Biotic and Abiotic Contributions to the Reduction of Environmental Bacteriogenic Fe-oxides at Circumneutral pH

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Although the formation of Fe-oxides at circumneutral pH in soils and streams has long been held to be an abiotic process, biomineralization of iron at these conditions has recently been recognized as a potentially widespread and important process. Consequently, the reactivity of environmental bacteriogenic Fe-oxides (BIOS) is significant but poorly understood. In this study, we investigate the biotic and abiotic factors controlling the reduction of BIOS at circumneutral pH and any accompanying phase changes. BIOS samples and synthetic 2-line ferrihydrite (2LFh) were incubated for 2 weeks under one oxic (~20% O_2) and two anoxic (100% N_2 and 95/5% N_2/H_2) conditions. Total Fe and Fe(II) concentrations in solution were measured throughout the incubations, and changes in mineralogy were detected with X-ray diffraction (XRD). Fe(II) production was consistent under both oxic and anoxic conditions in the presence of the Fe(II) complexing agent 1,10 phenanthroline. The average initial reduction rate of BIOS under these conditions, 1.65×10^{-10} mol m^{-2} min^{-1}, is consistent with reported values for microbial reduction of 2LFh. In the absence of the Fe(II) complexing agent under 95/5% N_2/H_2 conditions, addition of a microbial metabolism inhibitor (sodium azide) resulted in minimal Fe(II) production compared to incubations without the metabolism inhibitor. Additionally, XRD revealed the formation of goethite in the ferrihydrite-dominated BIOS samples under both oxic and 95/5% N_2/H_2 conditions. In contrast, 2LFh controls experienced minimal reduction and did not exhibit similar phase changes. Based on these results, we suggest that the activity of Fe-reducing bacteria may promote the reduction of BIOS and the conversion of ferrihydrite to more stable Fe-oxide minerals at circumneutral pH. The occurrence of anoxic microsites within the solid BIOS and stabilization of Fe(II) by organic matter may also contribute to the high rates of BIOS reduction observed under oxic conditions. Understanding the reduction mechanism(s) of BIOS will enhance our understanding of both Fe biogeochemical cycling and the bioavailability of environmental contaminants.