Mo(VI) incorporation into products of Fe(II)-induced Fe(III) (oxyhydr)oxide transformation

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Iron(III) (oxyhydr)oxides are important sinks for dissolved metal(loid)s in soils and sediments. However, these phases are often susceptible to reductive dissolution or transformation, which can promote repartitioning of adsorbed and co-precipitated metal(loid)s under anoxic conditions. Despite growing interest in Mo geochemistry, repartitioning behaviour during Fe(II)-induced Fe(III) (oxyhydr)oxide transformations is not fully understood. Previous research into Mo(VI) repartitioning during ferrihydrite transformation is limited to alkaline pH (8, 10) [1,2] with transformation induced by aqueous Fe(II) [1] or heat [2]. Although these studies report Mo(VI) incorporation into neoformed phases, reaction mechanisms remain enigmatic.

Here, we integrate results of two studies examining Mo repartitioning during Fe(II)-induced ferrihydrite and goethite [α-FeOOH] transformations. First, we examine repartitioning of adsorbed Mo(VI) under advective flow conditions in column experiments. Second, we examine repartitioning of adsorbed and co-precipitated Mo(VI) under static conditions in batch experiments. In both cases, Fe(II) introduction promoted lepidocrocite [γ-FeOOH] and goethite formation.

In the column experiments, transformation was induced by pumping anoxic solutions containing 0.2 or 2.0 mM aqueous Fe(II) to columns packed with ferrihydrite- or goethite-coated sand. An initial pH decrease from 7.0 to ~5.8 was accompanied by mobilization of 5 to 21% of initially adsorbed Mo(VI). Greater Mo mass release was associated with the ferrihydrite columns and the lower Fe(II) input solution.

For the batch experiments, ferrihydrite was prepared with varied amounts of adsorbed or co-precipitated Mo(VI). Transformation was promoted by addition of 0.5 mM Fe(II) to ferrihydrite suspensions at pH 5.0 and 6.5. Aqueous Fe(II) addition promoted transformation at pH 6.5 for ferrihydrite with co-precipitated Mo(VI).

Molybdenum K-edge EXAFS spectroscopy suggest that MoO_6 octahedra are incorporated into neformed Fe(III) (oxyhydr)oxides during Fe(II)-induced transformation. These findings offer insight into potential for Mo mobilization in soils and sediments subjected to redox transitions or oscillations.

[1] Gomez et al. (2013) *RSC Adv.* 3: 25812–25822. [2] Das and Hendry (2013) *Appl. Geochem.* 28: 194 – 201.