The influence of oxalate on Ni cycling through iron oxides

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Iron oxides are ubiquitous in soils and sediments and play a critical role in the geochemical distribution of trace elements and heavy metals through adsorption and coprecipitation [1]. Fe(II)-catalyzed recrystallization of iron oxides has been shown to cause incorporation of trace elements into the mineral structure as well as the release of preincorporated ions [2] [3]. The fate and transport of trace elements in iron oxide-bearing systems may be influenced by the presence of organic acids. Organic acids may bind trace elements in soluble complexes, compete with trace elements to sorb to surface sites, form ternary complexes with trace elements on the mineral surface, or result in ligand-promoted dissolution releasing incorporated metals into solution [4] [5]. All of these processes may affect the bioavailability of nutrients and sequestration of contaminants.

To better understand the impact organic acids have on trace element cycling, we investigated the effect of oxalate on Ni adsorption and release from goethite and hematite. Macroscopic adsorption studies suggest that oxalate suppresses Ni adsorption to the Fe oxides at pH 7 by forming Ni-oxalate complexes in solution. After accounting for solution complexation, oxalate also appears to alter the energetics of Ni adsorption. EXAFS spectroscopy shows that oxalate changes Ni adsorption mechanisms to goethite and hematite, suggesting the formation of Ni-oxalate ternary surface complexes. The addition of oxalate at pH 4 and 7 during Fe(II)-catalyzed recrystallization of goethite and hematite enhanced Ni released. Fe release to solution was low and increased stoichiometric dissolution caused by oxalate could not explain the excess Ni in the aqueous phase. This indicates that oxalate promoted further recrystallization. The effect of oxalate on Ni incorporation during Fe(II)-catalyzed recrstallization will also be discussed. This study identifies mechanisms through which oxalate, and likely other organic acids, modify trace metal interactions with iron oxides. These processes results in enhanced micronutrients availability and reduced sequestration of metals in iron oxides.

[1] Brown & Parks (2001) *Int. Geol. Rev.* **43**, 963-1073. [2] Frierdich et al. (2011) *Geology* **39**, 1083-1086. [3] Frierdich & Catalano (2012) *Environ. Sci. Technol.* **46**, 1519-1526. [4] Buerge-Weirich et al. (2002) *Environ. Sci. Technol.* **36**, 328-336. [5] Ha et al. (2009) *Langmuir* **25**, 5586-5593.