Microbial manganese reduction and its mineralogical record

JENA E JOHNSON[1]*, PRATIXA SAVALIA[2], BENJAMIN D KOCAR[3], SAMUEL M WEBB[4], KENNETH H NEALSON[2] AND WOODWARD W FISCHER[1]

[1]California Institute of Technology, Pasadena CA 91125 (*correspondence: jena@caltech.edu)
[2]University of Southern California, Los Angeles CA 90089
[3]Massachusetts Institute of Technology, Cambridge MA 02139
[4]Stanford Synchrotron Radiation Lightsource, Menlo Park CA 94025

The unseen manganese cycle is rich: Mn(IV)-oxide phases are a critical pool of oxidants in soils and aquifers, fresh-water and marine sediments. While manganese oxides enter sediments as Mn(IV) oxyhydroxides, subsequent geobiological processes during diagenesis produce a sedimentary record that is dominated by Mn(III)-oxide phases and Mn(II)-carbonates. This multi-electron reduction of solid Mn-oxide phases is mediated by both abiotic and biotic processes. The reaction pathways are complex and depend on a variety of conditions, including redox processes and rates of reduction, and the resulting products are hard to predict thermodynamically. We developed a novel approach to study the processes of Mn reduction via *Shewanella oneidensis* MR-1 in real time using synchrotron X-ray spectroscopy in stirred flow-through reactors. We capture spectra of the Mn phases every 15 minutes in 8-16 hr experiments. These real-time experiments highlight a Mn(III)-oxide intermediate and a final rhodochrosite product, which can be directly correlated to Mn(II)-carbonates in ancient sediments. We also show that in the presence of mM phosphate, a Mn(II)-phosphate phase forms rapidly as a secondary precipitate, which may be an analogue for modern high-phosphate soils. Manganese reduction in the presence of phosphate does not produce a Mn(III) intermediate, suggesting that despite evidence for two successive single-electron transfer reactions at the outer membrane [1], the microbially-mediated reduction mechanism effectively converts Mn(IV)-oxides to Mn^{2+} and the Mn(III)-oxide formation is the result of Mn^{2+}-Mn(IV)-oxide disproportionation [2]. These results provide an deeper understanding of the mechanics of Mn reduction and a way to invert observations of textures and mineralogy in Mn-rich sedimentary rocks for geobiological processes of Mn-reduction occuring in sediments.

[1] Lin *et al* (2012) *Geochimica et Cosmochimica Acta* **99**, 179-192 [2] Elzinga (2011) *Environmental Science & Technology* **45**, 6366-6372