

In Situ Falling Sphere Measurements of the Viscosity of Silicate Melts at High Pressures

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Introduction

Experimental measurements of viscosity are critical to understanding igneous processes in the Earth's mantle that control the rate of extraction of melts from partially molten source regions and the time scales for magma mixing. Traditionally, the settling velocity of a high-density sphere through a molten sample is determined from the initial and final positions of the sphere and elapsed settling time in a quench experiment. This velocity is used to solve Stokes' law for viscosity. These fall-and-quench experiments have generally been limited to 2.5 GPa in the piston cylinder device (e.g., Refs. 1 and 2). Kushiro [1] measured the viscosity of fully polymerized albite melt between 0.5 and 2 GPa at 1673K and found that the viscosity decreased by a factor of four over this pressure range. Brearley et al. [2] measured viscosities of diopside-albite melts and found that the viscosities of polymerized albite-rich melts decreased between 1 atm and 2.5 GPa, whereas the viscosities of depolymerized diopside melts increased between 0.5 and 1.5 GPa. Brearley et al. also reported a minimum viscosity in $\text{Ab}_{25}\text{Di}_{75}$ liquid at 1.2 GPa and 1873K. Mori et al. [3] extended fall-and-quench measurements of albite melt viscosity to 7 GPa in a multianvil apparatus and reported a negative pressure dependence generally consistent with that reported by Kushiro [1]. However, because of uncertainties in quench experiments, it is not feasible to extend these traditional falling sphere studies to higher pressures.

The *in situ* falling sphere technique, in which x-ray radiograph images record the movement of an x-ray opaque marker sphere through a molten sample, is the most promising approach to accurately measuring silicate melt viscosities at high pressures. Recent *in situ* studies of silicate melt viscosity have produced data on both polymerized [4] and depolymerized [5] compositions that are grossly consistent with the results of fall-and-quench experiments.

The main goal of the present study is to use the *in situ* falling sphere technique to determine the pressure dependence of the viscosity of dacite (67 wt.% SiO_2) melt. We use measured viscosities to evaluate the relationship between viscosity and self-diffusion.

Methods and Materials

We conducted *in situ* falling sphere viscosity measurements from 1.6 to 7 GPa between 1730 and 1950K, by using the 1000-ton press and the T-25 multianvil apparatus at GSECARS beamline station 13-ID-D at the APS [6]. The dacite glass powder used in these experiments was synthesized from laboratory reagents. Following Hazen and Sharpe [7], x-ray-opaque marker spheres were formed by explosively melting 0.1-mm-diameter Pt wire with an arc welder.

Assemblies were pressurized while cold. The temperature was increased slowly to $\sim 50\text{K}$ below the melting point, then increased rapidly at $\sim 800\text{K}$ per minute to the run temperature. The settling velocity of a Pt sphere was measured in radiographic images of the melt, which were recorded throughout the heating procedure to identify all movement of the sphere in the sample. Figure 1 shows a series of time-lapse images from one experiment. An energy-dispersive x-ray spectrum for the MgO-to-BN pressure standard was collected immediately following the fall of the marker, and the run pressure was determined by using the equation of state for MgO [8].

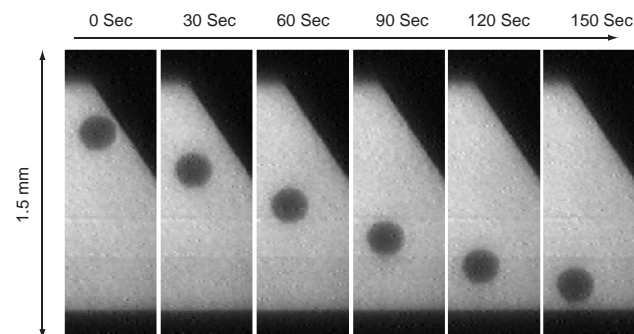


FIG. 1. Video images from a falling sphere experiment at 3.3 GPa and 1730K. The time interval between panels is 30 seconds. The Pt sphere (radius of $87.5\ \mu\text{m}$ in this experiment) is clearly visible as a dark shadow against the light grey sample. Dark regions are areas through which x-rays are not transmitted, including Pt discs at the top and bottom of the sample and tungsten carbide anvils in the upper right corner.

To determine the settling velocity of falling spheres, videotape recordings of experiments were converted to digital images for computer analysis. The digital images for each experiment were advanced frame by frame, and the position of the sphere was determined relative to a measuring grid overlain on the computer screen. The measuring grid was calibrated by using known distances in the radiograph image, such as the diameter of the marker sphere at atmospheric pressure. The resolution of the image leads to an uncertainty of 10 μm in distance estimates. Figure 2 shows the time-distance relationship used to determine the terminal velocity of the falling sphere. Nonlinear regions at the ends of the data set in Fig. 2 are present because the Pt sphere accelerates upon initial melting of the sample and slows as it approaches the bottom of the sample capsule.

Results and Discussion

The terminal velocities determined from time-distance relationships are used in Stokes' law to calculate viscosity with the Faxen correction for sample chamber wall effects [9]. Figure 3 shows the variation of dacite melt viscosity from 1.6 to 7 GPa, between 1730K and 1950K. These data show a negative pressure dependence that is

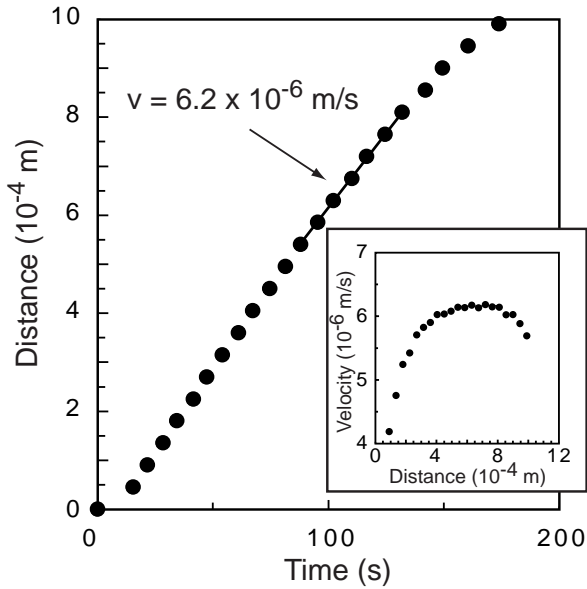


FIG. 2. Time-distance relationship for a falling sphere experiment conducted at 3.3 GPa and 1730K. This plot was used to determine the terminal velocity of the falling sphere. The slope of the least squares best fit line through the seven points between 90 and 130 seconds is the velocity used to calculate viscosity for this experiment. The inset shows the velocity-distance relationship for this experiment, with the plateau representing the terminal velocity of the falling sphere.

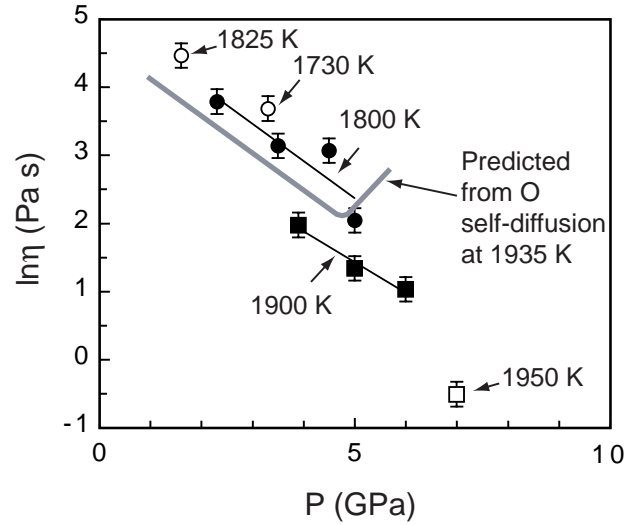


FIG. 3. Comparison of measured dacite viscosity with viscosity predicted from using the Eyring equation. The pressure dependencies for measured viscosities at 1800K (filled circles) and 1900K (filled squares) are shown by least squares best fit lines to these data. Additional data points are viscosities measured at 1825K and 1.6 GPa and at 1730K and 3.3 GPa (open circles), and at 7 GPa and 1950K (open square). The grey curve shows the trend of viscosities predicted by the Eyring equation, with O self-diffusion coefficients measured from 1 to 5.7 GPa at 1935K [10].

particularly well illustrated by the viscosities at 1800K and 1900K. Additional information on the pressure dependence of melt viscosity comes from the Eyring equation, which describes an inverse relationship between melt viscosity and the O self-diffusion coefficient. The grey curve in Fig. 3 shows that predicted viscosities for dacite melt, from using the Eyring equation and O self-diffusion coefficients from our earlier study [10], are generally consistent with measured viscosities up to ~ 5 GPa. However, above 5 GPa, the Eyring equation predicts an increase in viscosity with compression. This viscosity minimum is not evident from our *in situ* falling sphere experiments at least up to ~ 6 GPa.

Such comparisons of measured and predicted viscosities via the Eyring equation are critical in view of the common assumption that the Eyring equation can provide reliable estimates of melt viscosities at high pressures (e.g., Ref. 11). Figure 4 provides a more direct comparison of viscosities for our dacite composition. In general, the Eyring equation overestimates viscosity by 30% to 50%. The comparison in Fig. 4 further suggests that the discrepancy diminishes at higher pressures, although the apparent similarities may be fortuitous, given

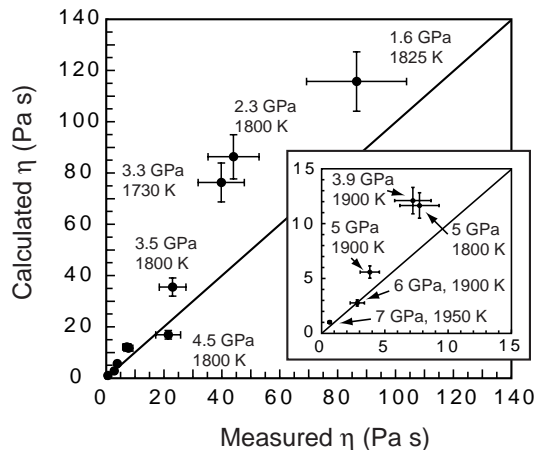


FIG. 4. Comparison of measured and calculated viscosities (η) of dacite. Viscosities measured at the APS are plotted on the abscissa, and calculated viscosities are plotted on the ordinate. The calculated viscosities were determined by using the Eyring equation ($\eta = kT/D\lambda$, where k is the Boltzmann constant, T is the absolute temperature, D is the O self-diffusion coefficient, and λ is the length of a diffusive jump) with a jump distance $\lambda = 2.8 \text{ \AA}$. The O self-diffusion coefficients are from Tinker and Leshner [10].

that the viscosity minimum predicted from oxygen self-diffusion is not substantiated by our *in situ* viscometry study, as shown in Fig. 3. One clear limitation of the Eyring equation is the assumption that both oxygen diffusion and viscous flow are accommodated by the activation of individual O^{2-} anions. This ionic model is certainly an oversimplification for network former diffusion in polymerized melts, where the formation and disassociation of high-coordinated Si or Al species are involved [10]. Our preliminary results highlight the importance of direct measurements of viscosity at high pressure by using the *in situ* falling sphere method, not only for establishing empirical relationships for melt rheology but also for understanding how, in detail, cooperative diffusion is linked to the disruption of chemical bonds that accommodate viscous flow in silicate

melts. Adam-Gibbs theory, which could accommodate a decoupling of motions associated with viscous flow and diffusion, may, in the future, be a more fruitful approach [12, 13].

Acknowledgments

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