Geochemical Perspectives Linking Arsenic Fate and Retention to Iron and Sulfur Cycling

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EPA
Environ Foundation

Arsenic in the Environment

- Arsenic not rare in the environment
  - “average soil”: about 10 mg As/kg

- Toxic environmental effects associated with arsenic not rare.
  - Effects of arsenic significant even at very low dissolved levels
  - Effects of arsenic are widespread

Cambodian rice field in As-impacted area

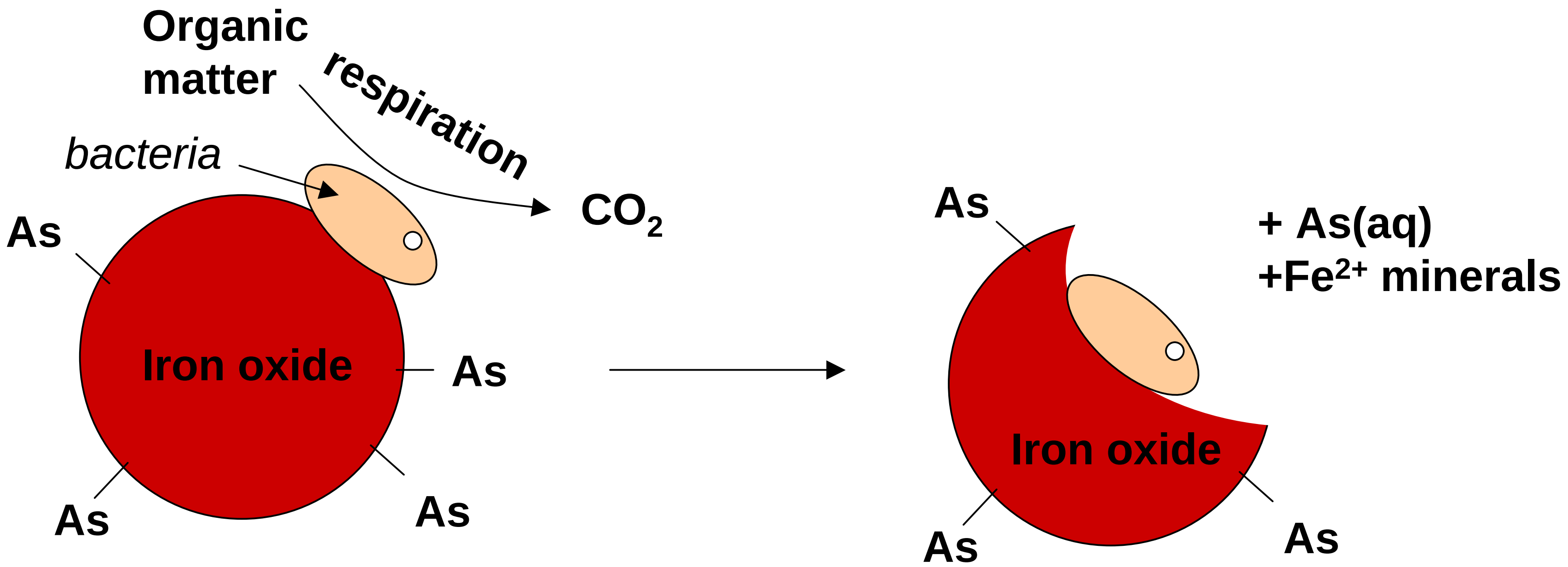
Natural Sources: Arsenic in Groundwater

- Arsenic concentrations in sediments in Bangladesh and Cambodia are not high. In fact, they are frequently **below** average.

- **Chemical Conditions** create elevated *dissolved* arsenic concentrations.
  - LANDFILLS (lined and unlined) are not unique, but are reactors in which pH and redox conditions are modulated by a combination of biological, chemical, and physical processes
    - Microbes
    - Electron Source (organic matter, H_2)
    - Terminal Electron Acceptors (Oxygen, Iron(III), Sulfate, CO_2)

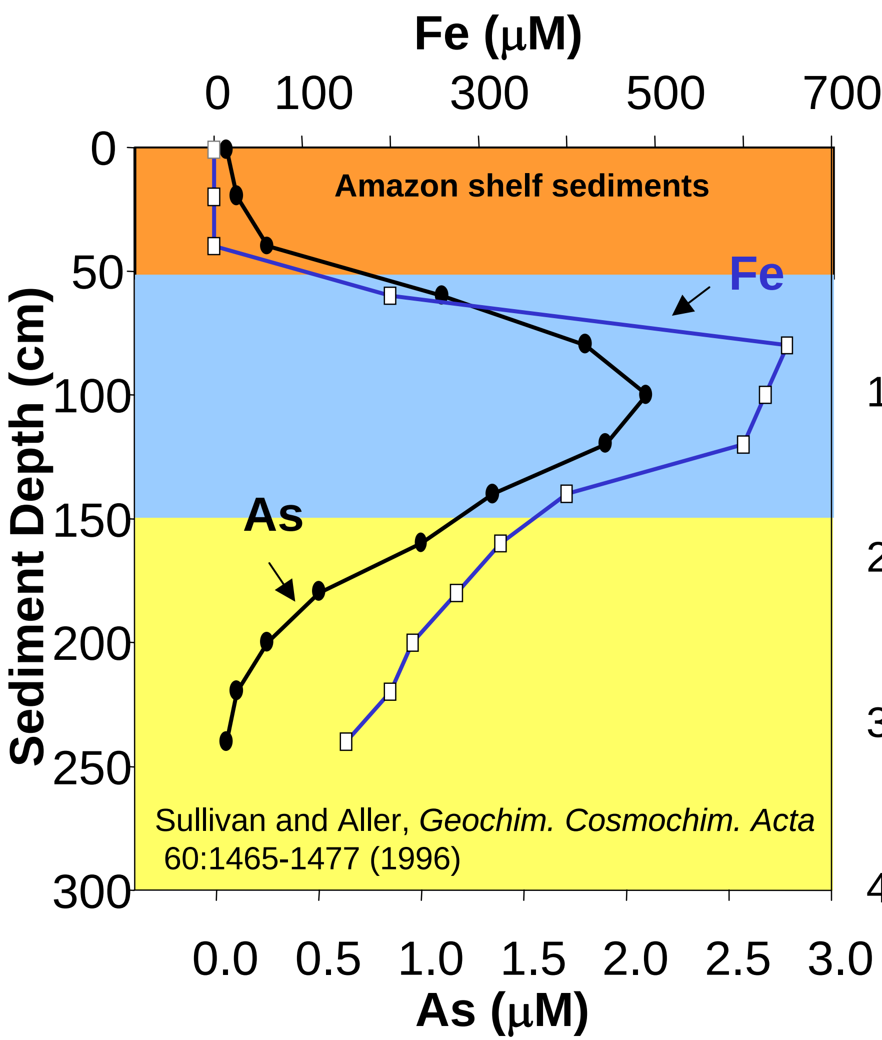

Protect Your Health
The soils and sediments in this area contain harmful levels of lead and other metals.
Small children and pregnant women are at the greatest risk from exposure.
KEEP CLEAN ! Wash your hands and face before you eat anything. Wash toys, bottles, and pacifiers if they have been in contact with soil or dust. Remove loose soil from your clothing, camping equipment, and pets before leaving the area. Wash all items when you return home.
EAT CLEAN ! Drink, cook, and wash only with water from home or other approved source. Do not use river water. Always eat at a table or clean surface off the ground. Clean fish thoroughly and eat only fish fillets.
PLAY CLEAN ! Children should play in grassy areas and avoid loose soil, dust, and muddy areas. No mud pies.
Healthy Choices......Healthy Kids !
For more information call Panhandle Health District / Kellogg at (208) 783-0707

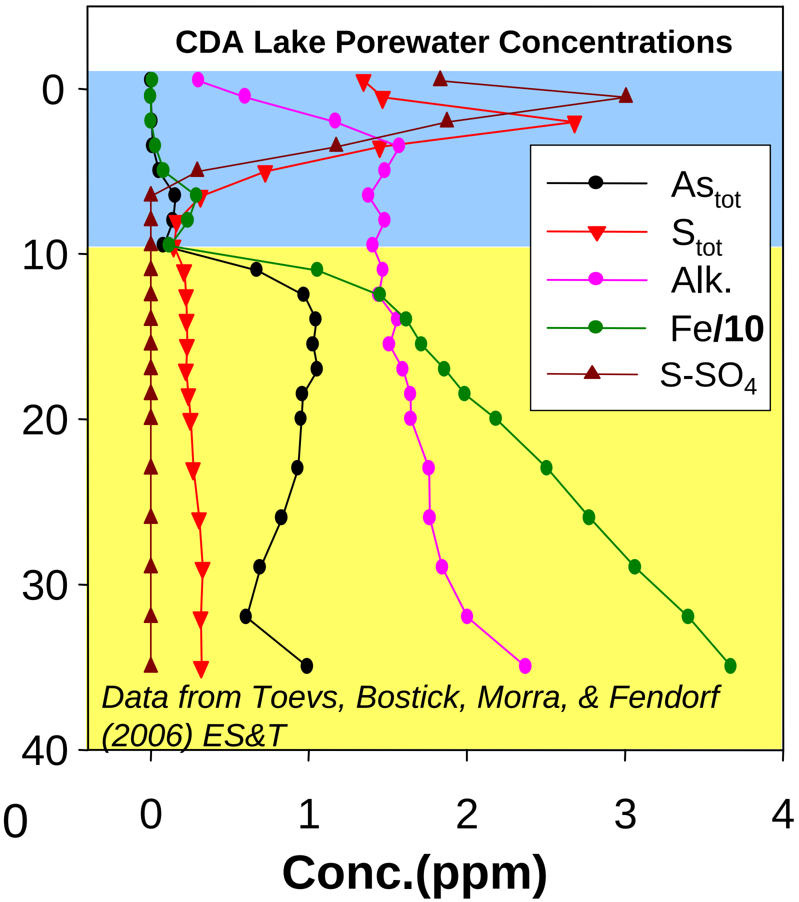
What Controls Dissolved Arsenic Concentrations in Wells?



- Arsenic is normally strongly retained by iron minerals
- *Microbes change (metabolize) the minerals in the soil and sediment, thereby releasing arsenic into groundwater.*
- *Conditions usually are reducing (usually +100 to -100 mV) where dissolved arsenic is found.*
- *Organic carbon quality and content critical to the development of reducing conditions*

Arsenic, Iron, and Sulfur Cycling





Trace Metal Retention and Release

Reduction:

$$Me\text{-}Fe(OH)_3 + OM \rightarrow Me(aq) + Fe^{2+} + CO_2 + H_2O$$

$$8Me\text{-}Fe(OH)_3 + HS^- + 15H^+ \rightarrow 8Me(aq) + 8Fe^{2+} + SO_4^{2-} + 20H_2O$$

However…

$$Fe(OH)_3\text{-}Me(sorb) \rightarrow FeOOH\text{-}Me(sorb) + H_2O$$

$$Me(aq) + Fe^{2+} + HS^- \rightarrow FeS\text{-}Me(sorb) + H^+$$

$$2As(aq) + 3HS^- \rightarrow As_2S_3 + 3H^+$$

$$Pb^{2+} + HS^- \rightarrow PbS + H^+$$

Arsenic Sequestration and Mobilization in Model Systems

- Oxic systems: Fe(III) oxides and sulfate
- Suboxic Systems: Fe(III) oxides $\rightarrow$ $Fe(II)_{aq}$, sulfate
- Anoxic Systems: Sulfate $\rightarrow$ sulfide, possibly Fe(III) oxides $\rightarrow$ $Fe(II)_{aq}$
- Field-Based Studies of As Cycling

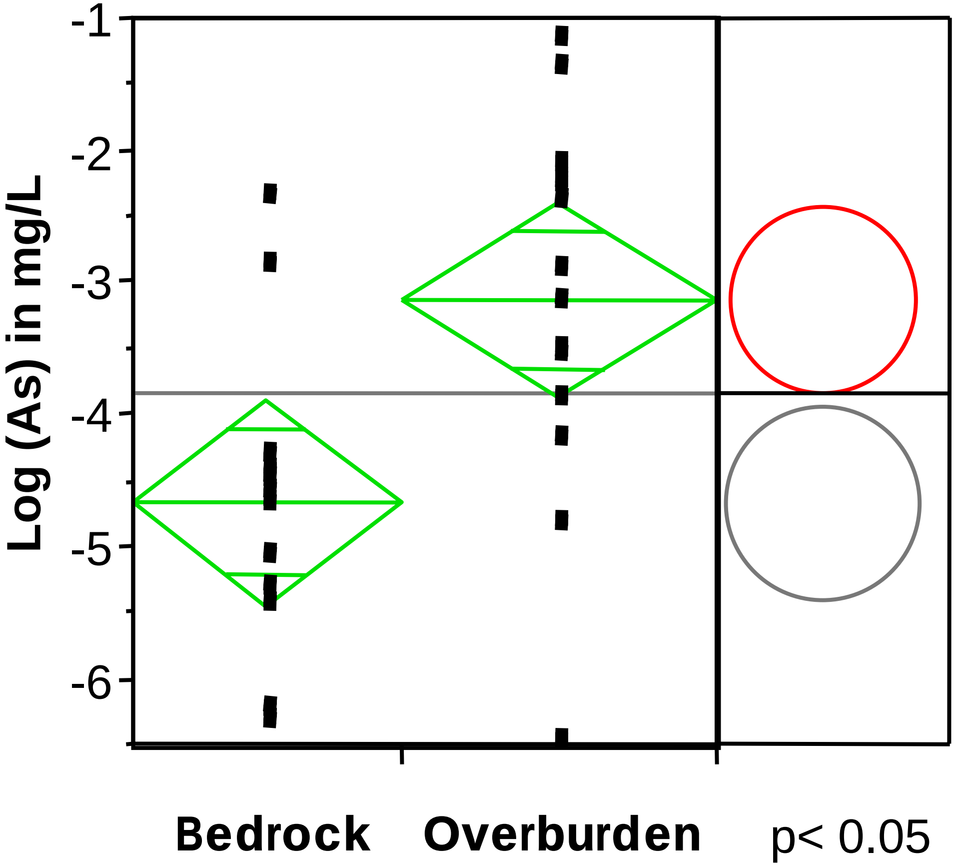
Arsenic-Iron-Sulfur Cycling in 3 Field Sites

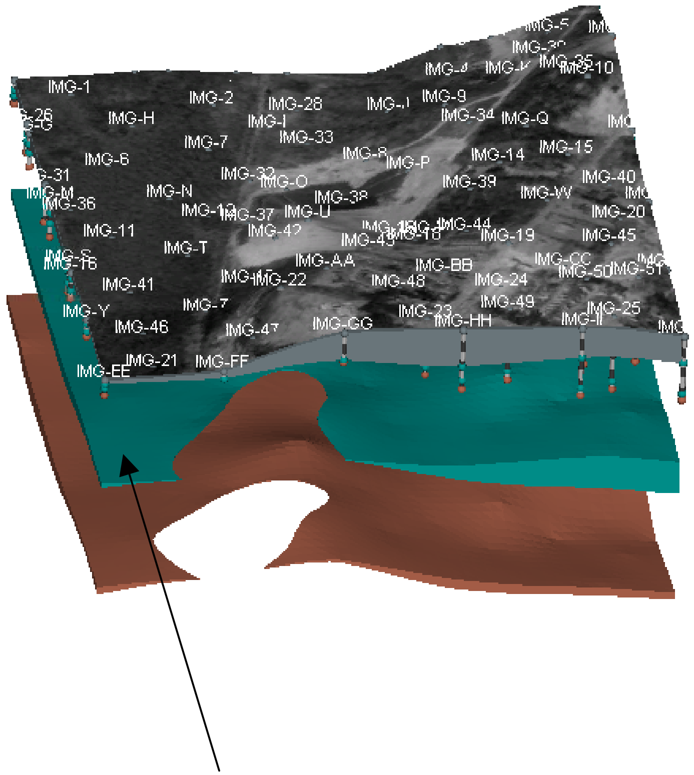
- Coakley Superfund Site (NH)
- Coeur d'Alene Mining District (ID)
- Cambodian Groundwater Systems

Collaborators (Dartmouth): Carl E. Renshaw, Jamie L. deLemos, Stefan Stürup, Xiahong Feng

Reference: de Lemos et al. (2005) ES&T

As Source: Overburden-Clay Aquitard



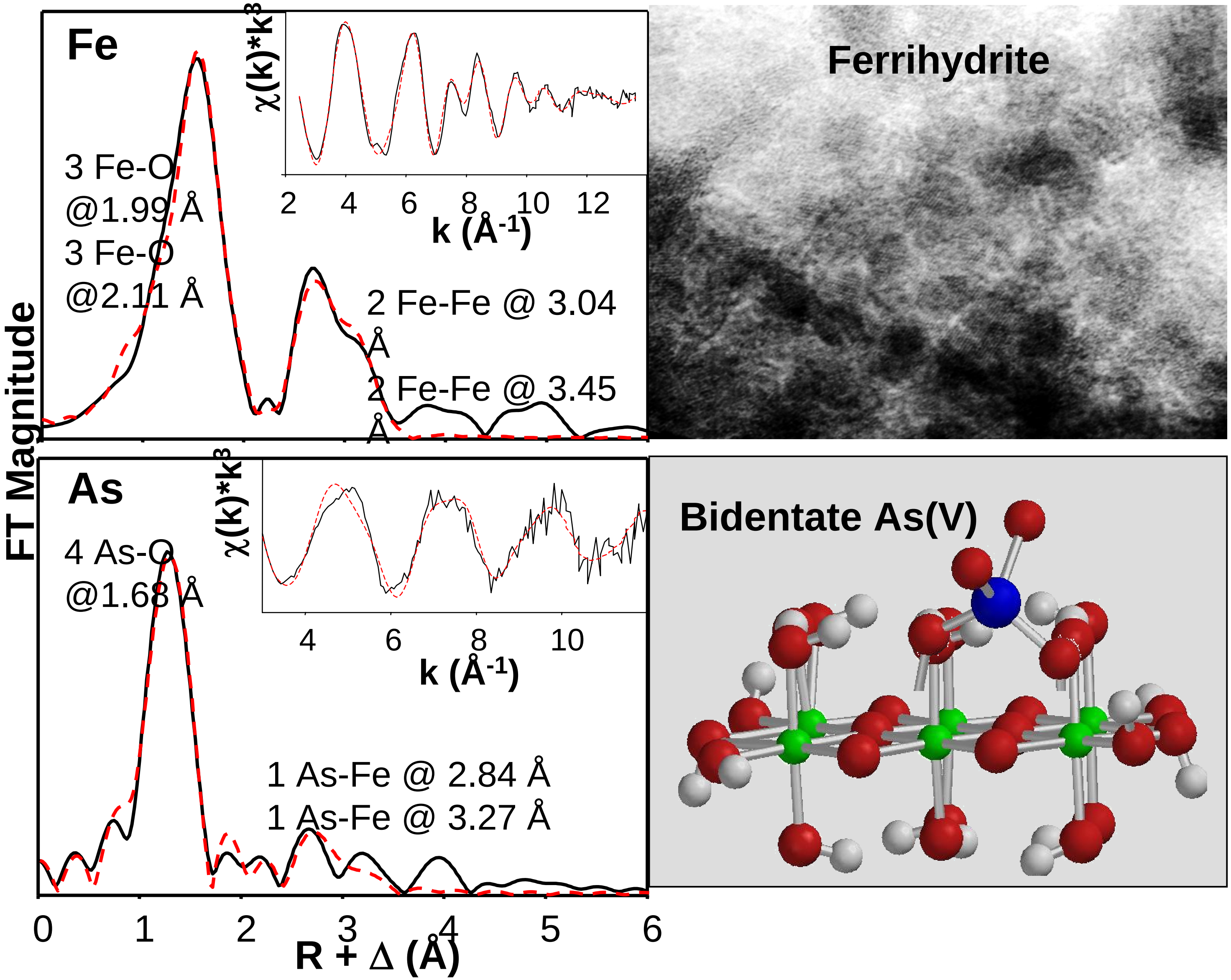


3-10m Thick Clay Layer

K = 7 x 10^{-7} cm/s

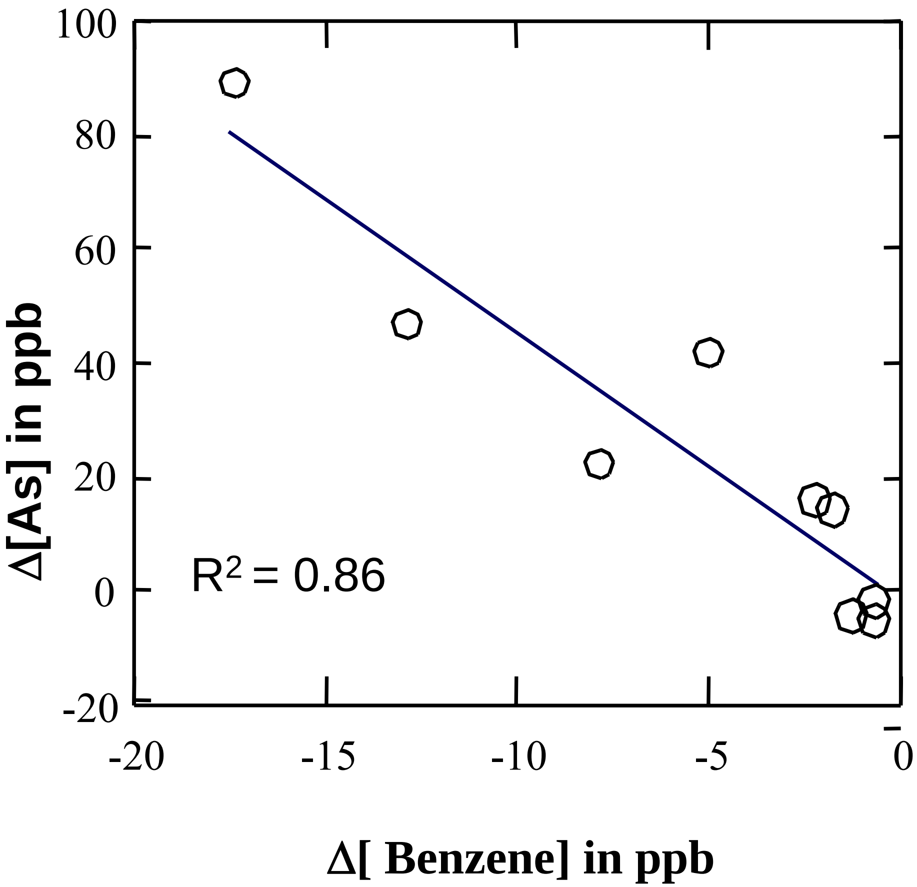
[As]~20 ppm

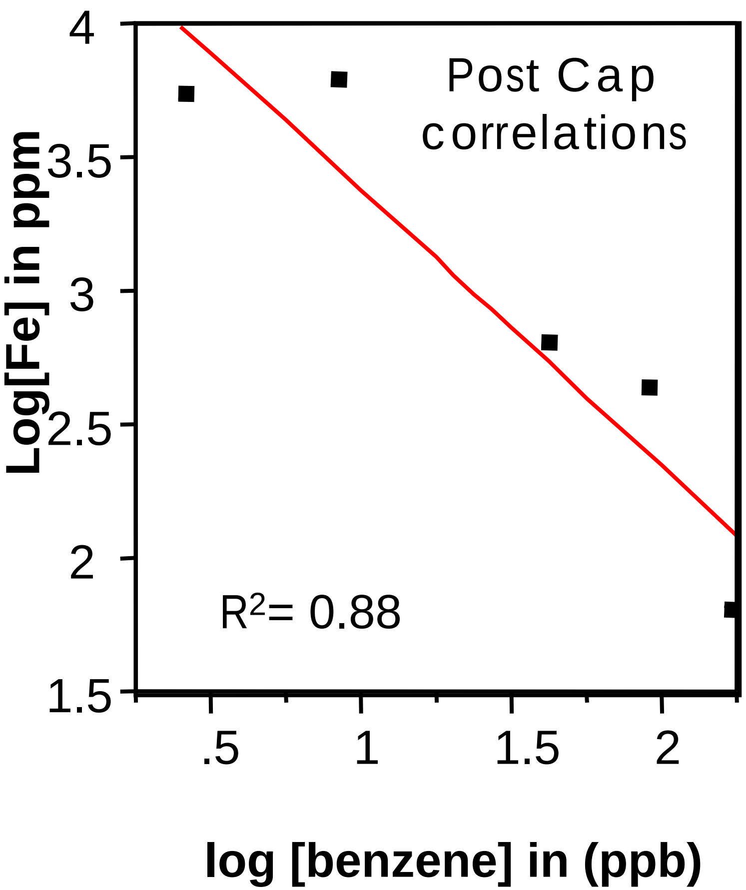
As Source : Characterization



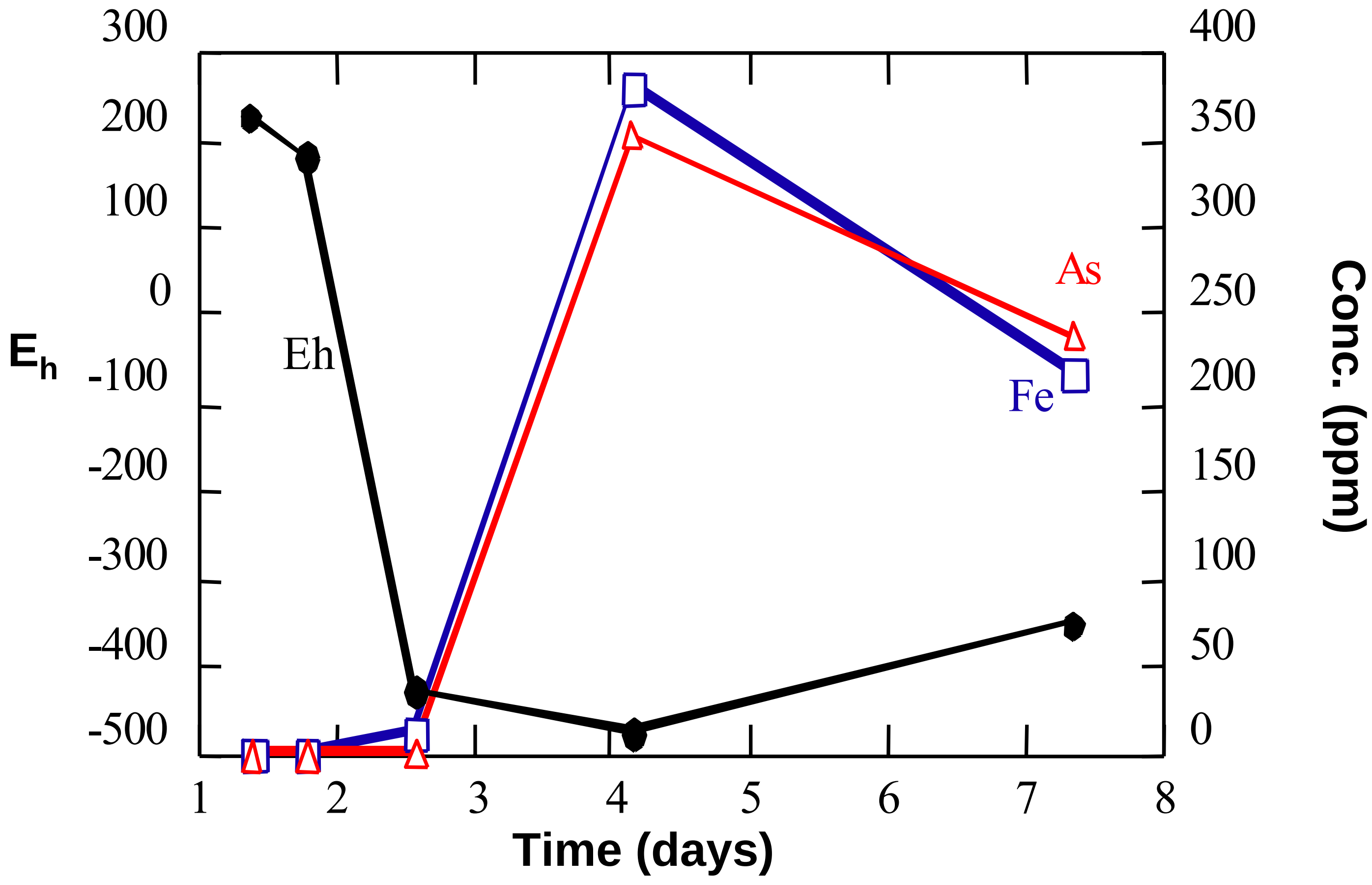
Coakley: Arsenic Mobilization & Natural Attenuation

$$30Fe(OH)_3 + C_6H_6 + 60H^+ \rightarrow 30Fe^{2+} + 6CO_2 + 78H_2O \quad \Delta G^o = -2359.96\ kJ$$





Coakley: Batch Experiments and Field Data



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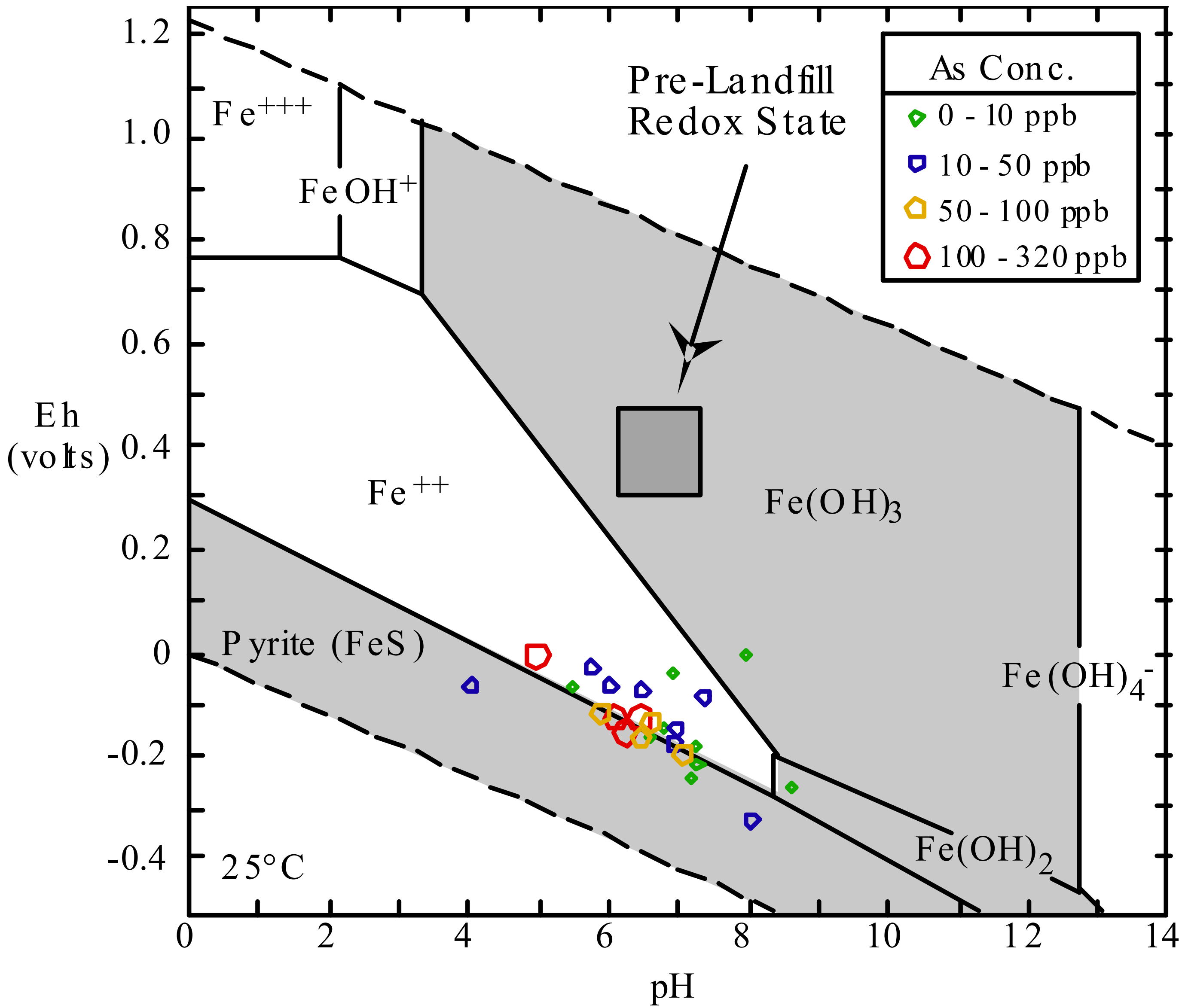
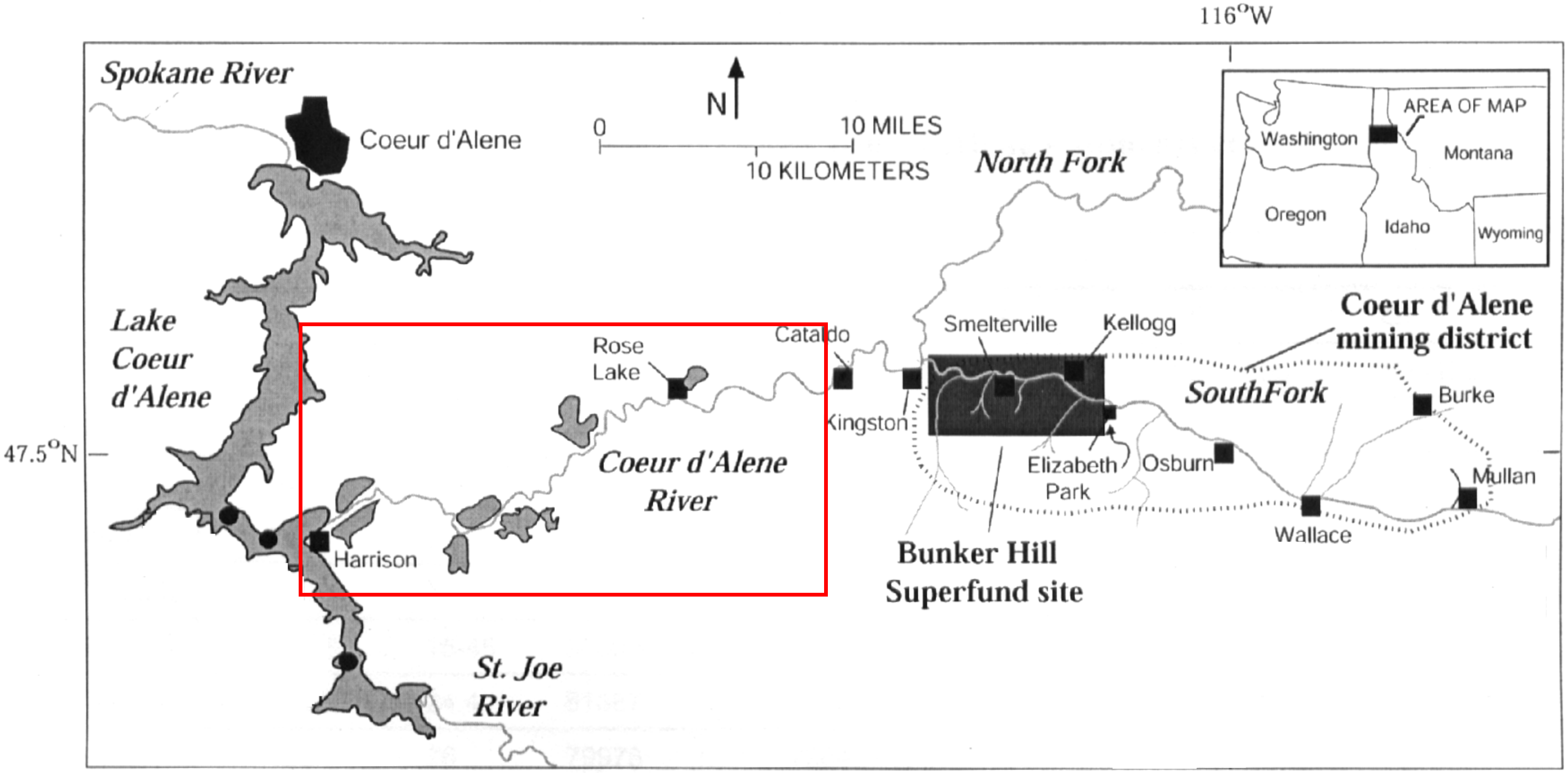


Arsenic-Iron-Sulfur Cycling in 3 Field Sites

- Coakley Superfund Site (NH)
- Coeur d'Alene Mining District (ID)
- Cambodian Groundwater Systems

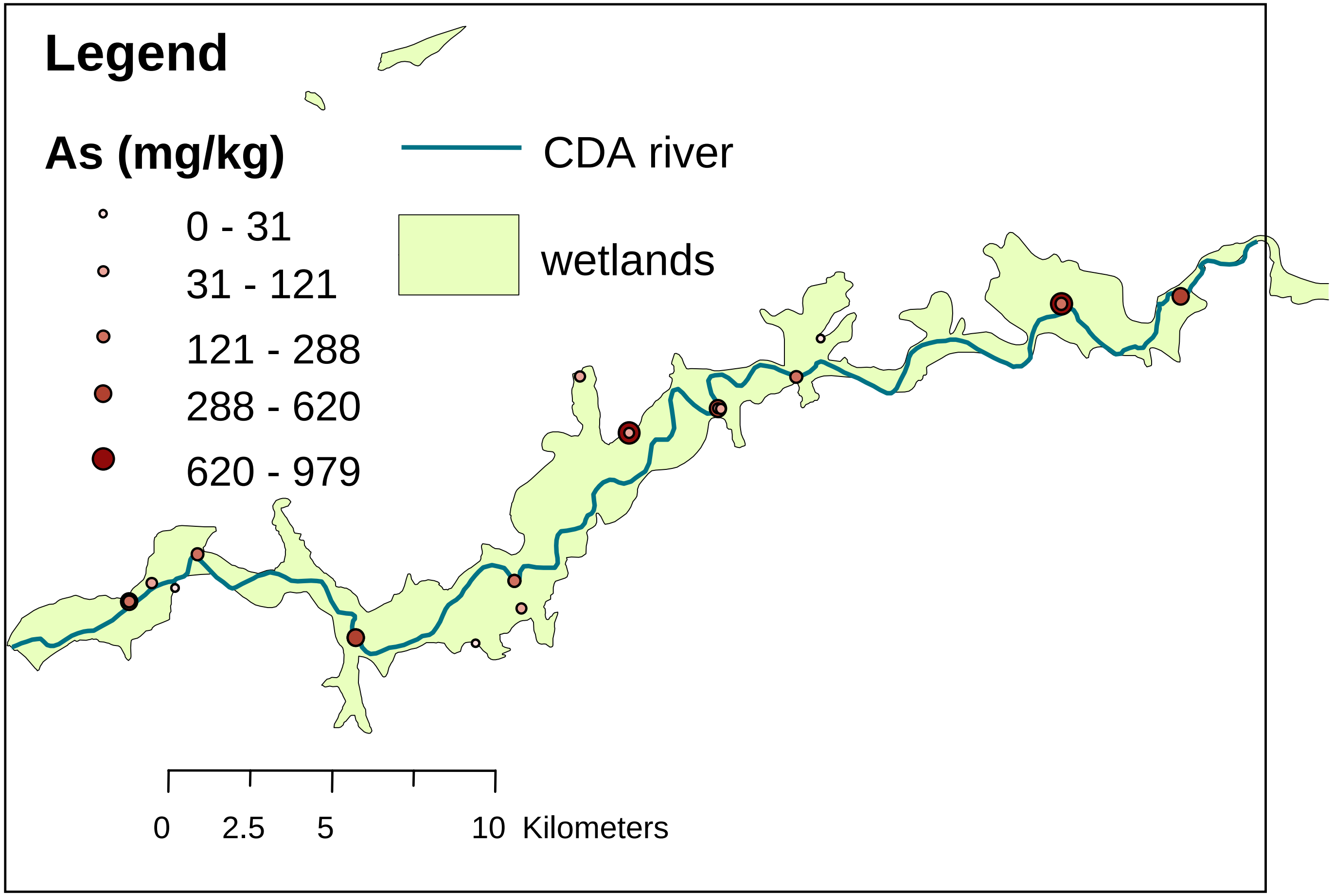
Collaborators: **Gretchen Gehrke (Dartmouth),)**
Gordon Toevs and Matt Morra (Univ. Idaho)
Scott Fendorf and Matt Polizzotto (Stanford)

Coeur d’Alene (CDA) Mining District, ID

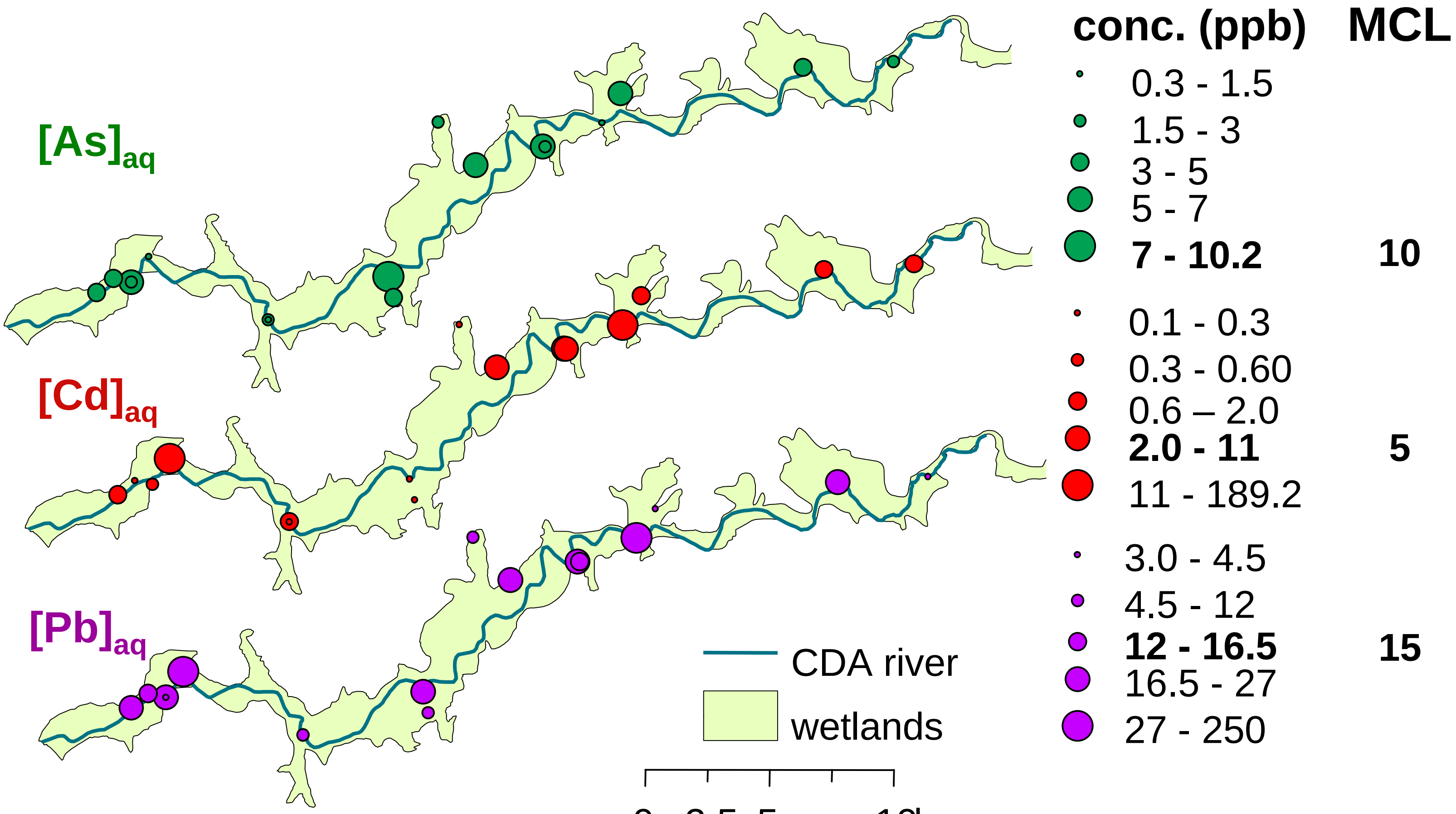


Downstream of the Lateral Lakes

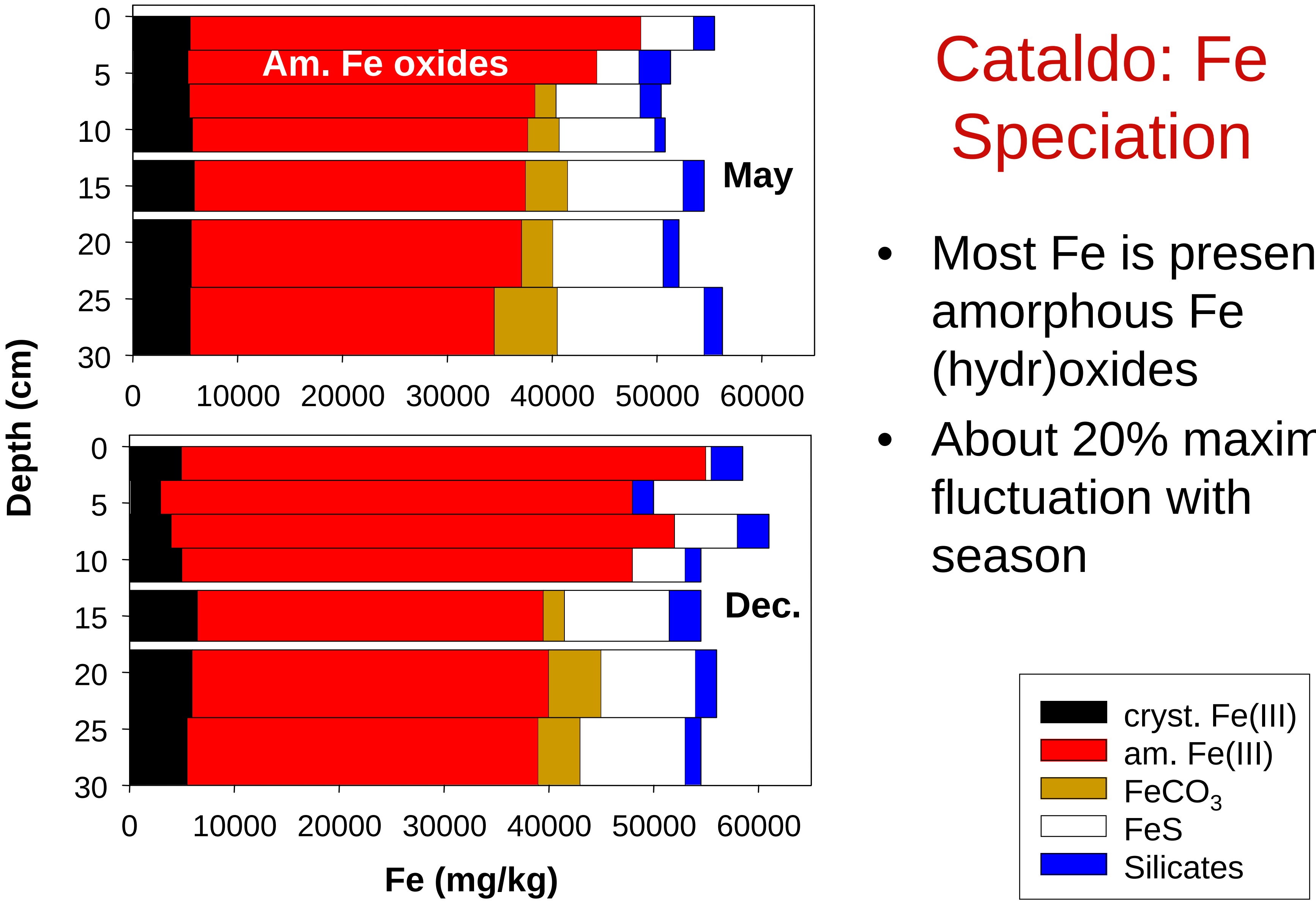
CDA: As Distribution (mg/kg)



CDA: Dissolved Contaminants



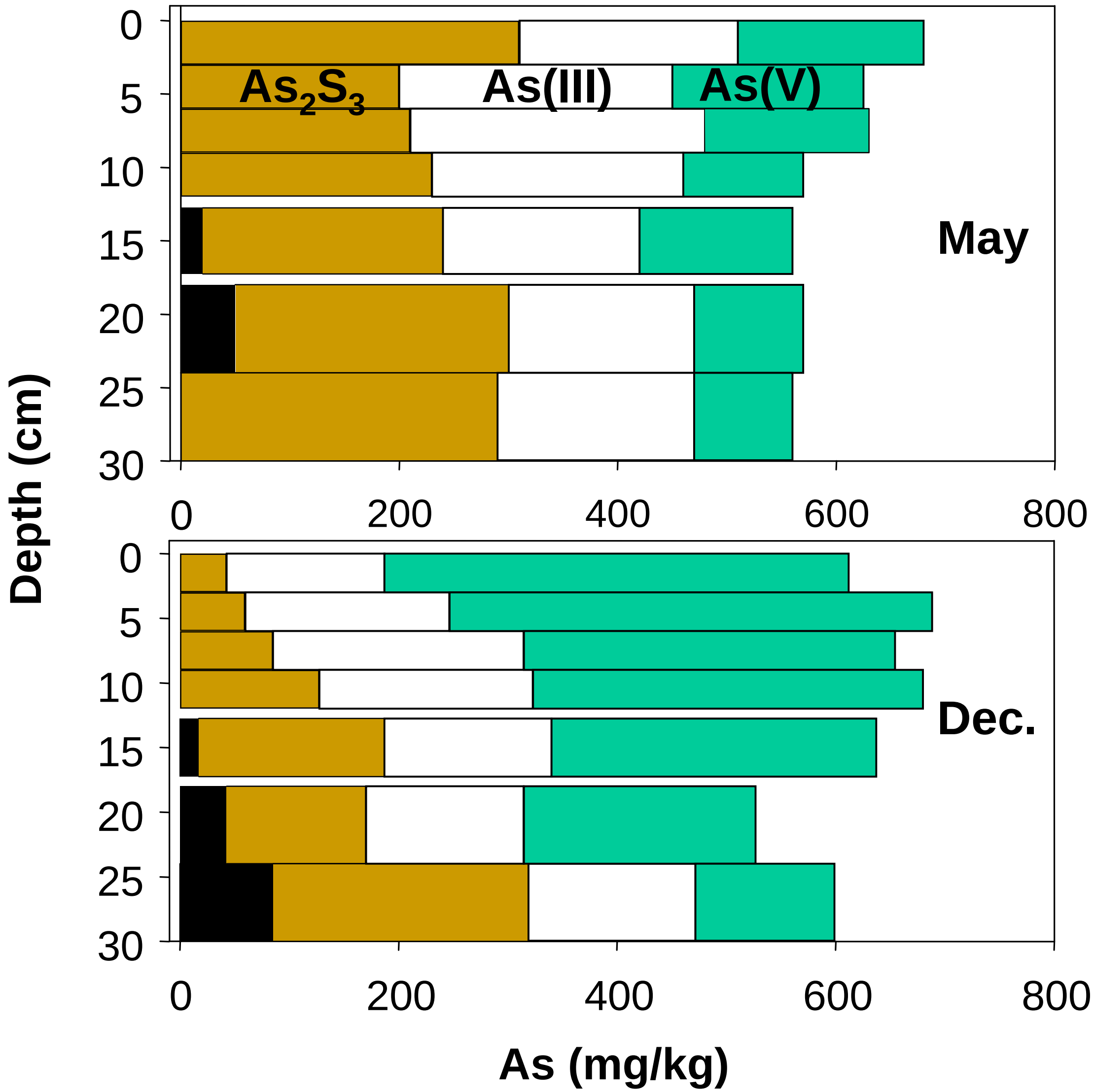
Selected contaminants often are correlated spatially, but in no obvious way with distance from source



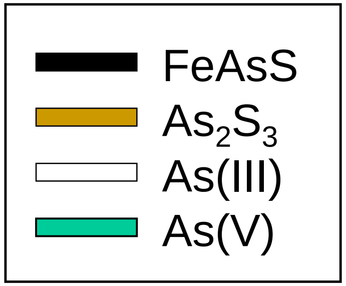
Cataldo: Fe Speciation

- Most Fe is present as amorphous Fe (hydr)oxides
- About 20% maximum fluctuation with season

Cataldo: As Speciation



- Large seasonal variation in the occurrence of reduced arsenic phases in Cataldo Wetland sediments

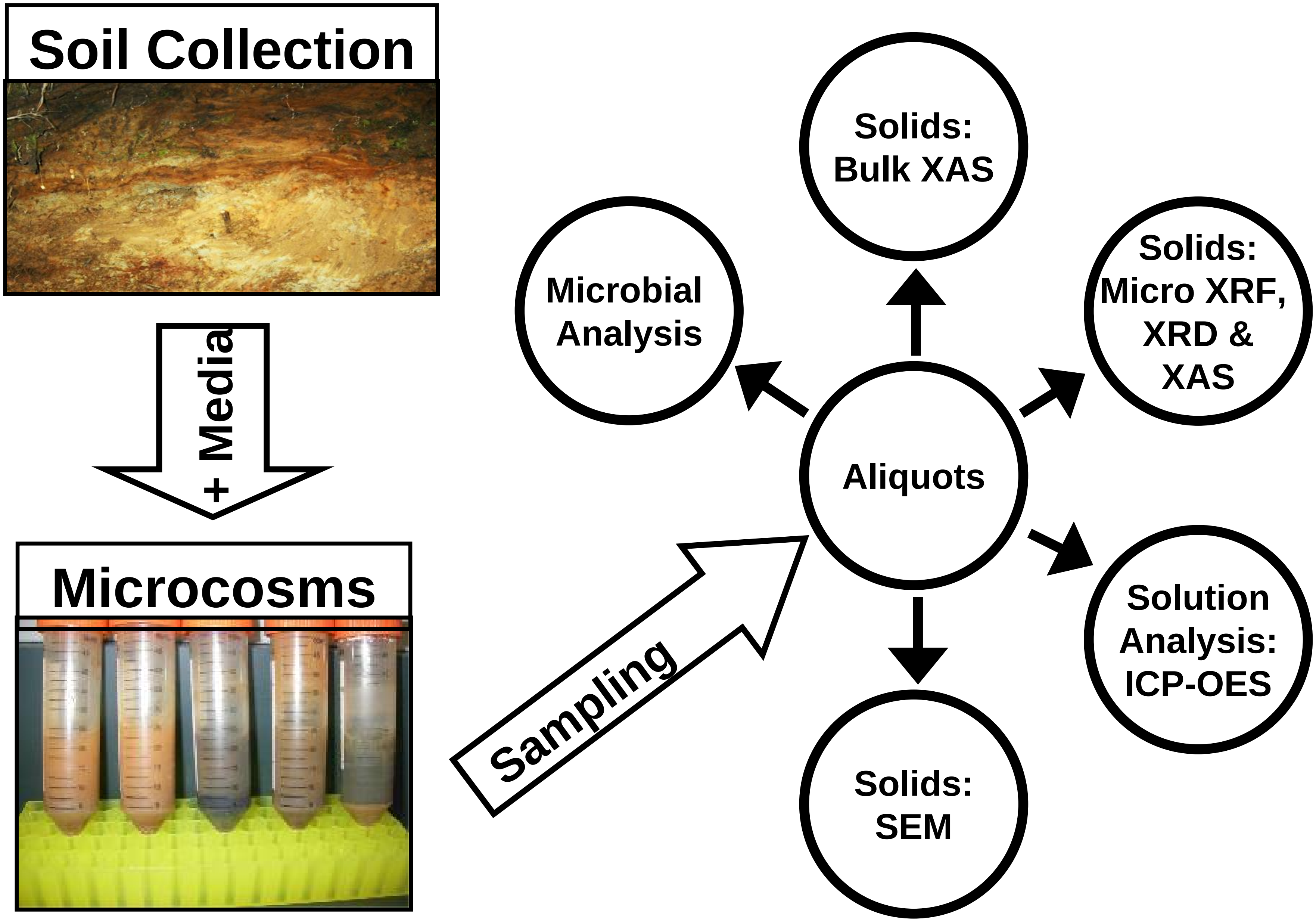


Experimental Studies of Sulfate Redox Transformations Coupled to As Levels: Coeur d’Alene Mining District

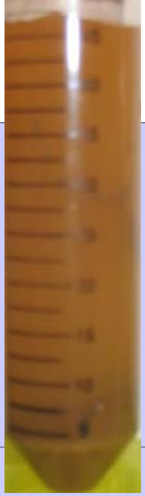
Students:
Andrew N. Quicksall
Samantha Saalfield
Joshua D. Landis

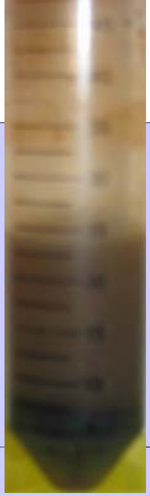
Coeur d’Alene River
At Swan Lake, ID

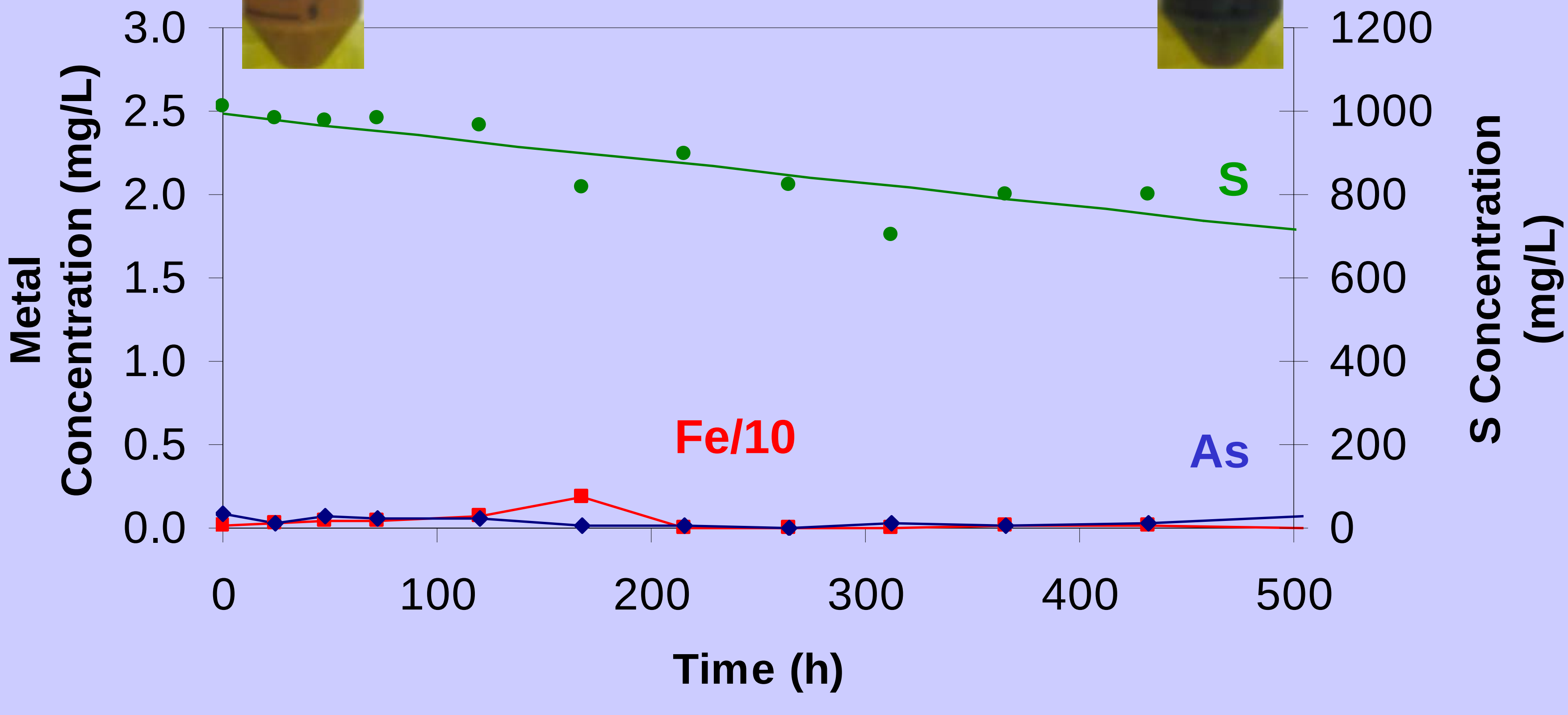
Incubations

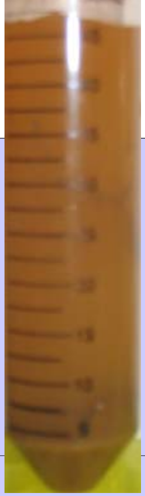


CDA Cataldo
Lactate Amended

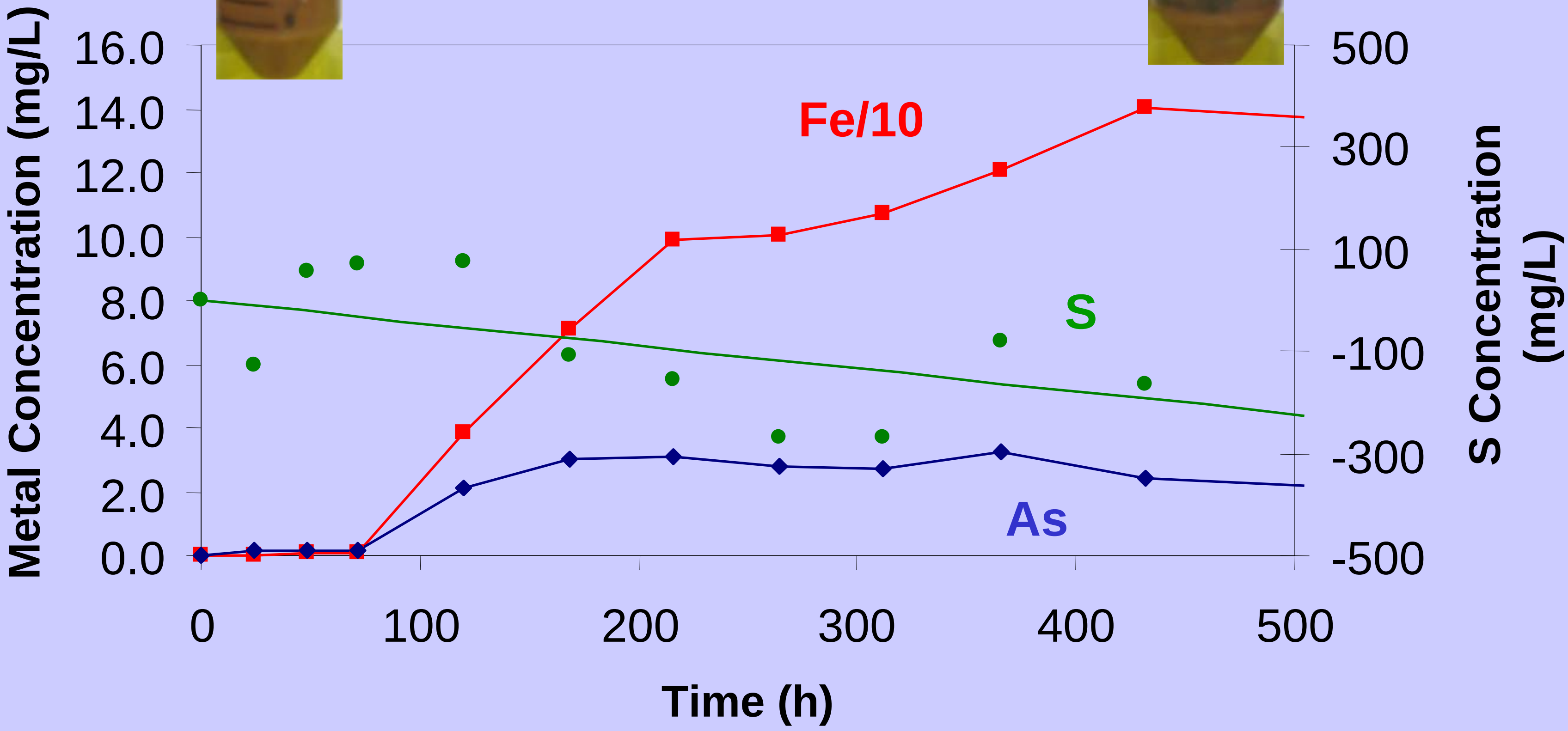






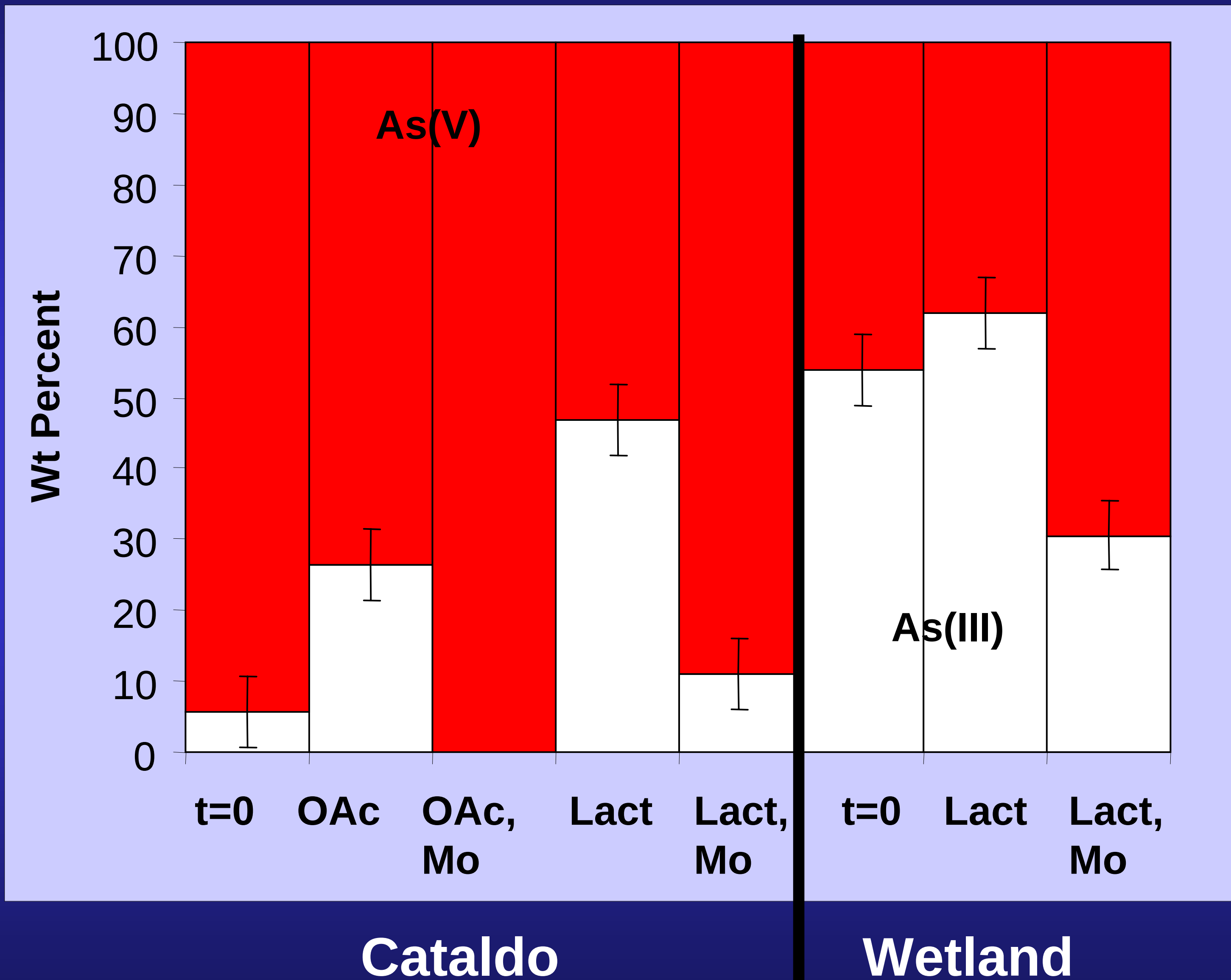


CDA Cataldo Lactate+Molybdate Amended

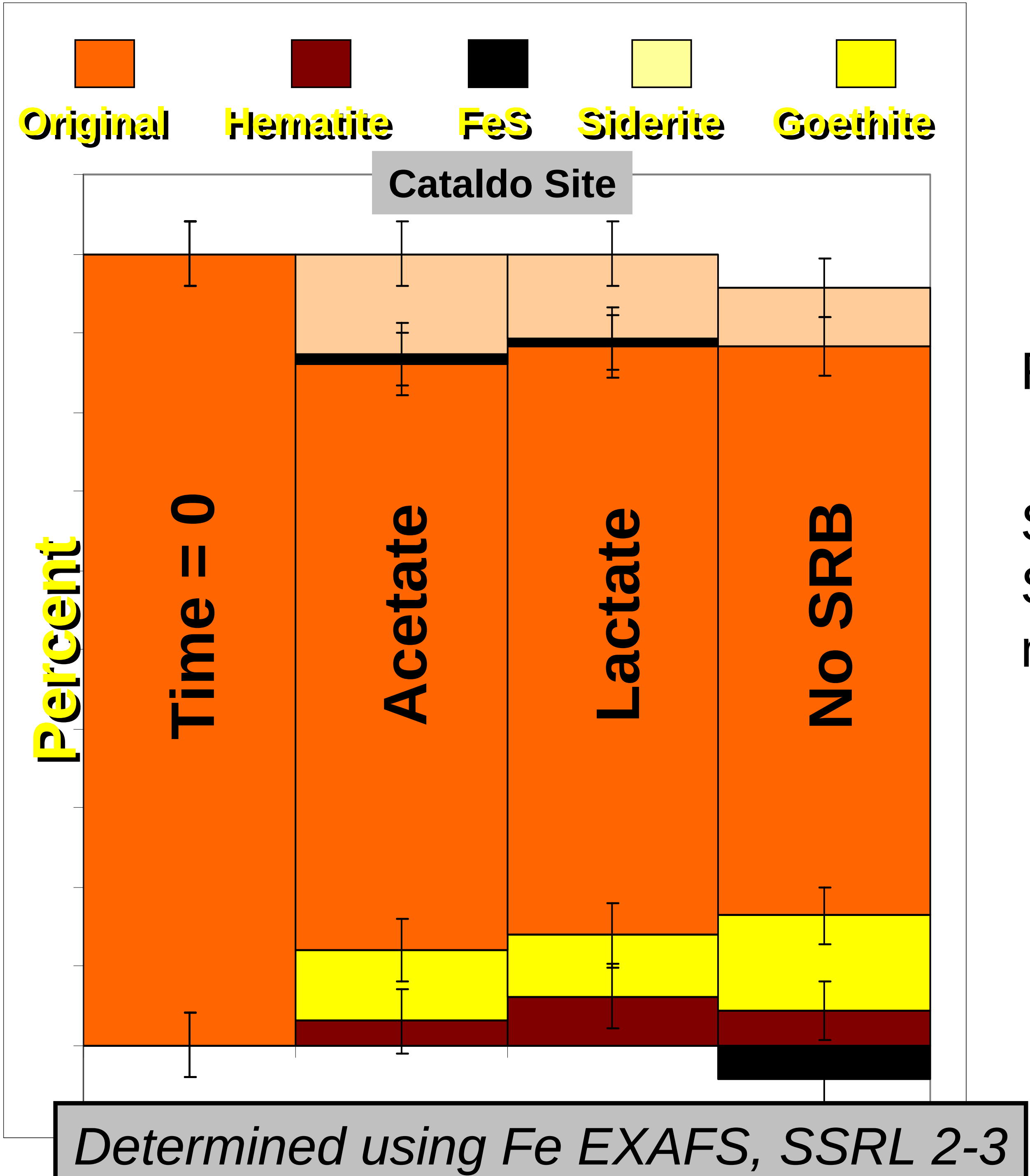


Plotted as Change from T=0

Solids: As Speciation



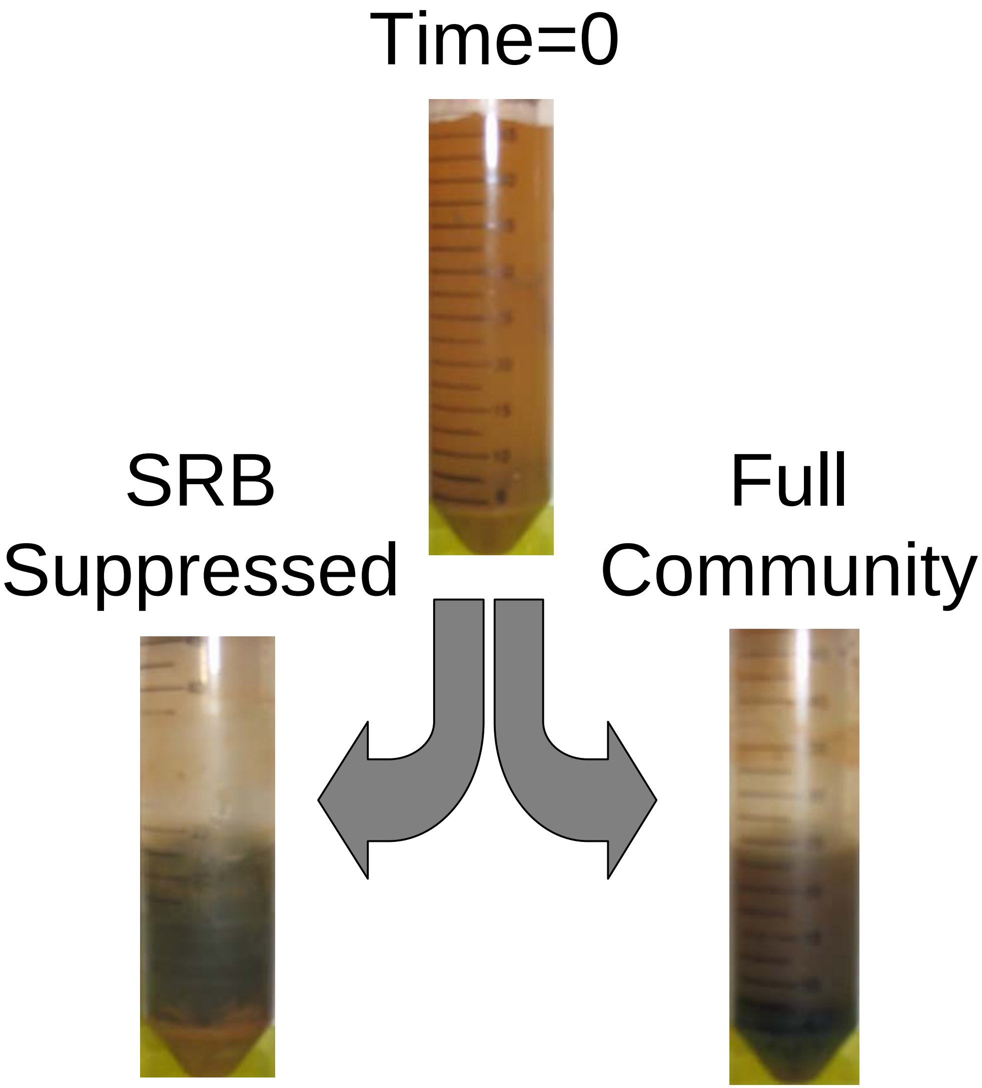
Determined using As XANES, SSRL 2-3



Solids: Fe Speciation

Fe(II) mineralization

Siderite present in SRB suppressed with net loss in FeS



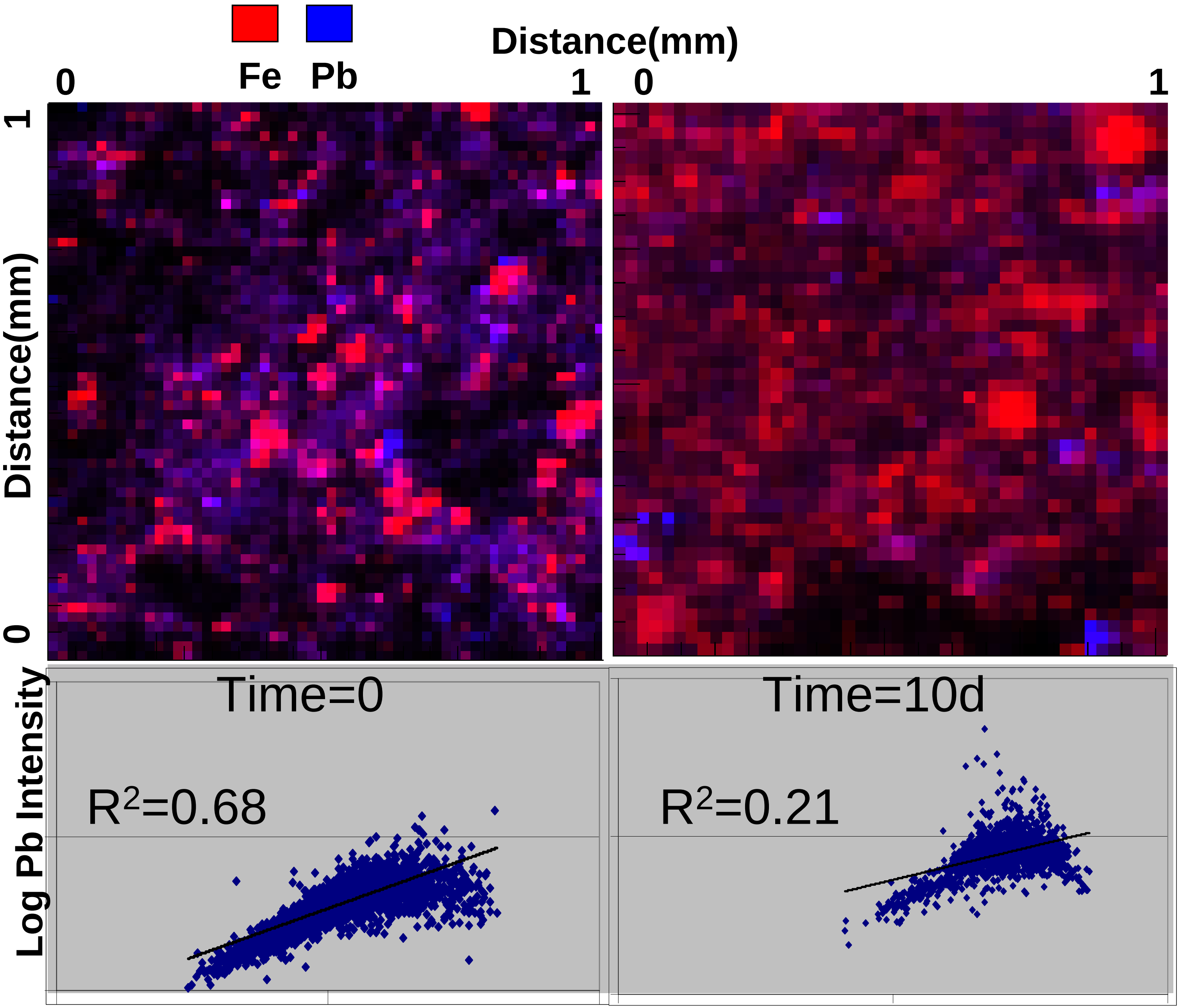
Changes as seen in representative microcosms

Temporal Change

Paired Fe and As Release in SRB Suppressed Microcosms

Fe and As were sequestered when FeRB and SRB were active

Soil Chemistry Cataldo Site



Fe-Pb Decoupling

“hot spot” generation

Determined via µXRF, NSLS x26A

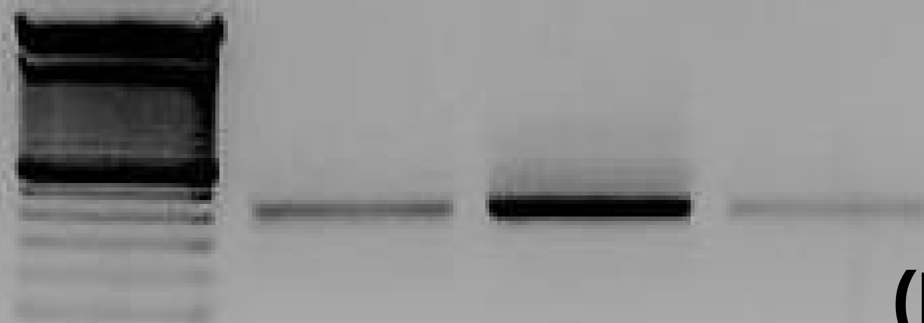
Microbial Ties

- The suppression via molybdate yields strong evidence for SRB involvement in trace element retention

- Can we explain this observation via direct methods to identify specific microbial populations?

Sequencing of cloned 16S rDNA soil extracts

Dominant Microbial Species



Lactate + Molybdate (SRB Suppressed)

Anaeromyxobacter dehalogenans (100%)

Metal Reducer
Particularly Fe
No S Reducers

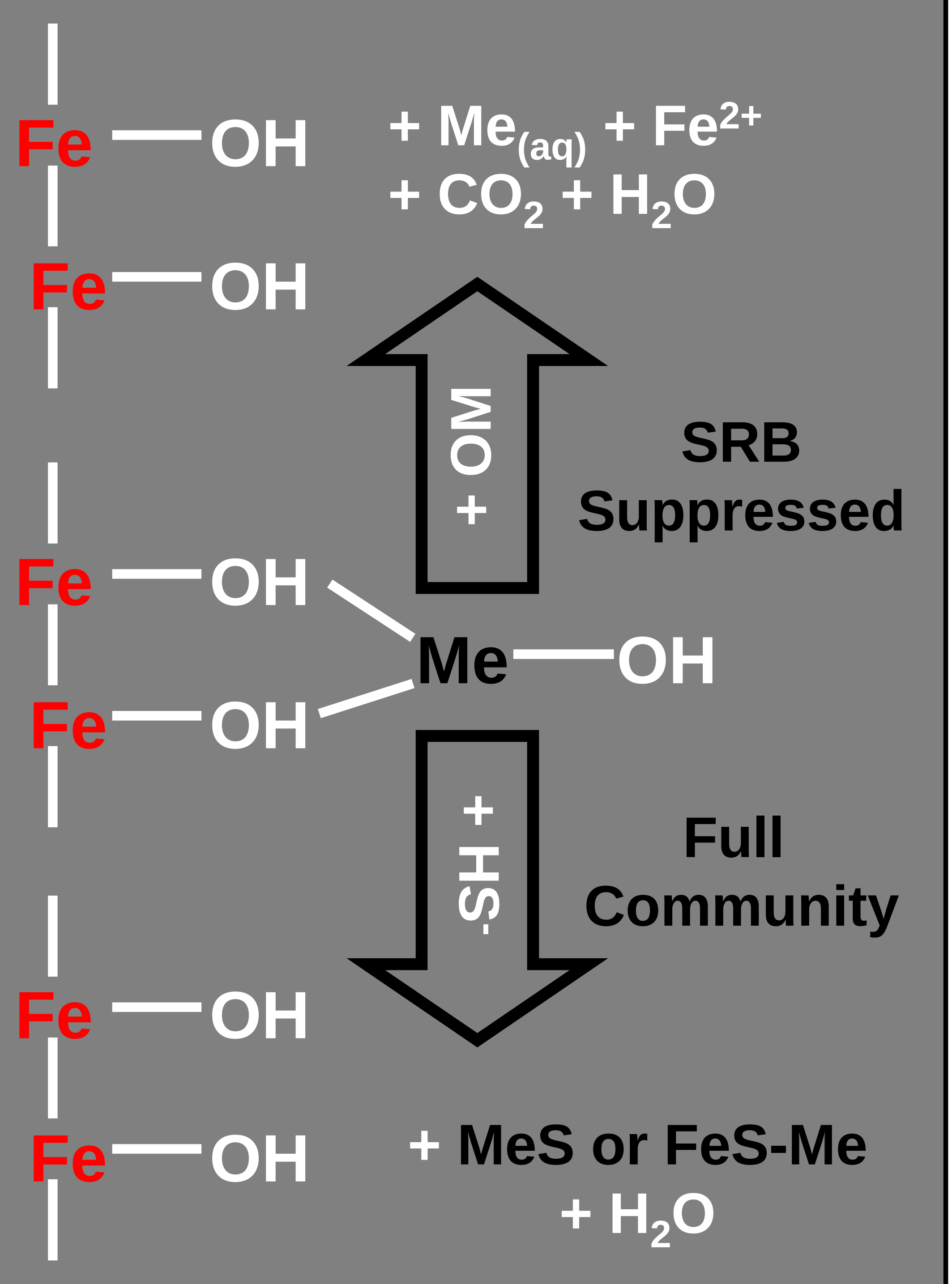
Lactate (Full Community)

Clostridia (89-91%)

Obligate Anaerobes
Many Can Reduce Fe

Desulfitobacterium hafniense (89%)

Can Reduce SO_4^{2-}



Observations:

- Iron reduction is central to the release of trace metals
- Mineral transformations govern trace metal sequestration

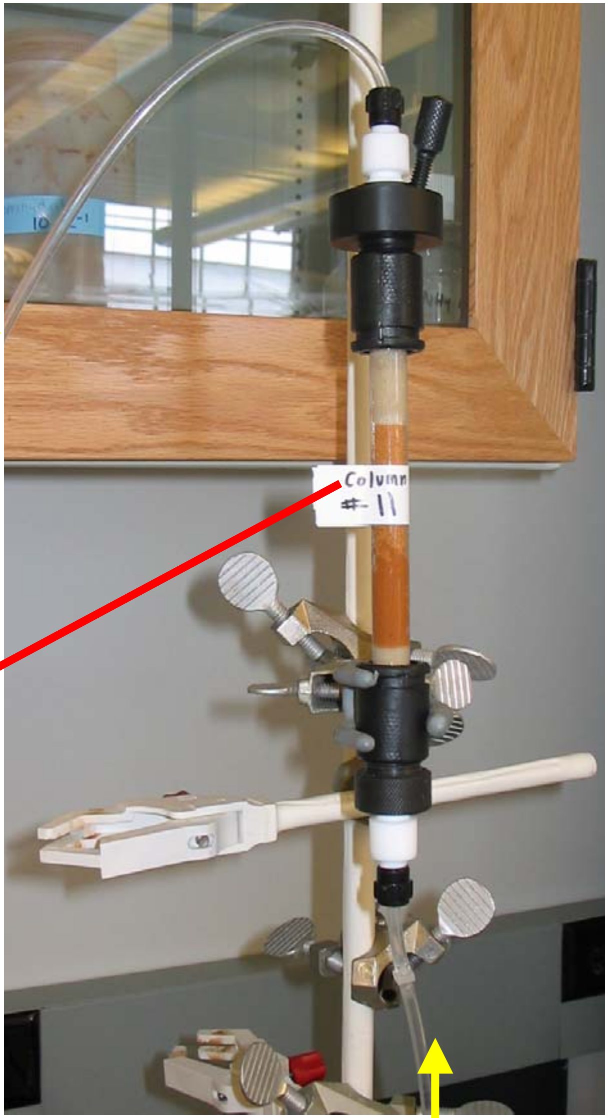
Implication:

- Solution Concentrations are ultimately governed by balanced Fe and S Reduction

PRIMARY EXPERIMENTAL METHODS

Flow-through experiments

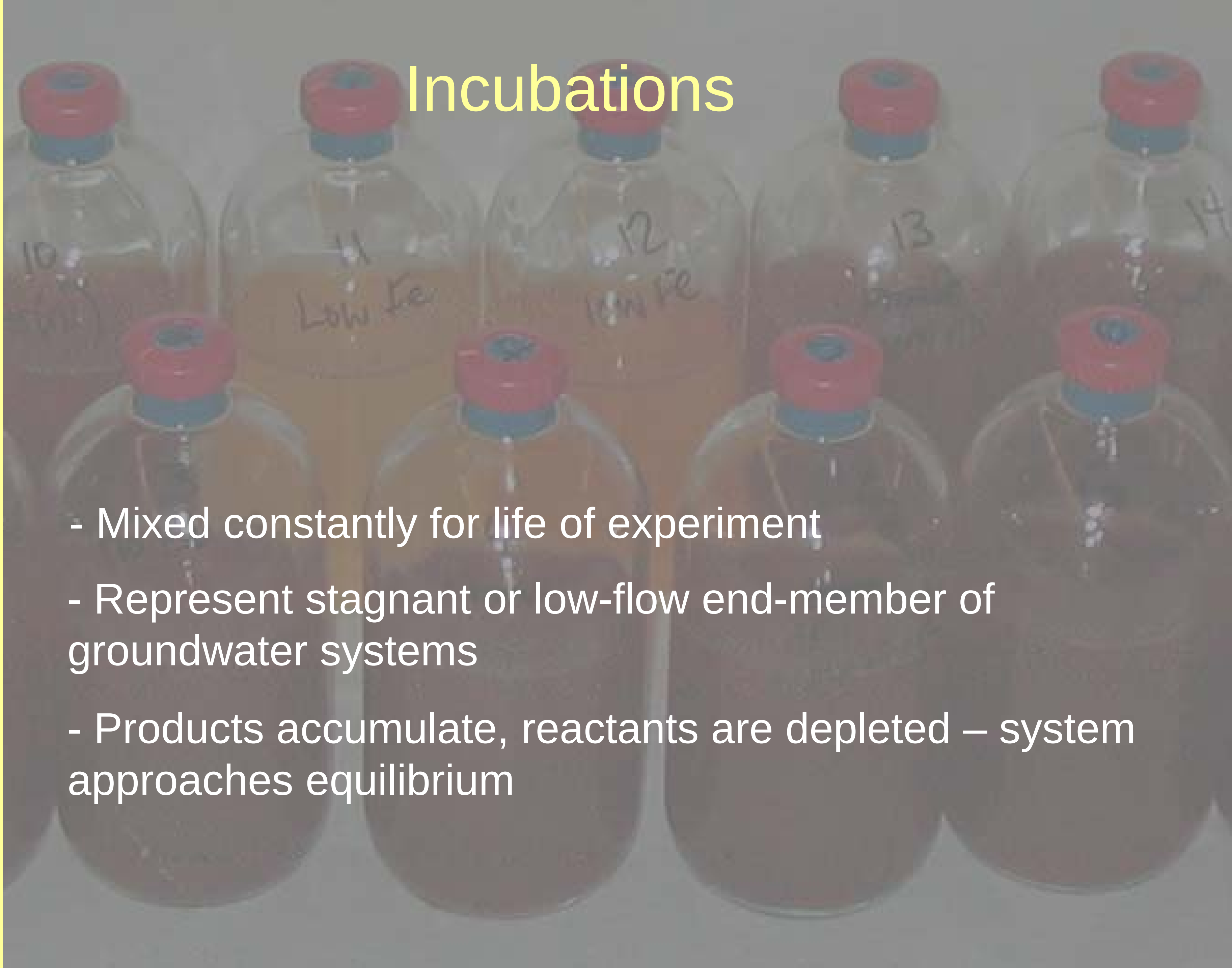
Effluent
(to fraction collector)



Iron-coated sand
(and/or arsenic
and/or microbes)

Influent

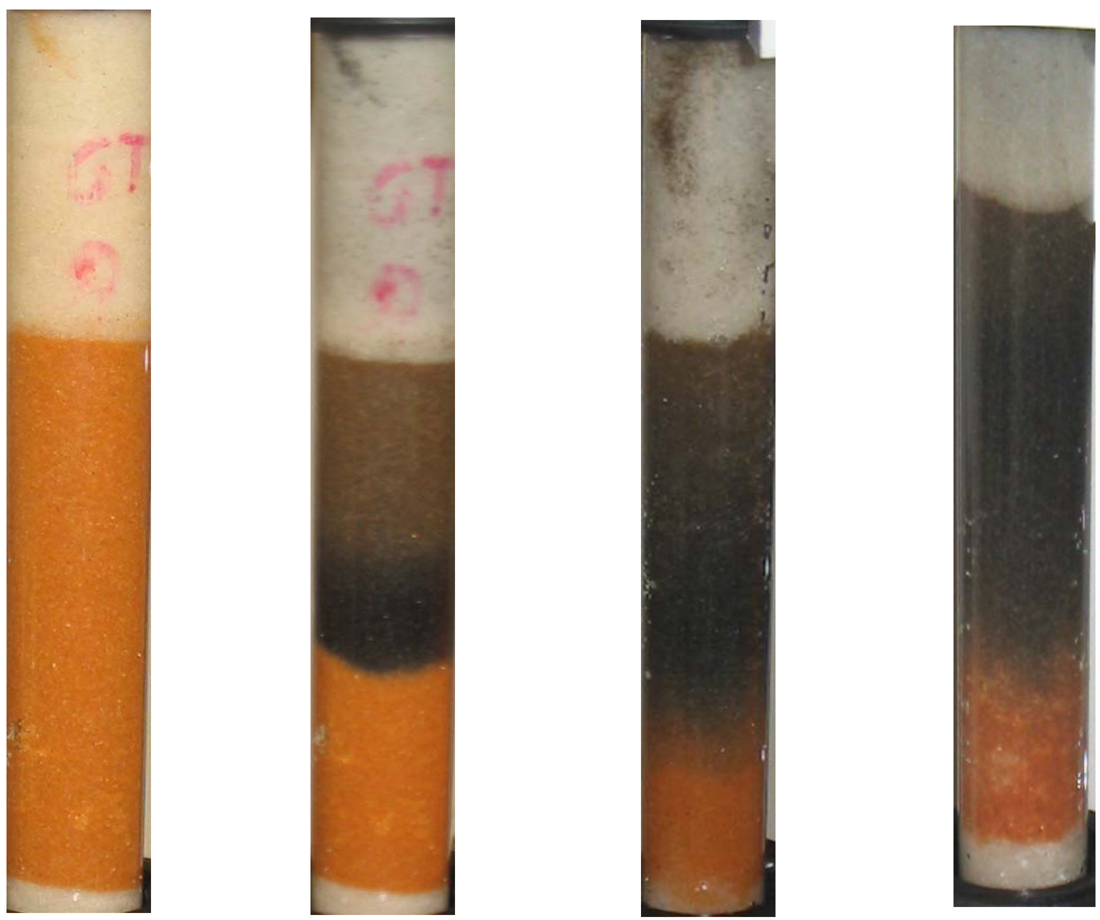
Incubations



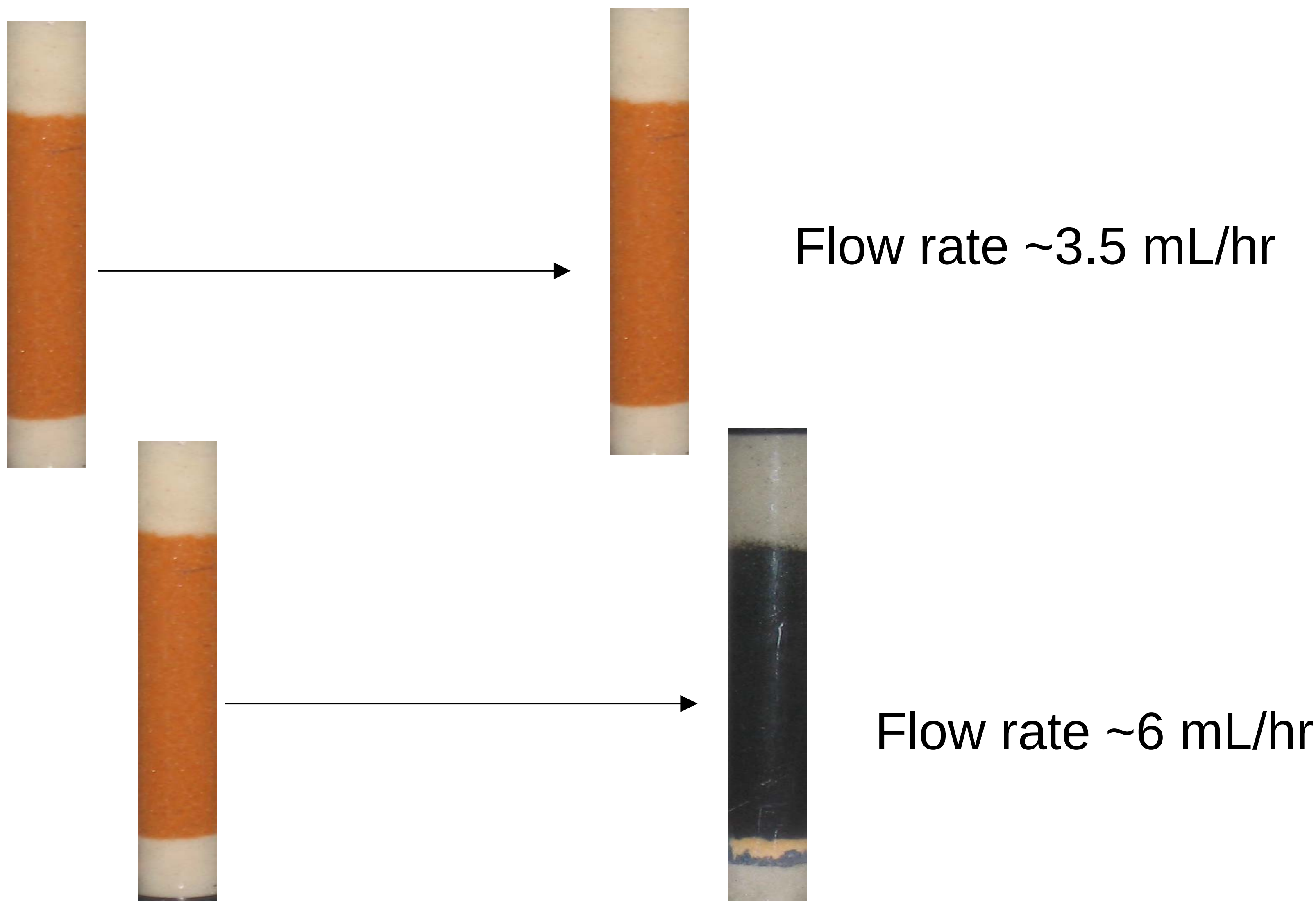
- Mixed constantly for life of experiment
- Represent stagnant or low-flow end-member of groundwater systems
- Products accumulate, reactants are depleted – system approaches equilibrium

How does sulfate input concentration affect mineralogy in *D. desulfuricans* columns?

5 µM 0.8 mM 10 mM 20 mM

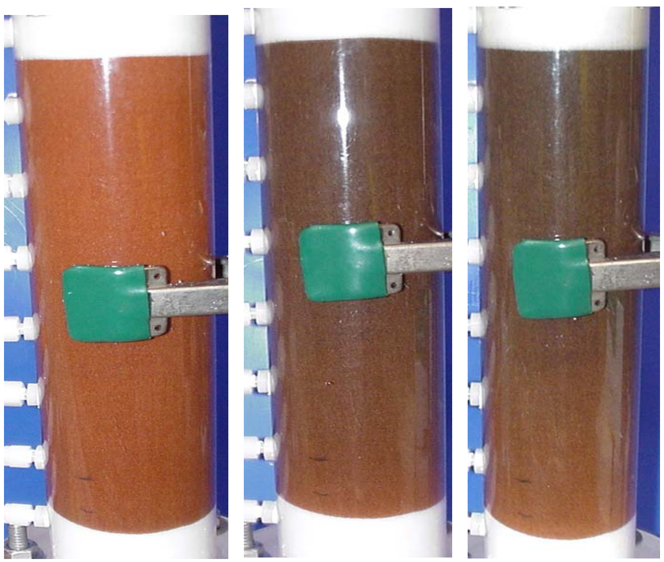


By what mechanisms does flow rate affect mineralogy in iron oxide-sulfide columns?

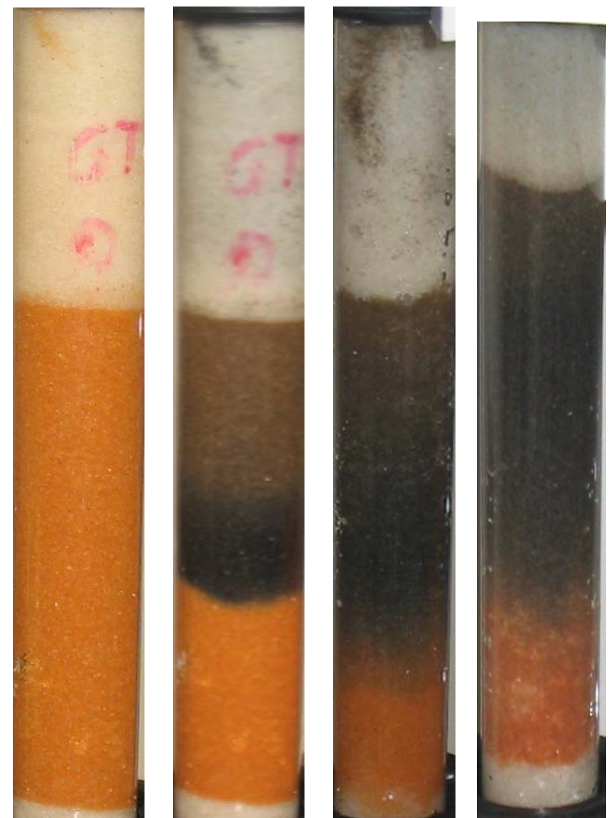


What determines which minerals form in SRB/FeRB systems?

- Magnetite formation



-Magnetite + iron sulfide formation

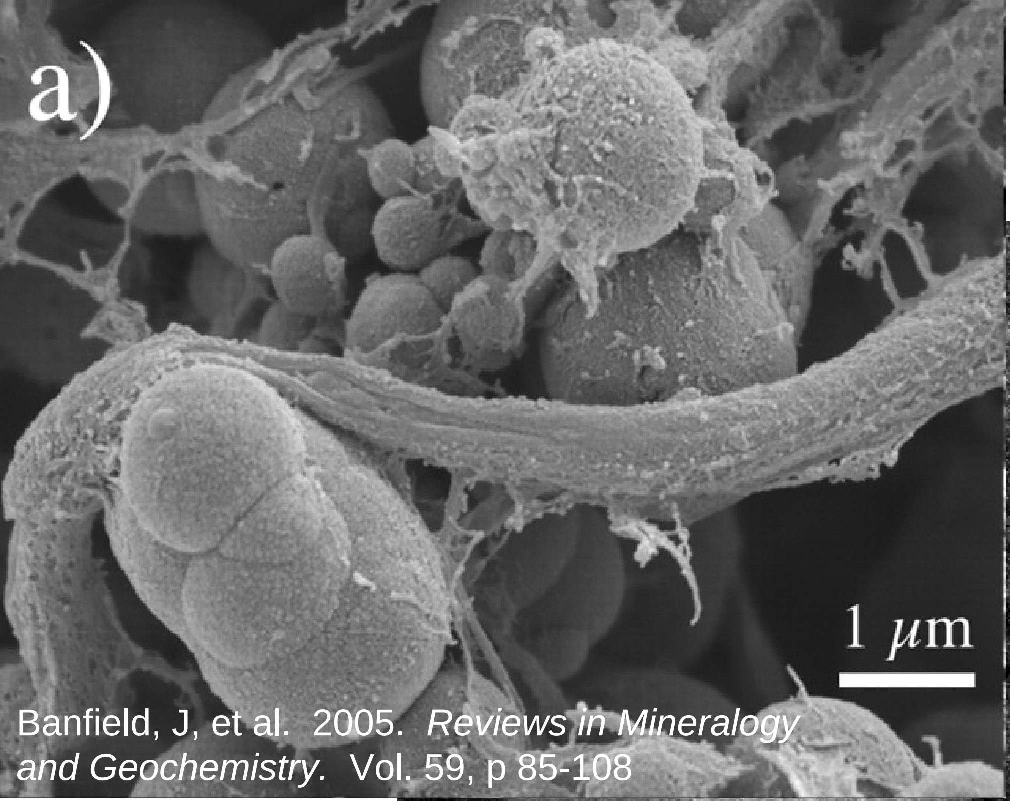


What mineral transformations occur under stagnant conditions in *D. desulfuricans* incubations?

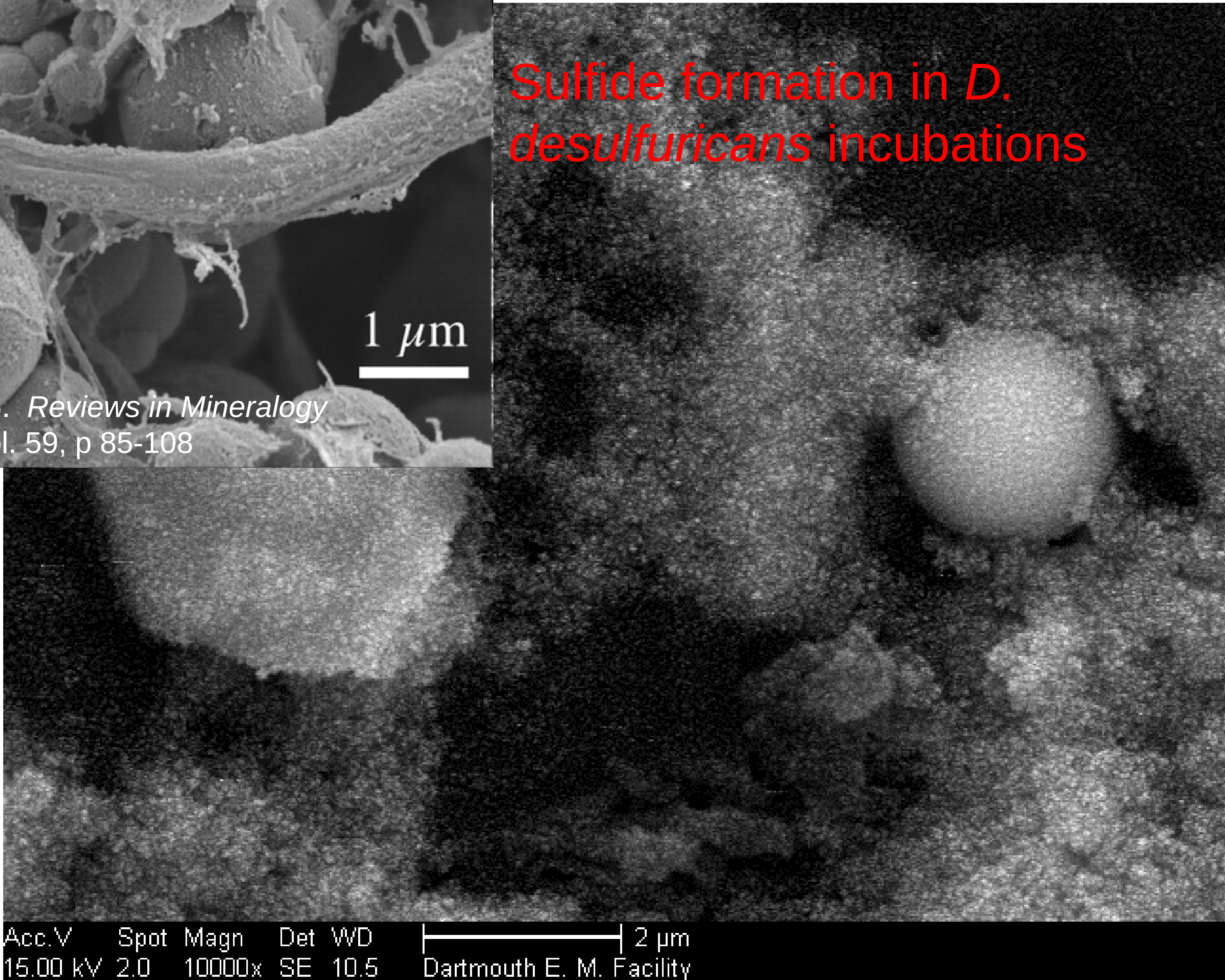
SRBs, 10 mM SO_4 No bugs

Only modest changes in Fe mineralogy (not enough carbon to reduce all Fe)

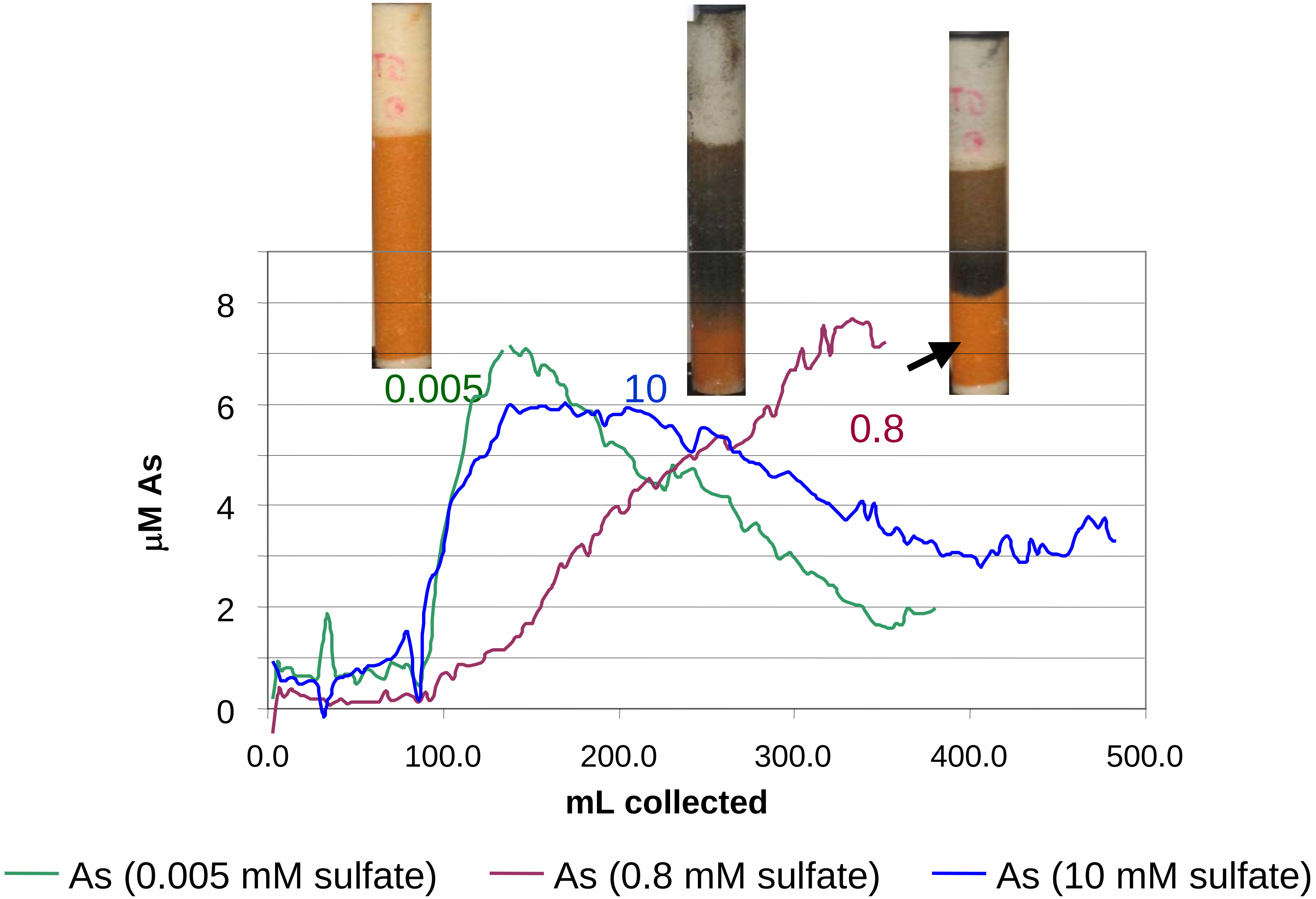
Sulfide formation in *D. desulfuricans* incubations



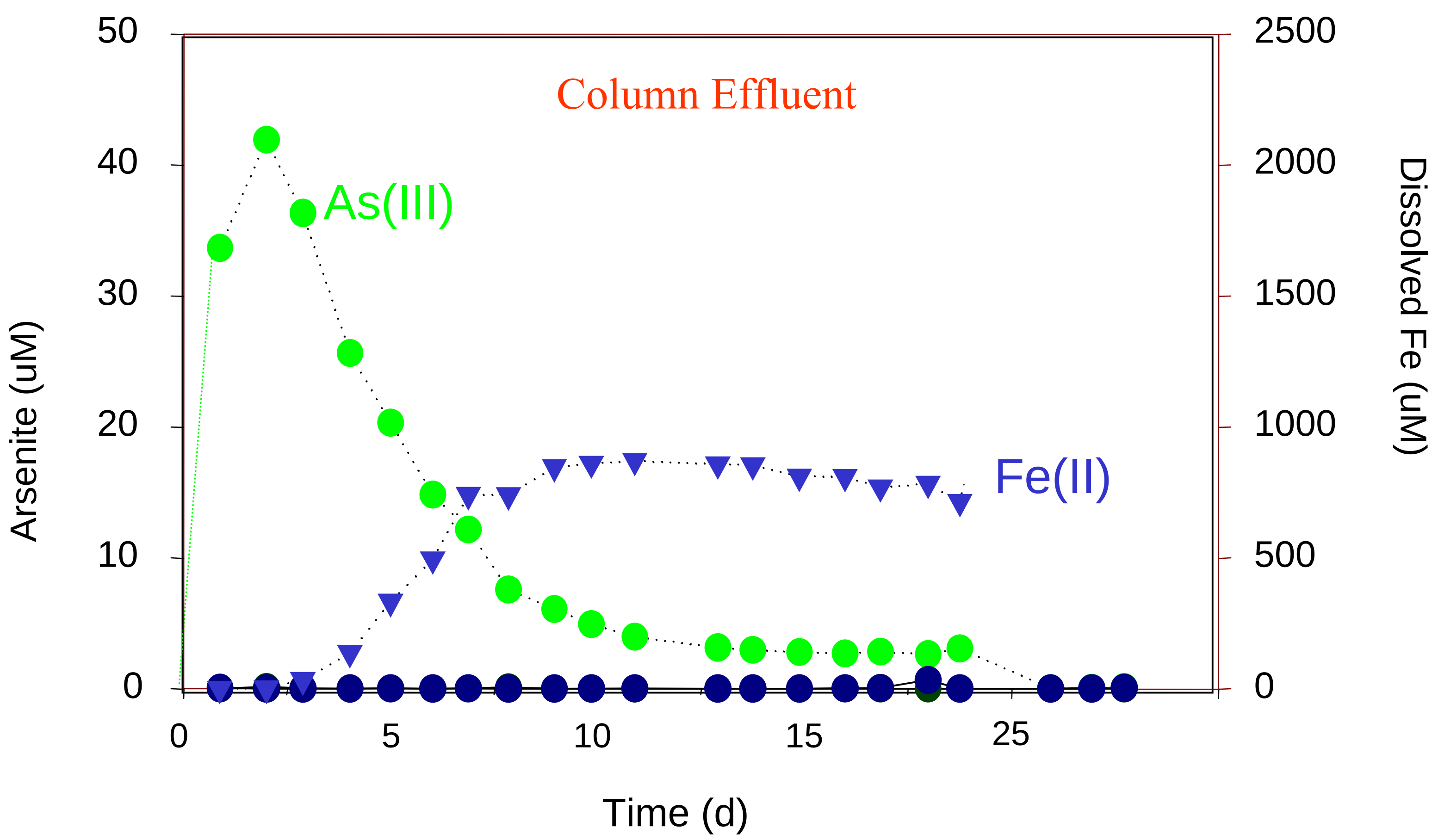
Banfield, J, et al. 2005. *Reviews in Mineralogy and Geochemistry.* Vol. 59, p 85-108



What mechanisms regulate arsenic release from *D. desulfuricans* columns?

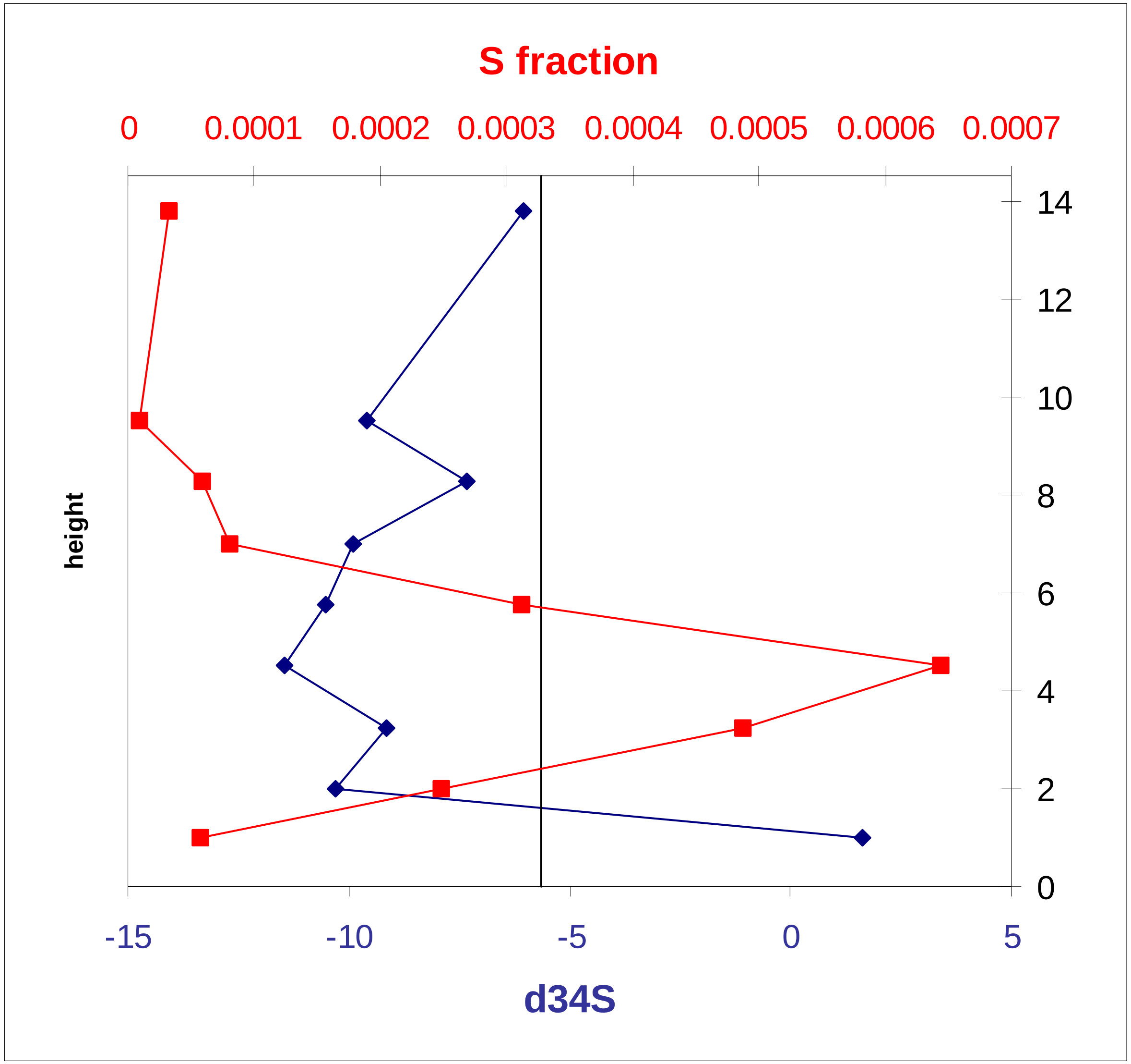


What causes differences in patterns of Iron and Arsenic release caused by SRBs and FeRBs?

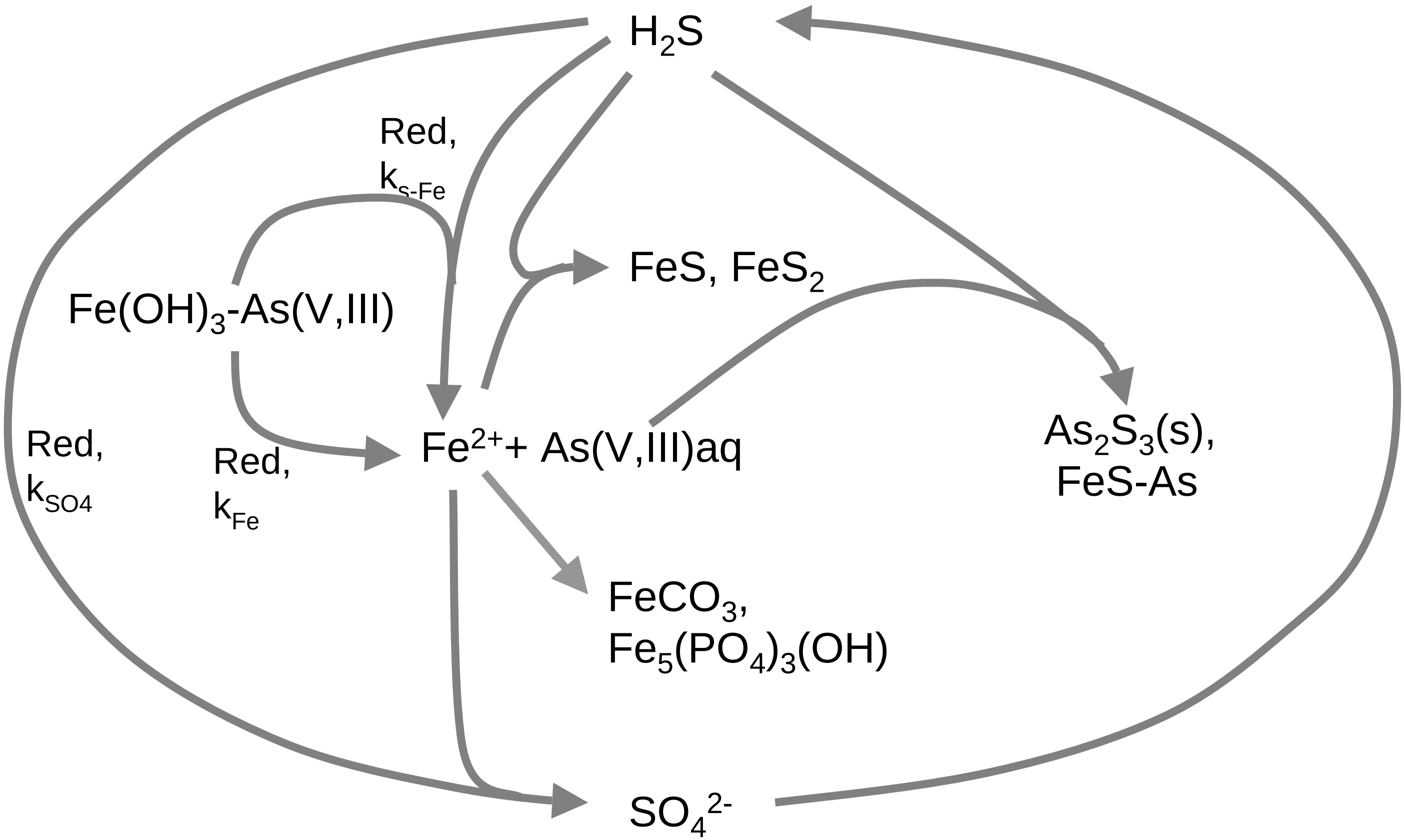


From Hansel, Fendorf, and Bostick 2004, unpublished

How do changes in $\delta^{34}S$ reflect sulfur cycling?



A more complete description of As fate



- It is necessary to include sulfate reduction to adequately describe arsenic concentrations.
- Kinetic processes are critical to regulating arsenic levels

Arsenic-Iron-Sulfur Cycling in 3 Field Sites

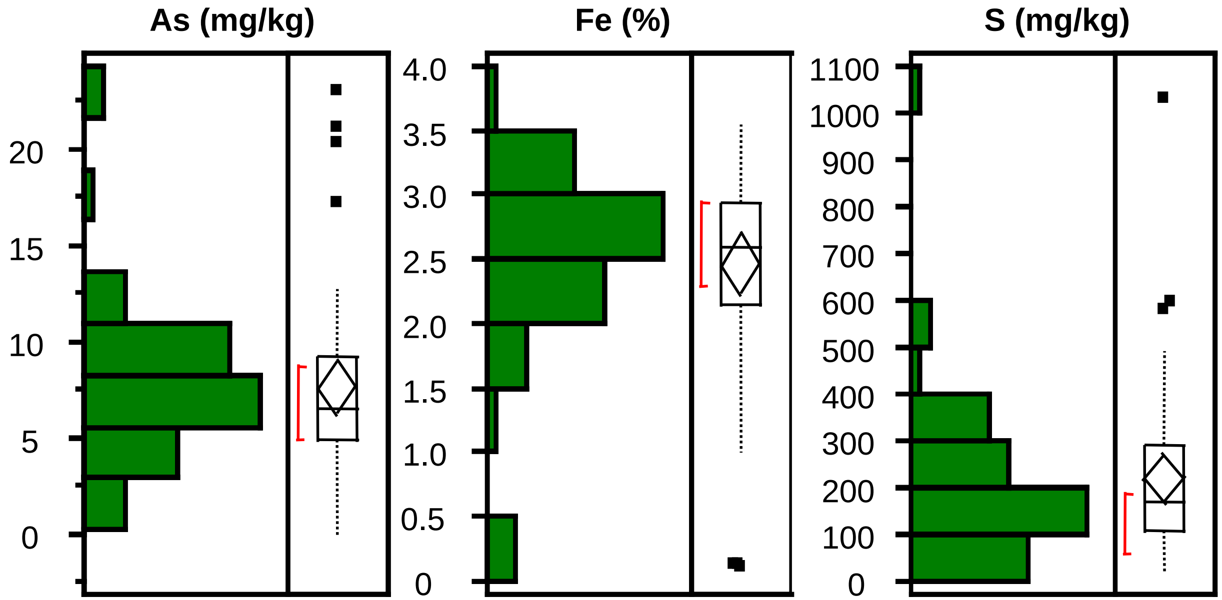
Coakley Superfund Site (NH)
Coeur d'Alene Mining District (ID)
Cambodian Groundwater Systems

Collaborators:

Mickey Sampson (Resources Development International, Cambodia)

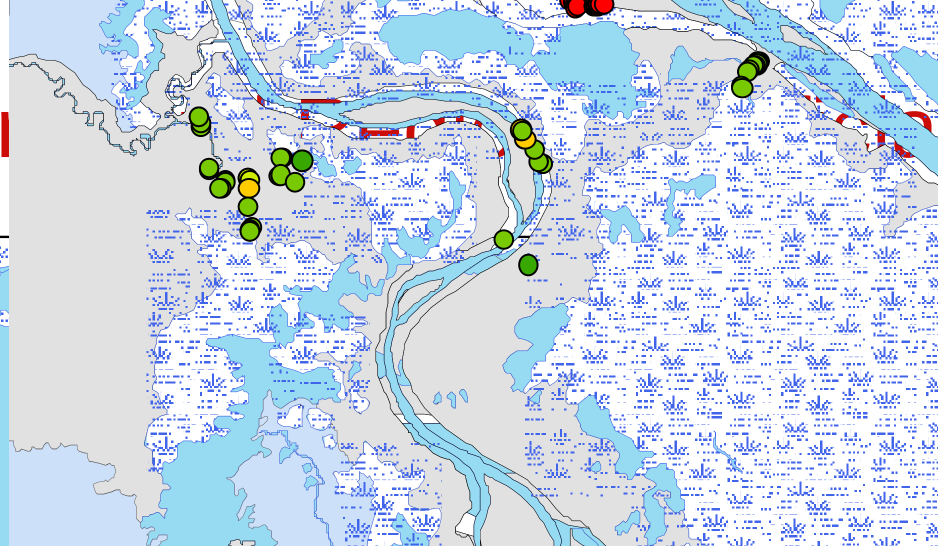
Elizabeth Hadzima
Gretchen Gehrke
Nick Papacostas
Joshua Landis
Jamie de Lemos

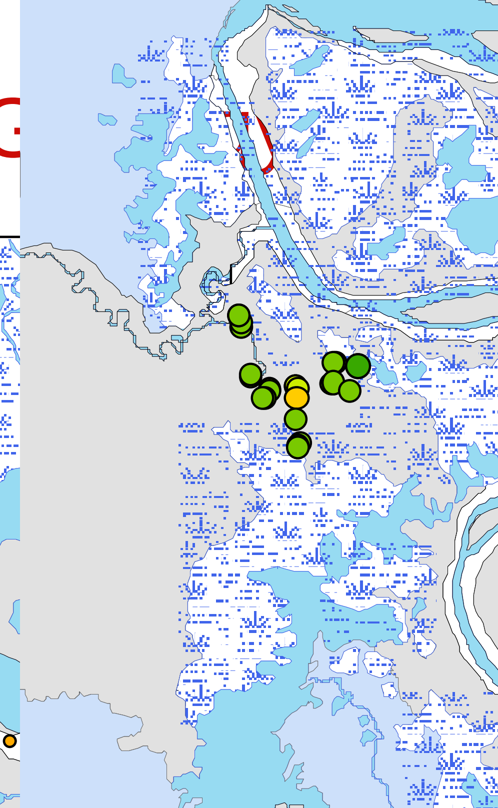
Soils and Sediments

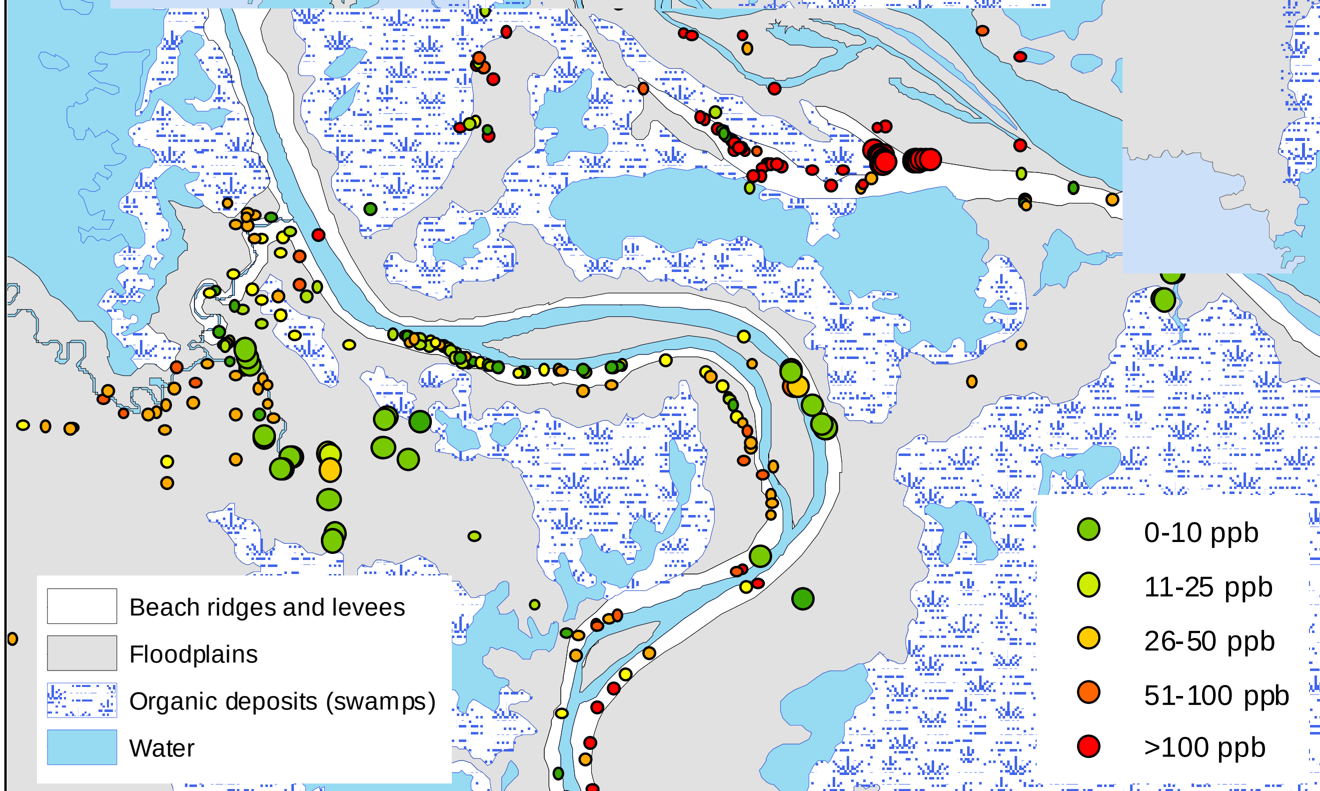


- Typical As, S and Fe levels
- Hard to determine composition of aquifer materials based on surficial environment

Arse G



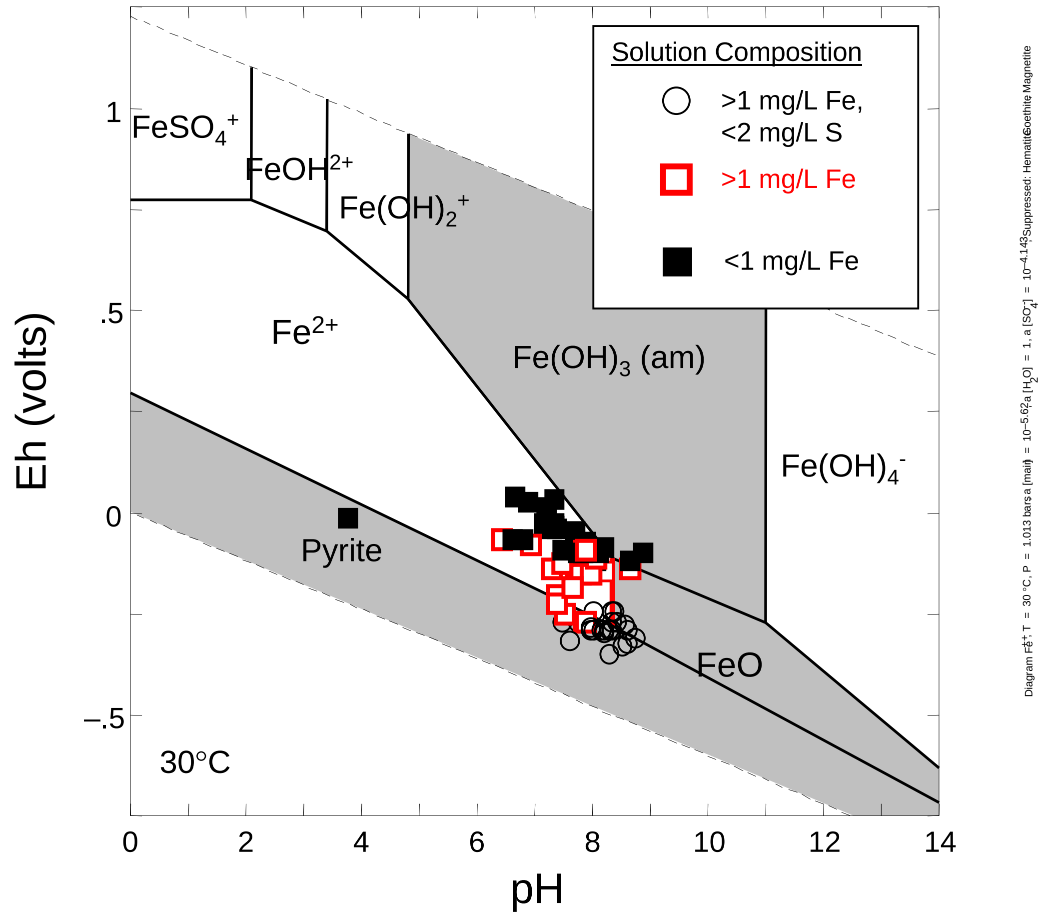




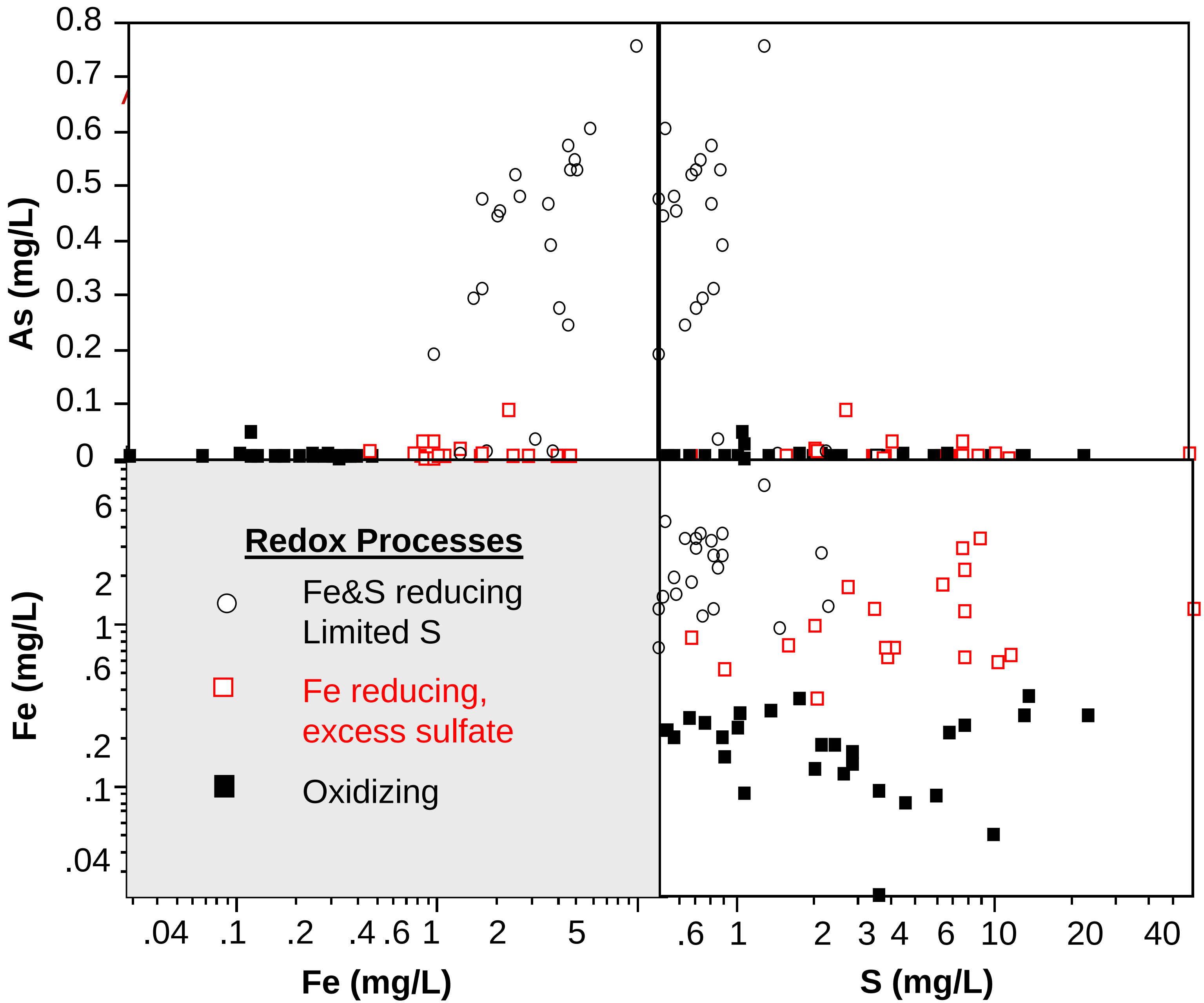
water_concentration_join

AS1890

Redox Processes: Sulfate and Iron reduction



- Redox Conditions indicate that sulfate reduction and/or Fe reduction is thermodynamically viable, concentration information indicates the extent to which they have occurred.



- Highly elevated As levels are most notably associated with waters high in Fe and low in sulfate