

## **Deciphering non-traditional isotope fractionation during solid-fluid interactions: Kinetic/thermodynamic challenges and pathways forward**

J. SCHOTT<sup>1</sup>, V. MAVROMATIS<sup>1</sup>, G.S. SALDI<sup>1,2</sup>, M. BLANCHARD<sup>1</sup>, M. MEHEUT<sup>1</sup>, E.H. OELKERS<sup>1,2</sup>

<sup>1</sup> Géoscience Environnement Toulouse, CNRS-Université de Toulouse, France (jacques.schott@get.omp.eu)

<sup>2</sup> Earth Science, University College London, Gower Street, London WC1E 6BT, United Kingdom

With the advent of multi collector plasma mass spectrometry, new advances in spectroscopic techniques, and the development of first-principles modeling of molecular structure and isotope effects, the past decade has seen the rapidly expanding application of ‘non-traditional’ metal stable isotopes in geochemistry, environmental sciences, biology, medicine, and archeology. The reliable use of stable isotopic tools to quantify solid-fluid interactions, however, requires further insights onto the elementary pathways and mechanisms that control the kinetics and thermodynamics of isotopic exchange. This presentation will review the key parameters controlling the mass dependence of reaction rates and equilibrium constants. It is shown that Transition State Theory and the principle of detailed balancing, applied to isotope fractionation during mineral standard growth, could yield the kinetic and equilibrium fractionation factors of a metal if the rate of dehydration of this metal is not significantly slower than that of the metal which controls the mineral growth rate, and it does not undergo a change of its coordination number during its incorporation in the solid lattice. Non-standard growth, involving the transient formation of an amorphous precursor followed by the formation of more stable mineral phases via near equilibrium dissolution-precipitation reactions, can likely lead to true isotopic equilibrium for both major and trace components. Accurate prediction of isotopic fractionation parameters from an atomistic approach based on first-principles or ab-initio modeling of atomic bonding is now largely possible. Each of these new approaches can be directly validated experimentally using the ‘three-isotope’ method, which allows determination of the *equilibrium* fractionation factor of metals between the solids and the aqueous species. In addition, the three isotope-method has been demonstrated to be successful for characterizing the rate of isotopic exchange between the solid and the fluid and thus predicting the conditions of preservation of the original isotopic signatures in natural minerals.