Characterization of Uranium Species in Sediments under Iron and Sulfate Reducing Conditions Using Synchrotron-Based Techniques

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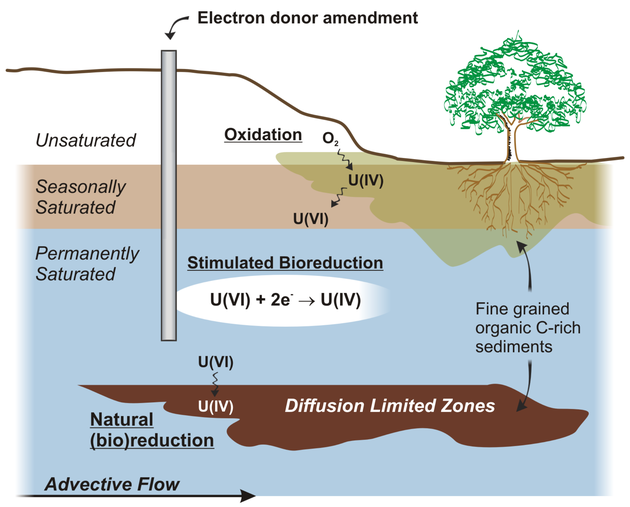
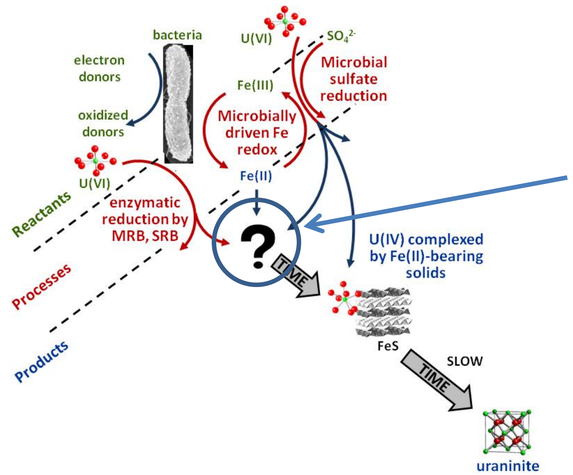
OBJECTIVES:

- To determine the chemical structure of uranium (IV) complexes found in subsurface sediments at Old Rifle, Colorado, a former uranium mill.
- To understand the biochemical process of uranium reduction under ironic and sulfuric reduction conditions.

INTRODUCTION:



- Large uranium plumes still persist in groundwater at legacy Department of Energy (DOE) due to past uranium extraction and processing.
- At Old Rifle, >34 million gallons of groundwater is contaminated with uranium.
- Such contamination is particularly problematic because it occurs at depth, is present in large volumes, and cannot be easily accessed for clean-up.
- One method of remediation being investigated is the bioreduction of soluble U(VI) to insoluble U(IV) complexes or uraninite (UO_2) through the *in-situ* stimulation of metal-reducing bacteria.
- Uranium complexes produced by metal-reducing bacteria can be characterized using X-ray absorption spectroscopy (XAS) and X-ray microscopy (XRM).



Previous data have shown other U(IV) complexes that are chemically and physically different from uraninite forming in the aquifer – U(IV) complexes eventually age into uraninite.

METHODS AND RESULTS:

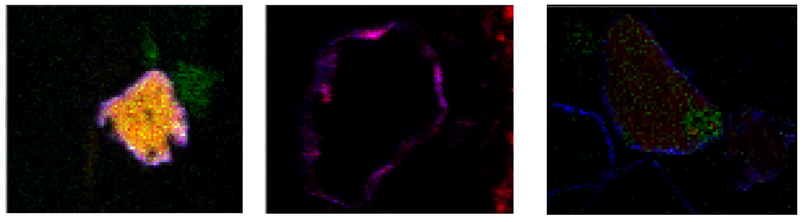
- Columns containing subsurface sediments from the Rifle test site were amended with acetate and uranium and flushed with groundwater for various duration.

Conditions of Sediment Columns

Column ID	Acetate (mM)	U(VI) (mM)	Reducing Stage	Length of Amendment (days)
2B	3	20	Iron	28 days
4A	12	20	Sulfate	14 days
4E	12	20	Sulfate	40 days

- During the initial days of amendment, iron reduction by metal-reducing bacteria is the dominant metabolic process.
- After ~30 days of amendment, shift to sulfate-reduction as the dominant terminal electron accepting process due to the growth of the sulfate-reducing bacteria population.

X-Ray Microscopy



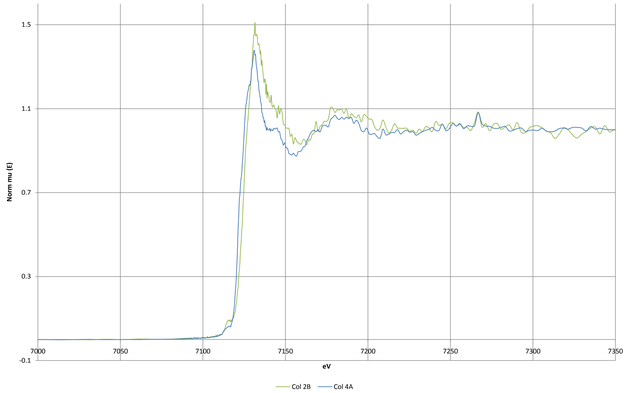
Fe = Red
U = Blue
S = Green

Col 2B **Col 4A** **Col 4E**

XRM images taken from sample sediment cross-section at energy level of 17220 eV.

- Uranium coat visible around Fe-S containing sediment in all three columns.

X-Ray Absorption Spectra



XAS was taken are the Fe-k edge at selected points on the sediment.

DISCUSSION:

- Uranium is shown to be highly associated with Fe-S coatings; uranium complexes bound to Fe-S structure
- Fe XANES of the sediment cross-section of column 2B and 4A show that the iron complexes contain Fe(II); XRM images show that the S is highly associated with Fe → possible iron complex is Fe(II)-S.
- As duration of sulfate reduction increases, sulfate concentration in sediment increases; however, uranium coating decreases → decrease in U(IV) production as sulfate-reducing bacteria dominate reducing process.

FURTHER STUDIES:

EXAFS on sediments need to be taken to distinguish the uranium complexes. Sediments will be amended at different time points during the transition between iron-reduction to sulfate-reduction phase.

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