Microbes, Minerals and Mixing: Revising Rayleigh models for isotope fractionation in natural porous media

Stable isotope ratios measured in aquifers and soils often show ‘effective’ fractionation factors which are lower than the intrinsic values measured under controlled laboratory conditions. Recent studies have demonstrated that transport effects are a principle cause for this disparity, and several models have been suggested which incorporate representations of fluid mixing such as a dispersion or diffusion coefficient to quantify isotope partitioning in natural systems. Here, I’ll motivate a new version of the classic Rayleigh equation which incorporates a non-uniform fluid travel time distribution. This approach avoids the addition of any new parameters to the classic model. Thus, any open, heterogeneous system in which stable isotope fractionation has been quantified with a Rayleigh model could potentially be reevaluated with this alternative.

I’ll explore the fidelity of this model through comparison with a reactive transport simulations of biologically-mediated stable isotope fractionation in homogeneous and spatially correlated heterogeneous flow fields. The validated approach is then used to reevaluate several stable isotope datasets obtained from through-flowing systems to (1) demonstrate agreement with laboratory values and (2) highlight the relationship between transport, reaction rates and apparent fractionation factors.