

Geochemistry of Hydrous Ferric Oxide Reduction by *Geobacter metallireducens*: Implications for Sustained Dechlorination of Tetrachloromethane

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The effect of changes in iron mineralogy on tetrachloromethane (TCM) dechlorination during microbial reduction of hydrous ferric oxide by *G. metallireducens* was followed during a 50-day incubation period. The first 10 days were marked by a rapid depletion of acetate accompanied by an increase in the proportion of Fe(II) in the solid phase from 1% to 30%. Aqueous Fe(II) concentrations peaked at day 8, then decreased, presumably via precipitation of siderite (FeCO₃), which was co-produced with nano-scale magnetite particles (Fe₃O₄). After 20 days of incubation, no further depletion of acetate or formation of ferrous iron were observed, indicating the cessation of microbial activity. Although *G. metallireducens* has previously been shown capable of directly mediating TCM dechlorination, the rates of degradation observed in this study suggest that dechlorination could be predominantly ascribed to reduced mineral surfaces throughout the incubation period.

Introduction and Approach:

The abundance of Fe(III) in fresh water sediments (Heron et al., 1994) and the ubiquity of dissimilative iron reducing bacteria (DIRB) in the subsurface (Coates et al., 1996) has generated great interest in the potential for contaminant transformation in iron reducing environments. As these environments are characterized by the presence of reduced solids (e.g. magnetite), both microbial and mineral-mediated reductive reactions can contribute to the transformation of highly chlorinated contaminants like TCM (Petrovskis et al., 1994; Kim and Picardal, 1999). It was recently demonstrated that TCM transformation in a one month old culture of *G. metallireducens*, using HFO as the electron acceptor, could be ascribed predominantly to reactions mediated by nano-scale magnetite particles generated by the bacteria (McCormick et al., 1998; McCormick and Adriaens, 2000). However, no information is available on the temporal changes in TCM reactivity that occur throughout the period of microbial iron reduction.

To address this question, *G. metallireducens* was incubated in a bicarbonate buffer with 140 mM hydrous ferric oxide as the electron acceptor, and 10 mM acetate as the electron donor. During the 50-day incubation period, the following parameters were monitored: (i) acetate, (ii) total protein, (iii) aqueous Fe(II) (iv) solid phase Fe(II) and Fe(III), (iv) redox potential and pH. In addition, at select time points, samples of the culture

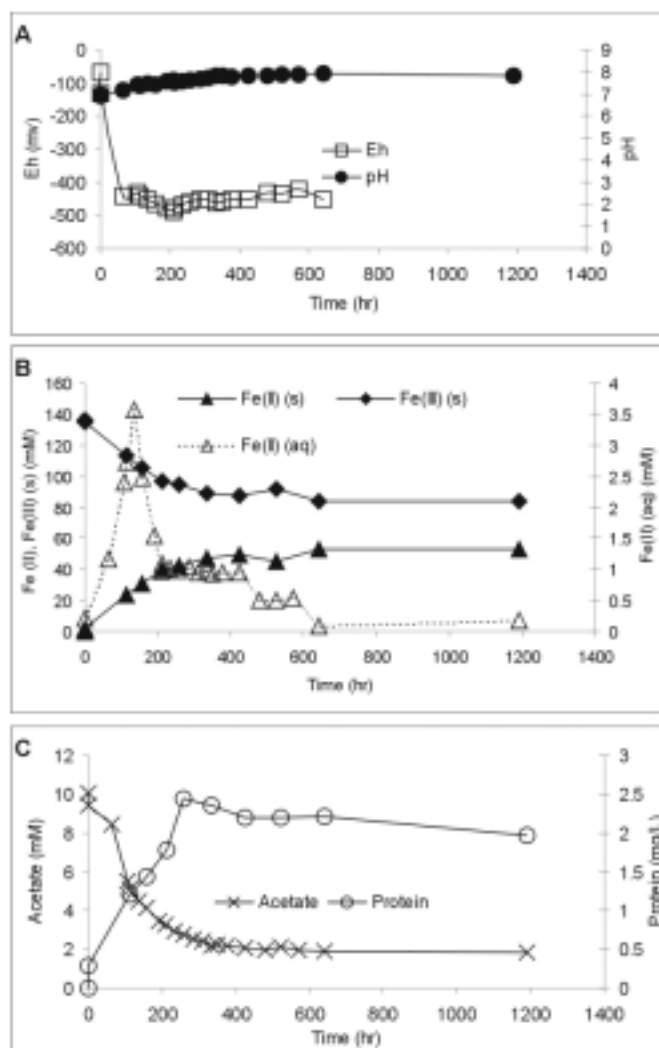
solids were collected and evaluated for their reactivity with TCM. These samples were then further characterized by X-ray diffraction (XRD), Raman spectroscopy, high resolution transmission electron microscopy, and BET surface area measurement. Comparing the pseudo-first order rate constant derived for each TCM degradation screening with previously obtained rate constants for TCM degradation by *G. metallireducens* (protein normalized) and biogenic magnetite (surface area normalized) should indicate if the reaction is predominantly biotic or abiotic in nature. Furthermore, methane, which has only been observed as a product of the abiotic reaction, can be used to indicate the presence of the abiotic reaction.

Results and Discussion:

The biogeochemical changes shown in Figure 1 provides some insights in the evolution of catalytic activity under iron-reducing conditions. Electron donor and acceptor analysis indicates that the solid phase distribution of Fe(II) and Fe(III) reflect a ratio exceeding that of the theoretical values of 1:2 expected for magnetite, while the electron donor is largely depleted during microbial iron-reduction. Aqueous Fe(II) increases during the first 8 days, when redox potentials drops sharply. Fe(II) (aq) then rapidly decreases, coinciding with the production of siderite as indicated by XRD. Raman spectroscopy confirmed the formation of siderite and indicated the presence of magnetite. Based on transmission electron microscopy, both micro- and nano-scale particles were present at the final time point, the latter attributed to magnetite. Based on total Fe(II), the final solids composition was estimated to consist of 92% magnetite and 8% siderite. The TCM degradation rates observed at each time point during the biogenesis experiment (starting at 5 days) indicate that dechlorination could be predominantly ascribed to abiotic surface reactions throughout the incubation period.

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Geochemical changes associated with the reduction of hydrous ferric oxide by *Geobacter metallireducens*. Changes in pH and Eh during microbial reduction (A), effective concentrations of ferric and ferrous iron in the solid and aqueous phases (B), and acetate consumption as well as total protein formation during cell growth (C).

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