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Biogeochemical cycling of organic carbon, uranium and sulfur in an alluvial aquifer

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Context

Uranium is a groundwater contaminant of concern in many DOE-LM and DOE-EM sites in the Colorado River Basin, USA. Under reducing conditions, the transformation of U(VI) to U(IV) results in its immobilization due to the relatively insoluble nature of U(IV). Natural reduction of uranium in organic-rich fine-grained sediments has been observed in several aquifers in the Colorado River basin, such as the U-contaminated Old Rifle and Naturita sites and is believed to be common at other similar sites. The release of uranium from these so-called Naturally Reduced Zones (NRZs) that are seasonally or perennially exposed to oxygenated groundwater is believed to help maintain the persistence of high dissolved U common to DOE sites in the Colorado River basin, presenting major challenges for site management and regulatory acceptance. Since microbial reduction of metals, sulfate, and other elements in NRZs is believed to be driven by enzymatic oxidation of organic carbon, the role of natural organic matter (NOM), the dominant electron donor in most subsurface environments, is central to this problem.

Objectives

1. Understand the biogeochemical linkages between C, S, and U in reduced sediments that help to control the redox status of the aquifer and the mobility of uranium.
2. Assess the structure and functionality of organic carbon in naturally reduced sediments and its association with other redox-sensitive elements (U, Fe, S)
3. Characterize the molecular- and nano-scale speciation of U in these sediments.
4. Develop process models for U(IV) product formation, transformation, and oxidation in aquifers.

Hypotheses

- U(IV) is reduced by NOM in low permeability zones:
- Reduced sediments have smaller particle size than non-reduced sediments
- When particle size decreases, C, U and S concentrations increase
- Organic carbon is co-located with Fe, S, U at the molecular scale

Site description

Old Rifle aquifer

- Former Uranium mill, with persistent U(VI) plume (up to 1.5 μmol/L).
- DOE's Integrated Field-Scale Research Challenge Site: several years of biostimulation at the aquifer scale.
- Presence of lenses of naturally reduced sediments.



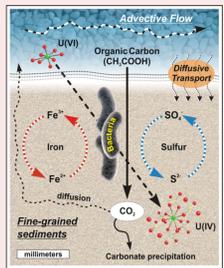
The Old Rifle aquifer, CO



Naturally Reduced Zones (NRZ)

- Documented in several sites in Western USA:
 - Rifle, CO (1,2)
 - Naturita, CO (3)
 - Midnite mine, WA (4)
- High levels of uranium, organic carbon, Fe and S reduced species
- May contain a significant fraction of the aquifer uranium inventory
- Different products of U(IV) observed:
 - Biogenic uraninite (2)
 - Monomeric forms of U(IV) (1)

- Zones of lower permeability (smaller particle size)
- Important role of organic carbon (OC) in their dynamics: electron donor, complexation sites

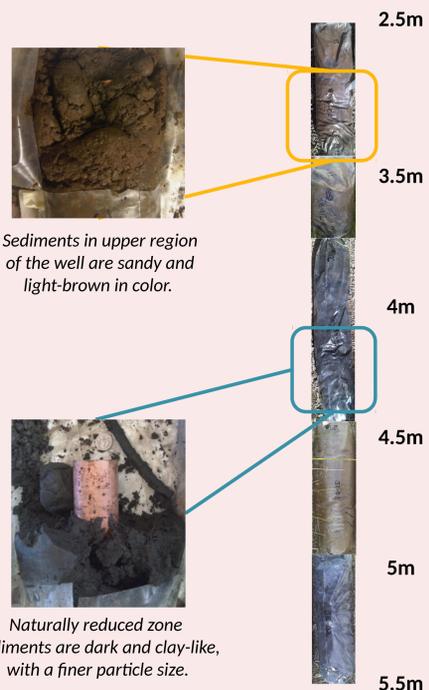


Biogeochemical cycling of C, Fe, S, U in fine-grained organic-rich sediments. In the presence of abundant indigenous OC and with diffusion-limitation conditions, microbial activity creates reducing conditions and reduces U, Fe and S.

Material and Methods

Well-core sampling

- 5 wells have been sampled at 0.25 ft depth intervals.
- Lenses of reduced sediment at different depths



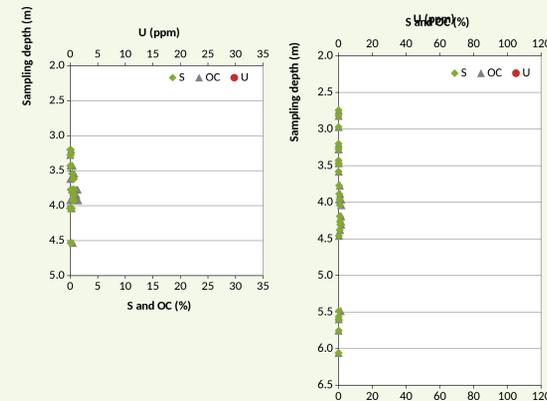
Sediments in upper region of the well are sandy and light-brown in color.

Naturally reduced zone sediments are dark and clay-like, with a finer particle size.

Sediments analysis

- Bulk composition:
 - XRF: S, U
 - Elemental analyzer: C, Organic C (OC)
- Bulk speciation of U, S, C: X-Ray Absorption Spectroscopy
- X-ray microscopy techniques:
 - OC, Fe, U: STXM
 - S, Fe, U: X-ray microprobe

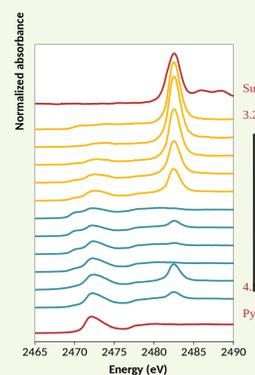
Bulk composition



Elemental concentrations in 2 adjacent wells from the Old Rifle aquifer

- Thin layer (50 cm) of sediments enriched in uranium
- Natural concentration of U up to 100 ppm, i.e. 200-fold higher than ambient
- Sediments enriched in U have high concentration of OC (>1%)
- Strong correlation between S, U, OC concentrations **at the macroscopic scale**

Bulk speciation

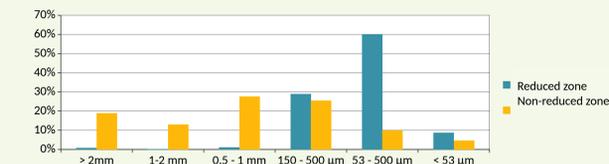


S K-edge XANES of natural sediments

- High variability of S speciation with depth:
 - Sediments in the upper region are oxidized (high sulfate peak at 2482 eV)
 - Sediments in lower regions present reduced forms of S (S⁻¹, S⁻²).
- In the reduced zone, S is mainly present as pyrite (peak at 2472 eV).
- Presence of monosulfide in top of reduced zone (peak at 2470 eV)

Results

Particle-size distribution



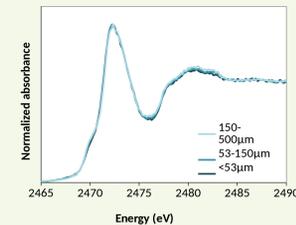
Particle size distribution of reduced and non-reduced sediments.

- ✓ Reduced sediments have a **smaller particle size** than non-reduced sediments

Fraction	U (ppm)	S (%)	OC (%)
Bulk	102	1.1	1.6
< 53 μm	78	1.5	1.2

Comparison between bulk and smallest particle size elemental composition

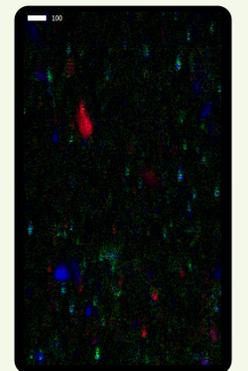
- ✗ OC, U and S are **not** mostly concentrated in the clay fraction of the sediments



S K-edge XANES of different size fractions of a naturally reduced sediment

- ✓ No change in S speciation in different particle size fractions

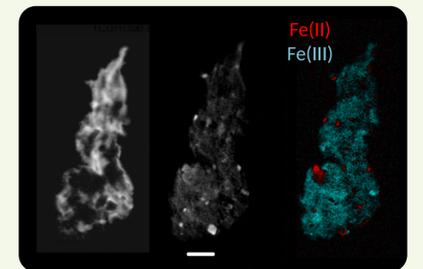
X-Ray Microscopy



S speciation: FeS is red, FeS₂ is green, S⁰ is blue.

Microprobe image of a reduced sediment (53-150 μm fraction)

- Variety of S species at the microscale
- Mainly pyrite grains (in agreement with bulk)



STXM analysis of a reduced particle (< 53 μm fraction) C map (left), Fe map (middle), Fe speciation map (right)

- Analysis of < 53 μm fraction: samples are too thick for good transmission signal at the C K-edge.
- Preliminary results on a grinded NRZ sample from another aquifer (Naturita site, CO) showed intra-particle heterogeneity of C speciation
- Natural U concentration is too low to be detected with field sediments
 - U-incubation experiments needed

Conclusions

- ✓ U is naturally concentrated in sediments in the Old Rifle aquifer, in locally reduced zones.
- ✓ Natural reduction of U occurs in sediments enriched in organic carbon
- ✓ Sulfur speciation shows the redox transition and seems independent of the particle size.
- ✓ Need other techniques to determine elemental association at the microscale

Upcoming work

- Determination of reduced U(IV) species using EXAFS.
- Detailed analysis of particle-size distribution of naturally reduced sediments.
- Analysis of organic carbon speciation in natural sediments using C K-edge NEXAFS and FTIR spectroscopy.
- Analysis of U-OC-S associations at the micro scale using STXM on incubated sediments (U-OC), X-ray microprobe (U-S), nano-SIMS (U-S) and FT-ICR-MS.

References

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