

Structure and reactivity of hydrated goethite (100) interface and Arsenic sorption: CTR and RAXR study

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Goethite (α -FeOOH), an abundant and highly reactive iron oxyhydroxide mineral phase found in soils and sediments, plays an important role in many natural processes. The reactivity of the goethite surface depends on the types of exposed surface functional groups which are a function of the structure and composition of the bulk material, the orientation of the exposed surface, and the chemical history of the surface, along with the interfacial water/ionic species. Hence determination of the molecular structure of the hydrated goethite interface and the precise mode of binding of sorbed species is critical to developing a fundamental understanding of the chemical reactions that control the fate of contaminants in natural aquatic systems. We used crystal truncation rod (CTR) diffraction to investigate the interface structure of the hydrated goethite (100) surface under environmentally relevant conditions [1]. The interface was found to be terminated by a relaxed double hydroxyl layer over which two ordered water layers occur with specific hydrogen bonding to the hydroxyl layers. These results give new fundamental information on water and hydroxyl structure at a geochemical interface, and indicate how sorption processes might be affected by functional group and water structure variations. We further examined arsenate sorption on the goethite (100) surface using both CTR and Resonance Anomalous X-ray Reflectivity (RAXR) methods, which we will compliment and add to the structural analysis. Preliminary results will be presented on the structural analysis of arsenate sorption on goethite (100) surfaces. Arsenate sorption on goethite has particular relevance to many contamination sites including Taiwan and Bangladesh.

[1] Ghose *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 1943–1953.

In vivo Hg MIF effect in epiphytes?

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We collected samples of the epiphyte *Tillandsia usenoides* (cf Spanish moss) along the eastern Coastal Plain of the U.S. from northern Florida to North Carolina and determined the relative abundances of Hg isotopes as permil deviations (δ) from NIST-SRM3133. In all moss samples analyzed, mercury possess a light isotope enrichment, with isotopes having even atomic mass number (A) varying according to mass fractionation (MF) laws. The δ values of odd-A isotopes ¹⁹⁹Hg and ²⁰¹Hg, when corrected for MF effects have distinct negative residuals $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$. Values of $\Delta^{199}\text{Hg}$ range from -0.25 to -1.20, with the average $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ being 1.05 ± 0.06 . These findings are virtually identical to those reported for lichen samples from Quebec, urban France, and Swiss Alps [1].

In addition we directly sampled atmospheric mercury vapor at multiple times during a year and water during a few rain events. Both mercury vapor and rainwater mercury exhibited a light isotope enrichment MF effect. However, vapor and water samples exhibit either no detectable mass-independent (MIF) Hg isotope effect, or one that is slightly positive ($\Delta^{199}\text{Hg} = \text{or } < +0.3$). The absence of a detectable MIF or such small positive values of $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ also characterize atmospheric samples we have collected elsewhere in the Northern Hemisphere but yet reported.

Consequently, we suggest that the negative $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ MIF isotope effect observed in these epiphytes is not an artifact of the atmosphere, but is due to processes within the plant. We cannot propose a mechanism. The data are consistent with a magnetic isotope effect (MIE). Photolytic processes drive the metabolism of plants, and the necessary radical pairs might be produced by this, by enzyme activity, or both.

[1] Carignan *et al.* (2009) *Environ. Sci. Technol.* **43**, 5660–5664.