

BEAMLINE

X23A2, X26A

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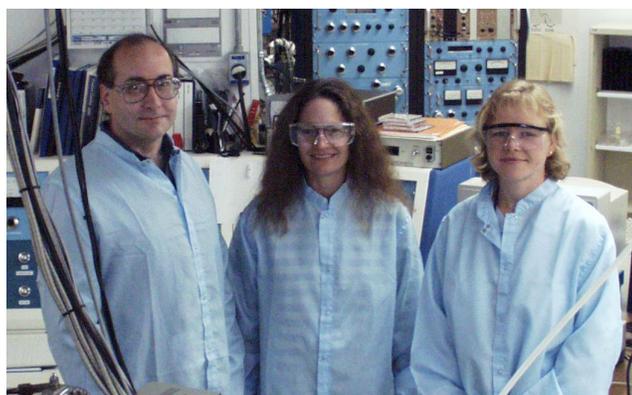
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Incorporation of Uranium with Iron Oxide Minerals

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The transport and biological availability of the toxic, radioactive element uranium (U) towards reduction to the less soluble U(IV) species may be limited by co-precipitation with Fe-oxide minerals. We examined the interaction dynamics between U(VI) and iron (Fe) oxides during crystallization by synthesizing Fe-oxide phases [0.5-5.4 mole %U/(U + Fe)] using U(VI) and Fe(III) solutions. Our studies show that U⁶⁺ is incorporated in Fe oxides as the uncommon uranate species (without axial O atoms) until saturation is reached whereby U(VI) forms crystalline U(IV)O₂²⁺ phases.



Author photo: Douglas B. Hunter, Martine C. Duff and Jessica Coughlin (left to right) in a laboratory at Westinghouse Savannah River Company's Savannah River Technology Center.

The geochemical speciation of uranium (U) influences its movement and biological availability in the environment. This information is often used to predict nuclear waste repository performance. In oxidized environments, U exists as the highly soluble uranyl [U(VI)O₂²⁺] species with two axial U=O double bonds at ~1.8 Å. In contaminated materials, solid phase U(VI) typically exists as the uranyl mineral, schoepite [UO₃·2H₂O]. Uranium(VI) can also exist as the less common uranate solid phase, which has at least three single U-O bonds and no axial double bonds. However, uranates have not been found in nature. The environmental mobility of U is influenced by many processes (**Figure 1D-E**). Another process that may influence U mobility is co-precipitation with other host minerals (**Figure 1F**). Uptake of U and other metals occurs during the formation of crystalline and amorphous Fe oxides but the local structure of U in these oxide materials has not been characterized.

Leaching of the synthetic U-Fe oxides typically removed most sorbed and solid phase U(VI) species leaving on average ~0.6 mol % U. X-ray diffraction and infrared spectroscopic studies (**Figure 2A-B**)

indicate that hematite (Fe₂O₃) formation is preferred over that of goethite (FeOOH) when the U level in the Fe-oxides exceeds 1 mol % U. Our studies with unleached U/Fe solids indicate a relationship between the mol % U in the Fe oxide, and the existence of the spectral features that can be assigned to uranyl species. These spectral features were undetectable in leached solids, suggesting solid phase and sorbed U(VI)O₂²⁺ species are extracted by leaching. Using uranium X-ray Absorption Fine Structure (XAFS) at NSLS Beamlines X23A2 and X26A, analyses of unleached solids containing <1 mol % U revealed that U(VI) exists with four O atoms at radial distances of 2.21 and 2.36 Å and Fe atoms at 3.19 Å (**Figure 2C**).

Due to the large size of UO₂²⁺ (~1.8 Å) relative to Fe³⁺ (0.65 Å), the UO₂²⁺ ion is unlikely to substitute for the Fe. Our results indicate that U⁶⁺ (~0.72-0.8 Å) is incorporated in the Fe oxides as uranate until a point of saturation is reached. Beyond this concentration, excess U precipitates as crystalline U(VI) phases resembling schoepite.

In summary, our findings indicate that the long-term association of U in the contaminated environment could result in structural incorporation of U in Fe oxide host phases. In nature, precipitation of pure U phases should occur at a kinetically faster rate than the structural incorporation of U into Fe oxides. Precipitation of U as pure mineral phases should be favored at high

dissolved U concentrations, whereas sorption and co-precipitation of U are most likely favored at lower U concentrations. In aged,

U-contaminated Fe-rich soils, uptake of U by Fe oxides may be significant since ~1 mol % U can be incorporated. The importance of

these mechanisms in U-contaminated materials has not been estimated.

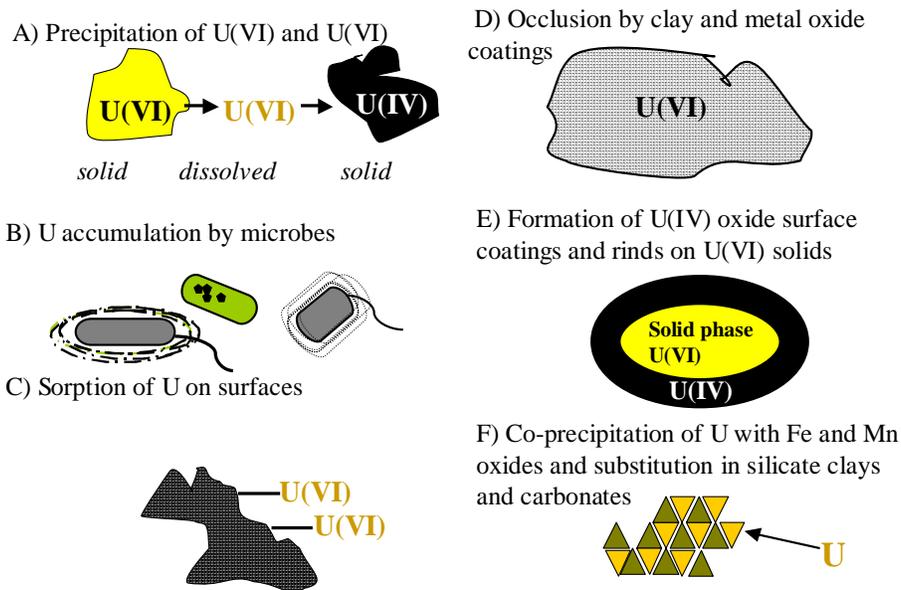


Figure 1. Mechanisms by which U mobility can be retarded in the surface and subsurface geologic environment. **A)** Precipitation of U(VI) and U(IV) phases. **B)** Microbial uptake (internal or external) of U. **C)** The sorption of U by organic or inorganic material such as humic acids and Fe oxides (respectively). **D)** Occlusion of U by clay and metal oxide coatings. **E)** Under reducing conditions, the formation of surface rinds of U(IV) on U(VI) minerals can also limit U mobility because U(IV) solids are less soluble. **F)** Co-precipitation of U with amorphous and crystalline host minerals may limit U mobility (adapted from Duff, Coughlin and Hunter, *Uranium Co-precipitation with Fe Oxide Minerals*. *Geochim. Cosmochim. Acta* 2002, **66**, 3533-3547.).

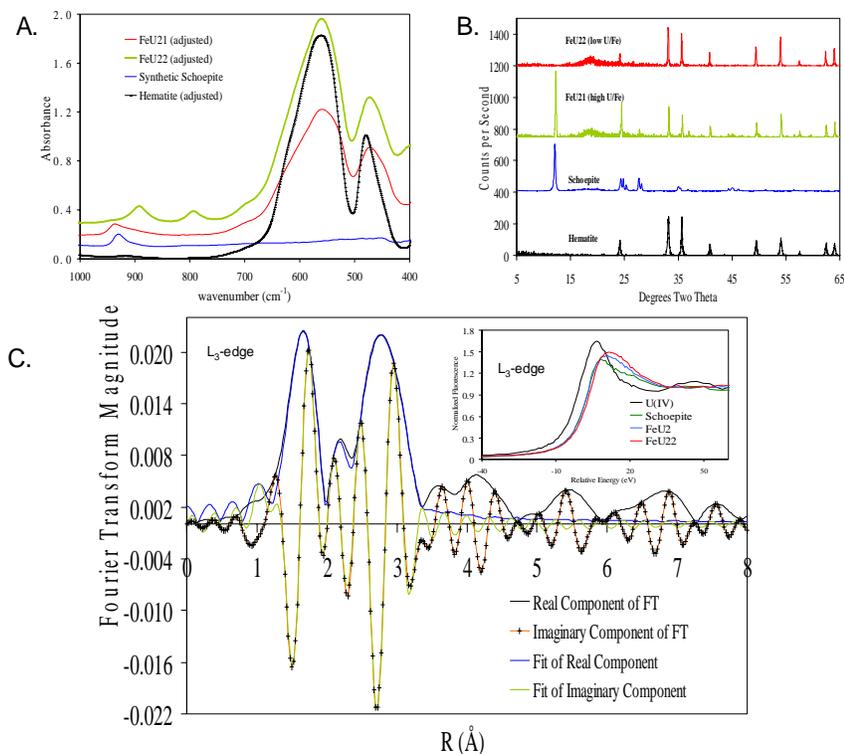


Figure 2. **(A)** Uranium XAFS spectra (L_3 edge) Fourier transform and fit data for the U-Fe oxide co-precipitate sample, FeU22. **Inset:** The U XANES spectra (L_3 edge) for U(IV)O₂, the U(VI) mineral meta-schoepite, the FeU2 and FeU22 U-Fe oxide co-precipitate samples. The XANES spectra for uranyl nitrate contained post-edge multiple scattering resonance (MSR) features typically observed for uranyl-containing solids (data not shown). **(B)** FTIR spectra for hematite, the synthetic U-Fe oxide co-precipitates (FeU21 and FeU22) and the synthetic mineral meta-schoepite. Three of the spectra for the samples are adjusted linearly so that their absorbance peaks are proportional to that of meta-schoepite and **(C)** Powder X-ray diffraction spectra for hematite, the synthetic U-Fe oxide co-precipitates and the synthetic (adapted from Duff, Coughlin and Hunter, 2002).