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 exerts a very strong 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* X-ray absorption Near Edge Structure (XANES) experiments at the iron K-edge. 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.

Chemical, isotopic and structural features associated with mineral-fluid systems far from equilibrium

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Despite the utility of the equilibrium approach in quantifying the elemental and isotopic behavior in mineral-fluid systems, there is mounting evidence that chemical (and isotopic) heterogeneity and disequilibrium are common features of the rock record. Systems far from equilibrium tend to undergo extensive dissolution and/or formation of complex leached layers and reaction zones. Structures within the reaction zone and at the reaction interface, as well as reaction mechanisms and reaction rates, are still poorly constrained for most important rock-forming minerals. Microscopic and nanoscopic characterizations of leached layers and reaction zones using advanced electron microscopy and SIMS, augmented by micro-FTIR and neutron scattering (NS) are contributing to a detailed picture of experimental transformation rates, the nature and extent of porosity generation, chemical and isotopic gradients and the structural relationships between the reaction zone and the unreacted precursor phases.

We have focused on several issues pertaining to the formation of a reaction zone, namely the rate of hydration and reaction rim formation; chemical and isotopic communication within the zone; the geometry of the reaction front and the generation of nano- or microscopic porosity within the zone or near the interior reactive interface. Using advanced imaging methods we have interrogated (a) hydration of periclase to brucite, (b) breakdown of dolomite to calcite, (c) cation exchange in alkali feldspars and plagioclase, and (d) alteration of olivine to serpentine. We observed varying extents of rim thickness, structural rearrangement and porosity development in these different systems depending on temperature, pressure, solution chemistry, and duration of interaction. These results provide new insights into the role disequilibrium plays in chemical reactions that drive element recycling and isotopic exchange.