

## How does metal adsorption cause isotopes to apportion?

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Using a combination of experimental, computational, and analytical approaches, we have determined the molecular-scale mechanism by which adsorption of molybdenum to birnessite (Mn oxyhydroxide) causes a large fractionation of Mo isotopes. Our work with Mo has led us to a more general hypothesis about how large isotope effects arise during adsorption of metals to minerals or other substrates.

From simple experiments we learned that, while the fraction of Mo adsorbed takes >72 hours to reach steady state, the isotopic fractionation between dissolved and adsorbed Mo is constant as a function of time and amount adsorbed. This kinetic discrepancy led us to suspect that isotope exchange occurs in solution between  $\text{MoO}_4^{2-}$ , the predominant aqueous species, and a trace aqueous species that is enriched in light isotopes and preferentially adsorbs to birnessite [1].

Density functional theory calculations identified  $\text{MoO}_3(\text{H}_2\text{O})_3$  as the species that equilibrates with  $\text{MoO}_4^{2-}$  with a fractionation factor nearly matching experimental results [2]. Recent Raman spectroscopic observations also confirm the existence of  $\text{MoO}_3(\text{H}_2\text{O})_3$  in solution [3]. Octahedral coordination of Mo in  $\text{MoO}_3(\text{H}_2\text{O})_3$  versus tetrahedral coordination in  $\text{MoO}_4^{2-}$  drives the isotope effect.

Preliminary analysis of EXAFS patterns from our samples indicate that adsorbed Mo is likely in octahedral coordination.

For the Mo-birnessite system, the key conditions leading to a large isotope effect are (1) lack of adsorption of the predominant species, (2) presence of a trace species with a different metal coordination environment, and (3) adsorption of the trace species to the surface. We predict substantial isotope fractionation for other metal-mineral combinations satisfying these conditions.

[1] Wasylenki *et al.* (in review) *Geochim. Cosmochim. Acta*.

[2] Weeks *et al.* (2007) *J. Phys. Chem. A* **111**, 12434.

[3] Oyerinde *et al.* (2008) *Inorg. Chimica Acta* **361**, 1000.

## Stable isotopic variations of a stalagmite from Indonesia and their comparison of meteorological data

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Stable isotopic variations (i.e.,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) of stalagmites have been widely recognized as a powerful tool to reconstruct paleoclimate/environment of terrestrial areas. Oxygen and carbon isotopic ratios of a stalagmite are known, however, to be as cumulative signals of complex climatic and hydrogeological processes. In order to assess the reliability of stable isotopic ratios of stalagmites as climate proxies, we performed the first systematic comparison between temporal variation in precipitation and those in stable isotopic ratios of a speleothem, by taking the travel time of groundwater into account.

First, we analyzed a stalagmite collected in Ciawitali Cave, West Java, Indonesia, and found that the number of growth bands is coincident with the uranium series disequilibrium age within the error. This is the first documentation of a stalagmite having annual bands in the Asian equatorial region. Next, annual variations of isotopic data were compared with that of precipitation since 1950, showing significant, negative correlations if the correction is not made for the travel time. This result suggests that stable isotopic ratios in stalagmites are applicable as effective proxies for ancient precipitation in the study area.