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Interference of manganese with iron acquisition by bacterial siderophores

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Plants and microorganisms can exude siderophores under Fe deficient conditions. These molecules, however, can upregulate the solubility of trace metals other than Fe. For example, laboratory studies show that Mn(III) can be mobilized from Mn minerals by siderophores, forming Mn(III)-ligand complexes (Mn(III)-L). While Mn(III) was historically considered to be an insoluble species due to its low solubility and redox instability, recent laboratory and field investigations suggest that the formation of Mn(III)-L may interfere with siderophore-assisted Fe acquisition strategies. However, knowledge of the formation and stability of Mn(III)-L under environmentally relevant conditions is limited.

In this study, we examined the mobilization of Mn(III) and Fe(III) complexed by deferoxamine B (DFOB), a terrestrial bacterial siderophore, in single and mixed Mn and Fe (hydr)oxide systems, including four minerals: manganite, birnessite, lepidocrocite and 2-line ferrihydrite. Batch kinetic experiments were conducted under oxic conditions at circumneutral pH where siderophores are typically exuded in response to Fe deficiency. We determined the rates of metal mobilization and complex decomposition and analyzed the fate of Mn(III)-DFOB upon interaction with Fe (hydr)oxides by using Mn-K edge X-ray absorption near-edge structure and extended X-ray absorption fine structure spectroscopy.

We observed that DFOB mobilized Mn(III) to varying extents from both manganite and birnessite even in the presence of Fe (hydr)oxides. Additionally, Mn(III)-DFOB formation and Mn-promoted DFOB oxidation interfered with Fe(III)-DFOB mobilization. This effect was larger in the presence of birnessite, where we found up to an 83 % decrease in Fe mobilization, than in the presence of manganite, where we found up to a 30 % decrease in Fe mobilization. The effect of lepidocrocite on the rates of Mn(III)-DFOB mobilization from both manganite and birnessite was marginal while in the presence of 2-line ferrihydrite, the rate decreased by a factor of 8 and the Mn(III)-DFOB concentrations decreased by up to 90 %. Interestingly, the decomposition rates of Mn(III)-DFOB were accelerated by the presence of Fe (hydr)oxides, leading to Mn precipitation on their surfaces and enhancing the oxidation of complexed DFOB. Our results suggest a new pathway of Mn redistribution and show that soil minerals can significantly limit biological Fe acquisition processes.