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Reductive Dissolution of Hematite by the Microbe Shewanella putrefaciens: Surface Transformations and Dissolution Pathways

Kevin Rosso (kevin.rosso@pnl.gov), **John Zachara** (john.zachara@pnl.gov) &
Steven Smith (steven.smith@pnl.gov)

W.R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, 99352, USA

In anaerobic near-surface environments, the respiration of dissimilatory iron-reducing bacteria (DIRB) couples the oxidation of organic matter to reduction of solid phase iron oxides. Apparently, microbes transfer electrons to ferric iron by direct attachment to the mineral surface, converting it to its more soluble reduced counterpart and leading to dissolution of the mineral phase. Iron release rates have shown a sensitive dependence on the oxide phase, crystallinity, and surface area in macroscopic microbial dissolution experiments (e.g. Roden and Zachara, 1996; Zachara et al., 1998). However, the dissolution pathways followed at the microscopic scale are unknown. Presumably, dissolution is predisposed to proceed heterogeneously across the mineral surface via the localized microbe-mineral contacts.

To begin to understand the dissolution process, we performed a series of atomic force microscopy (AFM) investigations to probe for microtopographic changes on the basal surfaces of tabular hematite single crystals that were exposed to the DIRB *Shewanella putrefaciens*, strain CN32. Batch samples were bioreduced to varying degrees by treatment with repeated cycles of inoculations and rinses, with intermittent sample extractions, overcoming surface passivation by sorbed ferrous iron and enhancing the formation of dissolution features. The redox-active humic acid analogue anthraquinone-2, 6-disulfonate (AQDS), a known electron shuttle catalyst for this system, was included in parallel experiments to test for possible influences on the dissolution mechanism. Synthetic hematite platelets were chosen because their composition, size, and habit could be consistently reproduced.

Basal surfaces typically displayed combinations of extensive, well defined terraces and irregular growth spirals, the latter consistent with layer growth about bulk dislocations as commonly found in natural tabular hematites (Sunagawa, 1962) (Fig. 1a). *Ex situ* AFM images of bioreduced platelets demonstrated that DIRB attachment to the surface was facile and predominantly preserved (Fig. 1b). Platelets were often densely populated, with no preferential distribution of cells with respect to surface microtopography. Residual cell features of organic composition were also observed, recently attributed to arise from natural cell detachment mechanisms (Fig. 1c). Dissolution features were easily found, as determined by comparison with similarly treated but non-bioreduced control samples. Two general types of characteristic dissolution features were observed, 1) uniformly distributed nanometer-scale surface pitting (Fig. 1d), and 2) crystallographically controlled, locally facile dissolution features (Figure 1c). The latter showed no spatial correlation with attached DIRB, and no evidence of a connection with localized cell activity. In contrast, they were structurally correlated to the apices of spiral growth features on the mineral surface, and often followed hexagonal lattice directions. No discernible concentration of dissolution features was found localized in the vicinity of the microbe-mineral contacts using high resolution AFM scans. Collectively, contrary to the anticipated localized dissolution behavior, distinctly non-local dissolution features were found. The observations are consistent with a chemical dissolution mechanism and lead to the conclusion that the operative microbial metabolic processes release biomolecules capable of attacking structural ferric iron. This non-local dissolution pathway is suggestive of a potentially important link between mineral structure and bioreactivity in this system.

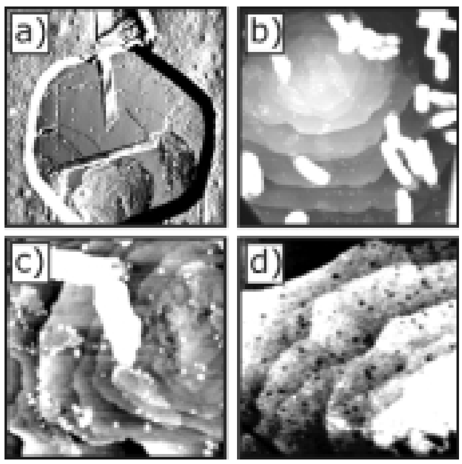

Figure 1: a) Deflection image of an unreacted hematite platelet (image 20 microns across) showing well defined basal terraces and spiral growth features. b) Topographic image of DIRB attached to basal surface and cell detachment features (8 microns). c) Topographic image of attached DIRB, cell detachment features, and dissolution features coincident with the apex of a growth spiral surrounding bulk dislocations (4 microns). d) Topographic image of nanometer-scale etch pits distributed uniformly across stepped basal terraces (3 microns).

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