

CHEMICAL OXYGEN DIFFUSION RATES IN SILICATE MELTS

Faculty

Samuel Kozak, Washington and Lee

Students

Judson Blazek, Washington and Lee

Jonathan Bull, Washington and Lee

Ann Farrell, Smith

Erica Smith, Smith

Visitor

John Brady, Smith

OXYGEN DIFFUSION AND REDOX EQUILIBRIA IN SILICATE MELTS

Samuel J. Kozak
Geology Department
Washington and Lee University
Lexington, Virginia

INTRODUCTION

Since oxygen is a major component in silicate melts, its kinetic transport through such melts and changes in redox equilibria resulting from such transport are of interest in the influence they exert on processes occurring in silicate melts. For example the redox state of iron will determine whether crystallization of compounds containing ferrous or ferric iron will form, thereby influencing the composition of residual magmas formed by differentiation.

MELT STRUCTURE

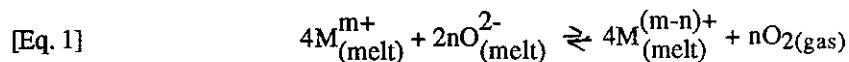
Oxygen in silicate melts can occur in tetrahedral coordination as a polymerized network member either as a bridging oxygen atom shared by adjacent tetrahedra or as oxygen which is bonded to metal cations, nonbridging oxygen. Oxygen can also occur as molecular oxygen occupying interstitial voids between polymerized tetrahedral units. Tetrahedrally coordinated cations such as Si^{+4} , Al^{+3} , and Fe^{+3} are termed network formers while non-tetrahedral metal cations are termed network modifiers, T-cations and M-cations respectively.

TYPES OF DIFFUSION

Diffusion of polymerized oxygen is referred to as network oxygen diffusion (NOD) while diffusion of interstitial molecular oxygen is referred to as chemical oxygen diffusion (COD). The type of diffusion rate which can be measured is dependent upon the experimental design.

NOD, also called self diffusion or tracer diffusion, occurs in the absence of a chemical gradient. A melt equilibrated at a particular oxygen fugacity, subsequently exposed to an atmosphere with the same oxygen fugacity will experience diffusion due to random motions with no net flux of oxygen (Dunn, 1986). The rate of diffusive exchange during such an experiment can be determined by isotopically tagging the oxygen in the atmosphere imposed after the initial equilibration. Quenched glasses obtained from such experiments show increasing concentrations of isotopically tagged oxygen as a function of time and allow the determination of the diffusion rate.

COD occurs in the presence of a chemical gradient. Melts doped with small amounts of a multivalent ion when exposed to an atmosphere of a known oxygen fugacity at a chosen temperature will develop a redox ratio for the dopant which is characteristic for the chosen experimental conditions if subjected to the chosen experimental conditions long enough for equilibrium to be achieved. These melts are then exposed to an atmosphere with a different oxygen fugacity. Depending upon the relative fugacities of the initial atmosphere and the second imposed atmosphere, a reducing or an oxidizing reaction will occur according to equation (1).



The redox ratio of the dopant changes as a function of time and hence allows one to determine the rate at which oxygen is entering or leaving the melt.

DIFFUSION RATE DETERMINATION

Experimental studies in this project were designed to measure COD rates or equilibrium redox ratios reached by means of COD.

COD rates were determined by exposing samples of a base composition which had been equilibrated under relatively reducing conditions to an oxidizing atmosphere for a variety of times ranging from fifteen minutes to twenty four hours. Earlier studies had demonstrated that 24 hours was sufficient time for redox equilibrium to be achieved, Redox ratios for individual samples were then analyzed by microtitration or by spectrometry to determine the amount of reduced multivalent dopant ion present. The amount of oxidized dopant ion was determined by difference with nominal or analyzed total dopant allowing determination of its redox ratio.

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).

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

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.

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

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

- Schreiber, H. D., Kozak, S. J., Fritchman, A. L., Goldman, D. S., and Schaeffer, H. A., 1986, Redox kinetics and oxygen diffusion in a borosilicate melt. *Physics and Chemistry of Glasses*, v. 27, no. 4, pp. 152-177.
- 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.
- Dunn, Todd, 1982, Oxygen diffusion in three silicate melts along the join diopside-anorthite. *Geochimica et Cosmochimica Acta*, v. 46, pp. 2293-2299.

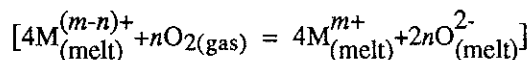
A DETERMINATION OF CHEMICAL OXYGEN DIFFUSION RATES IN THE SYSTEMS
ANORTHITE₈₀ DIOPSIDE₂₀ AND ANORTHITE₁₀₀
VIA IRON REDOX EXPERIMENTS

Judson M. Blazek
Department of Geology
Washington and Lee University
Lexington, Virginia

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 Anorthite₈₀ Diopside₂₀ and Anorthite₁₀₀ 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 An₈₀ Di₂₀ and An₁₀₀ 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.