

IRON REDOX CHARACTERISTICS AND CHEMICAL OXYGEN DIFFUSION  
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The redox behavior of iron under oxidizing conditions was examined for five melt compositions in the system Anorthite - Diopside. Samples were prepared by the fusion and quenching of constituent oxides and carbonates at 1450 °C. Samples were then doped with one weight percent iron, homogenized, remelted and quenched. Individual samples were then equilibrated in a carbon dioxide atmosphere at temperatures at which experimental runs were to be carried out. Time series were run for each of the compositions at a number of temperatures above or close to the liquidus in air, an atmosphere more oxidizing than that in which original equilibration had taken place. Samples were analyzed for  $[Fe^{+2}]$  by microtitration [1] and the redox ratio( $[Fe^{+2}]/[Fe^{+3}]$ ) determined by subtraction from nominal iron content.

Equilibrium iron redox ratios after equilibration under oxidizing conditions in an air atmosphere show a systematic increase with temperature. The same equilibrium ratios show no systematic variation with relation to melt composition or composition derived structural parameter, NBO/T [2]. Table 1 summarizes the equilibrium iron redox ratios for different compositions and temperatures.

TABLE 1. Experimentally determined equilibrium iron redox ratios (at  $fO_2=10^{-0.7}$  atm.) and NBO/T values.

	Di <sub>100</sub>	Di <sub>90</sub> An <sub>10</sub>	Di <sub>70</sub> An <sub>30</sub>	Di <sub>58</sub> An <sub>42</sub>	Di <sub>40</sub> An <sub>60</sub>
1475°C	.318	.317	.362	.315	.322
1425°C	.272	.291	.326	.276	.283
1375°C	—	.250	.264	.254	.250
1325°C	—	—	.240	.199	—
NBO/T					
	2.0	1.636	1.077	0.817	0.50

Chemical oxygen diffusion rates for melts of each of the compositions were determined at two or more temperatures above or close to liquidus temperatures by redox kinetics comparing experimental iron redox data from time series experiments with model derived profiles of iron redox values versus time. The model was one of gaseous diffusion through a flat surface, with the redox state of iron being used to determine the rate of oxygen diffusion into the melt. Calculated diffusion rates are summarized in Table 2.

TABLE 2. Chemical oxygen diffusion values calculated from regression equations of experimental chemical oxygen diffusion data versus structural parameter (NBO/T). Values  $\times 10^6$  cm<sup>2</sup>/sec. \* indicates calculated values for which no experimental values were obtained.

	Di <sub>100</sub>	Di <sub>90An<sub>10</sub></sub>	Di <sub>70An<sub>30</sub></sub>	Di <sub>58An<sub>42</sub></sub>	Di <sub>40An<sub>60</sub></sub>
1475°C	36.1	28.7	17.3*	12.0	5.6
1425°C	14.9	12.1	7.6	5.6	3.0
1375°C	4.9*	4.6	4.0	3.8	3.5
1325°C	4.6*	3.9*	2.8	2.3	1.7*
NBO/T	2.0	1.636	1.077	0.817	0.50

Diffusion rates vary directly with temperature and inversely with degree of melt polymerization (NBO/T). Diffusion coefficients determined in this study agree with chemical oxygen diffusion rates determined in other studies for similar melt compositions [1] but are one to two orders of magnitude slower than network oxygen diffusion coefficients determined via isotope tracer studies on melts of the same composition in the system Anorthite - Diopside [3].

REFERENCES [1] Schreiber, H. D., Kozak, S. J., Fritchman, A. L., Goldman, D. S., and Schaeffer, H. A., 1986, Physics and Chemistry of Glasses, V. 27.[2] Mysen, B. O., Virgo, D., and Seifert, F. A., 1985, American Mineralogist, V. 70.,[3] Dunn, Todd, Geochemica et Cosmochimica Acta, V. 46.