Control of Mn(III) on contaminant sorption by biogenic manganese oxides

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Manganese biomineralization proceeds through the enzymatic oxidation of aqueous Mn(II) to Mn(IV) and extracellular precipitation of MnO_2. This process is widespread and has large consequences for environmental processes including contaminant fate and trace element bioavailability due the high sorption reactivity of MnO_2.

In this work, we investigated the source of Mn(III) in biogenic MnO_2 and the implications for mineral reactivity. Sorbents were produced by varying the amount of $Mn(II)_{aq}$ provided to *Pseudomonas putida* GB-1 (50 to 1000 μM). The Mn(III) content of the resulting minerals was determined using wet chemical methods and the extent and mechanism of metal sorption was assessed by coupling Ni sorption isotherms and EXAFS spectroscopy. Additional sorption experiments (Zn and Pb) were conducted using the biogenic MnO_2 produced with 1000 μM Mn. Finally, the sorption behavior of abiotic MnO_2 containing either 0 or 35 mol% Mn(III) was also investigated.

Our results show that as the Mn concentration in the medium increased, the Mn(III) content of biogenic MnO_2 increased from 7 – 32 mol% and the loading of Ni on vacancy sites decreased from 23 to 6 mol%. However, minimal sorption of Ni at vacancy sites was observed for abiotic MnO_2 containing 35 % Mn(III). Sorption isotherms for Pb and Zn on biogenic MnO_2 showed considerably higher loadings for Pb (0.49 mol Pb mol^{-1} Mn) than for Zn (0.12 mol Zn mol^{-1} Mn). In addition, up to 4 mol% and 20 mol% of the Mn initially in the solid phase mobilized by Zn and Pb sorption, respectively.

The observed differences in metal surface loadings and accumulation of $Mn(II)_{aq}$ are consistent the capacity of the metals to displace interlayer Mn(III). Our results also highlight the different nature of biogenic and abiotic MnO_2 due to the admixing of the former with microbial biomass that has the potential to sustain the redox cycling of Mn between its three different oxidation states.