

Uranium Reduction and Structural Incorporation into Iron Oxides: Competing Sequestration Pathways Under Reducing Conditions

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Introduction

- Uranium (U) contamination in groundwater is an environmental and health risk at U mining, milling, processing, manufacturing, and disposal sites.
- Active research on *in situ* sequestration methods is underway at a variety of locations (e.g., Hanford, WA and Rifle, CO).
- Reductive precipitation of U as U(IV) is one such *in situ* technique.
 - Potential for re-oxidation to U(VI) leads to the risk of re-mobilization of contamination.
- U can become incorporated into Fe oxides during Fe oxide transformation.
 - Ferrihydrite, $\text{Fe}(\text{OH})_3 \rightarrow$ goethite, FeOOH
 - Ferrihydrite, $\text{Fe}(\text{OH})_3 \rightarrow$ magnetite, Fe_3O_4
- Incorporated U may be resistant to re-oxidation (e.g., Stewart et al., 2009; Ilton et al., 2010).
 - Potential long-term sink for U
- What conditions favor U incorporation vs. reductive precipitation as U(IV)?

Objectives

- Compare U reduction and incorporation into Fe oxides across a range of U and Fe(II) loadings during Fe(II)-induced transformation of ferrihydrite.
- Evaluate these two U sequestration pathways in environmentally-relevant conditions ($< 100 \mu\text{M}$ aqueous U, $> 1 \text{ mM}$ Ca and carbonate).

Methods

- Abiotic batch incubations
 - pH 7, $1 \mu\text{M}$ - 0.5 mM uranyl (UO_2^{2+}), 4 mM CaCl_2 , 3.8 mM KHCO_3
 - Ferrihydrite slurry ($\sim 180 \text{ mg L}^{-1}$), transformed with the addition of 0.3 mM or 3 mM Fe(II)
- Synchrotron x-ray analysis
 - X-ray absorption spectroscopy (XANES, EXAFS)
 - X-ray powder diffraction

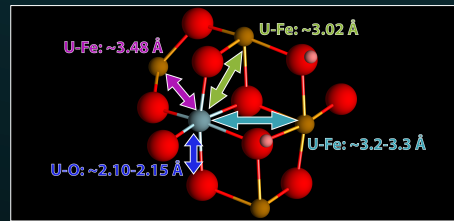


Figure 1. Conceptual model of U(VI/V) incorporation into goethite (FeOOH). Bond distances are based on XANES and EXAFS fits.

Results

- U-Fe distance at ~ 3.0 - 3.3 \AA suggests U incorporation into goethite (Figures 1 & 2).
- U is incorporated as U(VI) or U(V).
- At 0.3 mM Fe(II), ferrihydrite transformed to goethite; at 3 mM , a mixture of goethite and magnetite occurred (Figure 3).
- Uraninite precipitation was not observed at $\text{U} < 10 \mu\text{M}$ (Fig. 3); incorporation was observed.

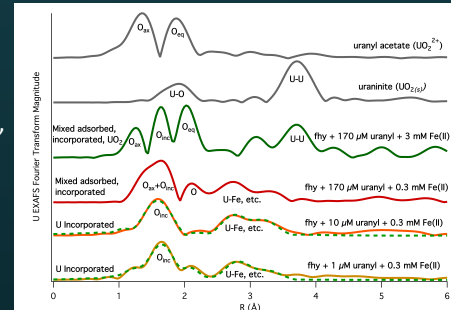


Figure 2. Uranium L_3 -edge EXAFS Fourier transform magnitude (solid lines) and example fits (dashed lines). A 30 mM KHCO_3 extraction removed adsorbed U from $1 \mu\text{M}$ and $10 \mu\text{M}$ samples, clarifying the spectra as U incorporated into goethite. The $170 \mu\text{M}$ spectra show mixtures of incorporated, adsorbed, and reduced U.

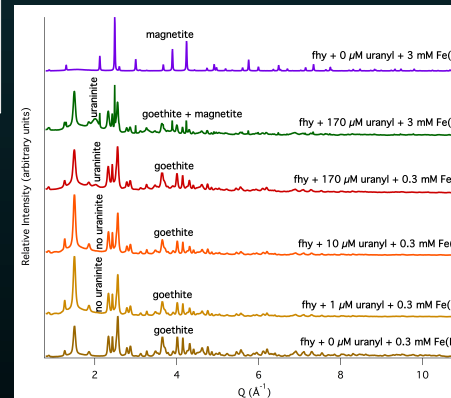


Figure 3. X-ray diffractograms of transformed ferrihydrite (fhy). Transformation was accomplished with Fe(II) in the presence uranyl (UO_2^{2+}), calcium, and carbonate. Uraninite precipitation occurred only at high UO_2^{2+} or Fe(II) loading.

Discussion

- U incorporation is a competitive sequestration pathway under reducing conditions.
 - Particularly when U and Fe loadings are low ($< 10 \mu\text{M}$ U, $300 \mu\text{M}$ Fe(II))
- U-Fe distance at ~ 3.0 - 3.3 \AA , U-O distance of ~ 2.10 - 2.15 \AA support the model developed by Nico et al. (2009) for U(VI/V) incorporation into goethite (Figures 1 & 2).
- U reduction becomes more prevalent at higher U ($> 0.1 \text{ mM}$) and 3 mM Fe(II) due to greater availability of U and/or reductant (Figure 3).

Conclusions

- U incorporation into Fe oxides can occur under field-relevant conditions.
- U is incorporated as U(VI,V) in octahedral sites in goethite.
- U incorporation into Fe oxides could represent a stable, long-term sink for U contamination.

Acknowledgements

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