Illuminating the mechanisms behind contaminant behavior in below-ground heterogeneous redox environments

Kristin Boye

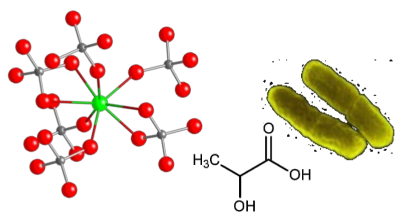
Associate Staff Scientist, SSRL/SLAC

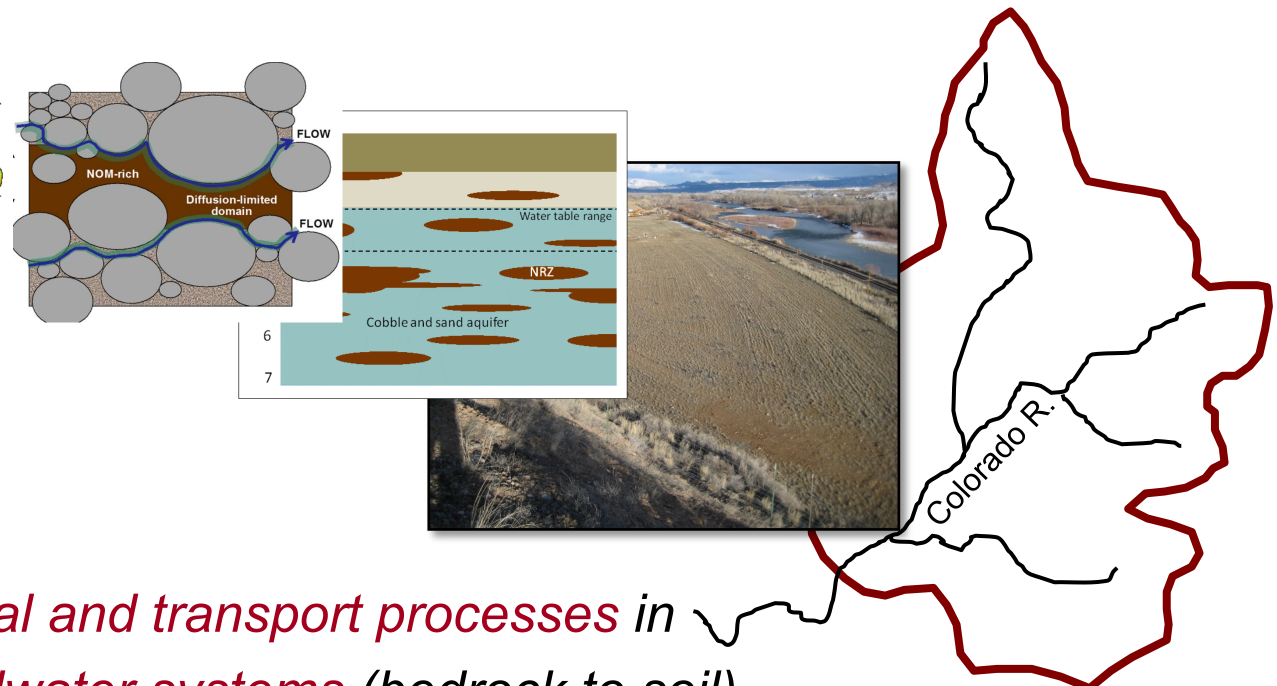
SLAC Groundwater Quality SFA

https://www-ssrl.slac.stanford.edu/sfa/

SLAC Groundwater Quality SFA

Molecular scale — Pore scale — Field scale





<u>Overarching Question:</u>

How do biogeochemical and transport processes in shallow alluvial groundwater systems (bedrock to soil) couple to one-another and control <u>water quality</u> under hydrologically variable conditions?

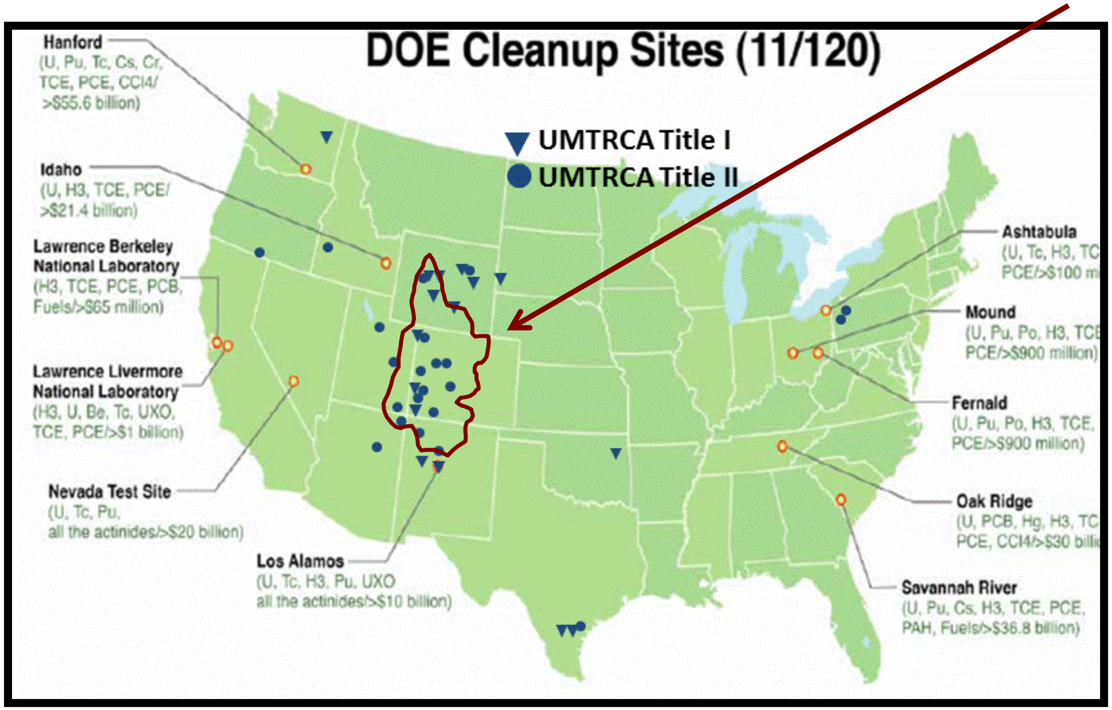
Contamination with **metal(loid)s** and **actinides**

DOE legacy and contaminant research sites

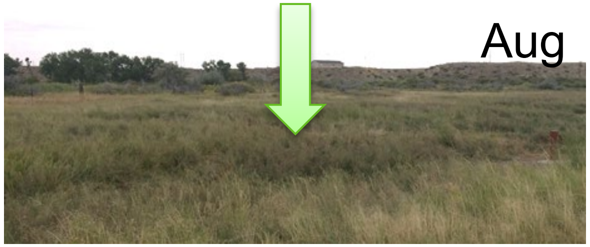
Uranium Mill Tailings Remediation Cleanup Action (UMTRCA)

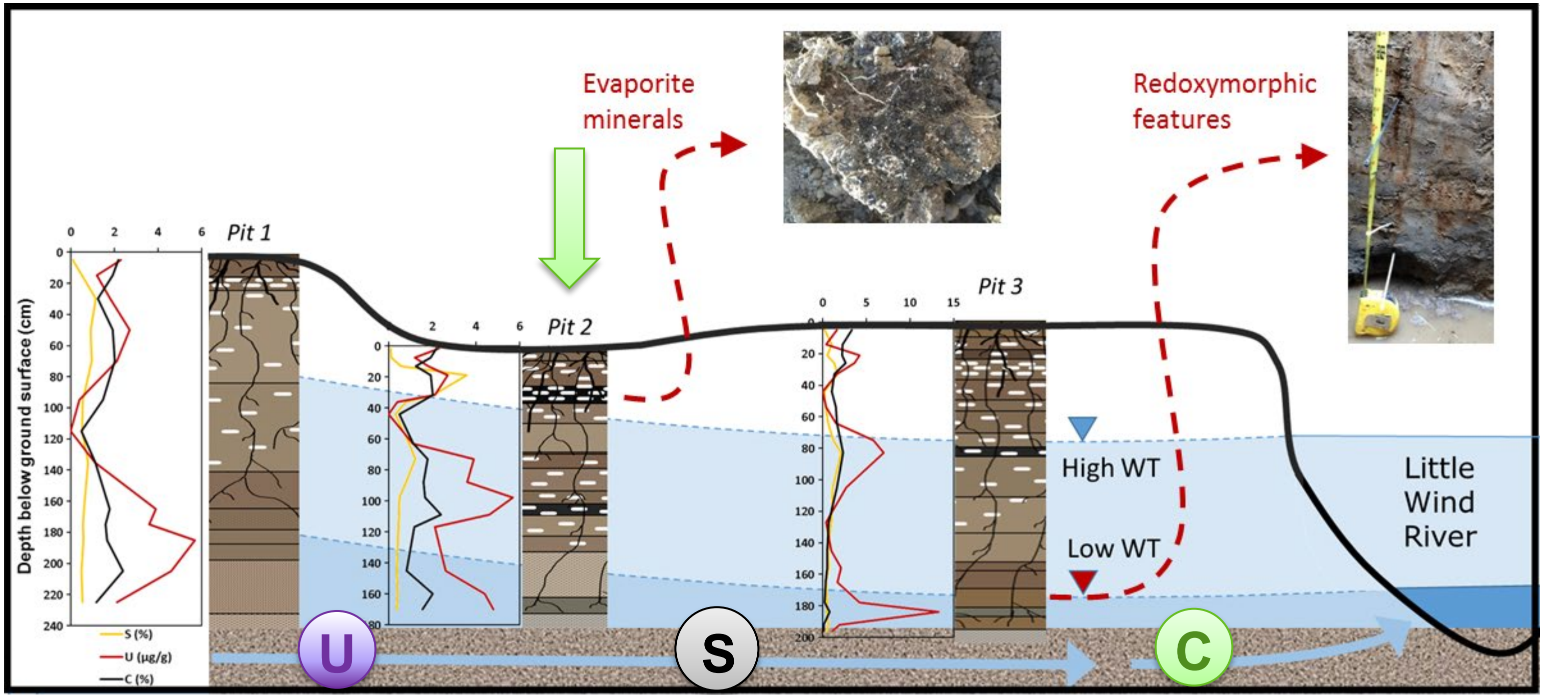
- Mill tailings, ore, and contaminated soil removed
- Groundwater still contaminated

Upper Colorado River Basin

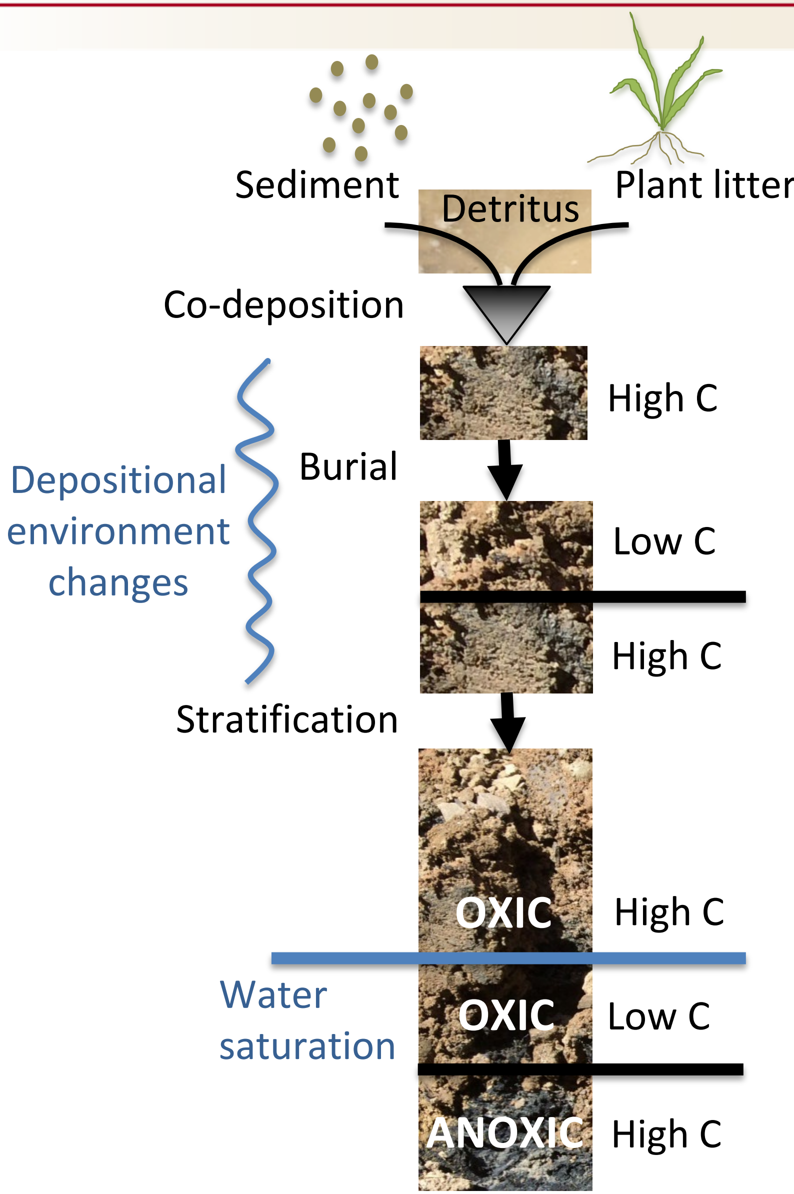


Floodplains exhibit dynamic hydrology





Floodplain Subsurface



Active meandering changes depositional environment over time

Organic matter often most abundant in finer sediments

Water saturation leads to oxygen depletion

“Naturally reduced zones” (NRZs)

Approaches to understanding contaminant behavior

Field measurements

Field samples

Field material

Experiments

Laboratory analyses

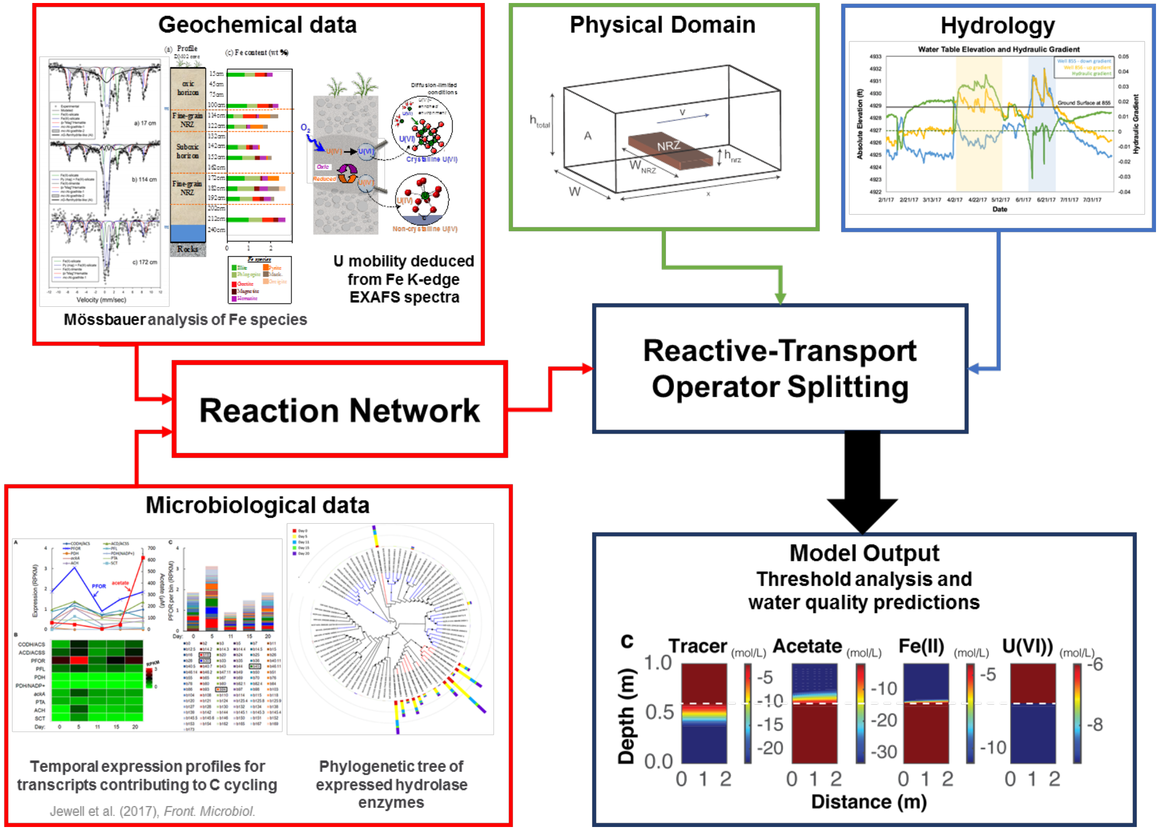
SLAC

Observables	Analyses
Aqueous concentrations	IC, ICP, TOC, colorimetric assays, microsensors
Redox conditions	Sensors (*in situ* or in lab)
Aqueous element speciation	IC, colorimetric assays, FT-ICR-MS, LC-ICP-MS
Solid phase concentrations	XRF, EA
Solid phase mineralogy, element speciation, spatial distribution/association	XRD, (μ)XANES, EXAFS, STXM, NanoSIMS, TEM, SEM, Mössbauer, extractions
Microbial community composition	16S iTAG sequencing
Microbial activity and function	Metabolomics, metagenomics, metatranscriptomics, qPCR, calorimetry, GC, MicroResp
Transport (rates/direction)	Tracers (*e.g.* Br, NO3, dyes, isotopes)

Develop a process-based systems understanding

Process representations for reactive transport models based on field and experimental data

- Generate accurate and precise predictions
- Transferrable between sites that function similarly
- Compliance with machine-learning capabilities for processing data and improve model



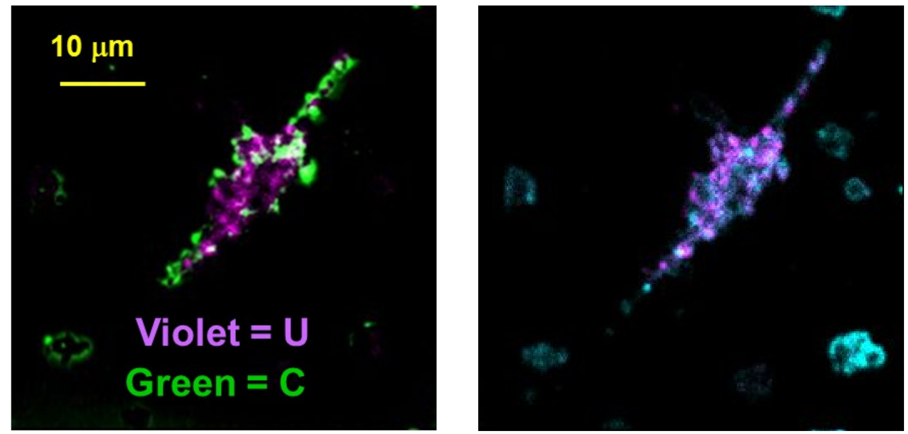
Sorption to Organic Matter Controls Uranium Mobility

Bulk U L_{III}–edge EXAFS combined with STXM (spatially resolved C speciation + Fe, Al, Si mapping), and NanoSIMS revealed:

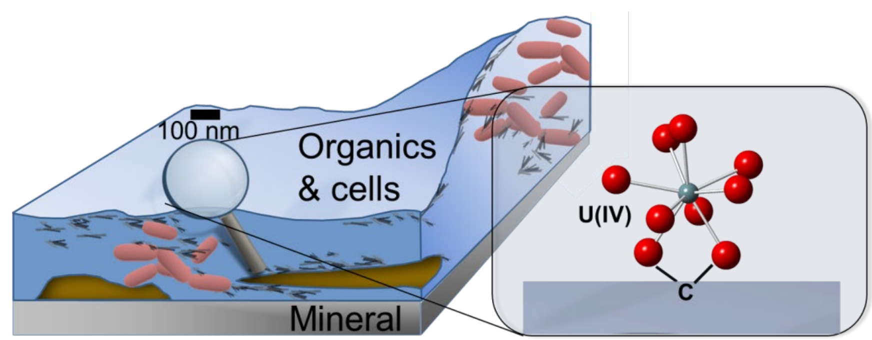
- U(IV) adsorb on organic carbon and organic carbon-coated clays → refutes previously assumed dominance of U(IV) minerals (e.g. uraninite)

This implies that **U(IV) is much more reactive and able to participate in repeated biogeochemical cycling** than previously thought

Sharon Bone



NanoSIMS images of cells colonizing detrital organic matter; Uranium binds to cells and interstitial organics.



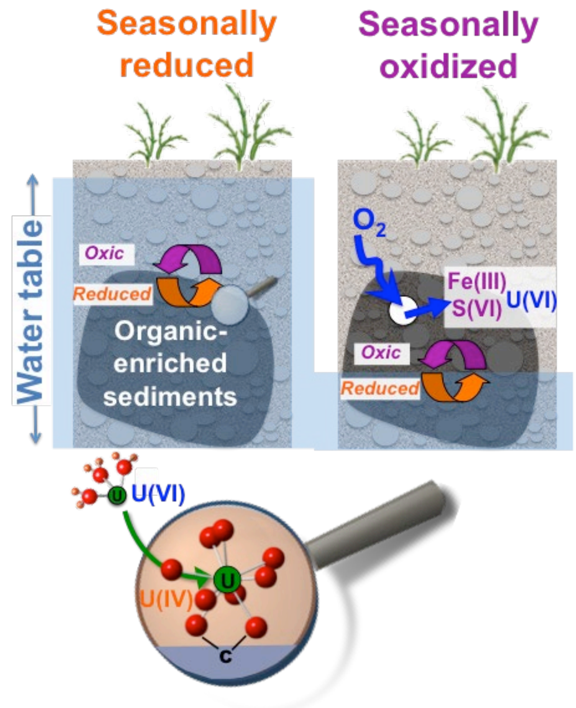
Bone *et al.* (2017) *PNAS* **114**(4), 711-716.

NRZs accumulate uranium regionally

Vincent Noël

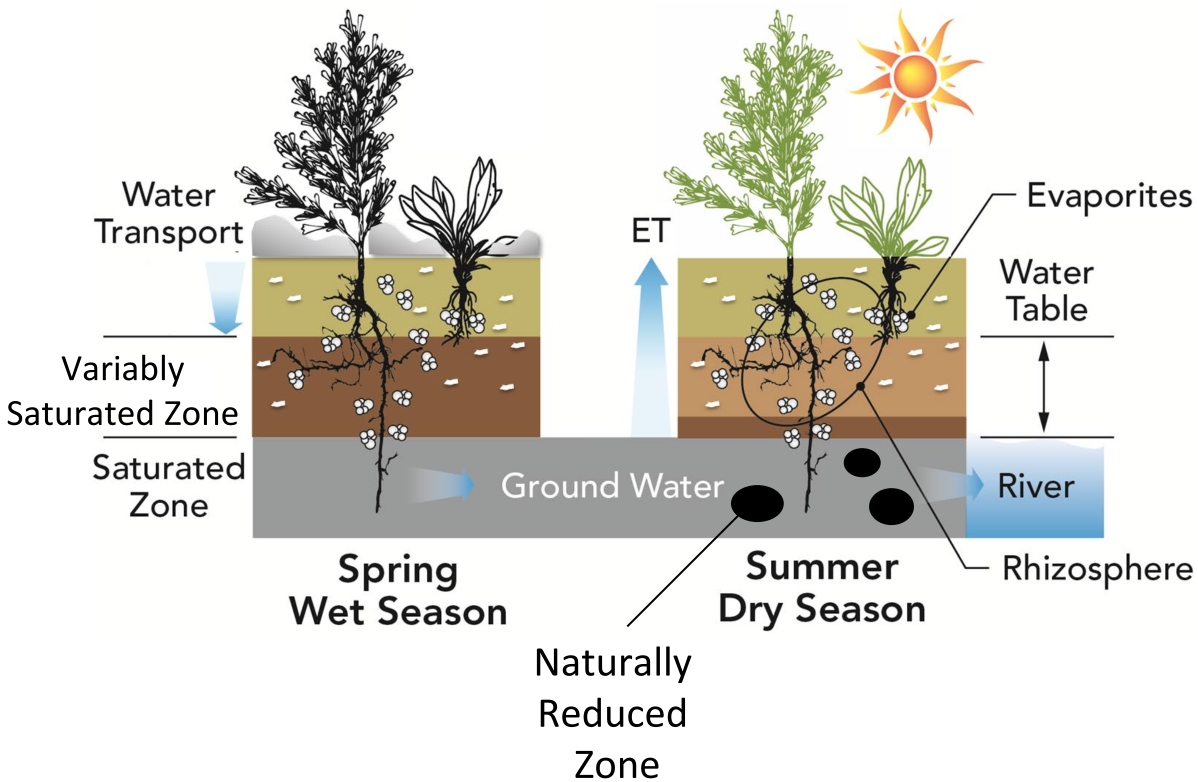
Bulk U L_{III}–edge EXAFS and XANES, S k-edge XANES, Fe k-edge XANES and EXAFS combined with mössbauer spectroscopy, FTICRMS, chemical extractions, and hydrological measurements show:

- NRZs are common, and strongly accumulate ***sulfides, U(IV), and thermodynamically preserved organic C*** compounds
- Seasonal redox cycles mobilize elements → strong ***vertical transport*** both UP (evapotrans) and DOWN (infiltration)
- U(IV) oxidation is faster than diffusion rate → ***U(VI) also accumulates in seasonal NRZs*** and is stable against reduction



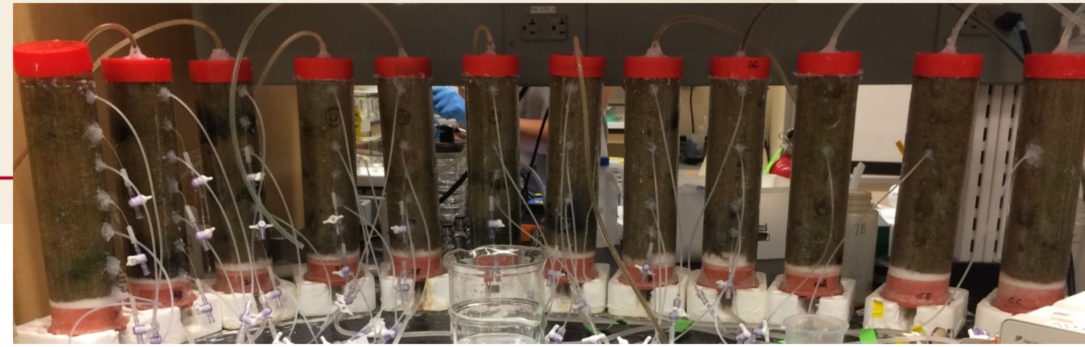
Boye et al. *Nat Geo Sci* **2017**, 10, 415-419
Noël, V. et al. *STOTEN* **2017a**, 603-604, 663-675
Noël, V. et al. *ES&T* **2017b**, 51, 10954-10964
Noël, *et al.* (2019) *Water Research* **152**, 251-263

Field data helps build conceptual models and develop hypotheses



But we need manipulative experiments (field and lab) to test hypotheses and parameterize model reaction networks

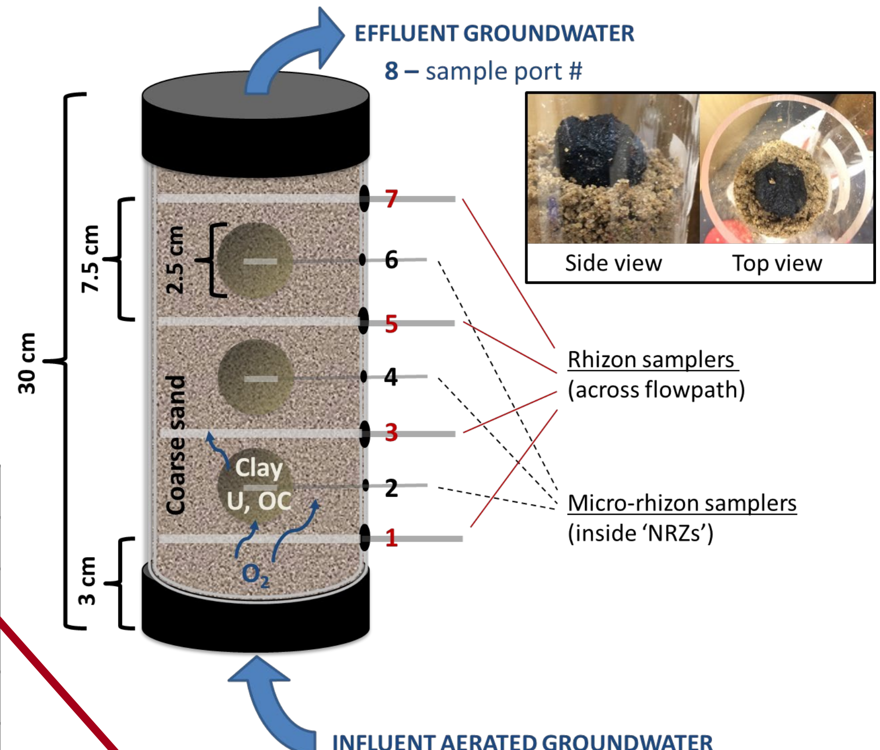
Magnitude of NRZ control on groundwater



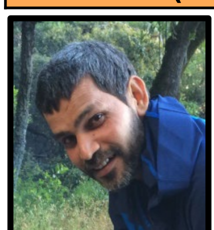
- Riverton aquifer sand
- 0, 1, 2, or 3 NRZs
- Artificial aerated groundwater
  - High SO_4, alkalinity (pH ~8)
  - U and NO_3 (last 2 weeks)
- 10 weeks, weekly water samples

Initial solid phase concentrations:

Constituent	NRZ sediment	Aquifer Sand
Total U (µg/g)	**69±4**	<0.4
Total As (µg/g)	0.7±0.1	1.2±0.4
Total S (mg/g)	**6.45±0.04**	**6.49±0.03**
Total C (mg/g)	**37.22±0.02**	0.028±0.002
Total Fe (mg/g)	**31±2**	7.1±0.3

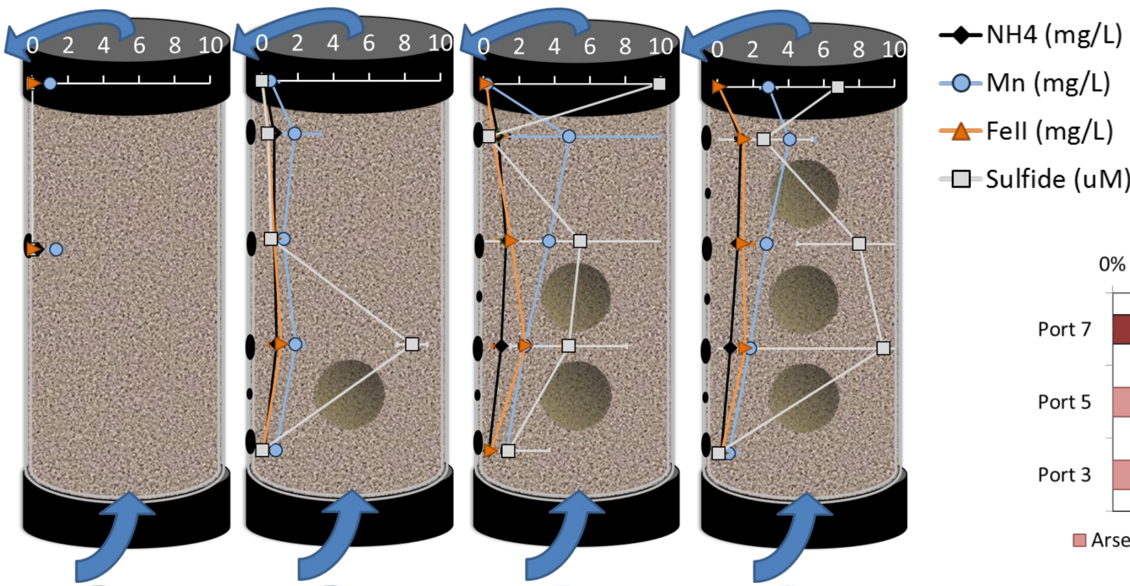


NOTE! Very low As concentrations

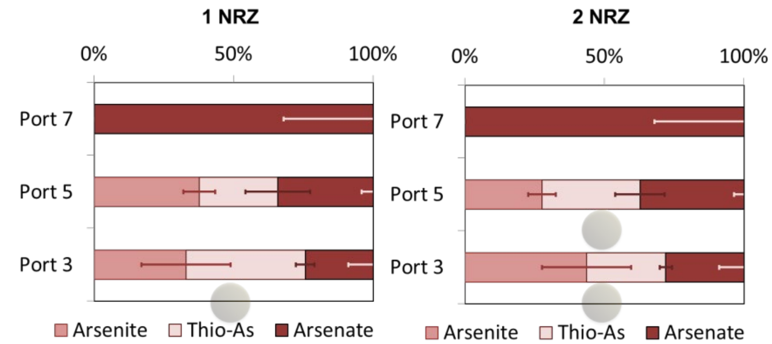


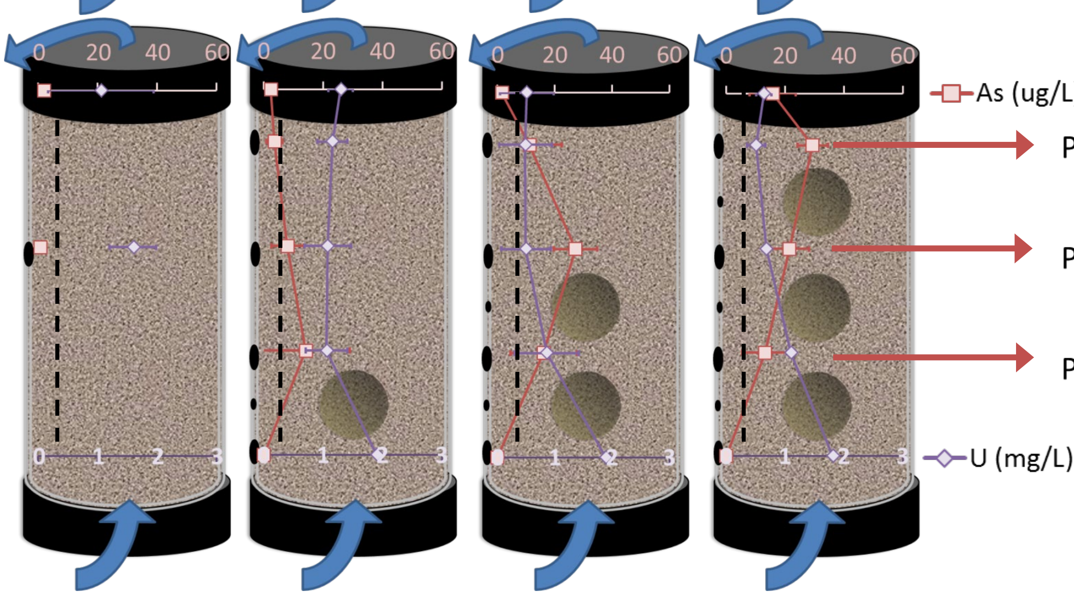
Naresh Kumar

End-point groundwater chemistry

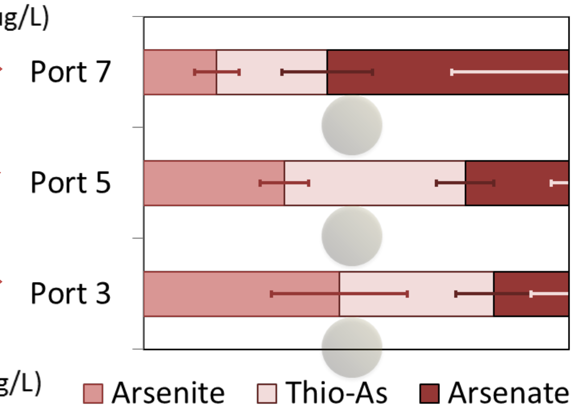


Reduced species outside NRZs



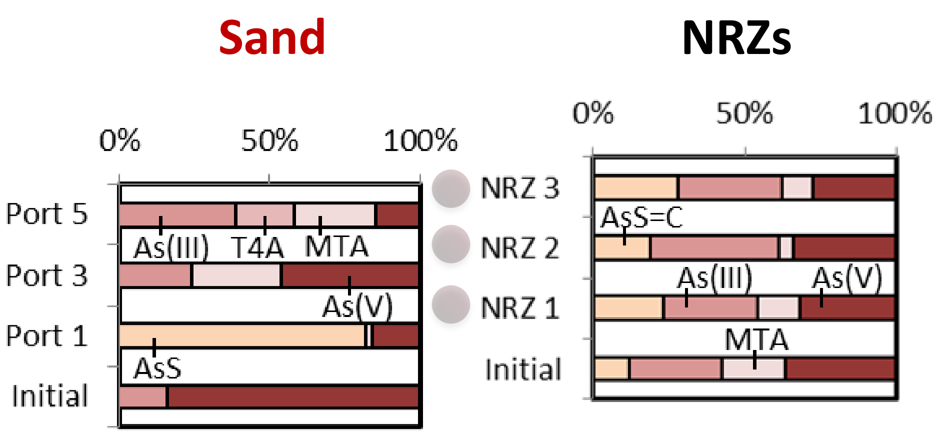


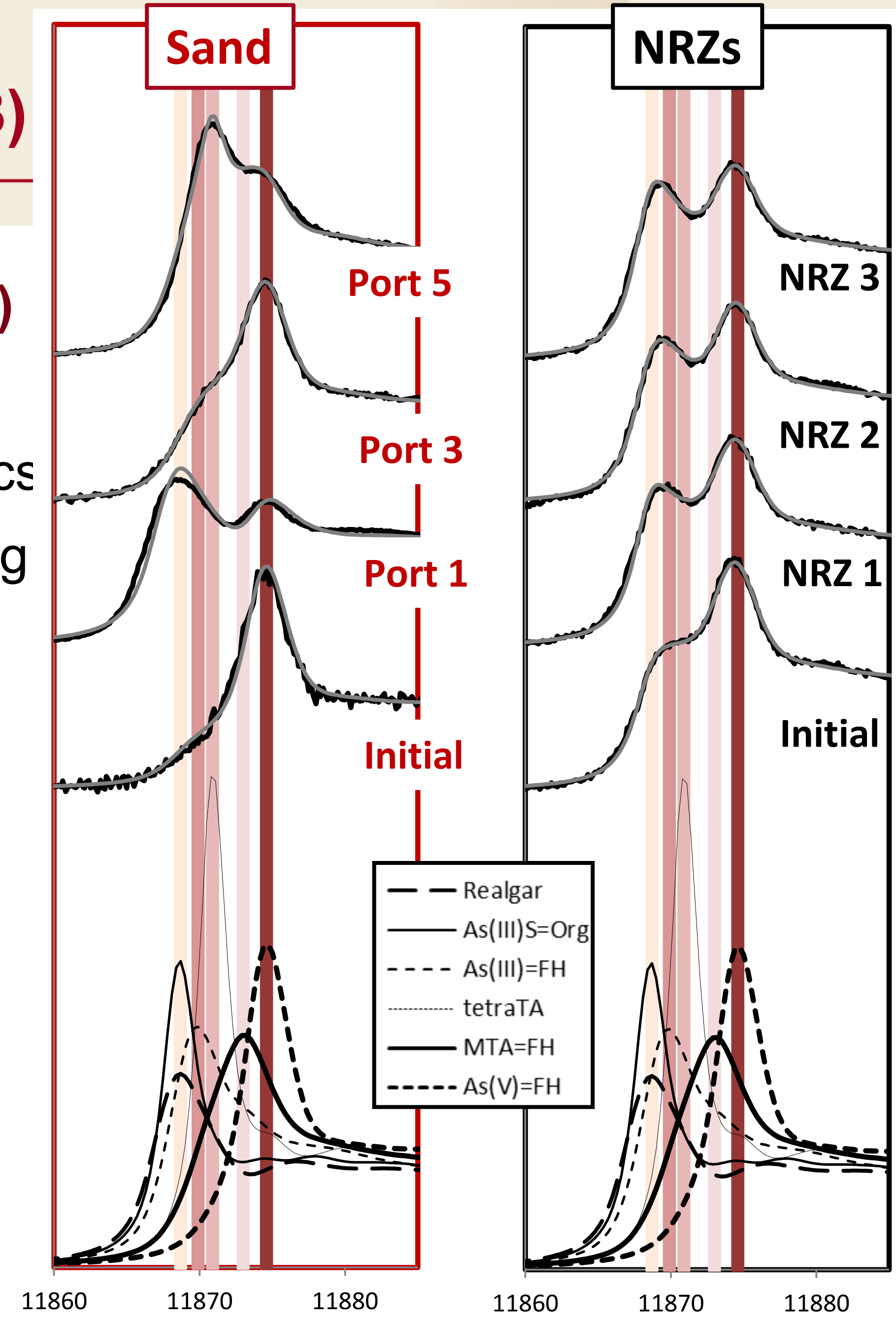
Aqueous As speciation



Bulk As XANES (SSRL BL 7-3)

- Initial As mostly as arsenate, **As(V)**
- As accumulation in **NRZs**:
  mainly AsS adsorbed to organics
- In **sand**, As speciation shifted along flowpath
  - AsS before first NRZ (port 1)
  - Thiolated As species after NRZs





µXRF and spot Fe XANES at SSRL BL 6-2

- Accumulation of Fe(II) on influent side of NRZ
- Depletion of Fe(II) and/or accumulation of Fe(III) on effluent side of NRZs
- Only Fe(II) inside NRZs (FeS, clay/org C)

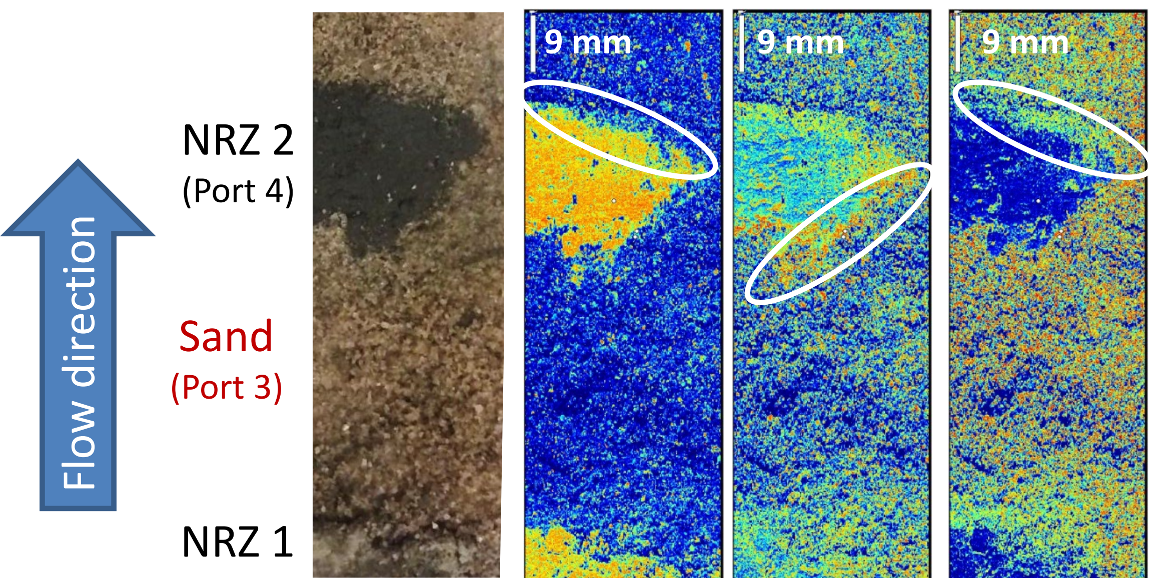
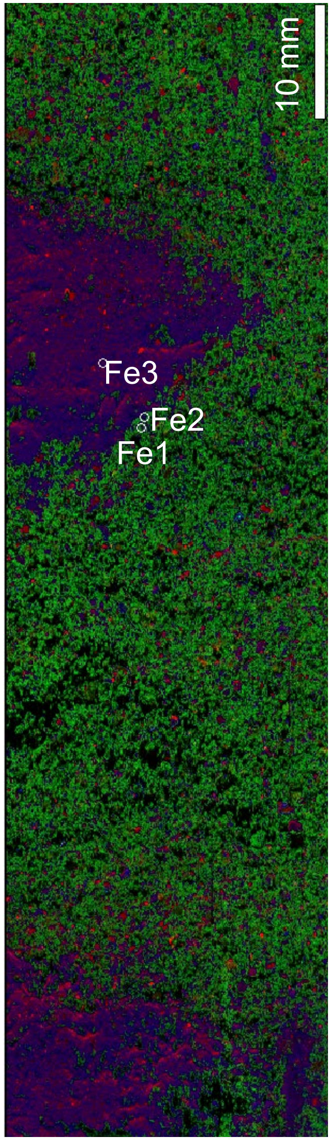
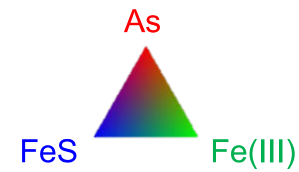
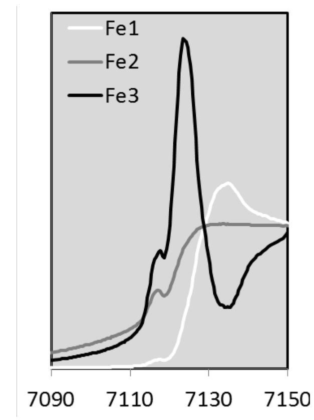


Photo of mapped region | Fe(II)-S (7123 eV) | Fe(II)-C/clay (7127 eV) | Fe(III)-O (7134 eV)



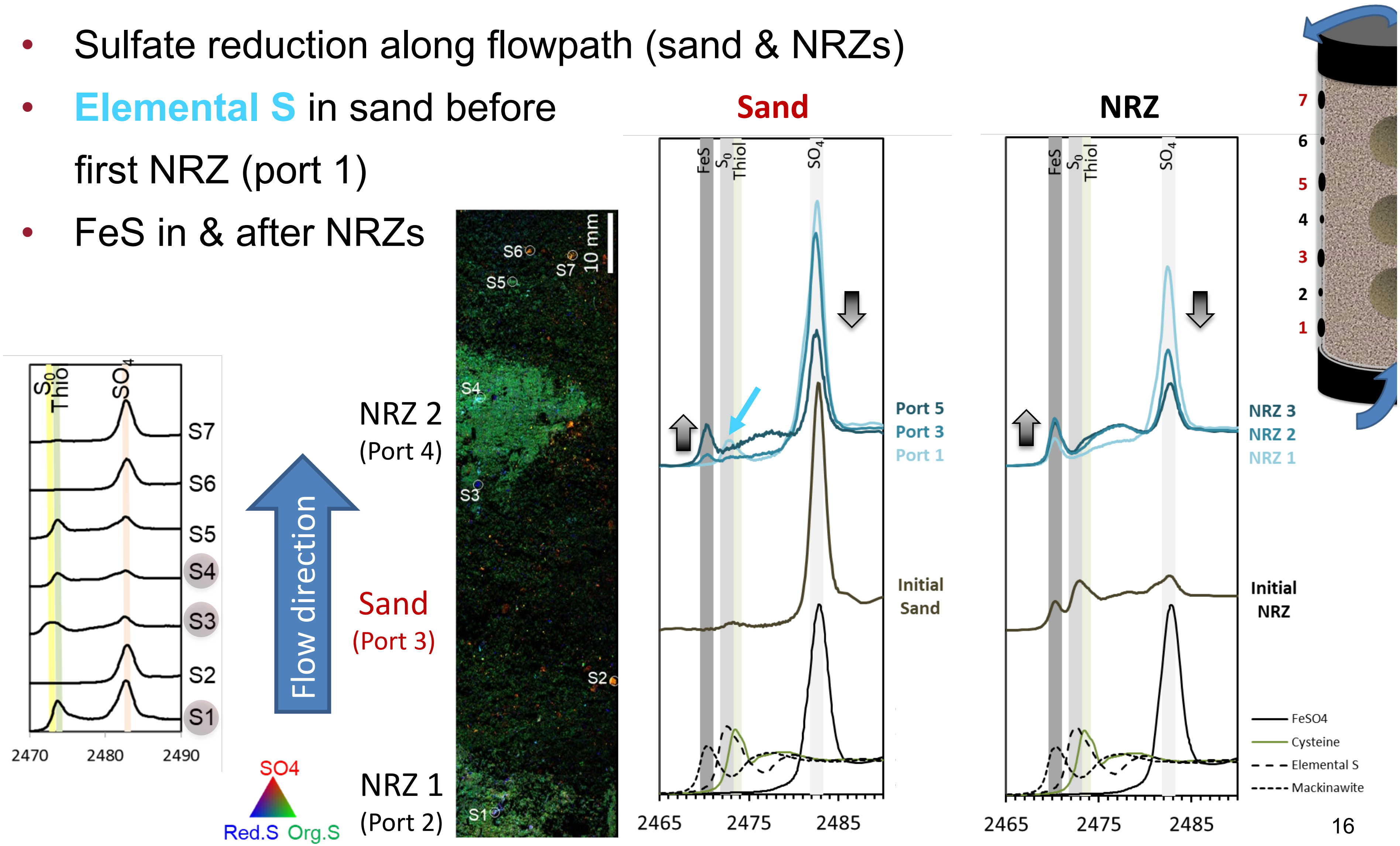




Fe1 = Fe(III) oxide
Fe2 = FeS
Fe3 = Fe(II)-clay/org C

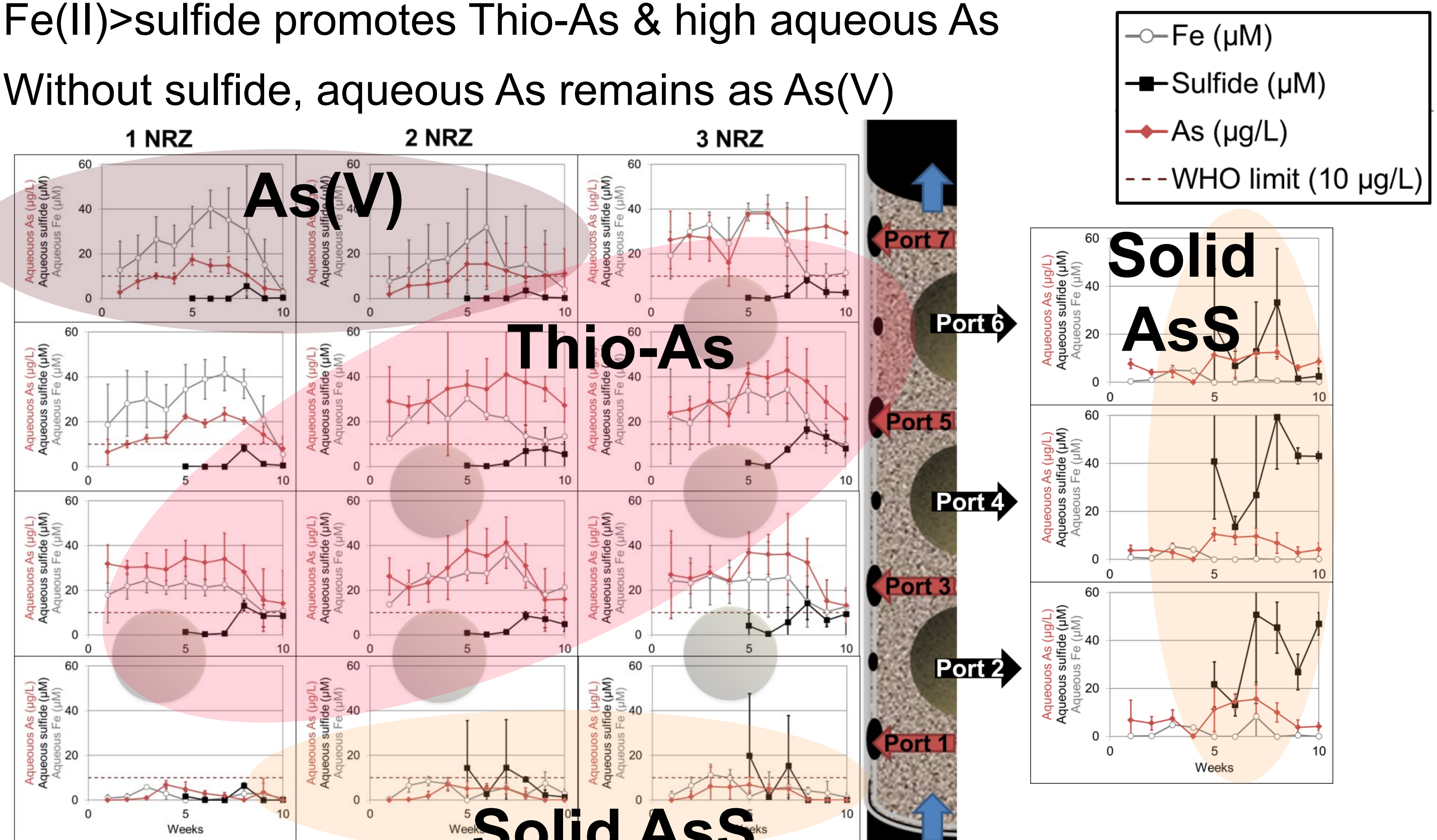
µXRF and spot S XANES at SSRL BL 6-2
Bulk S XANES at SSRL BL 4-3

- Sulfate reduction along flowpath (sand & NRZs)
- **Elemental S** in sand before first NRZ (port 1)
- FeS in & after NRZs

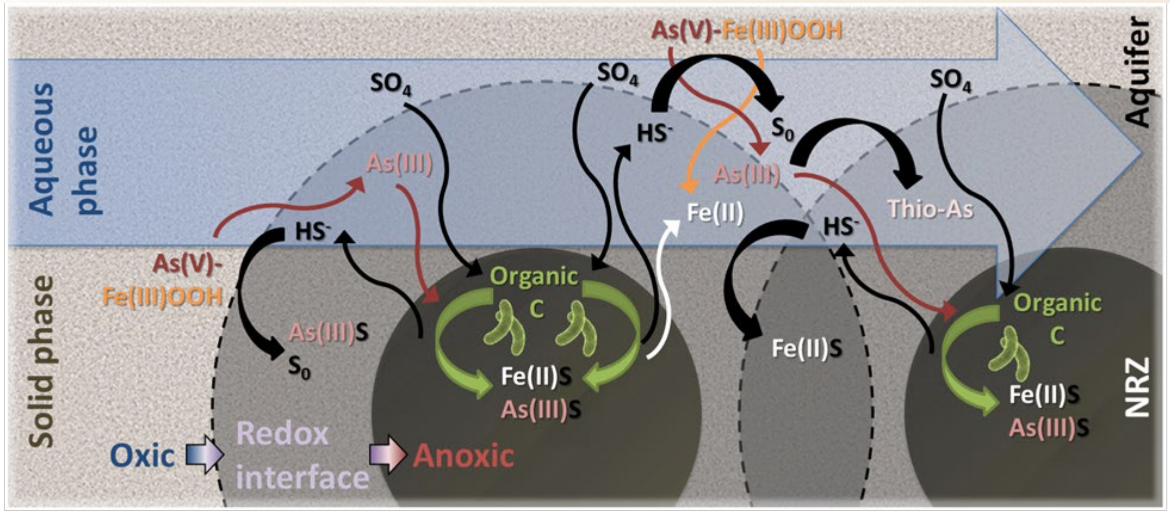


Both solid and aqueous phase speciation required to explain As behavior

- Solid phase AsS only forms where Fe(II)<sulfide and sulfide>>As
- Fe(II)>sulfide promotes Thio-As & high aqueous As
- Without sulfide, aqueous As remains as As(V)



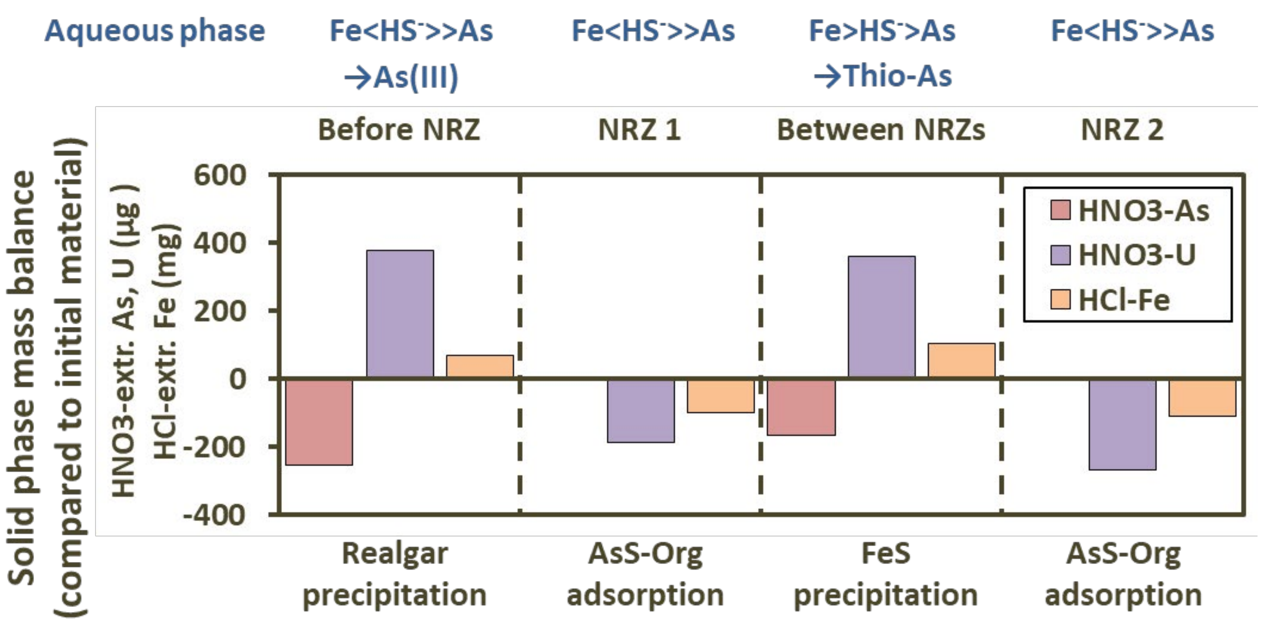
NRZs drove the system to locally reducing conditions in volumes >2 times their size

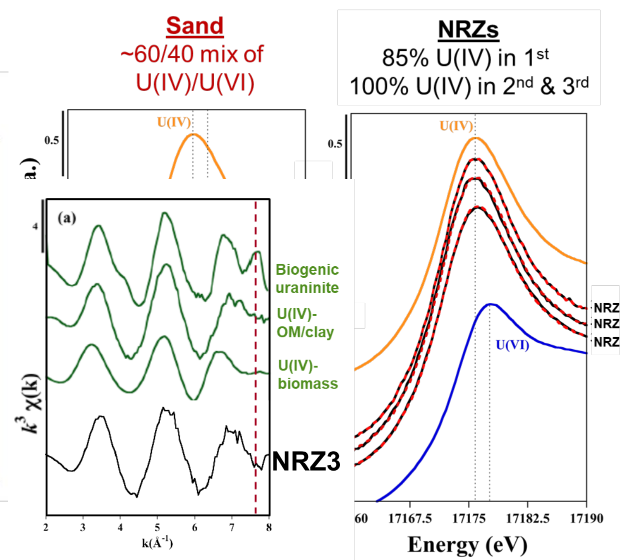


~20% Org-C was lost from NRZs:

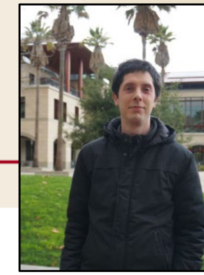
- 7.5% to sand
- 6.5% out as DOC
- 7% respired

U was transported to sand as U(IV)





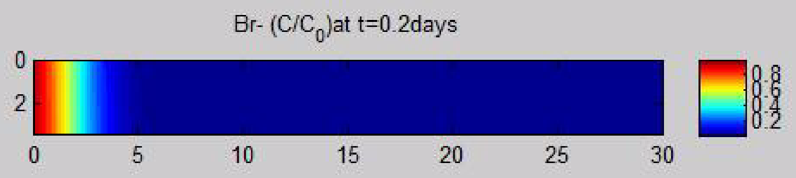
Process-based model development



Tristan Babey

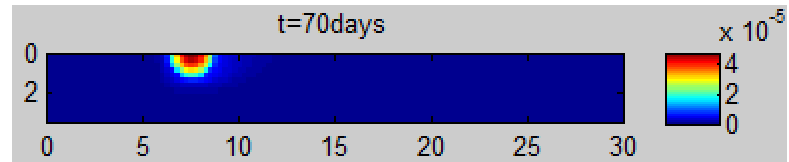
Currently: Calibration of the column experiments (reactive transport code CrunchFLow)

Transport calibration (Br tracer)

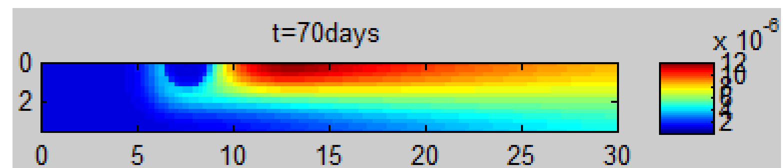


Geochemical model calibration

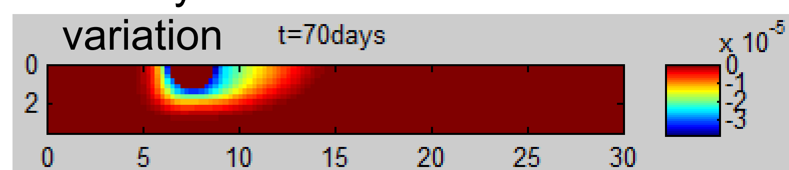
Sulfide (M)



Aqueous Fe(II) (M)



Ferrihydrite volume fraction variation



Future steps: Integration of the unsaturated flow dynamics (code Parflow-CrunchFlow) and development of field-scale model for the Riverton site (HPC cluster Sherlock, Stanford)

It takes a village…

SLAC

Naresh Kumar

Vincent Noël

Sharon Bone

SFA team at Riverton field site, Aug 2015

SLAC-SFA team

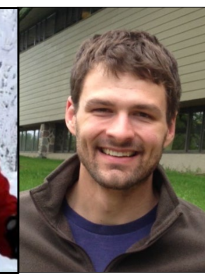
John R. Bargar

Scott Fendorf

Kate Maher

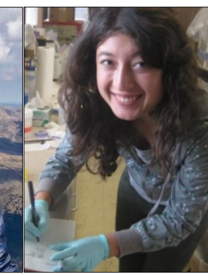
Chris Francis

Zach Perzan



Christian Dewey

Callum Bobb



Emily Cardarelli

Bradley Tolar

Tristan Babey

Northern Arapaho Tribe

Central Wyoming College

U.S. DEPARTMENT OF ENERGY | Legacy Management

Thank You!

SLAC-SFA team:
Vincent Noël, Naresh Kumar, Bradley Tolar, Tristan Babey
Zach Perzan, Emily Cardarelli, Callum Bobb, Christian Dewey
Sharon Bone, Juan Lezama Pacheco
John Bargar, Scott Fendorf, Chris Francis, Kate Maher

Stanford lab:
Lilia Barragan, Laura Spielman
Melanie Rose-Cahill, Alexander Ederer
Guangchao Li, Doug Turner
Fendorf group

SSRL:
Nick Edwards, Sam Webb, Erik Nelson
Matthew Latimer, Ryan Davis

EMSL:
Malak Tfaily, Rosalie Chu, Liliana Pasa-Tolic
John Cliff, Ravi Kukkadapu

Field work:
Dustin Proctor, George Sims
Sam Campbell, Ray Johnson, Ken Williams

Subsurface Biogeochemical Research

U.S. DEPARTMENT OF ENERGY | Office of Science

San Juan River, Shiprock, NM