Uranium speciation in FRC sediments before and after biostimulation

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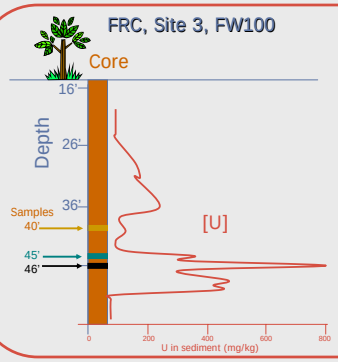
Introduction

Successful remediation strategies at the NABIR FRC and elsewhere will be based on detailed information, including the major U sources within the sediments throughout a contaminated volume containing a heterogeneous mixture of sediment phases. Because of the complexity of the FRC sediments with depth, the sources of U in the sediments will depended on the local chemical environment about the U atoms, which will vary with sample depth. X-ray absorption fine structure (XAFS) spectroscopy is ideally suited for these types of investigations, as measurements can be made on pristine sediments under anoxic conditions and at a variety of spatial scales. We have used XAFS spectroscopy to determine the valence state and chemical speciation of U at a variety of depths throughout the contaminated plume at site 3. Further, in concert with the "Criddle" FRC project; we have repeated these XAFS measurements on sediments from the same depth after biostimulation. The results provide unique information on the chemical speciation of U throughout the plume, both before and after biostimulation. We plan to correlate these results with other depth-dependent characterization results and contribute to a more complete understanding of the biogeochemical processes occurring as a results of biostimulation experiments described in the Criddle project.

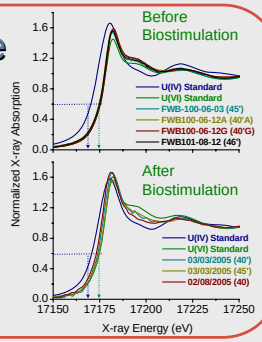


Uranium Sediments

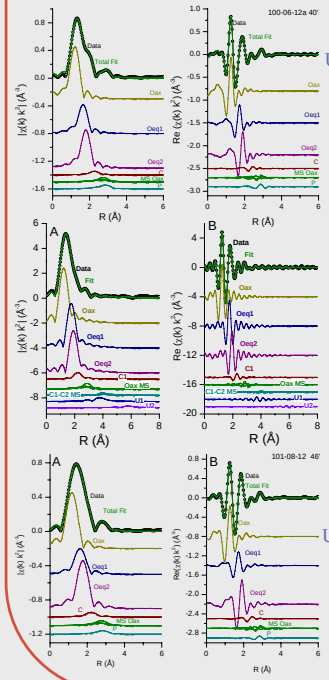
- The U profile shown below is for core FW103 which is close to FW100.
- Sediments from 40, 45, and 46 feet were collected from cores before biostimulation.
- Sediments were surged from 40 feet after one month cessation of biostimulation injections.
- Sediments were surged from 40 and 45 feet after weekly biostimulation injections.

XANES: Valence State

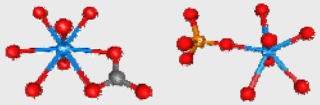
- The rise in the absorption edge for the sediment samples is at the energy value for U(VI) rather than the energy value for U(IV), as shown between the arrows.
- Before Biostimulation the U valence state is ~ 100% U(VI) at 40', 45', and 46'
- After Biostimulation the U valence state is (a) 80/20 U(VI)/U(IV) at 40' after weekly injections, (b) 90/10 U(VI)/U(IV) at 45' after weekly injections, and (c) 50/50 U(VI)/U(IV) after monthly cessation of injections.



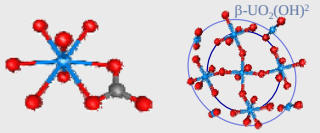
EXAFS spectra and model with depth before biostimulation



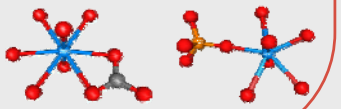
40 feet before biostimulation
Uranyl-Carbonates and Uranyl-Phosphates



45 feet before biostimulation
Uranyl-Carbonates and Uranyl-Oxides

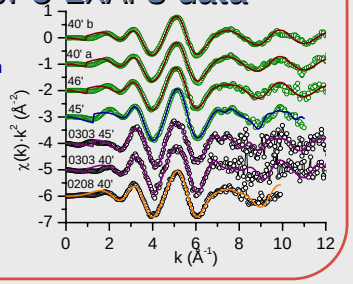


46 feet before biostimulation
Uranyl-Carbonates and Uranyl-Phosphates



Comparison of U EXAFS data

- Data before biostimulation from 40' and 46' are similar
- Data from before biostimulation from 45' shows a signal from a heavy atom (U) by the increased amplitude in the oscillations at high wave number.
- Data after weekly biostimulation (0303 45' and 40') shows Uranyl-P signal.
- Data after monthly cessation of injections (0208 40') is different from the other data.



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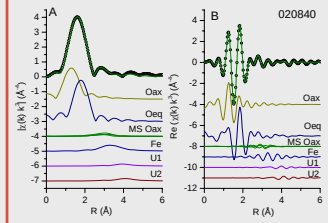
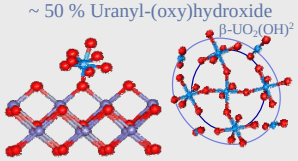
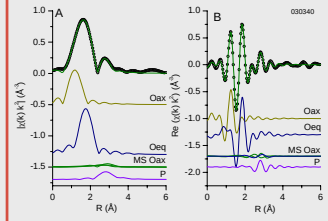
EXAFS spectra and model with depth after biostimulation

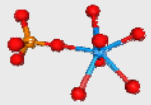


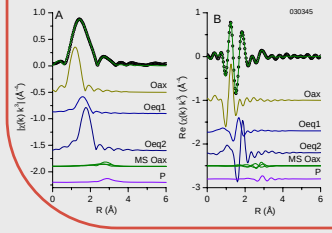
One month after cessation of biostimulation at 40 feet
~50 % U(IV)-Fe (oxy)hydroxide and ~ 50 % Uranyl-(oxy)hydroxide



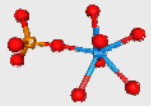


After weekly biostimulation at 40 feet
Uranyl Phosphates and ~ 10% U(IV)





After weekly biostimulation at 45 feet
Uranyl Phosphates and ~ 20% U(IV)



Before Biostimulation

- The analysis of the data from all three sampled depths showed U(VI) complexed by N- or C-containing ligands bound to uranyl in bidentate fashion (sharing two O atoms with the uranyl).
- The brownish (40-ft) and blackish (46-ft) sediments had some uranyl species complexed by P- or S-containing ligands bound in monodentate fashion (sharing one O atom with the uranyl).
- In contrast, the greenish-gray (45-ft) sediments contained 16 ± 11% of a β-UO2(OH)2-like phase, but no P- or S-containing ligands were detected.

After Biostimulation

- The analysis of the data from both samples (40-ft) and (45-ft) after weekly biosimultation indicates oxidized U(VI) bound to P- or S-containing ligands.
- The sample taken from the well after a one month period without biostimulation showed a 50/50 mixture of U(VI) and U(IV). The U(VI) is likely part of a uranyl oxide while the U(IV) is likely bound to Fe-oxides.

Conclusions

The U speciation within the sediments is affected by biostimulation. Before biostimulation, uranyl-carbonates are a major U species of solid phase materials sampled at all three depths. After biostimulation, no uranyl-carbonates are detected in the solid phase material. The process of weekly biostimulation seems to render the majority of the U within the sediments as U(VI) that is likely bound as uranyl phosphates. However, the speciation of U from the solids collected one month after the cessation of biostimulation is found to have a significant U(IV) component. This U(IV) is not in the form of uraninite. Rather, the U(IV) is likely sorbed to solid phase minerals consistent with 3*d* transition metal-(oxy)hydroxides. The U(VI) phase within these solids that was sampled one month after cessation of biostimulation is likely a uranyl-oxide.