AN EXAMINATION OF THE CHEMICAL OXYGEN DIFFUSION RATES IN THE SYSTEM ANORTHITE20 AND DIOPSIDE80 VIA IRON REDOX EXPERIMENTS

Ronald W. Niebo
Department of Geology
Washington and Lee University
Lexington, Virginia

Introduction

Experiments were performed on melts composed of Anorthite20 Diopside80 to determine the chemical oxygen diffusion coefficient at one atmosphere pressure at three different temperatures. The experimental temperatures were 1375, 1425, and 1475 degrees C.

Chemical diffusion is defined as the movement of components or constituent species in a melt from point to point within the melt along chemical potential gradients (Dunn, 1986). A chemical potential gradient defines the motion of the chemical from point to point in the melt. Chemical potential is analogous to gravitational systems in that the most stable state is the one of lowest potential. At equilibrium, potentials of neighboring states are equal (Best, 1982).

Oxygen will diffuse from an oxygen rich atmosphere into a sample with a lower oxygen content than the atmosphere. Diffusion rates can be determined by using an iron dopant to monitor changes in the oxygen content. Iron is used because when it is oxidized, it accepts an extra oxygen atom. The redox state of iron changes as oxygen enters or exits the system according to the general redox equation (Eq. 1)

$$[4M^{(m-n)+} + n\ O2_{(gas)} = 4M^{m+} + 2n\ O^{2-}\ ]$$
$$(melt) \qquad\qquad (melt) \qquad (melt) \qquad\qquad \textbf{Eq. 1}$$
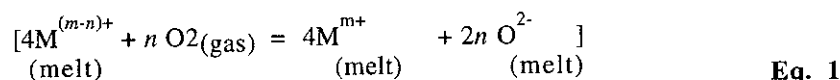
where M is the multivalent element in oxidized M^{m+}, and reduced, $M^{(m-n)+}$, species within the melt and n is the number of electrons transferred in the redox couple (Schreiber et al., 1986).

The experiments used small samples (400 mg) of An20 Di80 doped with %1 iron by weight. Each sample was equilibrated under reducing conditions (CO_2 atmosphere) to minimize the Fe^{+3} content. The reduced samples were remelted at a chosen temperature for varying lengths of time in a more oxidizing environment, air. A modified version of Fick's Second Law of Diffusion (Eq. 2) can be used to calculate the redox ratios at a given depth for a fixed time The results also allow one to calculate a diffusion coefficient which is the rate of diffusion.

$$\frac{x - x_o}{x_e - x_o} = \sum_{j=0}^{\infty} (-1)^j \times \left[erfc\frac{(2j+1)L - z}{2\sqrt{Dt}} + erfc\frac{(2j+1)L + z}{2\sqrt{Dt}} \right] \qquad \textbf{Eq. 2}$$

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 and D is the diffusion coefficient." (Kozak, 1991)

Experimental Procedures

A glass composed of An20 Di80 was prepared by melting the appropriate elemental materials in a platinum crucible at 1350° C for 24 hours in a Deltec high temperature bulk furnace. After quenching the glass in water, it was removed from the crucible and ground by hand into a fine powder. The powder was then weighed, doped with 1 wt% iron to make a 10g batch and mixed in a mechanical mixer to homogenize the materials. The doped An20-Di80+Fe sample was re-melted, quenched, and ground to a fine powder and separated into 18 400 mg lots. These lots were placed in 5 mm OD round platinum tubes of a constant geometry. Identical sample sizes and small platinum tubes were used to ensure a constant melt depth and minimize convection.

After separating the samples into 3 groups of 6, each sample was equilibrated at a specified temperature above its liquidus (1375° C, 1425° C, or 1475° C) in a reducing atmosphere of CO_2. This was done in a Deltec vertical tube furnace specially equipped to control the atmosphere. One of the reduced
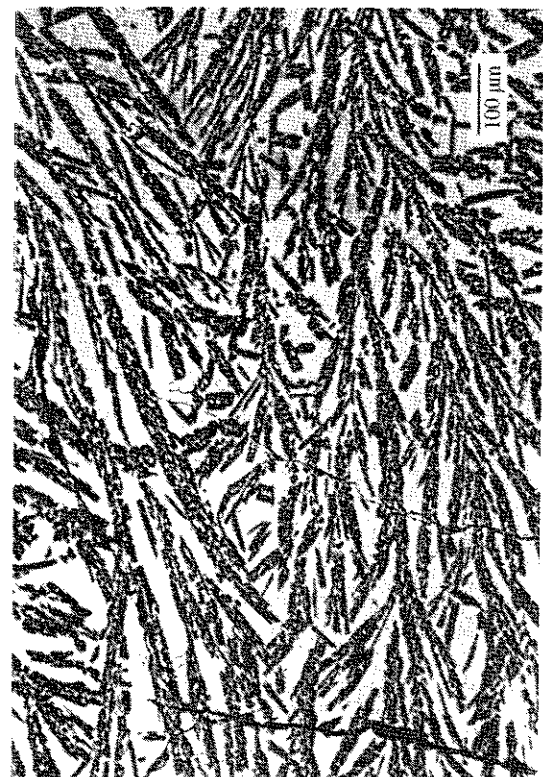
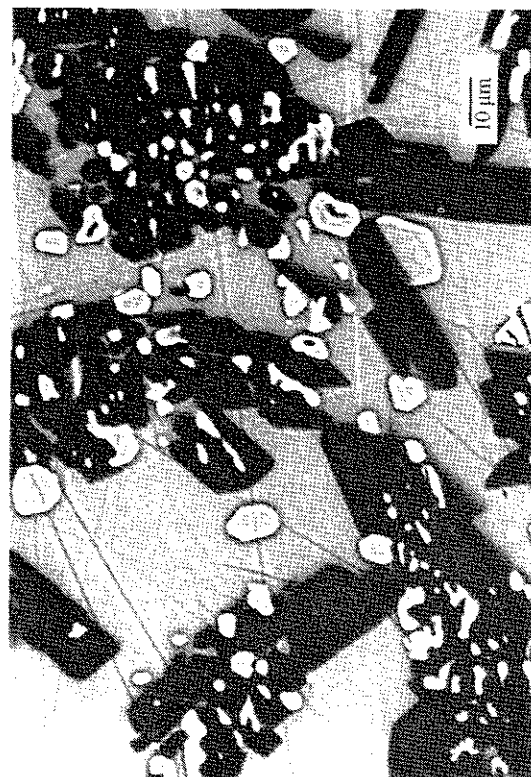Figure 2. Sample #214, 1140°C, 42 hrs.

Figure 4. Sample #214, 1140°C, 42 hrs.

Figure 1. Sample #213, 1150°C, 20 hrs.

Figure 3. Sample #205, 1160°C, 10 hrs.

samples from each group was set aside while the others were melted in air for different time periods at their respective temperature. The times were 15 min., 30 min., 45 min., 75 min., and 24 hours. Afterwards, the oxidized samples were removed from the platinum tubes and prepared for titration.

Titrations were conducted using standard cerric sulfate solution as a titrant and o- phenanthroline complex as a visual indicator to determine the redox state of the individual samples. Approximately 100 mg of sample was placed into a polypropylene digestion container along with a dry magnetic stirring bar. Inert argon was forced to flow through the system so that the sample would not oxidize during digestion. Two acids were used to digest the glass. A 10 ml aliquot of 1:1 (by volume) H_2SO_4: H_2O was added first and a 5 ml aliquot of 1:1 HF:H_2O was added later. 3.0g of crystalline boric acid was added later to complex excess fluoride. After complete digestion, the sample was removed from argon and titrated (Blazek, 1991).

50.0 ml of o-phenanthroline complex indicator was added to the sample. It caused the sample to take on a reddish hue. The sample was titrated to its clear/blue equivalence point using the cerric sulfate titrant. The amount of reduced iron could then be determined from Eq. 3.

$$Wt\% Fe^{+2} = \frac{.00698 * (ml\ Ce^{+4}\ to\ titrate\ sample\ -\ ml\ Ce^{+4}\ to\ titrate\ blank)}{(Grams\ of\ sample)} \qquad \textbf{Eq. 3}$$

The Fe^{+3} content was determined by subtracting the analyzed $\%Fe^{+2}$ from a nominal total iron content (1%) and the redox ratio, Fe^{+2}/Fe^{+3} calculated.

Modeling

For a given set of starting and final redox ratios, there exists only one diffusion coefficient which will yield a model redox ratio matching an experimental value for a given time. Eq. 4 uses values computed from Eq. 2 to "give the average value of the reduced ion concentration in the entire sample after a set time has been allowed for diffusion. The average concentration of the oxidized ion can be obtained by the difference of the total multivalent element concentration and the average concentration of the reduced ion" and the average redox ratios for the sample calculated (Schreiber et al., 1986).

$$\left[\overline{M^{(m-n)+}}\right] = \frac{[M]}{L}\int_0^L \frac{x(z,t)}{1+x(z,t)}dz \qquad \textbf{Eq. 4}$$

A computer program was written to solve the equation so that given a starting and final redox ratio, the weight percent iron in the system, the time in seconds for which the sample was oxidized, the sample depth, and a diffusion coefficient, the program calculated the average redox ratio for the chosen time. Keeping the starting and final redox ratios of the system, the melt depth, the weight percent iron, and time constant for each experiment, the diffusion coefficient was varied until the program gave the model redox ratio most closely matching the experimental redox ratio. This value was chosen as the diffusion coefficient operating during the experiment. The average of diffusion coefficients for different experiments at the same temperatures was assumed to be the diffusion coefficient operating at that experimental temperature. The model redox ratios for the chosen diffusion coefficient and the experimental redox ratios for experiments at 1475°C were each plotted with respect to time (Figure 1) and are similar to plots of data for other temperatures examined.

Results

Diffusion Coefficients

The log of the average diffusion coefficients for each temperature and the standard deviation for each group of averages are shown in Table 1.

Table 1 Diffusion coefficients and standard deviations for An_{20} Di_{80} at 1375°, 1425°, and 1475°C.

Temperature (°C)	Log of the Diffusion Coefficients	Standard Deviation
1375	-5.06	.137
1425	-5.10	.303
1475	-4.69	.519

Experimental Redox Ratios vs Modeled Redox Ratios in An_{20} Di_{80} System at 1475 Degrees C

Time in Seconds
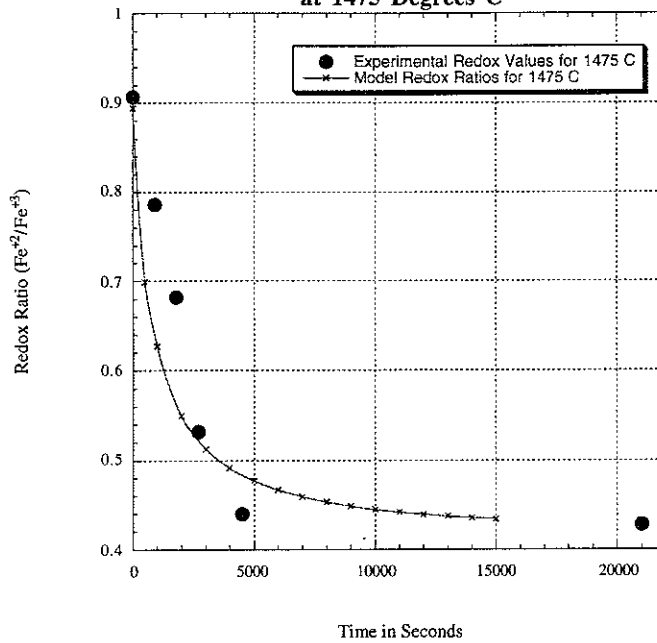
Figure 1. Each of the circles represents an experimental data point. The curve is the average theoretical diffusion coefficient with respect to time found by manipulation of Fick's Second Law. The last experimental point is actually located at 86,400 seconds. It has been moved in to 21,000 seconds for convenience.

Another way to determine a diffusion coefficient for each temperature in this system is to use the Arrhenius relationship (Eq. 5).

$$\log D = \frac{-E}{2.303RT} + \log Do \qquad\qquad Eq. 5$$

D is the diffusion coefficient, E is the activation energy, R is the universal gas constant, T is the temperature in degrees Kelvin for an experimental time series, and Do is the pre-exponential factor. The log of the diffusion coefficients are inversely related to the temperature in degrees Kelvin in a linear fashion. Since the relationship is linear, a least squares solution for all experimental data will yield a linear least squares equation relating log D to $1/T°K$. (Figure 2) Calculation of the diffusion coefficients by means of the equation for each experimental temperature will yield a value based on all of the data rather than that at just one temperature. The calculated diffusion coefficients are shown in Table 2.

Table 2 Diffusion coefficients An_{20} Di_{80} at 1375°, 1425°, and 1475°C calculated from best fit line on a plot of log D vs. $1/T°K$

Temperature (°C(	Log of the Diffusion Coefficients
1375	-5.13
1425	-4.95
1475	-4.77

198

Activation Energy

    Activation energy is related to the log of diffusion coefficients and the inverse of temperature in degrees Kelvin by means of the Arrhenius relationship (Eq. 6). Activation energy is equal to 2.303R multiplied by the slope of a least squares fit on a plot of log D and $1/T°K$. Figure 2 shows the least squares solution line and the value of its slope. The activation energy for $An_{20} Di_{80}$ is 47.47 Kcal/mol. The value is comparable with activation energies for other similar systems.

Log of Diffusion Coefficients vs Inverse of Temperature (K)
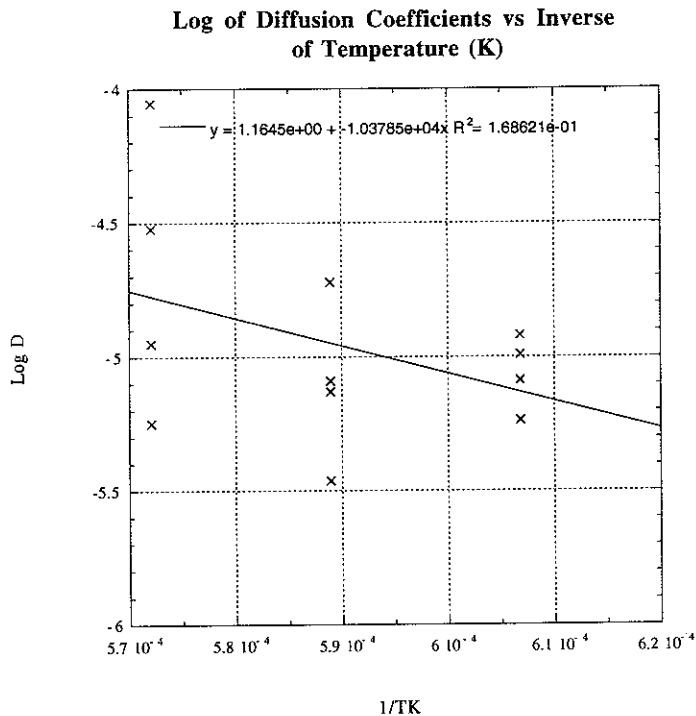
Figure 2. The log of each diffusion coefficient was plotted against the inverse of temperature (Kelvin). A linear curve was found and used to calculate diffusion coefficients. The slope of the line, 1.038×10^4, is used to calculate activation energy for $An_{20} Di_{80}$

References

Best, M. G., Igneous and Metamorphic Petrology. W. H. Freeman and Company; San Francisco, 1982.

Blazek, J., 1991, A Determination of Chemical Oxygen Diffusion Rates in the Systems Anorthite$_{80}$ Diopside$_{20}$ Via Iron Redox Experiments, *in* The Fourth Keck Research Symposium in Geology (Abstracts Volume): Franklin and Marshal College, Lancaster, PA, April 1991.

Dunn, T., 1986, Diffusion in silicate melts: an introduction and literature review. Mine Association of Canada, short course in silicate melts (Short Course Handbook vol 12), May 1986, p. 57 - 92.

Kozak, S., 1991, Oxygen Diffusion and Redox Equilibria in Silicate Melts, *in* The Fourth Keck Research Symposium in Geology (Abstracts Volume): Franklin and Marshal College, Lancaster, PA, April 1991.

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.

Measuring the Rates Between Cation Interdiffusion Between Dacite and Basalt

Gillian Rosenstein '95
Department of Geology
Smith College
Northampton, MA 01063

Introduction

Almost every geologist has observed in the field a mafic pillow or pod located inside a felsic magma, and there always has been scientific curiosity concerning the interaction between magmas of different bulk compositions. The purpose of this study was to determine how dacite, a silica-rich magma, and basalt, a silica-poor magma, interact during magma mixing. The effects of cation interdiffusion between dacite and basalt also were studied. Several questions posed during the design of the project include (1) "what are the details of the magma mixing process between a felsic and mafic magma?" (2) "how does the diffusion rate differ under various temperature conditions for each constituent species?" There are many different geologic instances where various magmas come in contact with one another and combine, e.g. volcanic regions or any landscape where intrusions, dikes, and sills are present.

To answer the questions about the interactions among magmas of different bulk compositions, it is necessary to recall that magma can be mixed by mechanical processes, forcible injection and convection, or by chemical diffusion. These experiments were designed to try and minimize mechanical mixing by inserting the more dense magma in the capsule first and then placing the less dense magma on top. This helped to ensure that the different chemical composition readings collected would be a consequence of diffusion. It is also important to note that the melting and crystallization temperatures for each magma are dependent upon their chemical compositions. The final mixture is usually a combination of these processes occurring simultaneously.

I designed experiments to place dacite and basalt in contact at high temperatures (800°C - 1200°C) and 1.0 GPa of pressure in order to observe the reaction between them. Dacite and basalt were chosen for use in this study because both are common magmas but have different bulk chemical compositions. The major chemical factor which influences crystallization temperature is the percentage amount of silica in the magma. The dacite used contained 64 percent SiO_2 whereas the basalt contained 50 percent SiO_2. Because SiO_2 crystallizes at a lower temperature, it crystallizes out of the melt relatively early. When it crystallizes out, it is removed from interacting with the other chemical elements in the melt. Because of this, the amount of crystallization is an important factor in determining the final product of the background melt in magma mixing, or determining the diffusion rate.

As magmas can be molten at various temperatures, experiments are conducted at temperatures 800° C to 1200° C. In all experiments the temperature is low enough to allow the basalt to begin crystallizing before the dacite. At these experimental temperatures, the basalt became crystalline while the dacite was still above its liquidus. When this happens, the dacite is limited in its mixing with the basalt and diffusion occurs slowly. In order to address the question of how diffusive mixing differs under various temperature conditions, it is helpful to understand diffusion. Diffusion is defined by Dunn (1986, p.57) as "the movement of constituent species of the melt from point to point within the melt". Constituent species usually move from an area of higher concentration to an area of lower concentration in an attempt to achieve homogeneity. In order to verify a diffusive effect, it is necessary to minimize all other factors and avoid mechanical mixing. Diffusion is the idea that the species in the melt move because part of their total energy is kinetic. This kinetic energy causes random motions of the particles in the melt.

Experimental Procedure

To investigate how temperatures affect the rate of diffusion, five different experiments were conducted at temperatures varying from 800°C - 1200°C at intervals of 100°C. All experiments in this study were conducted at a constant pressure of 1.0 GPa. For each pressure-temperature pair, one sample had 0 percent water by weight, and a second sample had 6 percent water by weight. All five different temperature experiments were conducted for 24 hours to allow for measurable diffusion to occur. In addition to these five experiments, a four day experiment at 800°C and a zero-time experiment at 1000°C were conducted. The purpose of the four day experiments was to determine whether diffusion rates were what was actually being measured in the other samples. This verification could be accomplished by comparing data from the four-day run data with the 24-hour run data. For example, if the distance measured by diffusion was proportional to the time at 800°C, calculated using Fick's equation, and all other relevant factors were