

A new Rayleigh model for fractionation in subsurface flow

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Stable isotope ratios measured in aquifers and rivers often show variable inferred fractionation factors. We demonstrate that for an irreversible reaction, the Rayleigh or distillation relationship between stable isotope fractionation and reactant concentration is compromised if fluid samples are composed of a range of water ages. Such mixed samples are rarely avoided in standard methods of sampling natural systems. As a result, application of a Rayleigh model commonly requires a diminished or effective fractionation factor relative to the intrinsic value obtained in the absence of transport effects. In contrast, variability in chemical parameters such as the reaction rate constant does not inherently impact the fractionation factor. Thus, in order to quantitatively apply intrinsic parameter values to a fractionating reaction occurring in porous media flow, the functional form of the relationship between reactant concentration and isotope fractionation requires revision. Here, we present a novel, generalized analytical solution for the relationship between fractionation and flow subject to non-uniform fluid travel time distributions. This model is demonstrated against multi-component reactive transport simulations of stable isotope fractionation in homogeneous and spatially correlated heterogeneous flow fields, and applied to a previously reported dataset of stable Cr isotope enrichment obtained from a heterogeneous aquifer. This work offers an updated functional form for the relationship between reactant concentration and isotope fractionation for a mixed-fluid sample, which we offer as a replacement for the traditional Rayleigh model in porous media flow.