

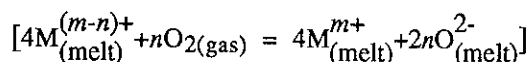
A DETERMINATION OF CHEMICAL OXYGEN DIFFUSION RATES IN THE SYSTEMS  
ANORTHITE<sub>80</sub> DIOPSIDE<sub>20</sub> AND ANORTHITE<sub>100</sub>  
VIA IRON REDOX EXPERIMENTS

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## Introduction

The diffusion coefficient of oxygen in silicate melts has been determined as a function of melt temperature by monitoring redox kinetics, the rate at which a multivalent element establishes equilibrium between its oxidized and reduced forms, within the melts (Schreiber *et al.*, 1986). The primary focus of this study is the determination of chemical oxygen diffusion rates in the systems Anorthite<sub>80</sub> Diopside<sub>20</sub> and Anorthite<sub>100</sub> at various temperatures ranging from 1500 to 1600 degrees C and 1575 to 1625 degrees C respectively. Iron was the redox couple chosen for these experiments. Previous experiments have shown that chemical oxygen diffusion rates are independent of the redox couple analyzed (Schreiber *et al.*, 1986). For an oxidation experiment, one in which the final imposed oxygen fugacity on the glass melt is greater than the initial oxygen fugacity, oxygen must diffuse into the melt to reestablish equilibrium. Since the melt contains a redox couple, the oxygen as it diffuses inward will react with the reduced species of the multivalent element according to the reaction expressed by the general redox equation in Eq. 1

[Eq. 1]



where M is the multivalent element in oxidized,  $M^{m+}$ , and reduced,  $M^{(m-n)+}$ , species within the melt and  $n$  is the number of electrons transferred in the redox couple.

In this study, the multivalent element, iron, was dissolved in the glass melts of base compositions at a specified temperature and oxygen fugacity and was allowed sufficient time to establish redox equilibrium. The geometry of the samples approximates that of a cylinder of fixed depth whose top is exposed to the experimental atmosphere. After an individual sample has been quenched, it is remelted at the same temperature but at a greater imposed oxygen fugacity for a set time. Thus the experimental constraints of the oxidation experiments require the diffusion of oxygen into the top of the cylinder.

The rate of diffusion of a gas through a flat surface can be calculated according to Fick's Law of Diffusion (Schreiber *et al.*, 1986). Consequently, profiles of the average concentration of oxygen and hence the redox ratios can be modeled through solution of the diffusion equation. Such profiles will be dependent on the assumed diffusion coefficient and on the time interval elapsed since the start of diffusion.

## Experimental Procedures

Glasses of base compositions An<sub>80</sub> Di<sub>20</sub> and An<sub>100</sub> were prepared in 25g lots by combining appropriate quantities of the elemental materials in a platinum crucible and fusing them for 24 hours at a temperature slightly above their melting points in a Deltec high temperature bulk furnace. The crucible was then removed from the furnace and immediately quenched in water. The resulting glass was removed from the crucible and ground into a fine powder using a mortar and pestle. A calculated amount of this powder was then doped with 1wt% iron, added as its oxide, to make up a total base sample of 10g. This 10g sample was then homogenized in a mechanical mixer and was subsequently melted, quenched, and ground again. Samples weighing 400 mg of the resulting glass powder were then loaded into cylindrical platinum capsules of a constant geometry. All samples contained the same weight of powder to ensure a constant melt depth; their small size was chosen to minimize convection. A series of 8 of these samples for each composition and chosen temperature was then pre-equilibrated for 24 hours in a Deltec vertical tube furnace which has been modified to maintain a controlled atmospheric composition. After synthesis in the reducing, carbon dioxide rich atmosphere, the melts were quenched to glasses so that each series consisted of 8 identical samples in terms of geometry, composition, melt temperature, and redox state.

Redox ratios (reduced/oxidized) of the dopant in different samples will vary as a function of time, decreasing when the sample has been exposed to a more oxidizing atmosphere than that in which it had been initially equilibrated or increasing when exposed to a more reducing atmosphere. A diffusion model based on Fick's Law of Diffusion (Goldman and Gupta, 1983) and modified by (Schreiber *et al.*, 1986) was programmed and used to calculate redox ratios as a function of time (Eq. 2).

$$[\text{Eq. 2}] \quad \frac{x^{-4/n} - x_0^{-4/n}}{x_e^{-4/n} - x_0^{-4/n}} = \sum_{j=0}^{\infty} (-1)^j \left[ \text{erfc} \frac{(2j+1)L-z}{2\sqrt{Dt}} + \text{erfc} \frac{(2j+1)L+z}{2\sqrt{Dt}} \right]$$

In the equation  $X_0$  and  $X_e$  are the initial and equilibrium redox ratios while  $X$  is the redox ratio for a particular depth,  $z$ , at any given time  $t$ .  $L$  is the total depth of the sample,  $D$  is the diffusion coefficient and  $n$  is the number of electrons involved in the redox couple.

Equation (2) will yield results for an oxidizing experiment. An analogous but slightly different equation will yield results for a reducing experiment. Details of the models and their derivations are given in Schreiber, 1986.

For model calculations, all experimental variables were set to those at which the experiment had been run. The diffusion coefficient was varied on sequential model calculations. The diffusion coefficient used for that model whose redox ratio versus time distribution most closely matched the experimental data was chosen as the diffusion coefficient most likely to be that controlling diffusion during the experimental runs.

### ACTIVATION ENERGY

The activation energy for COD can be determined by means of equation 3.

$$[\text{Eq. 3}] \quad \text{Log } D = \frac{-E}{2.303 RT} + \text{Log } D_0$$

In equation 3,  $D$  is the experimentally determined diffusion coefficient,  $E$  is the activation energy of diffusion in calories per mole,  $R$  is the gas constant,  $T$  is the temperature in degrees Kelvin of the experimental runs yielding  $D$  and  $D_0$  the Arrhenius pre-exponential function, a measure of the number of pathways available for diffusion.

### THE 1990 KECK EXPERIMENTAL PETROLOGY PROJECTS

Four students participated in the Keck Experimental Petrology project for 1990, two from Smith College, Ann Farrell and Erica Smith, and two from Washington and Lee University, Judson Blazek and Jonathan Bull. three elected to undertake chemical oxygen diffusion studies on parts of the systems Anorthite-Diopside and Albite Diopside. The fourth investigated the relationship between equilibrium redox ratios of iron and different imposed atmosphere oxygen fugacities at different temperatures at one atmosphere pressure.

### REFERENCES CITED

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- Goldman, D. S. and Gupta, P. K., 1983, Diffusion-controlled redox kinetics in a glassmelt. *Journal of American Ceramic Society*, v. 66, no. 3, pp. 188-190.
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Individual samples of each series were then remelted in air, a more oxidizing atmosphere, at the same temperature at which they had been equilibrated for 15, 30, and 45 minutes and for 1, 1.5, 2, and 24 hours respectively. Following syntheses, the melts were quenched and ground for redox analyses.

Redox microtitrations using standard ceric sulphate solution as titrant and o-phenanthroline complex as visual indicator were employed to determine the redox state of the individual samples (Schreiber *et al.*, 1986). Approximately 0.1000g of sample was placed into a clear polypropylene digestion container with a dry, magnetic stirring bar. Argon was forced to flow through the container to provide an inert atmosphere over the sample during glass digestion. The sulphuric and hydrofluoric acid solutions used in the digestions were specially treated in order to rid them of any active redox components. Under continuous argon flow, 10.00ml of a 1:1 (by volume) H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O solution were added to the digestion container, and the resulting slurry vigorously stirred for 5 minutes. Five milliliters of a 1:1 HF:H<sub>2</sub>O solution were then added to the slurry with ten additional minutes of stirring. After addition of the sulphuric and hydrofluoric acid solutions, the glass powder had been dissolved by the aqueous medium without disruption of the redox states initially present in the glass. Subsequently, 4.0g of crystalline boric acid were added with distilled water to the container in order to complex any excess fluoride in the solution. After about 5 more minutes, the solution was removed from the argon atmosphere for titration.

Precisely 50.0 microliters of o-phenanthroline complex were then added to this solution as a visual redox indicator. The solution turned red in the presence of this indicator. The solution was then titrated with a standard Ce (IV) sulfate solution to the colorless/blue endpoint. This titration procedure was employed for the Fe doped glasses because Fe (II) is selectively analyzed without interference from Fe (III) in solution. The average Fe (III) concentration could then be obtained by difference between the total iron content and analyzed Fe (II) content. Each series thus provided a set of redox ratios (Fe<sup>+2</sup>/Fe<sup>+3</sup>) as a function of oxidation time. As an example, experimental data for An<sub>80</sub> Di<sub>20</sub> at 1550 degrees C are shown in Figure 1.

## Modeling

With an assumed oxygen diffusion coefficient, the theoretical diffusion model, based on Fick's Law of Diffusion, can predict redox ratios as a function of time. Comparison of experimental redox data with redox values determined via the redox model for different diffusion coefficients allowed the determination of the redox ratio vs. time curve which most closely corresponded to the experimental data. An example of model determined diffusion curves for three different diffusion coefficients is shown in Figure 2. In Figure 3, the experimental data for An<sub>80</sub> Di<sub>20</sub> at 1550 degrees C are compared with these model diffusion curves to determine the actual diffusion coefficient.

## Results

### Diffusion Coefficients:

The determined diffusion coefficients for An<sub>80</sub> Di<sub>20</sub> and An<sub>100</sub> at the various experimental temperatures used are shown in table 1.

Table 1

	An <sub>80</sub> Di <sub>20</sub>	An <sub>100</sub>
Degrees C	Diffusion Coefficients	
1500	.000006	
1550	.0000012	
1575		.000010
1600	.0000199	.0000205
1625		.0000306

### Activation Energies:

Solution of the Arrhenius relationship,  $\log D = \frac{-E}{2.303RT} + \log D_0$ , yielded E, the activation energy of diffusion, for each composition. D is the measured diffusion coefficient, T is the temperature in degrees Kelvin for

Fig. 1  
An80 D:20 w/ 1% Fe  
at 1550 degrees C  
Experimental Data w/ Fitted Curve

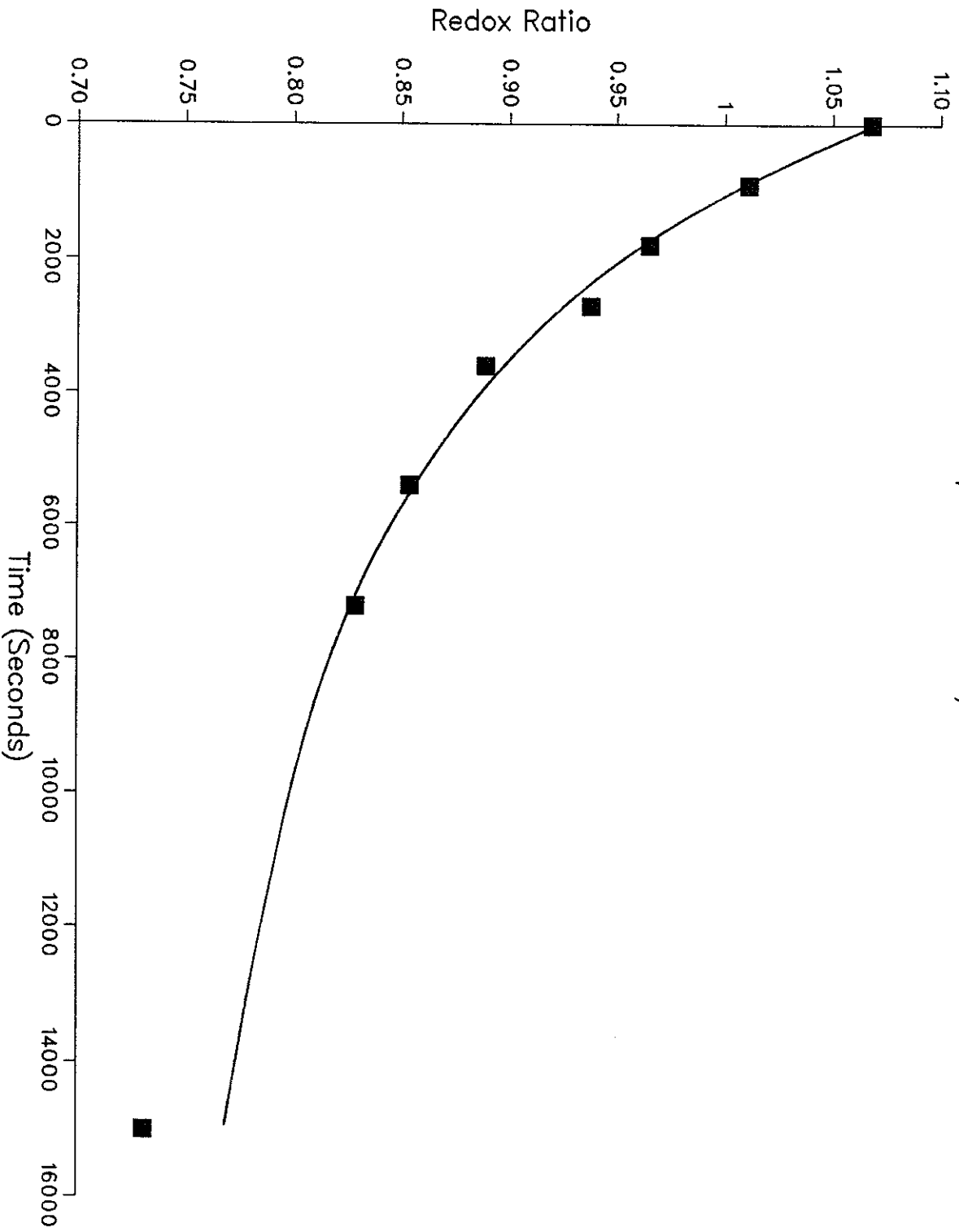
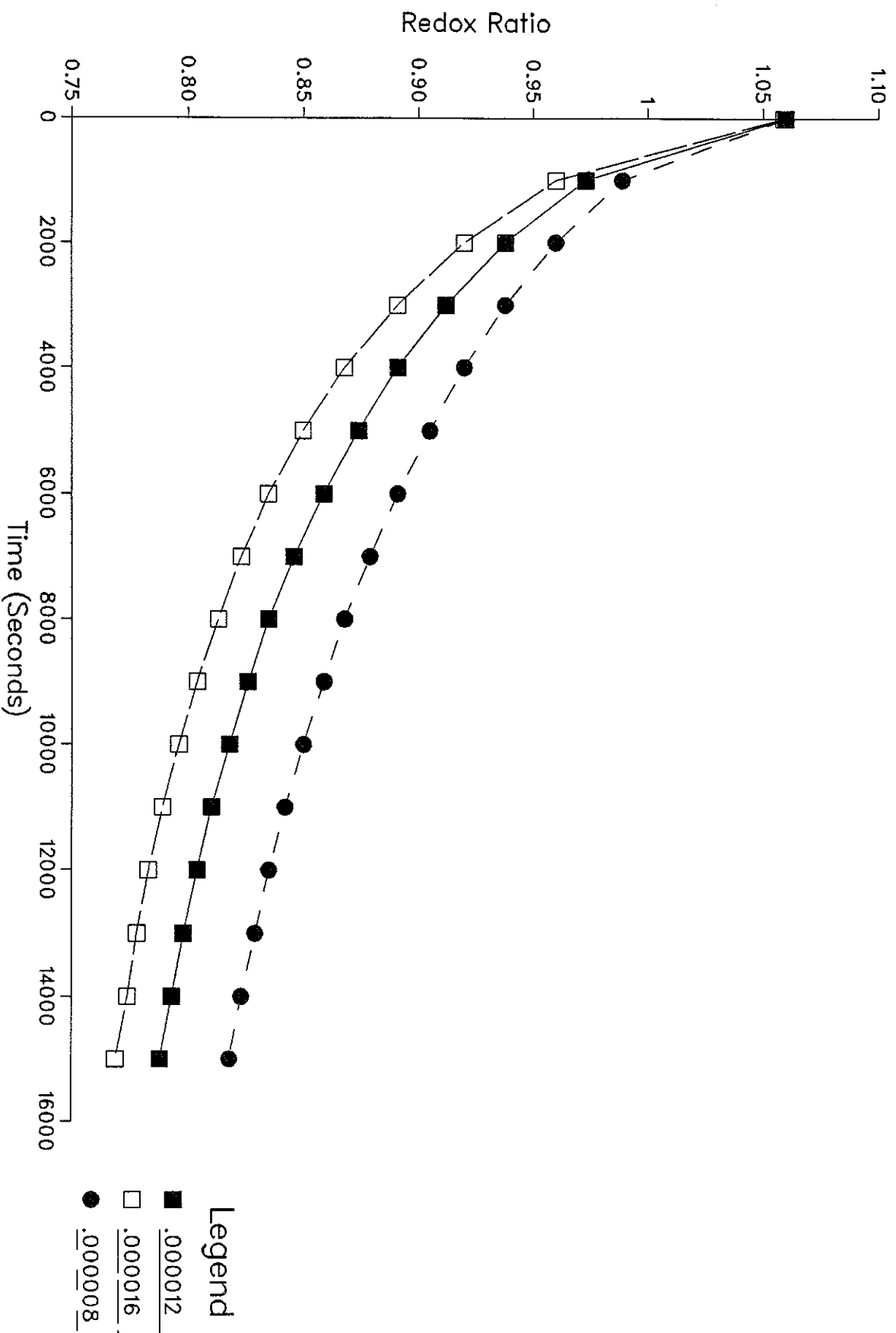


Fig. 2  
 An80 D120 w/ 1% Fe  
 at 1550 degrees C  
 Model Diffusion Curves



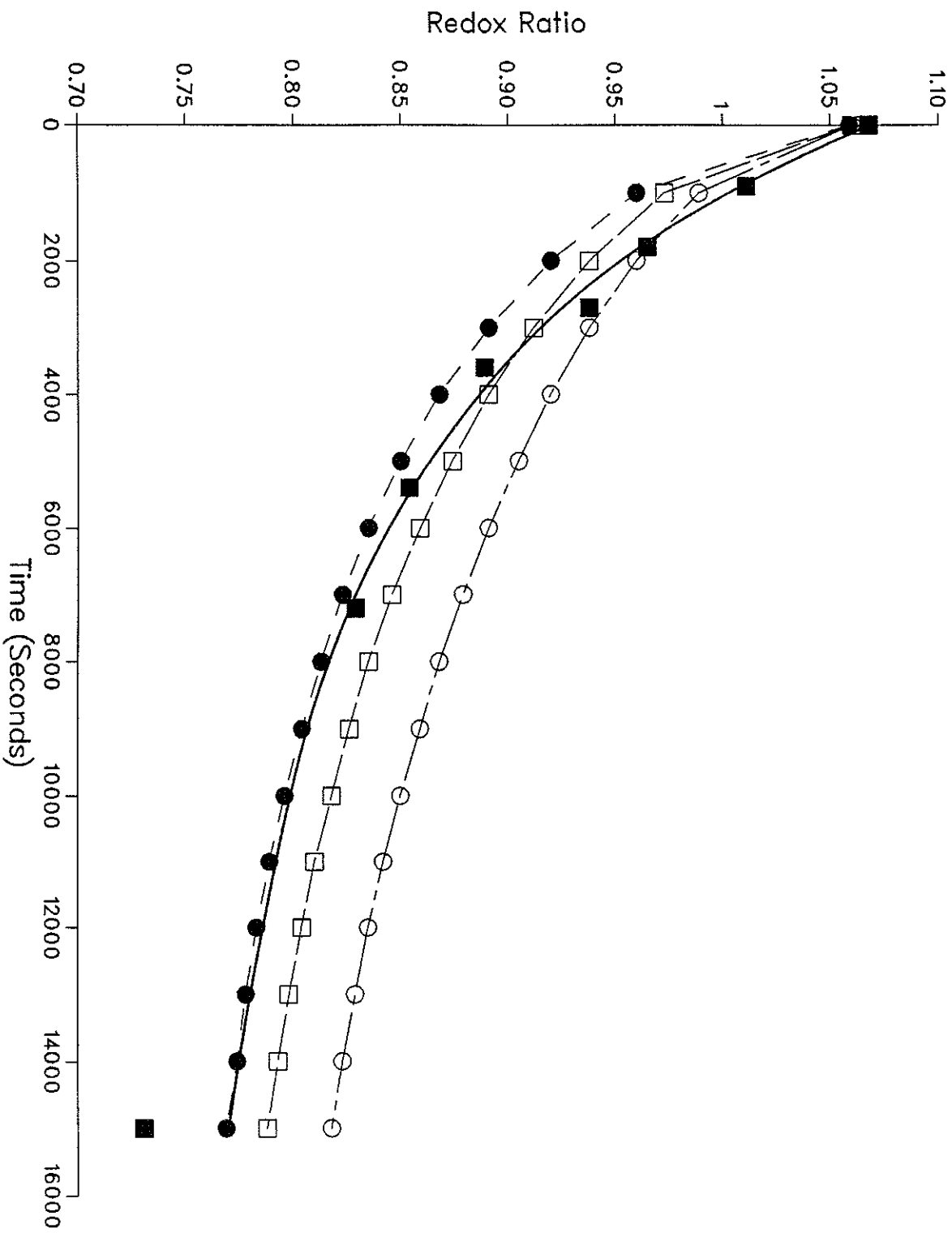


Fig. 3  
 An80 DI20 w/ 1% Fe  
 at 1550 degrees C  
 Determining the Actual Diffusion Coefficient

**Legend**

**Experimental Data**

- .000012
- .000016
- .000008

— — — — —

an experimental time series, R is the gas constant, and Do is the pre-exponential factor. The activation energy, the energy required to drive the diffusion process, determined for each composition is as follows:

An<sub>80</sub> Di<sub>20</sub>      79.34 Kcal/mole

An<sub>100</sub>            156.35 Kcal/mole

## References

Schreiber, H., Kozak, S., Fritchman, A., Goldman, D., and Schaeffer, H., 1986, Redox kinetics and oxygen diffusion in a borosilicate melt. *Physics and Chemistry of Glasses*, v. 27, no. 4, p. 152-177.

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## DEVELOPMENT OF AN IRON BASED GEOBAROMETER

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### INTRODUCTION

The effects of oxygen fugacity and temperature on equilibrium redox conditions in the geochemical standard basaltic compositions JB-1 and W-1 were investigated to provide a basis for the development of a geobarometer. Oxygen fugacity for a given atmospheric composition increases with increasing temperature at constant atmospheric pressure. The ratio of ferric to ferrous iron was used to measure the redox condition within a melt at equilibrium under an imposed oxygen fugacity and known temperature. Sack *et al* (1980), and Schreiber *et al* (1986), observed a definite correlation between increasing oxygen fugacities and decreasing redox values. The correlation is supported by experimental data obtained in this study (Table 1). Temperature effects on the equilibrium redox state of the melt are positively correlated; as temperature increases the redox ratio within the melt increases. This relationship reflects the effect of temperature on oxygen fugacity, in which higher oxygen fugacities are correlated with higher temperature (Sack, 1980). The relationship between oxygen fugacity and equilibrium redox values at known temperatures as observed in experimental data has permitted development of a graphical geobarometer (Figure 2). The barometer operates on the premise that given the redox state of a rock in nature, equilibrium oxygen fugacity conditions responsible for the redox state can be determined if the melting temperature of the rock is known.

### EXPERIMENTAL PROCEDURE AND ANALYSIS

The procedure followed for sample preparation and collection of data involves a series of furnace runs at atmospheric pressure to fuse the powdered samples into glass beads. Dissolution of these beads and subsequent titration of the solution measures the concentration of ferric ions in the bead at equilibrium.

Two-hundred milligrams of the powdered geochemical standard was placed in a shallow graphite crucible containing a five millimeter diameter platinum wire loop. The crucible was heated in a DT-31 bulk furnace at 1200 degrees C for one minute and then removed to quench the sample at room temperature, producing a glass bead. The glass bead was suspended in a DT-28 vertical tube furnace at the desired temperature and oxygen fugacity conditions for four hours to ensure redox equilibrium between the melt and the imposed atmosphere. Previous studies had indicated achievement of redox equilibria within four hours. Oxygen fugacity conditions within the furnace were controlled by mixtures of carbon dioxide and carbon monoxide gases. Samples were run at CO<sub>2</sub>/CO ratios of 50/50, 95/5, 100/0, and in air at 1200, 1275, and 1375 degrees C. Similar experimental runs were completed on both standard compositions.

After reaching equilibrium, samples were taken from the furnace and quenched at room temperature. The samples were removed from the platinum loop and ground into a fine powder using a clean alumina mortar and pestle. Ten to fifteen milligrams of the powder was placed into a covered plastic vessel and flushed with argon gas to remove excess oxygen. Ten milliliters of 1:1 H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O solution was then added to the vessel and allowed to react with the glass for five minutes while being stirred with a magnetic stirring rod. Five milliliters of 1:1 HF:H<sub>2</sub>O solution was then added and the mixture was stirred for an additional ten minutes. Four grams of crystalline boric acid was added and allowed to react for five minutes with the solution to complex any excess fluoride in the solution that might interfere with the subsequent titration.

The resulting solution contained Fe (II) and Fe (III) ions in the ratio in which they existed in the melt at equilibrium with the imposed atmosphere. Fifty microliters of 0.2M o-phenanthroline indicator was added to the solution, giving it a red-orange color. The sample was titrated using 0.00125M Ce (IV) sulfate solution. The amount of titrant used in reaching the colorless endpoint was recorded and compared to the amount necessary to neutralize a blank sample. Fe (II) in solution was calculated by equation 1.

$$[\text{Eq. 1}] \quad \text{Fe (II)} = \frac{\text{ml. Sample} - \text{ml. Blank}}{\text{mg. Sample}} * .00698$$

The equilibrium redox ratio was then calculated as the amount of Fe (II) divided by total Fe minus Fe (II).