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

Michael D. Rutter,[1] Richard A. Secco,[1] Takeyuki Uchida,[2] Liu Hongjian,[1] Yanbin Wang,[2] Mark L. Rivers,[2] and Stephen R. Sutton[2]

[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 cm^3/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 for the Earth's outer core, at the inner core boundary, of 1.6×10^{-2} Pa s. On this basis, we present a revised viscosity profile across the outer core. *INDEX TERMS:* 3924 Mineral Physics: High-pressure behavior; 1507 Geomagnetism and Paleomagnetism: Core processes (8115); 8124 Tectonophysics: Earth's interior—composition and state (8105)

1. Introduction

[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' viscometry 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].

2. Experimental

[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 thermo-elastic parameters available in the literature [*Sanloup et al.*, 2000; *Fei*, 1995; *Anderson and Isaak*, 1995; *Nasch and Steinemann*, 1995; *Holmes et al.*, 1989; *Kaiura 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 (*D*) 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 (*dD/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_η^*), defined as:

$$\Delta V_\eta^* = RT(\partial \ln \eta / \partial P)_T \qquad (1)$$

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 cm^3/mol.

[6] To date, there are only a few studies in which apparent activation parameters for Fe-FeS liquid transport properties have
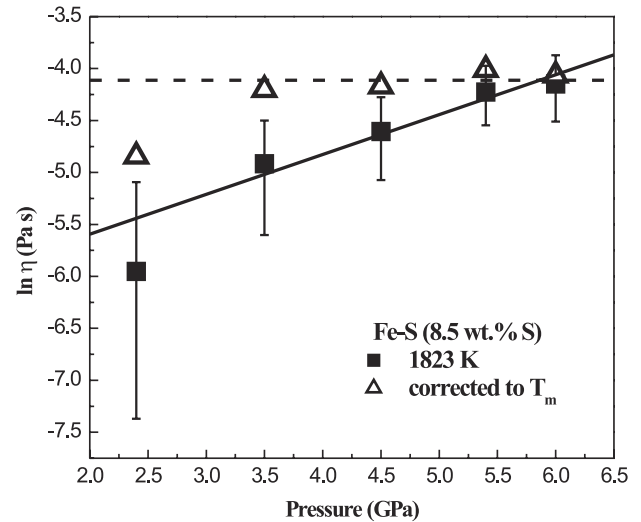
---
[1]Department of Earth Sciences, University of Western Ontario, London, Ontario, Canada.
[2]Consortium for Advanced Radiation Sources, The University of Chicago, Chicago, Il, USA.
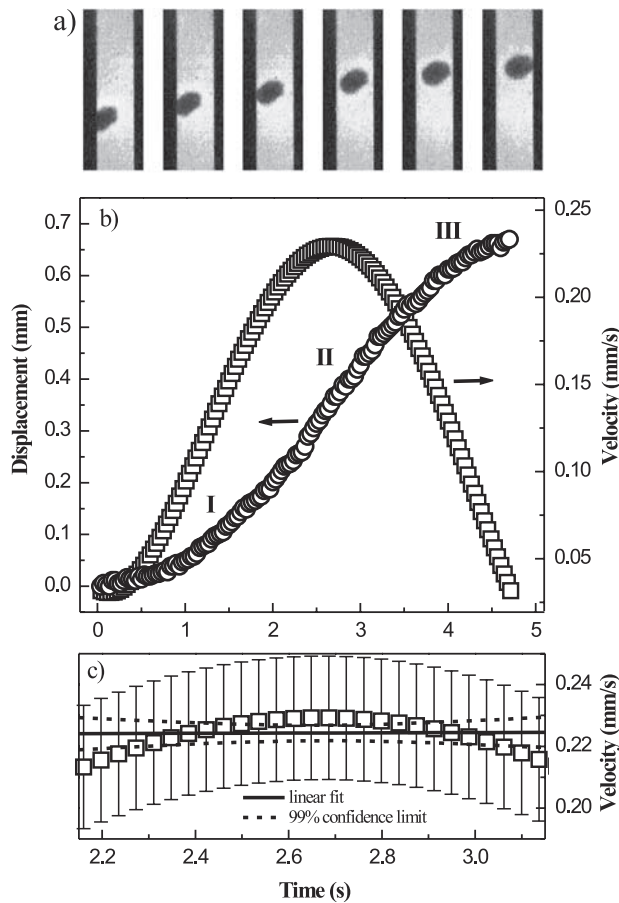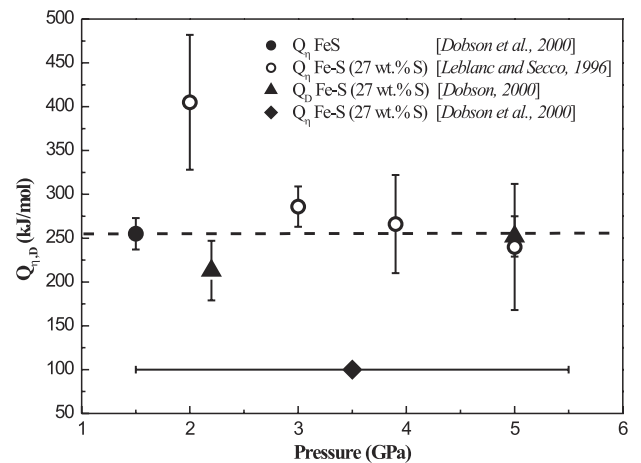
Figure 1. (a) Real-time, synchrotron X-ray radiographic, density contrast images, at 4.7 GPa and 1823 K, of a Pt-ruby sphere rising through an Fe-S (8.5 wt.% S) melt. Elapsed time between frames is 430 msec. Pt core is visible as a dark circle which rises as frames advance. The ruby mantle appears as a bright "halo" surrounding the Pt core. While small deviations from sphericity of the Pt core are visible, they are due to irregularities in the pit machined in the ruby mantle. Post-run sectioned pressure cell analysis indicates that the ruby mantle maintains its sphericity under pressure. Dark bands bracketing the sample are the WC anvils. (b) Displacement vs. time curve (left ordinate axis) for rising composite sphere. Open circles indicate measured displacement from real-time radiographic images. (I) indicates the acceleration phase, (II) the terminal velocity phase, and (III) the deceleration phase of the sphere's flight. Open squares indicate the velocity curve (right ordinate axis) determined from the derivative of a polynomial fit of the displacement vs. time data. (c) Expanded view of the terminal velocity section of the velocity curve. Within the error of the measurement, all the data shown represent a velocity plateau (ie. velocity is constant). Curvature of the data is an artifact of the polynomial fit to the data.

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 cm³/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 cm³/mol. *Leblanc and Secco* [1996], employing an *in-situ* electrical-detection technique, reported

Figure 2. Arrhenian plot of viscosity as a function of pressure for liquid Fe-S (8.5 wt.% S). Solid squares indicate viscosity values measured isothermally at 1823 K. Solid black line is the linear fit to the data whose slope gives the apparent activation volume (r = 0.95). Open triangles are viscosity values corrected to the melting temperature (T_m). Dashed line is the linear fit to the corrected viscosity values with a zero slope. Intersection of the dashed line with the y-axis gives a viscosity along the melting boundary of 1.6×10^{-2} Pa s.

Figure 3. Measured apparent activation energy of viscosity (Q_η) and diffusion (Q_D), for Fe-FeS liquids, as a function of pressure. The solid circle is the Q_η for FeS [*Dobson et al.*, 2000], open circles are the Q_η values for Fe-S (27 wt.% S) [*Leblanc and Secco*, 1996], solid triangles are the Q_D values for Fe-S (27 wt.% S) [*Dobson*, 2000] and the solid diamond is the Q_η for Fe-S (27 wt.% S) [*Dobson et al.*, 2000]. Horizontal dashed line is the Q_η (260 kJ/mol) used to correct the isothermal viscosity values in this study to the melting boundary.

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

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

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_η) and diffusion (Q_D) of Fe-FeS as a function of pressure, with the exception of Q_η determined by Terasaki et al. Eliminating the datum derived 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_η 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:

$$D\eta = k_B T / 2\pi a \qquad (2)$$

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 concentration have little effect on the viscosity of liquid Fe under pressure, supporting the dominance of Fe in controlling liquid viscosity [*Alfè 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:

$$\Delta V_\eta^* = gR(dT_m/dP) = Q_\eta(d \ln T_m/dP) \qquad (3)$$

where Q_η 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 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 × 10^{-6} m³ [*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 relegates 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
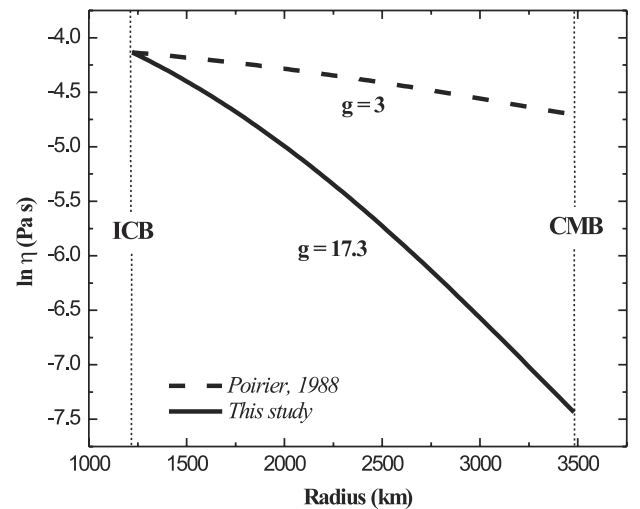
Figure 4. Viscosity profile across the Earth's outer core. Solid line is calculated with g = 17.3 from this study, thick dashed line is calculated with g = 3 [*Poirier*, 1988].

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]:

$$\eta = \eta_0 \exp(gT_m/T) \tag{4}$$

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 1.6×10^{-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.

References

Alfè, D., and M. J. Gillan, First-principles simulations of liquid Fe-S under Earth's core conditions, *Phys. Rev. B*, *58*(13), 8248, 1998.

Anderson, O. L. and D. G. Isaak, Elastic constans of mantle minerals at high temperature, in *Mineral Physics and Crystallography Handbook of Physical Constants*, edited by T. J. Ahrens, pp. 64–96, American Geophysical Union, Washington, 1995.

Brett, R., and P. M. Bell, Melting relations in the Fe-rich portion of the system Fe-FeS at 30 kb pressure, *Earth Planet. Sci. Lett.*, *6*, 479, 1969.

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.

Dobson, D. P., J. P. Brodholt, L. Vocadlo, and W. A. Crichton, Experimental verification of the Stokes-Einstein relation in liquid Fe-FeS at 5 GPa, *Mol. Phys.*, *99*(10), 773, 2001.

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

Fei, Y., Thermal expansion, in *Handbook of Physical Constants*, edited by T. J. Ahrens, pp. 29–43, American Geophysical Union, Washington, 1995.

Fei, Y., C. M. Bertka, and L. W. Finger, High-pressure iron-sulfur compound, Fe_3S_2, and melting relations in the Fe-FeS system, *Science*, *275*, 1621, 1997.

Holmes, N. C., J. A. Moriarty, G. R. Gathers, and W. J. Nellis, The equation of state of platinum to 660 GPa (6.6 Mbar), *J. Appl. Phys.*, *66*(7), 2962, 1989.

Kaiura, G. H., and J. M. Toguri, Densities of the molten FeS, FeS-Cu_2S and Fe-S-O systems-utilizing a bottom-balance Archimedean technique, *Can. Met. Quart.*, *18*, 155, 1979.

Kanzaki, M., et al., A new technique to measure the viscosity and density of silicate melts at high pressure, in *High Pressure Research in Mineral Physics*, edited by M. H. Manghnani, and Y. Syono, pp. 195–200, American Geophysical Union, Washington, 1997.

Kingery, W. D., Property Measurements at High Temperature, John Wiley and Sons Inc., New York, 1959.

Leblanc, G. E., and R. A. Secco, Viscosity of an Fe-S liquid up to 1300°C and 5 GPa, *Geophys. Res. Lett.*, *23*(3), 213, 1996.

Nasch, P. M., and S. G. Steinemann, Density and thermal expansion of molten manganese, iron, nickel, copper, aluminum and tin by means of the gamma-ray attenuation technique, *Phys. Chem. Liq.*, *29*, 43, 1995.

Nasch, P. M., M. H. Manghnani, and R. A. Secco, Anomalous behavior of sound velocity and attenuation in liquid Fe-Ni-S, *Science*, *277*, 219, 1997.

Poirier, J. P., Light elements in the Earth's outer core: A critical review, *Phys. Earth Planet. Int.*, *85*, 319, 1994.

Poirier, J. P., Transport properties of liquid metals and viscosity of the Earth's core, *Geophys. J.*, *92*, 99, 1988.

Rivers, M. L., et al., A new facility for high-pressure research at the Advanced Photon Source, in *Properties of Earth and Planetary Materials at high pressure and temperature*, edited by M. H. Manghnan, and T. Yagi, pp. 79–87, American Geophysical Union, Washington, 1998.

Sanloup, C., et al., Density measurements of liquid Fe-S alloys at high-pressure, *Geophys. Res. Let.*, *27*(6), 811, 2000.

Secco, R. A., High pressure measurements of viscosities of Fe-S liquids, in *High Pressure Science and Technology*, edited by S. C. Schmidt, J. W. Shaner, G. A. Samara, and M. Ross, pp. 947–949, American Institute of Physics Press, New York, 1994.

Secco, R. A., Viscosity of the outer core, in *Handbook of Physical Constants*, edited by T. J. Ahrens, pp. 218–226, American Geophysical Union, Washington, 1995.

Secco, R. A., R. F. Tucker, S. P. Balog, and M. D. Rutter, Tailoring sphere density for high pressure physical property measurements on liquids, *Rev. Sci. Instrum.*, *72*(4), 2114, 2001.

Terasaki, , et al., The effect of temperature, pressure, and sulphur content on viscosity of the Fe-FeS melt, *Earth Planet. Sci. Lett.*, *200*, 93, 2001.

Utsumi, W., D. J. Weidner, and R. C. Liebermann, Volume measurement of MgO at high pressures and high temperatures, in *Properties of Earth and Planetary Materials*, edited by M. H. Manghnani, and T. Yagi, pp. 327–333, American Geophysical Union, Washington, 1998.

Zhang, Y., and G. Guo, Molecular dynamics calculation of the bulk viscosity of liquid iron-nickel alloy and the mechanisms for the bulk attenuation of seismic waves in the Earth's outer core, *Phys. Earth Planet. Inter.*, *122*, 289, 2000.

─────────────

M. D. Rutter, R. A. Secco, and H. Liu, Department of Earth Sciences, University of Western Ontario, London, Ontario, Canada N6A 5B7.

T. Uchida, Y. Wang, and M. L. Rivers, and S. R. Sutton, Consortium for Advanced Radiation Sources, The University of Chicago, 5640 S. Ellis Ave., Chicago, Il 60637, USA.