

High-Resolution Mineralogical Characterization and Biogeochemical Modeling of Uranium Reduction Pathways at the NABIR Field-Research Center

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Abstract

The effectiveness and feasibility of bioremediation at the field scale cannot be fully assessed until the mechanisms of immobilization and U speciation in the solid matrix are resolved. However, characterization of the immobilized U and its valence states is extremely difficult, because microbially mediated mineral precipitates are generally nanometer (nm)-sized, poorly crystalline, or amorphous. We are developing combined field emission gun - scanning electron microscopy (FEG-SEM, at Indiana University) and FEG transmission electron microscopy (TEM, at Hopkins) to detect and isolate uranium containing phases; (2) method developments for TEM sample preparations and parallel electron energy loss spectroscopy (EELS) determination of uranium valence; and (3) to determine the speciation, fate, reactivity, valence states of immobilized uranium, using the state-of-the-art 300-kV, FEG-TEM.

We have obtained preliminary results on contaminated sediments from Area 3 at the Oak Ridge Field Research Center (FRC). TEM results show that the sediments contain numerous minerals, including quartz, mica/clay (muscovite and/or illite), rutile, ilmenite, zircon, and an Al-Sr-Ce-Ca phosphate mineral, none of which contain uranium above the EDS detection limit. Substantial U (up to ~2 wt.%) is, however, clearly associated with two materials: (1) the Fe oxyhydroxide and (2) clots of a chemically complex material that is likely a mixture of several nm-scale phases.

The Fe oxyhydroxide was identified as goethite from its polycrystalline SAED pattern and EDS analysis showing it to be very Fe-rich; the aggregate also displays one of several morphologies that are common for goethite. U is strongly sorbed to goethite in the FRC sediment, and the ubiquitous association with phosphorous suggests that complexes containing both U and P may play an important role in that sorption. Results from bulk analysis and SEM had previously demonstrated the association of U with Fe and thus suggested that U may be sorbed by Fe oxide or oxyhydroxide (Dr. Roh, image presented by David Watson). However, rigorous identification of the host minerals for U requires TEM results such as these involving imaging, electron diffraction, and spectroscopic analysis.

An even higher concentration of U occurs in the chemically complex material noted above. These "clots" are high in Fe but also contain C, O, Mg, Al, Si, P, S, Cl, K, Ca, Mn, and U. This chemical complexity strongly suggests that they consist of aggregates of carbonate, silicate, phosphate, and sulfate phases, and TEM images also suggest that they may be intergrowths of numerous exceedingly small nanoparticles. EELS and EFTEM studies should be able to resolve these various components and identify precisely where the uranium is in these complex materials.

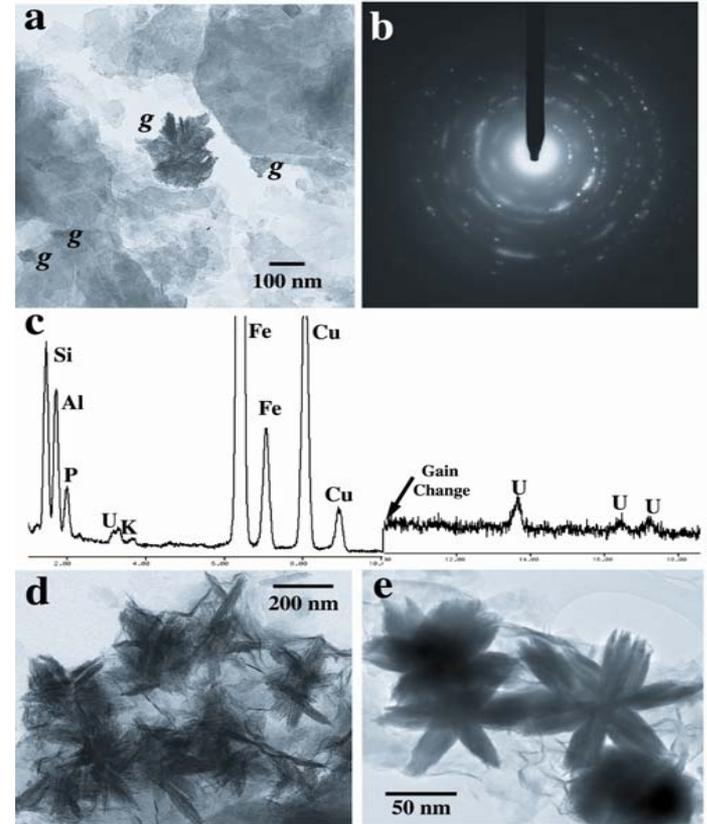
From the results, it is clear that the FEG-SEM and FEG-TEM can readily detect uranium in the FRC samples. The FEG-SEM allows a wide field of view of the samples and can detect U-rich aggregates as small as 20-30 nm. The FEG-TEM can then focus on these aggregates and use SAED, EDS, EFTEM, and PEELS techniques to determine the valence states, structures, and compositional data for these aggregates. This research will provide a crucial component for a complete understanding of the efficacy of uranium bioremediation.

Results from high resolution Transmission Electron Microscopy



Uranium isotope fractionation as another potential indicator of the mechanisms of uranium reduction

Experimental protocols for the precise measurement of ²³⁵U/²³⁸U by multiple-collector ICPMS (MC-ICPMS) have been developed at the ETH, Zürich. Using a Nu Instruments NuPlasma MC-ICPMS, we are able to resolve variations in ²³⁵U/²³⁸U at the 40 ppm level (2×10^{-4} ; 1 ppm = 1 part in 10^6) on sample sizes comprising 35 ng of uranium. Isotopic fractionation between ²³⁵U and ²³⁸U has been observed in low-temperature environments (Stirling *et al.*, Fall Meeting of the AGU, 2003). Variability in ²³⁵U/²³⁸U therefore offers the potential to differentiate biotic or abiotic uranium reductive mechanisms.



TEM results (a) Bright-field TEM image of a 300-nm goethite particle and three smaller particles ("g"), surrounded by clay. (b) Selected-area electron diffraction pattern from the central particle in part "a." (c) EDS spectrum from the central goethite particle in "a," showing that U is associated with goethite. (d) Aggregate consisting of both "wispy" and needle-shaped goethite. (e) Goethite "stars," which consist of three 60° penetration-twinned goethite needles.