

Oxidative scavenging of Tl by Mn oxide birnessite: Sorption and stable isotope fractionation

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Sorption processes at the mineral-water interface are a key control on the fate and mobility of trace-metals in natural biogeochemical systems. Recently, specific sorption mechanisms have been invoked to help explain observed stable isotope fractionation of trace-metals between (hydr)oxide mineral surfaces and aqueous solution (e.g., [1-3]). Inner-sphere complexation of trace-metals at (hydr)oxide surfaces involves the formation of chemical bonds between trace-metal species and surface functional groups and thus the opportunity for concentration of the heavy trace-metal isotope in the stronger bonding environment, be it aqueous species or sorbed complex (e.g., [2]). In addition to this mass-dependent isotope fractionation, fractionation of very heavy trace-metals is predicted to predominantly occur by nuclear volume, concentrating the heavier trace-metal isotope in the most oxidised trace-metal species [4].

Tl is one of the heaviest elements for which variation in natural stable isotope composition has been recorded. In particular, hydrogenetic, birnessite-rich marine ferromanganese (FeMn) crusts are enriched in the heavy ²⁰⁵Tl isotope with an isotope fractionation factor of ~20 ε²⁰⁵Tl-units (where ε²⁰⁵Tl = 10⁴ × (²⁰⁵Tl/²⁰³Tl_{sample} - ²⁰⁵Tl/²⁰³Tl_{NIST997})/²⁰⁵Tl/²⁰³Tl_{NIST997}) [5].

Using synchrotron spectroscopy we show a positive Tl-Mn spatial correlation in marine FeMn and the oxidation of Tl(I), present in seawater, to Tl(III) during inner-sphere complexation to hexagonal birnessite. On the other hand, Tl(I) is not oxidised during sorption to todorokite, the dominant Mn oxide in hydrothermal FeMn, and is sorbed as an outer-sphere complex probably at todorokite tunnel sites.

Our results support an oxidation fractionation mechanism [4] where Tl fractionates as a function of Tl oxidation by different Mn oxides.

Sorption experiments, XAS results and implications for Tl stable isotope signatures in FeMn will be discussed.

[1] Barling & Anbar (2004) *EPSL*. [2] Balistrieri *et al.* (2008) *GCA* [3] Pokrovsky *et al.* (2008) *GCA*. [4] Schauble (2007) *GCA* [5] Rehkämper *et al.* (2002) *EPSL*.

Experimental quantification of kinetic Mg-isotope fractionation during magnesite precipitation

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Magnesium (Mg) is one of the most abundant rock-forming elements in the Earth's crust, and displays mass-dependant isotopic fractionation in a range of terrestrial materials and settings [1]. Some of the largest measured Mg-isotope variations occur in carbonate rocks, with a ~2 ‰ δ²⁶Mg difference between dolostone and limestone suggesting a strong mineralogical control on Mg-isotopic compositions [2]. In this study a series of well-constrained magnesite (MgCO₃) precipitation and dissolution experiments have been performed to better understand Mg-isotope fractionation during carbonate formation.

Experiments were performed using synthetic MgCO₃ in open and closed-system reactors under varying temperature and P_{CO2} conditions [3]. Supersaturation of MgCO₃ in the closed-system solutions was induced by temperature increases of 30–50°C. This resulted in the precipitation of isotopically light MgCO₃, and a corresponding increase in the δ²⁶Mg composition of the solution. Δ²⁶Mg_{solid-solution} did not vary with temperature in these experiments, although isotopic equilibrium was attained faster at higher temperatures. Isotopically light MgCO₃ was also precipitated in the open-system experiments, as demonstrated by an increase in δ²⁶Mg compositions between the input and output solutions. Δ²⁶Mg_{solid-solution} in these experiments varied as a function of the MgCO₃ precipitation rate, with a larger Δ²⁶Mg_{solid-solution} associated with faster precipitation rates. A similar relationship was observed in open-system dissolution experiments, where a slightly larger Δ²⁶Mg_{solid-solution} was recorded during slower rates of dissolution.

These observations suggest that variations in MgCO₃ precipitation and dissolution rates are associated with kinetic mass fractionation effects that may have important consequences for the δ²⁶Mg variations found in nature.

[1] Young & Galy (2004) *Rev. Min. & Geochem.* **55**, 197-230. [2] Galy *et al.* (2002) *EPSL* **201**, 105-115. [3] Saldi *et al.* (2007) *GCA* **71**, A868.