

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

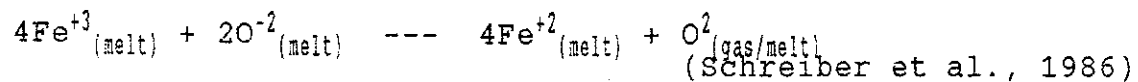
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INTRODUCTION

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:

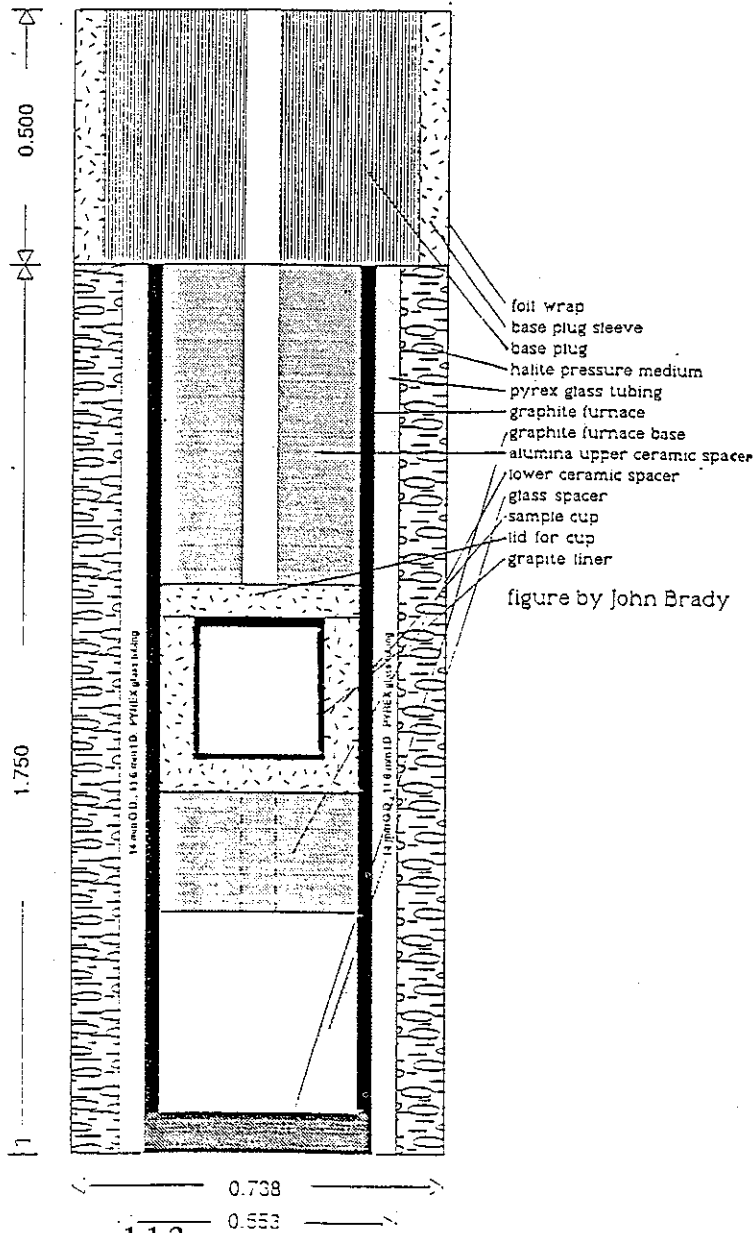


With this reaction in mind the two weight percent of Fe (along the hedenbergite line) was added to the system (see figure 1). Two percent was chosen so that a measurable Fe+2 signal would be achieved during titration without causing a significant change in the structure of the melt. 100g of anorthite30-diopside70 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

Table 1
STARTING GLASS COMPOSITIONS (WT%)

Reagent	An100	An75Di25	An50Di50
SiO ₂	45.19	45.37	48.61
Al ₂ O ₃	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



crucible from the furnace it was immediately quenched in water. The glass was then removed from the crucible and ground into a powder under acetone to prevent further change in the oxidization state. The sample was then placed in a graphite cup. The size of the cup was chosen that so the length (.338 inches) exceeded the diameter (.250 inches), to reduce the proportion of the diffusion from the ends of the cup. Because the sample is totally surrounded with graphite, oxygen lost will occur from the sides as well as from the top and bottom of the cup. Although we hoped to use the mathematical model of an infinite cylinder, compression and melting of the porous glass powder during the experiment, made a spherical model more appropriate. The cup was then placed in a furnace assembly, which in turn was placed in a piston cylinder press. Each of the runs in the press had three variables: pressure, temperature, and time (see table 1).

The sample was then pressurized and heated in steps. The temperature was raised first at a rate of 200 degrees per minute and then at 500 degrees per minute to the final value. After the final temperature is achieved (at a rate of 500 degrees per minute) these two variables are held constant while the time variable is measured (enacted). The sample was then quenched in air by turning off the power and slowly removing the pressure.

The temperature was measured with a tungsten/rhenium thermocouple which was standardize with a chromium/aluminum thermocouple.

After the each experiment the sample was removed from the graphite and ground into a powder, again under acetone to prevent oxidization. The powder was then weighed and dissolved in H₂SO₄ and HF. Boric acid was used as a buffer for the HF and Phenanthroline ferrous sulfate complex was used as an indicator. This solution was then titrated with a Cerium +4 solution (Schreiber et al., 1986).

RESULTS

Two graphs were plotted to show the relationship between the experimental data and the theoretical data. In figure 1, there is a notable change between the diffusion rates of oxygen under different temperatures at 7 Kb. Figure 2 show a similar relationship. When comparing the two figures, the rate of diffusion of oxygen is dependent upon the temperature more so than the pressure. This observation is not consistent with the expected theoretical results but can be explained though errors in the experimental procedure.

One such error can be found in the resulting glass sample. Due to the limitation of the sample assembly and the compression of the sample during the experiment, I used a spherical geometry model verses a cylindrical model. Error could have occurred during the titrations; there is uncertainty in the color change of the titrated solution and the reading of the meniscus, all of which are contributed to human error.

In conclusion, different temperatures and pressures effect the rate of oxygen diffusion in the system of anorthite₃₀-diopside₇₀.

TABLE # 1

PRESSURE (Kb)	TEMPERATURE (°C)	TIME (MINUTES)	SAMPLE	Fe+2 VALUES
7 Kb	1425	5	91 TAS 111	—
		20	91 TAS 110	—
	1500	5	91 TAS 101	1.28
		20	91 TAS 102	1.39
	1575	0	91 TAS 113	0.6
		5	91 TAS 103	1.34
20		91 TAS 104	1.50	
15 Kb	1500	5	91 TAS 106	1.20
		20	91 TAS 112	1.12
	1575	5	91 TAS 107	1.38
		20	91 TAS 109	1.60
	1650	5	91 TAS NOT DONE	—
		20	91 TAS NOT DONE	—

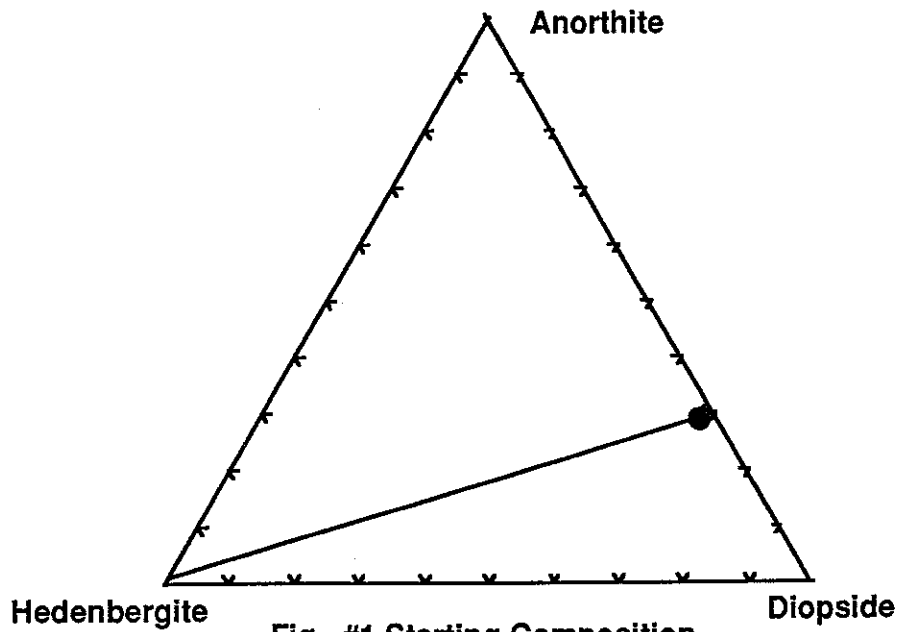


Fig. 2 Theoretical Diffusion Coefficient Curves
and Experimental Data at 7 Kbars

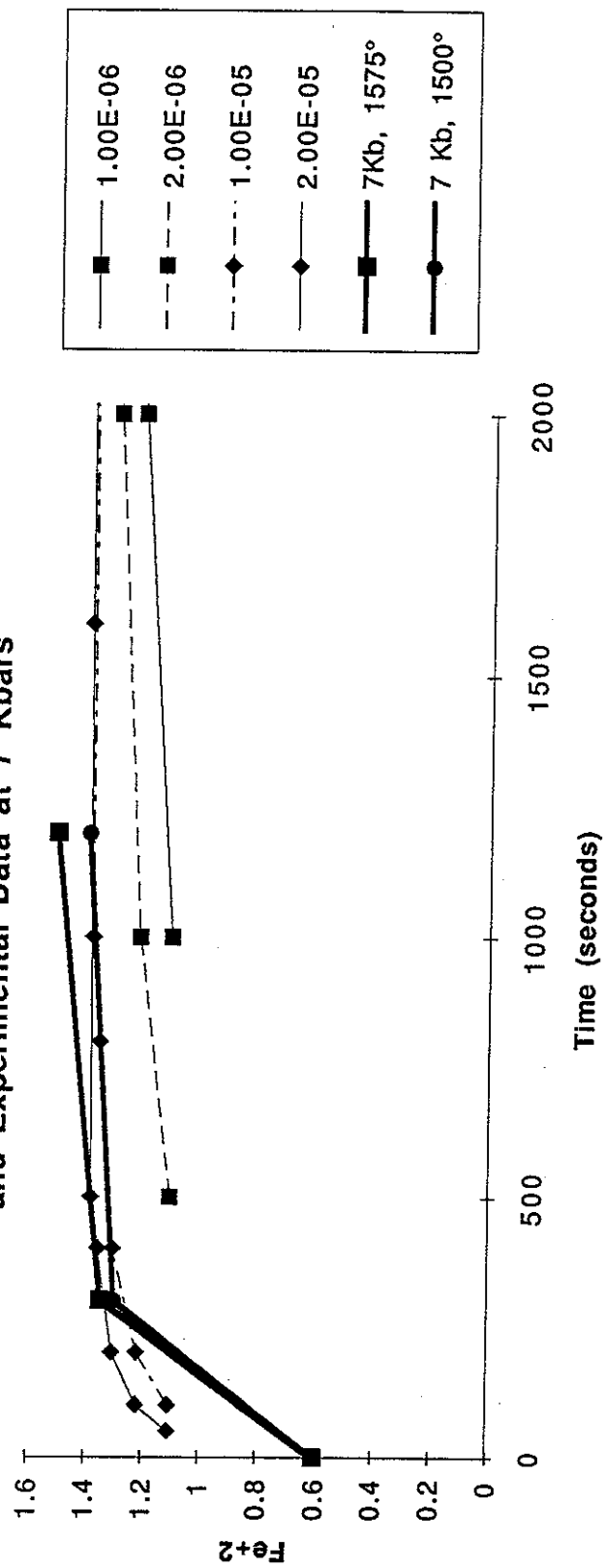
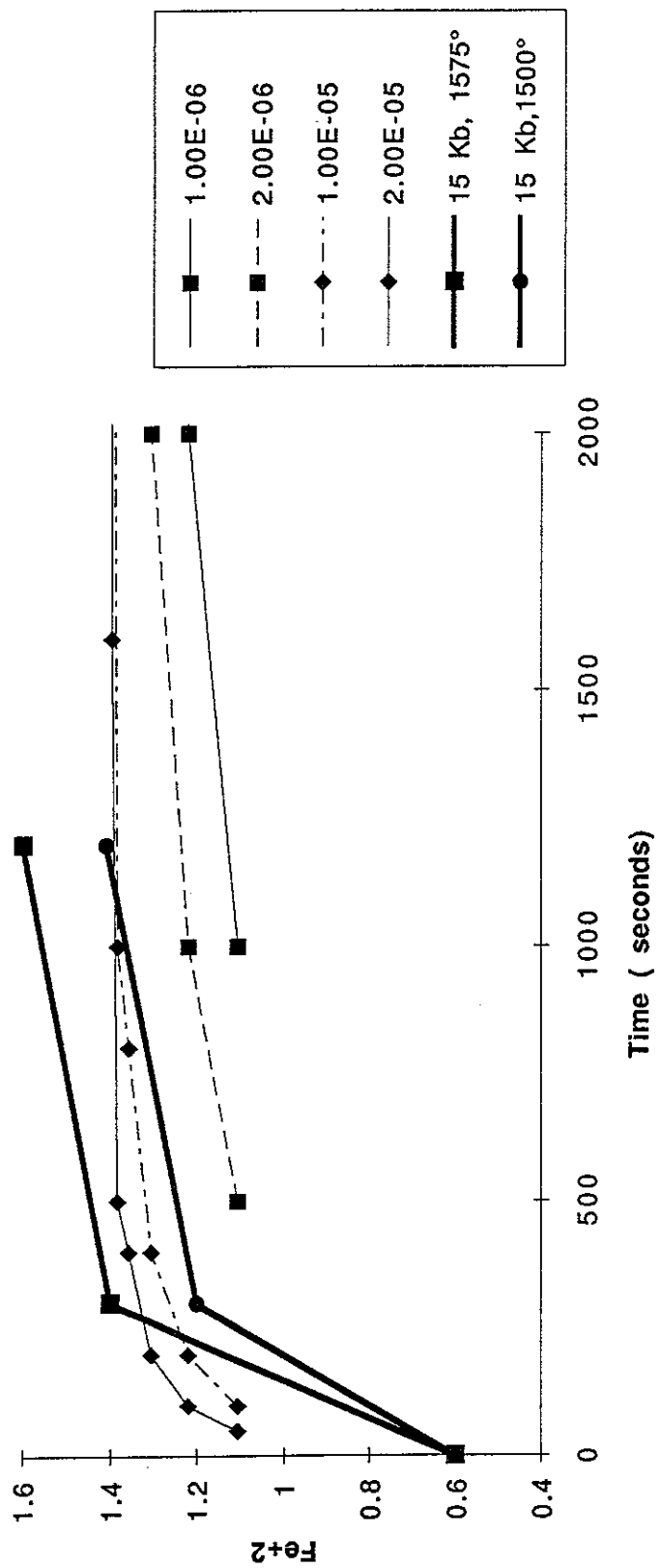


Fig. 3 Theoretical Diffusion Coefficient Curves
and Experimental Data at 15 Kbars



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AN EXPERIMENTAL DETERMINATION OF VISCOSITIES FOR MELT COMPOSITIONS ANORTHITE₂₅- DIOPSIDE₇₅ AND DIOPSIDE₁₀₀ 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 Anorthite₂₅-Diopside₇₅, 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