

## **Tungsten isotopes as a probe of reactions governing tungsten's removal from solution to sediment**

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Tungsten is of interest to geochemists for its potential as a paleoredox indicator in ancient marine sediments, but also because of its widespread use in modern military and industrial applications. The (erstwhile) US EPA declared this element an “emerging contaminant of concern” in 2012, because it is likely a carcinogen. Despite these diverse reasons for interest, few researchers have yet investigated the reactions governing tungsten and tungsten isotope distribution between natural waters and soils and sediments.

Partitioning of tungsten (W) between aqueous and solid phases in most terrestrial and marine environments is likely governed primarily by adsorption to particles of Mn, Fe, and Al oxyhydroxides. In addition to how much tungsten adsorbs under various conditions, crucial questions are how exactly W bonds to particle surfaces and how the concentrations and isotope ratios in the sorbed/solid pools relate to those in coexisting aqueous solutions. A few recent studies have employed X-ray absorption spectroscopy (XAS) to examine W sorption complexes directly, but that technique requires unrealistically high concentrations of tungsten. Because chemical speciation of W is known to vary strongly with concentration (and pH), environmentally relevant sorption mechanisms are likely inaccessible via X-ray spectroscopy. Hence, we are attempting to use tungsten stable isotopes to constrain speciation and adsorption mechanisms at concentrations relevant to co-precipitation with Mn and Fe oxyhydroxides in contaminated soils and in the deep oceans.

Interestingly, our experiments thus far show little difference in fractionation of W isotopes during sorption on ferrihydrite versus birnessite, although W's chemical cousin, Mo, displays rather different behavior for these two sorbent phases. Preliminary density functional theory calculations suggest that the observed fractionation is driven by equilibrium fractionation between aqueous  $\text{WO}_4^{2-}$  and a polymeric W-O surface complex.