

## **Contrasting effects on trace element fate of iron and manganese oxide transformations induced by electron transfer reactions**

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Biogeochemical cycling at redox interfaces generates chemical conditions where coexisting reduced and oxidized forms of iron and manganese coexist. In these settings dissolved Fe(II) induces coupled dissolution and precipitation of crystalline Fe(III) oxide minerals through electron transfer and atom exchange [1] [2]. Our prior work [3] [4] has shown that the resulting recrystallization of Fe oxides causes the repartitioning of trace metals such as Ni and Zn among the mineral surface, mineral bulk, and aqueous solution.

The coexistence of aqueous Mn(II) and solid Mn(IV/III) oxides at redox interfaces and the semiconductive properties of Mn oxides suggests that similar processes may occur in the Mn system. However, Mn oxide minerals occur as layered, turbostratic phylломanganates and Mn(II)-Mn(IV) comproportionation may occur, suggesting that electron transfer-induced Mn oxide transformations likely differ in character from those seen for Fe oxides. We have investigated the reactions of dissolved Mn(II) with Mn(IV/III) oxide minerals and the resulting effect on trace metal fate. At pH 4, Mn(II) binds to vacancy sites in the Mn oxide sheet, initially capping these sites and creating structural Mn(III). At higher loading, Mn(II)-binding not only forms structural Mn(III) but also induces a reduction in sheet symmetry and the apparent rotational ordering of adjacent phylломanganate layers. At pH 7, Mn(II) only substantially reacts with Mn oxides having high vacancy contents, and high Mn(II) concentrations induce phase transformations to MnOOH phases, as found previously [5]. Trace metal fate is largely unaffected at pH 7, but at pH 4 Mn(II) drives adsorbed Ni and Zn from interlayer vacancy sites to adsorption onto the edges of phylломanganate sheets. This transition in trace metal binding is correlated with the rotational ordering of the Mn oxide sheets. This work shows that the nature of Mn(II)-Mn(IV/III) oxide reactions, and the resulting impact on trace metals, is fundamentally different from what occurs in the Fe system.

[1] Rosso et al. (2004) *ES&T* **44**, 61. [2] Handler et al. (2014) *ES&T* **48**, 11302. [3] Frierdich et al. (2011) *Geology* **39**, 1083. [4] Frierdich and Catalano (2012) *ES&T* **46**, 1519. [5] Elzinga (2011) *ES&T* **45**, 6366.