

## A model for the isotope partitioning of weathering reactions in catchments

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Changes in the distribution of stable isotope ratios resulting from weathering reactions provide a constraint on the flux of solutes through the subsurface. To quantify relationships between concentration and isotope fractionation during weathering, we present a model that incorporates two factors: (1) rate-dependent fractionation and (2) heterogeneity in subsurface flow.

First, recent experimental and modeling studies demonstrate that the overall fractionation factor associated with isotope partitioning for a reversible reaction is rate dependent. This dependence can be quantified by replacing the common assumption of a constant overall fractionation factor with a model considering the relative influence of equilibrium and kinetic partitioning as a function of saturation state. We demonstrate the improvement gained from this modeling approach using a dataset of calcium isotope ratios associated with carbonate mineral precipitation.

Second, variability in the travel time of fluid through the subsurface limits the extent to which catchments can act as chemical reactors, and thus the extent of isotopic fractionation. We use numerical simulations of reactive flow through a hillslope composed of spatially correlated, heterogeneous flow fields to demonstrate how results for flux-weighted average concentrations and isotopic compositions differ from the case of a uniform flow field.

The combination of these two effects results in isotope ratios that are not readily quantifiable using simplified concentration-fractionation relationships (e.g., Rayleigh distillation). To overcome this limitation we have derived an analytical solution for the steady-state isotope ratio resulting from a reversible reaction subject to a non-uniform travel time distribution, which we validate against numerical results. The modeling approach outlined here offers a way to parameterize flux-averaged reactivity at the catchment scale, and we suggest that it represents an improved means of quantifying isotope ratios resulting from weathering reactions in the heterogeneous Critical Zone.