

Effect of metals on goethite and ferrihydrite redox potentials

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Metals are well known to substitute into and adsorb onto Fe minerals in soils and sediments. Little is known about how incorporated or adsorbed metals influence Fe mineral redox potentials and interfacial redox reactivity. To better understand the effect of metals on Fe mineral redox potentials, we measured open circuit redox potentials of goethite and ferrihydrite with metals either incorporated or adsorbed under anoxic conditions over a pH range of 5.5 to 7.0. Specifically, we compared the redox potentials of Ni-, Zn-, Cu-, and Al-substituted goethite and ferrihydrite with those of unsubstituted goethite and ferrihydrite. Ni incorporation into goethite as well as Ni sorption onto goethite shifted redox potentials between 50 and 200 mV more positive (i.e., more oxidizing) than unsubstituted goethite. X-ray absorption spectroscopy (XAS) suggests that the lower stability of Ni-goethite is due to a greater accumulation of strain energy caused by two additional protons attaching to Ni-O octahedra. Strain energy in Zn-goethite is partly dissipated by generation of Fe lattice vacancies which are protonated to maintain charge balance. Somewhat surprisingly, we found that Zn and Cu incorporation had little effect on goethite redox potentials. Additional work is underway to measure redox potentials of Al-substituted goethite as well as metal substituted ferrihydrite, and to investigate any links between redox potential and Fe(II)-Fe(III) electron transfer. In addition, we are exploring how metal substitution into goethite and ferrihydrite influences mineral reactivity by measuring reduction rates of nitroaromatic compounds.