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Viscosity of Liquid Fayalite up to 9 GPa

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Abstract

The viscosity of liquid fayalite (Fe\textsubscript{2}SiO\textsubscript{4}) was determined up to 9.2 GPa and 1850 °C using in situ falling sphere viscometry and X-ray radiography imaging. The viscosity of liquid fayalite was found to decrease with pressure, reducing by a factor of 2.5 between ambient pressure and 9.2 GPa. The results are in contrast with previous studies on depolymerised silicate melts which found viscosity to increase with pressure. In accordance with recent in situ structural measurements on liquid fayalite, the viscosity decrease is likely a result of the increase in Fe-O coordination with pressure. In addition, temperature is found to have little effect on the viscosity at high pressure. The results show that liquid silicate viscosities need to be considered on an individual basis and can be strongly dependent on the melt structure and composition. This has important implications for models of planetary differentiation. In particular, terrestrial bodies with high Fe contents and reducing mantle conditions are likely to have had very mobile melts at depth.
1. Introduction

The viscosity of liquid silicates (i.e. magmas) is a fundamental property that influences igneous processes, as it controls the transport properties of magmas in planetary interiors. As such, viscosity of liquid silicates will have been an important controlling factor in influencing the formation of the terrestrial planets during the existence of the potential magma oceans. Many of the previous studies on silicate melt viscosity at high pressure were carried out on aluminosilicate melts e.g. basalt and andesite (Kushiro et al., 1976), jadeite (Kushiro, 1976; Suzuki et al., 2011), and albite (Suzuki et al., 2002). Viscosity was found to decrease significantly with increasing pressure in these melts.

Despite its importance for magma ocean systems, the viscosity of depolymerised silicate melts at high pressure has not been extensively studied due to experimental difficulties, including high melting temperatures and very low melt viscosities. Liquid diopside (CaMgSi$_2$O$_6$) (Brearley et al., 1986; Taniguchi, 1992; Reid et al., 2003) and peridotite (Liebske et al., 2005) are the only depolymerised silicate melt viscosities determined experimentally so far. The viscosity of these liquids was found to initially increase with pressure, but decrease above $\sim$9-10 GPa.

It is also important to investigate the physical properties of iron-rich liquid silicates because the FeO content of the planets is highly variable, estimated to range from 3 wt% in Mercury’s mantle (Robinson and Taylor, 2001), to 22 wt% in the lunar and martian mantles (Cahill et al., 2009; Baratoux et al., 2011). This may lead to important differences in the processes occurring in the respective magma oceans of planets. In addition, Fe can ex-
ist in different oxidation states (2+, 3+) which has been shown to influence silicate melt viscosity e.g. (Liebske et al., 2003; Bouhifd et al., 2004; Chevrel et al., 2014). Additionally, there is no data for depolymerised, low viscosity Fe-rich liquids, and computational methods have only investigated Mg-rich liquid viscosities such as MgSiO$_3$ (Karki and Stixrude, 2010) and Mg$_2$SiO$_4$ (Ghosh and Karki, 2011). Therefore, experimental determination of high-P physical properties of such Fe-rich liquids is required.

Here we present viscosity experiments carried out on the molten iron-rich end member of olivine, fayalite (Fe$_2$SiO$_4$), a highly depolymerised silicate, up to 9.2 GPa. The results are discussed by comparison with recent *in situ* structural measurements (Sanloup et al., 2013a) in order to determine the relationship between the melt structure and viscosity at high pressure.

2. Experimental Methods

2.1. High pressure techniques

Experiments on molten fayalite up to 9.2(6) GPa and 1850(95)$^\circ$C were performed using a Paris-Edinburgh press. Natural fayalite supplied by Alfa Aesar was powdered and packed inside a graphite capsule. The cell-assembly (Sakamaki et al., 2012; Sanloup et al., 2013a) shown in Fig. 1, is optimized to allow a large vertical access to the sample and to limit the extrusion of cell materials, even at high $P$-$T$ conditions. The cell design uses low density materials such as boron epoxy and graphite to allow maximum transparency for X-rays. Zirconia was used for thermal insulation and to stabilise the cell. MgO caps + packed pyrex power were inserted above and below the graphite capsule in order to prevent the oxidation of iron and the consequen-
tial decomposition of fayalite at high $T$ (Sanloup et al., 2013a). A rhenium sphere was inserted at the top of each capsule to enable it to fall through the sample upon melting. To enable proper falling, a thin layer of sample was inserted to cover the sphere. The pressure was determined from the cell-volume of the MgO ring pressure-transmitting medium, which uses the $P-V-T$ relation of MgO derived by simultaneous elastic wave velocity and in situ X-ray measurements by Kono et al. (2010) and accounts for the pressure difference between the sample and the MgO ring. X-ray diffraction patterns of the MgO pressure-transmitting medium were collected at 100°C below the liquidus and after the spheres had fallen to determine the pressure. The temperature was determined from previous calibration measurements of the cell-assembly (Kono et al., 2014).

Figure 1: Schematic cross section of the cell assembly; adapted from Sakamaki et al. (2012). Dimensions are given in mm.
2.2. Viscosity measurements

High pressure falling sphere viscometry, in combination with in situ X-ray imaging (Kono et al., 2013), was carried out at beamline 16-BM-B, High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source, Argonne National Laboratory, USA. The sample was pressurised at room temperature and the temperature was then gradually raised to approximately 100°C below the liquidus. The sample was then rapidly heated to a super-liquidus set-point temperature, until either melting or the target $T$ of 1600°C was achieved. The difference between the X-ray absorption coefficients of the rhenium sphere and silicate melt allows for clear imaging of the sphere falling through the melt. The viscosity of liquid fayalite is extremely low, therefore a high speed video camera (Photron FASTCAM SA3) was used to collect images of the falling spheres at a rate of 250 frames per second. The imaged descent path of the sphere was used to calculate a distance/time curve, from which it is possible to calculate the terminal velocity $v_s$ of the sphere. The viscosity $\eta$ of the liquid can then be calculated using Stokes law:

\[
\eta = \frac{2gr_s^2(\rho_s - \rho_l)W}{9v_sE} \tag{1}
\]

where $r_s$ is the radius of the sphere, $\rho_s$ and $\rho_l$ are the densities of the sphere and the liquid respectively at a given pressure and temperature, and $g=9.803$ m·s$^{-2}$ is the acceleration due to gravity. $W$ and $E$ are correction factors that account for the wall and end-effects of a finite cylindrical container (Faxén, 1922) of radius $r_c$ and height $h_c$ are given by:

\[
W = 1 - 2.104 \left( \frac{r_s}{r_c} \right) + 2.09 \left( \frac{r_s}{r_c} \right)^3 - 0.95 \left( \frac{r_s}{r_c} \right)^5 \tag{2}
\]
The radii $r_s$ of the rhenium spheres, as determined from X-ray shadowgraph images using the high resolution camera, ranged between 54-93 $\mu$m, where the largest uncertainty was $\pm$ 2 $\mu$m. The density of the spheres was calculated using the third-order Birch-Murnaghan equation of state, accounting for the thermal expansion of rhenium ($6.63 \times 10^{-6}$ K$^{-1}$), using data from Vohra et al. (1987). The density of liquid Fe$_2$SiO$_4$ at high pressure was taken from Sanloup et al. (2013a) who determined the density of liquid fayalite at 1627°C up to 7.5 GPa. These measurements were in good agreement with Thomas et al. (2012) who determined the density of fayalite liquid using shock wave, sink/float and ultrasonic experiments and with shock wave experiments carried out by Chen et al. (2002). For experimental runs not carried out at 1627°C, thermal expansion was accounted for using a thermal expansion coefficient of 4.8 $\times$ 10$^{-5}$ K$^{-1}$ (Agee, 1992).

The maximum uncertainty in $P$ and $T$ was $\pm$ 0.6 GPa and $\pm$ 95°C, respectively. The $P$ uncertainty resulted in an uncertainty in the determination of the liquid and rhenium sphere density at high pressure. The largest error in the liquid density was 1.5%, while the largest error in the sphere density was 1.1%, and are therefore relatively minor. Due to the small sphere size used in our study, the uncertainty in the measurement of the sphere radii also contributes to the overall viscosity uncertainty. The high-resolution X-ray radiography set-up had an image resolution of $\pm$ 2 $\mu$m. (Kono et al., 2014).

However, it is the uncertainty in the terminal velocity determination
that plays the dominant role in the precision of the viscosity measurements (Brizard et al., 2005). In this study, the terminal velocities were determined with standard deviations of ± 2-6%. In addition, an error in terminal velocity may arise if the shape of the sphere deviates from spherical. The actual terminal velocity of an ellipsoid particle \(v_e\) may be found by multiplying \(v_s\) by a shape factor \(S\) (Kerr and Lister, 1991). Our most elliptical sphere had an aspect ratio of \(c/a = 0.85\), which corresponds to a shape factor of 0.998 and thus a 0.2% error in the terminal velocity calculation. Indeed, the effect of an elliptical shape is small even at \(c/a = 0.5\), which results in \(S = 0.96\), thus corresponding to only a 4% error in terminal velocity. Therefore, the effect of sphere shape in our study can be considered to be negligible on the final viscosity result. The overall uncertainty in the final viscosity values, determined by standard error propagation, was <10%.

3. Results

3.1. Fayalite liquid viscosity

The experimental conditions, sphere diameter \(d_s\), terminal velocity and viscosity results are presented in Table 2. X-ray shadowgraph images of the rhenium sphere falling during one of the experimental runs (Run B13, 5.1 GPa, 1650 °C) are shown in Fig. 2a. A plot of the sphere falling distance against time for this run is shown in Fig. 2b. The points show a good fit to the straight line, indicating that the sphere reached a constant terminal velocity after an initial acceleration. The velocity/time plot for the rhenium sphere of experiment B13 is shown in Fig. 2c. After the initial acceleration, the sphere reaches a “velocity plateau”,
The viscosity of liquid fayalite decreased along the liquidus (Run A) from 76.0 ± 6.7 mPa·s at ambient pressure, 1250°C (Shiraishi et al., 1978), to 30.7 ± 2.6 mPa·s at 9.2 GPa, 1850°C (Fig. 3a and 3b). Viscosity decreased rapidly from ambient pressure to around 4 GPa, after which it decreased much more slowly. In order to confirm that the viscosity decrease was due to increasing pressure and not increasing temperature, the viscosity of liquid fayalite was measured as a function of pressure along the 1600°C isotherm, within ±50°C (Run B). At 1600°C, the viscosity of liquid fayalite decreased from 51.4 ± 4.0 mPa·s at 1.3 GPa, to 34.3 ± 2.6 mPa·s at 6.3 GPa (Fig. 3a), suggesting that increasing pressure is indeed the main cause of the viscosity decrease along the fayalite liquidus.

Table 1: Experimental run conditions, results and uncertainties

<table>
<thead>
<tr>
<th>Run</th>
<th>$P$ (GPa)</th>
<th>$T$ (°C)</th>
<th>$d_s$ (μm)</th>
<th>$v_s$ (mm·s$^{-1}$)</th>
<th>$\eta$ (mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A5</td>
<td>2.0 ± 0.5</td>
<td>1350 ± 70</td>
<td>173 ± 2</td>
<td>3.7 ± 0.1</td>
<td>51.8 ± 2.8</td>
</tr>
<tr>
<td>A10</td>
<td>3.6 ± 0.5</td>
<td>1550 ± 80</td>
<td>171 ± 2</td>
<td>5.1 ± 0.2</td>
<td>37.9 ± 3.6</td>
</tr>
<tr>
<td>A12</td>
<td>6.3 ± 0.5</td>
<td>1600 ± 80</td>
<td>185 ± 2</td>
<td>6.4 ± 0.2</td>
<td>34.3 ± 2.6</td>
</tr>
<tr>
<td>A8</td>
<td>9.2 ± 0.6</td>
<td>1850 ± 95</td>
<td>185 ± 2</td>
<td>7.2 ± 0.1</td>
<td>30.7 ± 2.6</td>
</tr>
<tr>
<td>B17</td>
<td>1.3 ± 0.5</td>
<td>1580 ± 80</td>
<td>183 ± 2</td>
<td>4.0 ± 0.2</td>
<td>51.4 ± 4.0</td>
</tr>
<tr>
<td>B14</td>
<td>2.8 ± 0.5</td>
<td>1570 ± 80</td>
<td>155 ± 2</td>
<td>4.0 ± 0.2</td>
<td>41.5 ± 3.7</td>
</tr>
<tr>
<td>B11</td>
<td>3.8 ± 0.5</td>
<td>1600 ± 80</td>
<td>133 ± 2</td>
<td>3.2 ± 0.1</td>
<td>40.5 ± 2.7</td>
</tr>
<tr>
<td>B7</td>
<td>4.3 ± 0.5</td>
<td>1640 ± 80</td>
<td>108 ± 2</td>
<td>2.3 ± 0.1</td>
<td>40.4 ± 3.6</td>
</tr>
<tr>
<td>B13</td>
<td>5.1 ± 0.5</td>
<td>1650 ± 85</td>
<td>173 ± 2</td>
<td>5.3 ± 0.2</td>
<td>37.1 ± 2.3</td>
</tr>
</tbody>
</table>

where the sphere is deemed to have reached its terminal velocity.
3.2. Sample Analysis

After the experiments, the samples were quenched and recovered for electron microprobe analysis at EMMAC (The Edinburgh Materials and Micro-Analysis Centre), University of Edinburgh. The analyses were performed on a CAMECA SX100 electron microprobe with a 15 kV accelerating voltage.
Figure 3: (a) The viscosity of liquid fayalite as a function of pressure. The black squares are values obtained along the fayalite liquidus (Run A), with the temperature indicated. The grey squares are values obtained along the 1600°C isotherm (Run B). The ambient pressure measurement is from Shiraishi et al. (1978) at 1250°C. The trend is a guide for the eye. (b) The $P$-$T$ conditions of each run obtained along the fayalite liquidus (Run A) in relation to the Fe$_2$SiO$_4$ phase diagram. The viscosity values are shown in mPa·s beside each $P$-$T$ point.

and a 1 µm beam, with a current of 30 nA. Table 2 shows the average composition of quenched fayalite obtained by the electron microprobe analysis.

In one of the highest $P$ runs (A12, 6.3 GPa), a very small amount of interstitial areas richer in FeO were detected. This was not the case for the other samples (e.g. the example illustrated in Fig. 4) where only fayalite crystals were detected. Whilst this suggests minor oxidation in the sample with FeO in some of the interstices, we consider it to be unimportant for the following reasons: (i) Sanloup et al. (2013a) used Mössbauer spectroscopy to quantify the ratio of Fe$^{3+}$ to Fe$^{2+}$ in fayalite after high $P$-$T$ experiments and found no evidence for the presence of Fe$^{3+}$ within the experimental uncertainty ($\sim$1%) when the same cell assembly as in the present study was used, and (ii) the decomposition of fayalite could be tracked in situ upon melting as Fe-rich blobs were apparent on the X-ray radiographs due to their strong absorption
contrast with the silicate melt. For the data presented here, no heterogeneity was detected *in situ* by X-ray radiography. We did however detect a Re-Fe alloy on the rim of some of the recovered spheres. The rims were significant, up to 40 µm in thickness, however we must conclude that this growth occurred after the fall as no growth in the size of the spheres was detected during the fall within the error of ± 2 µm, and the Fe-rich rim would have been very visible on the radiographs and this was not observed. We therefore consider interaction between the spheres and the sample during the experiments to be negligible.

<table>
<thead>
<tr>
<th>oxide</th>
<th>wt%</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>29.34</td>
<td>0.15</td>
</tr>
<tr>
<td>FeO</td>
<td>65.25</td>
<td>0.41</td>
</tr>
<tr>
<td>MgO</td>
<td>0.63</td>
<td>0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>4.29</td>
<td>0.14</td>
</tr>
<tr>
<td>Total</td>
<td>99.54</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Mean composition from 41 analyses on the quenched fayalite samples. Data is given in oxide wt% along with the standard deviation (δ). The sample is natural fayalite and contains approximately 4.3 wt% MnO, 0.6 wt% MgO and trace amounts of CaO.

A Philips XL30CP scanning electron microscope (SEM) at EMMAC and the Institute of Petroleum Engineering, Heriot Watt University was used to image the samples. A back scattered electron (BSE) image of experimental run A5 is shown in Fig. 4.
Figure 4: A BSE SEM image of experimental run A5. The sample was quenched as 100% fayalite crystals. The rhenium sphere can be seen in the bottom left side of the sample. The dark material surrounding the sample is the graphite capsule.

4. Discussion

4.1. Viscosity and structure of liquid fayalite at high pressure

Liquid fayalite exhibits an average Fe-O coordination number (CN) of 4.8 (2) at ambient pressure which arises from the co-existence of approximately 60% FeO$_4$ and 40% FeO$_6$ units (Drewitt et al., 2013). With increasing pressure up to 7.5 GPa, energy dispersive X-ray diffraction measurements show that the average Fe-O CN increases to 7.2 (3) (Sanloup et al., 2013a). However, it is not possible to determine the relative proportions of different FeO$_x$ species as the real-space resolution of the high pressure diffraction measurements is limited. The proposed viscosity decrease in liquid fayalite is therefore likely due to the increase in Fe-O coordination with pressure.
This is particularly significant in the light of work that demonstrates that
the Mg$_2$SiO$_4$ glass structure network largely consists of MgO$_x$ polyhedra
(Kohara et al., 2004). If we assume that Fe$_2$SiO$_4$ behaves in the same way,
then an increase in Fe-O coordination would result in the melt structure
becoming more depolymerised, thus resulting in a decrease in viscosity. In
addition, higher coordinated cations are characterised by longer and thus
weaker cation-oxygen bonds, which is thought to lower the activation barri-
ers to self-diffusion, and hence leads to a further reduction in viscosity (Waff,
1975; Reid et al., 2003; Liebske et al., 2005).

At high $P$, a silicate melt is expected to reach a densely packed state after
which there are no further changes in cation coordination (i.e. a viscosity
minimum). The viscosity minimum will vary for silicate melts of different
composition. The four- to six-fold Si coordination change occurring between
20-35 GPa (Sato and Funamori, 2010; Sanloup et al., 2013b) might not nec-
essarily influence fayalite melt as it is thought to consist of isolated silica
tetrahedra with a structure built from FeO$_x$ polyhedra. Indeed, the effect of
the Si coordination change is still unknown for even the most polymerised
silicate melts, as viscosity experiments have so far been limited to below 13
GPa. In order to complement theoretical studies, further experimental stud-
ies on silicate melts at high pressure are needed in order to fully understand
the effects of the various pressure induced structural changes in relation to
melt viscosity.

4.2. The effect of temperature on the viscosity of fayalite melt

It is noteworthy that the viscosity values measured at 1600°C are not
lower than those measured at lower temperatures (within the error bars).
In fact, when the isotherm and liquidus viscosity values are plotted on the same diagram (Fig. 3a), the values all fit on the same trend. This suggests that at high \( T \), temperature may have very little effect on viscosity and that pressure is the controlling variable.

A weak \( T \)-dependency implies that the liquid is fragile, i.e. it has a non-Arhenian viscosity behaviour. Depolymerised silicate melts have been shown to be fragile liquids at 1 bar (Giordano et al., 2008). In fayalite melt, this fragile behaviour is reinforced at high \( P \) following its structural rearrangements. The changes that occur at high \( P \), i.e. the increase of Fe-O CN and strengthening of the medium-range order (Sanloup et al., 2013a), are likely to further increase the liquid fragility. This effect has been shown for SiO\(_2\) and Na\(_2\)O-SiO\(_2\) melts from a computational approach (Barrat et al., 1997; Micoulaut and Bauchy, 2013), whereby the liquid goes from strong to fragile and becomes less viscous as the Si-O CN increases from 4 to 6.

4.3. The effect of pressure on the viscosity of silicate melts

A summary of previous experimental studies on the viscosity of silicate melts is shown in Fig. 5. A viscosity decrease at high pressure has been previously documented in many polymerised silicate melts e.g. jadeite (Kushiro, 1976; Suzuki et al., 2011) and albite (Suzuki et al., 2002). The decrease in viscosity of polymerised melts at high pressure is much greater than in our depolymerised fayalite melt. Liquid fayalite viscosity decreased by a factor of 2.5 between 0-9 GPa, whereas liquid jadeite viscosity decreased by a factor of 10 between 0-2.4 GPa (Kushiro, 1976), a much smaller pressure range. Since fayalite melt is already highly depolymerised, structural changes will have a less significant effect on the melt viscosity.
Of experimentally determined viscosities, fayalite is thus far the most depolymerised silicate melt to have been measured. Previous studies on depolymerised melts (diopside (Brearley et al., 1986; Taniguchi, 1992; Reid et al., 2003) and peridotite (Liebske et al., 2005)) found the viscosity to initially increase with pressure, but decrease above \( \sim 9-10 \) GPa. However, simula-
tions on liquid MgSiO$_3$ found an anomalous pressure-dependence similar to what has been reported for polymerised melts, with the viscosity reaching a minimum value near 5 GPa, and then increasing upon further compression (Karki and Stixrude, 2010).

The anomalous inverse pressure-viscosity relationship of polymerised silicate melts has often been attributed to depolymerisation in the melt via the increase in Al$^{3+}$ coordination with oxygen e.g. (Waff, 1975; Kushiro, 1976). Particular emphasis has therefore been placed on the determination of aluminosilicate glass structure at high pressure. Allwardt et al. (2007) reported the significant presence of 5-fold coordinated aluminium in a range of aluminosilicate glasses at 3 GPa, however the relative proportions of the 4-,5- and 6-fold coordinated Al was highly variable between glasses of different compositions. On the other hand, Poe et al. (2001) found no significant changes in Al coordination below 6 GPa. Other explanations for the anomalous viscosity behaviour of silicate melts include the negative thermal expansion coefficient of the liquid (Schmelzer et al., 2005) and a reactive ion transfer model, whereby the O$^{2-}$ self-diffusivity increases with increasing pressure, resulting in a viscosity decrease (McMillan and Wilding, 2009). However, a recent theoretical study by Bauchy et al. (2013) attempted to relate viscosity and diffusivity of silicate melts at high pressure, but could not find a definitive relationship. The clear discrepancies in the literature, combined with the additional problem that high pressure Si-O and Al-O bond arrangements have been found to return to tetrahedral coordination upon decompression (Williams and Jeanloz, 1988), demonstrate the need for the in situ determination of the structure of silicate melts. The experimental
difficulties associated with the in situ determination of liquid structures has resulted in very few studies possessing both viscosity and in situ structural data. Exceptions include the present study and Sakamaki et al. (2013), who measured the viscosity and structure of basaltic magma.

Our results show that cations other than Al\(^{3+}\) experience coordination changes over the 0-10 GPa pressure range. It is likely, on the basis that molten fayalite exhibits different behaviour to other depolymerised melts such as diopside and peridotite, that a catch-all theory for the behaviour of depolymerised silicate melts at depth is not appropriate. Behaviour should be considered on an individual basis and may be strongly dependent on the melt structure and composition.

4.4. Geological Implications

Our results hold particular significance for FeO-rich planetary magmas existing in reduced environments. Our experiments were carried out under reducing conditions and the final sample composition was found to contain Fe\(^{3+}/\sum\ \text{Fe}\ \leq 0.01\) (Sanloup et al., 2013a). The present day Moon and Mars are estimated to have high-mantle iron contents (up to 22 wt% FeO (Cahill et al., 2009; Baratoux et al., 2011)) in a reducing environment (Sato et al., 1973; Herd et al., 2002). \(fO_2\) has been found to have an effect on melt viscosity e.g. Lieske et al. (2003); Bouhifd et al. (2004); Chevrel et al. (2014) all found a drop in silicate melt viscosity with a reduction in Fe\(^{3+}/\sum\ \text{Fe}\).

Lacks et al. (2007) carried out molecular dynamics simulations to calculate viscosity along the MgO-SiO\(_2\) join to investigate the effect of composition and pressure on transport properties. At atmospheric pressure, viscosity was
found to vary by more than 3 orders of magnitude along the compositional join, however at pressures > 15 GPa, the viscosity varied by less than an order of magnitude over the entire compositional range. If the FeO-SiO$_2$ system behaves in the same way, then planetary magma viscosities will be particularly sensitive to FeO content at lower pressures. Our results suggest that the increase in $P$ along the magma ocean adiabat will favour a decrease in melt viscosity of a FeO-rich magma, and may be most important at upper mantle depths. Additionally, the viscosity decrease may be particularly pronounced in more reducing conditions, such as those considered to be present in Mars and the Moon. Bodies that are less FeO rich (such as Mercury) may have a less pronounced negative pressure effect (or it may not be present at all) and it is therefore worth considering when modelling processes occurring in planetary magma oceans.

Due to the lack of data on silicate melts at high pressure, assumptions about the viscosity of depolymerised melts at depth have often been made. Solomatov and Stevenson (1993) assumed that the viscosity of depolymerised melts would increase with depth due to closer interatomic spacing. Tonks and Melosh (1990, 1993) assumed no pressure effect on silicate melt viscosity in their global magma ocean model. Our results however, show that depolymerised silicate melts may exhibit a hitherto unexpected decrease in viscosity at depth. Viscosity will have been an important influencing property on the chemical evolution of the early terrestrial bodies due to the fact that convection (Davaille and Jaupart, 1993), crystal settling (Solomatov and Stevenson, 1993), cumulate overturn (Elkins-Tanton et al., 2003), and chemical diffusion (Rubie et al., 2003) are much more efficient in low viscosity melts. However,
more work is needed to understand the properties of other silicate melts relevant to magma ocean compositions across a larger pressure range. Whilst the existence of a fayalitic magma ocean in a planetary body is unlikely, it is nevertheless important to measure the properties of simple end-member compositions so that we can begin to understand how different compositional mixtures influence planetary magma viscosity and processes.

5. Conclusions

In situ falling sphere viscometry was performed on liquid fayalite (Fe$_2$SiO$_4$), a highly depolymerised, Fe-rich silicate melt, up to 9.2 GPa and $\sim$1850°C. This is the most depolymerised silicate melt studied so far, and the viscosity was found to decrease by a factor of 2.5 over the measured pressure range. It is likely that this decrease is a result of the increase in Fe-O coordination with pressure (Sanloup et al., 2013a). In polymerised melts, the structural transformation of tetrahedrally coordinated cations (such as Al$^{3+}$) to higher species has often been cited as the cause of the anomalous viscosity behaviour of silicate melts. Hitherto, it has often been assumed that depolymerised silicate melts will not exhibit anomalous viscosity behaviour at depth. Our results show that this assumption is not appropriate, and that the behaviour of silicate melts at depth should be considered on an independent basis for melts of different composition. This has important implications for models of planetary differentiation. In particular, terrestrial bodies with high Fe contents and reducing mantle conditions are likely to have had very mobile melts at depth.
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Kushiro, I., Yoder, H. S., Mysen, B. O., 1976. Viscosities of basalt and an-


Poe, B. T., Romano, C., Zotov, N., Cibin, G., Marcelli, A., 2001. Compression mechanisms in aluminosilicate melts: Raman and XANES spec-


