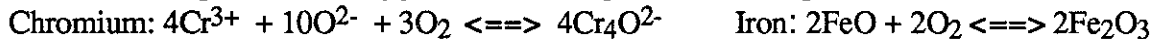


## Diffusion of Oxygen Through a Melt of Composition 80% Diopside and 20% Albite

Ann Farrell  
Geology Department  
Smith College  
Northampton, MA 01063

This study was undertaken with the purpose of determining oxygen diffusion coefficients for a silicate melt of a composition between diopside and albite, 80% diopside and 20% albite by weight. The diffusion of oxygen was observed by doping the melt with a multivalent element to record oxygen activity through the redox ratios of the ion. When the reduced multivalent ion is reheated in the presence of oxygen the following reactions take place:



With this redox reaction it is possible to gauge oxygen diffusion through the melt by testing for the presence of oxidized species of the ion dopant.

Less than 5 weight percent of a multivalent element was added to the melt in order to avoid the possibility of the ion acting as a network modifier and changing the structure of the melt, or the results for diffusion through the melt (Schreiber et al. 1986). The standard sample preparation was as follows:

1. The desired bulk composition was prepared from oxides of the elements representing diopside and albite, which were mixed together, and heated beyond the liquidus for melting and homogenization.
2. Less than 5 weight percent of a multivalent ion was added to the powdered homogenized melt, in this instance 0.1 weight percent chromium or 1% iron was added.
3. The doped samples were then heated beyond the liquidus in a reducing  $\text{CO}_2$  atmosphere for 24 hrs.
4. For periods of time from 15 min to 24 hrs the reduced samples were reheated above the liquidus at a specific temperature in an atmosphere of ambient  $\text{O}_2$ , then quickly removed and quenched in air.

Redox ratios for the melt were then determined through one of two methods. The standard method, titration, involved dissolving the quenched melt in acid under an inert argon atmosphere to prevent further oxidation and titrating the glass solution with a cerrium indicator to determine the amount of FeO present. Knowing the amount of FeO added to the sample the redox ratio was calculated. The redox ratios ( $\text{Fe}^{+2}/\text{Fe}^{+3}$  and  $\text{Cr}^{+3}/\text{Cr}^{+6}$ ) were plotted as a function of the amount of time the sample spent in air (Fig. 1). From the redox ratio plot a diffusion coefficient was determined by matching the plot with a best fit line based on mathematical models (see Erica Smith this volume). Iron is the standard multivalent ion used in titration, but since chromium was used for spectrophotometer work, both iron and chromium were used.

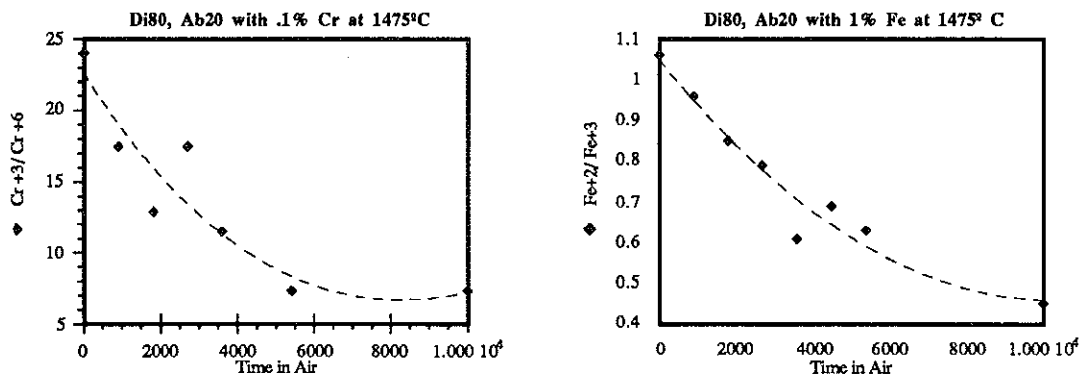


Fig. 1 Plot of redox ratios versus time in air

A UV-visible spectrophotometer was also used to determine redox profiles of the melt. This was done by imbedding the quenched glass in a plastic mold and slicing out a thin sliver of the glass, which was polished to remove any relief. When the glass sliver was placed in the spectrophotometer and wavelengths of light from 350 to 800 nm were passed through, absorption peaks at specific wavelengths were registered according to the relative presence of the oxidized or reduced ions. (Schreiber, unpublished)

The use of a spectrophotometer to determine redox profiles for the melt was explored because of the relative ease and nondestructive nature of the method in comparison with titration. Spectrophotometer readings allow for a two dimensional view of diffusion through the capsule by providing redox ratios for many points both down and across the sample. This is in contrast to the titration method that provides only an average redox value for the melt. There is also the possibility of obtaining a diffusion coefficient for a sample at a specific temperature with only one sample, rather than a whole time series. The quenched glass was imbedded in a plastic mold, and a thin sliver of the glass was sliced out, and polished to remove any relief on the glass that would create noise and affect wavelength absorption values. When the glass sliver was placed in the spectrophotometer wavelengths of light from 350 to 800 nm were passed through, and absorption values were registered at 620 and 430nm to determine the relative presence of oxidized (Cr +6) and reduced (Cr+3) ion.

Oxygen is believed to diffuse monotonically within the melt, based on results of melts doped with titanium where oxygen diffusion was easily identified through the color changes observed in the oxidized titanium. The color changes showed progressive solid fronts between the oxidized and reduced titanium down through the capsule with time in air (Schreiber et al., 1986). With the spectrophotometer, then, the peaks of Cr +6 should decrease continuously with depth in the sample. This relationship, however, was not observed (Fig 2.) while the Cr +6 initially decreased, high peaks were found at the bottom of the sample, rather than the expected low peaks.

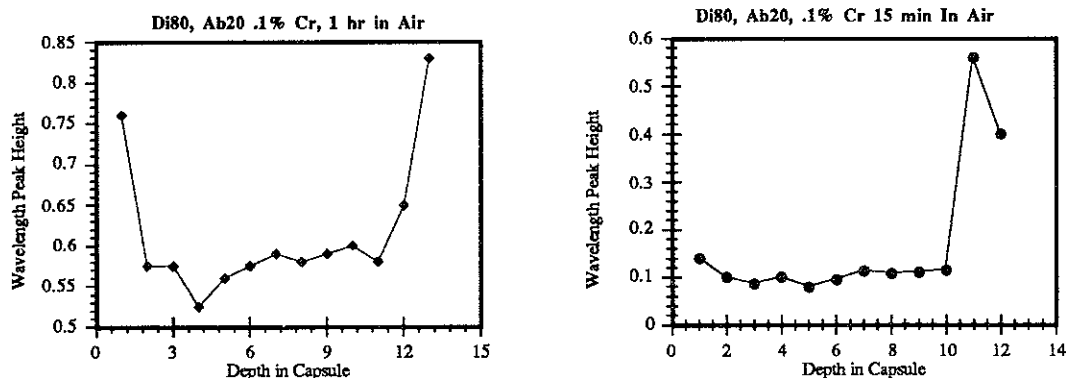


Figure 2. Plot of Cr+6 absorption peak height versus depth in capsule for samples in air for 1 hr and 15 minutes.

The absorption peaks for chromium in the +6 state were significantly more sensitive than the Chromium +3 peaks. This may be due in part to the background noise that polishing failed to quiet. Because of the relative positions of the +3 and +6 wavelength absorption values there may be an additive effect.

#### References Cited:

Schreiber et. al. "Redox Kinetics and Oxygen Diffusion In a Borosilicate Melt." *Physics and Chemistry of Glasses* Vol. 27 No.4 August 1986.