shown in Figure 6, suggest that the viscosity at 1825 °C decreases by ~0.8 log units as pressure increases from 1 bar to 10 GPa. The viscosity at 1 bar and 1825 °C, estimated from Figure 5, lies on the extrapolation of the high-pressure data, even though the experimental techniques on which the 1-bar and high-pressure estimates are based are completely different. The correspondence between the 1-bar viscosity

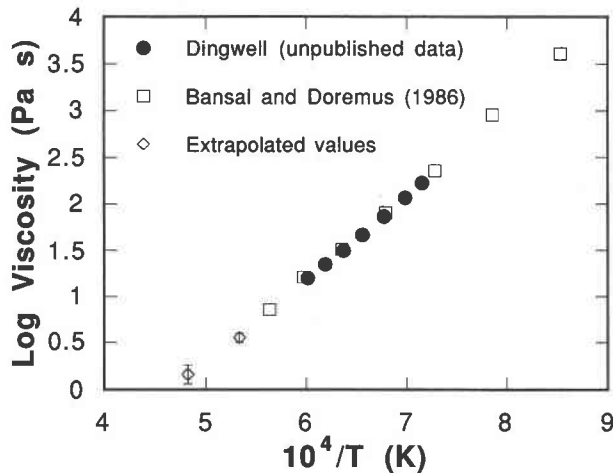


Fig. 5. Viscosity of Na₂Si₄O₉ liquid as a function of inverse temperature ($10^4/T$) at 1 bar. Viscosities at 1825 and 1625 °C are estimated by extrapolation of the lower temperature data.

estimate and the extrapolation of the high-pressure estimates at 1825 °C supports the applicability of Equation 3 and also suggests that O diffusivities are not significantly affected by traces of H₂O in the melts.

The values of O self-diffusivity determined at 1625 and 1825 °C (Table 1), yield a value for the activation energy (Q) of 55 ± 17 kJ/mol at 4 GPa, which is very low compared with $Q = 174$ – 180 kJ/mol obtained from the 1-bar viscosity data in the temperature range 900–1500 °C (Fig. 6). The estimated activation energy at 4 GPa is also very low compared with $Q = 255$ kJ/mol, determined for O self-diffusion in jadeite liquid at 1.5 GPa (Shimizu and Kushiro, 1984). This result, although based on limited data at only two temperatures (1825 and 1625 °C), suggests that the activation energy decreases very significantly with increasing pressure; such a trend has also been observed by Kushiro (1980) for the viscous flow of jadeite liquid, for which the activation energy decreases from 335 kJ/mol at 0.8 GPa to 188 kJ/mol at 2.1 GPa. These results indicate that the fragility of jadeite and Na₂Si₄O₉ liquids increases with pressure (Angell, 1988). It must be emphasized, however, that our activation energy estimate is based on a very limited data set obtained over a narrow temperature range, and therefore it may not be reliable. There are significant technical difficulties involved in obtaining data over a significantly larger temperature range in order to obtain a more reliable estimate of Q . Because of the position of the liquidus (Kanzaki et al., in preparation), temperatures of the present study can only be extended in an upward direction. However, at temperatures significantly higher than those of the present study (e.g., >2000 °C) the choice of capsule material becomes problematic (see Stebbins and Sykes, 1990), temperature measurement becomes less reliable, times required to achieve experimental conditions become longer, and the possibility of convective mass transport increases.

There are indications from the results of this study that

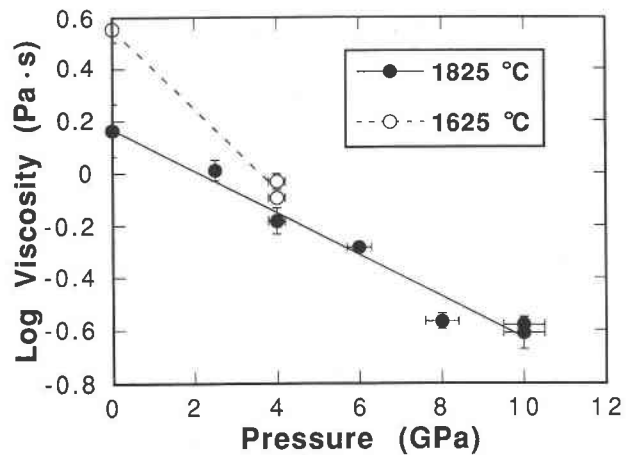


Fig. 6. Viscosity of Na₂Si₄O₉ liquid as a function of pressure at 1825 and 1625 °C. The 1-bar estimates are the extrapolated values shown in Fig. 5. The high-pressure viscosities are estimated from the O-diffusivity results using the Eyring relation (Eq. 3).

the activation volume for O diffusion and viscous flow increases with temperature (as discussed above, see also Fig. 6) and that the activation energy decreases with increasing pressure. If that is the case, a more complex version of Equation 2 is clearly required to describe the dependence of the rates of these processes on pressure and temperature (e.g., Watson, 1979).

SUMMARY AND CONCLUSIONS

The results of this study demonstrate that O diffusivity in Na₂Si₄O₉ liquid at 1825 °C increases over the pressure range 2.5–10 GPa by ~ 0.6 log units. This trend is similar to that observed for O self-diffusion in jadeite liquid (Shimizu and Kushiro, 1984) and may be related to an increasing concentration of fivefold-coordinated Si in the liquid, as predicted previously. Assuming the validity of the Eyring relationship, the results also predict a decrease in viscosity of ~ 0.8 log units over the pressure range 1 bar to 10 GPa and a significant decrease in the activation energy for viscous flow and O diffusivity with increasing pressure.

The extension of the present study to the determination of faster O diffusivities may be possible by analyzing the resulting ¹⁸O concentration profiles in terms of a model of diffusion between two noninfinite bodies. For example, using a sample length of 1.5–2.0 mm and diffusion times of ~ 1 min it should be possible to estimate viscosities as low as 10^{-2} Pa·s, provided the validity of the Eyring relationship can be demonstrated and provided convective mass transport does not occur. In contrast, measuring such low viscosities by falling-sphere viscometry would be virtually impossible.

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