Towards evaluating the viscosity of the Earth’s outer core:  
An experimental high pressure study of liquid Fe-S (8.5 wt.% S)

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[1] In-situ high pressure viscosity measurements, using synchrotron X-ray radiography, have been carried out on liquid Fe-S (8.5 wt.% S) at pressures up to 6 GPa and at 1823 K. Here we show that (i) the effect of pressure on the isothermal viscosity is substantial, with an apparent activation volume of 5.8 cm³/mol; and (ii) viscosity is constant along the pressure dependent melting boundary. Assuming the independence of viscosity along the melting boundary up to core pressures, our results yield a viscosity boundary.  

[2] The viscosity of the Earth’s outer core, which is composed of iron with some light alloying elements [Poirier, 1994], is an essential property necessary to understand and model core processes such as the geodynamo and heat flow through the outer core. However, current viscosity estimates of outer core liquids are poorly constrained [Secco, 1995]. Due to the experimental challenges in measuring viscosity of liquids under high pressure, current techniques rely on clever modifications of the traditional Stokes’ viscosity method. This involves measuring the velocity with which a probe sphere moves through a pressurized melt, and employing Stokes’ law to determine the melt viscosity. Previous experimental measurements had difficulties in resolving sphere velocity (quench and probe, electro-detection) [Secco, 1994; Leblanc and Secco, 1996] or suffered from swift reaction between the probe sphere and the sample (X-ray radiography) [Dobson et al., 2000; Terasaki et al., 2001]. We employ a synchrotron X-ray radiographic method to image, in-situ, the velocity of the probe sphere [Kanzaki et al., 1997], combined with a novel technique of sphere shielding to eliminate all reaction between sphere and melt [Secco et al., 2001].  

[3] We chose Fe-S (8.5 wt.% S) as a possible candidate outer core composition based on seismological, geochemical and mineral physics constraints [Poirier, 1994]. Samples were synthesized at high pressure and temperature, prior to viscosity experiments, from mixtures of FeS and Fe (99.9% and 99.99% purity, respectively). In order to isolate the siderophile Pt probe sphere from the sample, a technique was developed to produce composite spheres made of a Pt core surrounded by a ruby mantle. High pressure and temperature, in-situ, viscosity experiments were performed in a 250-ton DIA-type high pressure apparatus at beamline 13 BM-D, Advanced Photon Source, Argonne National Laboratory [Rivers et al., 1998]. Experimental temperatures were monitored with a W3%Re-W25%Re thermocouple. Temperature gradients within the experimental cell were estimated to be ±50 K/mm and pressure was determined using the equation of state for MgO [Utsumi et al., 1998].  

[4] Sample viscosity was calculated from terminal sphere velocity using a corrected form of Stokes’ equation [Faxen, 1925; Kingery, 1959]. Densities of the composite sphere and sample at high pressure and temperature were determined by applying the high temperature 3rd order Birch-Murnaghan equation of state for ruby, Pt and Fe-S (8.5 wt.% S) with all thermelastic parameters available in the literature [Sanloup et al., 2000; Fei, 1995; Anderson and Isaak, 1995; Nasch and Steinemann, 1995; Holmes et al., 1989; Kaitura and Toguri, 1979].  

3. Results and Discussion

[5] Figure 1a displays a real-time sequence of images showing a composite sphere, with high X-ray absorption, rising through the sample melt at 4.7 GPa and 1823 K, with a time interval between frames of 430 ms. Dark vertical bars bracketing the lighter sample region are the tungsten carbide (WC) anvils of the press which frame the window into the central third of the high pressure liquid sample. The dark Pt core is clearly visible, and the ruby mantle appears as a light “halo” surrounding the core. The ruby mantle is an effective barrier between the melt and the platinum core, as it remains intact during the length of the experiment. All post-run samples, examined by electron probe micro-analysis, reveal uniform sample composition and no reaction between the sample, Pt core and sample container. The displacement (Δ) vs. time (t) curve of the ascent of the sphere through the melt (Figure 1b) shows the acceleration (stage I), terminal velocity (II) and deceleration (III) phases of sphere motion. The terminal velocity of the sphere, as shown by the maximum of the velocity plot (dΔ/dt) in Figures 1b and 1c, was used to calculate sample viscosity. The pressure dependence of viscosity, up to 6 GPa, is plotted in Figure 2 (solid squares). The effect of pressure on the isothermal viscosity is substantial and can be quantified through the apparent activation volume of viscosity (ΔV//), defined as:

\[
\Delta V// = RT(\partial \ln \eta / \partial P)_T
\]

(1)

where \( R \) is the universal gas constant, \( T \) is temperature and \( P \) is pressure. The error associated with the lowest pressure viscosity value was too large for it to be used to calculate the apparent activation volume and therefore in all fitting procedures it was excluded. Apparent activation volume obtained from a linear fit to the data is 5.8 cm³/mol.

[6] To date, there are only a few studies in which apparent activation parameters for Fe-FeS liquid transport properties have
been determined. Dobson et al. [2000] and Terasaki et al. [2001] have recently measured the viscosity of Fe-FeS liquids, using a similar technique as we employed but with unshielded Pt, Au, W and Ir probe spheres. Although the magnitude of their measurements ($10^{-2} - 10^{-3}$ Pa s) agree with this study, reaction between the sphere and melt, and incongruent melting of the FeS phase in their samples limits their ability to accurately determine apparent activation parameters. When examining pure FeS, which is free from incongruent melting, Dobson et al. find a negligible effect of pressure on viscosity and an apparent activation energy of 250 kJ/mol. We note that a large effect of temperature and a small effect of pressure on viscosity is thermodynamically unlikely. Terasaki et al. measure an apparent activation energy and volume of 30 kJ/mol and 1.5 cm$^3$/mol respectively, for Fe-FeS, which indicates that the effect of pressure on viscosity cannot be ignored. It is interesting to point out that a further examination of their data, including only values that are measured in what can only be a homogeneous melt, yields an apparent activation volume of 6.7 cm$^3$/mol. Leblanc and Secco [1996], employing an in-situ electrical-detection technique, reported
viscosity data for Fe-S (27 wt.% S) in a range of pressure and temperature similar to this study. The magnitude of the viscosity values they found was greater than we report, however we expect their derivatives of viscosity, with respect to temperature and pressure, to be acceptable. They found large values for both derivatives.

[7] Figure 3 illustrates all existing literature values of apparent activation energy of viscosity \(Q_v\) and diffusion \(Q_d\) of Fe-FeS as a function of pressure, with the exception of \(Q_v\), determined by Terasaki et al. [2000], in which apparent activation energy was determined from individual viscosity experiments over a wide pressure range (1.5–5.5 GPa, solid diamond) by Dobson et al. [2000], the majority of the values suggests a negligible effect of pressure and composition on \(Q_v\) and \(Q_d\), and cluster about a value of 260 kJ/mol. The independence of apparent activation energy on sulfur content (and on pressure, as illustrated in Figure 3) implies that large viscous flow units, which were previously postulated as a possible cause of high viscosity of Fe-FeS melts under pressure in an early study [Leblanc and Secco, 1996] can be ruled out. As a corollary, this suggests that Fe is the dominant component controlling the viscosity. Furthermore, recent experiments of Fe self diffusion in FeS(eutectic) liquids [Dobson, 2000], in which apparent activation energy was determined and apparent activation volume was approximated (~9 cm³/mol), suggest that Fe is linked more strongly to controlling diffusion than S. Through the Stokes-Einstein equation:

\[
D \eta = k_BT/2\pi a
\]

which describes the recently examined relationship [Dobson et al., 2001] between the diffusivity, \(D\), of a particle with diameter \(a\) and the viscosity of the surrounding liquid (where \(k_B\) is the Boltzmann constant), a comparison between the results of this study and diffusion data is feasible. In agreement with the results of our measurements, apparent activation volume for diffusion indicates a large pressure effect. Similarly, first-principles and molecular dynamics simulation studies have shown that S and Ni concentrations have little effect on the viscosity of liquid Fe under pressure, supporting the dominance of Fe in controlling liquid viscosity [Alfé and Gillan, 1998; Zhang and Guo, 2000].

4. Geophysical Implications

[8] Acknowledging that variations in S content, within the range of low S, has nearly constant effect on the activated energy of viscosity and diffusion we accept the apparent activation energy of viscosity from LeBlanc and Secco, and Dobson et al., and diffusion from Dobson as representative values for Fe-S (8.5 wt.% S) [Leblanc and Secco, 1996; Dobson et al., 2000; Dobson, 2000]. Poirier demonstrated that activation volume is related to activation energy [Poirier, 1988] through the following equation:

\[
\Delta V^* = gR(dTm/dP) = Q_A(d\ln Tm/dP)
\]

where \(Q_A\) is apparent activation energy and \(g = Q/RT_m\). Using the melting data for Fe-S (8.5 wt.% S) [Brett and Bell, 1969; Fei et al., 1997] \((dT_m/dP = 30\text{ K/GPa})\), the apparent activation volumes, calculated with equation (3) using the afore-mentioned apparent activation energies, are given in Table 1. In addition, using an atomic volume at the melting temperature of \(9.85 \times 10^{-6} \text{ m}^3\) [Kaiura and Toguri, 1979], the calculated and measured apparent activation volumes, within the error, are ~40% of the atomic volume (Table 1). The self-consistency of these values demonstrates that the dynamic fluid properties of Fe-S (8.5 wt.% S) can be scaled to the pressure dependent melting temperature. This allows the isothermal viscosity values at 1823 K, presented in Figure 2, to be corrected to the melting temperature using an apparent activation energy of 260 kJ/mol. The corrected data points, which are plotted in Figure 2 as the open triangles, fall along a horizontal line and show that viscosity is constant along the melting boundary.

[9] The coefficient between the apparent activation energies of transport processes and the melting temperature, \(g\) (equation 3), determined by this study \((g \approx 17)\) is much higher than typical liquid metals values \((g \approx 3)\) [Poirier, 1988] and more consistent with that of solid metals. In both solids and liquids, transport processes can be described in terms of vacancy formation and migration volume. While in solids both factors control transport, the high concentration of vacancies in liquids regulates transport control to migration volume, where migration volume is one tenth the activation volume [Poirier, 1988]. Nasch et al. [1997] have demonstrated anomalous behavior of sound velocity in liquid FeNi(5 wt.% Ni)S(10 wt.% S). Assuming that Ni has little effect on the bulk properties of Fe, the mechanism by which the addition of 10 wt.% S gives rise to anomalous behavior of sound velocity could also increase the migration volume of Fe-FeS resulting in \(g\) values approaching those of solids. In a similar study to that which we present here, Rutter et al. [submitted] have measured the apparent activation

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**Table 1.** Experimental and Semi-Empirical Determination of Apparent Activation Volume of Viscosity and Diffusion for Liquid Fe-S (8.5 wt.%S) at 1823 K

<table>
<thead>
<tr>
<th>Property</th>
<th>Sulfur Content (wt.%S)</th>
<th>Determination Method</th>
<th>Apparent Activation Volume (cm³/mol)</th>
<th>Fraction of Atomic Volume</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>8.5</td>
<td>Measured</td>
<td>5.8</td>
<td>0.59 ± 0.24</td>
<td>this study</td>
</tr>
<tr>
<td>Viscosity</td>
<td>27</td>
<td>Calculated</td>
<td>4.03</td>
<td>0.40 ± 0.12</td>
<td>Leblanc and Secco [1996]</td>
</tr>
<tr>
<td>Viscosity</td>
<td>33</td>
<td>Calculated</td>
<td>4.28</td>
<td>0.43 ± 0.03</td>
<td>Dobson et al. [2000]</td>
</tr>
<tr>
<td>Diffusion</td>
<td>27</td>
<td>Calculated</td>
<td>4.23</td>
<td>0.42 ± 0.04</td>
<td>Dobson [2000]</td>
</tr>
</tbody>
</table>

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**Figure 4.** Viscosity profile across the Earth’s outer core. Solid line is calculated with \(g = 17.3\) from this study, thick dashed line is calculated with \(g = 3\) [Poirier, 1988].
volume for pure liquid Fe and find remarkable agreement with the semi-empirical framework for transport in liquid metals, ruling out the possibility that the result for Fe-S (8.5 wt.% S) is an experimental artifact.

[10] The effect of pressure on viscosity can be related to the pressure dependent melting temperature as follows [Poirier, 1988]:

$$\eta = \eta_0 \exp(gT_m/T)$$

(4)

Since the inner core boundary (ICB) of the earth is a solidification front, our experimental results can be applied directly, without extrapolation, to the ICB, giving a viscosity of $1.6 \times 10^{-2}$ Pa s. Using the viscosity for the outer core at the ICB and $g \approx 17$ (found in this study), and $T_m = 4766$ K and $dT_m/dP = 10$ K/GPa [Poirier, 1988], and assuming that temperature varies adiabatically in the core, the viscosity profile of the outer core can then be re-evaluated using equation (4) as shown in Figure 4. The addition of S into the melt causes the viscosity to decrease to a value close to two orders of magnitude smaller at the core mantle boundary than the previous estimate based on the viscosity of pure Fe.

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References


Dobson, D. P., $^{57}$Fe and Co tracer diffusion in liquid Fe-FeS at 2 and 5 GPa, Phys. Earth Planet. Inter., 120, 137, 2000.

Dobson, D. P., et al., In situ measurement of viscosity of liquids in the Fe-FeS system at high pressures and temperatures, Amer. Min., 85, 1838, 2000.


Faxen, H., Gegenseitige einwirkung zweier kugelen, die in einer zähnen flüssigkeit fallen, Ark. Mat. Astron. Fys., 19, 1, 1925.


Fei, Y., C. M. Bertka, and L. W. Finger, High-pressure iron-sulfur compound, FeS$_2$, and melting relations in the Fe-FeS system, Science, 275, 1621, 1997.


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