Characterization of organic carbon in sediments from Old Rifle, CO, a former uranium mill

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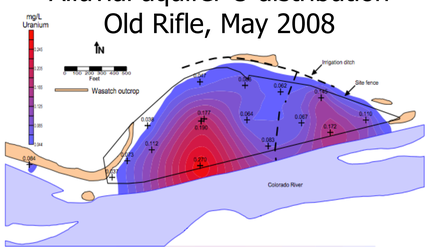
Background

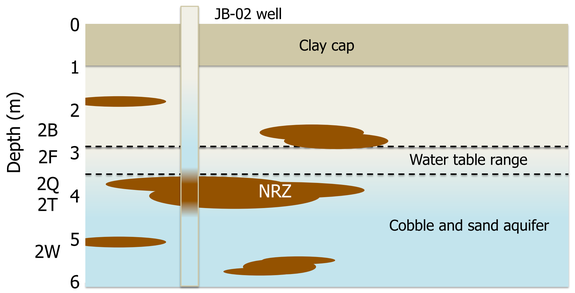
- The Old Rifle site in western CO covers an area of 52.6 m² and has over 129 million liters of uranium-contaminated groundwater
- Naturally reduced zones (NRZs) are thin pockets of silt-, clay-, and organic-rich sediments that contain reduced U
- U mobility depends on its valence state: oxidized U(VI) is highly soluble while reduced U(IV) precipitates easily



Oxidized		Reduced
U(VI) + 2e	↔	U(IV)
Soluble		Insoluble

Objective

- What makes the NRZs special for uranium reduction? Previous studies have shown a correlation between increased organic carbon (OC) and U(IV) within NRZs. U(IV) complexes eventually age into naturally occurring uraninite, also known as pitchblende
- The objective of this study is to better understand the differences in the OC content (not only concentration but also functional groups) in the NRZ of the JB-02 well compared to outside the NRZ



Methods

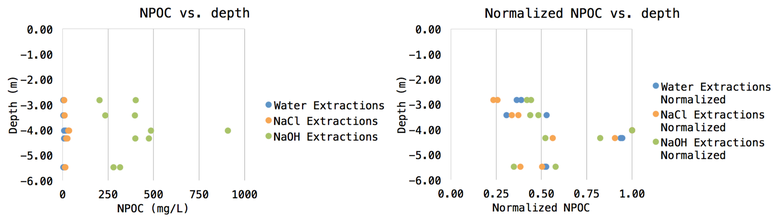
- Sediments were collected from the JB-02 well at Old Rifle and of these sediments, subsamples were taken at depths of 2.8 m (2B), 3.4 m (2F), 4.0 m (2Q), 4.3 m (2T), and 5.5 m (2W). 2Q lies completely within the NRZ, while 2T is at its lower edge
- These samples were analyzed through three chemical tests:
  1. Non-purgeable organic carbon (NPOC)
  2. Permanganate oxidizable carbon (POXC)
  3. X-ray absorption spectroscopy (XAS)

Extractions

- 2 g of sediment were extracted using three different solvents: 20 mL H_2O, 20 mL NaCl and 20 mL NaOH
- The extractions were analyzed for NPOC and by XAS

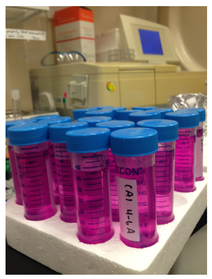
NPOC Results and Analysis

- NPOC gives a reliable estimate of OC content
- Highest NPOC concentration observed in NaOH extracts
- When normalized, 2Q had the highest amount of NPOC across all three extraction methods

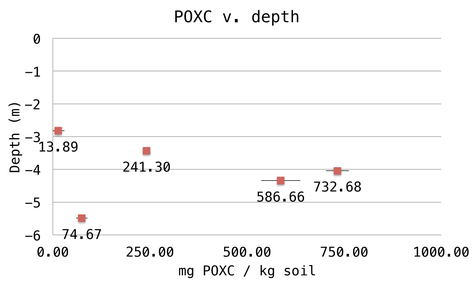


POXC Results and Analysis

- POXC serves as a proxy for biodegradable C. Past studies have shown that the reduction of U may be impacted by microbial processes
- Using an ultraviolet-visible (UV-Vis) spectrophotometer, absorbance measurements can be converted to POXC concentrations
- 2Q has the highest POXC concentrations, while 2T is not far behind
- Compared to the total C present at each depth, 2F actually has the highest percentage POXC, but 2Q and 2T have much higher total C present



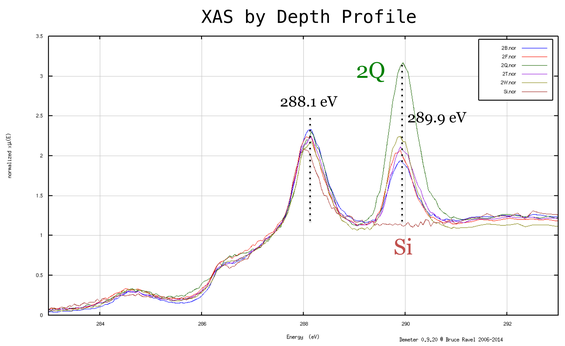
Using UV-Vis (background), absorbance at 550 nm is used to measure the amount of $KMnO_4$ still present within samples. This number is indicative of the amount of biodegradable C



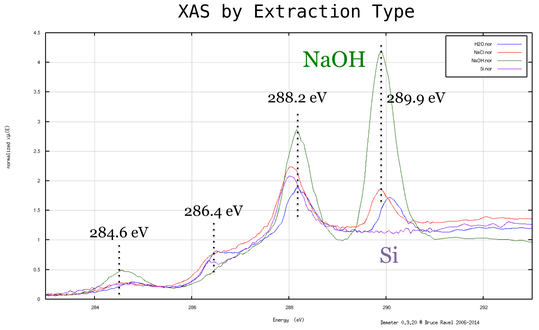
Depth	Name	% C	% POXC (mass POXC / mass total C)
2.8	2B	0.217	0.639
3.4	2F	0.322	7.492
4.0	2Q	1.674	4.376
4.3	2T	1.492	3.931
5.5	2W	0.236	3.159

XAS Results and Qualitative Analysis

All depths show weak peaks 288.1 eV and moderate to high peaks at 289.9 eV, with 2Q having a much higher intensity peak.



- NaOH extractions showed a weak peak at 284.6 eV
- Both NaCl and NaOH showed moderate peaks at 288.1-228.6 eV
- H_2O and NaCl showed moderate peaks at 289.9 eV, while NaOH showed a much more intense peak at 289.9 eV



Peak Assignments for C forms obtained from C (1s) NEXAFS			
Photon energy (eV)	Transition	C form	Functionality
284.3	1s-π*	C=C	Quinone
285-285.3	1s-π*	C=C	Unsaturated/aromatic; graphitic
286.4	1s-π*	C=O	Ketone, carbonyl substituted aromatic
287.1-287.3	1s-3p/σ* 1s-π*	C-H C-OH	Aliphatic Phenol-OH, aliphatic-OH
288-288.5	1s-3p/π*	C=O	Carboxyl; aldehyde
288.6	1s-p*	NC=O	Amide
288.9-289.2	1s-p*	C-C	Alkyl
289.2-289.3	1s-3pσ*	C-O	Alcohols; secondary alcohols in polysaccharides, hemicellulose and cellulose, propyl side chains and methoxyl carbons of lignin
289.9-290	1s-π*	$(O^-)_2C=O$	Carbonate
291.2-291.6	1s-σ* exciton	C-C	Extensive conjugated aromatic sheets

Conclusions

- NPOC confirms that extracts from 2Q and 2T have greater concentrations of OC
- POXC shows that 2Q and 2T have a greater amount of biodegradable C
- Sediments within the NRZ (2Q, 4.0 m) have higher amounts of carboxyl and/or aldehyde groups. However, a slight shift relative to the Si wafer and H_2O extracts may also indicate amides.
- There are significant peaks at 289.9 eV, indicating carbonate.
- NaCl extracts indicate the presence of phenols and/or aliphatic alcohols at 287.3 eV and alcohols at 289.2 eV.
- Both H_2O and NaCl extracts have a peak at 286.4 eV, indicating ketones and/or carbonyl substituted aromatics.

Further studies

- What functional groups are important for U reduction?
- How do these complexes form?
- What role do sulfur and iron play in these complexes?
- How can the XAS data be processed to better distinguish peaks?

Acknowledgements

Thank you John Bargar, Morris Jones, Sharon Bone, Ted Raab, Marco Keiluweit, and Michael Schaefer for your guidance and support in this research.
Thank you Scott Fendorf, Guanghao Li, Doug Turner and Juan Lezama Pacheco for lab use and instrument support.
And finally thank you STAR for making this opportunity possible.

This material is based upon work supported by the Chevron Corporation, Howard Hughes Medical Institute, the National Marine Sanctuary Foundation, National Science Foundation, and S.D. Bechtel, Jr. Foundation. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the funders.
The STAR program is administered by the Cal Poly Center for Excellence in STEM Education (CESAME) on behalf of the California State University.