

An “ion-by-ion” model for kinetic isotope fractionation during mineral dissolution

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A number of studies have observed kinetic isotope fractionation during mineral dissolution. To date, such fractionation has been observed for Mg isotopes during olivine dissolution, and for Fe isotopes during hornblende, mica and goethite dissolution. Such isotope effects, which are also not predicted by the typical kinetic description of mineral dissolution, provide constraints on the processes occurring at the mineral surface during dissolution, and contribute to our general understanding of kinetic and equilibrium isotope partitioning. To investigate the processes that control Mg isotope fractionation during olivine (Fo₉₂) dissolution, we performed a series of batch experiments consisting of a three-phase system of water (\pm NaCl), olivine, and supercritical CO₂ at conditions relevant to *in situ* mineral carbonation (*i.e.* 60°C, 100 bar PCO₂). In addition to monitoring the changes in solution composition through time, we measured the $\delta^{26}\text{Mg}$ of the dissolved Mg during the early stages of dissolution. In all experiments, Mg concentrations increase rapidly for the first 2 days then increase at a constant but slower rate until the experiments are stopped (80 to 100 days). Analysis of the solid reaction products using a variety of techniques (e.g., XPS, SIMS and TEM) indicates the formation of a Si-rich, Mg-depleted layer on the olivine surface as quickly as 2 days after the experiment is started (before the bulk solution reaches silica saturation). The $\delta^{26}\text{Mg}$ of the dissolved Mg decreases by approximately 0.4‰ in the first stages of the experiment and then approaches the value of the initial olivine (-0.35‰) as the steady state dissolution rate is approached.

We attribute the preferential release of ²⁴Mg to a kinetic effect associated with the formation of a Si-rich surface layer that develops as protons exchange for Mg²⁺. To test this hypothesis, we developed an ion-by-ion model for olivine dissolution. This model is able to reproduce the early rapid dissolution rate, the long-term dissolution rate, and constrain the early state isotopic fractionation. The inclusion of Mg isotopes in this study demonstrates the utility of coupling stable metal isotope fractionation with theory to constrain interfacial mass transfer processes and how isotopes are partitioned during heterogeneous reactions.