Viscosity of Liquid Fayalite up to 9 GPa

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Abstract

The viscosity of liquid fayalite (Fe_2SiO_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.

11 1. Introduction

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

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

30 It is also important to investigate the physical properties of iron-rich
31 liquid silicates because the FeO content of the planets is highly variable,
32 estimated to range from 3 wt% in Mercury's mantle (Robinson and Taylor,
33 2001), to 22 wt% in the lunar and martian mantles (Cahill et al., 2009; Bara-
34 toux et al., 2011). This may lead to important differences in the processes
35 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_2SiO_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_2SiO_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) °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-

60 tial decomposition of fayalite at high T (Sanloup et al., 2013a). A rhenium
 61 sphere was inserted at the top of each capsule to enable it to fall through
 62 the sample upon melting. To enable proper falling, a thin layer of sample
 63 was inserted to cover the sphere. The pressure was determined from the
 64 cell-volume of the MgO ring pressure-transmitting medium, which uses the
 65 P - V - T relation of MgO derived by simultaneous elastic wave velocity and *in*
 66 *situ* X-ray measurements by Kono et al. (2010) and accounts for the pressure
 67 difference between the sample and the MgO ring. X-ray diffraction patterns
 68 of the MgO pressure-transmitting medium were collected at 100 °C below
 69 the liquidus and after the spheres had fallen to determine the pressure. The
 70 temperature was determined from previous calibration measurements of the
 71 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.

72 2.2. Viscosity measurements

73 High pressure falling sphere viscometry, in combination with *in situ* X-ray
 74 imaging (Kono et al., 2013), was carried out at beamline 16-BM-B, High Pres-
 75 sure Collaborative Access Team (HPCAT) at the Advanced Photon Source,
 76 Argonne National Laboratory, USA. The sample was pressurised at room
 77 temperature and the temperature was then gradually raised to approximately
 78 100 °C below the liquidus. The sample was then rapidly heated to a super-
 79 liquidus set-point temperature, until either melting or the target T of 1600 °C
 80 was achieved. The difference between the X-ray absorption coefficients of the
 81 rhenium sphere and silicate melt allows for clear imaging of the sphere falling
 82 through the melt. The viscosity of liquid fayalite is extremely low, therefore
 83 a high speed video camera (Photron FASTCAM SA3) was used to collect
 84 images of the falling spheres at a rate of 250 frames per second. The imaged
 85 descent path of the sphere was used to calculate a distance/time curve, from
 86 which it is possible to calculate the terminal velocity v_s of the sphere. The
 87 viscosity η of the liquid can then be calculated using Stokes law:

$$\eta = \frac{2gr_s^2(\rho_s - \rho_l)W}{9v_sE} \quad (1)$$

88 where r_s is the radius of the sphere, ρ_s and ρ_l are the densities of the sphere
 89 and the liquid respectively at a given pressure and temperature, and $g=9.803$
 90 $\text{m}\cdot\text{s}^{-2}$ is the acceleration due to gravity. W and E are correction factors that
 91 account for the wall and end-effects of a finite cylindrical container (Faxén,
 92 1922) of radius r_c and height h_c are given by:

$$W = 1 - 2.104 \left(\frac{r_s}{r_c} \right) + 2.09 \left(\frac{r_s}{r_c} \right)^3 - 0.95 \left(\frac{r_s}{r_c} \right)^5 \quad (2)$$

$$E = 1 + 3.3 \left(\frac{r_s}{h_c} \right) \quad (3)$$

93 The radii r_s of the rhenium spheres, as determined from X-ray shadow-
 94 graph images using the high resolution camera, ranged between 54-93 μm ,
 95 where the largest uncertainty was $\pm 2 \mu\text{m}$. The density of the spheres was
 96 calculated using the third-order Birch-Murnaghan equation of state, account-
 97 ing for the thermal expansion of rhenium ($6.63 \times 10^{-6} \text{ K}^{-1}$), using data from
 98 Vohra et al. (1987). The density of liquid Fe_2SiO_4 at high pressure was taken
 99 from Sanloup et al. (2013a) who determined the density of liquid fayalite
 100 at 1627°C up to 7.5 GPa. These measurements were in good agreement
 101 with Thomas et al. (2012) who determined the density of fayalite liquid us-
 102 ing shock wave, sink/float and ultrasonic experiments and with shock wave
 103 experiments carried out by Chen et al. (2002). For experimental runs not
 104 carried out at 1627°C , thermal expansion was accounted for using a thermal
 105 expansion coefficient of $4.8 \times 10^{-5} \text{ K}^{-1}$ (Agee, 1992).

106 The maximum uncertainty in P and T was $\pm 0.6 \text{ GPa}$ and $\pm 95^\circ\text{C}$, re-
 107 spectively. The P uncertainty resulted in an uncertainty in the determination
 108 of the liquid and rhenium sphere density at high pressure. The largest error
 109 in the liquid density was 1.5%, while the largest error in the sphere density
 110 was 1.1%, and are therefore relatively minor. Due to the small sphere size
 111 used in our study, the uncertainty in the measurement of the sphere radii
 112 also contributes to the overall viscosity uncertainty. The high-resolution X-
 113 ray radiography set-up had an image resolution of $\pm 2 \mu\text{m}$. (Kono et al.,
 114 2014).

115 However, it is the uncertainty in the terminal velocity determination

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

129 **3. Results**

130 *3.1. Fayalite liquid viscosity*

131 The experimental conditions, sphere diameter (d_s), terminal velocity and
 132 viscosity results are presented in Table 2.

133 X-ray shadowgraph images of the rhenium sphere falling during one of
 134 the experimental runs (Run B13, 5.1 GPa, 1650 °C) are shown in Fig. 2a.
 135 A plot of the sphere falling distance against time for this run is shown in
 136 Fig. 2b. The points show a good fit to the straight line, indicating that the
 137 sphere reached a constant terminal velocity after an initial acceleration. The
 138 velocity/time plot for the rhenium sphere of experiment B13 is shown in Fig.
 139 2c. After the initial acceleration, the sphere reaches a “velocity plateau”,

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

Table 1: Experimental run conditions, results and uncertainties

140 where the sphere is deemed to have reached its terminal velocity.

141 The viscosity of liquid fayalite decreased along the liquidus (Run A) from
142 76.0 ± 6.7 mPa·s at ambient pressure, 1250 °C (Shiraishi et al., 1978), to
143 30.7 ± 2.6 mPa·s at 9.2 GPa, 1850 °C (Fig. 3a and 3b). Viscosity decreased
144 rapidly from ambient pressure to around 4 GPa, after which it decreased
145 much more slowly. In order to confirm that the viscosity decrease was due
146 to increasing pressure and not increasing temperature, the viscosity of liquid
147 fayalite was measured as a function of pressure along the 1600 °C isotherm,
148 within ± 50 °C (Run B). At 1600 °C, the viscosity of liquid fayalite decreased
149 from 51.4 ± 4.0 mPa·s at 1.3 GPa, to 34.3 ± 2.6 mPa·s at 6.3 GPa (Fig. 3a),
150 suggesting that increasing pressure is indeed the main cause of the viscosity
151 decrease along the fayalite liquidus.

Figure 2: (a) A series of X-ray radiography images showing the rhenium sphere (radius $86.5 \mu\text{m}$) descent through liquid Fe_2SiO_4 from experiment B13 at 5.1 GPa and 1650°C . Every 4th frame is shown between 8 and 120 ms. (b) The results of the sphere fall analysis for each frame during experiment B13. The points show a good fit to a straight line and the constant gradient before the sphere reaches the bottom of the capsule indicates that terminal velocity was achieved. (c) The velocity/time plot of the rhenium sphere in experiment B13. Points on the flat section of the graph either side of the red line were deemed to have achieved terminal velocity, which is first reached after 30 ms. The sharp deceleration at 130 ms occurs as the sphere approaches the bottom of the capsule.

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 the P - T conditions of each run obtained along the fayalite liquidus (Run A) in relation to the Fe_2SiO_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. 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. In addition, 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. Additionally, the use of rhenium spheres does not seem to have resulted in a reaction between the melt and the sphere, as the FeO content of the sample does not appear to have been affected, as shown in Table 2.

oxide	wt%	δ
SiO ₂	29.34	0.15
FeO	65.25	0.41
MgO	0.63	0.01
CaO	0.03	0.01
MnO	4.29	0.14
Total	99.54	

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.

170 A Philips XL30CP scanning electron microscope (SEM) at EMMAC and
171 the Institute of Petroleum Engineering, Heriot Watt University was used to
172 image the samples. A back scattered electron (BSE) image of experimental
173 run A5 is shown in Fig. 4.

174 4. Discussion

175 4.1. Viscosity and structure of liquid fayalite at high pressure

176 Liquid fayalite exhibits an average Fe-O coordination number (CN) of
177 4.8 (2) at ambient pressure which arises from the co-existence of approxi-
178 mately 60% FeO₄ and 40% FeO₆ units (Drewitt et al., 2013). With increas-
179 ing pressure up to 7.5 GPa, energy dispersive X-ray diffraction measurements
180 show that the average Fe-O CN increases to 7.2 (3) (Sanloup et al., 2013a).
181 However, it is not possible to determine the relative proportions of differ-
182 ent FeO_x species as the real-space resolution of the high pressure diffraction
183 measurements is limited. The proposed viscosity decrease in liquid fayalite

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.

184 is therefore likely due to the increase in Fe-O coordination with pressure.
 185 This is particularly significant in the light of work that demonstrates that
 186 the Mg_2SiO_4 glass structure network largely consists of MgO_x polyhedra
 187 (Kohara et al., 2004). If we assume that Fe_2SiO_4 behaves in the same way,
 188 then an increase in Fe-O coordination would result in the melt structure
 189 becoming more depolymerised, thus resulting in a decrease in viscosity. In
 190 addition, higher coordinated cations are characterised by longer and thus
 191 weaker cation-oxygen bonds, which is thought to lower the activation barriers
 192 to self-diffusion, and hence leads to a further reduction in viscosity (Waff,
 193 1975; Reid et al., 2003; Liebske et al., 2005).

194 At high P , a silicate melt is expected to reach a densely packed state after
 195 which there are no further changes in cation coordination (i.e. a viscosity

196 minimum). The viscosity minimum will vary for silicate melts of different
 197 composition. The four- to six-fold Si coordination change occurring between
 198 20-35 GPa (Sato and Funamori, 2010; Sanloup et al., 2013b) might not nec-
 199 essarily influence fayalite melt as it is thought to consist of isolated silica
 200 tetrahedra with a structure built from FeO_x polyhedra. Indeed, the effect of
 201 the Si coordination change is still unknown for even the most polymerised
 202 silicate melts, as viscosity experiments have so far been limited to below 13
 203 GPa. In order to complement theoretical studies, further experimental stud-
 204 ies on silicate melts at high pressure are needed in order to fully understand
 205 the effects of the various pressure induced structural changes in relation to
 206 melt viscosity.

207 *4.2. The effect of temperature on the viscosity of fayalite melt*

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

214 A weak T -dependency implies that the liquid is fragile, i.e. it has a
 215 non-Arrhenian viscosity behaviour. Depolymerised silicate melts have been
 216 shown to be fragile liquids at 1 bar (Giordano et al., 2008). In fayalite
 217 melt, this fragile behaviour is reinforced at high P following its structural
 218 rearrangements. The changes that occur at high P , i.e. the increase of Fe-O
 219 CN and strengthening of the medium-range order (Sanloup et al., 2013a),
 220 are likely to further increase the liquid fragility. This effect has been shown

for SiO_2 and $\text{Na}_2\text{O-SiO}_2$ 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

Figure 5: A summary of experimental studies on the viscosity of silicate melts. The temperature is also given for each composition. Black squares: fayalite at 1600 °C, this study; filled circles: peridotite at 2013 °C (Liebske et al., 2005); open circles: peridotite at all T (Liebske et al., 2005); blue triangles: jadeite at 1350 °C (Kushiro, 1976); green diamonds: jadeite at 1650 °C (Suzuki et al., 2011); grey hexagons: diopside at 1600 °C (Brearley et al., 1986); filled stars: diopside at 1800 °C (Taniguchi, 1992), highest pressure point from Reid et al. (2003) at 1730 ± 100 °C; open stars: diopside at all T (Reid et al., 2003); navy pentagons: albite at 1600 °C, first 3 points from Brearley et al. (1986), points at 3.3 and 4.6 GPa from Suzuki et al. (2002); magenta triangles: $\text{K}_2\text{MgSi}_5\text{O}_{12}$ at 1300 °C (Kushiro, 1977); orange triangles: $\text{Na}_2\text{Si}_3\text{O}_7$ at 1175 °C (Kushiro, 1976).

A summary of previous experimental studies on the viscosity of silicate

226 melts is shown in Fig. 5. A viscosity decrease at high pressure has been pre-
 227 viously documented in many polymerised silicate melts e.g. jadeite (Kushiro,
 228 1976; Suzuki et al., 2011) and albite (Suzuki et al., 2002). The decrease in
 229 viscosity of polymerised melts at high pressure is much greater than in our
 230 depolymerised fayalite melt. Liquid fayalite viscosity decreased by a factor of
 231 2.5 between 0-9 GPa, whereas liquid jadeite viscosity decreased by a factor of
 232 10 between 0-2.4 GPa (Kushiro, 1976), a much smaller pressure range. Since
 233 fayalite melt is already highly depolymerised, structural changes will have a
 234 less significant effect on the melt viscosity.

235 Of experimentally determined viscosities, fayalite is thus far the most de-
 236 polymerised silicate melt to have been measured. Previous studies on depoly-
 237 merised melts (diopside (Brearley et al., 1986; Taniguchi, 1992; Reid et al.,
 238 2003) and peridotite (Liebske et al., 2005)) found the viscosity to initially
 239 increase with pressure, but decrease above ~ 9 -10 GPa. However, simula-
 240 tions on liquid MgSiO_3 found an anomalous pressure-dependence similar to
 241 what has been reported for polymerised melts, with the viscosity reaching a
 242 minimum value near 5 GPa, and then increasing upon further compression
 243 (Karki and Stixrude, 2010).

244 The anomalous inverse pressure-viscosity relationship of polymerised sil-
 245 icate melts has often been attributed to depolymerisation in the melt via
 246 the increase in Al^{3+} coordination with oxygen e.g. (Waff, 1975; Kushiro,
 247 1976). Particular emphasis has therefore been placed on the determination
 248 of aluminosilicate glass structure at high pressure. Allwardt et al. (2007)
 249 reported the significant presence of 5-fold coordinated aluminium in a range
 250 of aluminosilicate glasses at 3 GPa, however the relative proportions of the

251 4-,5- and 6-fold coordinated Al was highly variable between glasses of dif-
 252 ferent compositions. On the other hand, Poe et al. (2001) found no signif-
 253 icant changes in Al coordination below 6 GPa. Other explanations for the
 254 anomalous viscosity behaviour of silicate melts include the negative thermal
 255 expansion coefficient of the liquid (Schmelzer et al., 2005) and a reactive
 256 ion transfer model, whereby the O^{2-} self-diffusivity increases with increas-
 257 ing pressure, resulting in a viscosity decrease (McMillan and Wilding, 2009).
 258 However, a recent theoretical study by Bauchy et al. (2013) attempted to re-
 259 late viscosity and diffusivity of silicate melts at high pressure, but could not
 260 find a definitive relationship. The clear discrepancies in the literature, com-
 261 bined with the additional problem that high pressure Si-O and Al-O bond
 262 arrangements have been found to return to tetrahedral coordination upon
 263 decompression (Williams and Jeanloz, 1988), demonstrate the need for the
 264 *in situ* determination of the structure of silicate melts. The experimental
 265 difficulties associated with the *in situ* determination of liquid structures has
 266 resulted in very few studies possessing both viscosity and *in situ* structural
 267 data. Exceptions include the present study and Sakamaki et al. (2013), who
 268 measured the viscosity and structure of basaltic magma.

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

276 4.4. Geological Implications

277 Our results hold particular significance for FeO-rich planetary magmas
278 existing in reduced environments. Our experiments were carried out under
279 reducing conditions and the final sample composition was found to contain
280 $\text{Fe}^{3+}/\sum \text{Fe} \leq 0.01$ (Sanloup et al., 2013a). The present day Moon and Mars
281 are estimated to have high-mantle iron contents (up to 22 wt% FeO (Cahill
282 et al., 2009; Baratoux et al., 2011)) in a reducing environment (Sato et al.,
283 1973; Herd et al., 2002). fO_2 has been found to have an effect on melt vis-
284 cosity e.g. Liebske et al. (2003); Bouhifd et al. (2004); Chevrel et al. (2014)
285 all found a drop in silicate melt viscosity with a reduction in $\text{Fe}^{3+}/\sum \text{Fe}$.
286 This appears to be composition-dependent as only a slight decrease was ob-
287 served in the less polymerised basaltic compositions measured by Liebske
288 et al. (2003) and Bouhifd et al. (2004). Lacks et al. (2007) carried out molec-
289 ular dynamics simulations to calculate viscosity along the MgO-SiO₂ join to
290 investigate the effect of composition and pressure on transport properties.
291 At atmospheric pressure, viscosity was found to vary by more than 3 or-
292 ders of magnitude along the compositional join, however at pressures > 15
293 GPa, the viscosity varied by less than an order of magnitude over the entire
294 compositional range. If the FeO-SiO₂ system behaves in the same way, then
295 planetary magma viscosities will be particularly sensitive to FeO content at
296 lower pressures. Our results suggest that the increase in P along the magma
297 ocean adiabat will favour a decrease in melt viscosity of a FeO-rich magma,
298 and may be most important at upper mantle depths. Additionally, the vis-
299 cosity decrease may be particularly pronounced in more reducing conditions,
300 such as those considered to be present in Mars and the Moon. Bodies that

301 are less FeO rich (such as Mercury) may have a less pronounced negative
302 pressure effect (or it may not be present at all) and it is therefore worth
303 considering when modelling processes occurring in planetary magma oceans.

304 Due to the lack of data on silicate melts at high pressure, assumptions
305 about the viscosity of depolymerised melts at depth have often been made.
306 Solomatov and Stevenson (1993) assumed that the viscosity of depolymerised
307 melts would increase with depth due to closer interatomic spacing. Tonks
308 and Melosh (1990, 1993) assumed no pressure effect on silicate melt viscosity
309 in their global magma ocean model. Our results however, show that depoly-
310 merised silicate melts may exhibit a hitherto unexpected decrease in viscosity
311 at depth. Viscosity will have been an important influencing property on the
312 chemical evolution of the early terrestrial bodies due to the fact that convec-
313 tion (Davaille and Jaupart, 1993), crystal settling (Solomatov and Stevenson,
314 1993), cumulate overturn (Elkins-Tanton et al., 2003), and chemical diffusion
315 (Rubie et al., 2003) are much more efficient in low viscosity melts. However,
316 more work is needed to understand the properties of other silicate melts rel-
317 evant to magma ocean compositions across a larger pressure range. Whilst
318 the existence of a fayalitic magma ocean in a planetary body is unlikely, it
319 is nevertheless important to measure the properties of simple end-member
320 compositions so that we can begin to understand how different compositional
321 mixtures influence planetary magma viscosity and processes.

322 5. Conclusions

323 *In situ* falling sphere viscometry was performed on liquid fayalite (Fe_2SiO_4),
324 a highly depolymerised, Fe-rich silicate melt, up to 9.2 GPa and $\sim 1850^\circ\text{C}$.

325 This is the most depolymerised silicate melt studied so far, and the viscosity
326 was found to decrease by a factor of 2.5 over the measured pressure range.
327 It is likely that this decrease is a result of the increase in Fe-O coordination
328 with pressure (Sanloup et al., 2013a). In polymerised melts, the structural
329 transformation of tetrahedrally coordinated cations (such as Al^{3+}) to higher
330 species has often been cited as the cause of the anomalous viscosity behaviour
331 of silicate melts. Hitherto, it has often been assumed that depolymerised sil-
332 icate melts will not exhibit anomalous viscosity behaviour at depth. Our
333 results show that this assumption is not appropriate, and that the behaviour
334 of silicate melts at depth should be considered on an independent basis for
335 melts of different composition. This has important implications for models
336 of planetary differentiation. In particular, terrestrial bodies with high Fe
337 contents and reducing mantle conditions are likely to have had very mobile
338 melts at depth.

339 **Acknowledgments**

340 We thank C. Kenney-Benson for providing cell-assembly parts, J.W.E.
341 Drewitt for his assistance with data acquisition, electron microprobe analy-
342 ses and useful discussions during preparation of the manuscript, C. Hayward
343 for his help with electron microprobe analyses and R. Askew and J. Buckman
344 for their assistance with the scanning electron microscope. High-pressure ex-
345 periments were performed at HPCAT (Sector 16), Advanced Photon Source
346 (APS), Argonne National Laboratory. HPCAT operations are supported by
347 DOE-NNSA under Award No. DE-NA0001974 and DOE-BES under Award
348 No. DE-FG02-99ER45775, with partial instrumentation funding by NSF.

349 APS is supported by DOE-BES, under Contract No. DE-AC02-06CH11357.
350 This work was supported by the Engineering and Physical Sciences Research
351 Council and the European Research Council under the European Commu-
352 nity's Seventh Framework Programme (FP7/20072013 Grant Agreement No.
353 259649 to C.S.).

354 **References**

- 355 I. Kushiro, H. S. Yoder, B. O. Mysen, Viscosities of basalt and andesite melts
356 at high pressures, *Journal of Geophysical Research* 81 (1976) 6351–6356.
- 357 I. Kushiro, Changes in viscosity and structure of melt of $\text{NaAlSi}_2\text{O}_6$ compo-
358 sition at high pressures, *Journal of Geophysical Research* 81 (1976) 6347–
359 6350, doi:<http://dx.doi.org/10.1029/JB081i035p06347>.
- 360 A. Suzuki, E. Ohtani, H. Terasaki, K. Nishida, H. Hayashi, T. Sakamaki,
361 Y. Shibazaki, T. Kikegawa, Pressure and temperature dependence of the
362 viscosity of a $\text{NaAlSi}_2\text{O}_6$ melt, *Physics and Chemistry of Minerals* 38 (2011)
363 59–64, doi:<http://dx.doi.org/10.1007/s00269-010-0381-4>.
- 364 A. Suzuki, E. Ohtani, K. Funakoshi, H. Terasaki, T. Kubo, Viscosity of albite
365 melt at high pressure and temperature, *Physics of Chemistry and Minerals*
366 29 (2002) 159–165, doi:<http://dx.doi.org/10.1007/s00269-001-0216-4>.
- 367 M. Brearley, J. E. Dickinson, C. Scarfe, Pressure dependence of melt vis-
368 cosities on the join diopside-albite, *Geochimica et Cosmochimica Acta* 50
369 (1986) 2563–2570, doi:[http://dx.doi.org/10.1016/0016-7037\(86\)90210-3](http://dx.doi.org/10.1016/0016-7037(86)90210-3).

- 370 H. Taniguchi, Entropy dependence of viscosity and the glass-transition
371 temperature of melts in the system diopside-anorthite, *Contributions to Mineralogy and Petrology* 109 (1992) 295–303, doi:
372 <http://dx.doi.org/10.1007/BF00283319>.
- 374 J. E. Reid, A. Suzuki, K. Funakoshi, H. Terasaki, B. T. Poe, D. C. Rubie, E. Ohtani, The viscosity of $\text{CaMgSi}_2\text{O}_6$ liquid at pressures up to 13
375 GPa, *Physics of the Earth and Planetary Interiors* 139 (2003) 45–54, doi:
376 [http://dx.doi.org/10.1016/S0031-9201\(03\)00143-2](http://dx.doi.org/10.1016/S0031-9201(03)00143-2).
- 378 C. Liebske, B. Schmickler, H. Terasaki, B. T. Poe, A. Suzuki, K. Funakoshi,
379 R. Ando, D. C. Rubie, Viscosity of peridotite liquid up to 13 GPa: Implications for magma ocean viscosities, *Earth and Planetary Science Letters*
380 240 (2005) 589–604, doi:<http://dx.doi.org/10.1016/j.epsl.2005.10.004>.
- 382 M. S. Robinson, G. J. Taylor, Ferrous oxide in Mercury’s crust and
383 mantle, *Meteoritics and Planetary Science* 36 (2001) 841–847, doi:
384 <http://dx.doi.org/10.1111/j.1945-5100.2001.tb01921.x>.
- 385 J. T. S. Cahill, P. G. Lucey, M. A. Wieczorek, Compositional variations
386 of the lunar crust: results from radiative transfer modeling of central
387 peak spectra, *Journal of Geophysical Research* 114 (2009) E09001, doi:
388 <http://dx.doi.org/10.1029/2008JE003282>.
- 389 D. Baratoux, M. J. Toplis, M. Monnereau, O. Gasnault, Thermal history of
390 Mars inferred from orbital geochemistry of volcanic provinces, *Nature* 472
391 (2011) 338–342, doi:<http://dx.doi.org/10.1038/nature09903>.

- 392 C. Liebske, H. Behrens, F. Holtz, R. A. Lange, The influence of pressure
393 and composition on the viscosity of andesitic melts, *Geochimica et Cos-*
394 *mochimica Acta* 67 (2003) 473–485, doi:[http://dx.doi.org/10.1016/S0016-](http://dx.doi.org/10.1016/S0016-7037(02)01139-0)
395 [7037\(02\)01139-0](http://dx.doi.org/10.1016/S0016-7037(02)01139-0).
- 396 M. A. Bouhifd, P. Richet, P. Besson, M. Roskosz, J. Ingrin, Redox
397 state, microstructure and viscosity of a partially crystallized basalt
398 melt, *Earth and Planetary Science Letters* 218 (2004) 31–44, doi:
399 [http://dx.doi.org/10.1016/S0012-821X\(03\)00641-1](http://dx.doi.org/10.1016/S0012-821X(03)00641-1).
- 400 M. O. Chevrel, D. Baratoux, K. Hess, D. B. Dingwell, Viscous
401 flow behavior of tholeiitic and alkaline Fe-rich martian basalts,
402 *Geochimica et Cosmochimica Acta* 124 (2014) 348–365, doi:
403 <http://dx.doi.org/10.1016/j.gca.2013.08.026>.
- 404 B. B. Karki, L. P. Stixrude, Viscosity of MgSiO_3 at Earth’s mantle conditions:
405 implications for an early magma ocean, *Science* 328 (2010) 740–742, doi:
406 <http://dx.doi.org/10.1126/science.1188327>.
- 407 D. Ghosh, B. Karki, Diffusion and viscosity of Mg_2SiO_4 liquid at high pres-
408 sure from first-principles simulations, *Geochimica et Cosmochimica Acta*
409 75 (2011) 4591–4600, doi:<http://dx.doi.org/10.1016/j.gca.2011.05.030>.
- 410 C. Sanloup, J. W. E. Drewitt, C. Crépeau, Y. Kono, C. Park, C. McCam-
411 mon, L. Hennem, S. Brassamin, A. Bychkov, Structure and density of
412 molten fayalite at high pressure, *Geochimica et Cosmochimica Acta* 118
413 (2013a) 118–128, doi:<http://dx.doi.org/10.1016/j.gca.2013.05.012>.

- 414 T. Sakamaki, Y. Wang, C. Park, T. Yu, G. Shen, Structure of jadeite melt
415 at high pressures up to 4.9 GPa, *Journal of Applied Physics* 111 (2012)
416 112623, doi:<http://dx.doi.org/10.1063/1.4726246>.
- 417 Y. Kono, T. Irifune, Y. Higo, T. Inoue, A. Barnhoorn, *P-V-T* relation
418 of MgO derived by simultaneous elastic wave velocity and in situ X-ray
419 measurements: A new pressure scale for the mantle transition region,
420 *Physics of the Earth and Planetary Interiors* 183 (2010) 196–211, doi:
421 <http://dx.doi.org/10.1016/j.pepi.2010.03.010>.
- 422 Y. Kono, C. Park, C. Kenney-Benson, G. Shen, Y. Wang, Toward comprehen-
423 sive studies of liquids at high pressures and high temperatures: Combined
424 structure, elastic wave velocity, and viscosity measurements in the Paris
425 Edinburgh cell, *Physics of the Earth and Planetary Interiors* 228 (2014)
426 269–280, doi:<http://dx.doi.org/10.1016/j.pepi.2013.09.006>.
- 427 Y. Kono, C. Kenney-Benson, C. Park, G. Shen, Y. Wang, Anomaly in the
428 viscosity of liquid KCl at high pressures, *Physical Review B* 87 (2013)
429 024302, doi:<http://dx.doi.org/10.1103/PhysRevB.87.024302>.
- 430 H. Faxén, Der Widerstand gegen die Bewegung einer starren Kugel in
431 einer zähen Flüssigkeit, die zwischen zwei parallelen ebenen Wänden
432 eingeschlossen ist, *Annalen der Physik* 373 (1922) 89–119, doi:
433 <http://dx.doi.org/10.1002/andp.19223731003>.
- 434 Y. K. Vohra, S. J. Duclos, A. L. Ruoff, High-pressure x-ray diffraction studies
435 on rhenium up to 216 GPa (2.16 Mbar), *Physical Review B* 36 (1987) 9790–
436 9792, doi:<http://dx.doi.org/10.1103/PhysRevB.36.9790>.

- 437 C. W. Thomas, Q. Liu, C. B. Agee, P. D. Asimow, R. A. Lange, Multi-
 438 technique equation of state for Fe_2SiO_4 melt and the density of Fe-bearing
 439 silicate melts from 0 to 161 GPa, *Journal of Geophysical Research: Solid*
 440 *Earth* 117 (2012) B10206, doi:<http://dx.doi.org/10.1029/2012JB009403>.
- 441 G. Q. Chen, T. J. Ahrens, E. M. Stolper, Shock-wave equation of state of
 442 molten and solid fayalite, *Physics of the Earth and Planetary Interiors* 134
 443 (2002) 35–52, doi:[http://dx.doi.org/10.1016/S0031-9201\(02\)00080-8](http://dx.doi.org/10.1016/S0031-9201(02)00080-8).
- 444 C. B. Agee, Isothermal compression of molten Fe_2SiO_4 , *Geophysical Research*
 445 *Letters* 19 (1992) 1169–1172, doi:<http://dx.doi.org/10.1029/92GL01064>.
- 446 M. Brizard, M. Megharfi, C. Verdier, Absolute falling-ball viscometer: eval-
 447 uation of measurement uncertainty, *Metrologia* 42 (2005) 298–303, doi:
 448 <http://dx.doi.org/10.1088/0026-1394/42/4/015>.
- 449 R. C. Kerr, J. R. Lister, The effects of shape on crystal settling and on the
 450 rheology of magmas, *The Journal of Geology* 99 (1991) 457–467.
- 451 Y. K. Shiraishi, K. Ikeda, A. Tamura, T. Saitô, On the viscosity and density
 452 of the molten FeO-SiO_2 system, *Transactions of the Japan Institute of*
 453 *Metals* 19 (1978) 264–274.
- 454 S. Kohara, K. Suzuya, K. Takeuchi, C. K. Loong, M. Grimsditch,
 455 J. K. R. Weber, J. A. Tangeman, T. S. Key, Glass formation at the
 456 limit of insufficient network formers, *Science* 303 (2004) 1649–1652, doi:
 457 <http://dx.doi.org/10.1126/science.1095047>.
- 458 H. S. Waff, Pressure-induced coordination changes in magmatic liquids, *Geo-*
 459 *physical Research Letters* 2 (1975) 193–196.

- 460 T. Sato, N. Funamori, High-pressure structural transformation of SiO_2
461 glass up to 100 GPa, *Physical Review B* 82 (2010) 184102, doi:
462 <http://dx.doi.org/10.1103/PhysRevB.82.184102>.
- 463 C. Sanloup, J. W. E. Drewitt, Z. Konôpková, P. Dalladay-Simpson, D. M.
464 Morton, N. Rai, W. van Westrenen, W. Morgenroth, Structural change
465 in molten basalt at deep mantle conditions, *Nature* 503 (2013b) 104–107,
466 doi:<http://dx.doi.org/10.1038/nature12668>.
- 467 D. Giordano, J. K. Russell, D. B. Dingwell, Viscosity of magmatic liquids:
468 A model, *Earth and Planetary Science Letters* 271 (2008) 123–134, doi:
469 <http://dx.doi.org/10.1016/j.epsl.2008.03.038>.
- 470 J. Barrat, J. Badro, P. Gillet, A strong to fragile transition in a
471 model of liquid silica, *Molecular Simulation* 20 (1997) 17–25, doi:
472 <http://dx.doi.org/10.1080/08927029708024165>.
- 473 M. Micoulaut, M. Bauchy, Anomalies of the first sharp diffraction
474 peak in network glasses: Evidence for correlations with dynamic and
475 rigidity properties, *Physica Status Solidi B* 250 (2013) 976–982, doi:
476 <http://dx.doi.org/10.1002/pssb.201248512>.
- 477 I. Kushiro, Phase transformation in silicate melts under upper mantle condi-
478 tions, in: M.H. Manghnani and S. Akimoto (Ed.), *High-Pressure Research*
479 *Applications in Geophysics*, Academic, 25–37, 1977.
- 480 J. R. Allwardt, J. F. Stebbins, H. Terasaki, L. Du, D. J. Frost, A. C. With-
481 ers, M. M. Hirschmann, A. Suzuki, O. E., Effect of structural transitions
482 on properties of high-pressure silicate melts: ^{27}Al NMR, glass densities,

483 and melt viscosities, *American Mineralogist* 92 (2007) 1093–1104, doi:
 484 <http://dx.doi.org/10.2138/am.2007.2530>.

485 B. T. Poe, C. Romano, N. Zotov, G. Cibin, A. Marcelli, Compression mecha-
 486 nisms in aluminosilicate melts: Raman and XANES spectroscopy of glasses
 487 quenched from pressures up to 10 GPa, *Chemical Geology* 174 (2001) 21–
 488 31, doi:[http://dx.doi.org/10.1016/S0009-2541\(00\)00304-1](http://dx.doi.org/10.1016/S0009-2541(00)00304-1).

489 J. W. P. Schmelzer, E. D. Zanotto, V. M. Fokin, Pressure dependence
 490 of viscosity, *The Journal of Chemical Physics* 122 (2005) 074511, doi:
 491 <http://dx.doi.org/10.1063/1.1851510>.

492 P. F. McMillan, M. C. Wilding, High pressure effects on liquid viscosity and
 493 glass transition behaviour, polyamorphic phase transitions and structural
 494 properties of glasses and liquids, *Journal of Non-Crystalline Solids* 355
 495 (2009) 722–732, doi:<http://dx.doi.org/10.1016/j.jnoncrysol.2009.01.036>.

496 M. Bauchy, B. Guillot, M. Micoulaut, N. Sator, Viscosity and
 497 viscosity anomalies of model silicates and magmas: A numer-
 498 ical investigation, *Chemical Geology* 346 (2013) 47–56, doi:
 499 <http://dx.doi.org/10.1016/j.chemgeo.2012.08.035>.

500 Q. Williams, R. Jeanloz, Spectroscopic evidence for pressure-induced coor-
 501 dination changes in silicate glasses and melts, *Science* 239 (1988) 902–905,
 502 doi:<http://dx.doi.org/10.1126/science.239.4842.902>.

503 T. Sakamaki, A. Suzuki, E. Ohtani, H. Terasaki, S. Urakawa, Y. Katayama,
 504 K. Funakoshi, Y. Wang, J. W. Hernlund, M. D. Ballmer, Pondered melt

505 at the boundary between the lithosphere and asthenosphere, *Nature Geo-*
506 *science* 6 (2013) 1041–1044, doi:<http://dx.doi.org/10.1038/ngeo1982>.

507 M. Sato, N. L. Hickling, J. E. McLane, Oxygen fugacity values of Apollo 12,
508 14 and 15 lunar samples and reduced state of lunar magmas, *Proceedings*
509 *of the Lunar Science Conference* 4 (1973) 1061–1079.

510 C. D. K. Herd, L. E. Borg, J. H. Jones, J. J. Papike, Oxygen fugac-
511 ity and geochemical variations in the martian basalts: implications for
512 martian basalt petrogenesis and the oxidation state of the upper mantle
513 of Mars, *Geochimica et Cosmochimica Acta* 66 (2002) 2025–2036, doi:
514 [http://dx.doi.org/10.1016/S0016-7037\(02\)00828-1](http://dx.doi.org/10.1016/S0016-7037(02)00828-1).

515 D. J. Lacks, D. B. Rear, J. A. Van Orman, Molecular dynamics in-
516 vestigation of viscosity, chemical diffusivities and partial molar vol-
517 umes of liquids along the MgO–SiO₂ join as functions of pres-
518 sure, *Geochimica et Cosmochimica Acta* 71 (2007) 1312–1323, doi:
519 <http://dx.doi.org/10.1016/j.gca.2006.11.030>.

520 V. Solomatov, D. Stevenson, Suspension in convective layers and style of dif-
521 ferentiation of a terrestrial magma ocean, *Journal of geophysical Research*
522 98 (1993) 5375–5390, doi:<http://dx.doi.org/10.1029/92JE02948>.

523 W. B. Tonks, H. J. Melosh, The physics of crystal settling and suspension in
524 a turbulent magma ocean, in: N.E. Newsom and J.H. Jones (Ed.), *Origin*
525 *of the Earth*, Oxford University Press, New York, 151–174, 1990.

526 W. B. Tonks, H. J. Melosh, Magma ocean formation due to giant

527 impacts, *Journal of geophysical Research* 98 (1993) 5319–5333, doi:
528 <http://dx.doi.org/10.1029/92JE02726>.

529 A. Davaille, C. Jaupart, Thermal convection in lava lakes,
530 *Geophysical Research Letters* 20 (1993) 1827–1830, doi:
531 <http://dx.doi.org/10.1029/93GL02008>.

532 L. T. Elkins-Tanton, E. M. Parmentier, P. C. Hess, Magma ocean fractional
533 crystallization and cumulate overturn in terrestrial planets: Implications
534 for Mars, *Meteoritics and Planetary Science* 38 (2003) 1753–1771, doi:
535 <http://dx.doi.org/10.1111/j.1945-5100.2003.tb00013.x>.

536 D. C. Rubie, H. J. Melosh, J. E. Reid, C. Liebske, K. Righter,
537 Mechanisms of metal-silicate equilibration in the terrestrial magma
538 ocean, *Earth and Planetary Science Letters* 205 (2003) 239–255, doi:
539 [http://dx.doi.org/10.1016/S0012-821X\(02\)01044-0](http://dx.doi.org/10.1016/S0012-821X(02)01044-0).