

## Bacterial reduction of crystalline Fe<sup>3+</sup> oxides in single phase suspensions and subsurface materials

JOHN M. ZACHARA,\* JAMES K. FREDRICKSON, SHU-MEI LI, DAVID W. KENNEDY,  
STEVEN C. SMITH, AND PAUL L. GASSMAN

Pacific Northwest National Laboratory, Richland, Washington 99352, U.S.A.

### ABSTRACT

Microbiologic reduction of synthetic and geologic Fe<sup>3+</sup> oxides associated with four Pleistocene-age, Atlantic coastal plain sediments was investigated using a dissimilatory Fe reducing bacterium (*Shewanella putrefaciens*, strain CN32) in bicarbonate buffer. Experiments investigated whether phosphate and anthraquinone-2, 6-disulfonate, (AQDS, a humic acid analogue) influenced the extent of crystalline Fe<sup>3+</sup> oxide bioreduction and whether crystalline Fe<sup>3+</sup> oxides in geologic materials are more or less reducible than comparable synthetic phases. Anaerobic incubations (10<sup>8</sup> organisms/mL) were performed both with and without PO<sub>4</sub> and AQDS that functions as an electron repository and shuttle. The production of Fe<sup>2+</sup> (solid and aqueous) was followed with time, as was mineralogy by X-ray diffraction. The synthetic oxides were reduced in a qualitative trend consistent with their surface area and free energy: hydrous ferric oxide (HFO) > goethite > hematite. Bacterial reduction of the crystalline oxides was incomplete in spite of excess electron donor. Biogenic formation of vivianite [Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O] and siderite (FeCO<sub>3</sub>) was observed; the conditions of their formation was consistent with their solubility. The geologic Fe<sup>3+</sup> oxides showed a large range in reducibility, approaching 100% in some materials. The natural oxides were equally or more reducible than their synthetic counterparts, in spite of association with non-reducible mineral phases (e.g., kaolinite). The reducibility of the synthetic and geologic oxides was weakly effected by PO<sub>4</sub>, but was accelerated by AQDS. CN32 produced the hydroquinone form of AQDS (AHDS), that, in turn, had thermodynamic power to reduce the Fe<sup>3+</sup> oxides. As a chemical reductant, it could reach physical regions of the oxide not accessible by the organism. Electron microscopy showed that crystallite size was not the primary factor that caused differences in reducibility between natural and synthetic crystalline Fe<sup>3+</sup> oxide phases. Crystalline disorder and microheterogeneities may be more important.