

Formation of manganese-desferrioxime B complexes by dissolution of manganese oxides

OWEN W. DUCKWORTH AND GARRISON SPOSITO

Division of Ecosystem Sciences, University of California, Berkeley, CA 94720, USA (owen@nature.berkeley.edu, gsposito@nature.berkeley.edu)

Recent laboratory and field studies suggest that Mn(III) forms persistent aqueous complexes with high-affinity ligands. Aqueous Mn(III) species thus may play a significant, as-yet largely unexplored role in biogeochemical processes. To that end, we have studied the interaction of desferrioxime B (DFOB), a common tri-hydroxamate siderophore, with manganese. DFOB stabilizes Mn(III) for the pH range 7.0-11.3, forming a Mn(III)HDFOB⁺ complex.

The Mn(III)HDFOB⁺ complex may be formed by DFOB-promoted dissolution of solid Mn-oxides (Figure 1). At pH > 6.5, the dissolution of manganite (γ -MnOOH) in the presence of DFOB is predominantly a non-reductive ligand-promoted reaction whose rate (R_L) is proportional to the adsorbed surface concentration of DFOB. At pH < 6.5, Mn²⁺ is the dominant species resulting from manganite dissolution, thus implicating a reductive dissolution pathway (R_R).

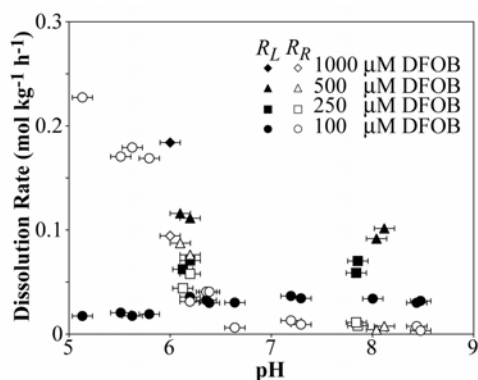


Figure 1. DFOB-Promoted dissolution of γ -MnOOH at 25°C in 0.1 M NaCl and 10 mM buffer.

The results of this study suggest that Mn(III)-siderophore complexes may be readily produced by Mn-oxide dissolution. The formation of these complexes may have implications for the biogeochemical cycling of manganese, redox-active elements, and siderophores in natural environments.

Effects of siderophores on Pb adsorption to kaolinite

PATRICIA MAURICE¹, BHOOPESH MISHRA²,
 ELIZABETH HAACK¹ AND BRUCE BUNKER²

¹Dept. of Civil Engineering & Geological Sciences, University of Notre Dame, Notre Dame, IN 46556, USA (pmaurice@nd.edu)

²Dept. of Physics, University of Notre Dame, Notre Dame, IN 46556, USA

Siderophores are low molecular weight organic ligands synthesized by aerobic microorganisms to acquire Fe under conditions of Fe stress. In addition to Fe (III), siderophores may complex other metals such as Pb. This study compared the effects of trihydroxamate siderophores desferrioxamine-B (DFO-B), desferrioxamine-D₁ (DFO-D₁), desferrioxamine-E (DFO-E), and monohydroxamate siderophore-like ligand acetohydroxamic acid (aHA) on Pb adsorption to kaolinite (KGa-1b) at pH 4.5 to 9, in 0.1 M NaClO₄, at 22°C, in the dark. At pH > 6, all of the studied ligands decreased Pb adsorption to kaolinite: aHA by 5 to 40% and DFO-B, DFO-D₁ and DFO-E by 30 to 75%. However, DFO-B enhanced adsorption at pH ~5 to 6.5, which we hypothesized to be due to adsorption of the doubly positively charged PbH₃(DFO-B)²⁺ complex, which occurs in this pH range. EXAFS results confirmed that this is indeed the case. EXAFS results also showed that Pb adsorption to kaolinite in the presence of DFO-B is dominated by Pb-DFO-B species at pH ≥ 5. Overall, our results demonstrate that siderophores may have different effects on Pb adsorption and mobility through porous media depending upon the siderophore structure and the pH; comparison with other studies suggests sensitivity to mineral structure as well.