PRESSURE DEPENDENCE OF MELT VISCOSITIES ON THE ANORTHITE-DIOPSIDE JOIN

Nicole Fraser
Department of Geology
Smith College
Northampton MA, 01063

INTRODUCTION

Three factors appear to control the environment in which a magma will crystallize: availibility of an escape route to the earth's surface, the eruptive force of the magma (enhanced by volatiles such as H_2O, CO_2, and O_2) and the viscosity of the melt. A very fluid, low-viscosity melt has a better chance of reaching the surface than a more viscous material. Under average crustal pressure (1-2 kbar) the viscosity of basaltic melts is only 10^3 g/cm·s, due to the low $(SiO_4)^{-4}$ content. While the viscosity of granitic melts is 10^6 g/ cm·s, a significant difference. Yet there is a need to study silicate melts in their originating environments, specifically deeper than the crust and into the upper mantle to understand the igneous processes such as crystal fractionation, melt separation from the source region and melt aggregation, which requires these systems to be viewed under upper mantle correlated temperatures and pressures. In the upper mantle, pressure may influence the actual melt structure. Two manifestations of a change in melt structure are viscosity and density, this study focuses on viscosity's role.

A relationship between pressure and viscosity has been observed for several compositions of silicate melts. Most viscosity measurements on anhydrous melt compositions of interest have shown a decrease in viscosity with increasing pressure. However, melts such as albite, jadeite, and anorthite have highly polymerized melt structures at one atmosphere. The ratio of non-bridging oxygens to tetrahedrally arranged cations in all of these melts is less than one (Scarfe, 1986). In contrast, recent measurements on relatively depolymerized melts with the ratio of non-bridging oxygens to tetrahedrons greater than one (for instance: diopside) have shown viscosity increases with pressure for these melts.

The differences in structure between a highly polymerized melt (NBO/T<1) and a depolymerized melt (NBO/T>1) suggest that there may be two mechanisms of viscous flow. Flow mechanisms in highly polymerized melts have been studied by Day and Rindone (1962) and Taylor and Rindone (1970). They modelled the flow as silica rich clusters bonded by weak tetrahedron-oxygen bonds, where the tetrahedron is formed by a cation other than Silica. During viscous flow the tetrahedron-oxygen bonds break. Bockris *et al.*, (1955) studied the depolymerized melts, their proposed model is that silica tetrahedra and cations are the flow components. Scarfe (1986) says that there is no consensus on the mechanisms of flow in silicate melts.

Kushiro (1976, 1978) found that the highly polymerized jadeite-albite melts show a negative pressure dependence of viscosity. Scarfe *et al.*(1979, 1986) observed that relatively depolymerized melts of diopside and sodium metasilicate composition display a positive pressure dependence of viscosity. A contrasting relationship occurs in diopside-albite melts (Scarfe *et al.*,1986). Viscosity of diopside and albite compositions at 1600°C have a positive and negative pressure dependence, respectively. Melts of an intermediate composition display an initial decrease in viscosity with increasing pressure until approximately 12 kbar and then an increasing relationship.

Another interesting relationship is that between viscosity and the diffusion of oxygen (O^{2-}) anions at high pressures. Shimizu and Kushiro (1984) found an inverse relationship in jadeite and diopside melts. Dunn and Scarfe (1987) found a similar inverse relationship in an andesite melts. Dunn (1983) studied three basaltic liquids' oxygen diffusivity under pressure, as well. He proposes a model that predicts oxygen chemical diffusivities from melt viscosities. The model suggests that oxygen chemical diffusion is comparable to divalent cation diffusivities in low-viscosity melts, but that oxygen diffuses much more slowly than do cations in high-viscosity melts. These observations raise the question as to the whether viscosity is rate limited by the diffusion of oxygen at high pressures.

In this study, I have observed the pressure dependence of the viscosity of melts on the anorthite end of the anorthite-diopside join, at mole percents: An_{100}, $An_{75}Di_{25}$, and $An_{50}Di_{50}$. The conditions of the experiments were 1500°C and 1600°C and 7.5 kbar and 15 kbar (pressures corresponding to depths of approximately 23 km and 46 km respectively, which places these near or below the Mohorovicic related to the presence of molecular water. Further studies are required to evaluate this relationship.

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discontinuity beneath continental crust and into the upper mantle). This join was chosen for a variety of reasons. Viscosity data for one atmosphere along the anorthite-diopside join were available (Scarfe, 1983). Secondly, The diopside end of the system was being studied by David Tinker of Carleton College and diffusion studies of the same join were examined by Shelley Fain of Trinity College and Tori Swarmer of Beloit College. Thirdly, the albite-diopside join examined by Scarfe (1986) is of similar interest. Finally, the join is an analog for natural melts of basaltic composition.

EXPERIMENTAL PROCEDURES

Viscosity data were collected using falling sphere viscometry techniques (Shaw, 1963). Glasses were made in 25 percent mole intervals along the Di-An join from oxides (Fisher Scientific Company Reagents: SiO_2, Al_2O_3 and $CaCO_3$; Aldrich Chemical Company Reagents: MgO), see Table 1. The oxides were mixed and heated at one atmosphere for thirty minutes at 1500°C in platinum crucibles. The resulting glass was then crushed in an alumina mortar for fifteen minutes. Platinum spheres of 50 microns and smaller were made from a platinum wire of .025 mm diameter (Johnson Matthey Electrical Co.) according to the method described by Hazen and Sharpe (1983). An electric current was run through the wire using a 157.4 volt DC arc welder. The wire melted instantly and cooled in the shape of spheres as the molten wire dropped.

Next, the powdered glass was placed into a graphite capsule and tapped down using a flat surface (a slotted screw) to insure a smooth surface for the spheres. The ridge created by the screw was intended to be on the same level as the top of the cup and was accounted for after the final layer of glass was placed. Four to five spheres of various sizes were placed on top of the glass using a vacuum manipulator. Then a fine layer of glass was placed on top, so the spheres would not adhere to the graphite cap, once the sample was melted. The graphite cup was inserted into a pyrophyllite cup, then into a salt-pyrex-graphite assembly covered with lead foil. See Figure 1.

A 3/4" piston-cylinder press was used. The sample temperature was monitored by a W-Re thermocouple inserted directly into the assembly. First, the endload pressure was raised to 5000 psi. Next, the sample pressure was brought to eighty percent of the final value. Then, the sample was heated to 200° short of the final temperature at a rate of 200°C/minute. During the dwell of three minutes, the pressure was raised to the final value. Next, at a rate of 400°C/minute temperature was raised to the final value. Run durations were two hours, thirty minutes and five minutes. The programwas set to quench at 10,000°C/minute. The actual quench rate varied from this and was monitored and recorded by hand.

At the end of the experiment, the assembly was stripped of as much lead foil, salt and pyrex as possible so as not to disturb the sample itself. Then, the sample was photographed using an x-ray diffraction machine for an exposure of five minutes. A negative image of the sample and the spheres was produced. The positions of the spheres are visible on the negative, the radius can be determined using a micrometer.

RESULTS

Stoke's law was used to calculate the velocity of the spheres:

$$v = 2a^2 \cdot g \cdot \Delta\rho / 9\eta$$

"v" is the settling velocity of the spheres, measured in m/sec and "a" is the radius of the sphere, in m. "g" is the acceletation of gravity, 9.8 m/sec^2. "$\Delta\rho$" is the difference between the density of the spheres (21.45 x 10^3 kg/m^3) and the melt (approximately 3 x 10^3 kg/m^3). "η" is the viscosity of the melt, measured in newtons but converted to poises by using a factor of 0.1 (1 poise = .1 newton·sec/m^2). The data collected from the 1500°C, 7.5 kbar run of $Anorthite_{100}$, showed all of the spheres at the bottom for all three runs: two hours, thirty minutes and five minutes. From this result only a maximum viscosity can be found. By manipulating Stoke's law the equation may read:

$$\eta = t \cdot 2a^2 \cdot g \cdot \Delta\rho / 9d$$

Where "t" is the length of the run in seconds, and "d" is the distance travelled (4.5 mm = .0045m). The radius of the largest sphere was approximately 25 microns (2.5 x 10^{-5} m). A maximum value of 16.7 poises was found.

Relative to the data of anorthite melts at in air, this maximum value, if it is close to 16.7 poises, meets the predictions of this experiment. In air at 1500°C and 1600°C, are 69 and 27 poises respectively (Scarfe *et al.*, 1983). This is a significant decrease from 69 poises to 16.7 and could potentially be less because it is a maximum value. The viscosity of the experimental melt has declined with pressure just as predicted with another highly polymerized melt, albite, studied by Scarfe (1986). Whether this comparison can be made or not is questionable, the viscosity of albite is significantly higher than that of anorthite. Albite under similiar conditions has a viscosity of 346 poises, over twenty times that of anorthite.

Taylor and Brown (1979) proposed that the sturcture of the studied anorthite melts consists of four-membered rings of SiO_4 and AlO_4 tetrahedra with a non-bridging oxygen to tetrahedron ratio of 0, just like that of the albite structure. As a result of this datum an expectation would be that there is a mixture of highly polymerized, network structures to depolyerized chain, sheet and mononmer stuctures as the experimental composition moves along the join from anorthite to diopside.

The implications of this datum as applied to the melt structure of anorthite-diopside melts is negligible. More data needs to be collected on the other compositions. Also, absolute values need to found instead of maximum values, to do this the system conditions need to be adjusted. Lowering the temperature and working upwards to a limit has been suggested, but the liquidus of anorthite is 1553°C and this study is very close to that already. Another obstacle to lowering the temperature is that Scarfe's (1983) data at one atmosphere does not extend below 1350°C. Despite these barriers, the maximum value of 16.7 is enlightening and does point to the decrease in viscosity with increasing pressure for a highly polymerized melt.

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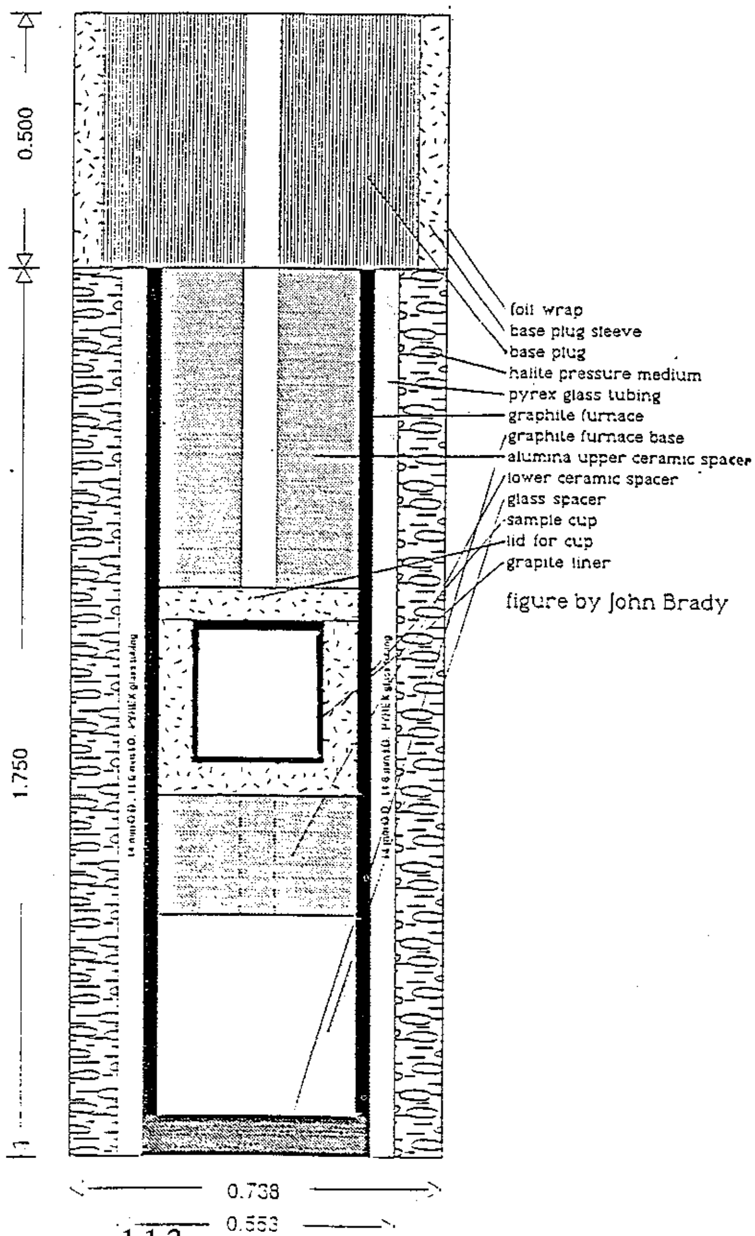
Table 1
STARTING GLASS COMPOSITIONS (WT%)

Reagant	An100	An75Di25	An50Di50
SiO2	45.19	45.37	48.61
Al2O3	36.65	29.31	20.52
MgO	0.00	3.72	8.19
CaO	20.15	21.30	22.68
NBO/T	0.00	0.33	1.2

Figure 1
SALT-PYREX-GRAPHITE ASSEMBLY
Scale: 1" = 0.389



THE EFFECTS OF HIGH TEMPERATURE AND HIGH PRESSURE ON THE DIFFUSION OF OXYGEN IN A ANORTHITE30-DIOPSIDE70 SILICATE MELT

Tori A. Swarmer
Department of Geology
Beloit College
Beloit, Wisconsin

INTRODUCTION

The primary purpose of this study was to determine the effect of temperature and pressure on the diffusion coefficient of oxygen in a silicate melt of 30 weight percent anorthite and 70 weight percent diopside. The composition of anorthite30-diopside70 was chosen for its low liquidus cotectic, its stable melt structure with the change of temperature, and its comparability to existing one atmosphere data. Some of the preexisting data comes from last years Keck study group and from Todd Dunn of the University of Alberta, Canada. The Keck group studied chemical oxygen diffusion rates in silicate melts (Blazek, 1991; Smith, 1991), while Todd Dunn studied the chemical diffusivity of oxygen in andesite and basaltic melts (Dunn, 1986). It is hoped that the new diffusion data can be used to indicate the pressure variations of the different diffusion processes with depth.

METHOD

Measuring the diffusion rate of oxygen through a melt of any composition is very difficult. Changes in oxygen concentration (dissolved oxygen) are so small that they can only be detected by either isotopic exchange, oxygen bubble dissolution, redox kinetics, or electro-chemistry (Schreiber et al., 1986). Redox kinetics was the method chosen to measure the rate of oxygen diffusion in the melt of anorthite30-diopside70. Although the redox monitoring can be achieved with many multivalent elements, iron was chosen as the tracer for the oxygen. The addition of oxygen to the melt by diffusion will change ferrous iron (Fe+2) to ferric iron (Fe+3), according to the reaction:

$$4Fe^{+3}_{(melt)} + 2O^{-2}_{(melt)} \;---\; 4Fe^{+2}_{(melt)} + O^{2}_{(gas/melt)}$$

(Schreiber et al., 1986)

With this reaction in mind the two weight percent of Fe (along the hedenbergite line) was added to the system (see figure 1). Two percent was chosen so that a measurable Fe+2 signal would be achieved during titration without causing a significant change in the structure of the melt. 100g of anorthite30-diopside70 glass were prepared by combining weighed amounts of the appropriate reagent grade oxide chemicals and by fusing them in a platinum crucible for 24 hours at 1500 degrees C. This length of time was used to homogenize the sample to a largely oxidized form. Allowing the melt to equilibrate in an oxidizing environment ensured that most of the iron was in the +3 valence state. Upon removal of the