

## **Transformation of Fe(III) (hydr)oxides under oscillating redox conditions**

MATTHEW GINDER-VOGEL\*, JACQUELINE MEJIA  
AND ELIZABETH TOMASZEWSKI

Environmental Chemistry and Technology, Dept. of Civil and  
Environmental Engineering, University of Wisconsin –  
Madison, 660 N. Park St., Madison, WI 53706

\*mgindervogel@wisc.edu

Understanding the linkage between microbial activity and geochemical processes, as influenced by the cyclical nature of environmental systems remains poorly understood. In particular, while the transformation of Fe(III) (hydr)oxide minerals under reducing has been extensively investigated, mineralogical evolution under cyclically reducing and oxidizing conditions has been studied under only a few conditions. Additionally, the role of oxidant (e.g.,  $\text{NO}_3^{2-}$  vs.  $\text{O}_2$ ), rate of oxidation, and reduction mechanism in determining the ultimate crystallinity of the resultant Fe (hydr)oxide minerals is poorly characterized. In abiotic cycling studies with ferrihydrite, utilizing either  $\text{Fe(II)SO}_4$  or  $\text{Fe(II)Cl}_2$  as the reductant and  $\text{O}_2$  as the oxidant, we find that ferrihydrite is consumed during the first reduction half cycle and the mineralogy stabilizes at a mixture of maghemite and goethite after two complete redox cycles (e.g., increased Fe (hydr)oxide crystallinity). However, in systems where redox cycling is biologically driven the crystallinity of the resultant Fe (hydr)oxides is determined by a combination of oxidant and oxidation rate. Ferrihydrite, lepidocrocite, and goethite were all reduced using a natural inoculum and then oxidized either by the introduction of either  $\text{O}_2$  (abiotic oxidation) or  $\text{NO}_3^{2-}$  (biotic oxidation). After several complete redox cycles, increasing Fe (hydr)oxide crystallinity is observed when  $\text{NO}_3^-$  is used as the oxidant and decreasing crystallinity when  $\text{O}_2$  is used as the oxidant. This work demonstrates that both reduction mechanism (abiotic/biotic) and oxidant play a pivotal role in determining the ultimate mineralogy Fe (hydr)oxides in redox active environments.