Adsorption of Mn(II) at the surface of birnessite: Characterization of sorption products by XRD and EXAFS analyses

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Manganese oxides are among the most reactive mineral phases found in the environment and exert a strong control on the chemistry of soil and sediments through adsorption and redox reactions [1]. Here, results from experiments characterizing the interaction between Mn^{2+} and hexagonal birnessite, which typifies the phyllomanganates found in natural aquatic systems, are presented for a variety of reaction conditions.

Experiments were performed at varying pH (3.0-7.0) and Mn^{2+} concentrations (0.5 – 4 mM) under both oxic and anoxic conditions. Reacted solids were washed and dried, and characterized by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Under all conditions studied, the XAS results indicate an increase in Mn^{III} content of the reacted solids relative to non-reacted birnessite, consistent with electron transfer between surface sorbed Mn^{2+} and structural Mn^{IV}. For samples reacted at pH 7.0, XAS and XRD results show that reaction with Mn^{2+} results in transformation of birnessite into manganite (γ-MnOOH), a tunnel-structured Mn^{III} phase. No differences in reaction products were observed between samples reacted under oxic and anoxic conditions, suggesting that oxidation of Mn^{2+} by O2 is of secondary importance in these systems.

The results of this study indicate that Mn^{2+} acts as a reductant of birnessite under the conditions applied. Transformation of birnessite into γ-MnOOH during interaction with Mn^{2+} resembles the transformation of bacteriogenic vernadite (δ-MnO2) into feitknechtite (β-MnOOH) resulting from reaction with Mn^{2+} at concentrations > 0.5 mM observed by Bargar *et al.* [2], and can be explained in terms of a thermodynamic driving force resulting from lowering Eh by introduction of Mn^{2+} facilitating transformation. The kinetics and pathway (s) of transformation, and the effects of and consequences for adsorbed trace impurities are the subject on ongoing research.

[1] Post (1999) *Proceedings of the National Academy of Science of the USA* **96**, 3447–3454. [2] Bargar *et al.* (2005) *American Mineralogist* **90**, 143–154.

Emerging patterns in deep-sea microbial iron mats

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There is growing evidence that Fe-oxidizing bacteria (FeOB) are the primary mediators of Fe-oxyhydroxide deposition at Fe (II)-rich marine hydrothermal vents. One clade of bacteria in particular, the candidatus class ‘Zetaproteobacteria’ has been found consistently in iron-rich microbial mats. Thus far, this class is represented by only one cultivated genus, *Mariprofundus* an obligately lithotrophic FeOB that is a microaerophile. *Mariprofundus* forms a helical stalked comprised primarily of Fe-oxydroxide. We have investigated Fe-mats at Loihi Seamount, an active undersea volcano (950 mbsl) in the Pacific for over five years. These studies reveal total numbers of bacteria remain quite constant in active mats at Loihi, as does population structure as revealed by tRFLP. Both tRFLP and SSU rRNA gene clone libraries indicate Zetaproteobacteria are consistently present, and dominant features of tRFLP profiles, or numerically dominate clone libraries. Phylogenetic analysis indicates that the cultured *Mariprofundus* strains are relatively rare compared to other uncultivated members of the Zetaproteobacteria. Colonization of microslides by FeOB at different vents consistently show that stalk-forming FeOB initiate colonization. Gross morphological characterization of the mats reveal at least four morphotypes, *Mariprofundus*-like helical stalks, a Y-shaped tubular oxide, long tubular sheaths, and particulate oxides. The stalks, Y-structures, and particulate oxides are most common, while the sheaths are rare and sporadic. Specific cell types have been linked to stalks, Y-structures, and sheaths. Bulk analysis suggests that the vast majority of these structures are devoid of cells, suggesting active growth is restricted to specific zones within the mats. Overall, these results suggest that Fe-mats are stable communities dependent upon a continuous source of Fe (II) with internal structure composed of unique populations of FeOB, most of which remain a mystery.