

The source and persistence of kinetic isotope effects in ionic minerals

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Ionic minerals in contact with aqueous solution are dynamic environments in which ions continuously attach to and detach from surface sites, leading to reorganization of surface structure and composition. The relative magnitude of ion attachment and detachment fluxes depends on the fluid composition at the mineral-aqueous interface, and growth occurs when the forward ion flux is greater than the reverse. Kinetic isotope fractionation arises from the mass-dependent rates of ion attachment to and detachment from active surface sites. While fractionation during ion attachment is likely governed by the mass-dependence of ion desolvation kinetics, fractionation during detachment (i.e. metal-ligand exchange) likely depends on the bond energetics of surface sites. Both processes are areas of active research.

We will present the framework and application of a model that uses classical crystal growth theory to predict solid-aqueous kinetic isotope fractionation during mineral growth. The isotopic composition of growing minerals depends on (1) equilibrium partitioning between constituent aqueous species, and (2) isotope enrichment at the surface due to net attachment and detachment fluxes. The slow nature of solid-state diffusion precludes extensive isotope exchange between phases, so all measured isotope fractionation factors reflect to some degree the surface conditions during growth. Trends in isotopic composition preserved in deep-sea carbonates will be re-evaluated in light of these new perspectives on the nature of the mineral-aqueous interface.