

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

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Goethite (α -FeOOH), an extremely common and reactive phase found in soils and sediments, plays an important role in many natural processes including the transport and sequestration of environmental contaminants, and the biological availability and geochemical cycling of iron. 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. 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 contrast. Arsenate sorption on goethite has particular relevance to many contamination sites including Taiwan and Bangladesh.

Mercury isotopic signature of the atmosphere

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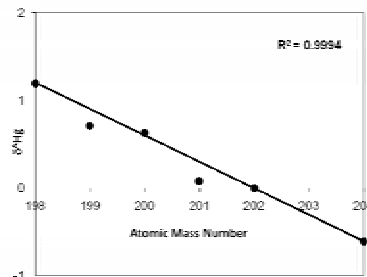
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Previously we reported measurements of the isotopic composition of atmospheric mercury trapped in the epiphyte Spanish moss. All samples exhibited a common isotope effect. When normalized to the NIST-3133 standard and corrected for mass-dependent fractionation, Hg from the moss samples exhibit a depletion of the odd neutron number isotopes ¹⁹⁹Hg and ²⁰¹Hg. Because ¹⁹⁹Hg and ²⁰¹Hg are depleted in nearly equal amounts, we attributed this mass-independent fractionation (MIF) to a magnetic isotope effect (MIE) in accordance with the nearly equal nuclear magnetic moments of the two odd A isotopes. The figure below illustrates this effect where ¹⁹⁹Hg and ²⁰¹Hg deviate from the mass dependent relationship.

We could not preclude the possibility that this MIF resulted from catalytic reactions of enzymes within the plant. Also, while we assumed that the bulk of the Hg represented elemental mercury vapour taken up by the air plant, we were also aware of the



possibility that in fact it might be Hg (II) that was deposited by wet deposition on the plant. In the latter case, the observed isotope effect could be an artefact of one or more of the possible atmospheric oxidation paths and not representative of atmospheric Hg. A refined procedure permitting precise isotopic analyses of as little as 7ng of mercury has made it possible to characterize atmospheric mercury vapour directly. The Mercury is trapped on gold plated sand in a quartz tube. Air is passed through this gold trap by a pump, and a flow meter with an adjustable needle valve is used to control and measure the flow rate. Once the sampling is complete, mercury is thermally purged from the gold trap, and carried by a helium stream into concentrated nitric acid containing chloride, where it is completely oxidized to Hg (II). At a concentration of 1ppb the Hg (II) is reduced in a hydride generator, and the evolving cold mercury vapour is analyzed in a NEPTUNE MC-ICP-MS. Analyses of atmospheric mercury vapour have revealed a clear negative isotopic anomaly with respect to the odd-A isotopes that is currently indistinguishable from that found in the epiphytes. Multiple isotope effects promise to significantly contribute to a better understanding of the dynamics of the mercury cycle.