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Redox-Linked Conformation Change Observed for Adsorbed Metal-Reducing Bacterial Cytochromes

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Fate of ferric-hydroxide associated U(VI) during biological magnetite formation

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In situ microbial metal reduction for the immobilization of toxic metals and radionuclides is an area of current research as a means of remediating contaminated ground water. The reduction of iron may result in the formation of magnetite concurrent with the reduction of soluble uranyl ions. The fate of adsorbed or co-precipitated uranium during iron reduction and magnetite formation remains was investigated.

Uranium-doped biogenic magnetite slurries were produced during fermentative reduction of uranium-doped ferric hydroxide precursor by cultures of *Thermoanaerobacter* strain TOR-39 [1]. The resultant suspensions were incubated at 65°C followed by room-temperature storage in crimp-sealed serum bottles with butyl rubber caps. Subsets of samples were analyzed by U L_{III}-edge X-ray absorption near edge spectroscopy (EXAFS) at the Advanced Photon Source and dropped onto TEM grids in an anaerobic chamber.

TEM imaging of the slurries revealed the presence of magnetite, unreduced FeOOH precursor, as well as needle-like crystal structures of akaganéite. Electron diffraction patterns confirmed the presence of magnetite and akaganéite in the slurries. Additionally, diffraction patterns were used to identify the presence of uraninite. EDS spectra of isolated magnetite crystals indicated small amounts of associated uranium.

EXAFS data indicate the presence of a biogenic UO_2 phase. Theoretical model fits identify 5 to 6 nearest-neighbor uranium atoms (compared to 12 in the standard UO_2 structure) suggesting the formation of UO_2 nanoparticles. The model fits also identify a uranyl-Fe phase suggesting the sorption of uranyl to magnetite or the FeOOH precursor and a a uranyl-carbon signal possibly due to organic-U complexes.

[1] Moon *et al.* (2007) *J. Microb. Meth.* **70**, 150–158.

Redox-linked conformation change observed for adsorbed metal-reducing bacterial cytochromes

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We investigated the adsorption of cytochromes from different organisms to oxides. The adsorption of periplasmic cytochromes including STC from *Shewanella oneidensis* MR-1 (So) and PpcA from *Geobacter sulfurreducens* (Gs) was compared to that of outer-membrane cytochromes (OmcB from Gs and OmcA and MtrC from So). STC, OmcA and MtrC adsorption was measured with the protein in the reduced and oxidized states.

Adsorption was monitored using optical waveguide lightmode spectroscopy (OWLS), which gives the mass of adsorbed protein alone, and quartz crystal microbalance with dissipation (QCM-D), which gives the total adsorbed mass including associated solvent. Previous work has shown that OWLS and QCM-D results together correlate with protein density. The detection of density change upon oxidation and reduction indicates of changes in protein conformation.

Periplasmic cytochromes are invariably more dense than outer-membrane cytochromes, which are unusually low density. This likely reflects the different functional roles of the proteins. Periplasmic and outer-membrane proteins react oppositely to redox; STC is less dense in the reduced form, while OmcA and MtrC are more dense in the reduced form. This result implies significant change in protein structure or folding upon reduction, in turn implying the importance of conformation change in catalysis of electron transfer. Disspation results show that both MtrC and OmcA are 'floppy' relative to more compact STC or cytochrome *c*.

Recent proteomic evidence suggests that both periplasmic and outer-membrane cytochromes are found in abundance in extracellular biofilm matrix, consistent with the idea that they are part of a functional extracellular electron transport network. Homology modeling suggests adaptations for interaction with metals, metal oxyanions, and minerals.

Evidence is mounting that the outer-membrane cytochromes are conformationally labile 'nanomachines' that direct electron transfer to solids.