The Effect of Variation of Iron Content on Redox Monitored Oxygen Diffusion Experiments in a Silicate Melt

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These experiments were undertaken to determine the variation in oxygen diffusion coefficients based on a change in iron content in a silicate melt. The oxygen diffusion coefficient and related multivalent element redox ratios, which is the ratio of multivalent ions, in our study of Fe^{+2}/Fe^{+3}, changes the bulk structure of the melt and thus has an affect on the density and viscosity (Dickenson and Hess, 1986), crystallization sequence (Hill and Roeder, 1974), liquid immiscibility (Naslund, 1983), and liquid fractionation (Osborn, 1959). The oxygen diffusion coefficient varies with temperature, composition and oxygen fugacity (Kozak, 1991). At Washington and Lee University under Keck funding a group of students worked in this area of study in 1990. Oxygen diffusion coefficients for melts of Anorthite 80% Diopside 20% were measured (Blazek, 1991). One of the purposes of my study was to look at what error might have been introduced into experiments of this kind. The multivalence of iron allows its use as a tracer in the movement of oxygen in the melt structure by chemical oxygen diffusion or COD (Kozak, 1991). A change in oxygen fugacity in the atmosphere sets up a chemical gradient that causes the movement of oxygen in order to keep the concentration of O_2 equal. Because the diffusion is monitored by the ratio of Fe^{+2} to Fe^{+3} this movement can be measured by the change in the redox ratio. In diffusion experiments using isotopes of oxygen as the indicator of diffusion, the results for the diffusion coefficient vary from those measured using iron as a tracer (Dunn, 1982). This may be due due to the reaction of dissolved oxygen with iron in the melt structure and thus the slowing of the diffusion process. Fe^{+2} reacts with O_2 molecules producing Fe^{+3} and single oxygen ions which are incorporated into the network structure. This reaction produces a disequilibrium in the oxygen fugacity of the O_2 in solution with that in the atmosphere. Oxygen molecules from the atmosphere then diffuse into the melt equilibrating the oxygen fugacity in the melt with that in the atmosphere (Eqn. 1). My project is to look at the affect of iron concentrations on the magnitude of oxygen diffusion over different times.

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

***Equation One:** Redox equilibrium of multivalent iron (Farrell, 1991)*

The melt chosen was the Anorthite 80% Diopside 20% which was studied in the summer of 1990. The mixtures were made up of a composition of anorthite-diopside-hedenbergite along the line of 75.69 molar percent anorthite which is on the Anorthite-Diopside line at $An_{80}Di_{20}$. This method allowed the addition of iron without modifying the melt structure. Increasing iron in weight percent substituted for magnesium and moved the composition from diopside to hedenbergite (Figure 1). Experimental glasses were composed of 1.00%, 3.00%, and 5.01% iron by weight. The glass was made from Fisher reagent grade powdered oxides and, except for the introduction of the iron oxide in the first stage of the mixing rather than after the primary homogenization, the procedure for composing the glass is the same as conducted by Keck students in 1990 (Farrell, 1991). The glasses were analyzed by scanning electron microscope (SEM) with an energy dispersive system (EDS) after homogenization to confirm composition and full homogenization. The melt was then crushed into a powder and samples of about 300mg were mixed with Duco liquid cement so that the powder could be stuck onto a platinum loop and placed into the furnace to form a bead. In previous experiments it has been found that platinum forms a solid solution with iron in the sample thus causing iron in the melt in contact with the wire to react with the platinum (Schreiber et al., 1986). The amount of Pt in contact with my beads allows for only negligible loss of iron to the wire (Presnall and Brenner, 1974). Another problem encountered when trying to form the experimental beads was that of iron reduction. When first making beads this summer the sample amount of powder was placed in a graphite crucible with the platinum loop all of which was then put into a bulk furnace above the melting temperature of the powder. The powder melted into a bead and surface tension between the melt and the wire loop caused the melt to stick onto the loop. However, when some of the powder from the beads was analyzed I found that the graphite had reduced the iron in the sample even with as little time as 5 minutes. Therefore I abandoned this technique in favor of using Duco cement. The

cylindrical holes; (4) measure twice, saw once; (5) write everything in your lab book, even the most obvious things; (6) weigh everything at every opportunity; (7) remove the outer layer of cylindrical metal stock prior to applying high stress; (8) water under pressure in the lab should be confined; (9) salt causes rust; (10) 50 micron marbles are difficult to shoot; (11) Virginia is hot and humid in July -- except in caves; (12) graphite dust permeates everything; (13) the Civil War has not been forgotten.

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mixture of Duco and powder was placed onto a platinum loop and suspended in a Deltec furnace at 1500°C to form a 6mm diameter bead. The amount of wire used was kept to a minimum to avoid solution with the iron while still long enough to provide sufficient surface tension to hold the bead. The temperature of the Deltec furnace was calibrated with a $Pt/Pt_{90}Rd_{10}$ thermocouple accurate within ± 5°C which in turn had been calibrated with a chromium alloy thermocouple. The beads were allowed to equilibrate in CO_2 for three hours under reducing conditions. The beads were then placed in an air atmosphere at 1500°C for a time series consisting of :00 minutes (fully reduced), :05 minutes, :15 minutes, :30 minutes, and overnight runs which were done to equilibrate the beads in an oxidizing atmosphere. All quenches were air quenches with a time of 20 seconds or less from removal from the hot spot to fully cooled. Effects of the quench media may give a poor reading in the redox ratio due to the partitioning of atoms in four fold or six fold coordination and the consequential change of Fe^{+2} to Fe^{+3} to fit into the denser glass (Dyar et al., 1987). This change in iron valence would occur in the spot in the bead which cooled the slowest, which would be the center. In oxidizing experiments the reduced iron in the center of the bead would tend to oxidize slightly thus increasing the weight percent of Fe^{+3} and decreasing the redox ratio. However, by trying to quench the beads in a cold ice bath the beads were disfigured and tended to fracture which would change the diffusion rate if the bead were to be run again. After the time series each set of beads was powdered and titrated in an inert argon atmosphere using a $cerium^{+4}$ solution and a phenanthroline ferrous sulfate indicator to determine the weight percent of Fe^{+2}

$$\text{wt\% } Fe^{+2} = \frac{.00578 * (Ce^{+4}\text{ titrate ml }_{[\text{sample}]} - Ce^{+4}\text{ titrate ml }_{[\text{blank}]})}{\text{grams of sample}}$$

Equation 2: *Determination of the weight percent Fe^{+2}*

where the constant .00578 is an experimental constant derived from the titration of samples with known Fe^{+2} weight percents (Eqn. 2). Then by using the original weight percent iron in the melt and subtracting the Fe^{+2} weight percent, the weight percent of Fe^{+3} and the redox ratio were determined.

The data presented in Table 1 and the graphsshows that there is a correlation between the iron content in the melt and the measured redox ratio. The samples that had 3.00% and 5.01% iron showed an increase in the redox ratio over the samples with 1.00% iron. As the amount of iron in the melt slows down the amount of oxygen going into the melt, then the Fe^{+3} decreases and the redox ratio, Fe^{+2}/Fe^{+3}, increases. The difficulty in measuring 1.00% iron by colorimetric titration is probably the reason for the poor data for the 1.00% samples. I have more confidence in the 3.00% and 5.01% samples as these show the expected decrease in Fe^{+2}, and the decrease in the redox ratio with the longer time in air.

I intend to continue this research and hope firstly to obtain more accurate data especially at 1.00% iron. I will be sending samples to be analyzed using Mössbauer spectroscopy which has been shown to be more accurate than wet chemical titrations at low iron content (Dyar et al., 1987). Secondly I will be repeating the time series at different temperatures to obtain an activation energy for the system. Finally, I would like to see if the activation energy is changed by the change in iron content.

Figures

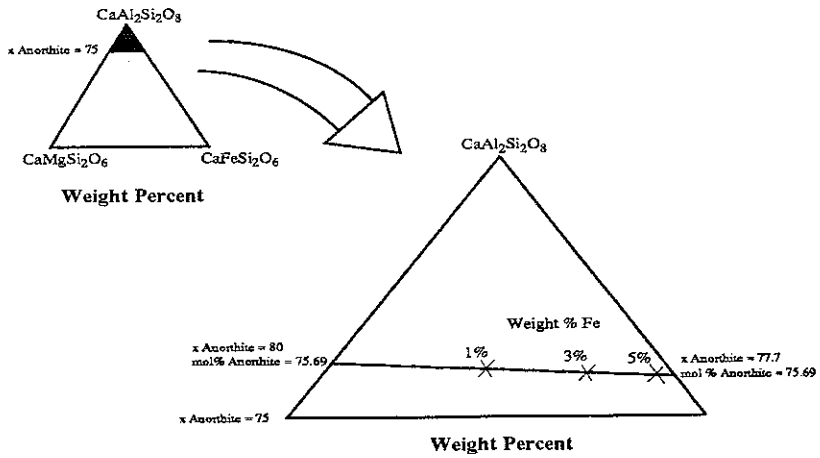
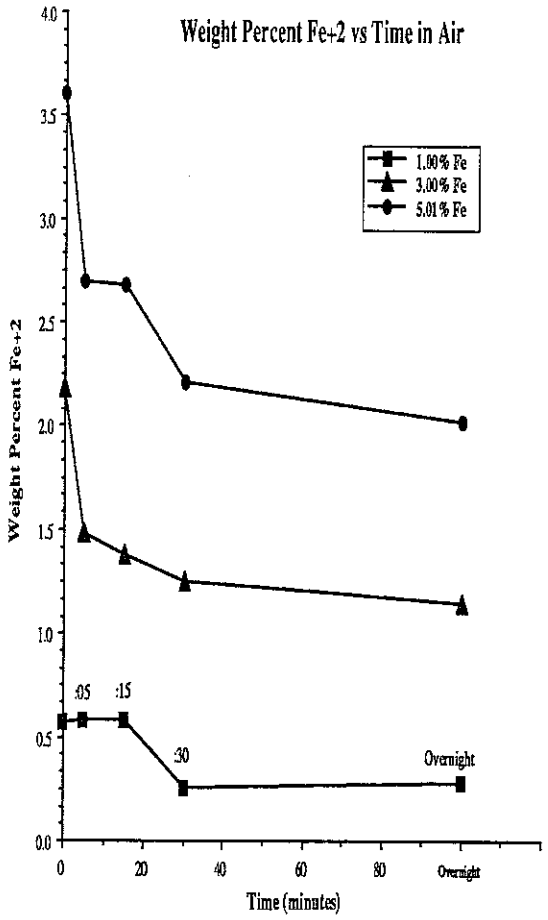


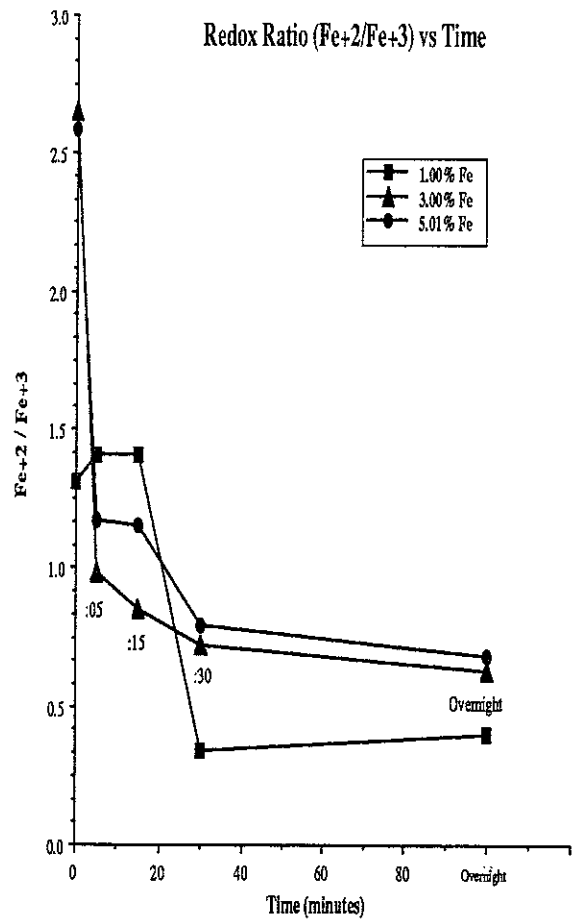
Figure 1: *Plot of experimental compositions on the Anorthite-Diopside-Hedenbergite triangle*

Time	Fe^{+2} weight percent and **Redox Ratio (Fe^{+2}/Fe^{+3})**					
Hours:minutes	**1.00 weight % iron**		**3.00 weight % iron**		**5.01 weight % iron**	
0:00 CO2 Equilibration	.57	**1.31**	2.18	**2.65**	3.61	**2.59**
0:05	.58	**1.41**	1.48	**.98**	2.70	**1.17**
0:15	.68 .58	**2.11*** **1.41***	1.38	**.85**	2.68	**1.16**
0:30	.26	**.34**	1.25	**.72**	2.21	**.79**
Overnight	.28	**.40**	1.15	**.63**	2.02	**.68**

* Two titration values recorded

Table 1: Redox ratios and Fe^{+2} weight percents for varying experimental times and compositions





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The Effect of Pressure and Water Content on Chemical Diffusion of Oxygen in an $An_{30}(Di_{98}Hd_2)_{70}$ Silicate Melt

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Introduction

The major goal of this study is to measure the effect of pressure and water content on chemical diffusion of oxygen through a basaltic silicate melt [$An_{30}(Di_{98}Hd_2)_{70}$] at elevated temperatures. As both pressure and temperature are increased, the rate of oxygen diffusion through a melt is also expected to increase (Dunn, 1983). As pressure is increased, the distance between atoms becomes smaller, requiring less energy for these atoms to migrate and thus the diffusion coefficient increases with pressure. As temperature is increased, atoms have on average a greater amount of kinetic energy and can migrate more easily; thus, the diffusion coefficient also increases with temperature. Earlier studies have not fully quantified the role of water in oxygen diffusion, particularly at high pressure. The experiments described here were designed in an effort to determine the effect of water on the diffusion coefficient of oxygen in a basaltic melt at pressure (7 kbar) similar to that in the mid- to deep crust or uppermost mantle.

The composition used in this study was chosen for several reasons. Previous diffusion studies similar to the one conducted here used melts composed of 30% anorthite + 70% diopside (Kozak, 1991) because of their similarity to basalt. This composition is the eutectic composition in the absence of water (Presnall et al., 1978), thus allowing the temperatures used in the experiments to be as low as possible while still remaining above the solidus in the dry runs. Hedenbergite was added to obtain the two percent iron needed to monitor the changing oxygen fugacity resulting from diffusion.

Methods

The Fe^{+2} - Fe^{+3} oxidation - reduction couple was used to monitor the oxygen diffusion rate. The powdered oxides were heated above the liquidus and allowed to equilibrate in an oxygen-rich environment so that most iron would be in the form of ferric (+3) iron. The melt was then quenched to a glass and subsequently ground into a powder in an alumina mortar and pestle. In each run, the powdered glass was placed in a graphite cup with a 0.25 inch diameter cylindrical hole to achieve reducing conditions, i.e., as oxygen diffuses out of the sample to the graphite the ferric iron would be reduced to ferrous iron. An appropriate amount of water was added to some of the powders to achieve either 4 or 8 weight % water (Table 1). A pressure of 7 kbar (hot piston in) was applied in all runs, using a piston-cylinder apparatus at Smith College. The powders (+/- water) were heated at a rate of 200°C per minute to a specific temperature above the liquidus, held at this temperature for either 5, 10 or 20 minutes (Table 1), then quenched to a glass pellet. When the experiment is done at a temperature below the liquidus, crystallization happens too fast to measure the diffusion coefficient for the liquid.

Next, each glass pellet was crushed in an alumina mortar and pestle and dissolved in an hydrofluoric - sulfuric acid solution. Each dissolution took place in an argon environment to prevent atmospheric oxygen from entering the system. Titrations were performed on each sample solution to determine the amount of ferrous (+2)