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Viscosity and density of Fe–S liquids at high pressures

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Abstract

High P, T measurements of viscosity and density of Fe–S liquids are reported. Viscosity was measured using Stokes method and synchrotron radiographic techniques for real-time imaging of a falling/rising composite sphere in Fe–S liquids. For P up to 4 GPa and T up to 1523 K, measured viscosities are of the order of 10^{-2}–10^{-3} Pa s. Density of Fe–10 wt% S liquids was measured using the sink/float method with composite spheres. The high P density data indicate a density increase of 29% between 1 atm and 15 GPa at 1923 K.

1. Introduction

Viscosity and density of liquid Fe alloys are fundamental properties for models of the composition and dynamics of the cores of planetary bodies with magnetic fields, including the Earth and some of the Jovian satellites. Consequently, there is a need to understand the pressure and temperature effects on the viscosity and density of outer core liquids through experimental studies. Unfortunately, direct measurements on candidate core liquids at extreme pressures (P) and temperatures (T) are fraught with difficulties because of the high T needed to melt Fe-bearing systems and their reactivity with pressure cell materials. We describe experiments using a novel design of probe sphere for measurement of the viscosity and density of Fe–S liquids.

2. Experimental details

Samples for viscosity studies were synthesized at high P, T from mixtures of FeS and Fe and cut to a cylindrical shape using electrical-discharge machining (EDM). A small pit was made by EDM at the bottom of the sample to accept the probe sphere. In order to isolate the siderophile Pt sphere from the sample, a new technique [1] to produce composite spheres made of a Pt core surrounded by a ruby mantle was used. In addition to preventing a reaction

between the Pt and Fe–S sample, this technique allows the density of the composite sphere to be tailored by adjusting the relative radii of the core (125–250 μm) and mantle (250–500 μm). High P, T *in situ* viscosity experiments were performed in a 250-ton DIA-type high-pressure apparatus at beamline 13 BM-D, advanced photon source (APS), Argonne National Laboratory. Temperatures were monitored with a $W_{97\%}Re_{3\%}$–$W_{75\%}Re_{25\%}$ thermocouple. During each experiment, the temperature was ramped slowly ($\sim$100 K min^{-1}) to 1073 K where the sample equilibrated for 20 min. After the equilibration period, the temperature was increased rapidly ($\sim$50 K s^{-1}) to 1373 K, followed by an abrupt jump ($\sim$500 K s^{-1}) to 1823 K. Temperature gradients within the experimental cell were measured by replacing the $FeS_{(8.5\ wt\%)}$ sample with NaCl in a separate experiment and collecting energy dispersive x-ray diffraction patterns (EDXRD) from the entire sample region at a step size of 300 μm, with a Ge detector. With this method temperature gradients within the cell are indicated by corresponding shifts in energy of the EDXRD peaks for NaCl according to the Decker equation of state (EOS) [2], assuming pressure is uniform throughout the sample. At temperatures up to 1073 K, there was no peak shift at various locations in the sample, signifying temperature gradients were not detectable within the resolution of the method ($\pm$50 K). At maximum experimental temperatures, above the melting point of NaCl, the vertical flight of all probe spheres indicated the absence of convection in the sample attesting to small temperature gradients. Pressure was determined using the EOS for MgO [3]. Viscosity was measured using Stokes method coupled with synchrotron radiographic techniques for real-time imaging of a falling/rising composite sphere.

Density of Fe–10 wt% S liquids was measured in high-pressure–temperature experiments carried out at the University of Western Ontario in cubic anvil and multi-anvil (Walker-type) presses and at the Bayerisches Geoinsitut in a multi-anvil apparatus using the sink/float method. Tailored density composite spheres were also used with either Pt or WC core spheres and either ruby or sapphire mantles. Microprobe analyses confirm chemical composition integrity of sphere and sample composition. Density of probe spheres was determined by first measuring volumes of core and mantle components of composite spheres at different stages of sectioning of recovered samples by area analysis of backscattered electron images. These reference volumes were then extrapolated to the experimental run conditions using known EOS parameters for sphere components.

3. Results and discussion

The x-ray absorption contrast of Pt/sample is greater than ruby/sample and hence only the Pt core sphere is observed as it falls through the liquid sample shown in the real-time sequence of images in figure 1. Electron microprobe analyses on recovered and sectioned pressure cells confirm the lack of interaction between the composite sphere and Fe–S melt and they confirm the chemical homogeneity of the sample. An example of a recovered and ground pressure cell is shown in the backscattered electron image in figure 2. The bright Pt core and the dark ruby mantle are easily distinguished. The ruby mantle is clearly an effective barrier between the melt and the Pt core as it remains intact during the length of the experiment. Geometry measurements of the initial composite sphere components allow sphere density to be determined by applying the third-order Birch–Murnaghan EOS and using the known elastic constants and thermal expansivity for ruby [4], and the EOS for Pt [5]. The density of the sample was determined from the EOS and thermal expansion of Fe–S liquid [6–8].

The radiographic images were analysed to determine a sphere travel versus time plot. Shown in figure 3 are the measured distance versus time and the derived velocity versus time data. The sigmoidal shape of the distance data is indicative of the acceleration, terminal velocity and deceleration phases of sphere motion. The terminal velocity of the sphere, used to calculate

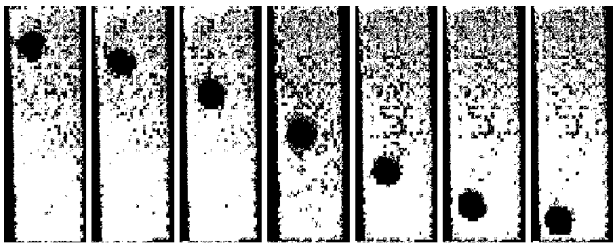

Figure 1. Synchrotron radiographic images of a Pt–ruby composite sphere falling in liquid Fe–29 wt% S at 2.6 GPa and 1373 K. Images are separated in time by 62 ms.

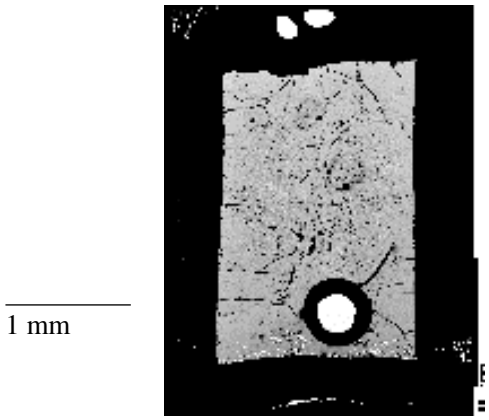

Figure 2. Photograph of recovered and ground pressure cell showing descended composite sphere (Pt core and ruby mantle) in Fe–29 wt% S after a viscosity experiment at 1.5 GPa and 1273 K.

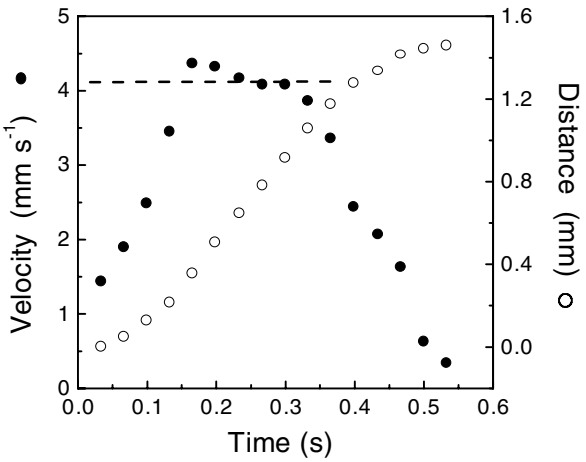

Figure 3. Distance and velocity of falling composite sphere versus time in Fe–29 wt% S liquid, at 2.6 GPa and 1373 K. Velocity is determined by point-to-point derivatives of the distance data. Dashed line is terminal velocity.

the viscosity of the samples, was determined by the maximum of the velocity versus time plot, as shown by the dashed line in figure 3.

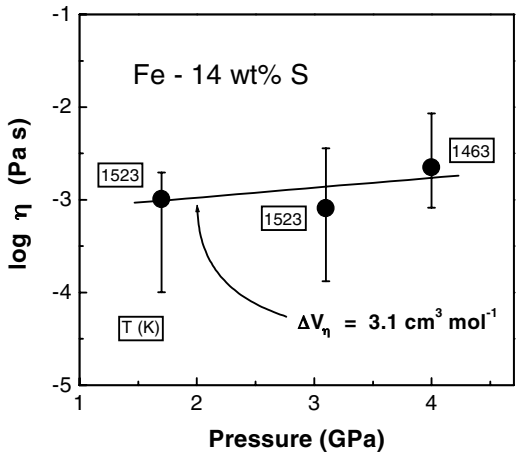

Figure 4. P-dependence of viscosity of Fe–14 wt% S at ∼1500 K.

Viscosity was calculated using a modified form of Stokes's equation which includes terms for wall and end effect corrections [9]. The measured viscosities for Fe–14 wt% S at ∼1500 K between 1.5 and 4.0 GPa are of the order of 10^{-3} Pa s, as shown in figure 4, and for Fe–29 wt% S at 1200–1400 K between 1.0 and 2.5 GPa are of the order of 10^{-2}–10^{-3} Pa s. The P-dependence of the viscosity allows the calculation of activation volume of viscosity from

$$\Delta V_\eta = RT(\partial \ln \eta / \partial P)_T \tag{1}$$

where R is the gas constant. A linear fit to the data in figure 4 yields a value of 3.1 cm^3 mol^{-1} for ΔV_η which is in good agreement with the activation volumes for viscosity reported by LeBlanc and Secco [9] for Fe–27 wt% S in a similar P, T-range using the electro-detection technique of *in situ* sphere velocity determination.

Density data were collected up to 15 GPa at 1773 and 1923 K. A recovered composite sphere with a WC core and sapphire mantle following a 4.5 GPa, 1773 K experiment is shown in figure 5. The density results obtained at 1923 K of several sink/float experiments are shown in figure 6. Comparison is made with temperature-corrected density measurements of liquid Fe–10 wt% S obtained at lower pressures using an x-ray absorption technique [8]. Also shown is the extrapolation of the x-ray data based on the high-temperature Birch–Murnaghan EOS (BMEOS) using K_{0T}- and K'_{0T}-values from [8] and thermal expansion values from [6, 7]. The high-pressure density results confirm the validity of the use of EOS parameters for this composition up to 15 GPa. The results apply directly to the interiors of Jovian satellites Io and Ganymede, for which moment of inertia and magnetic field data from the Galileo orbiter suggest presence of liquid cores with densities in the 5–8 g cm^{-3} range [10]. Our density values indicate that for the calculated internal pressures of these satellites, Fe–10 wt% S is a likely candidate composition.

4. Conclusions

This report demonstrates the composite sphere technique for high-P, T measurements of viscosity and density, using Stokes's method with synchrotron radiography and sink/float, respectively. The shielded design and tailored density attributes of composite spheres allow core-type, ferrous liquid alloys to be investigated without chemical interaction between sphere and melt.

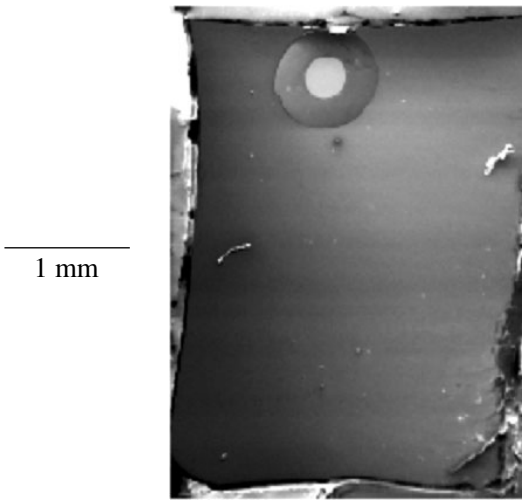

Figure 5. Example of float behaviour of a composite sphere with a WC core and sapphire mantle, at 4.5 GPa, 1773 K.

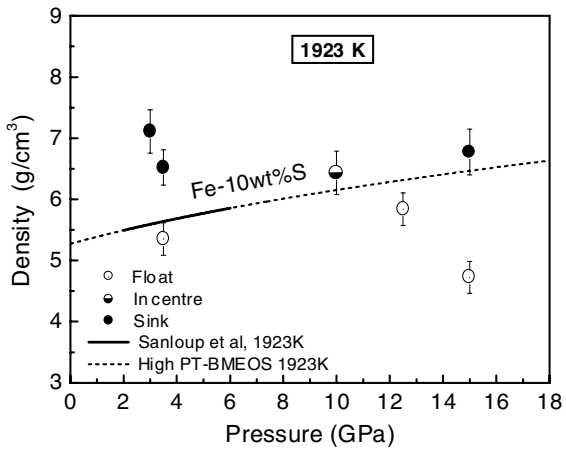

Figure 6. Compression of Fe–10 wt% S liquid at 1923 K.

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