

Trace metal isotope fractionation during adsorption to Mn oxyhydroxide: mechanisms, patterns, and further questions

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Adsorption to mineral surfaces is often the first step when dissolved trace metals are removed from the water column and associated with sediment. Many factors govern the concentrations and isotopic compositions of adsorbed trace metals, and recent research has yielded some mechanistic insight into those factors. Whether the set of atoms adsorbed is the same set eventually incorporated within a mature sediment is unclear (and unlikely), and this complication demonstrates the need to better understand how adsorbed metals become more permanently incorporated in sediments.

My colleagues and I have conducted simple experiments in the past five years to quantify metal stable isotope fractionation during adsorption of several paleoceanographically important trace metals (Mo, U, Zn, Cd, Ni) to the mineral birnessite, a predominant phase in hydrogenetic ferromanganese crusts. In all of these experiments, the lighter isotopes of the metal in question have preferentially adsorbed. Our results indicate that we are measuring equilibrium, rather than kinetic, isotope effects.

In some cases (Mo and U), the fractionations we see in our experiments exactly match the fractionations observed in nature between dissolved metal in seawater and metal in young ferromanganese crusts. This strongly suggests a direct relationship between adsorption and final incorporation of these trace metals. EXAFS spectra from experimental and natural samples demonstrate that the observed isotope effects are driven by differences in coordination chemistry between dissolved and adsorbed metals. [1,2]

For Zn, Cd, and Ni, the fractionations observed in experiments do not match what is observed in nature. Chemical and mineralogical (and perhaps biological) differences between our simple experimental systems and nature may be the cause for the discrepancies. Other hypotheses involve additional reactions occurring during incorporation of metal into mineral structures or following burial that can modify the set of trace metal atoms and the metal isotope ratios initially associated with sediment. These hypotheses and their implications for isotope paleoproxies will be discussed.

[1] Wasylenki et al. (2011) *Geochim. Cosmochim. Acta* **75** 5019-5031. [2] Brennecka et al. (2010) *Env. Sci. Tech.* **45**, 1370-1375.

Anomalous Fractionations of Sulfur Isotopes during High Temperature Reactions between Solid Organic C- and Oxidized S Compounds

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Until recently, many researchers have thought that UV-photolysis of volcanic SO₂ gas in an O₂-poor (i.e., $pO_2 < 10^{-6}$ atm) atmosphere created the anomalous isotope fractionations of sulfur isotopes (AIF-S) found in many (but not all) sedimentary rocks >2.4 Ga in age. However, we suggest that redox reactions between solid organic compounds (e.g., kerogen in sedimentary rocks) and oxidized S-bearing compounds (e.g., SO₄²⁻, SO₂) at elevated temperatures (T > ~150°C) may have created most (if not all) AIF-S signatures in nature, based on the following discoveries: (1) SO₂ photolysis using a broad-band UV lamp, which simulates the UV spectra of the sunlight, produced the AIF-S signatures that differed significantly from those in natural rocks [1, 2]; (2) AIF-S signatures occur in some post-2.4 Ga samples, including the ~1.8 Ga black shales in Finland [3], and most interestingly in SO₄ in pollutants in the Beijing air, which were produced by the burning of pyrite-rich coals [4]; (3) Shales with large AIF-S signatures are characteristically kerogen- and pyrite-rich black shales that deposited under the influence of large-scale submarine hydrothermal activity [5]; and (4) The reduced S-bearing compounds, generated from reactions among simple amino acid crystals, sulfate crystals and H₂O at 150-200°C, possess variable AIF-S signatures ($\Delta^{33}S = 0.2$ to +13‰; $\Delta^{36}S = -1.3$ to +1.1‰), and most of the data ~~are~~ match with those in sedimentary rocks [6, 7]. Reactions using some complex organic compounds did not produce AIF-S. The results of these laboratory experiments, and also those of our recent study on reactions between activated carbon and SO₂(g) at 150-200°C, suggest that variable fractionations of S isotopes occur during: (i) adsorption of oxidized S-species on the surfaces of solid C-bearing compounds; (ii) series of reduction of the adsorbed S-species on/in the solid; and (iii) desorption of the reduced S-compounds. The isotope effects during (i) and (iii) are probably due to the chemisorption isotope effects proposed by Lasaga et al. (2008) [8], which may affect on one or more S isotopes, whereas those during (ii) may be caused by the magnetic isotope effects that affect only on ³³S.

Therefore, the AIF-S record in sedimentary rocks may indicate the evolutions of the biosphere (species and abundances) and environments (e.g., influence of submarine hydrothermal activity) rather than of the atmosphere.

[1] Naraoka and Poulson (2008) *GCA* **72**, A671; [2] Masterson et al. (2011) *EPSL* **306**, 253-260; [3] Young et al. (2009) *GSA Ann. Mtg. Absts_165626* [4] Ding et al. *GCA* **70**, A142; [5] Kaufman et al. (2007) *Science* **317**, 1900-1903; [6] Watanabe et al. (2009) *Science* **324**, 370-373; [7] Oduro et al. (2011) *PNAS*. doi: 10.1073/pnas.1108112108; [8] Lasaga et al. (2008) *EPSL* **268**, 225-238.