

Reduction of U by adsorbed vs. surface-precipitated Fe(II) at model cell surfaces

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We investigated the effect of Fe-Fe proximity on the reduction of U(VI), using aqueous suspensions containing Fe(II) and carboxyl-functionalized microspheres as an abiotic model of bacterial cell-surface associated Fe(II). Fe K-edge and U L-edge X-ray absorption fine-structure spectroscopy (XAFS) was used to determine the valence state and atomic environment of the adsorbed species, while acid-base titrations and batch-sorption experiments provided information on proton release and metal uptake as a function of pH. In the binary (Fe + carboxyl surface) system we observe two regimes of Fe(II) sorption: mononuclear at circumneutral pH and 1 mM Fe and polynuclear at conditions just below saturation with respect to bulk Fe(OH)₂(s) formation. In the ternary system (U + Fe + carboxyl surface) we did not observe U(VI) reduction when Fe(II) was sorbed as mononuclear species; however, U(VI) was reduced to uraninite nanoparticles when Fe(II) was adsorbed as a polynuclear species. Our results suggest that Fe-Fe coordination is necessary for U(VI) reduction by Fe(II) in the absence of electron-shuttling agents or conductive surfaces. This abiotic study also elucidates the physico-chemical processes that may be occurring at and near the charged cell surface.

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The geomicrobiology of surficial geochemical anomalies

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Dispersion halos occur in soil horizons above buried ore bodies that possess geochemical signals originating from the buried ore (Cameron et al., 2004). The model by Hamilton et al. (2004) describe a reduced column that forms above buried sulfides, facilitating the transport of reduced iron (and base metals) to the soil surface where it is oxidized and precipitates (immobilising the base metals).

Aerobic heterotrophic bacteria, anaerobic heterotrophic bacteria, dissimilatory sulfate reducing bacteria (SRB) and acidophilic iron oxidizing bacteria were enumerated in samples collected from the Cross Lake dispersion halo environment. The heterotrophic bacterial counts were generally enhanced within this environment; with the anaerobic heterotrophic bacteria counts exceeding those of the aerobic heterotrophic bacteria. Also, low populations of SRB were enriched over mineralization suggesting that low concentrations of sulfate are being transported to the surface from the ore body. Acidophilic iron oxidising bacteria were not recovered from these samples, suggesting that chemical oxidation may be responsible for the mobilisation of the geochemical signatures from the ore. The enhanced bacterial biosphere suggests that one of the roles for bacteria in these systems is to maintain the reduced column above the buried sulphide deposit, which then facilitates the transport of dissolved metal species to the surface. The relationship between bacteria, oxidation-reduction potential (ORP), spontaneous potential (SP), selective leach extractions, and soil gas hydrocarbons (SGH) then, appears to be a contemporary process that could be examined under laboratory conditions to improve understanding of these systems.

References

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