Monitoring Uranium Attenuation at a Uranium Recovery Site in Texas: Stable Isotope Ratios as Proxies for U(VI) Remediation

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Outline

• Introduction to roll-front U deposits, ISR sites, redox-reactions affecting U mobility

• Redox sensitive isotope systems – detecting remediation
  – U “stable” isotopes
  – Se stable isotopes
  – Mo stable isotopes
  – S stable isotopes

• Additional tracers of U migration - U activity ratios as indirect indicators of U removal

• Future work – promises and challenges
Significance of This Study

• What happens to U after restoration, in terms of fate and cycling?
• Is naturally occurring U reduction likely?
• How much information can we get from U concentration measurements? How do we know if reduction is occurring?
• Characterization of reactions affecting uranium mobility at postmining ISR sites
Uranium Roll-front

Groundwater flow crosses an oxidation/reduction interface in the sandstone

Primary reductant for U deposition – fault derived $\text{H}_2\text{S} +$ microbial activity
Reduction- Oxidation Gradient

Dahlkamp, 2010
Se, U and Mo Enrichment within the Roll-front System

Dahlkamp, 2010
In Situ Recovery by O$_2$ Injection

Oxidation during mining

Se(0)/Se(-II) (Ferroselite) $\rightarrow$ Se(IV)/Se(VI) (Selenate/Selenite)

U(IV) (Uraninite) $\rightarrow$ U(VI)

Mo(IV) (Molybdenite) $\rightarrow$ Mo(VI) (Molybdate)

S(-II) (Pyrite/Marcasite) $\rightarrow$ S(VI) (Sulfate)

~50% of world uranium mining is ISR operations
Reduction as Remediation

U(VI) → U(IV)

Uranyl Mobile

Uranous Immobile

Fe(III) → Fe(II)

Fe(II) - Minerals

Bacteria

CO₂ + H₂O

C, H₂

U(IV) → U(VI)

U(VI) → U(IV)
Reduction- Oxidation Gradient

Path of decreasing Eh as solution passes roll front:
- FeS$_2$ $\rightleftharpoons$ Fe(OH)$_3$
- Se $\rightleftharpoons$ SeO$_3^{2-}$
- V$_2$O$_4$ $\rightleftharpoons$ V$_4$O$_4^{2+}$

More reducing:
- Se reduction
- U reduction
- Mo reduction

Dahlkamp, 2010
Usual Kinetic Isotope Fractionation

- Isotopes: Atoms with different numbers of neutrons
- Reduction fractionates stable isotopes: Transition metals and lighter elements

- Lighter isotopes react faster
- Remaining reactant (e.g., Se(VI)) is enriched in heavier isotopes (e.g., $^{82}\text{Se}$)
Natural Abundance of Se Isotopes

\[ \delta^{82}\text{Se}(\text{‰}) = \left[ \frac{(^{82}\text{Se}/^{76}\text{Se})_{\text{Sample}}}{(^{82}\text{Se}/^{76}\text{Se})_{\text{NIST3149}}} - 1 \right] \times 1000 \]

Precision: \( \delta^{82/76}\text{Se}: <0.15\% \) (2σ)
U Isotope fractionation

- $^{238}\text{U}$ (99.27%), $^{235}\text{U}$ (0.72%), $^{234}\text{U}$ (0.005%)

- Effectively stable at environmental time scale

- Reduction induces isotopic fractionation

- For heavy elements (U, Hg), size and shape of the nucleus affect bonding

- $^{238}\text{U}$ is more reactive than $^{235}\text{U}$

$$\delta^{238}\text{U} = \left[ \frac{\left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{Sample}}}{\left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{CRM 112-A}}} - 1 \right] \times 1000\%$$

Precision: $\delta^{238}\text{U}$: $<0.1\%$ (2σ)
Definitions

\[ \delta^{82}\text{Se}(\%o) = \left[ \frac{(^{82}\text{Se}/^{76}\text{Se})_{\text{Sample}}}{(^{82}\text{Se}/^{76}\text{Se})_{\text{NIST3149}}} - 1 \right] \times 1000 \]

\[ \alpha = \frac{R_{\text{Product}}}{R_{\text{Reactant}}} \]

\[ \epsilon = 1000 \times (\alpha - 1) \]

\[ \epsilon \approx \delta_{\text{product}} - \delta_{\text{reactant}} \]
Isotope Ratios as Indicators of Reduction

- Concentrations sensitive to dilution and adsorption
- With progressive reduction, groundwater becomes enriched in:
  - $^{235}$U
  - $^{82}$Se
  - $^{98}$Mo
  - $^{34}$S

- U, Se, S isotope ratios can be used to detect reducing conditions in groundwater
- To determine the extent of remediation, the enrichment factor $\epsilon$ must be determined

![Graph showing fraction of U(VI) reduced vs. $\delta^{238}$U (‰)]
Rosita U Mine History and Sampling Locations

- **PAA1**: Production - 1990 to 1992, restoration - 2005-2008
- **PAA2**: Production - 1995 to 1999, restoration - 2001-2005
- **PAA4**: Un-mined

Basu et al., 2015 (ES&T)
Objectives

• Detection of U(VI) reduction and reducing environments from redox sensitive isotope systems (U, Se, Mo, S)
  – 32 groundwater samples from within, upgradient and downgradient of the ore zone

• $^{234}\text{U}/^{238}\text{U}$ signature of the groundwater

• Isotopic characterization of U ore
Results
Uranium Concentrations in Rosita Groundwater
Geochemistry of Rosita Groundwater

Basu et al., 2015 (ES&T)
U Isotopes in Rosita Groundwater

\[ \delta^{238}U (\%) \]

U in ore (μg/g)

\[ \ln(U(\text{VI}) \, \mu g/L) \]

\[ \delta^{238}U (\%) \]

\[ \varepsilon = 0.48\% \]

Basu et al., 2015 (ES&T)
Se Isotopes in Rosita Groundwater

Basu et al., 2015 (in prep)
Mo Isotopes in Rosita Groundwater

Reduction?
\[ \varepsilon = -1.2\% \pm 0.2\% \]

Dissolution/dilution
Mo Isotopes: Correlation with Eh?

![Graph showing correlation between Mo isotopes and Eh values with data points and contour lines indicating different isotope ratios and Eh ranges.](image)
Unmined Area at Rosita
## Unmined PAA4 Transects

<table>
<thead>
<tr>
<th></th>
<th>Western Transect</th>
<th>Mo (Total) (µg/L)</th>
<th>Eastern Transect</th>
<th>Mo (Total) (µg/L)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Se(VI) (µg/L)</td>
<td>U(VI) (µg/L)</td>
<td></td>
<td></td>
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<tr>
<td>MW 154</td>
<td>109</td>
<td>104</td>
<td>11</td>
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<td>BL 39</td>
<td>9</td>
<td>1474</td>
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<td>MW 149</td>
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<table>
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<tr>
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<th>Western Transect</th>
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<tr>
<td></td>
<td>δ\textsuperscript{82}Se</td>
<td>δ\textsuperscript{238}U</td>
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<tr>
<td>MW 154</td>
<td>2.19‰</td>
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<td>MW 149</td>
<td>0.48‰</td>
<td>0.79‰</td>
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**Se(VI) reducing**

**U(VI) Reducing**
S isotopes in Rosita Groundwater

U in ore (μg/g)

δ³⁴S (‰)

U(VI) in groundwater (mg/L)

Upgradient MW - PAA1
Ore Zone BL Well - PAA1
Ore Zone BL Well - PAA2
Upgradient MW - PAA2
Downgradient MW - PAA1
Ore Zone BL Well - PAA3
Downgradient MW - PAA3
Upgradient MW - PAA4
Ore Zone BL Well - PAA4
Downgradient MW - PAA4
Rosita U Ore

Ore Zone groundwater

U Ore

Basu et al., 2015 (ES&T)
Tracer for U Migration – U Activity Ratios

- In solid materials, $^{234}\text{U}/^{238}\text{U}$ should be in secular equilibrium (=1)
- When $^{234}\text{Th}$ is ejected in the surrounding medium, groundwater can acquire high $^{234}\text{U}/^{238}\text{U}$
- $^{234}\text{U}/^{238}\text{U}$ in solid can become less than 1
U Activity Ratios at Rosita

![Graph showing U activity ratios](image)

Basu et al., 2015 (ES&T)
U Activity Ratios at Rosita

- Ore Zone groundwater has very low U activity ratios (~0.75)
- Downgradient wells have higher U activity ratios nearing the secular equilibrium value 1
- This pattern suggests natural loss of U (U removal) between ore zone and downgradient wells

<table>
<thead>
<tr>
<th></th>
<th>Upgradient</th>
<th>Ore Zone</th>
<th>Downgradient</th>
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<tbody>
<tr>
<td>PAA 3</td>
<td>MW 129</td>
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<td>MW 75</td>
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<td>1.22</td>
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<td>0.94</td>
<td>0.77</td>
<td>0.8</td>
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</table>
Conclusions

• $^{238}\text{U}/^{235}\text{U}$ in Rosita groundwater indicate U(VI) reduction
• $^{82}\text{Se}/^{76}\text{Se}$ are indicators of Se reduction and possibly the onset of U(VI) reduction
• $^{98}\text{Mo}/^{95}\text{Mo}$ may suggest strong reducing environments capable of efficient U(VI) reduction
• U activity ratios ($^{234}\text{U}/^{238}\text{U}$) are effective tracers for ore zone U – also suggest U removal downgradient of the ore zone
• S isotopes are additional tracers for ore zone groundwater
Future Work and Remaining Challenges

- Determination of the size of isotopic fractionation for the relevant reductants at each site
- Determination the reduction kinetics
- Characterization the U ore – XANES, EXAFS (ongoing, presence of U-Ti species suggest an alternative pathway for U immobilization and ore genesis)
- Characterization of the distribution of the reductants/reducing capacity (ongoing)
- Rate of reduction and the magnitude of fractionation can be incorporated in the reactive transport models to accurately predict the fate of U at ISR sites
- Need to incorporate the effects of non-redox processes (dispersion, sorption-desorption, diffusion limitation) on isotopic fractionation
Isotopic and Geochemical Tracers for U(VI) Reduction and U Mobility at an In Situ Recovery U Mine

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ABSTRACT: In situ recovery (ISR) uranium (U) mining mobilizes U in its oxidized hexavalent form (U(VI)) for effective dissolution of U from the roll-front U deposit. Postmining natural attenuation of residual U(VI) at ISR mines is a potential remediation strategy. Detection and monitoring of naturally occurring radionuclide concentrations are important for successful implementation of this remediation strategy. We used the isotopic tracers 3H/U (3H/3H0), 13C/12C, 18O/16O activity ratios, and 234U/238U (3H), and geochemical measurements of U ore and groundwater collected from SU wells located within the upgradient and downgradient of a roll-front U deposit to detect U(VI) reduction and U mobility at an ISR mining site at Rainton, TX, USA. The 3H/3H0 in Rainton groundwater varies from 0.678 ± 0.004 to 0.699 ± 0.004, with a 3H activity indicative of naturally occurring reducing environments conducive to U(VI) reduction. Additionally, characteristic 13C/12C activity ratio of U(VI) in groundwater and U(VI) in groundwater from upgradient wells. The concurrent decrease in U(VI) concentration and 3H/3H0 with an e of 0.40±0.03 to 0.49±0.03 in Rainton and other similar ISR mining sites supports the use of U isotope-based detection of natural attenuation of U(VI) at Rainton and other similar ISR mining sites.