

Sequestration of Pb by hydrous manganese oxide-coated clay

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Mn oxide-coated clay and similar fine-grained fractions have been noted as surfaces that control the behavior of metal contaminants in the environment. The objective of this study was to better understand the effect of coatings on the sorption behavior of Pb. Macroscopic adsorption experiments and X-ray absorption spectroscopy (XAS) were conducted to study sorption mechanisms.

Discussion of results

Hydrous manganese oxide (HMO) coatings were prepared according to Boonfueng et al. (2005). Adsorption edges and isotherms revealed that sorption was dominated by the Mn oxide phase. In XAS analysis one type of coordination environment was observed; sorption was invariant of pH, ionic strength, and loading. Specifically, we found approximately 1.7 ± 0.3 atoms of oxygen in the first shell at a distance of 2.29 ± 0.06 Å and 1.0 ± 0.4 atoms of manganese in the second shell at 3.59 ± 0.08 Å. Therefore, the sorption affinity and capacity of the coating was consistent with that of discrete oxide where Pb ions formed inner-sphere complexes. For a contact time up to 4 months, an additional 60% of the sites became occupied and the lead structure was consistent with short-term samples. This slower sorption process was modeled as intraparticle surface diffusion as there was no evidence of surface precipitation or solid solution formation. Best fit diffusivities ranged from 10^{-20} to 10^{-18} cm²/s.

Conclusions

Pb sorption to HMO coated-clay was invariant of pH, ionic strength, and concentration; inner-sphere complexation of Pb involved 1.7 ± 0.3 atoms of oxygen in the first shell at a distance of 2.29 ± 0.06 Å and 1.0 ± 0.4 atoms of manganese in the second shell at 3.59 ± 0.08 Å. This average structure was also observed as a function of time where as much as a 60% increase in adsorption occurred; the result suggests internal surface sites are no different than external ones. Best fit diffusivities ranged from 10^{-20} to 10^{-18} cm²/s, and therefore hydrous Mn oxide present as either coatings or discrete particles acts as an important sink for metal ions.

Reference

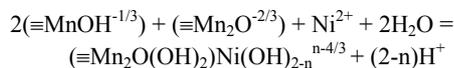
Boonfueng T., Axe L. and Xu, Y. (2005) *J. Colloid Interface Sci.* 281, 80-92.

Sorption of Ni by marine Fe-Mn nodules and crusts: Surface complexation and structural incorporation of Ni in birnessite

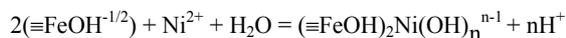
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Marine ferromanganese crusts and nodules contain very high (up to 2 wt. %) Ni contents yet the concentration of Ni in seawater is only ~10 nM. We measured the sorption of Ni(II) onto synthetic birnessite and goethite from pH 3 – 8. EXAFS spectra show that, at pH 8.0, Ni is adsorbed to the birnessite surface by forming a tridentate complex with two edge-sharing MnO₆ polyhedra. We developed a surface complexation model (multisite 1pK with diffuse layer) for Ni on birnessite based on the reactions



(with n=0,1). For Ni sorbing to goethite, we fit our sorption edge to the equilibria



(with n=0,1). Our surface complexation models show that, at the pH of seawater and below, Ni will be strongly preferentially sorbed by birnessite over goethite. This agrees with the Ni-Mn correlation observed in Fe-Mn nodules and crusts. We then characterised the crystal chemistry of Ni in several natural marine ferromanganese crust and nodule samples from the North Pacific. EXAFS spectra show that Ni has been structurally incorporated by replacement of Mn⁴⁺ in the phyllosilicate layer. The surface complex observed in our experiments must be a precursor to structural incorporation of Ni as the nodule grows. Using our surface complex stability constants, we show that in seawater at pH 8.3 the sorption of Ni by marine phyllosilicate phases limits the aqueous concentration of free Ni²⁺ to pM levels. The observed nM concentrations of total dissolved Ni presumably result from Ni complexation by organic ligands. Such ligands must be essential for making biolimiting nutrients available for primary productivity; in their absence, sorption of Ni by birnessite would preclude its bioavailability.