

Tungsten sorption on birnessite and concomitant stable W isotope fractionation at conditions relevant to environmental transport

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The potential toxicity of tungsten to human health (*e.g.*, cancer, heart, lung, and kidney diseases) led to this element's designation in 2003 as an “emerging contaminant of concern”^[1], but few studies have yet investigated transport and fate of W in the environment. Tungsten mobility is likely primarily controlled by sorption to nanoparticulate Mn- and/or Fe-oxyhydroxides^[2]. In a previous experimental study, we reported a persistent increase in the amount of W sorbed on birnessite from solutions with [W] >500 ppb, even beyond 500 hours (*pH* 5 or 8, very low ionic strength)^[3]. We hypothesized that a polymeric W-O precipitate nucleated on the birnessite [001] surface, enabling continued growth and possibly unlimited sorption capacity. The W stable isotope fractionation between dissolved and sorbed W evolved slightly over time in a manner consistent with this hypothesis and inconsistent with any simple equilibrium or kinetic isotope effect. Here, we aimed to determine whether those results bear out at low tungsten concentrations relevant to actual contaminated soils (≤ 100 ppb).

As observed at higher W concentrations, the amount of W sorbed on birnessite slowly increased for at least 530 hours, with varied magnitude of isotopic fractionation ($\delta^{183/182}\text{W}_{\text{dissolved-sorbed}}$ ranged from +0.21 to +0.88‰). In some reactors, we spiked the solution with ¹⁸⁶W partway through, to monitor the extent of exchange between dissolved and sorbed W over time. The isotope data have significant scatter, but, to first order, they reflect incomplete isotopic exchange between the solution and the full volume of the surface precipitate as it continues to thicken over time. We infer that we are again observing a mixture of kinetic and equilibrium fractionation at any given time point, regardless of the initial dissolved [W]. The important implication of our results is that, even at field-relevant [W], birnessite may be capable of sorbing an enormous amount of W in the form of surface precipitates and may therefore greatly attenuate W mobility in contaminated soils and aquifers.

^[1] US CDC, 2003, <http://www.cdc.gov/nceh/clusters/Fallon>

^[2] Bednar et al. 2008 *JEnvQual* 37,229

^[3] Wasylenki et al. 2020 *ChemGeol* 558,119836