

Bamfordite precipitation contributes to Mo(VI) coordination changes during Fe(II)-induced ferrihydrite transformation

**DR. VALERIE A. SCHOEPPER, PHD, JULLIETA E. LUM
AND MATTHEW B. J. LINDSAY**

University of Saskatchewan

Presenting Author: valerie.schoepfer@usask.ca

Iron(III) (oxyhydr)oxides are important controls on contaminant and nutrient mobility and bioavailability in soils, sediments, and aquifers. However, changing redox conditions trigger transformation of ferrihydrite and other metastable phases, and promote repartitioning of associated elements.

Molybdenum is essential in biological systems as it occupies the active site of key enzymes involved in global biogeochemical N, C, and S cycles. Excessive exposure to this redox-active transition metal can also negatively affect human and animal health. Aqueous Mo(VI) concentrations are often controlled by sorption and co-precipitation reactions with ferrihydrite. Despite potential mobility and bioavailability implications, Mo(VI) repartitioning during Fe(III) (oxyhydr)oxide transformation is poorly understood.

Recent studies report extensive Mo(VI) retention during Fe(III) (oxyhydr)oxide transformations coupled with corresponding Mo(VI) coordination changes from tetrahedral to octahedral. Although this coordination change is apparent under varied redox and temperature conditions, pH-dependence and reaction mechanisms are unknown. Arai [1] hypothesized that bamfordite [$\text{FeMo}_2\text{O}_6(\text{OH})_3 \cdot \text{H}_2\text{O}$] precipitation may occur following Mo(VI) adsorption onto goethite at $\text{pH} < 4$. This hydrated Fe(III) molybdate phase contains MoO_6 octahedra and its precipitation may explain previous results. However, the contribution of bamfordite precipitation to Mo retention during Fe(III) (oxyhydr)oxide transformation reactions is unknown.

Here, we examine Mo(VI) repartitioning during Fe(II)-induced ferrihydrite transformation. We test the hypothesis that bamfordite precipitation contributes to Mo(VI) retention and coordination changes during ferrihydrite transformation. We conducted batch experiments at different conditions including pH_0 (6.5, 5.0), Mo(VI) loading (0, 25, 100 $\mu\text{mol Mo g}^{-1}$ ferrihydrite), and Mo(VI) uptake mechanism (sorption, co-precipitation). We examined initial and reacted solids by X-ray diffraction (XRD), transmission electron microscopy-selected area electron diffraction (TEM-SAED), and X-ray absorption spectroscopy (XAS) to identify phase transformations and determine Mo coordination and bonding.

Combined XRD and TEM-SAED analyses reveal phase transformations limited to ferrihydrite surfaces except in the pH_0 6.5 co-precipitation experiment. TEM-SAED analysis confirmed the presence of nanoscale bamfordite in all reacted solids and Mo K-edge EXAFS modelling indicates Mo(VI) coordination and bonding are consistent with bamfordite. Our results indicate that bamfordite precipitation contributes to Mo retention during Fe(II)-induced ferrihydrite transformation which could explain