

## Impact of birnessite on arsenic and iron speciation during microbial reduction of arsenic-bearing ferrihydrite

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Arsenic, a widespread redox-active and potentially toxic metalloid, occurs predominantly as As(V) adsorbed to Fe(III)-(hydr)oxides or, to a lesser extent, Mn-oxides in oxic soils. Under oxygen-limiting conditions, the microbially mediated reductive dissolution of Fe(III)-(hydr)oxides mainly liberates dissolved As(V), which is subsequently reduced to the more mobile As(III). Manganese oxides have been shown to rapidly oxidize As(III) and Fe(II) under oxic conditions, thus reducing the mobility of As. However, the net effect of Mn-oxides on the microbially mediated reductive release of As and Fe is still poorly understood. Therefore, we investigated the microbial reduction of As(V)-bearing ferrihydrite by *Shewanella* sp. ANA-3 at near-neutral pH in the presence of different concentrations of birnessite. We employed wet chemical analyses and X-ray absorption spectroscopy to follow reduction kinetics of Mn(III/IV), Fe(III), and As(V). Additional abiotic experiments were performed to explore the reactivity of birnessite towards As(III) and Fe(II) in the presence of Mn(II), Fe(II), ferrihydrite, or deactivated bacterial cells. In comparison with the birnessite-free control, the highest birnessite concentration of 3.1 mM Mn resulted in 78% less Fe and 47% less As reduction at the end of the biotic experiment. After Mn-oxide exhaustion, we observed a constant molar ratio of As/Fe reduction in all treatments, equaling the molar As/Fe ratio in the original ferrihydrite. Our abiotic experiments revealed that As(III) oxidation by birnessite was inhibited by Mn(II), Fe(II), and ferrihydrite. In contrast, the oxidation of Fe(II) by birnessite was equally fast under all conditions. We conclude that in the presence of birnessite, microbially produced Fe(II) is rapidly re-oxidized and precipitates as As-sequestering poorly crystalline Fe(III)-(hydr)oxides. Our results imply that the ability of Mn-oxides to oxidize As(III) in reduced environments is limited by the formation of Fe(III)-(hydr)oxides and surface passivation processes. The validity of this conclusion is currently being tested in a column experiment using As-contaminated soil.