Oxygen Diffusion, Viscous Magmatic Flow, Garnet Synthesis, and Other Adventures in Experimental Petrology

John B. Brady, Department of Geology, Smith College, Northampton, MA 01063
Samuel J. Kozak, Department of Geology, Washington and Lee University, Lexington, VA 24450

Introduction

The Virginia Experimental Petrology Project convened at Washington and Lee University is in many ways a continuation of the 1990 Keck Experimental Petrology Project (Kozak, 1991). As in 1990, the focus of the project was on the kinetics of processes in silicate melts that are simple chemical analogs of natural basalts. However, the availability of new 3/4" piston-cylinder presses, purchased in part with Keck funding, opened a number of new avenues for research for 1991. Three students elected to continue the work on oxygen diffusion, two of these projects involving high pressures. Two students chose to study the viscosity of these melts, a physical property that is related to diffusion. One student undertook the high pressure synthesis of a series of garnets, connecting with ongoing work at Smith College. Two challenges unify the experimental petrology projects: (1) overcoming the kinetics of rapid (or slow!) processes and (2) mastering obdurate equipment.

Kinetics

Geologists are time experts, collectors of chronometers. We use these timepieces to uncover critical evidence for earth models. Although erosion rates, sea-floor spreading rates, and radioactive decay constants are on the menu for introductory geology classes, other important rates such as those of chemical diffusion and viscous flow are not normal fare for geology undergraduates. This neglect is due in part to the somewhat complicated math required to interpret and apply diffusion and viscosity data. However, mathematical solutions to the equations for many important problems are known (*e.g.* Crank, 1975) and numerical solutions to many other problems are as close as the nearest spreadsheet program. Results of the 1990 and 1991 Keck experimental petrology projects demonstrate that the kinetics of diffusion and flow can be part of the undergraduate curriculum.

Oxygen is the most abundant element in the crust of the earth. It occupies most of the space and, with silicon, forms the structural framework of most minerals and magmas. The movement of oxygen by diffusion is important for many processes, processes whose rates and consequences may constitute useful geochronometers. For example, in silicate melts oxygen diffusion is necessary for crystal growth, isotopic exchange, and redox equilibria. Oxygen diffusion data can provide vital information about melt structure. Although several studies of oxygen diffusion in basalt-analog melts are available (*e.g.* Dunn, 1982, 1983; Blazek, 1991; Farrell, 1991; Smith, 1991), a number of interesting issues remain.

Most diffusion experiments study the rate of homogenization of a chemical discontinuity. Two principal types of experiment have been used to measure oxygen diffusion in silicate melts. The method used by the Keck projects is to change the oxygen fugacity of an "atmosphere" in contact with the melt and to monitor the flux of oxygen into or out of the magma by measuring the oxidation state of iron in glasses quenched from the melt after experiments of various durations. The other method is to make a melt enriched in ^{18}O, hold the melt in air for various times, and to measure the change of $\delta^{18}O$ in the quenched glass as a function of the duration of the experiment. Interestingly, these two measurement techniques do not yield the same oxygen diffusivity: the isotopic experiments yield diffusivities that are typically two orders of magnitude lower than the redox-monitored experiments.

One explanation for this difference is that the oxygen isotopic exchange experiments do not change the bulk chemical composition of the magma, whereas the redox-monitored experiments actually change the number of oxygen atoms in the melt. It has been shown (Darken, 1948) that the bulk composition change may provide an extra driving force for diffusion. However, this extra force probably cannot explain the large difference in measured diffusivities. A more likely explanation is that the redox-monitored experiments record the diffusion of O_2 molecules dissolved in the silicate melt. Dissolved O_2 could move without the breaking of strong silicon-oxygen bonds that form the melt structure or "network." To change the value of $\delta^{18}O$ for the melt, all of the oxygen in the melt is involved, silicon-oxygen bonds of the network would need to be broken, and this should reduce the measured diffusion rate.

To investigate the consequences of experimental design, Robert Cooper is studying the effect of iron content on one atmosphere, redox-monitored diffusion measurements. More iron means that more oxygen needs to diffuse into or out of the sample to change the iron redox ratio and this effect has not been accounted for in published results. If the operating mechanism is diffusion of low concentrations of dissolved O_2, then increasing the amount of iron in the sample should decrease the apparent diffusivity. Robert Cooper's experiments should provide a guide to removing the quantitative effects of the Fe redox reaction on the oxygen diffusivity obtained. The magnitude of the decrease in apparent diffusivity will also provide information on the concentration of O_2 in the magma.

Tori Swarmer is studying the effect of pressure on redox-monitored oxygen diffusivities. Although diffusivities invariably increase with increasing temperature, the effect of increased pressure cannot be predicted with certainty. The size of any pressure effect on oxygen diffusion may depend on the relative contributions of network oxygen and dissolved O_2. Shelly Fain is also studying oxygen diffusion at elevated pressure, but she has focused on the consequences of having H_2O in the melt. If the H_2O exists as OH^-, then some of the Si-O bonds in the network would be replaced by weaker Si-OH bonds that would facilitate the diffusion of network oxygen. However, if only diffusion of O_2 molecules is important, water should have a minimal effect.

Viscous flow and oxygen diffusion are related theoretically by the Eyring equation, which appears to describe well the viscosity and diffusivity data for a number of silicate melts (Yinnon and Cooper, 1980). The conceptual basis behind the Eyring equation is that both diffusion and viscous flow require the thermally activated breaking of network Si-O bonds. While the results of oxygen isotope diffusion studies of model basalts appear to conform to the Eyring equation, redox-monitored diffusion experiments do not. In part to explore these relations at elevated pressures, two students are measuring viscosities of basalt-analog melts as a function of composition and pressure. Nicole Fraser is studying anorthite-diopside melts rich in the anorthite component. David Tinker is studying anorthite-diopside melts rich in the diopside component. It is expected that the anorthite-rich melts will have a highly polymerized, feldspar-like framework silicate structure and, therefore, a higher viscosity than the diopside-rich melts with a less polymerized, pyroxene-like silicate chain structure. The effect of pressure and the properties of melts of intermediate compositions are less-easily predicted.

Equilibrium

Garnet is one of the most common minerals in metamorphic rocks. Because of its composition and high atomic density, garnet figures prominently in many geothermometers and geobarometers. Diffusion in garnet is slow and, therefore, garnets retain high temperature information even in slowly-cooled regional metamorphic rocks. However, because diffusion in garnet is so slow, it is difficult to complete experimental studies of reactions involving garnet. Equilibrium is elusive. If the thermodynamic properties of garnet were well-known, reactions involving garnet could be more accurately modeled, leading to improved geothermometers and geobarometers.

Dina Venezky elected to synthesize a suite of garnets at high pressure. To minimize the chemical complexity, she is growing garnets with compositions in the ternary system almandine-pyrope-spessartine. X-ray and spectroscopic data on these garnets should provide important constraints on garnet solution models. Eventually, the garnets will be used in garnet-biotite exchange experiments at Smith.

Equipment

Experimental petrology has its foundations in theory, but meaningful results are obtained only after many close encounters with a variety of complex equipment. Both engineering knowledge and artistic skills are needed to succeed in these endeavors. All members of our group gained both in activities ranging from shaping graphite on a lathe to extracting glass from platinum crucibles. A look at the sample assembly figured in some of the abstracts that follow will yield an appreciation of the complexity of these experiments.

Because the piston-cylinder presses were new, all were involved in the plumbing, wiring, calibration, and general debugging of the presses and related experimental procedures. Many false starts gave us a real appreciation for the work of other experimentalists: numbers are obtained only at a considerable expenditure of time and personal energy. The following is a small sampling of lessons learned: (1) metal is stronger than rubber O-rings and human flesh; (2) it is easy to deform stainless steel with a hydraulic press; (3) large cylindrical samples do not fit into small

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.

Acknowledgements

This project would not have been possible without the heroic efforts and advice of many people. We would like to give special thanks to John Ayers, Steve Weaver, Steve Bohlen, Eric Brewer, Jack Cheney, John Elrod, Bob Freed, John Harlow, Cathryn Manduca, Mata McGuire, Peter McNutt, Bob Merritt, Paula Seager, Diane Smith, Bob Thren, Bruce Watson, and Greg Young.

References

Blazek, J.M. (1991) A determination of chemical oxygen diffusion rate in the systems anorthite$_{80}$-diopside$_{20}$ and anorthite$_{80}$ via iron redox experiments: *in* H.H. Woodard, Editor, *Fourth Keck Research Symposium in Geology*, Franklin and Marshall College, 84-85.

Crank, J. (1975) *The Mathematics of Diffusion:* Oxford University Press, London, 414p.

Darken, L.S. (1948) Diffusion, mobility and their interrelation through free energy in binary metallic systems: *American Institute of Mining and Metallurgical Engineers Transactions*, **175**, 184-201.

Dunn, T. (1982) Oxygen diffusion in three silicate melts along the join diopside-anorthite: *Geochimica et Cosmochimica Acta*, **46**, 2293-2299.

Dunn, T. (1983) Oxygen chemical diffusion in three basaltic liquids at elevated temperatures and pressures: *Geochimica et Cosmochimica Acta*, **47**, 1923-1930.

Farrell, A. (1991) Diffusion of oxygen through a melt of composition 80% diopside and 20% albite: *in* H.H. Woodard, Editor, *Fourth Keck Research Symposium in Geology*, Franklin and Marshall College, 97-98.

Kozak, S.J. (1991) Oxygen diffusion and redox equilibria in silicate melts: *in* H.H. Woodard, Editor, *Fourth Keck Research Symposium in Geology*, Franklin and Marshall College, 84-85.

Smith, E.S. (1991) Chemical diffusion of oxygen in anorthite$_{20}$-diopside$_{80}$ melts: *in* H.H. Woodard, Editor, *Fourth Keck Research Symposium in Geology*, Franklin and Marshall College, 99-101.

Yinnon, H, and Cooper, A. (1980) Oxygen diffusion in multicomponent glass-forming silicates: *Physics and Chemistry of Glasses*, **21**, 204-211.

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

Robert Allen Cooper
Department of Geology
Amherst College
Amherst, MA 01002-5000

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