



Kinetics and Mechanisms of Redox Reactions in Silicate Melts: a Diffusion Problem ?

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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. 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 is of particular importance. Whereas the diffusivities of all these cations tend to converge at the high-temperature limit, a strong decoupling is observed at glass transition temperatures. The diffusivity of oxygen and network-former cations becomes much lower than that of network-modifier cations. This decoupling exerts an influence on the kinetics and mechanisms of redox reactions. In redox reactions, diffusion of oxygen is the rate-limiting factor only at superliquidus temperatures whereas 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 high temperature X-ray Absorption Near Edge Structure (XANES) experiments at the iron K-edge. To compare 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 natural iron lavas will be presented. In particular we will discuss the kinetics of iron redox reactions obtained on depolymerized melt such as basalt and komatiite or on polymerized melt such as phonolite and rhyolite.