

The self-diffusion of silicon and oxygen in diopside ($\text{CaMgSi}_2\text{O}_6$) liquid up to 15 GPa

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Abstract

The self-diffusivities of silicon and oxygen in diopside ($\text{CaMgSi}_2\text{O}_6$) liquid have been measured at pressures and temperatures up to 15 GPa and 2300°C, using a 1200-tonne multi-anvil apparatus. Diffusion couples were prepared using finely ground, diopside glass, half of which was enriched in tracer isotopes ^{18}O (5%) and ^{30}Si (12%). Results indicate that silicon and oxygen self-diffusivities are coincident (within an accuracy range of 10% RSD, 1σ) up to 13 GPa and show an initial decrease with pressure up to 11 GPa (oxygen self-diffusivities are $9.8 \times 10^{-10} \text{ m}^2/\text{s}$ at 3 GPa and $3.9 \times 10^{-10} \text{ m}^2/\text{s}$ at 11 GPa) after which there is an increase with pressure up to 15 GPa ($9.1 \times 10^{-10} \text{ m}^2/\text{s}$) at 2000°C. The activation energy of self-diffusion of both silicon and oxygen was calculated to be 267 kJ mol^{-1} , with no observable pressure effect up to 3 GPa. Self-diffusivity is inversely proportional to viscosity, the relationship between these properties being well approximated by the Eyring equation using the diameter of an oxygen anion as the translation distance. The calculated viscosities are in good agreement with previous direct viscosity measurements at lower pressure although the previously found high positive activation volumes were not reproduced. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

An understanding of the transport properties of silicate melts is essential for modelling geological processes such as magma ascent, convection and crystal fractionation. As a consequence, much work has been carried out on the determination of properties such as viscosity and diffusion in silicate melts. However, because of the applications to volcanology

and crustal melting, as well as experimental difficulties, most studies have been carried out at relatively low pressures and on highly polymerised silicate compositions (Webb and Dingwell, 1990; Bottinga and Weill, 1972). Studies at higher pressures would enable modelling of melt-related processes in the mantle, such as magma ocean convection and crystal settling, large- and small-scale melt migration and generation. There is a paucity of data that covers high-pressure properties, forcing assumptions to be made. For example, Solomatov and Stevenson (1993) assumed that completely depolymerised melts would

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have a pressure dependence similar to that of molecular liquids, where viscosity increases in proportion to decreasing distance between molecules. Tonks and Melosh (1990, 1993) assumed no pressure effect on the viscosity of silicate melts of mantle composition when modelling convection in a hypothetical, global magma ocean up to 1000 km in depth. Other models of magma ocean evolution do not even consider viscosity (Ohtani, 1985).

The paucity of data on the pressure dependence of silicate melt rheology above 3 GPa is, in part, due to the difficulty in measuring properties such as viscosity in high pressure apparatus. The large capsule size used with the piston cylinder apparatus has allowed falling-sphere viscometry to be used extensively over the past 20 years at pressures up to 3 GPa (Kushiro, 1976; Scarfe et al., 1987). For pressures higher than 3–4 GPa, a multianvil apparatus is required with small sample capsule volumes (ca. 11 mm³ in our experiments up to 10 GPa). Falling-sphere viscometry in multianvil apparatus becomes very imprecise, therefore, without a method of in-situ sphere detection, such as electrodedetection (LeBlanc and Secco, 1996) or the use of synchrotron radiation to image X-ray absorbency contrasts between the sphere and melt (Kanzaki et al., 1987).

An alternative to measuring viscosity directly at high pressure is to measure the self-diffusivities of network forming ions and to use the Eyring relation to estimate viscosity:

$$D = \frac{k_B T}{\eta \lambda} \quad (1)$$

In Eq. (1): D = diffusion coefficient of Si or O, k_B = Boltzmann constant (1.38×10^{-23} J K⁻¹), T = temperature (K), λ = translation distance of the diffusing ion (taken to be 2.8 Å, the diameter of O²⁻ anion) and η = viscosity (Pa s).

This method has been utilised successfully in a number of studies at high pressure (up to 15 GPa) for highly polymerised silicate and aluminosilicate melts (Rubie et al., 1993; Poe et al., 1997). Measuring the self-diffusion coefficients of silicon and oxygen is a relatively straightforward procedure in which one half of the sample capsule is packed with glass powder enriched in tracer isotopes (e.g. ³⁰Si and

¹⁸O) and separated from the non-enriched half by a smooth, flat interface. Rapid heating is used (2500°C/min) in order to minimise diffusion before the desired temperature is reached. Profiles of silicon and oxygen isotopic concentrations within the samples are analysed using secondary ionisation mass spectrometry (SIMS).

A diopside composition was chosen for this study in order to understand the pressure dependence on the transport properties of more depolymerised melts. The non-bridging oxygen to tetrahedral cation ratio (NBO/T) of diopside is 2, which is within the range of peridotite compositions and therefore of relevance to mantle processes. Much previous work has been carried out to determine the rheology of this composition, both at atmospheric pressure and up to 2.5 GPa, giving a good comparison base for further work.

2. Experimental procedure and starting materials

2.1. Preparation of diopside glass

Diopside (CaMgSi₂O₆) composition glass was made in a *Deltac* furnace with starting materials MgO, CaCO₃, and SiO₂. A Pt stirring rod was used to homogenise the melt. The glass was crushed and ground to a fine powder and used as the non-enriched component of the diffusion couple. Diopside glass enriched in ³⁰Si and ¹⁸O was made in smaller batches (1 g), and fused at 1450°C under a reducing atmosphere to minimise oxygen exchange. Enriched isotopes were acquired as silica granules (³⁰Si) and water (¹⁸O). To form ¹⁸O enriched silica, the following procedure was used (Jaeger et al., 1993). The enriched water was added dropwise to cold silicon tetrachloride under a nitrogen atmosphere. The resulting gelatinous precipitate was dehydrated overnight in a vacuum oven at 250°C. The remaining gel was then heated to 1000°C under a reducing atmosphere for 2 h to remove volatiles and to form crystalline silica. This silica was incorporated into the synthesis of the enriched diopside glass. Two batches were made with final enrichments of approximately ¹⁸O/(¹⁸O + ¹⁶O) = 3% and 5% and ³⁰Si/

Table 1

Experimental run conditions and results for the silicon and oxygen self-diffusion in diopside liquid at high pressure

Pressure (GPa)	Temperature (°C)	Duration (s)	Si diffusion coefficient (m ² /s)	O diffusion coefficient (m ² /s)
3	1800	120	9.5E – 10	9.0E – 10
3	1900	90	1.0E – 09	9.0E – 10
3	2000	120	9.4E – 10	9.2E – 10
6	2000	120	5.9E – 10	5.7E – 10
7	2000	120	1.0E – 09	9.1E – 10
9	2200	90	4.3E – 10	4.0E – 10
11	2200	60	3.9E – 10	3.3E – 10
12	2200	60	6.3E – 10	5.4E – 10
13	2200	60	7.3E – 10	6.3E – 10
14	2300	60	8.8E – 10	5.6E – 10
15	2250	60	9.1E – 10	6.2E – 10

(³⁰Si/²⁸Si) = 12% and 15% (natural percentage ¹⁸O = 0.2% and ³⁰Si = 3.1%).

2.2. Experimental conditions and procedure

Experiments were performed in a 1200-tonne multianvil press. The run conditions and durations are summarised in Table 1. Samples were contained within cold-sealed, Re capsules with a volume of 11 cm³ (3–10 GPa; 18 mm octahedral edge length) or

5.5 cm³ (10–15 GPa; 14 mm octahedral edge length). The pressure assembly was a MgO octahedron containing a stepped, cylindrical LaCrO₃ furnace (Fig. 1) and W₇₅-Re₂₅/W₉₇-Re₃ thermocouple. In all cases, the diffusion couples were assembled with the enriched half below the non-enriched half to avoid convection due to gravitational instability.

The diffusion experiments were carried out at the desired pressure using the following automated heating routine: heating at 1000°C/min to 800°C; 800°C

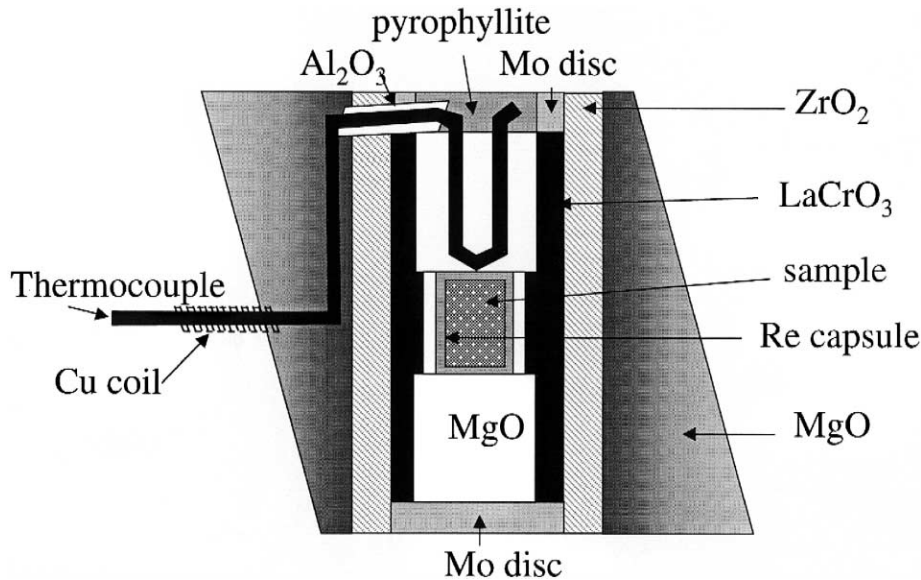


Fig. 1. Multianvil sample assembly.

for 30 s; heating at 2500°C/min from 800°C to the desired temperature (2000–2300°C). Quench was rapid, with an initial rate estimated to be 500°C/s. A zero-time experiment (heating only until the desired temperature has been reached and then immediately quenching), taken to 7 GPa and 2000°C, showed negligible diffusion. Quench crystallisation becomes more pronounced with increasing pressure. Samples quenched above 6 GPa were characterised by completely interlocking, feathery, quench crystals.

2.3. Analyses and data reduction

The analysis of self-diffusion profiles, defined by the isotope ratios $^{30}\text{Si}/(^{30}\text{Si} + ^{28}\text{Si})$ and $^{18}\text{O}/(^{18}\text{O} + ^{16}\text{O})$, were carried out using SIMS at Edinburgh University, UK (Cameca 4f, all samples up to 11 GPa) and GeoForschungsZentrum Potsdam, Germany (Cameca 6f, samples 12–15 GPa). A Cs^+ ion beam (spot size 30–40 μm) was used to measure the relative concentrations of ^{28}Si , ^{30}Si , ^{18}O and ^{16}O isotopes. O^{17} and Si^{29} were not measured, leading to

a maximum additional inaccuracy on the resulting self-diffusion coefficients of 5% (RSD, 1σ). It can be seen from Fig. 2 that, although the diffusion profiles utilise the entire length of the sample capsule, the original concentrations of the diffusion couple are preserved at either end after heating. Maps of ^{18}O and ^{30}Si over a cross-section of a sample capsule show isopleths parallel with the top and bottom of the capsule (Fig. 3) illustrating that no observable convection took place.

Diffusion profiles were fitted using a non-linear least-squares approximation for self-diffusion between two finite bodies (Crank, 1975):

$$C(x, t) = \frac{C_1 + C_2}{2} + \frac{C_1 - C_2}{2} \times \sum_{n=1}^8 \frac{1}{n} \exp\left[\frac{-Dn^2\pi^2 t}{l^2}\right] \times \cos\left[\frac{n\pi x}{l}\right] \sin\left[\frac{n\pi x_i}{l}\right]. \quad (2)$$

In Eq. (2), $C(x, t)$ is the ratio $^{18}\text{O}/(^{18}\text{O} + ^{16}\text{O})$ at time t over distance x , C_1 and C_2 at the initial

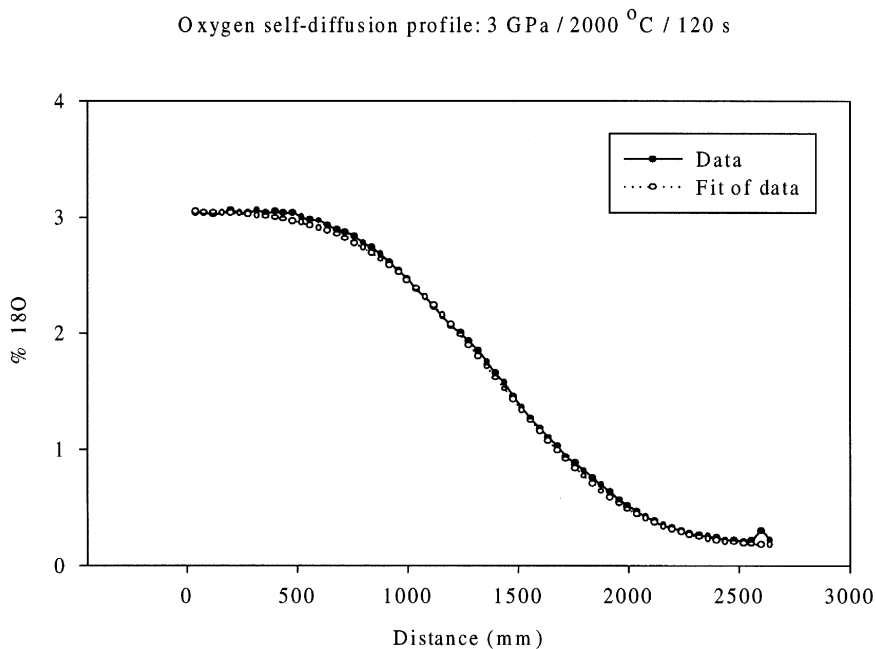


Fig. 2. Self-diffusion profiles defined by the percentage of ^{18}O from a sample capsule run at 3 GPa, 2000°C for 120 s. ^{18}O initial enrichment was 3%. Isotopic analyses were carried out using a Cameca 4f SIMS at Edinburgh University, Scotland.

% ^{18}O map of a sample cross section (11 GPa / 2200 °C / 60

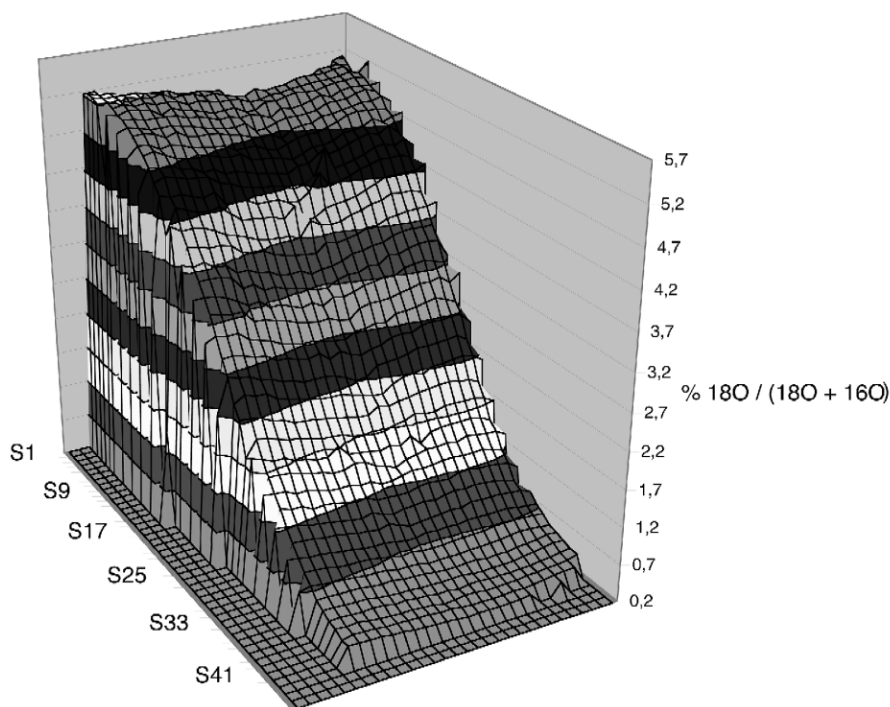


Fig. 3. A 3-dimensional representation of a mapped section across a sample capsule run at 11 GPa, 2200°C for 60 s. Each point on the map is defined by the percentage ^{18}O . Ratio-isopleths are parallel with the top and bottom of the sample capsule, illustrating the absence of convection.

concentrations at the two end members of the diffusion couple, l is the total length of the diffusion couple (length of sample capsule), x_i is the location of the interface, D is the diffusion coefficient.

3. Results

The self-diffusivities of silicon and oxygen in diopside liquid at 2000°C are coincident up to 13 GPa within a margin of inaccuracy of 10% RSD (Fig. 4). The self-diffusion coefficients for silicon and oxygen decrease with pressure from 3 to 11 GPa, consistent with previous measurements at lower pressures, and increase again from 11 to 15 GPa. The diffusivities at 7 GPa are relatively high and are not consistent with the trend shown by the rest of the data. The activation energy of self-diffusion was found to be 268 kJ mol⁻¹, derived from a fit of

oxygen data over a temperature range of 1600–2000°C and pressure range of 1 atm–3 GPa (Fig. 5). The temperature dependence of silicon self-diffusion was also well approximated by this fit. For comparison, previous literature data (Shimizu and Kushiro, 1984, 1991; Dunn, 1982) and those data from our experiments carried out above 8 GPa were extrapolated to 2000°C using this activation energy.

The determined self-diffusion coefficients were used to estimate viscosity using the Eyring equation (Fig. 6). Direct, falling-sphere viscosity data from Scarfe et al. (1987) and Brearley et al. (1986) were used as comparison after extrapolation to 2000°C using an activation energy of viscous flow of 155 kJ mol⁻¹ (Scarfe et al., 1987). Viscosity measured at 2039°C and 1 atm, by Urbain et al. (1982), is also plotted for comparison. In terms of accuracy, the data derived from the Eyring equation are in excellent agreement with the falling-sphere data (Fig. 6).

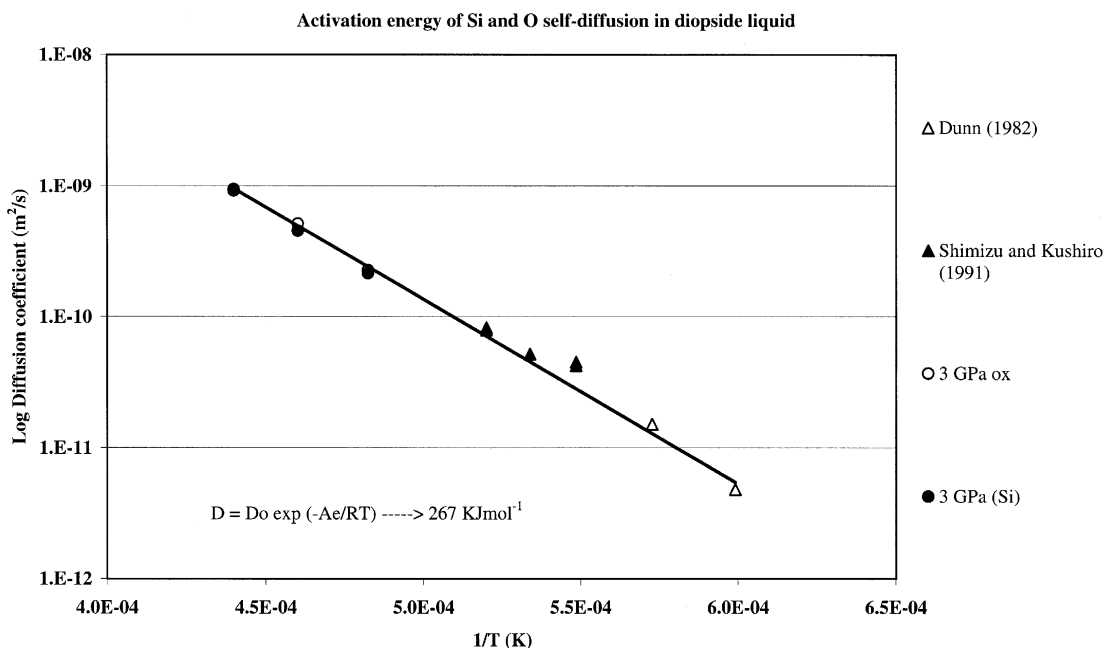


Fig. 5. The temperature dependence of the self-diffusion of silicon and oxygen. If negligible pressure effect is assumed, an Arrhenius temperature dependence gives an activation energy of 267 kJ mol^{-1} for a fit of the log oxygen self-diffusion data. The silicon self-diffusion is also well approximated by this fit. In the equation given, D = diffusivity, D_0 = pre-exponential constant, A_e = activation energy, R = gas constant and T = absolute temperature.

However, the strong positive activation volume shown by the falling-sphere data is not reproduced by the diffusivity data.

4. Discussion

A strong pressure effect on silicon and oxygen self-diffusivities has been observed for highly polymerised silicate and aluminosilicate melts. For some compositions, a change in activation volume from negative to positive has been shown with increasing pressure (Poe et al., 1997). The rheological properties of depolymerised silicate liquids are not likely to have such complex pressure dependence but instead are expected to be more like those of molecular liquids where the distance between the molecules or re-arranging units is inversely proportional to viscosity. This behaviour would result in an increase of viscosity with increasing pressure or positive activation volume (Solomatov and Stevenson, 1993). Consistent with this, previous literature data on the viscosity of diopside liquid (Scarfe et al., 1987; Brearley et al., 1986; Schulze et al., 1999) have

shown positive activation volumes up to 2.5 GPa (measurements carried out at less than 1650°C). This has also been shown for silicon self-diffusion in the same pressure and temperature range (Shimizu and Kushiro, 1991), although activation volumes were less positive.

The extended pressure range used in this study has allowed us to test extrapolations made from lower pressure data. With an activation volume consistent with previous diffusivity measurements, we find a decrease in silicon and oxygen diffusivity with pressure from 3 GPa. A minimum in diffusivity is seen at 11 GPa followed by an increase with pressure up to 15 GPa. Our measured diffusivities at 15 GPa are therefore higher, by approximately 0.5 log units, than those derived from extrapolations of previous low pressure silicon self-diffusion data corrected to 2000°C (Shimizu and Kushiro, 1991). Eyring-derived viscosity estimates from self-diffusion data at 15 GPa are orders of magnitude lower than the linear extrapolation of low pressure viscosity data. This suggests that either the pressure–viscosity relationship is not linear over the range

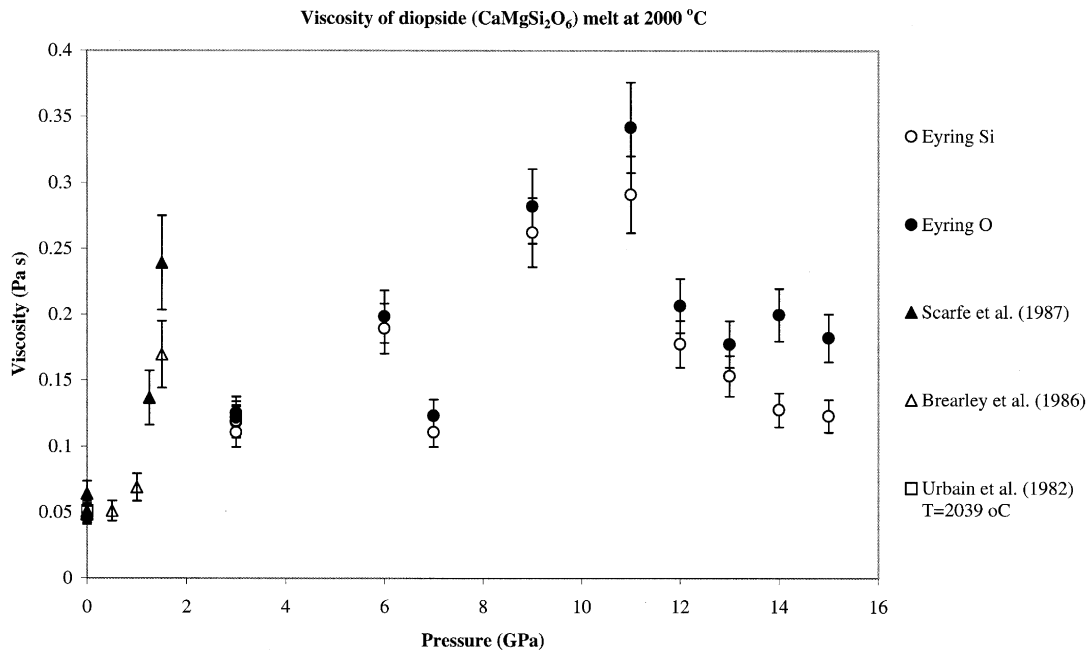


Fig. 6. Eyring-derived viscosity estimates from self-diffusion data at 2000°C, compared with previous falling-sphere viscosity measurements on diopside liquid. Falling-sphere data was temperature corrected to 2000°C assuming an Arrhenius temperature dependence. For comparison, viscosity measured at 2039°C from Urbain et al. (1982) is shown. Inaccuracy bars of 10% RSD are illustrated for the data derived from this study.

from 1 atm to 15 GPa or that the Eyring equation is unsuitable for relating self-diffusion and viscosity in a diopside composition as was also found by Dunn (1982) in his study at 1 bar (1400°C). To validate the relationship, Dunn suggested an increase in the translation distance (λ) from the size of an oxygen anion to that of a SiO_4^{4-} species. However, in this study, an increase in λ would create a worse correlation between direct and “Eyring derived” viscosity values. The discrepancy here lies not with the absolute viscosity values derived from the Eyring equation but with the magnitude of the activation volumes of each data set. A recent study by Schulze et al. (1999) on the viscosity of liquids along the anorthite–diopside compositional join shows that with increasing temperature the magnitude of the pressure effect on viscosity is reduced. It is possible, therefore, that the temperatures used in this study to reach super-liquidus conditions were high enough to suppress the pressure effect. At lower temperatures, a higher activation volume would therefore be expected.

If the Eyring relation is valid, the activation energy of self-diffusion should be similar to that of

viscous flow (Wasserman et al., 1993). However, the activation energy derived in this study is approximately double that determined for viscous flow in diopside liquid by Scarfe et al. (1987) and Urbain et al. (1982). It is, however, consistent with the activation energy for silicon diffusion in many other silicate liquids (Chakraborty, 1995). In contrast, Shimizu and Kushiro (1991) found a lower activation energy (180 kJ mol^{-1}) for silicon self-diffusion in diopside over a relatively narrow temperature range. It may be argued that using data measured at different pressures invalidates the activation energy determination. However, it should be noted that extrapolating the data to lower pressures would have the effect of slightly increasing the diffusion coefficients and would therefore increase the activation energy further.

5. Conclusions

The self-diffusivities of silicon and oxygen in diopside liquid decrease with pressure from $9.8 \times$

10^{-10} m²/s, at 3 GPa, to 3.9×10^{-10} m²/s, at 11 GPa, after which they increase with pressure up to 15 GPa (9.1×10^{-10} m²/s). A change in activation volume is therefore seen at approximately 11 GPa. The self-diffusion of silicon and oxygen are coincident up to 13 GPa within an accuracy of 10% RSD. The activation energy of self-diffusion for both silicon and oxygen is 267 kJ mol⁻¹, determined over a temperature range of 1400–2000°C (and a pressure range of 1 atm–3 GPa). The coincidence of the activation energy for both silicon and oxygen suggests that they have similar mechanisms of self-diffusion over the range of conditions measured. The validity of the Eyring equation to relate viscosity and self-diffusion in diopside liquid is not supported by the relatively high activation energies of self-diffusion measured in this study compared to those previously measured for viscous flow. However, it provides viscosity estimates for diopside liquid that are in good agreement, in terms of absolute values, with pre-existing, direct viscosity measurements up to 3 GPa. The marked positive activation volume observed in the direct viscosity measurements was not reproduced by Eyring derived viscosity estimates. This could be due to a reduction of the pressure-effect at high temperatures and/or the inability of the Eyring equation to relate viscosity and self-diffusion in depolymerised silicate liquids.

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