

Uranium (VI) Incorporation in Crystalline Iron Oxide Minerals

J. Coughlin, M. C. Duff, D. B. Hunter, and P. M. Bertsch (U. Georgia)

coug5204

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Introduction: The incorporation of uranium (U) into the structures of naturally occurring mineral phases may be one method by which the aqueous transport of U in the environment can be retarded. In oxidized systems, the most stable oxidation state of U is the U(VI) ion, which is known to have a strong affinity for Fe oxide minerals. In the dissolved form U(VI) exists as the uranyl $[\text{U(VI)O}_2^{2+}]$ species, which has two axial U=O bonds. Solid phase U(VI) can exist as the UO_2^{2+} species [as in the mineral schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$)] or as the less common uranate species, which has three or more single U-O bonds (for example, UO_6) and no axial bonds. In the absence of high levels of complexing ligands such as carbonate, dissolved U species have a high affinity for iron (Fe) oxide minerals including hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$).

Methods and Materials: To examine the dynamics of potential interactions between U and Fe oxides, we synthesized mg amounts of Fe-oxide phases using solutions of known amounts of dissolved U(VI) and Fe(III) ranging from 0.5 to 6 mole % U/Fe. We then applied techniques such as microprobe-X-ray absorption fine-structure (micro-XAFS) spectroscopy (at NSLS), wet chemical digestions, X-ray diffraction, thermogravimetric analyses, scanning electron microscopy, in addition to Fourier transform infrared, microprobe luminescence and Raman spectroscopy to examine the incorporation of U(VI) into the synthetic Fe-oxide minerals and we identified what crystalline Fe oxides were formed. Synthetic Fe oxides were acid digested before and after leaching with concentrated solutions of carbonate [to remove sorbed and solid phase U(VI)] and oxalate [to remove sorbed and solid phase U(VI), in addition to U associated with amorphous Fe oxides].

Results: Collectively, the micro-spectroscopic analyses of particles of unleached, Fe oxide solids indicate uranyl species predominate at high U(VI) loadings. XAFS studies with unleached solids at loadings below 1 mol % U indicate that U(VI) is incorporated octahedrally in the Fe oxides as uranate. The data show that the U-O bond is lengthened, which signifies that the U-O bond has more single bond character (i.e., U(VI) is present as uranate). Due to the size of UO_2^{2+} (~1.80 Å) relative to that of Fe^{3+} (0.65 Å), the UO_2^{2+} ion is not likely to be structurally incorporated into Fe oxides. The findings suggest U^{6+} (0.8 Å) can be incorporated into Fe oxides as a uranate species until a point of saturation is reached, and that beyond this excess precipitating U(VI) forms discrete crystalline uranyl phases that resemble schoepite. These results provide compelling evidence that U can be incorporated within Fe oxides.

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