Diffusion of Ferric and Ferrous Iron in Silicate Melts

Introduction: Understanding the behaviour of iron in silicate melts at different oxygen fugacities is crucial to the understanding of igneous petrogenesis. Because of the differing charges of ferric and ferrous iron they can potentially diffuse through melts at significantly different rates. The differing rates of diffusion can act as a fractionation mechanism of ferric and ferrous iron during crystal growth, crystal dissolution, the separation of a fluid phase from the melt, and the mixing of two melts. This fractionation can ultimately affect the stability and fractionation mechanism of ferric and ferrous iron during crystal growth, crystal dissolution, the separation of a fluid phase and the mixing of two melts. This fractionation can ultimately affect the stability and distribution of minerals during crystallization of the magma. In particular, the stability of magnetite (Fe₃O₄) is critically dependent upon the concentration of Fe³⁺ in the melt. Furthermore, the results of this study can have industrial applications in the manufacture of iron-containing glasses.

Methods and Materials: Bajt et al. (1994, 1995) have demonstrated that the energy of the pre-edge peak in the X-ray absorption near-edge structure (XANES) spectra can be used to accurately determine the ferric/ferrous ratio in silicate crystals and glasses (quenched melts). XANES spectra of a series of experiments designed to investigate the dissolution of iron metal into a synthetic silicate melt of the composition of the diopside-anorthite eutectic were measured. In these experiments an alumina capsule contained a ~1 mm³ cube of iron metal surrounded by the melt. The iron was allowed to dissolve for times varying from 20 minutes to 16 hours at temperatures between 1300°C and 1500°C and then the sample was quenched, mounted in epoxy and ground open to reveal the cube and the glass surrounding it. Typical experiments displayed little evidence for significant iron dissolution of the cube: all corners were still at approximately right angles. Electron microprobe analysis of the melt interface.

Results: Because of the calibration problems only three experiments at 1315°C have been analyzed and used for the measurement of ferric and ferrous iron diffusion coefficients (e.g. Fig. 1). The diffusion profiles demonstrate that as expected ferrous iron diffuses more rapidly than ferric iron. At 1315°C in air the diffusion coefficient for Fe²⁺ in this system is 7.2 x 10⁻¹² m² s⁻¹ and for Fe³⁺ is 2.5 x 10⁻¹² m² s⁻¹. At an oxygen fugacity equivalent to the wüstite-magnetite oxygen fugacity (log fO₂ = - 7.5) the diffusion coefficient of ferrous iron is 9.8 x 10⁻¹³ m² s⁻¹; unfortunately the diffusion coefficient for ferric iron could not be measured in this experiment because no profile was discernable.

Conclusions: Measurements of Fe³⁺ and Fe²⁺ diffusion in a silicate melt at 1315°C support the hypothesis that oxidation state exerts a significant effect on the diffusion of a cation. These preliminary results demonstrate clearly that ferric and ferrous iron diffuse at different rates in the silicate melt investigated and that oxygen fugacity exerts a significant effect on the diffusion of both iron species. The difference in diffusion coefficients at the temperature studied is significant enough to potentially create fractionation between ferric and ferrous iron by diffusive processes in natural magmatic systems.

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