GONZÁLEZ HOLGUERA Julia (2018): Reactivity of MnO_2 in bacteria–mineral assemblages

Abstract

Layer-type manganese oxides (MnO_2) are secondary phase nanoparticulate minerals ubiquitous in soils, sediments and water bodies. Because their high surface area and negative surface charges promote metal sequestration on their surfaces, MnO_2 are recognized to affect the mobility and bioavailability of contaminants in both natural and engineered systems. In addition, high valent Mn species are among the strongest oxidants in natural systems. Naturally occurring MnO_2 are precipitated by microorganisms and therefore often occur admixed with organic molecules and intact bacterial cells. The association of mineral phases with organic and biological components can significantly affect the mineral's reactivity through passive organo-mineral interactions that may lead to partial reduction of the oxide, the redox recycling of oxidized Mn [Mn(III) and Mn(IV)] and by exposing the mineral to the cells metabolic activity.

The objective of this thesis was therefore to study the reactivity of MnO_2, both its affinity towards metals and towards organic reductants, in bio-mineral assemblages. We used suspensions of biogenic MnO_2, precipitated by the Mn(II)-oxidizing model *Pseudomonas putida* GB-1, and of the abiotic δ-MnO_2. By combining sorption isotherms and EXAFS spectroscopy, we showed that the loading of cations on MnO_2 depends largely on their capacity to displace Mn(III) already present on the mineral. We then evaluated the effect of pH on Mn(III, IV) reduction in δ-MnO_2 and biogenic MnO_2 suspensions. We finally conducted a literature review to identify the knowledge gaps regarding the coupled interactions between Mn and C in natural systems.

The results from this thesis provide a better understanding of the impact of the biological matrix on the reactivity of biogenic MnO_2. We showed that the scavenging properties of the mineral are strongly affected by the bacteria's presence, both because a Mn(III)-enrichment of the oxide can influence the capacity of the mineral to adsorb cations and because the microbial metabolic activity can undermine the stability of the mineral. Similarly, the role Mn species can play as oxidants is strongly affected by local pH changes that the metabolic activity can establish. Furthermore, the presence of Mn(II)-oxidizers in biogenic MnO_2 provides the system with the capacity to regenerate high valent Mn species, a necessary condition to overcome the imbalance between the electron reducing equivalent of soil C residues and the electron accepting capacity of high valent Mn. These findings are necessary to the comprehension of the reactivity of MnO_2 in natural systems.