

Choosing a model for isotope fractionation in complex systems

JENNIFER L. DRUHAN¹, CARL I. STEEFEL²
AND KATE MAHER¹

¹Department of Geological and Environmental Sciences,
Stanford University, Stanford CA 94305, USA

²Earth Sciences Division, Lawrence Berkeley National
Laboratory, Berkeley, CA, 94720, USA

In practice, a wide range of models have been employed to describe the partitioning of stable isotopes between reactant and product species during heterogeneous reactions. These approaches vary in complexity and degree of parameterization from simple Rayleigh distillation to transition-state-theory to ion-by-ion descriptions of isotopic partitioning associated with mineral growth and dissolution. Under carefully constructed laboratory conditions, the advantages of more rigorous models can be shown. The question remains, however: when faced with the need to quantify an observed isotope fractionation at the field scale, which model is appropriate?

We will present examples of metal stable isotope fractionation during secondary mineral formation to study the conditions under which particular models are necessary to reproduce observed behavior. We suggest that a distillation model is insufficient to describe isotopic partitioning associated with a reversible departure from equilibrium. Moving to a more rigorous description raises a critical issue: namely that analytical solutions for the description of isotope fractionation during reversible reactions are based on the assumption that the isotopic composition of the mineral surface is at steady state. This assumption is not valid for systems in which the saturation state can vary. Therefore a numerical modeling approach is adopted to employ isotope-specific transition-state-theory rate laws. We demonstrate that for most conditions, this method can accurately reproduce the observed trend in metal stable isotope fractionation during mineral growth. However, important exceptions are noted, such as when the ratio of reactant ions in solution approaches unity. Laboratory studies have demonstrated that the rate of mineral growth may be influenced by this ratio, which is not described by a transition-state-theory rate law. As a result under these conditions an ion-by-ion growth model is employed to accurately describe stable isotope partitioning.