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

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Outline

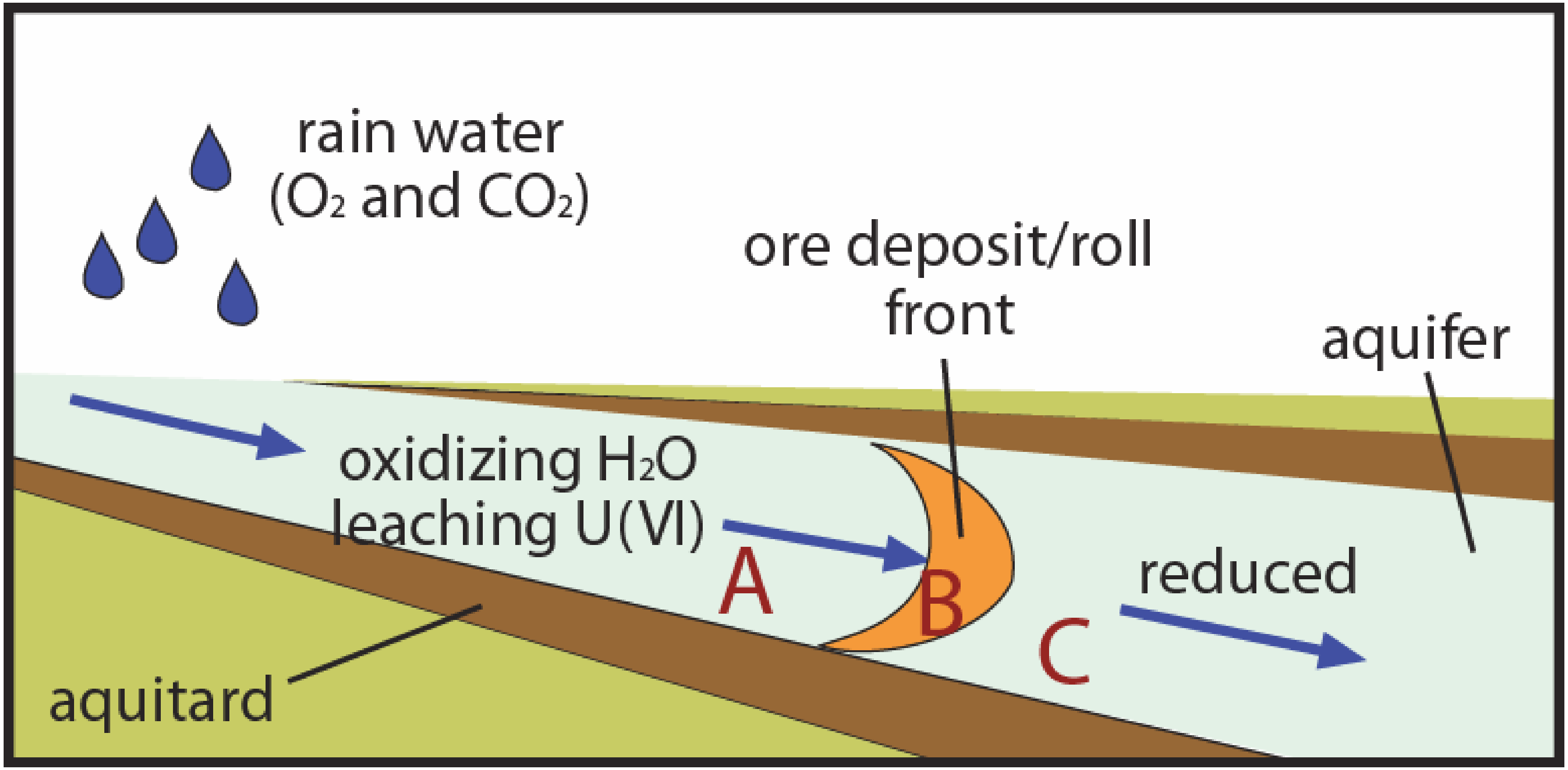
- Introduction to roll-front U deposits, ISR sites, redox-reactions affecting U mobility
- Redox sensitive isotope systems – detecting remediation
  - U “stable” isotopes
  - Se stable isotopes
  - Mo stable isotopes
  - S stable isotopes
- Additional tracers of U migration - U activity ratios as indirect 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

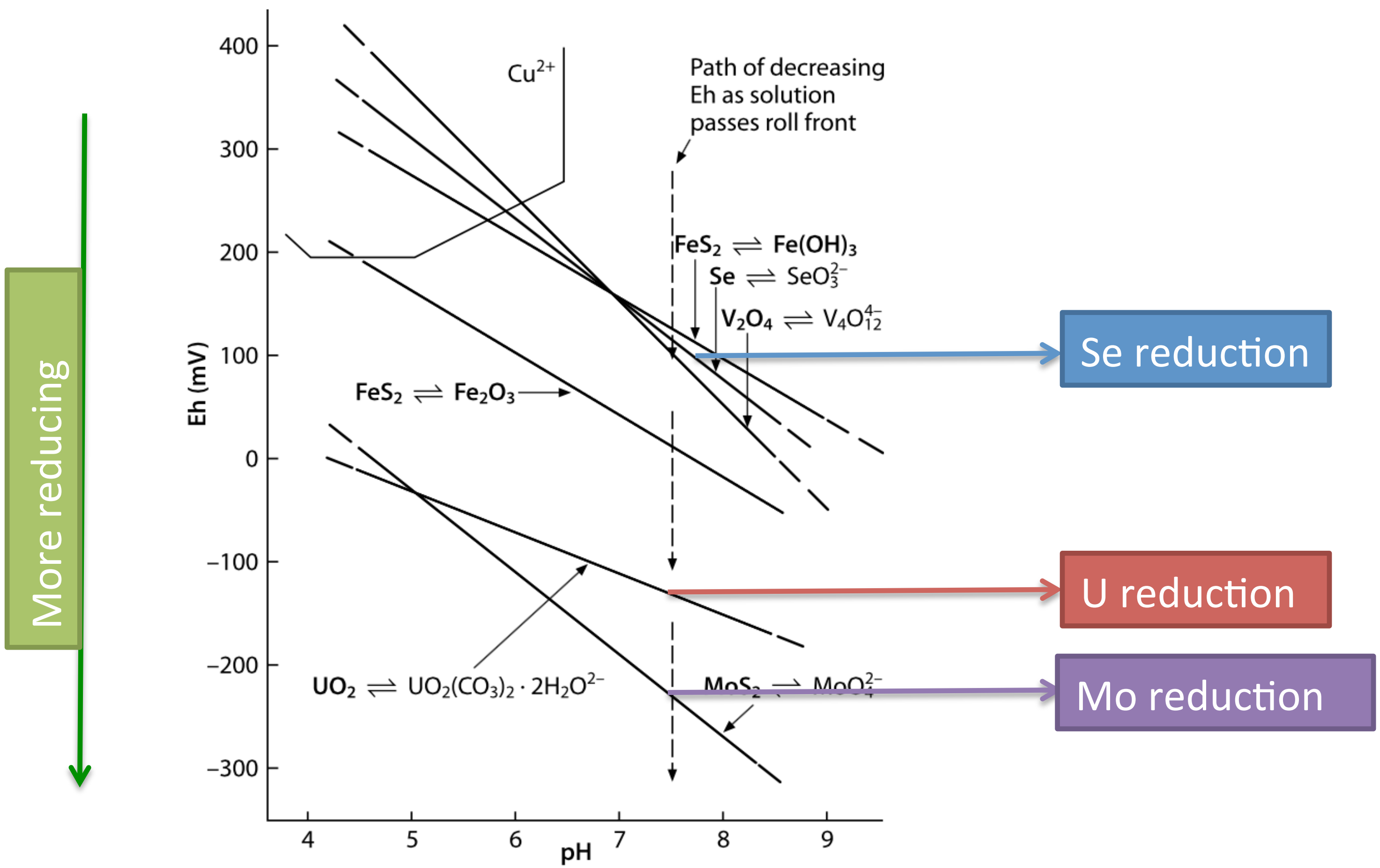
Uranium Roll-front

Groundwater flow crosses an oxidation/reduction interface in the sandstone



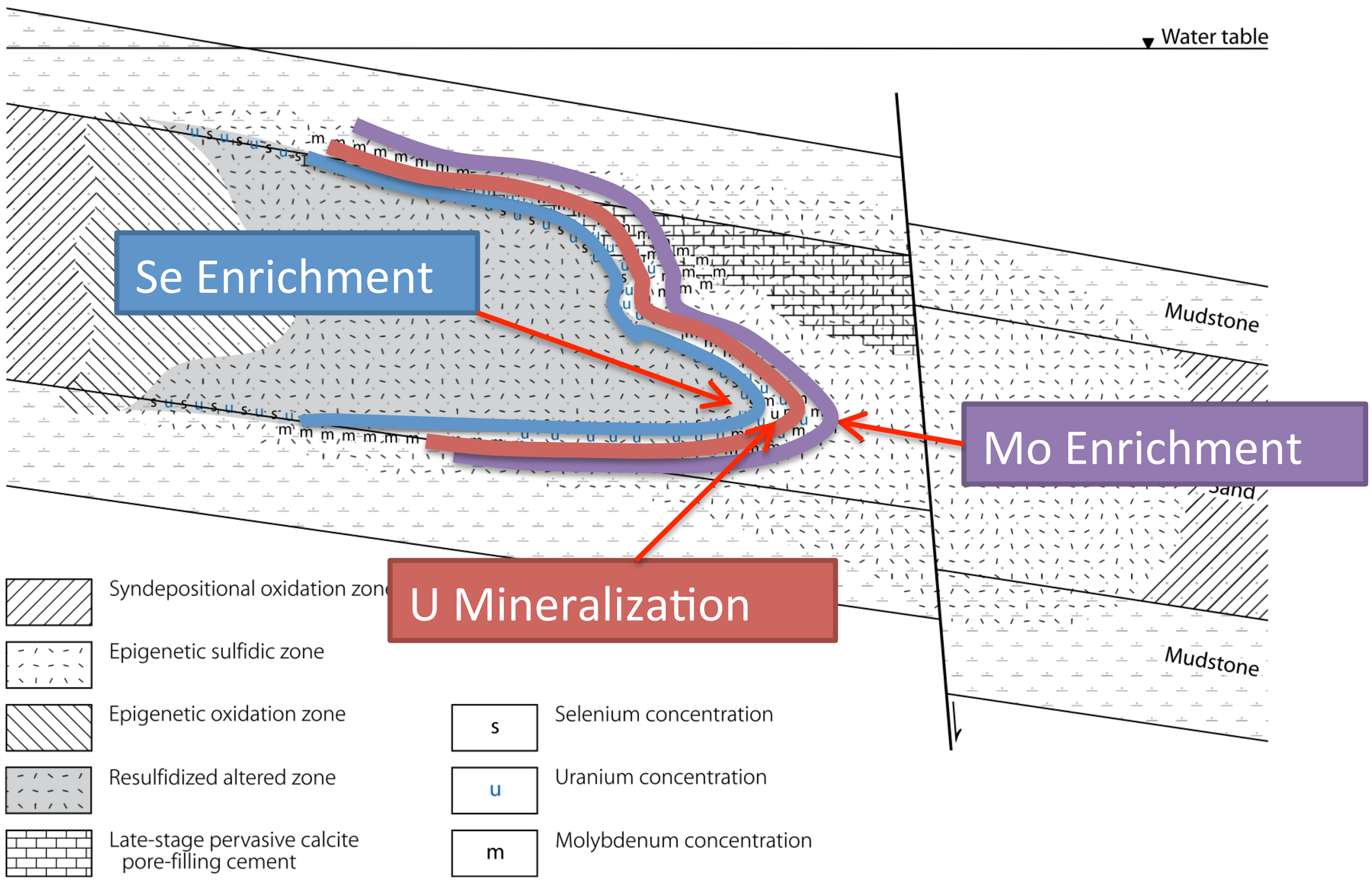
Primary reductant for U deposition – fault derived H_2S + microbial activity

Reduction- Oxidation Gradient



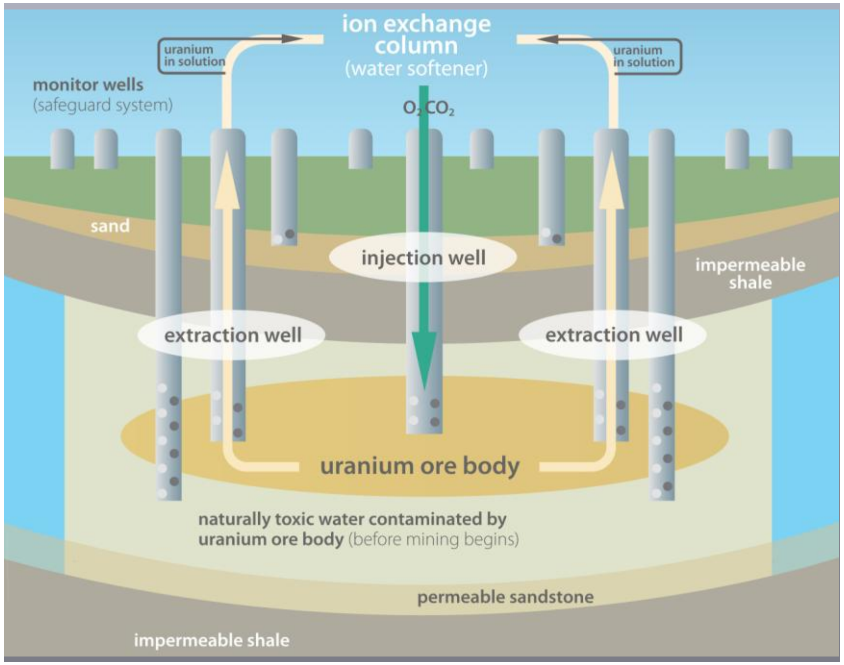
Dahlkamp, 2010

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) → Se(IV)/Se(VI) (Selenate/ Selenite)

U(IV) (Uraninite) → U(VI)

Mo(IV) (Molybdenite) → Mo(VI) (Molybdate)

S(-II) (Pyrite/Marcasite) → S(VI) (Sulfate)

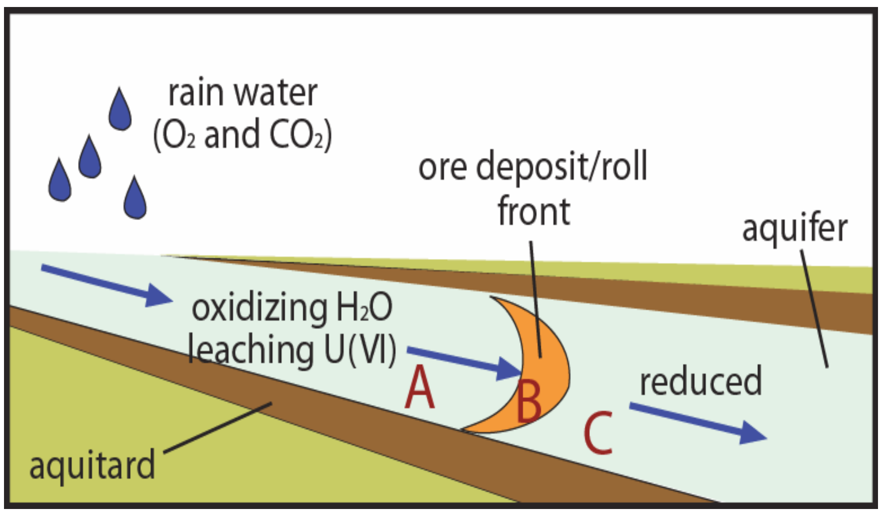
~50% of world uranium mining is ISR operations

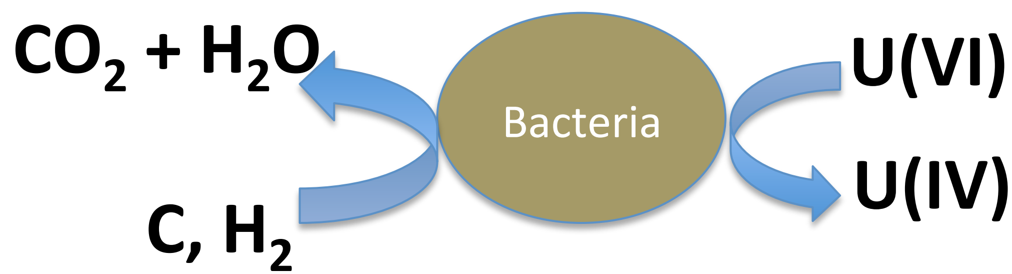
Reduction as Remediation

$U(VI) \longrightarrow U(IV)$

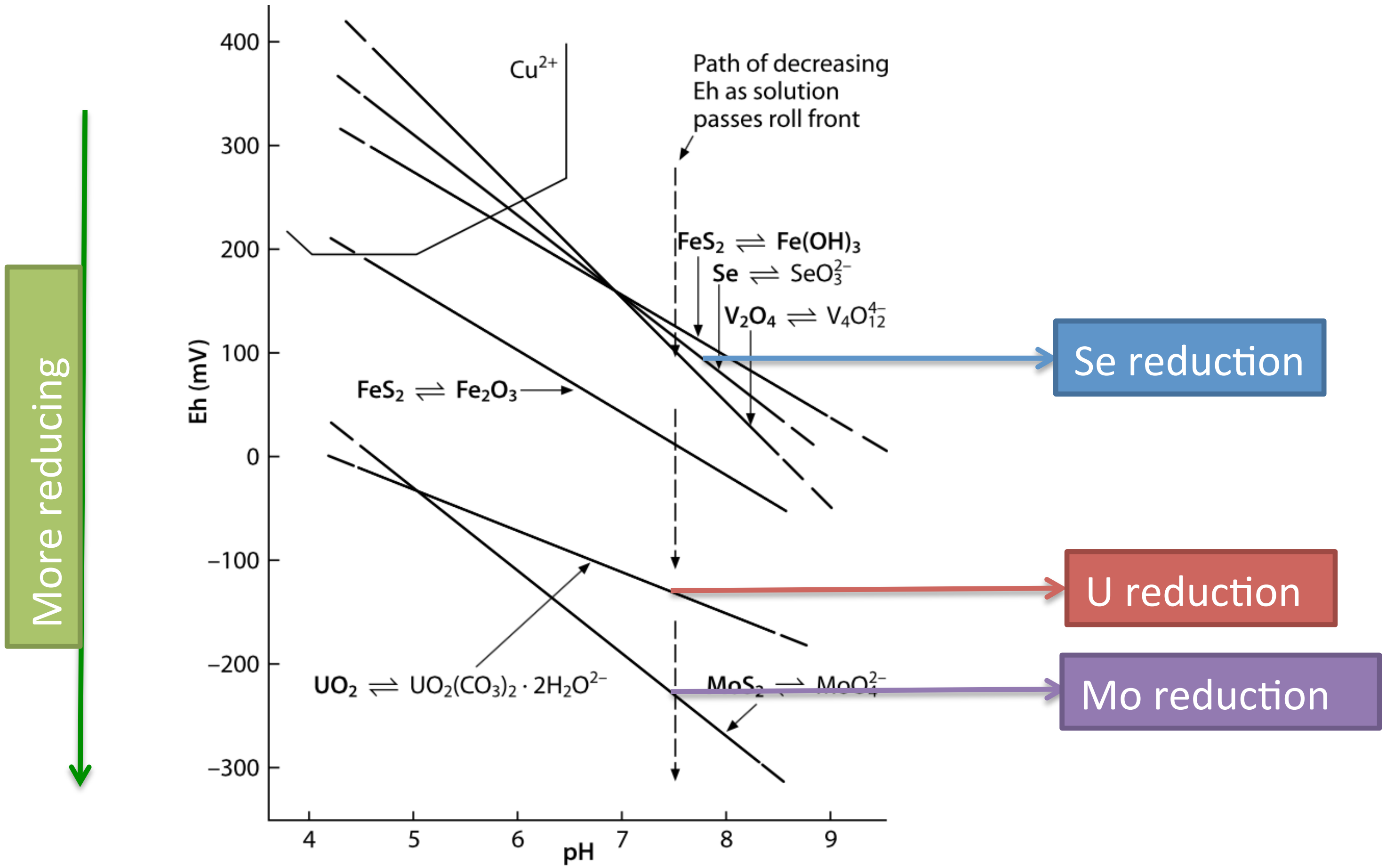
Uranyl
Mobile

Uranous
Immobile





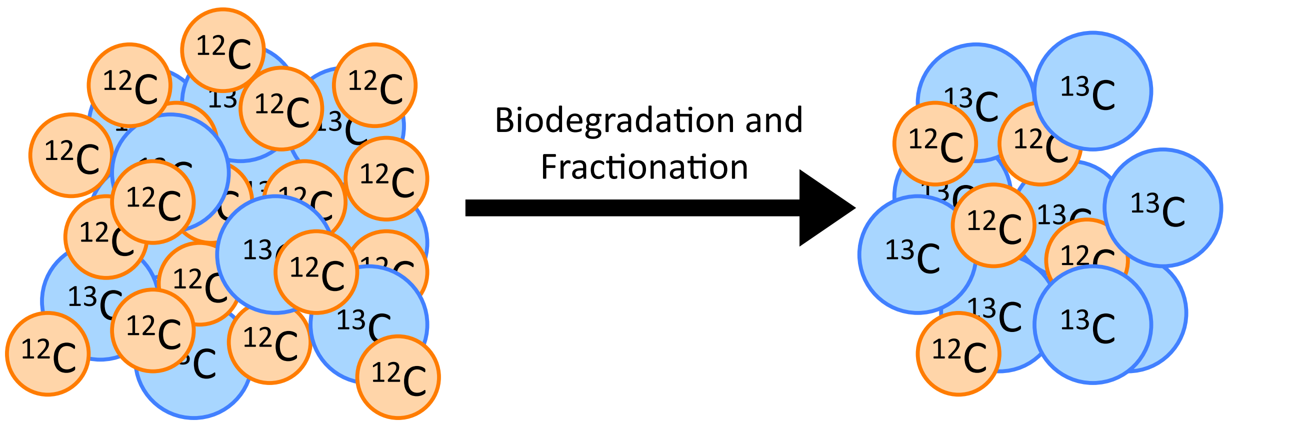
Reduction- Oxidation Gradient



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}Se)

Natural Abundance of Se Isotopes

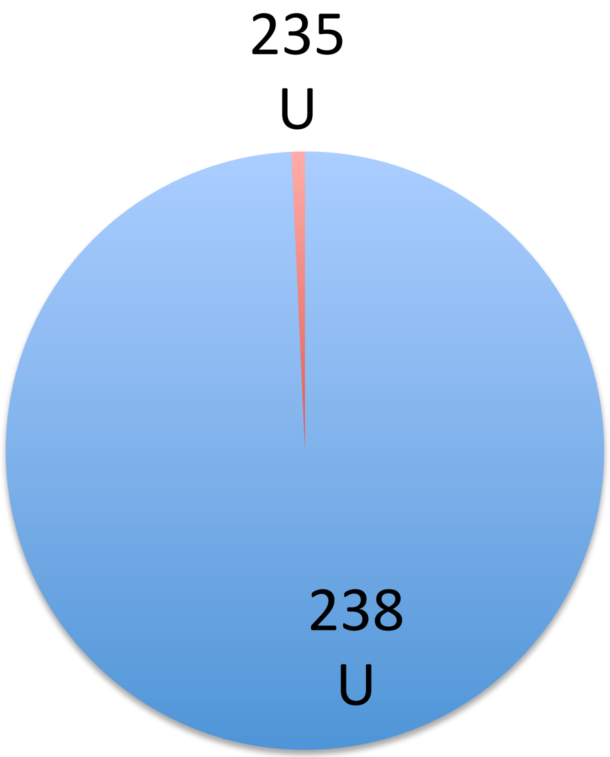
0.889 **9.366** 7.635 23.772 49.607 **8.731**

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

Precision: $\delta^{82/76}$Se: <0.15‰ (2σ)

U Isotope fractionation

- ^{238}U (99.27%), ^{235}U (0.72%), ^{234}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}U is more reactive than ^{235}U



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

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

Definitions

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

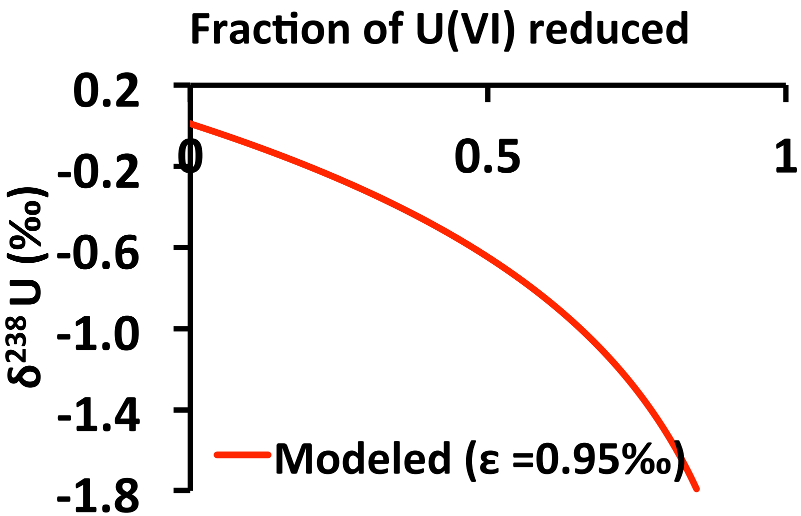
$$\alpha = \frac{\mathrm{R}_{\mathrm{Product}}}{\mathrm{R}_{\mathrm{Reactant}}}$$

$$\varepsilon = 1000 * (\alpha - 1)$$

$$\varepsilon \approx \delta_{\mathrm{product}} - \delta_{\mathrm{reactant}}$$

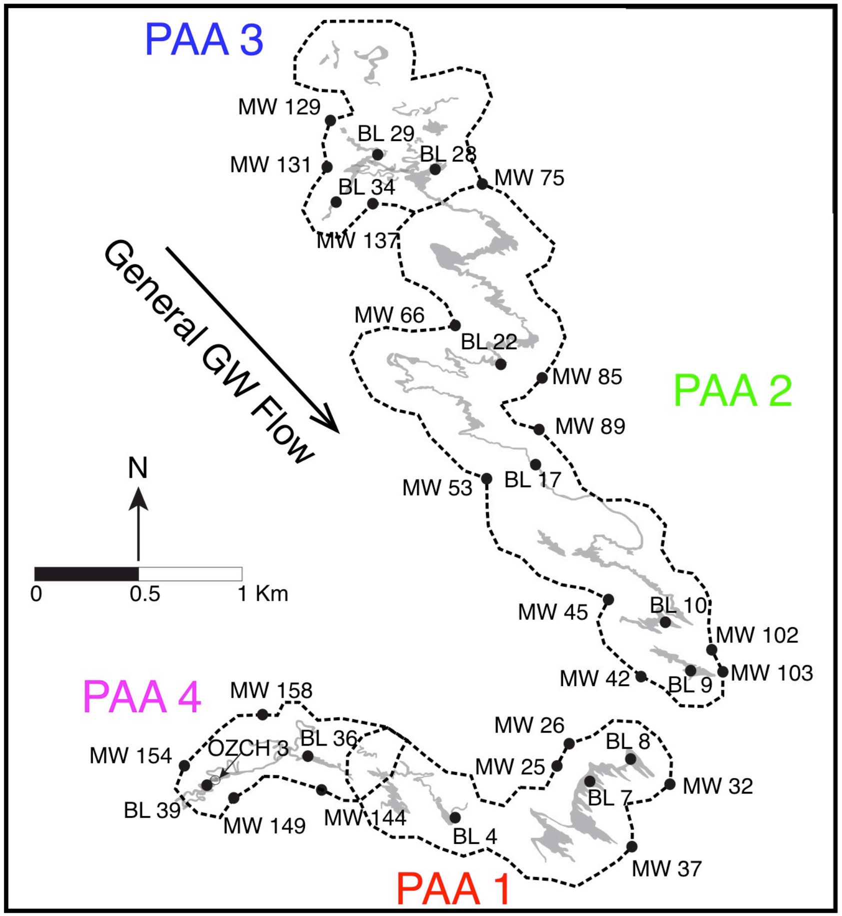
Isotope Ratios as Indicators of Reduction

- Concentrations sensitive to dilution and adsorption
- With progressive reduction, groundwater becomes
  - enriched in ^{235}U
  - enriched in ^{82}Se
  - enriched in ^{98}Mo
  - enriched in ^{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 ε must be determined

Rosita U Mine History and Sampling Locations



Basu et al., 2015 (ES&T)

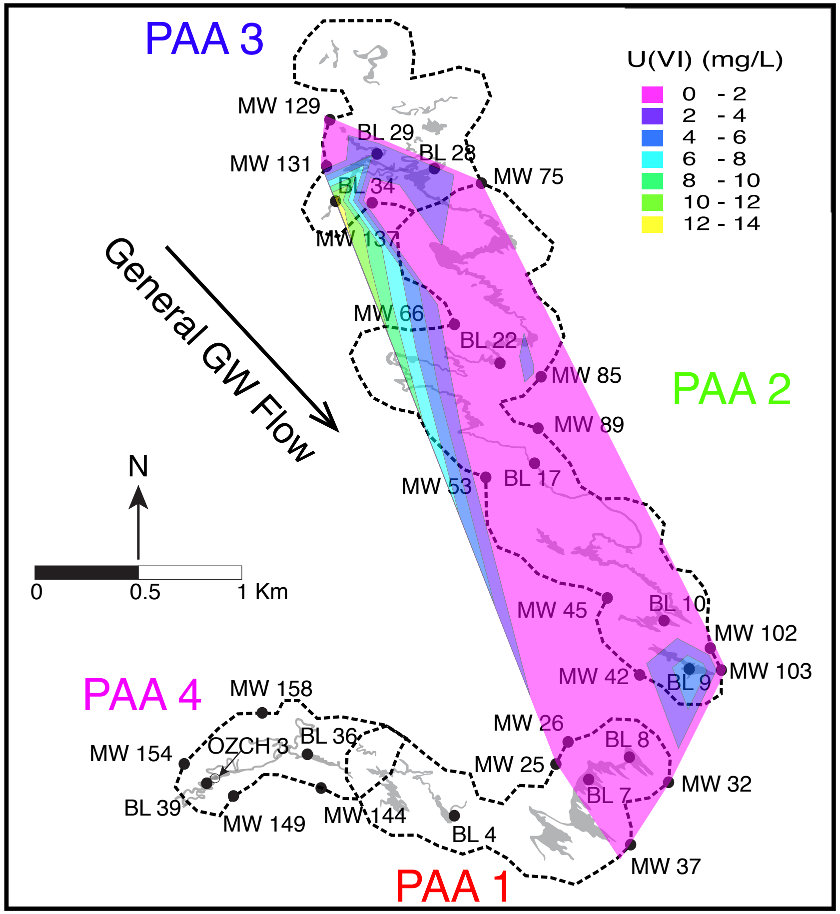
- PAA1: Production - 1990 to 1992, restoration - 2005-2008
- PAA2: Production - 1995 to 1999, restoration - 2001-2005
- PAA3: Production – 1999 to 1997, 2008, 2012
- PAA4: Un-mined

Objectives

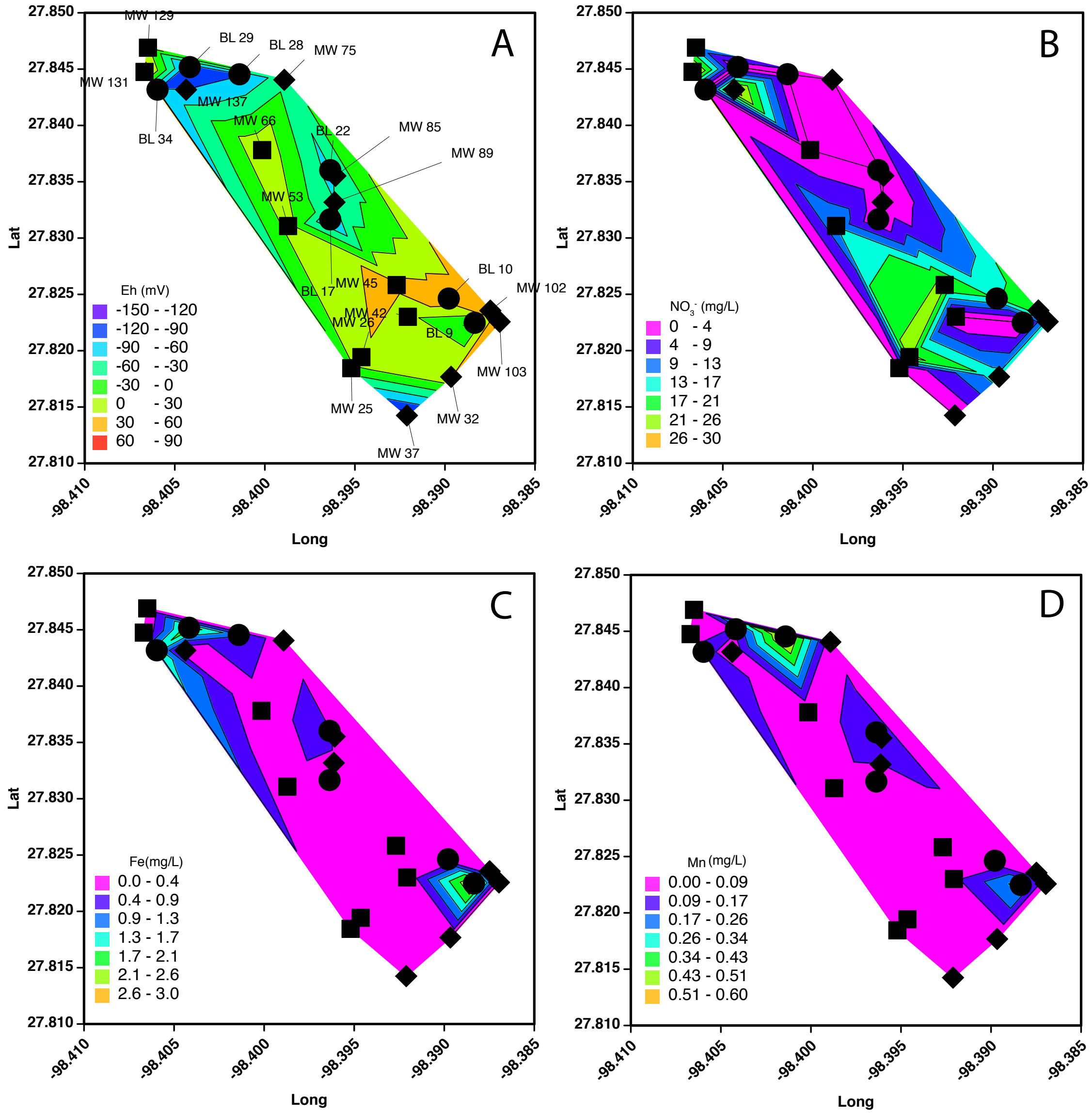
- Detection of U(VI) reduction and reducing environments from redox sensitive isotope systems (U, Se, Mo, S)
  - 32 groundwater samples from within, upgradient and downgradient of the ore zone
- $^{234}U/^{238}U$ signature of the groundwater
- Isotopic characterization of U ore

Results

Uranium Concentrations in Rosita Groundwater

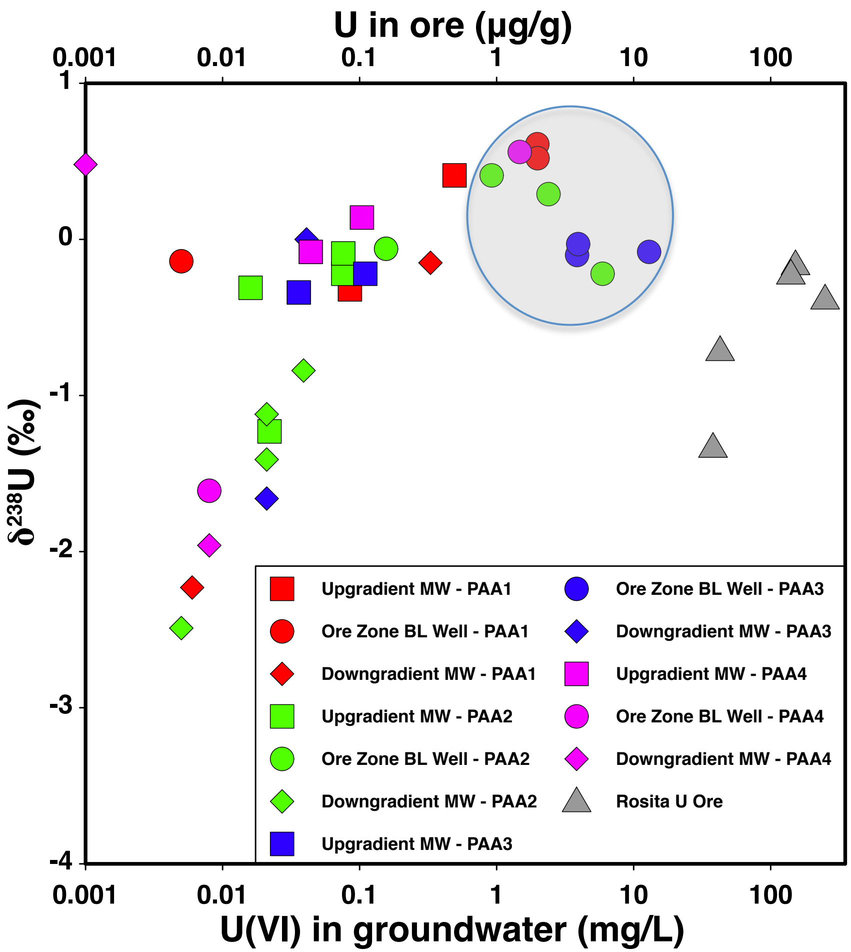


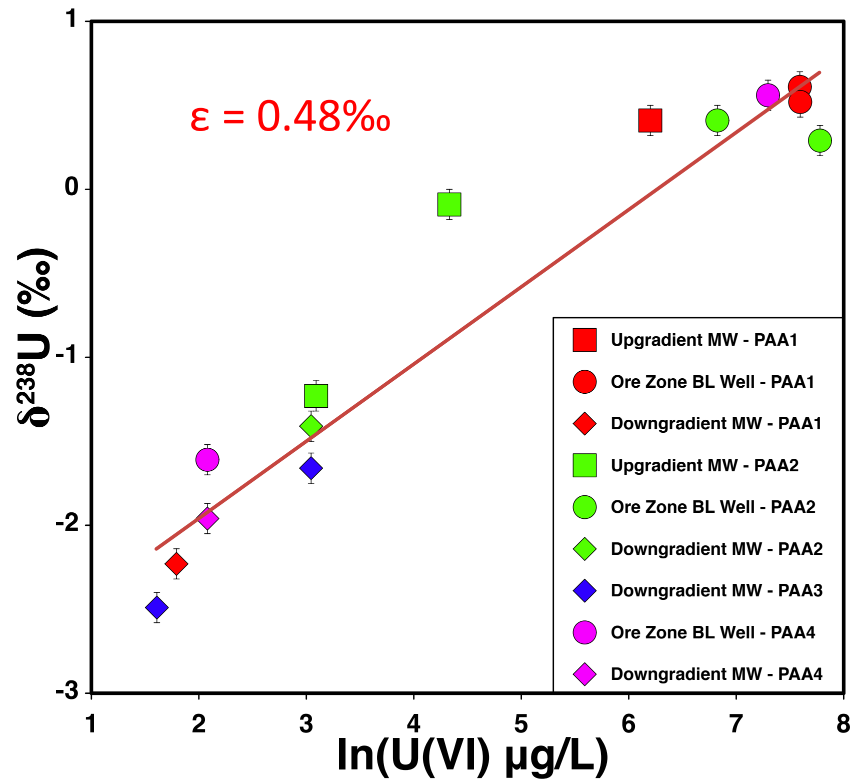
Geochemistry of Rosita Groundwater



Basu et al., 2015 (ES&T)

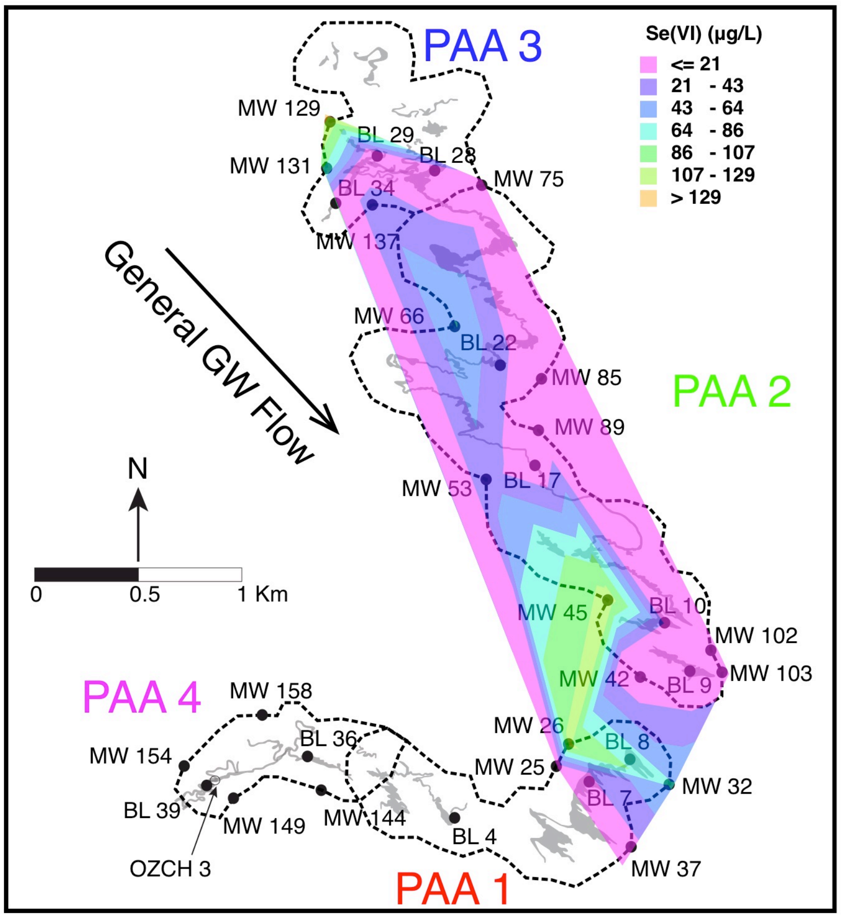
U Isotopes in Rosita Groundwater

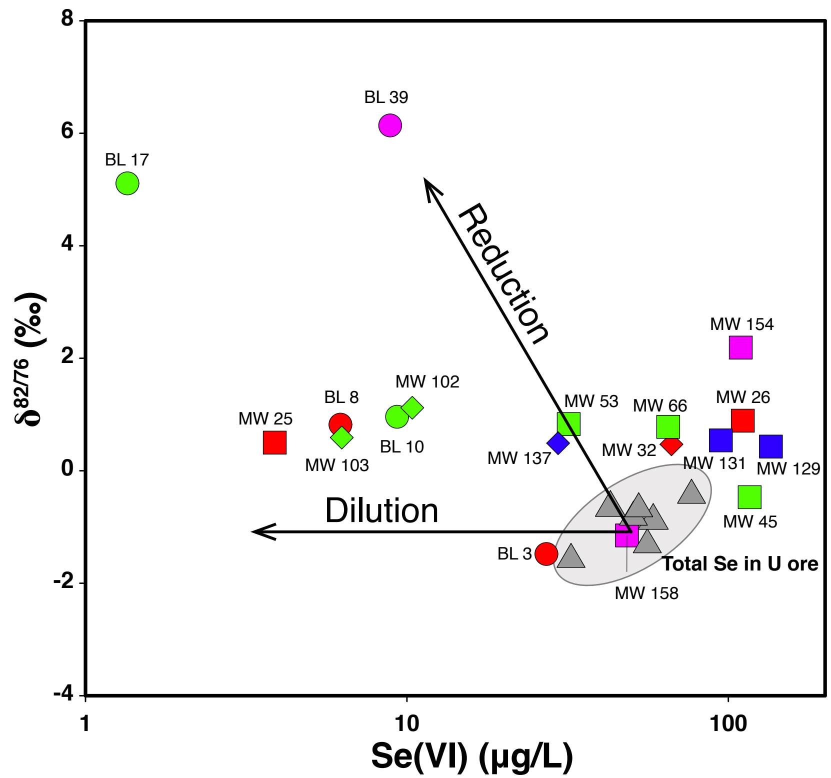




Basu et al., 2015 (ES&T)

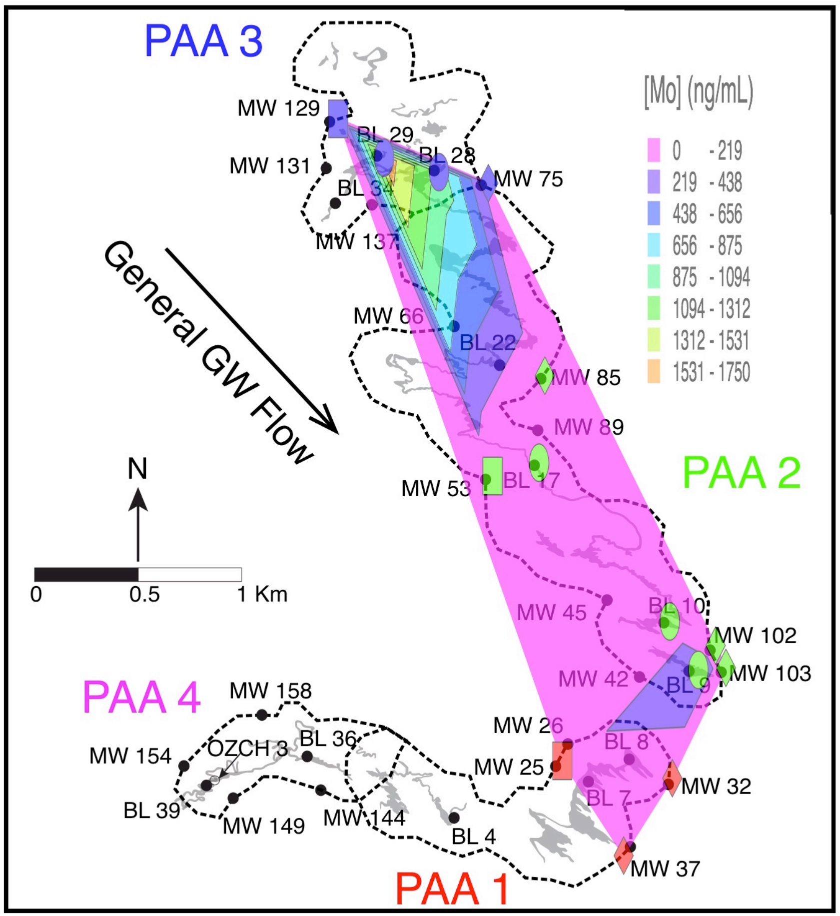
Se Isotopes in Rosita Groundwater

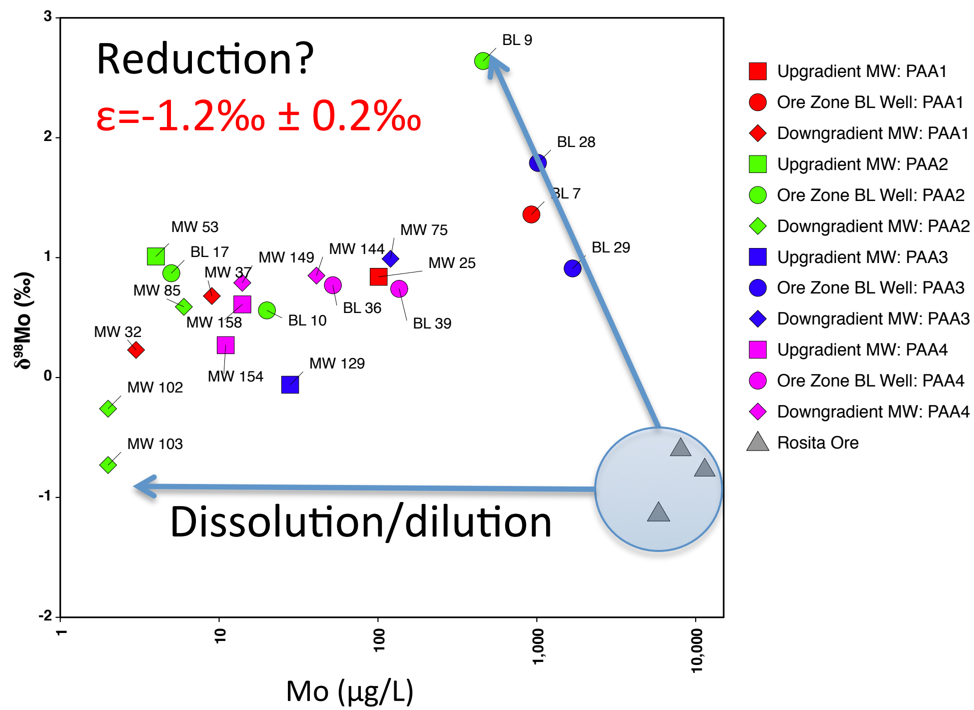




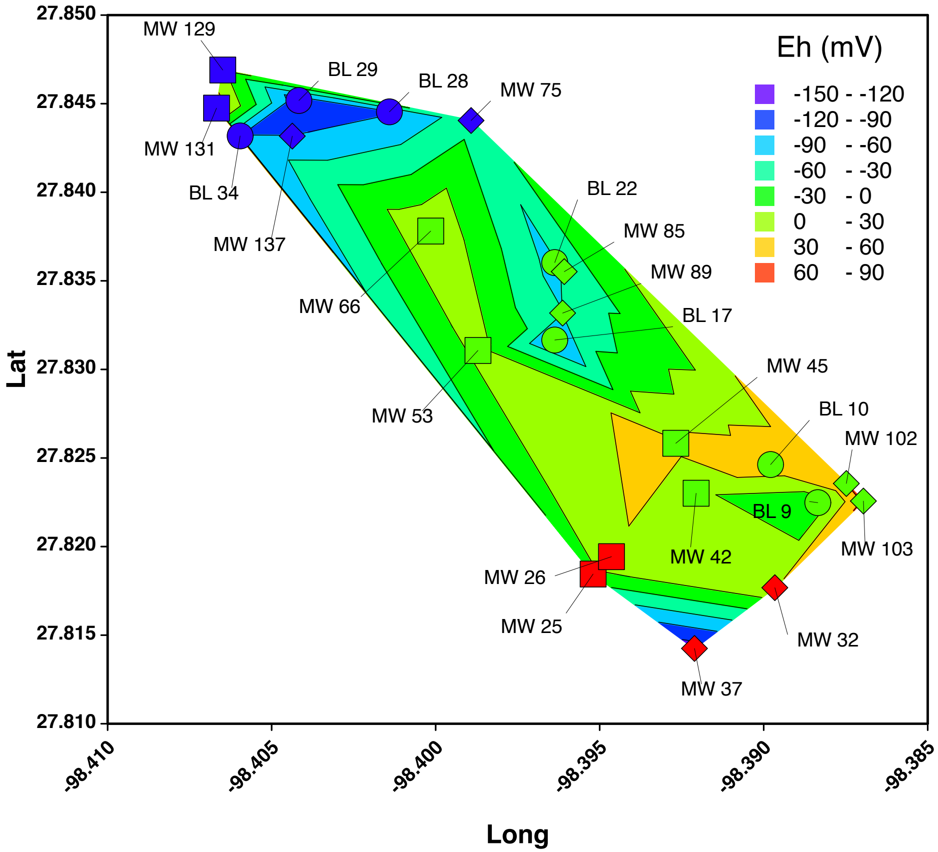
Basu et al., 2015 (in prep)

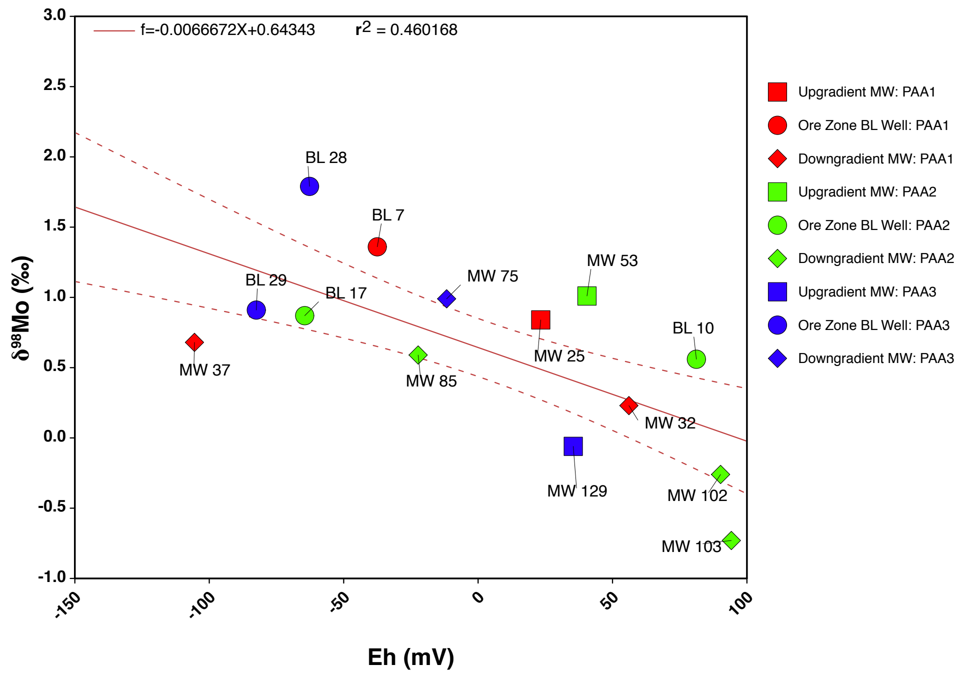
Mo Isotopes in Rosita Groundwater



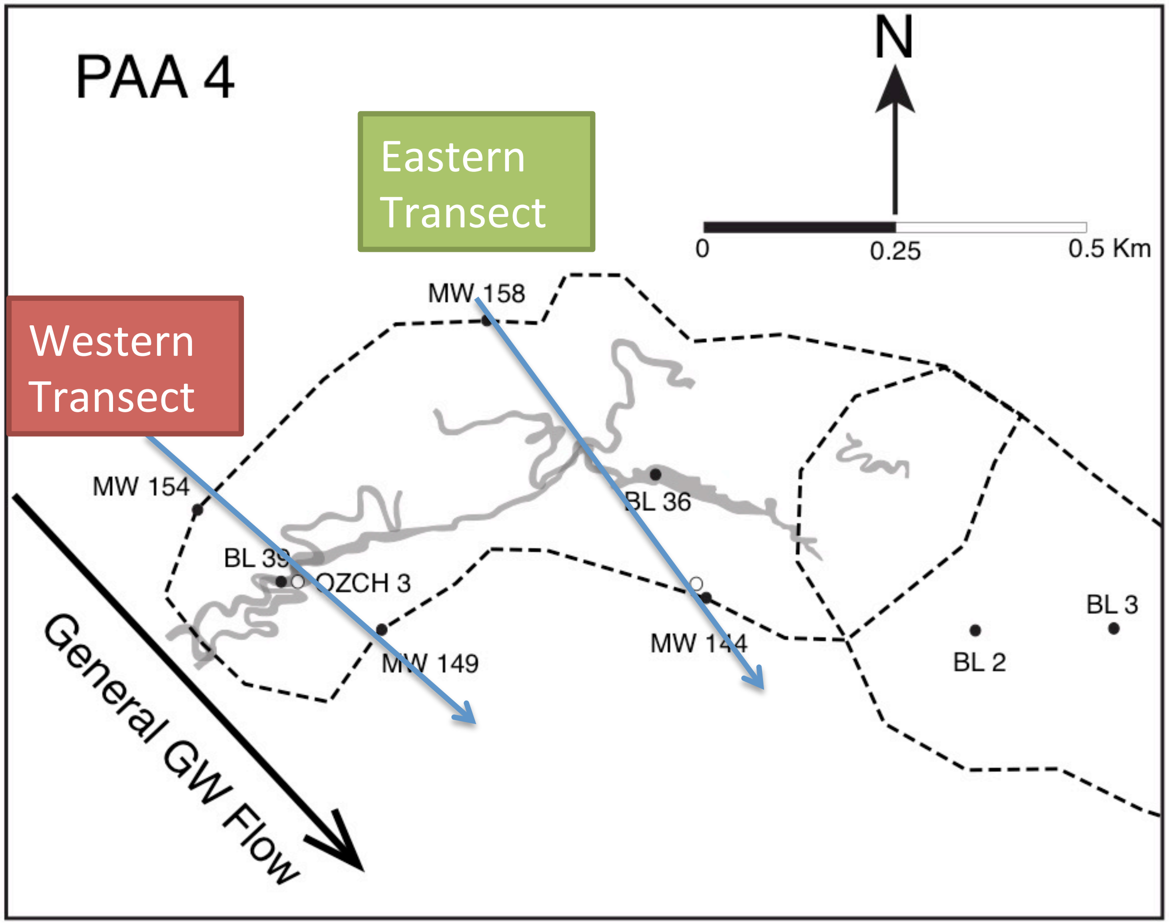


Mo Isotopes: Correlation with Eh?





Unmined Area at Rosita



Unmined PAA4 Transects

Western Transect	Se(VI) (µg/L)	U(VI) (µg/L)	Mo (Total) (µg/L)
MW 154	109	104	11
BL 39	9	1474	136
MW 149	0	1	14

Eastern Transect	Se(VI) (µg/L)	U(VI) (µg/L)	Mo (Total) (µg/L)
MW 158	48	44	14
BL 36	0	8	52
MW 144	0	8	41

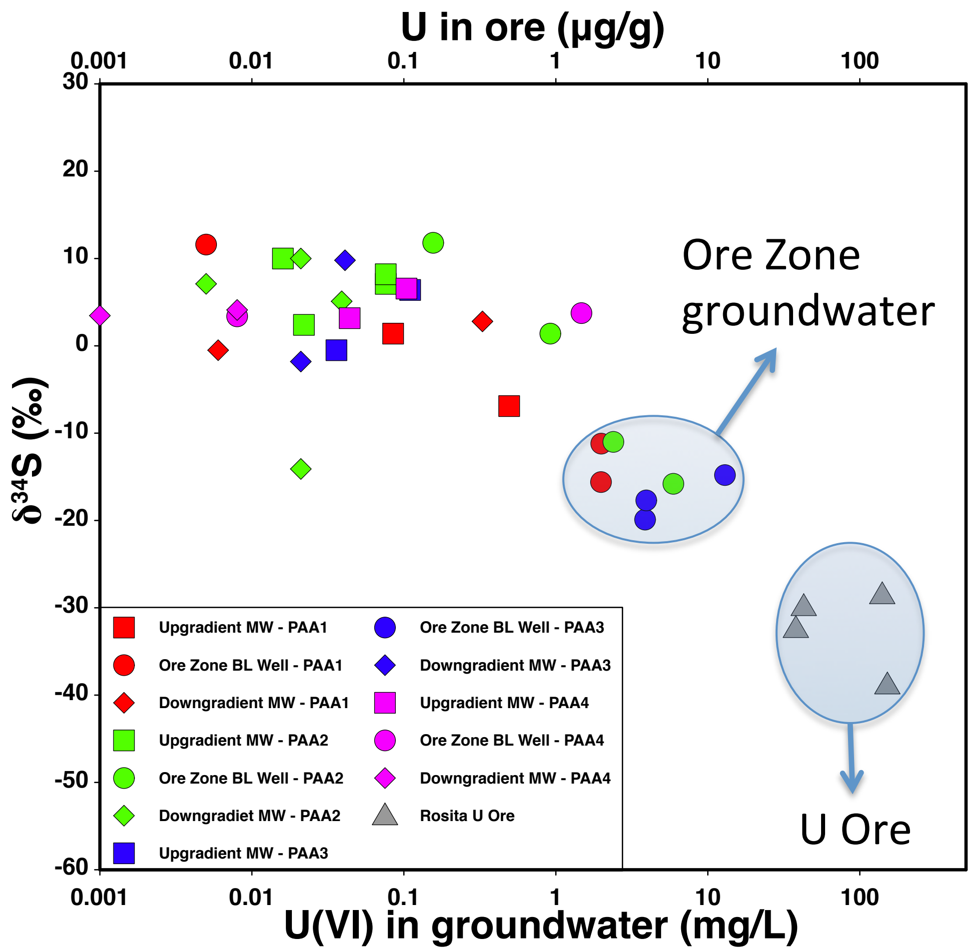
Western Transect	δ^{82}Se	δ^{238}U	δ^{98}Mo
MW 154	2.19‰	0.14‰	0.27‰
BL 39	6.14‰	0.56‰	0.74‰
MW 149		0.48‰	0.79‰

Eastern Transect	δ^{82}Se	δ^{238}U	δ^{98}Mo
MW 158	-1.15‰	-0.08‰	0.61‰
BL 36		-1.61‰	0.77‰
MW 144		-1.96‰	0.85‰

Se(VI) reducing

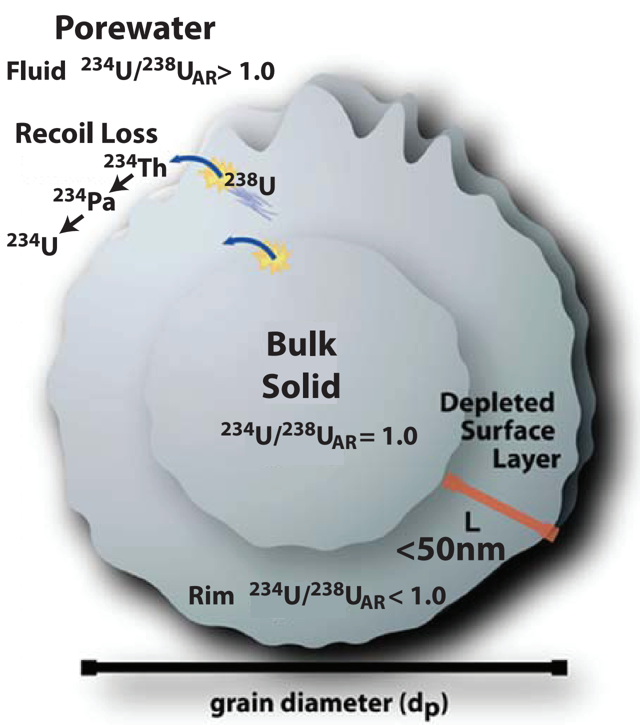
U(VI) Reducing

S isotopes in Rosita Groundwater



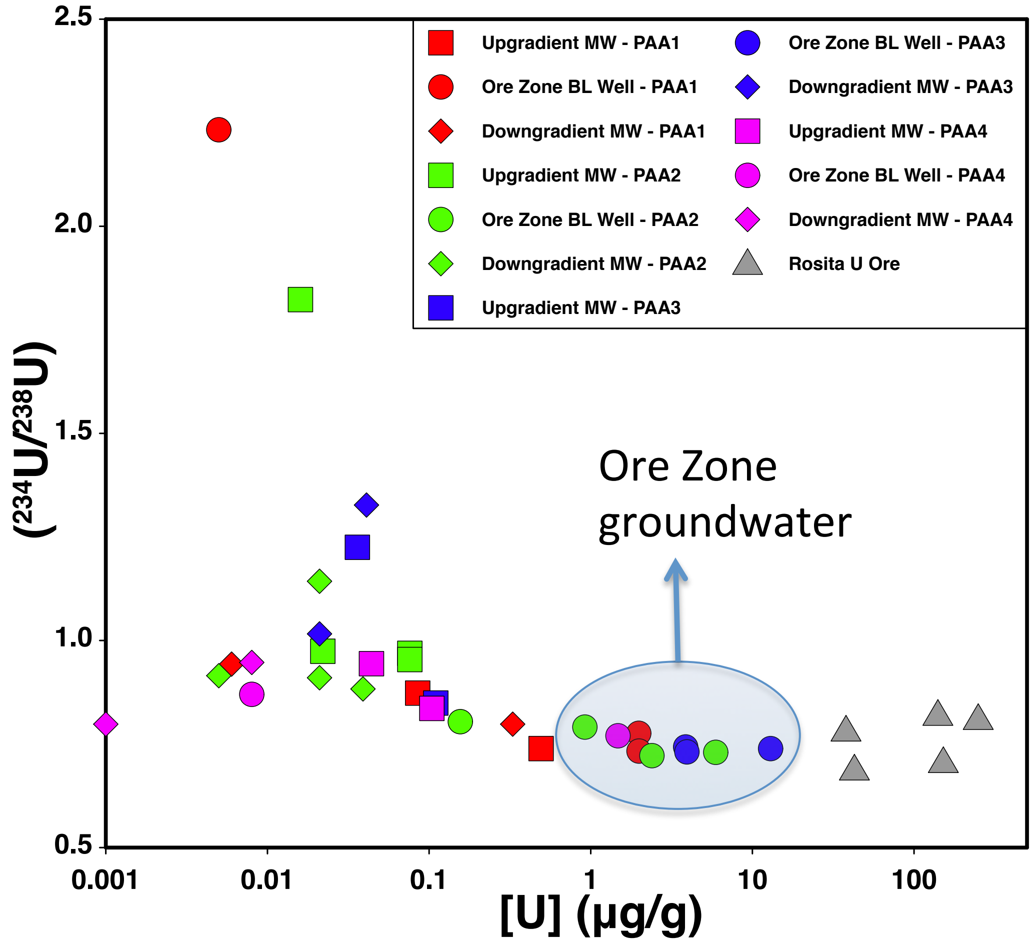
Basu et al., 2015 (ES&T)

Tracer for U Migration – U Activity Ratios



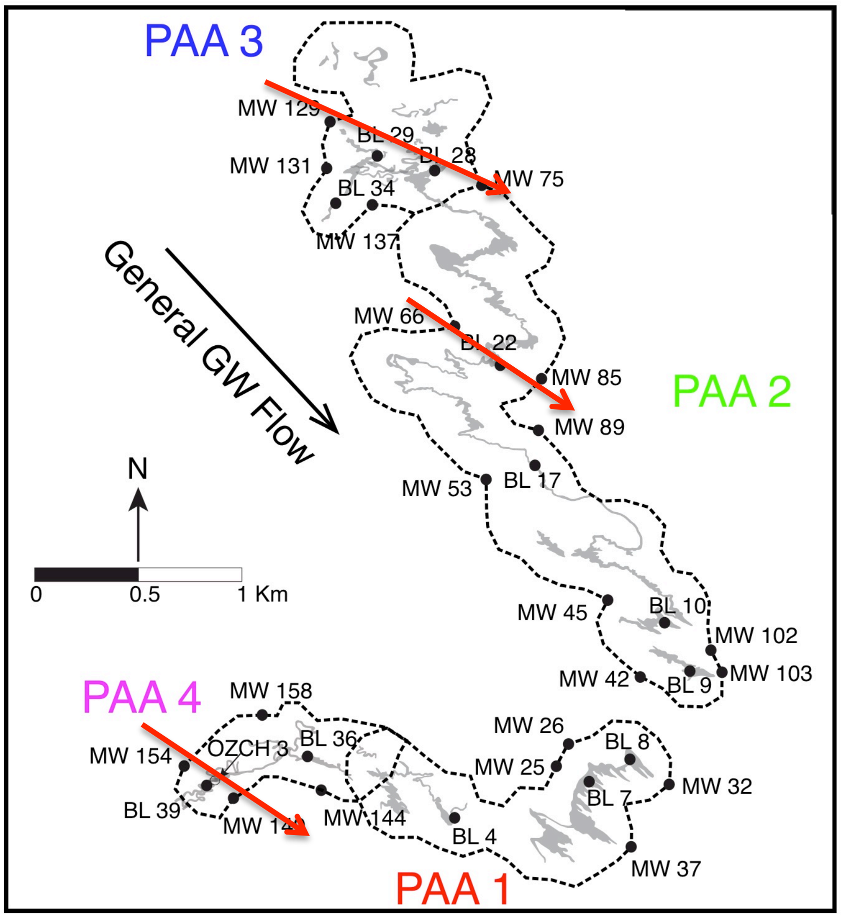
- In solid materials, $^{234}U/^{238}U$ should be in secular equilibrium (=1)
- When ^{234}Th is ejected in the surrounding medium, groundwater can acquire high $^{234}U/^{238}U$
- $^{234}U/^{238}U$ in solid can become less than 1

U Activity Ratios at Rosita



Basu et al., 2015 (ES&T)

U Activity Ratios at Rosita



	Upgradient	Ore Zone	Downgradient
	MW 129	BL 28	MW 75
PAA 3	1.22	0.74	1.02
	MW 66	BL 22	MW 85
PAA 2	0.95	0.72	0.91
	MW 158	BL 39	MW 149
PAA 4	0.94	0.77	0.8

- 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

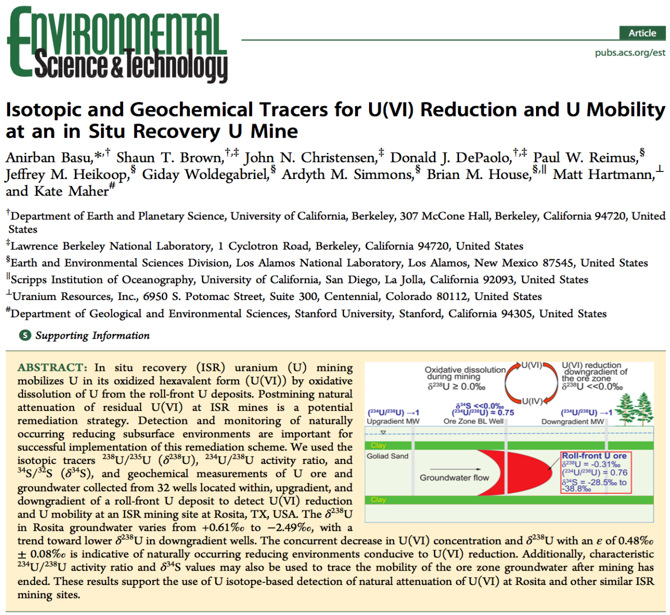
Conclusions

- $^{238}U/^{235}U$ in Rosita groundwater indicate U(VI) reduction
- $^{82}Se/^{76}Se$ are indicators of Se reduction and possibly the onset of U(VI) reduction
- $^{98}Mo/^{95}Mo$ may suggest strong reducing environments capable of efficient U(VI) reduction
- U activity ratios ($^{234}U/^{238}U$) 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-desoprtion, diffusion limitation) on isotopic fractionation

Questions?



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Isotopic and Geochemical Tracers for U(VI) Reduction and U Mobility at an in Situ Recovery U Mine

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Supporting Information

ABSTRACT: In situ recovery (ISR) uranium (U) mining mobilizes U in its oxidized hexavalent form (U(VI)) by oxidative dissolution of U from the roll-front U deposits. Postmining natural attenuation of residual U(VI) at ISR mines is a potential remediation strategy. Detection and monitoring of naturally occurring reducing subsurface environments are important for successful implementation of this remediation scheme. We used the isotopic tracers $^{238}U/^{235}U$ ($\delta^{238}U$), $^{234}U/^{238}U$ activity ratio, and $^{34}S/^{32}S$ ($\delta^{34}S$), and geochemical measurements of U ore and groundwater collected from 32 wells located within, upgradient, and downgradient of a roll-front U deposit to detect U(VI) reduction and U mobility at an ISR mining site at Rosita, TX, USA. The $\delta^{238}U$ in Rosita groundwater varies from +0.61‰ to −2.49‰, with a trend toward lower $\delta^{238}U$ in downgradient wells. The concurrent decrease in U(VI) concentration and $\delta^{238}U$ with an ε of 0.48‰ ± 0.08‰ is indicative of naturally occurring reducing environments conducive to U(VI) reduction. Additionally, characteristic $^{234}U/^{238}U$ activity ratio and $\delta^{34}S$ values may also be used to trace the mobility of the ore zone groundwater after mining has ended. These results support the use of U isotope-based detection of natural attenuation of U(VI) at Rosita and other similar ISR mining sites.