

Adsorption of isotopically light tungsten to birnessite

LAURA E. WASYLENKI¹ AND AUGUSTUS T. SCHAEFER¹

¹Department of Geological Sciences, Indiana University, Bloomington, Indiana USA, lauraw@indiana.edu, schaefea@indiana.edu

Tungsten has been declared an “emerging contaminant of concern” by the US Environmental Protection Agency [1], since it has been linked to leukemia clusters near mines in the western US [2] and has caused rice field contamination in China [3]. Despite the widespread use of tungsten and recent recognition of associated health hazards, remarkably little work has yet been conducted to understand the transport and fate of this heavy metal in the environment.

As dissolved tungsten flows in shallow groundwater, adsorption to particles of minerals such as manganese, iron, and aluminum oxyhydroxides is likely the principal process that acts to immobilize the contaminant. In addition to the amount of tungsten that adsorbs, a crucial question is how exactly W bonds to the mineral surfaces and how stable it will be in that chemical form. Previous work [4] [5] has employed EXAFS analysis to determine the structures of surface complexes, but unrealistically large concentrations of tungsten are needed for that technique, especially at environmentally relevant pH conditions, where aqueous speciation changes significantly with concentration.

We anticipate that W stable isotope ratios will be highly sensitive to the coordination chemistry changes that others have documented thus far for W adsorption reactions [4] [5], and thus we have begun conducting experiments to determine W isotope systematics during adsorption to synthetic birnessite. Initial experiments at pH ~8 indicate an easily resolvable fractionation of $\Delta^{183/182}\text{W}_{\text{sorbed-dissolved}} = -0.30 \text{ ‰}$ (analytical uncertainty is ± 0.04 , 2sd). The fraction of W adsorbed in these experiments spans a range of 55-93 %, so we can infer from nearly constant $\Delta^{183/182}\text{W}_{\text{sorbed-dissolved}}$ that the observed fractionation reflects a closed-system equilibrium process, with rapid and continuous exchange of W between solution and surface. Given the previous EXAFS work on Fe and Al oxyhydroxides [4] [5], we hypothesize that this effect is due to tetrahedral coordination of W by O in solution versus octahedral, polymerized coordination on the birnessite surface.

[1] US EPA (2012) Technical Fact Sheet EPA 505-F-11-005.

[2] Koutsospyros et al. (2006) *J. Hazardous Mat.* **136**, 1-19.

[3] Lin et al. (2014) *PLoS One* **9(3)**, e91981.

[4] Lorenz et al. (2011) *Goldschmidt Conf. Abstr.* 1357.

[5] Hur & Reeder (2012) *Amer. Chem. Soc. Abs. ENVR* 487.