diffusion-fundamentals

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Diffusion in Silicate Melts: Kinetics and Mechanisms of Redox Reactions

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Diffusion in silicate melts plays a fundamental role in all magmatic processes in nature as well as in the glass industry. Of particular importance is the diffusivity contrast that occurs between the so-called network-former (e.g., Si, Al) and network-modifier (e.g., alkali and alkaline-earth) cations. Whereas the diffusivities of all these cations tend to converge at the high-temperature limit, a strong decoupling is observed when the glass transition is observed. Scaling with the viscosity of the melt, the diffusivity of oxygen and network-former cations then becomes much lower than that of network-modifier cations.

This decoupling has considerable influence on crystallization because the crystals that precipitate irreversibly at strong degrees of supercooling are nonstoichiometric and show anomalously high concentrations of the most mobile elements. This decoupling also exerts a very strong influence on the kinetics and mechanisms of redox reactions. In both instances the mechanisms that operate do not ensure minimization of the Gibbs free energy of the system, but allow it to decrease fastest to a point where the system becomes trapped in a metastable state.

In redox reactions, this feature means that diffusion of oxygen is the rate-limiting factor only at superliquidus temperatures. At lower temperatures, the kinetics of these reactions is controlled instead by diffusion of alkaline-earth or alkaline cations coupled to a flux of electron holes. For iron redox reactions, we have investigated these effects quantitatively from the glass transition up to 2100 K by in situ X-ray absorption Near Edge Structure (XANES) experiments at the iron K-edge. Near the glass transition, similar kinetic experiments have yielded the same results. To rationalize in a simple way the observations made, we have introduced the concept of redox diffusivity from the time required to achieve redox equilibrium at a given temperature. Comparisons of these redox diffusivities with the diffusivities of oxygen, network-forming and network-modifying cations then allow one to distinguish the temperature range where a given redox mechanism predominates. The results obtained in this way for a variety of alkali and alkaline-earth iron silicates will be presented.