Metal reduction and formation of nanometer-sized magnetites by facultative iron-reducing bacteria isolated from inter-tidal flat sediments

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Although microbe-metal interactions play important roles in the metal geochemistry and organic matter degradation in the tidal flat sediments, studies of microbial metal reduction and iron biomineralization are beginning to be studied. The objectives of this study were to explore Fe(III) and metal reduction by the facultative metal-reducing bacteria isolated from the inter-tidal flat sediments, Southwestern coast of Korea as well as to examine microbial reduction of Fe(III) oxide hydroxides and biomineralization of Fe iron oxides by fermentation processes. Taxonomic characterization of the strains isolated from inter-tidal flat sediments indicated that they belong to genus of *Shewanella* sp. The bacteria were able to reduce $FeCl_3$, Fe(III)-citrate, FeOOH and metals including As(V) and Se(V) using short chain fatty acids as the electron donors. The Fe(III)-reducing bacteria were capable of reducing both akaganeite and ferrihydrite during glucose fermentation. By comparison of iron minerals formed by *Shewanella* sp.during reduction of the iron oxyhydroxides at room temperature, it was shown that *Shewanell*a sp. formed 2 ~ 3 nm-sized magnetite (Fe_3O_4) particles by akaganeite reduction, whereas the bacterium formed mainly X-ray amorphous iron oxides by ferrihydrite reduction. These results suggest that microbial reduction of metals and formation of nm-sized magnetites by fermentation processes at near ambient temperatures may influence the biogeochemical cycles of carbon and metals in subsurface environments. Knowledge concerning such bio-solid state processes may be important in the synthesis and production of nm-sized ferromagnetic materials.

Using copper isotopes to distinguish biotic and abiotic effects on acid mine drainage

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Recent experiments have shown that abiotic leaching of chalcopyrite causes greater Cu isotope fractionation between original mineral (Cu_{min}) and leachate Cu (Cu_{aq}) ($\Delta_{aq\text{-}min} = \delta^{65}Cu_{aq} - \delta^{65}Cu_{min} = 0.92\text{-}1.63 \pm 0.23‰$) than in the presence of *Acidithiobacillus ferrooxidans* ($\Delta_{aq\text{-}min} = 0.10\text{-}0.53 \pm 0.23‰$), a known Fe- and S-oxidizing Proteobacterium. Additional mineral-free experiments show that Cu associated with *A. ferrooxidans* cells (Cu_b) is isotopically enriched relative to Cu_{aq} in the medium ($\Delta_{b\text{-}aq} = 2.2 \pm 0.23‰$). Thus, cells are a sink for enriched Cu_{aq}, accounting for the smaller biotic $\Delta_{aq\text{-}min}$ fractionation during chalcopyrite dissolution.

In an effort to find similar abiotic and biotic fractionation signatures in a natural setting, we surveyed the Cu isotopic composition of primary minerals and stream water affected by acid mine drainage in an enargite- and chalcopyrite-containing drainage located in southwestern Colorado, USA. The $\delta^{65}Cu$ values measured for local enargite ($\delta^{65}Cu = -0.01 \pm 0.12‰$) and chalcopyrite ($\delta^{65}Cu = 0.16 \pm 0.12‰$) are within the general range of previously reported values for terrestrial primary Cu sulfides ($-1 < \delta^{65}Cu < 1$). These mineral samples show lower $\delta^{65}Cu$ values than stream waters ($\delta^{65}Cu = 1.36 - 1.74 \pm 0.12‰$). The average fractionation between chalcopyrite and stream samples ($\Delta_{aq\text{-}min} = 1.4 \pm 0.17‰$) is similar to that for previous abiotic chalcopyrite leach experiments.

Interestingly, the observed biotic $\Delta_{aq\text{-}min}$ fractionation signature is not detected in the field. Mass balance supports the likelihood that the fraction of leached Cu that associates with microorganisms is less significant in the open field system compared to the closed batch experiments. Experiments designed to test potential Cu isotope fractionation during sorption of Cu_{aq} onto *A. ferrooxidans* cells and onto mineral surfaces are ongoing. Our results suggest that Cu isotope measurements are a useful tool for better understanding Cu sources and mobility in the environment, and will aid in both ore prospecting and toxic metal remediation.