

Effects of Ni(II) and Zn(II) substitution on goethite redox potentials

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Metal incorporation into iron (Fe) minerals is well known to affect the properties and behavior of Fe minerals in soils and sediments. Little, however, is known about how incorporated metals influence Fe mineral redox potentials and ultimately interfacial redox reactivity. To better understand the effect of metal doping on Fe mineral redox potentials, we measured the continuous open circuit redox potentials of metal-substituted goethite under anoxic conditions over pH range of 5.5 to 7.0 using various electron transfer mediators. Specifically, we compared the redox potentials of Ni- and Zn- substituted goethite with those of unsubstituted goethite. We hypothesized that vacancies and structural instability introduced by the Ni and Zn incorporation into the goethite structure would increase the goethite|Fe(II) redox potential [1,2]. Surprisingly, we found that Zn incorporation had little effect on goethite redox potentials with both Zn-substitute and unsubstituted goethite closely aligning over a pH range of 5.8 to 7.0. At the lowest pH of 5.5, however, the Zn-substitute redox potential was slightly higher. In contrast, Ni-goethite and unsubstituted goethite potentials differed significantly over the full pH range. Interestingly, the Ni-goethite potentials closely matched the theoretical potentials expected for ferrihydrite|Fe(II) redox couple. Our findings suggest that Ni-substitution is destabilizing the goethite structure to have redox potentials more similar to ferrihydrite despite no evidence for the presence of a ferrihydrite impurity. Additional work is underway to correlate the structure of Ni and Zn substitution with goethite redox reactivity using *ab initio* molecular dynamics coupled with Ni and Zn extended X-ray absorption fine structure spectroscopy (EXAFS). Our work will provide important insights into how incorporated metals influence Fe mineral redox potentials and ultimately interfacial redox reactivity in soils and sediments.

[1] Association of Defect and Zinc in Hematite, Bylaska, E. J., et al. (2019). *Environmental Science & Technology* 53(23), 13687-13694.

[2] The Role of Defects in Fe(II)-Goethite Electron Transfer, Notini, L. et al. (2018). *Environmental Science & Technology* 52(5), 2751-2759.