

Towards a mechanistic understanding of metal isotope fractionation using spectroscopic and theoretical approaches

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The fractionation of metal stable isotopes provides a powerful tool to understand and predict transport and fate of dissolved metals in the environment. However, a general mechanistic explanation for isotope fractionation within natural systems has been extremely elusive, in part because all natural fluid-solid interfaces in the environment are characterized by variable crystallinity, porosity, and redox potential. Natural interfaces are also decorated with sorbed inorganic and organic molecules, microbial biofilms, and mineral precipitates in contact with exceedingly complex solutions. Knowledge of the speciation of metals is thus critical for understanding the resulting metal isotope signatures. Here we provide several examples of the power of spectroscopic studies combined with theoretical considerations surrounding metal ion speciation to provide new information about the processes governing metal stable isotopes in the environment. For example, the coupling of EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy with stable isotope analyses has improved our understanding of how speciation of solutions and surface complexes control isotope fractionation. Similarly, knowledge of the coordination of ions in solution and at surfaces enables the extension of theories for electron transfer to predict the kinetics and isotope effects associated with oxidation-reduction reactions. These types of studies show great promise for unraveling a fascinating world of yet unknown isotope effects, but require continued innovation in surface science and spectroscopy as well as new theoretical developments.