

Reduction of aqueous U^{VI} by Fe^{II}: Effect of Ti^{IV} on the speciation of U^{IV}

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The solubility and mobility of uranium, a radionuclide contaminant at many sites, is highly dependent on its valence state and speciation. Transformation of aqueous U(VI) to U(IV) under the (bio-)reducing conditions found in many subsurface environments can decrease U solubility due to the precipitation of U(IV) dioxide (uraninite), a process that has been studied extensively for uranium remediation. However, recent evidence suggests that U(VI) reduction can produce complexed U(IV) species in the solid phase, such as U(IV)-phosphate precipitates or surface-adsorbed U(IV) atoms. The molecular speciation and the stability of non-uraninite U(IV) phases is poorly understood, even though this knowledge is essential in predicting uranium behavior at contaminated sites or in the design of nuclear waste repositories.

As part of understanding uranium transformations under iron reducing conditions, we examined the reduction of U(VI) by Fe(II) in the presence of Ti(IV). Ti(IV) is commonly present in natural magnetite and has been observed in the magnetic sediment fraction at the Hanford nuclear site. Titanium-doped magnetite nanoparticles of varying Ti content (Fe_{3-x}Ti_xO₄, 0 < x < 0.5) were synthesized and reacted with aqueous U(VI) in the presence and absence of bicarbonate. Analysis of the solids by U L_{III} edge x-ray absorption spectroscopy (XANES and EXAFS) indicated that Ti incorporation did not affect the ability of magnetite to reduce U(VI) to U(IV). Reactions with pure magnetite resulted in the formation of uraninite (dioxo-bridged UO₂). In contrast, reactions with Ti-doped magnetite resulted in a phase that lacked dioxo bridges between the U(IV) atoms. The latter phase was distinct from the U(IV) mineral brannerite (UTi₂O₆), suggesting that U(IV) was stabilized as a mononuclear surface complex. To understand the nature of Ti-complexed U(IV) species, U(VI) was co-precipitated with Fe(II) in the presence of carboxyl-functionalized microbeads and increasing amounts of Ti(IV). Analysis of the resulting solids indicated complete reduction of U(VI) to U(IV) and the formation of an inner-sphere U(IV)-Ti complex at Ti:U ratios as low as 1:1. The refined U(IV)-Ti distance of 3.43 Å suggests the formation of a bidentate corner-sharing complex between Ti octahedra and U(IV).

Active Carbon Cycling in Deep Subsurface Fracture Environments: Insights from RNA, Lipid and Isotopic Analyses

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This study undertook identifying 1) the metabolically active microbial communities of deep fracture water by comparison of cDNA (from RNA = active community) and DNA (total community) sequences; and 2) the C source of the active microbial community by comparing the compound specific $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of the PLFA and the $\Delta^{14}\text{C}$ of the DNA with the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of the CH₄, DIC, DOC and the $\delta^{13}\text{C}$ of the organic acids. In this talk we will present this data for a borehole located at 1.3 kmbls. in the Beatrix Au Mine.

Comparison of the cDNA and DNA results for both Archaea and Bacteria indicates that the composition of the active community differs from that of the total DNA community. *Methanobacterium* is part of the active community, though in low abundance compared to the Bacteria. *D. audaxviator* found in both DNA and cDNA nifH results indicating that N₂ is occurring *in situ*. cDNA library also yielded pmoA gene indicating that active methanotrophy is also occurring.

The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of the CH₄ is consistent with methanogenesis. The $\Delta^{14}\text{C}$ of the PLFA agrees with the $\Delta^{14}\text{C}$ of the DNA and along with the $\delta^{13}\text{C}$ of the PLFA and the $\Delta^{14}\text{C}$ of the CH₄ indicate that the active microbial community is obtaining most of its carbon from the CH₄.