



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

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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 desferrioxamine B (DFOB), a common tri-hydroxamate siderophore, with manganese. We determined stability constants for both Mn(II) and Mn(III) complexes with DFOB, and found that desferrioxamine B 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. 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). The change in dissolution mechanism from ligand-promoted to reductive can be attributed to a change either in the chemical speciation of the surface or in the thermodynamic driving force within the system.

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 waters, sediments, and soils.