

# AN EXPERIMENTAL DETERMINATION OF VISCOSITIES FOR MELT COMPOSITIONS ANORTHITE<sub>25</sub>- DIOPSIDE<sub>75</sub> AND DIOPSIDE<sub>100</sub> AT ELEVATED PRESSURES AND TEMPERATURES

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## INTRODUCTION

The physical and chemical properties of silicate melts are important factors in answering the petrological questions of magma genesis and in describing the mechanics of magma flow and mixing. These properties are subject to such changes in the physical structure of the melts as the coordination of the metals and the degree of polymerization. Since Bowen examined the ternary system albite-anorthite-diopside in 1915, it has been studied systematically in terms of its phase relations (Scarfe et al., 1983). But relatively little work has been done to describe the petrologically important aspects of the physical properties. The bulk of the work done on the Keck research projects at Washington and Lee University examined some of these physical properties in detail. Work in 1990 described the diffusion rates of oxygen through compositions along this join under atmospheric conditions, and diffusion studies at high pressures and with water-saturated melts were undertaken in 1991 (see Fain and Swarmer, this volume). The effect of iron doping was also tested in regard to the diffusion rates under atmospheric conditions (see Cooper, this volume). Because of the broad applications of this knowledge, and because it has been thoroughly studied in other regards, the system diopside-anorthite was chosen to determine the viscosity changes under elevated pressure and temperature.

Loosely defined, viscosity is a measure of the internal shear necessary for a material to flow. This is determined by a number of factors inherent in the physical structure of the melt. One of these is the coordination of the metals present in the melt. The coordination numbers of different metal determines the internal strength of the melt by varying the geometry of the melt structure; this may include tetrahedra, chains, and sheets. The extent of the order determined by this geometry is also important. If the melt has a long-range order, it is polymerized; in general, the greater the polymerization, the greater the viscosity. One indicator of the degree of polymerization is the "nonbridging oxygen per silicon ratio" (NBO/Si). The higher the NBO/Si ratio, the less order is present in the melt, and measured viscosity will be lower. The effects of individual bond strengths must also be considered. All of these factors are vary under elevated pressures and temperatures.

This study was devised in part as a correlate to work done on this system by Scarfe et al. (1983), which focused on viscosity changes with temperature at 1 atmosphere of pressure. The viscosity decreased with higher temperatures. While they studied the changes at constant pressure, this project concerns the changes with different pressures as well as temperatures occurring in compositions with mole percents Anorthite<sub>25</sub>-Diopside<sub>75</sub>, the same composition doped with 2 weight percent iron, and 100 percent Diopside. Another Keck project begun in the summer of 1991 concentrated on the other end of the Anorthite-Diopside join (see Fraser, this volume). For most compositions, the viscosities in related systems and natural basalts have been shown to decrease under higher pressure and temperature conditions.

## MATERIALS AND METHODS

The experiments were performed in a piston-cylinder apparatus capable of controlling both temperature and pressure. The pressure was regulated by two hydraulic presses, one above and one below the sample. Hydrostatic pressure was applied on the sample assembly by a pyrex cylinder and halite sleeves. The temperature was controlled by running an electric current through a graphite furnace surrounding the sample. The sample consists of a synthetic basalt composition in a graphite cup lining a pyrophyllite cup, all of which is placed as close as possible to the center of the sample assembly with the aid of alumina spacers (see figure 1).

Reagent grade oxides, carbonates, and quartz were used to make synthetic compositions of the diopside-anorthite mixtures for the experiments. Compositions were made in the proportions 25 mole percent anorthite-75 mole percent diopside, a similar composition doped with 2 weight percent iron, and 100 percent diopside. The appropriate amounts of the reagents were mixed and shaken thoroughly, then fused in a bulk furnace for 12 hours at 1500°C to ensure their homogenization. The resulting glasses were then powdered for distribution in the sample assemblies.

For each viscosity experiment, the powder was tightly packed into a graphite cup 6mm in length, with a diameter of about 5mm. In each of these graphite cups, three platinum spheres (radii of 40-60 microns) were placed

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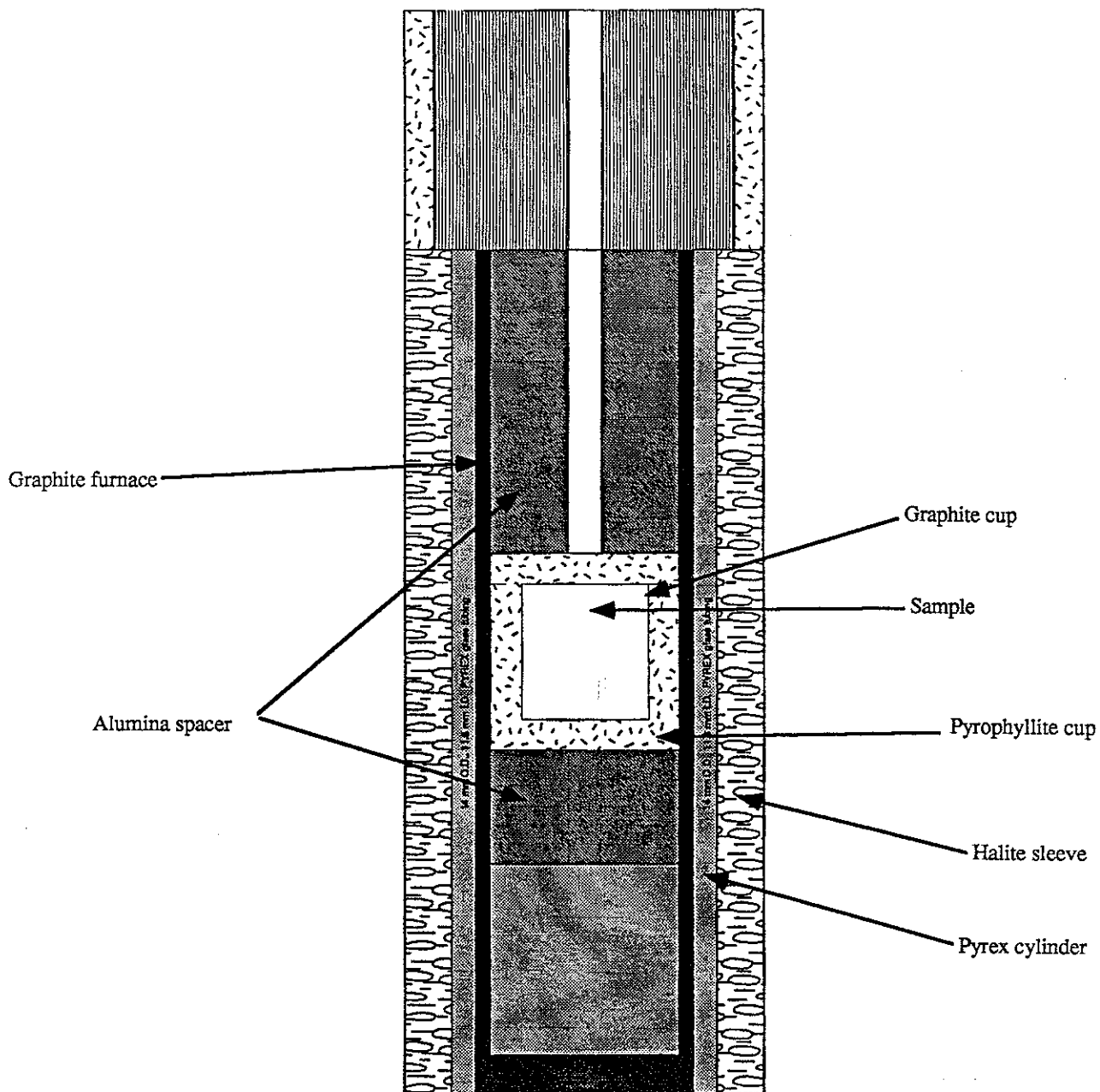


Figure 1. Sample assembly for viscosity measurements.  
The assembly is 3/4 inches long.

on the surface of the powder, followed by a thin (0.5-1.0mm) layer of the powder. The overlying layer was intended to prevent the spheres from adhering to the graphite lid that seals the cups.

The platinum spheres were created following the method used by Hazen and Sharpe (1983). Platinum wire with a diameter of 0.01mm was exploded using an arc welder and running a current through the wire. The exploding wire creates liquid drops of platinum that cool quickly into spheres before they land and can be collected.

The experiments used the "falling sphere" method of viscometry, whose theoretical basis lies in Stokes' Law:

$$\eta = 2a^2g\Delta\rho/9v \text{ eq. 1}$$

where  $\eta$  is the viscosity of the melt in poise,  $a$  is the radius of the sphere in m,  $g$  is the acceleration due to gravity in  $m/s^2$ ,  $\Delta\rho$  is the difference in density between the sphere and the surrounding medium in  $kg/m^3$ , and  $v$  is the velocity of the falling sphere in m/s. The radii of the spheres can be measured using an objective micrometer on a microscope,  $g$  is a known constant,  $\Delta\rho$  can be calculated using the known density of platinum (21.45) and the measured densities of natural basaltic melts. The velocity can be calculated following the experimental run.

The falling sphere method can be interpreted literally as a measure of how fast the platinum spheres fall through the melt. The melt forms when the sample is heated above the liquidus temperature. The "hot piston in" method was used for the experimental runs, meaning that the pressure was raised to 80 percent of the final pressure, the temperature was increased slightly, the pressure was raised to the final level, and the temperature was adjusted as quickly as possible (200°C per minute) to its final level. After the run had been completed, the melt was quenched by shutting off the power to the piston cylinder press. This has the effect of freezing the platinum spheres in place. Their position can be determined by taking actual-size, x-ray photographs of the sample. Measuring the distance in the picture, and knowing the time of the experimental run, the velocity is easily calculated for substitution into (equation 1).

## PROBLEMS

In addition to the possibility of having the platinum spheres stick to the graphite lid as mentioned earlier, there are a number of other problems associated with the falling sphere method of viscometry. The root of the problems uncovered so far lies in the viscosity of the melts in the diopside-anorthite system. While Scarfe et al. (1983) cited sources as saying that the viscosities in this system were "systematically high," initial runs have produced only limited results because the platinum spheres have reached the bottom of the graphite cup at some time during the experimental run. This makes it necessary to use smaller spheres to avoid having them fall so quickly; it is not feasible to use less-dense material under these conditions because of the risk of having the spheres melt, or react with the experimental composition, and because of the difficulty in producing spheres of a different composition. Another possible solution to the problem is to run the experiments at subliquidus temperatures, where the melt should be more viscous. That will allow successful experimental runs while still showing the effects of pressure that have not been previously examined in this system. Restrictions on the sample size and the length of each experiment are also dictated by the piston cylinder press.

Initially, it may seem that shortening the experimental runs would eliminate some of the problems that have arisen, but the precision of the piston cylinder puts some lower limit on the length of the runs. One complication inherent in the apparatus is the thermal gradient present from one end of the sample assembly to the other. The temperature ranges from under 100°C to over 1000°C in the sample assembly, a distance of only a few centimeters. This problem is accentuated by the fact that the computer-controlled thermostat has a tendency to overshoot when going up to the final temperature, and it is uncertain whether the piston cylinder is capable of maintaining constant temperature for runs lasting less than a minute.

## EXPECTED RESULTS

Experiments completed in the summer of 1991 did not yield meaningful results. Because the work was interrupted in the Fall, experimental data are currently being collected. When the technical problems mentioned above were addressed, it became apparent that the viscosities measured for this system at 1 atmosphere of pressure suggested higher viscosities at higher pressures than were observed. Therefore, the compositions will have to be studied at lower temperatures than originally intended. But because Scarfe et al. (1983) included subliquidus temperatures in their experiments, it will still be possible to compare that study with this one. Each of the experimental compositions will be studied under three temperatures at 7.5 and 15 kbar. Over the entire system, it is likely that the viscosity will decrease with increased temperature and pressure. This is in some cases likely due to

the energy present in the system that is sufficient to break bonds in the melt. The effect of the pressure is potentially the most interesting part of the problem. Previous work has suggested coordination changes of the metals present in the melt structure with higher pressure (Stolper, 1987). Within the system, a greater amount of diopside has the effect of depolymerizing the melt and reducing the viscosity. Viscosities of natural basalts have been measured as 40 poise at 1350°C and 15 kbar (Kushiro et al., 1976). We can expect similar results for the synthetic compositions under these conditions, and predict lower viscosities with higher pressures and temperatures. The relative rates of change in viscosities with these changes will probably differ from the changes in other compositions and will be the most interesting and useful results.

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# THE SYNTHESIS AND CHARACTERIZATION OF Mg-Fe-Mn GARNETS

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## INTRODUCTION

Garnet is a common mineral in metamorphic rocks that can be used with other minerals both as a geothermometer and as a geobarometer. The general structural formula for garnet is  $X_3Y_2Z_3O_{12}$  where X is in eight-fold coordination, Y is in six-fold coordination and Z is in four-fold coordination. Winchell (1933) divided the garnets into two groups: ugrandites, where Ca is in the X site, and pyrospites, where Ca is not in the X site. The ugrandites include: uvarovite ( $Ca_3Cr_2Si_3O_{12}$ ), grossular ( $Ca_3Al_2Si_3O_{12}$ ), and andradite ( $Ca_3Fe_2Si_3O_{12}$ ). The pyrospites include: pyrope ( $Mg_3Al_2Si_3O_{12}$ ), almandine ( $Fe_3Al_2Si_3O_{12}$ ), and spessartine ( $Mn_3Al_2Si_3O_{12}$ ).

Most garnets have compositions that lie near but between the two series (end member garnets rarely occur in nature). Various methods have been used to determine the compositions of natural garnets as a function of their physical properties. Historically certain properties such as unit cell size ( $a_0$ ), specific gravity (G), and refractive index (n) are most often used because they are comparatively easy to measure. Ford (1915) was the first to try to relate the refractive index (n), specific gravity (G), and lattice constant (a) to composition. Since Ford (1915) many other diagrams have been compiled, Stockwell (1927), Fleischer (1937), Kennedy (1947), etc. These earlier predictions were made by measuring the properties of natural garnets and then extrapolating to the pure end-members. Skinner (1956) used synthetic end-member garnets to determine the lattice constant (a), molar volume (V), density (r), and refractive index (n). He found that his data were comparable to those of Stockwell (1927) and Fleischer (1937) for the unit cell sizes of the pyrospite series. Sriramadas (1957) put the data from Skinner (1956) into diagram form relating the chemical compositions as a function of the unit cell edges and refractive indices. Winchell (1958) added the specific gravity (G) to the diagrams made by Sriramadas. This project extends this earlier work into the pyrospite ternary.

## EXPERIMENTAL

Garnets of composition Alm<sub>60</sub>Py<sub>20</sub>Sps<sub>20</sub>, Alm<sub>70</sub>Py<sub>30</sub>, Alm<sub>30</sub>Py<sub>10</sub>Sps<sub>60</sub>, Alm<sub>50</sub>Py<sub>10</sub>Sps<sub>40</sub>, and Alm<sub>60</sub>Py<sub>40</sub> were synthesized using a 3/4" piston-cylinder device from glasses made by J. B. Brady. End member glasses were made by melting mixes of oxides in graphite crucibles at 1 atm for 30 minutes at 1500°C. They were then crushed and ground under acetone for one hour. Crushed glass from each end member composition was weighed in appropriate amounts and ground together for an hour to achieve homogeneity. Two hundred to four hundred milligrams of the powder were then packed into a graphite container. The graphite container with lid was placed inside a fired pyrophyllite container and lid, which was held at the midpoint of the furnace. The furnace consisted of a graphite cylinder inside of a pyrex sleeve. The remaining space is filled from the bottom by a graphite plug, a glass plug, and a corundum plug. Above the sample container is another corundum plug with a hole for the thermocouple. The whole furnace was then placed inside a halite sleeve as shown in Figure 1.

The furnace assembly was then wrapped in lead foil and inserted into the piston-cylinder device along with a W-Re thermocouple to monitor temperature. The endload was applied, and the ram pressure was raised to about 7 kilobars. The temperature was then raised to 1250°C using the hot piston in technique (Bohlen 1984). First the temperature was raised to 800°C then during a dwell time of three minutes the