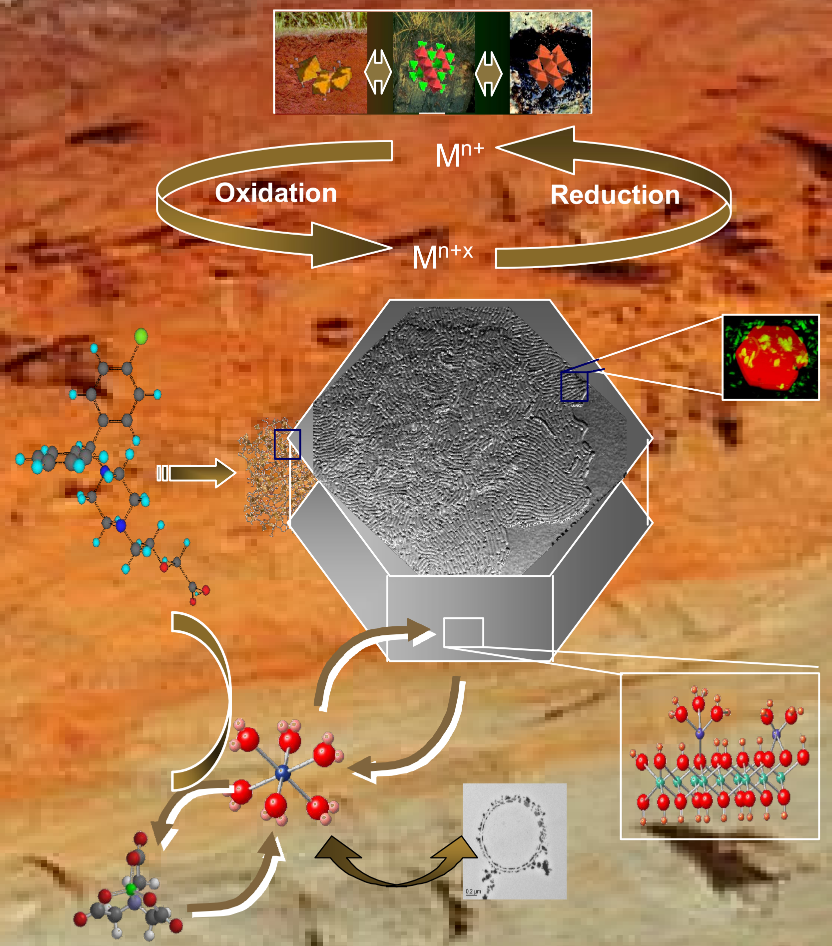
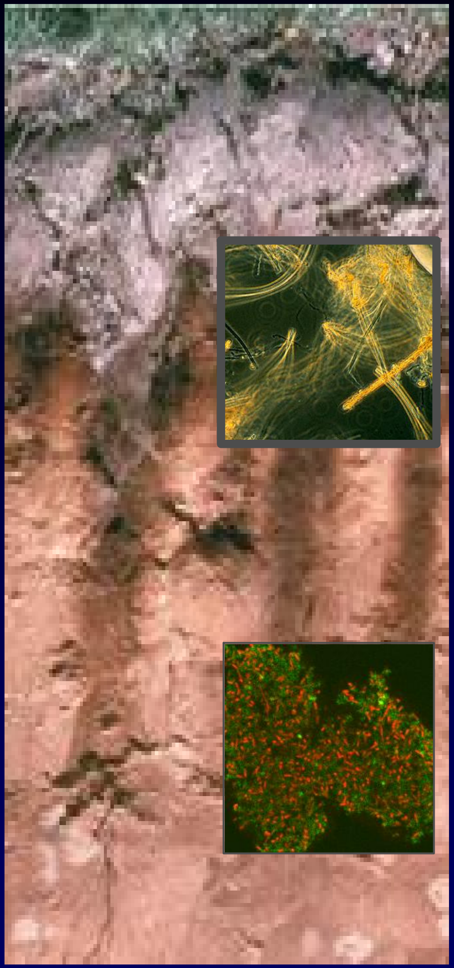
Heterogeneity in Bioreduction and Resulting Impacts on Contaminant Dynamics



Scott Fendorf
Stanford University

CONTRIBUTORS

- Shawn Benner, Boise State University
- Deborah Bond, USGS
- Matt Ginder-Vogel, Stanford University
- Colleen Hansel, Stanford University
- Jim Neiss, Stanford University
- Peter Nico, LBNL
- Kristin Revill, RHE
- Brandy Stewart, Stanford University
- Bruce Wielinga, MFG Incorp.

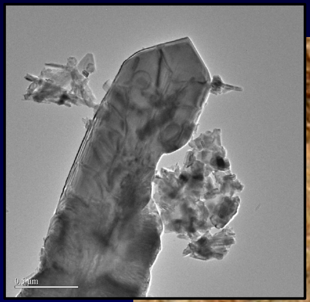


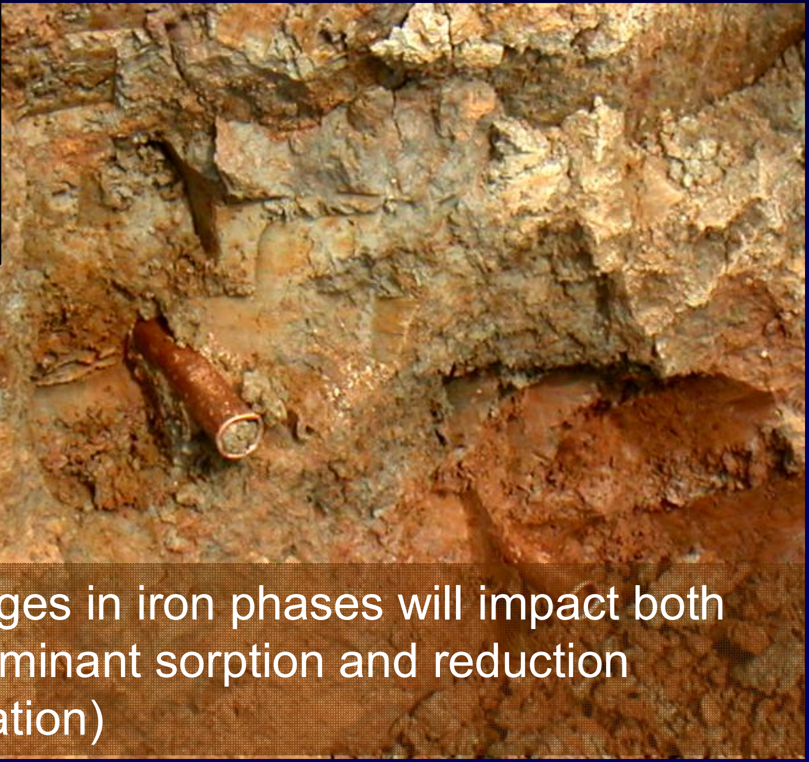
COLLABORATORS

- Yuri Gorby, Alice Dohnalkova, John Zachara, PNNL
- Phil Jardine, Scott Brooks, Tracy Banks, ORNL

FUNDING: DOE-NABIR/ERSP

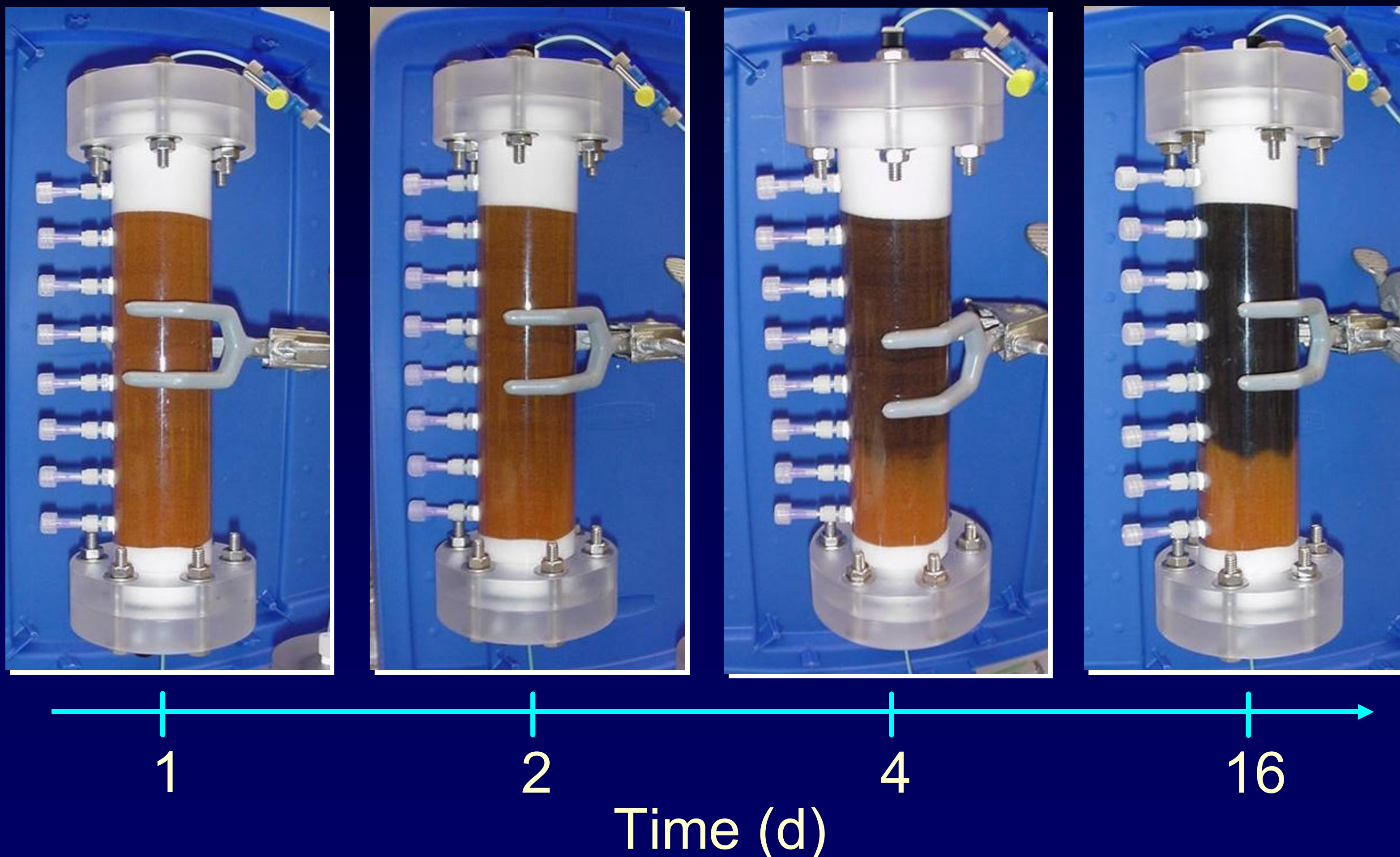
Transformations and Variation In Iron





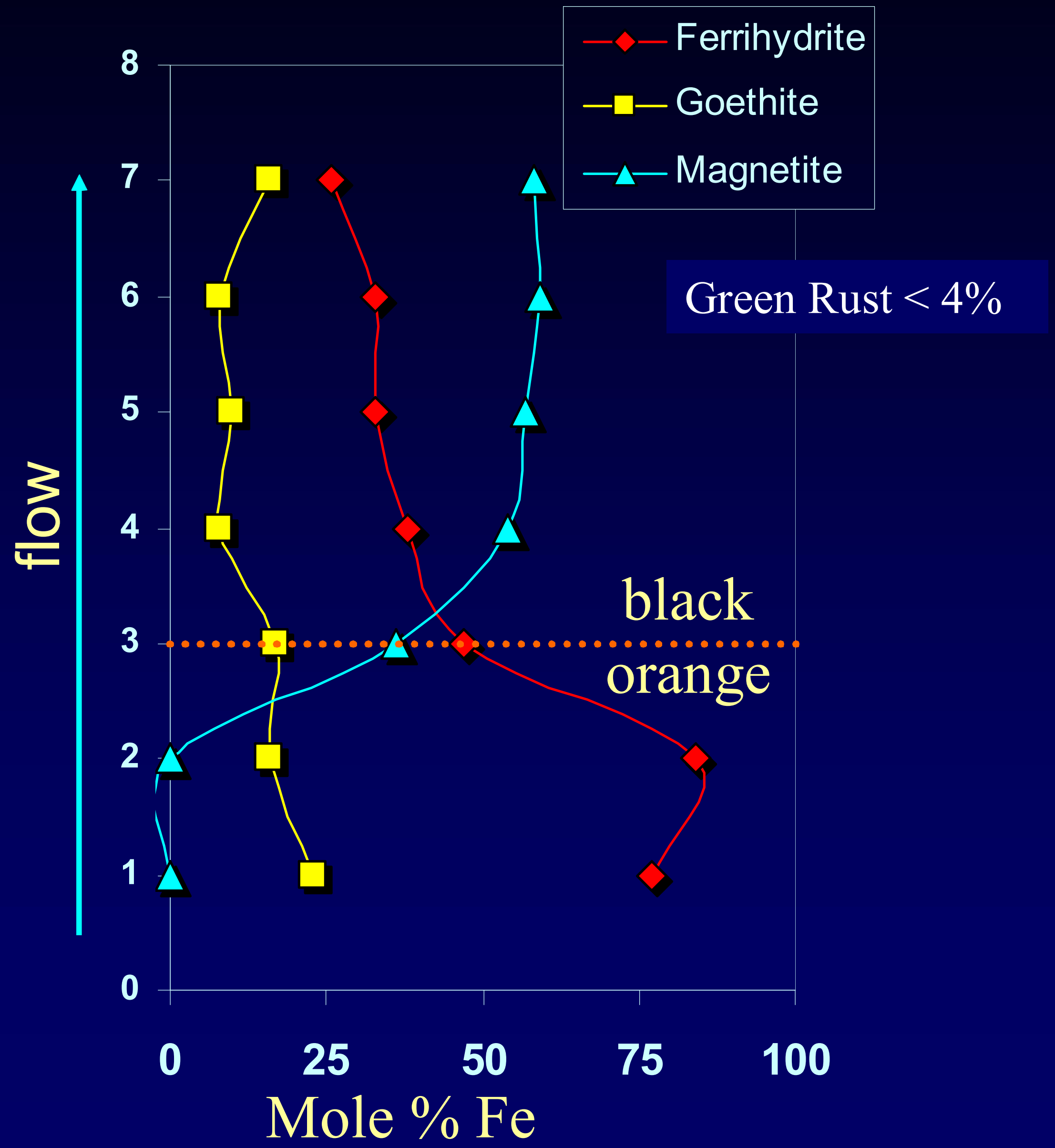
Changes in iron phases will impact both contaminant sorption and reduction (oxidation)

Reductive Transformation of Iron

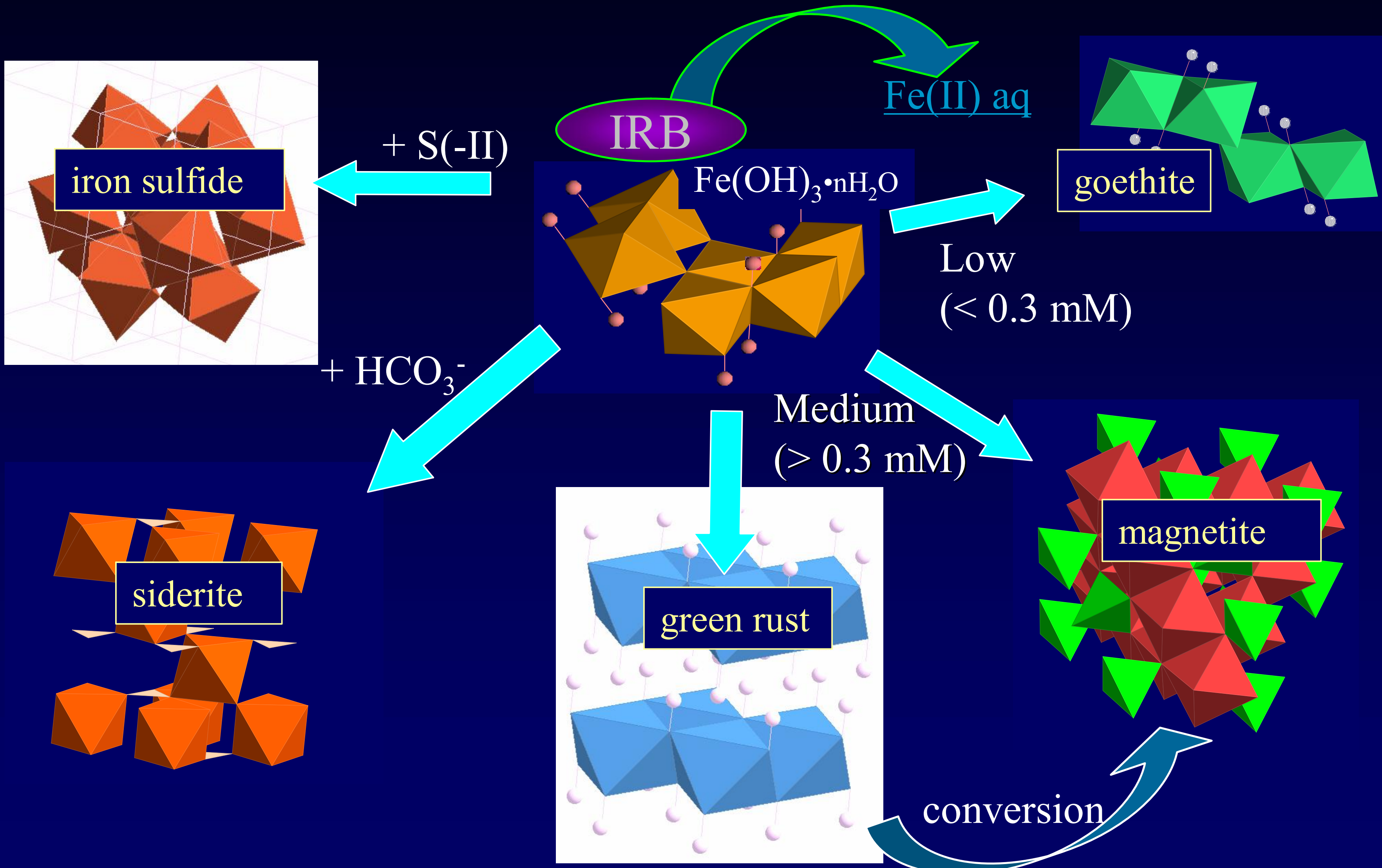


- *S. putrefaciens* strain CN32 inoculated ferrihydrite coated quartz-sand
- pH 7, 3 mM lactate

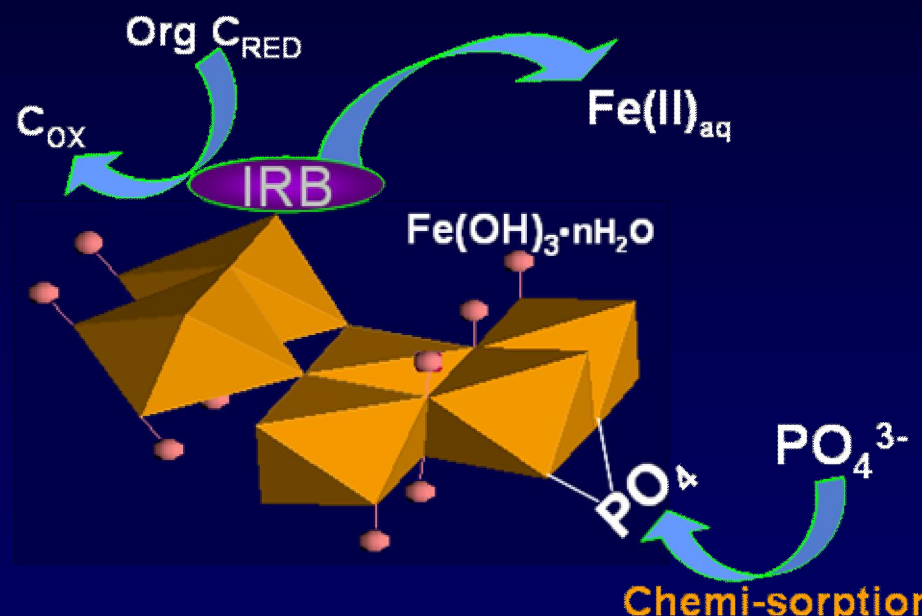
Solid-phase Distribution



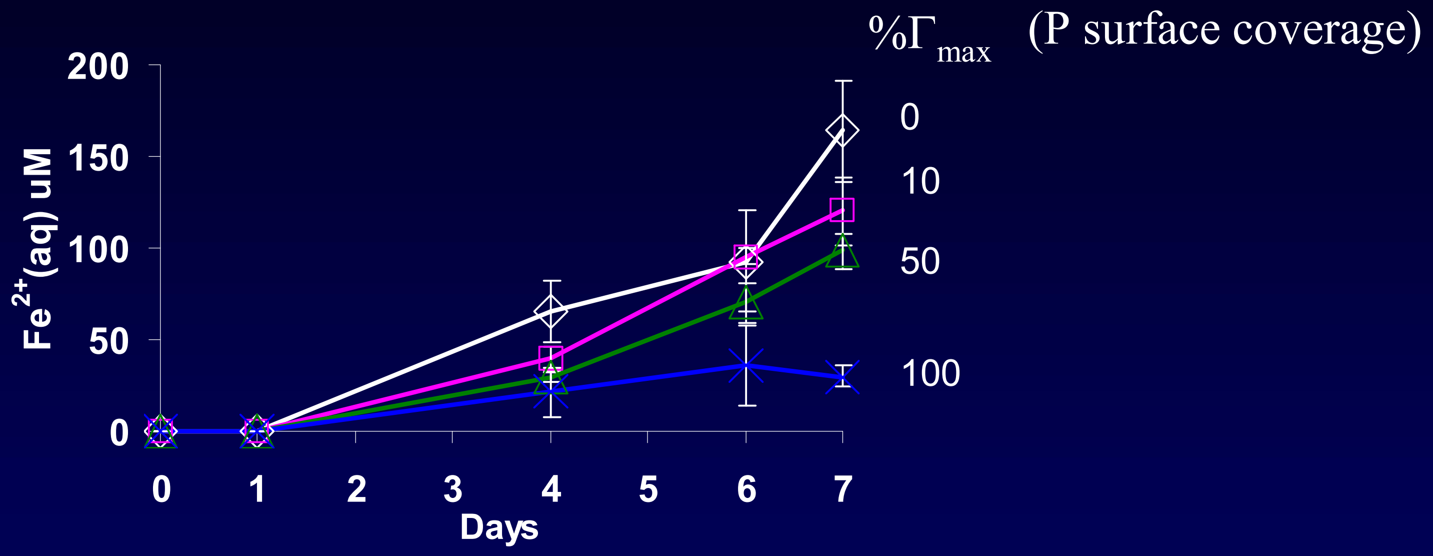
Iron Biomineralization

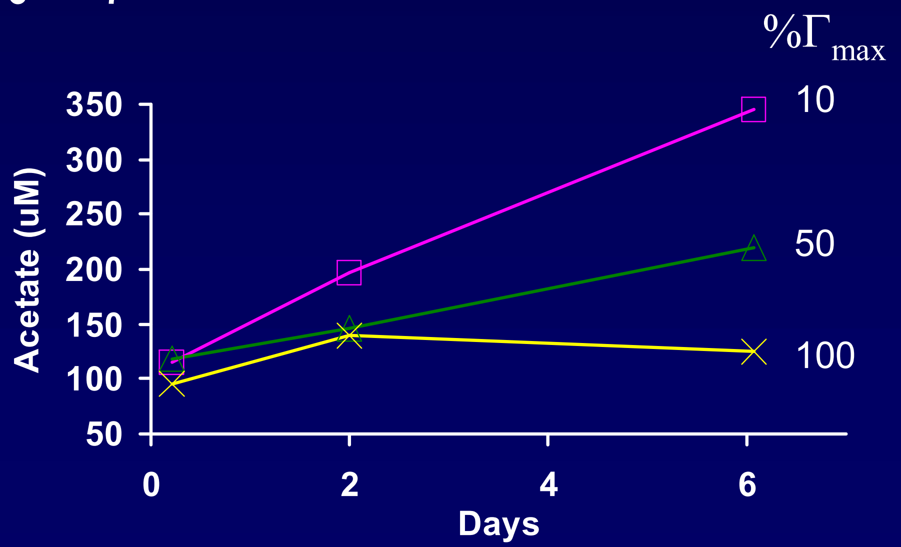


Alteration in Surface Composition

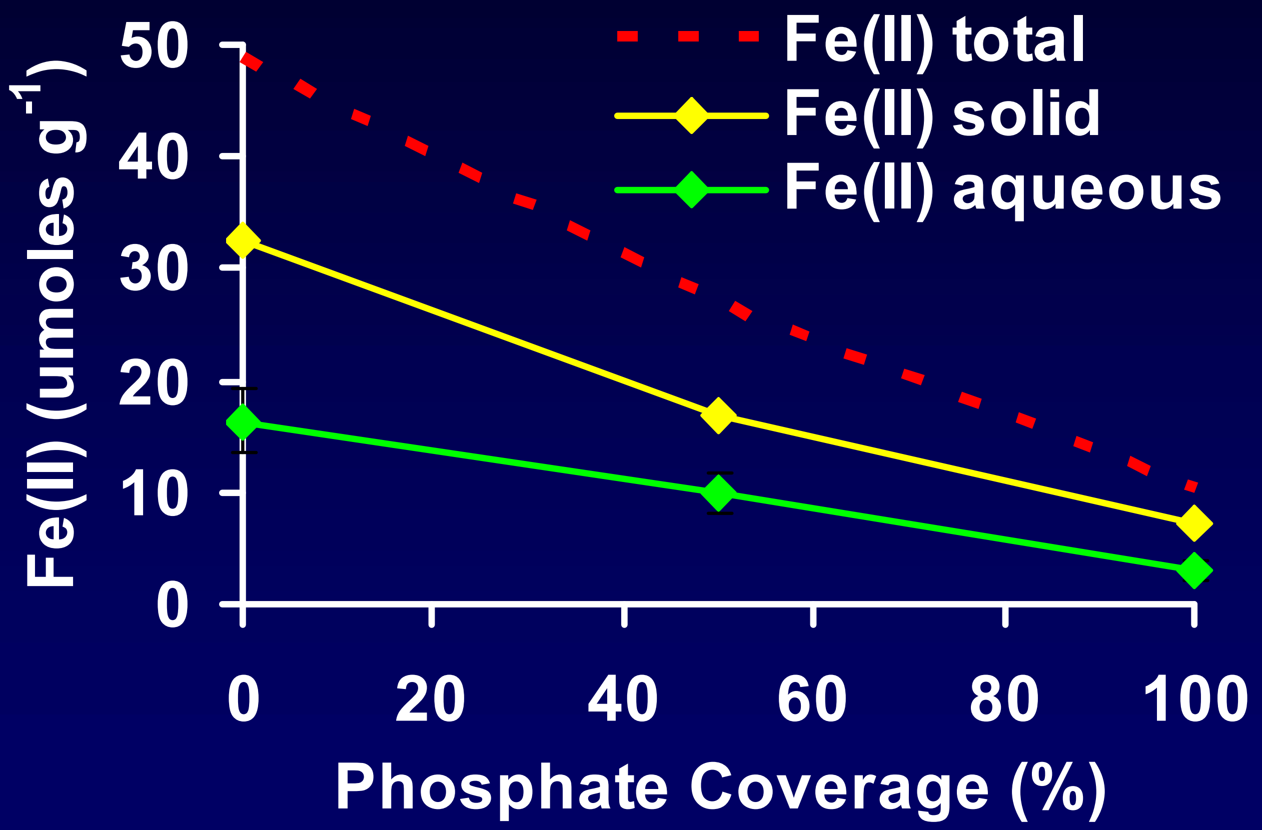


Ferrihydrite Reduction: Impact of Phosphate



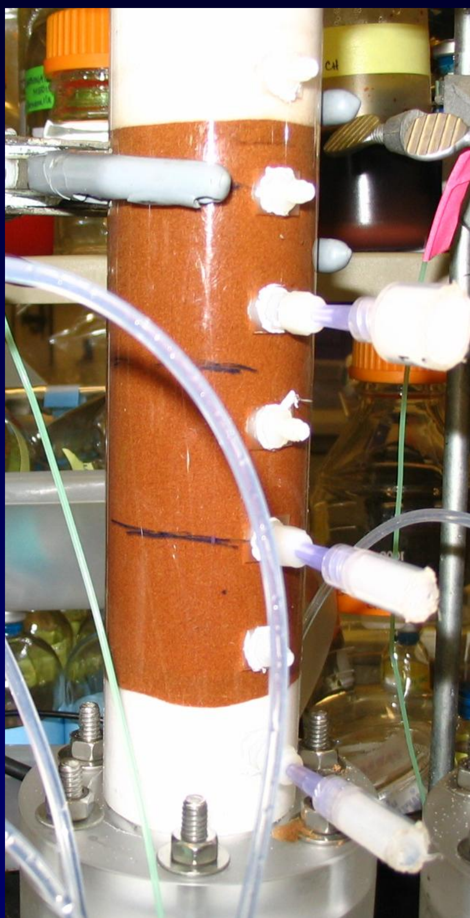


Alteration of Ferrihydrite Reactivity by Phosphate

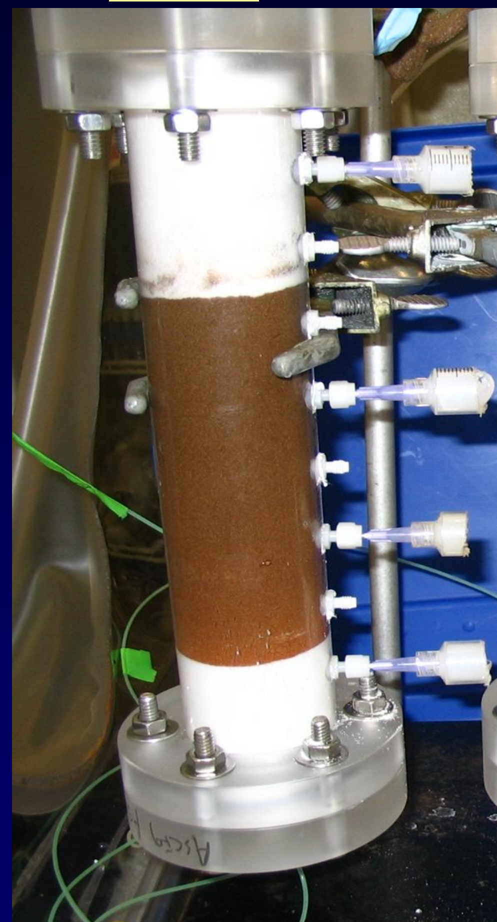


Fe Biomineralization: Impact of Phosphate

Day 1



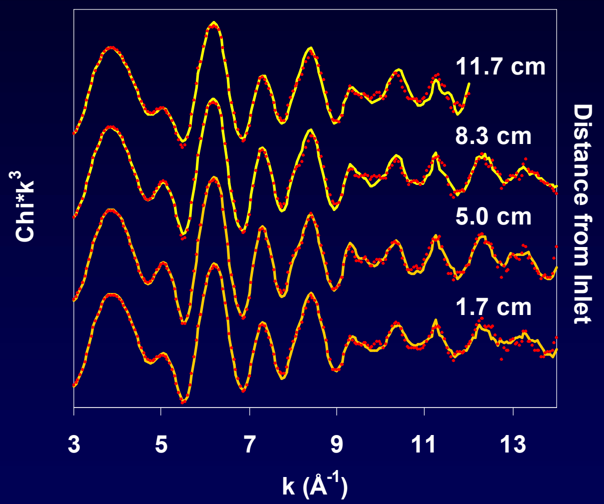
Day 17
with P



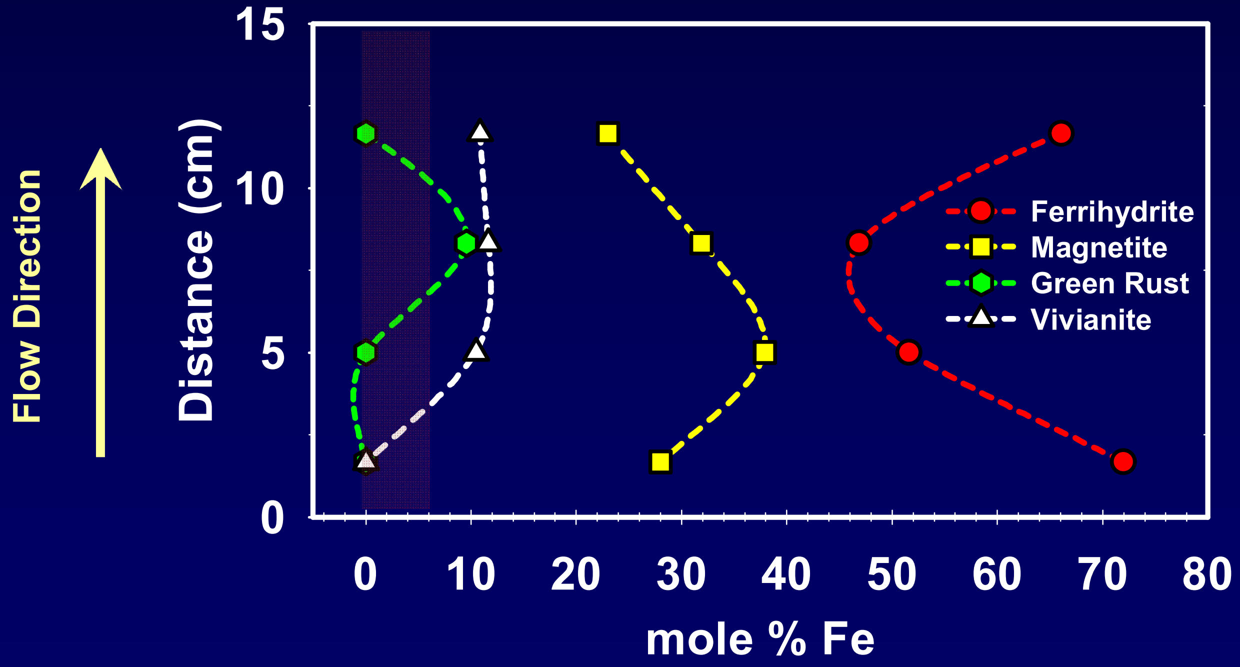
Day 17
without P

Biomineralization Products with Phosphate

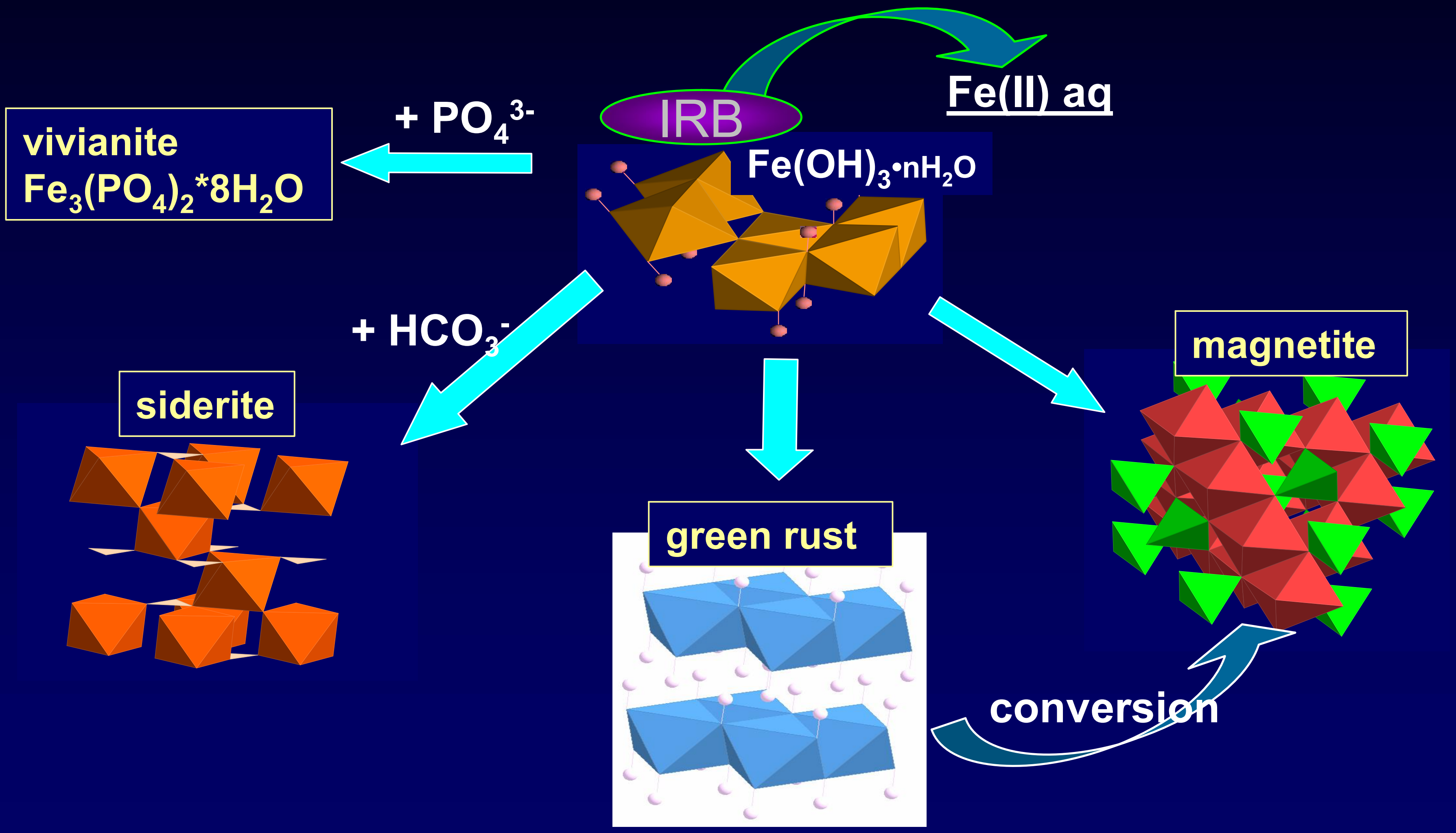
Fe EXAFS



Column Day 17

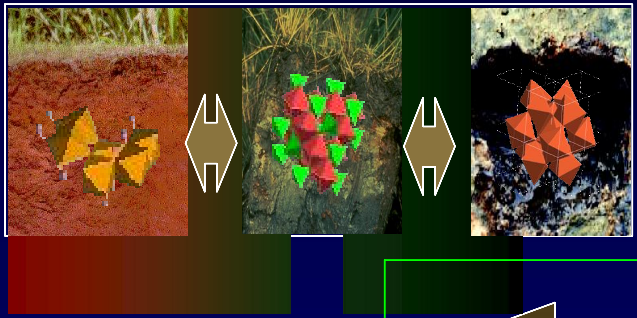


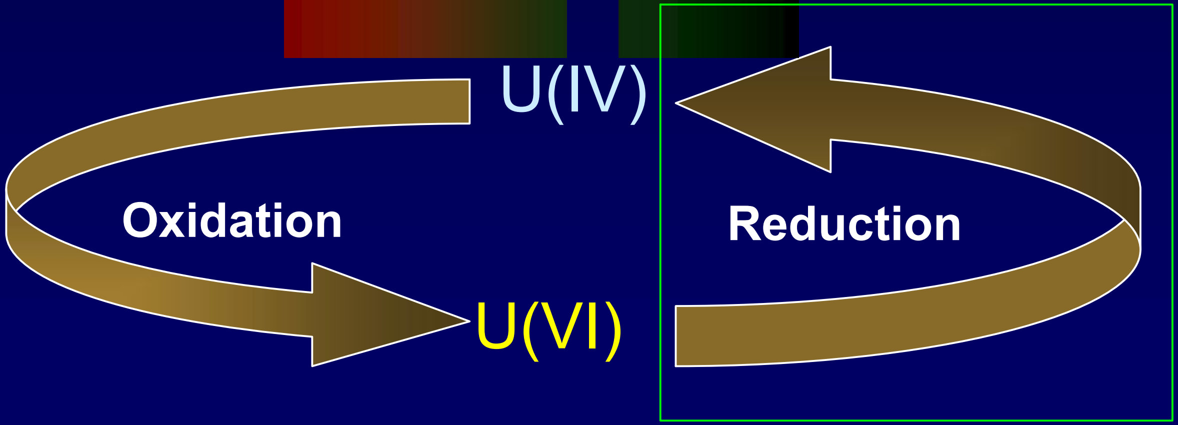
Iron Biomineralization with P



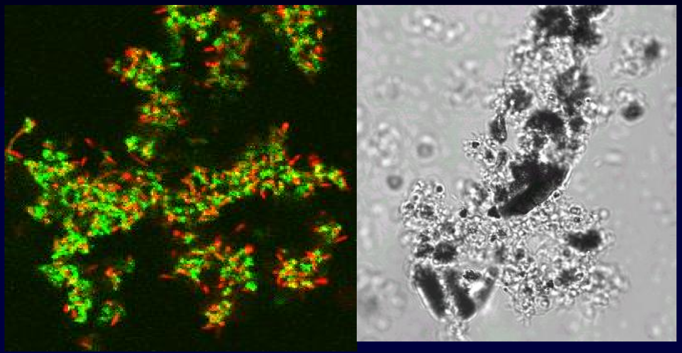
Impacts of Iron Transformation:

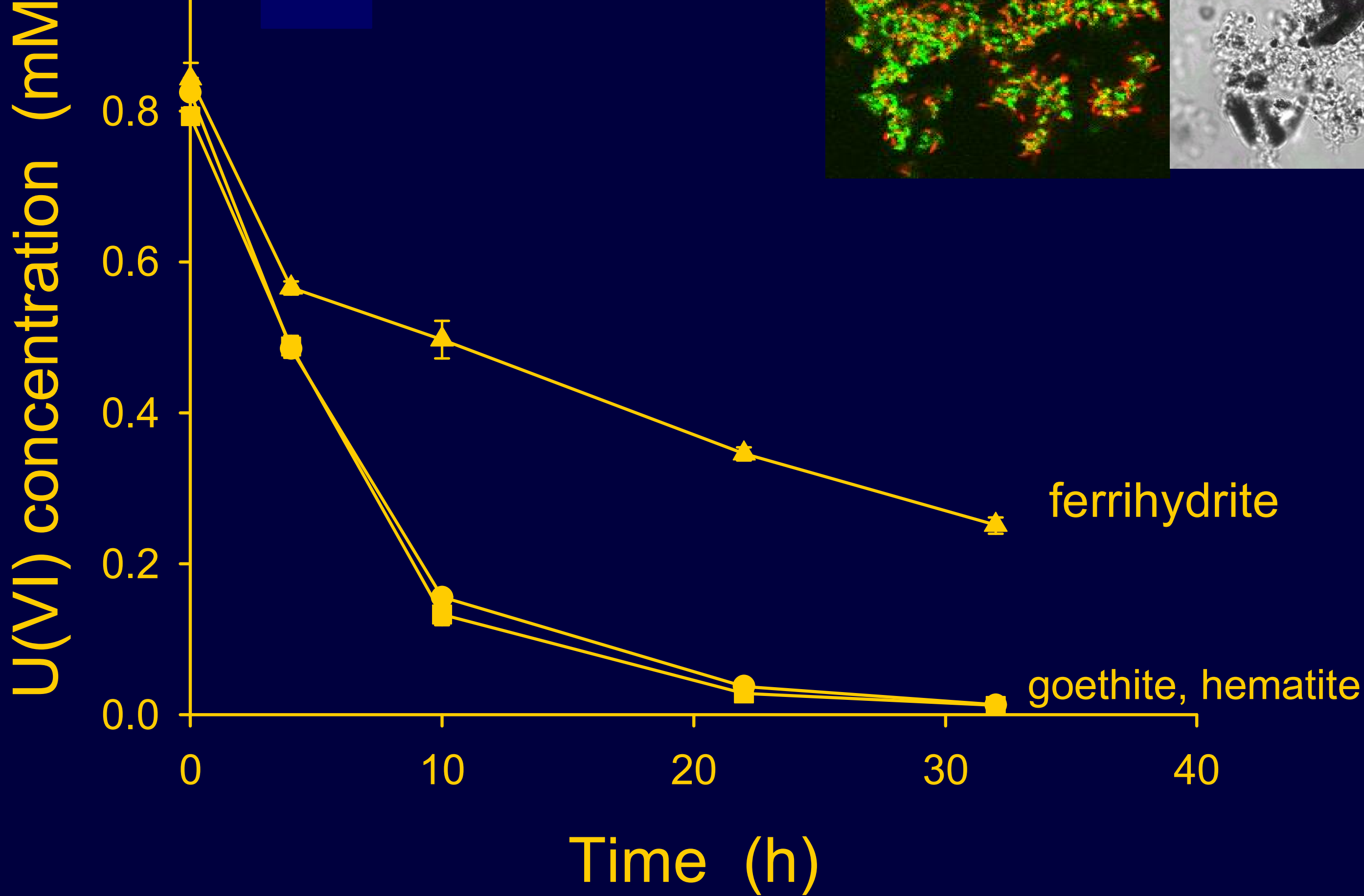
Reduction of Uranium



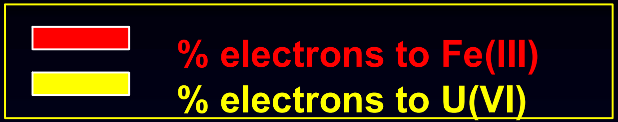


Uranyl Reduction by *Shewanella alga*

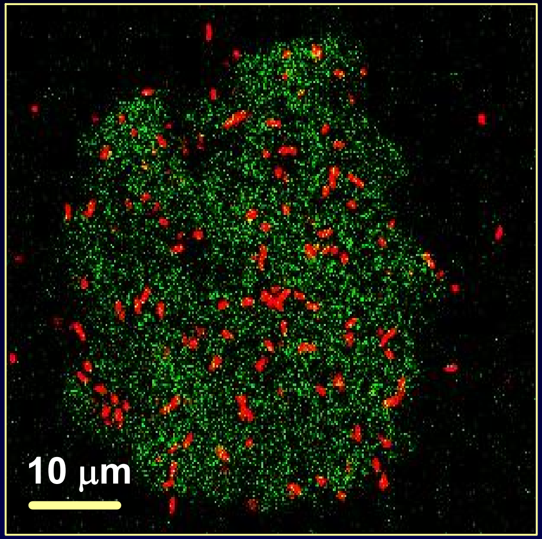


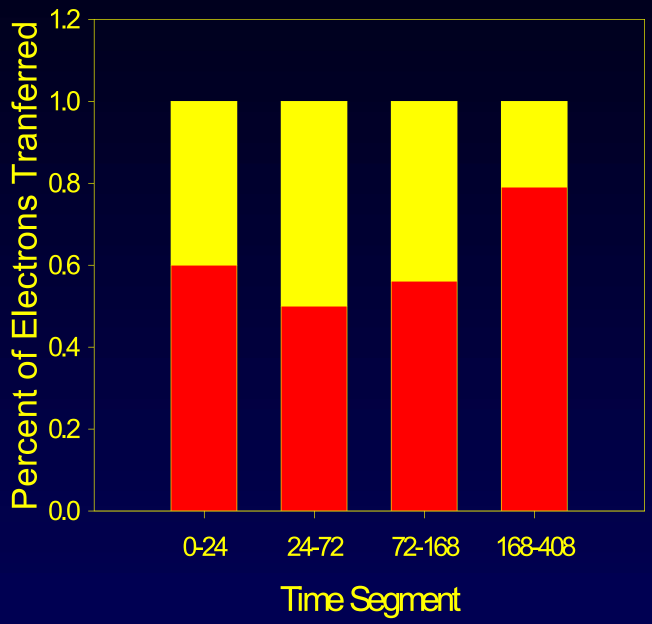


U(VI)-Fe(III) Reduction

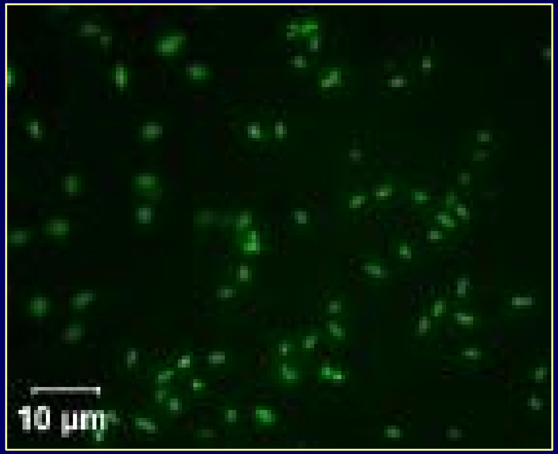


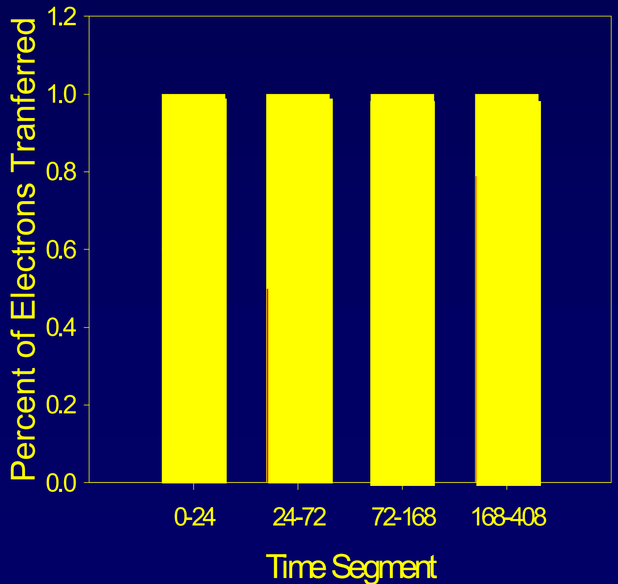
Nutrient-rich



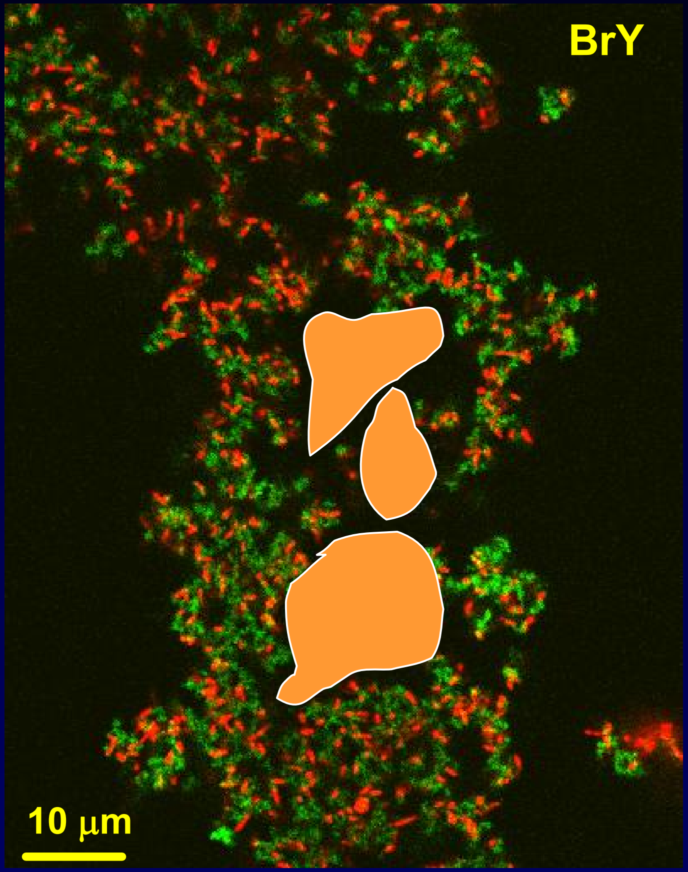


Nutrient-poor

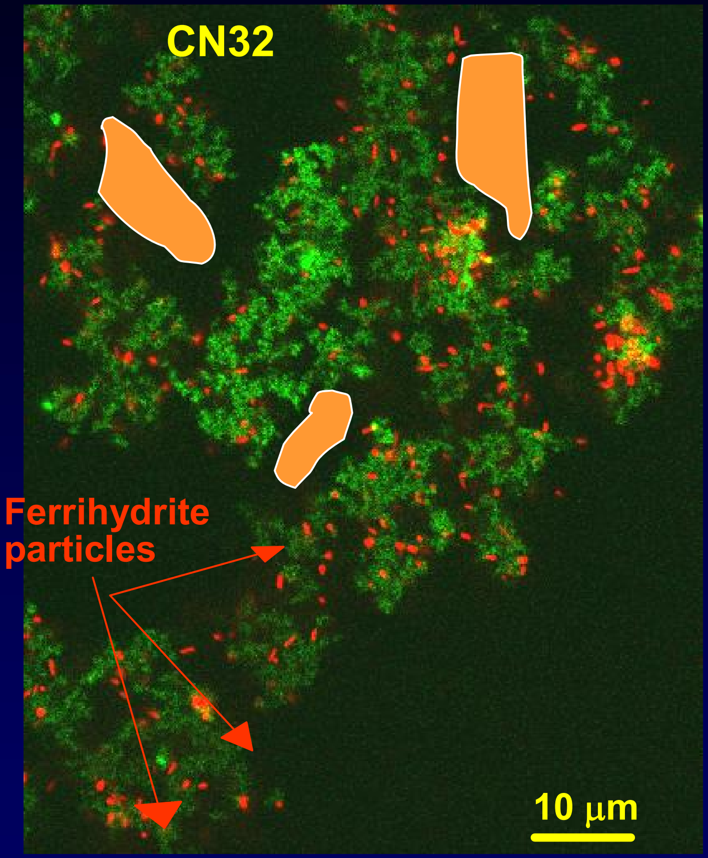


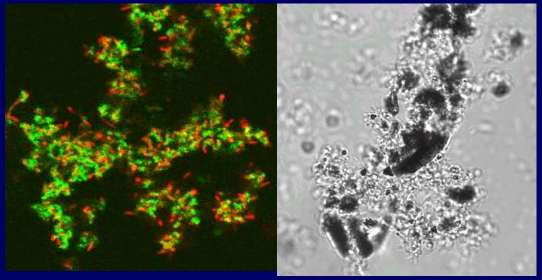


Uranyl Reduction by *Shewanella* sp.



CSLM Image

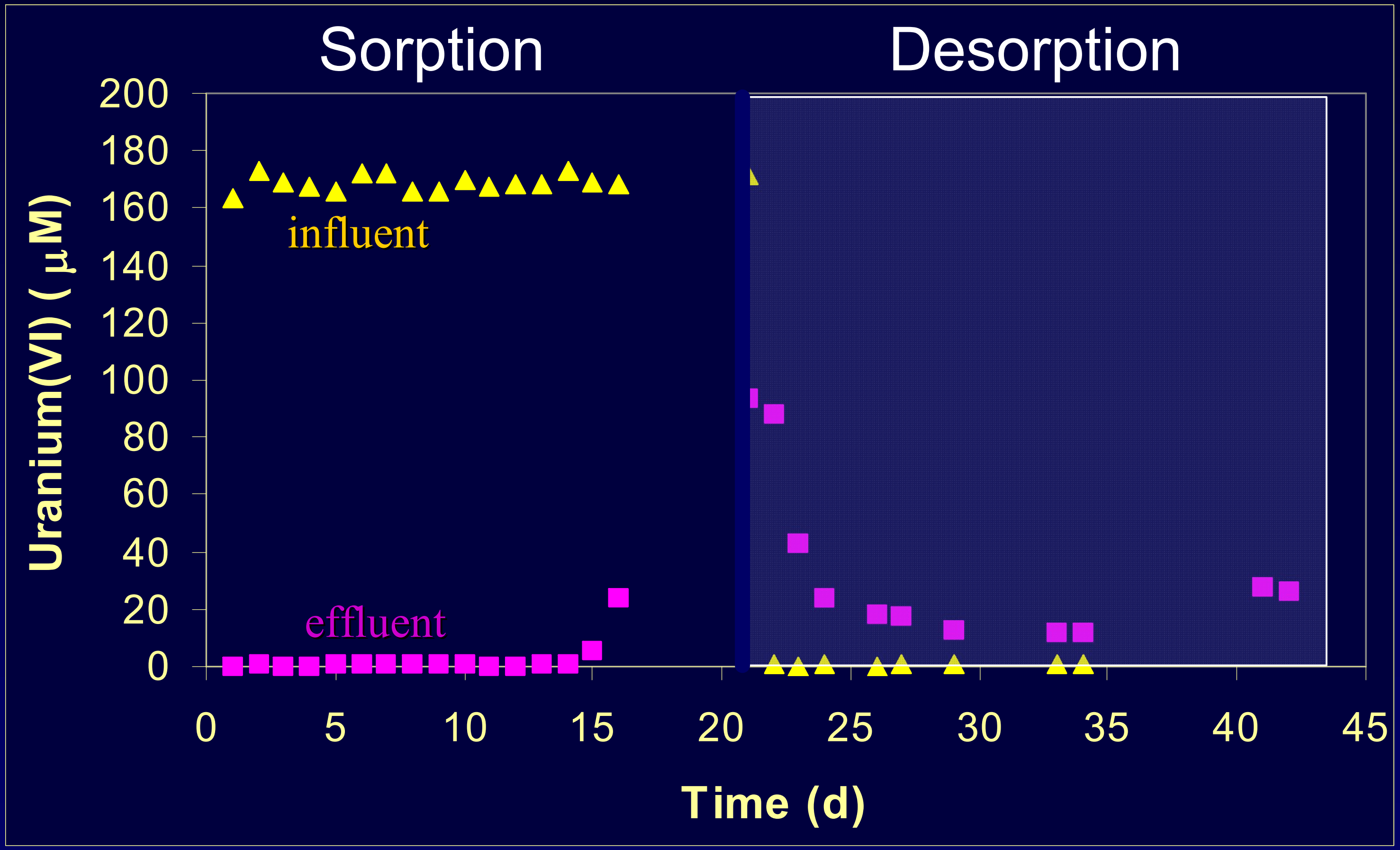




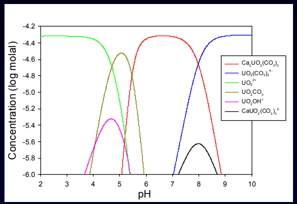
Phase Contrast Image

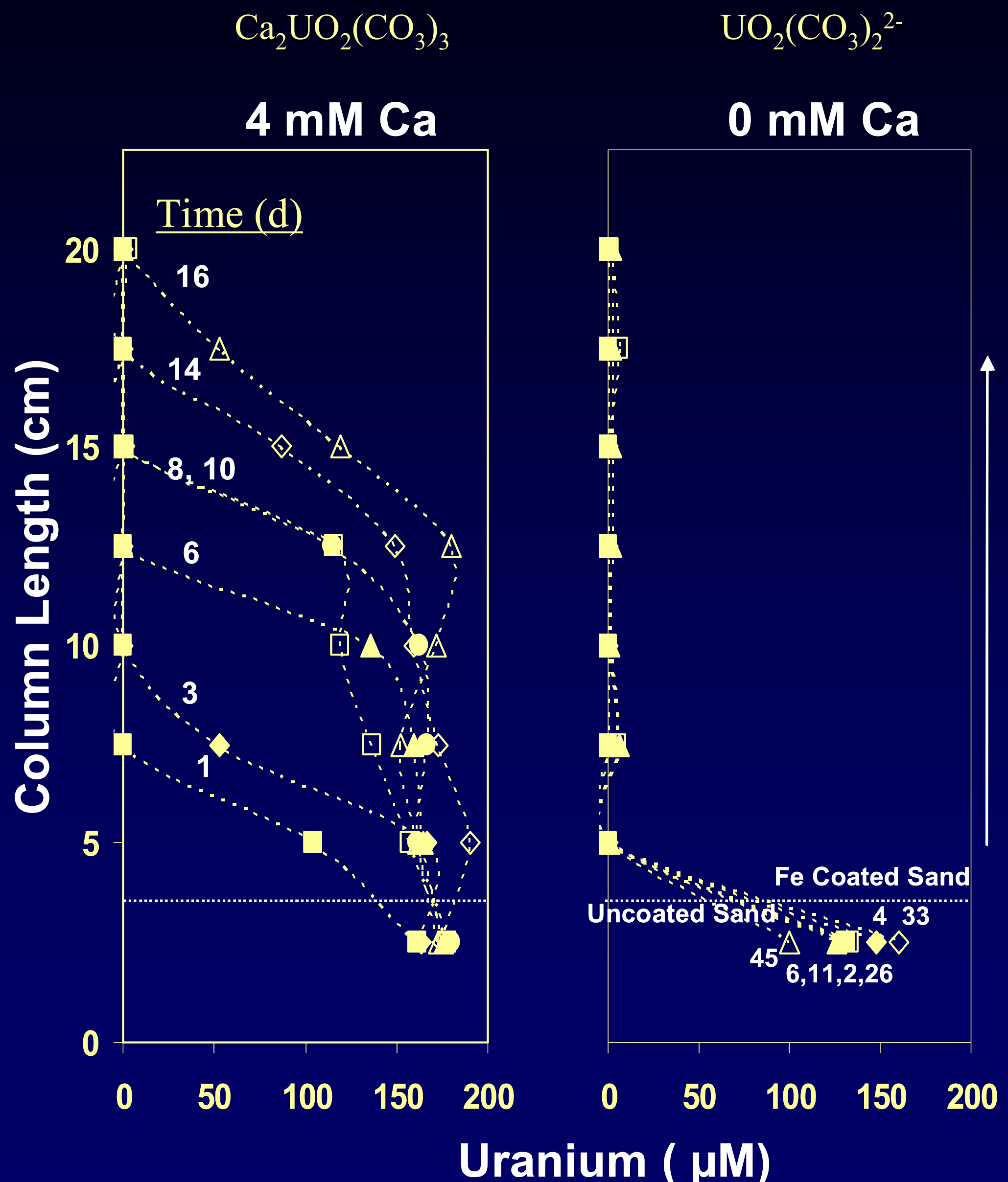
Reactive Transport of Uranium

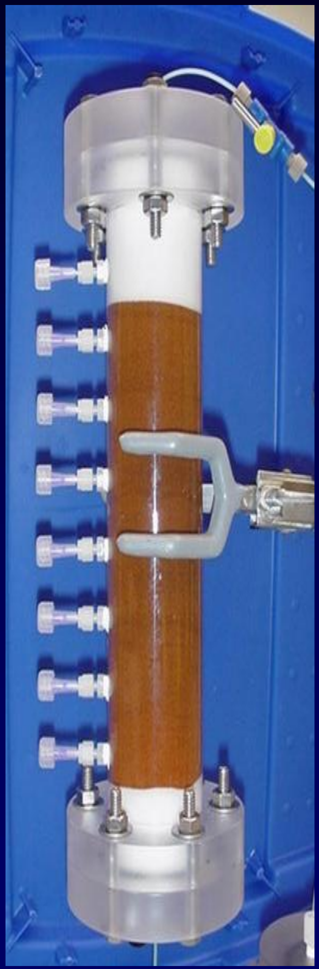
Calcite buffered uranyl/lactate feed solution



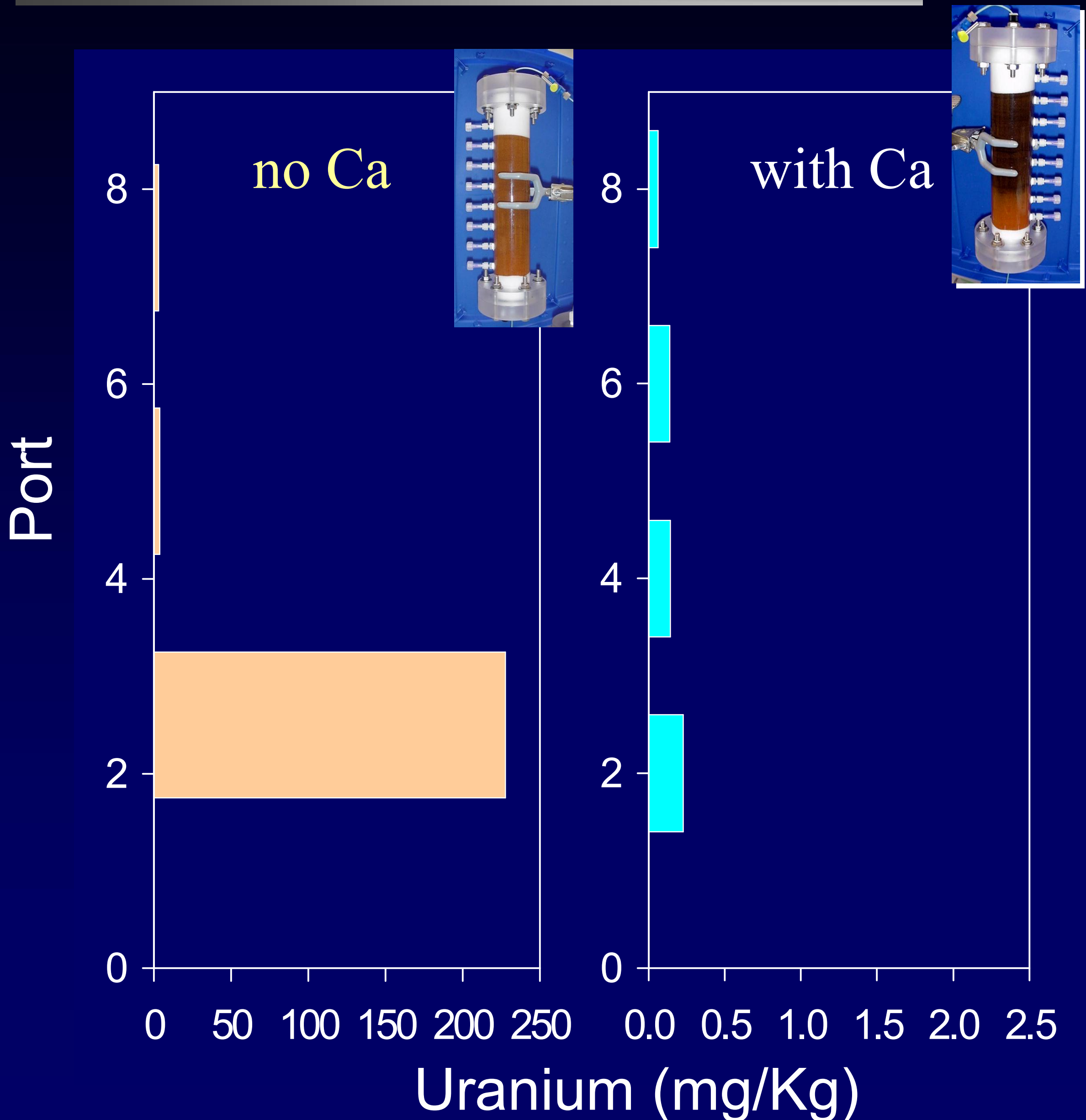
Transport of Uranium: Pore-water Concentration

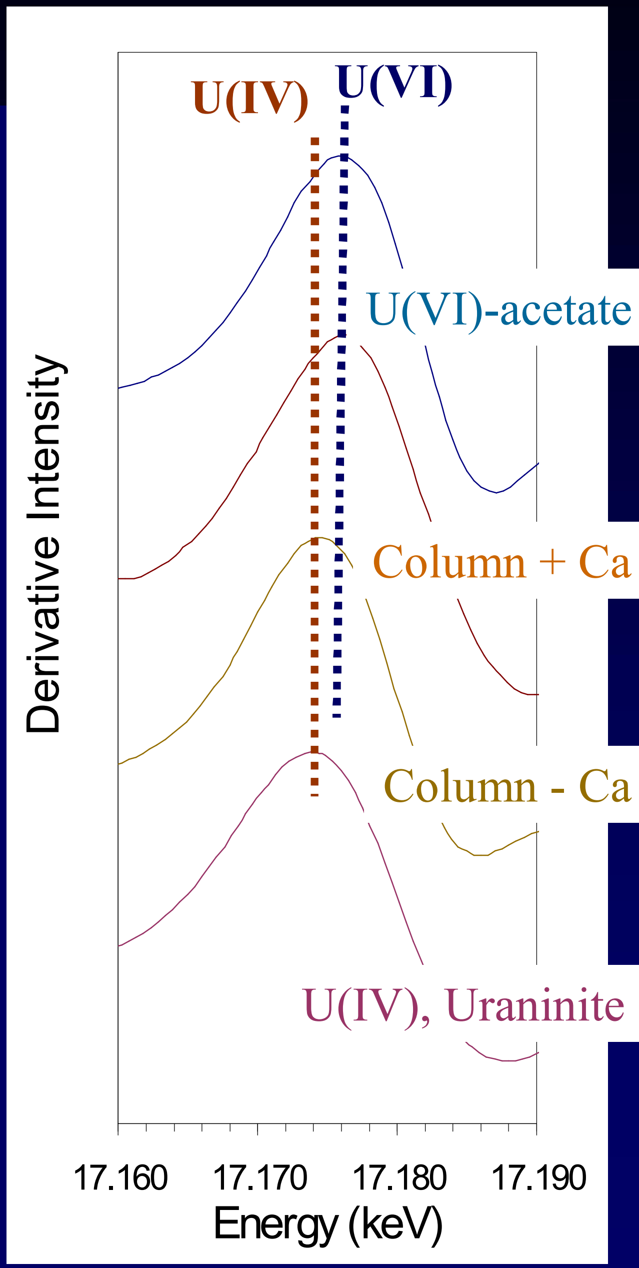




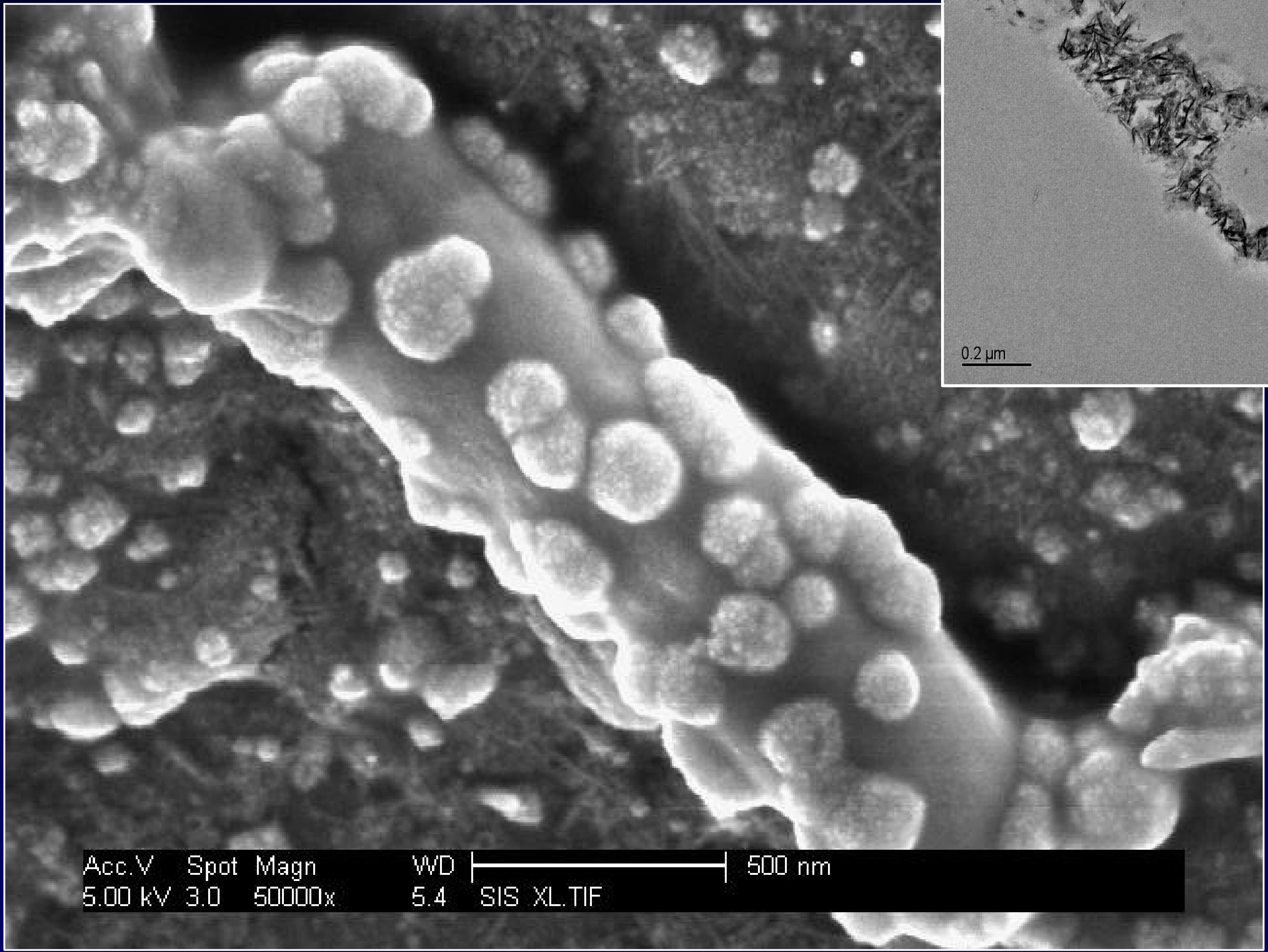


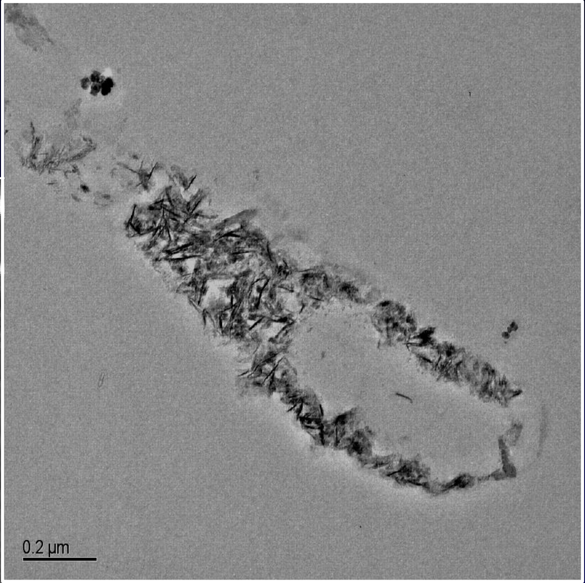
Uranium Sequestration





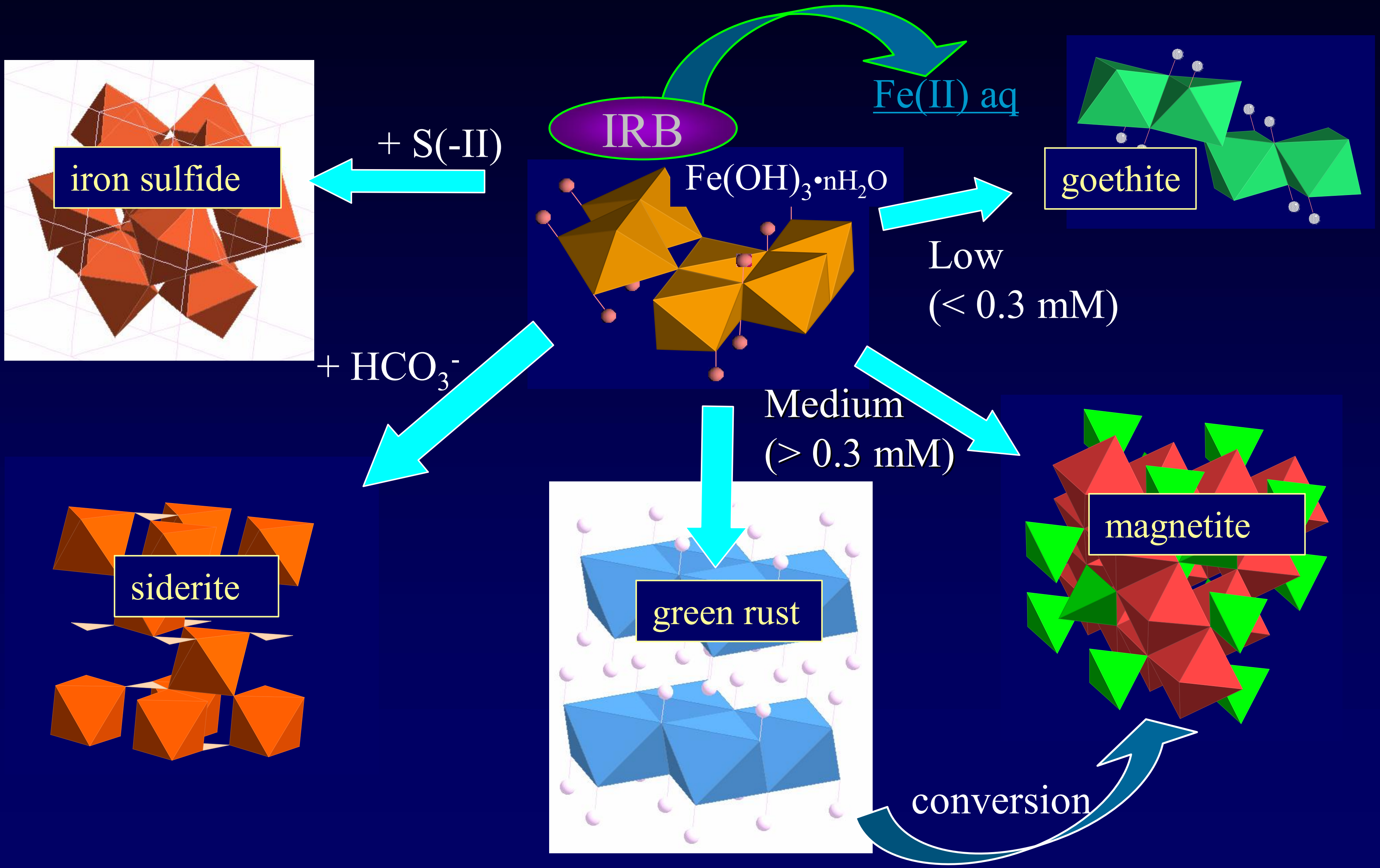
Uraninite Deposition



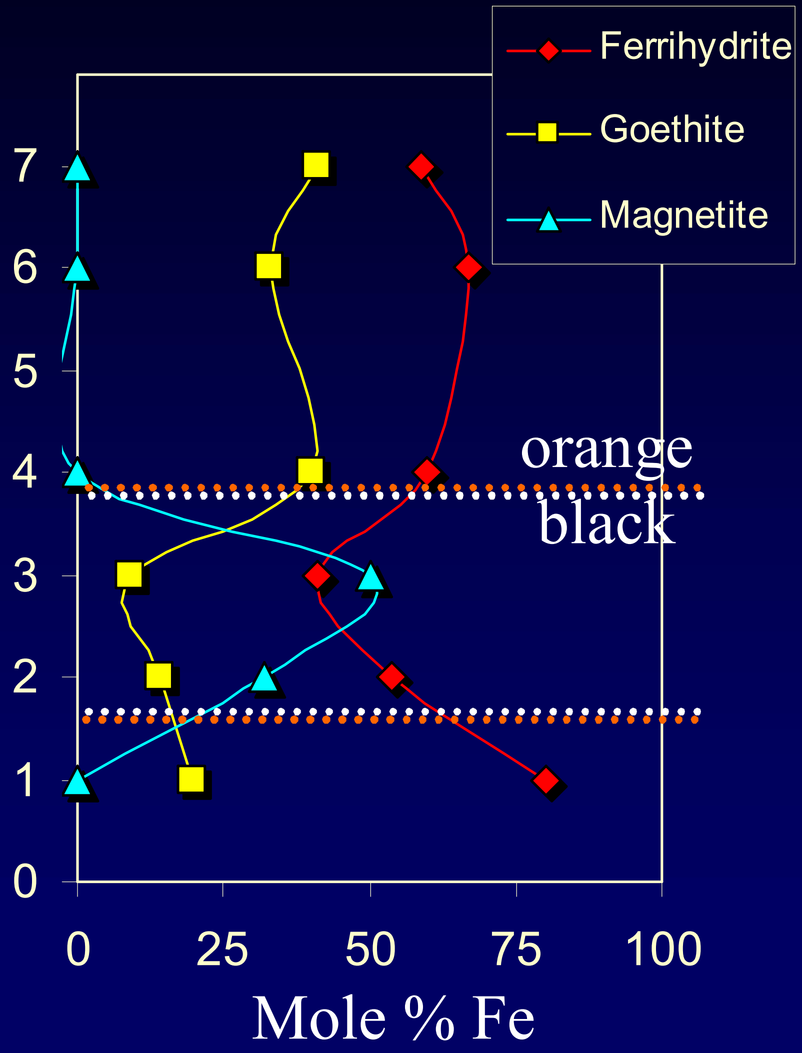


Physical-Biogeochemical Linkage

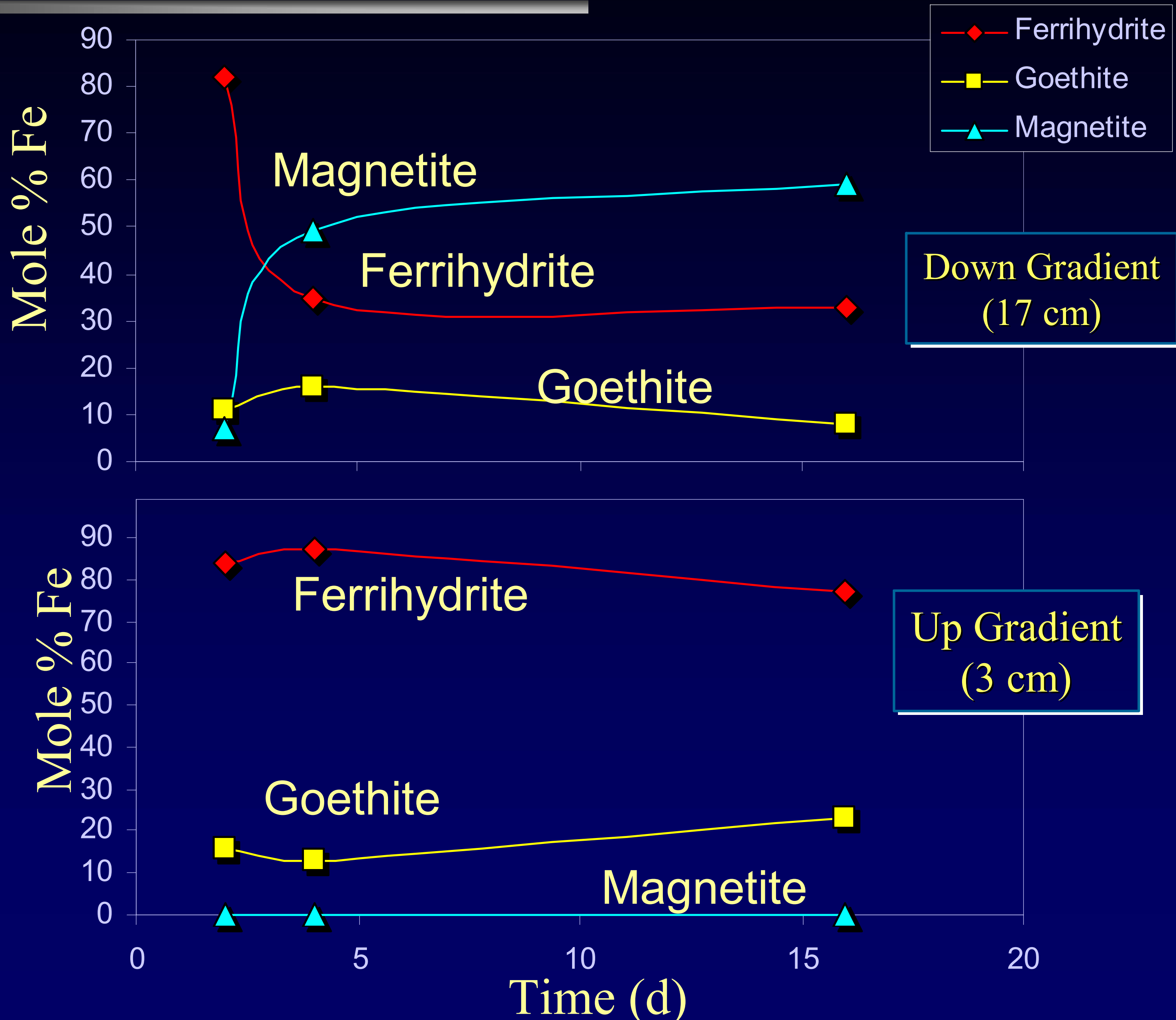
Iron Biomineralization



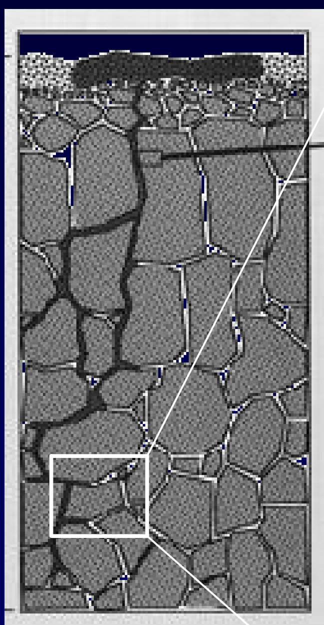
Spatial Heterogeneity in Biogeochemical Processes

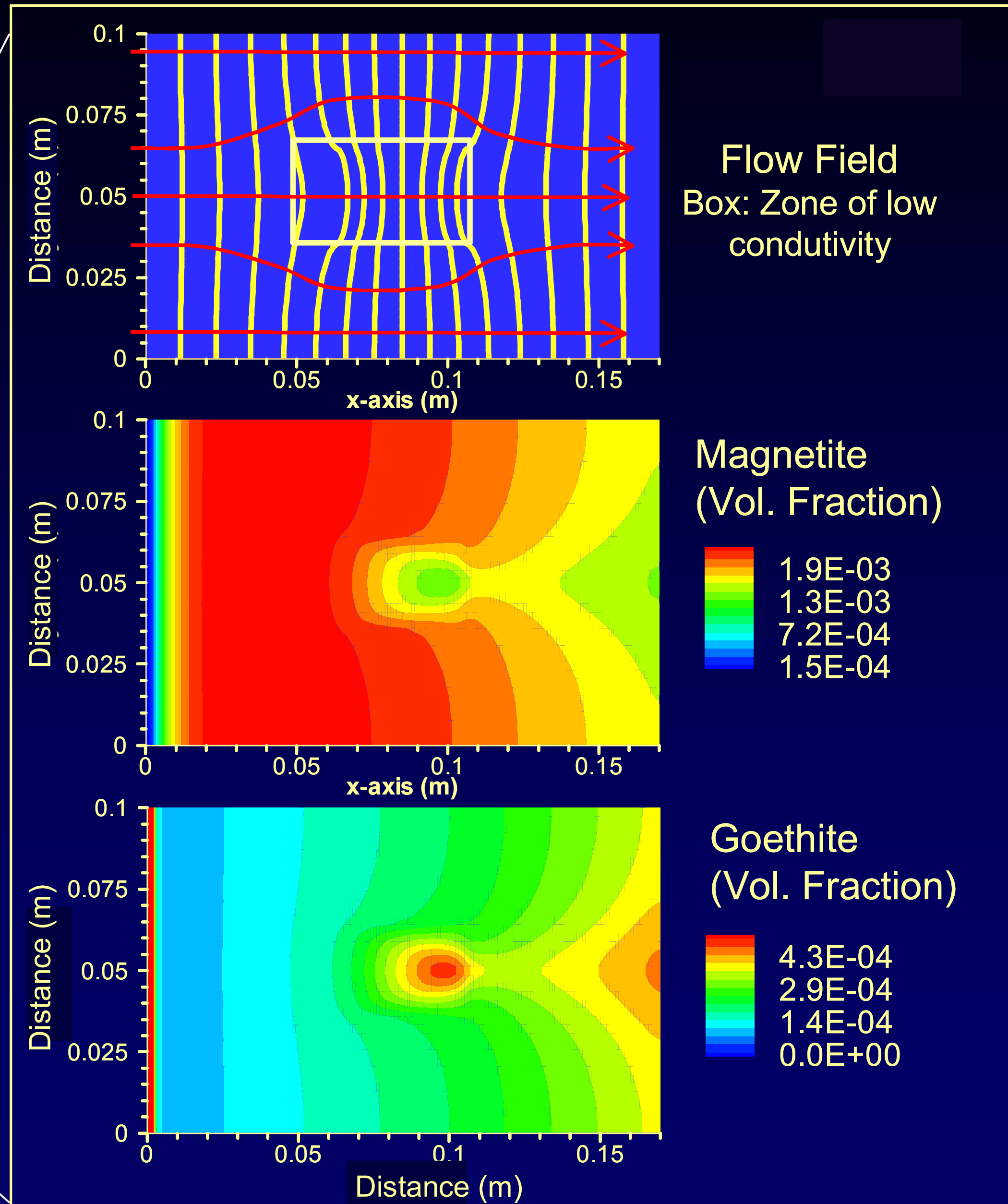


Solid-Phase Evolution

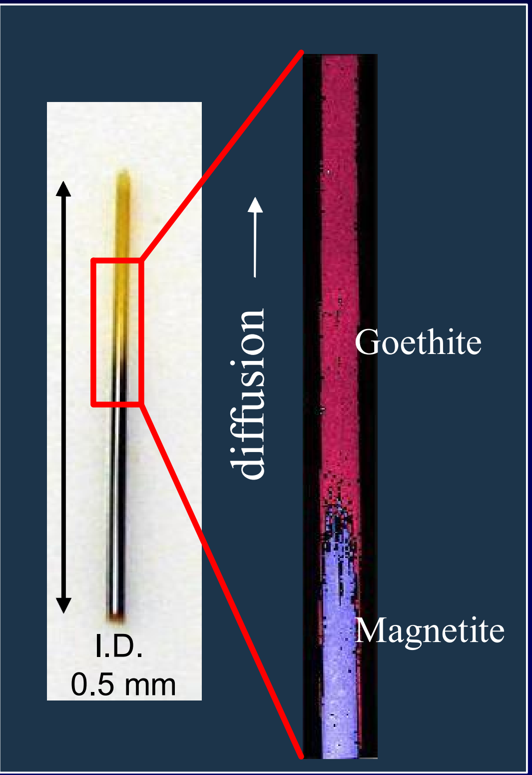


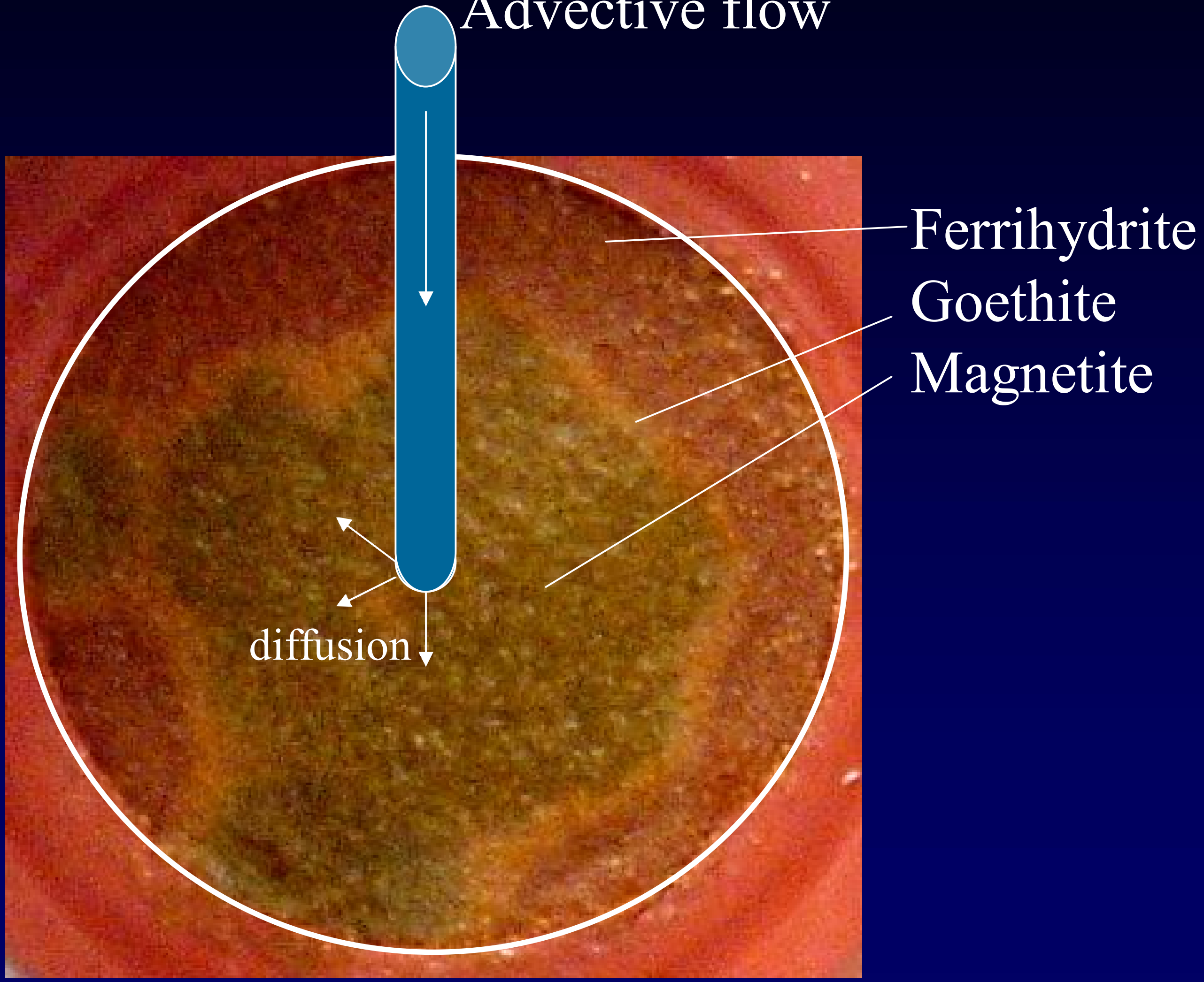
Heterogeneity in Iron Biomineralization



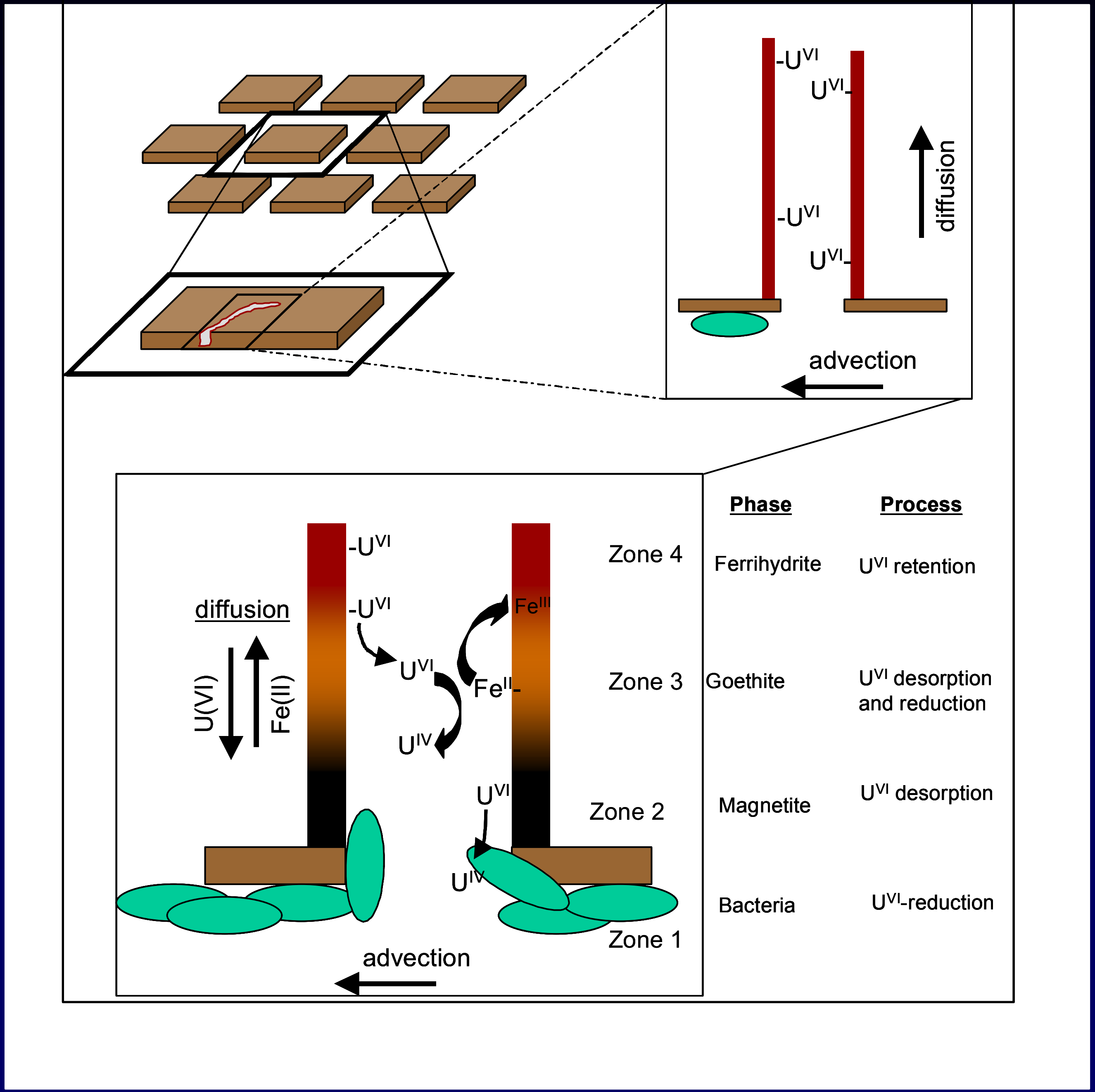


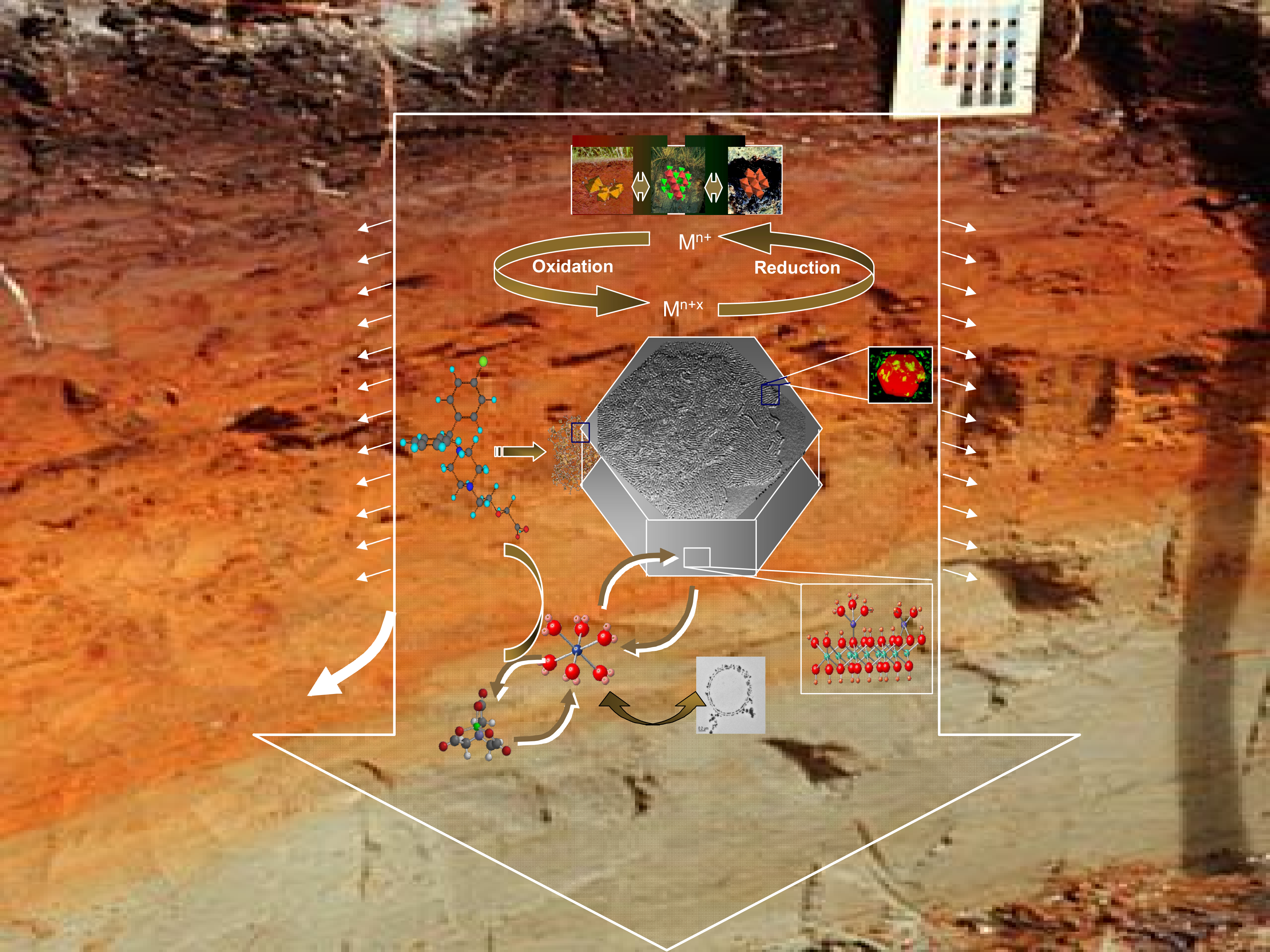
Biomineralization within Physically Complex Media





Pore-scale Heterogeneity in Uranium Dynamics

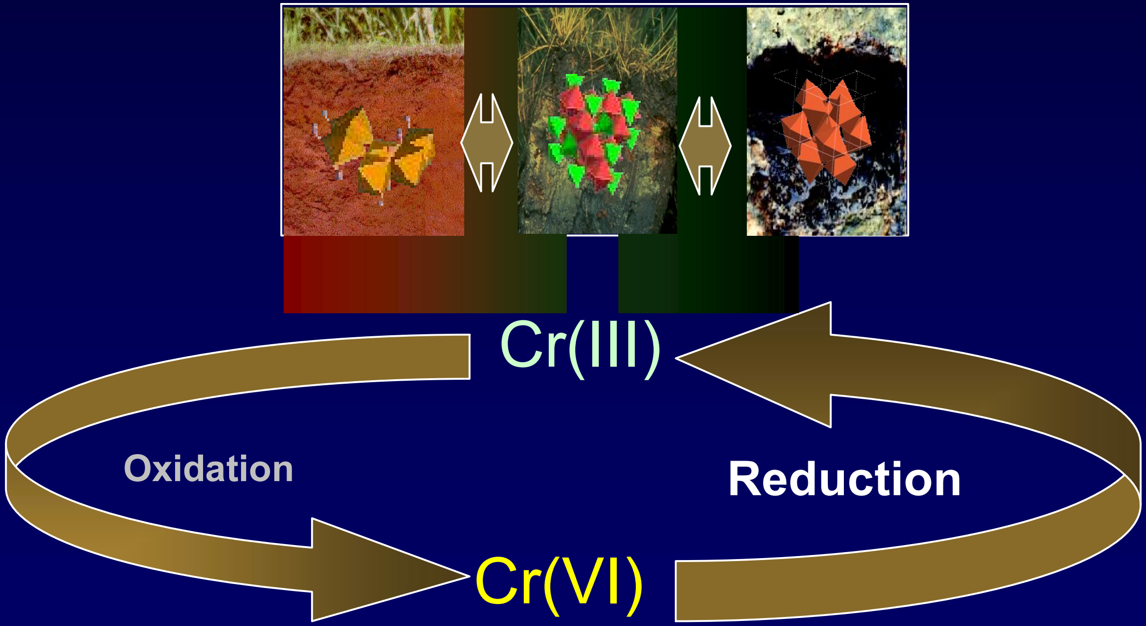




M^n+
Oxidation
Reduction
M^n+x

Impacts of Iron Transformation:

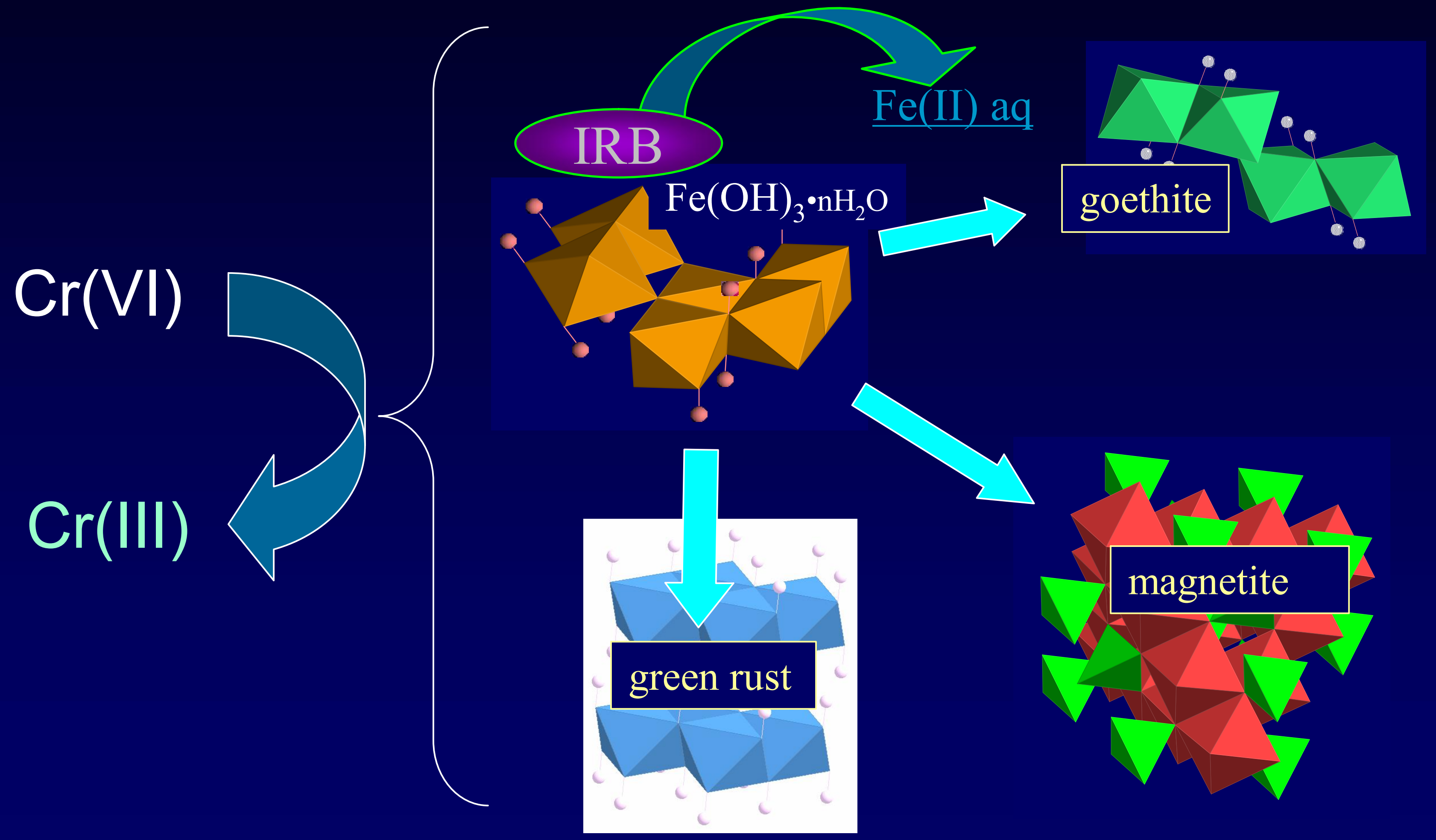
Reduction of Chromium



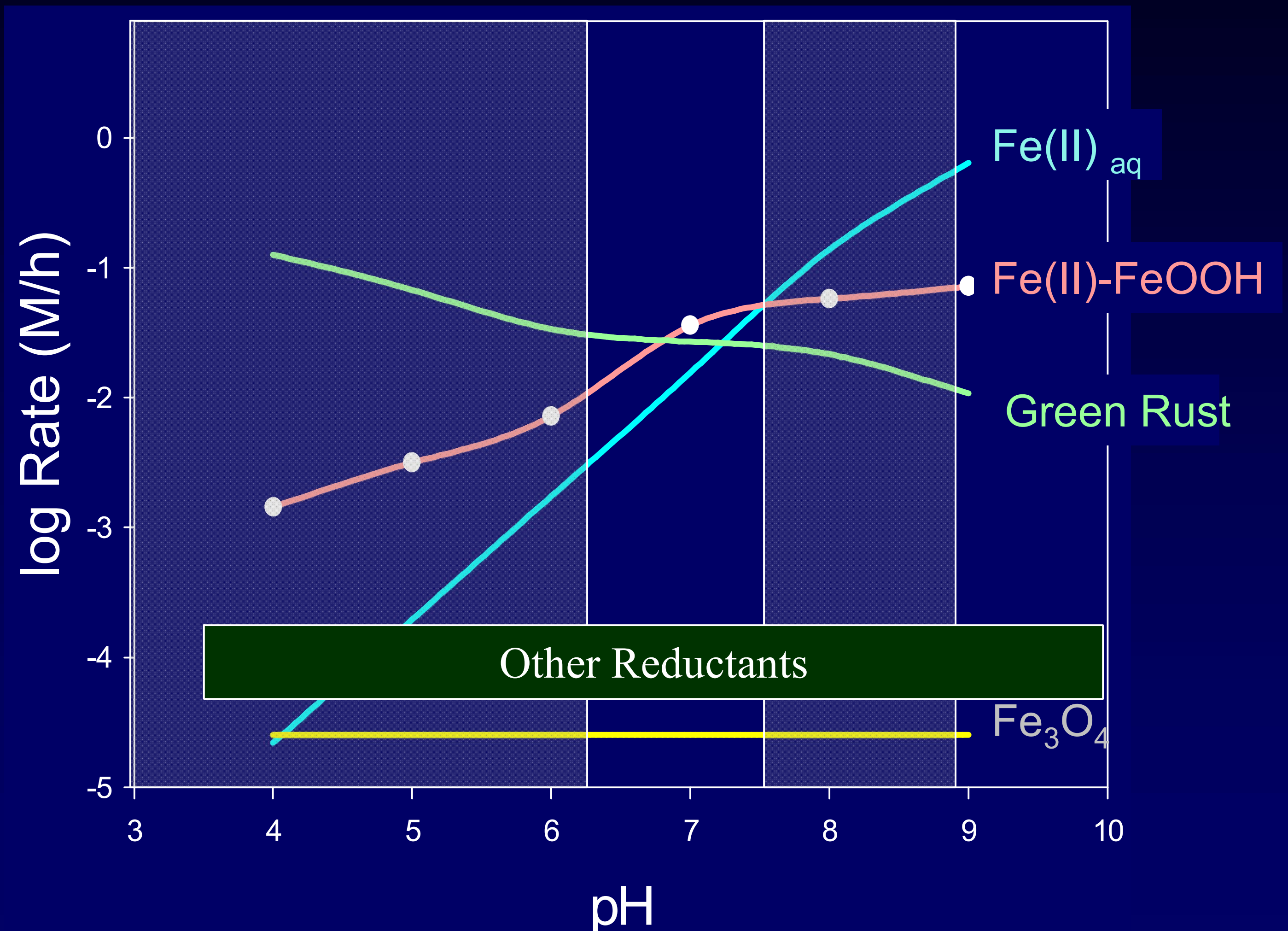
Reductants of Chromate

- Dissolved Fe(II)
- Dissolved (S-II)
- Soluble and particulate organic molecules/material
  - mineral catalyzed
  - photoinduced
- ‘Reduced’ Minerals
  - Fe(II) bearing
  - ‘reduced’ sulfur (-II, 0, …)
- Bacteria (enzymatic reduction)

Impact of Biomineralization on Chromium Dynamics



Comparative Rates of Reduction

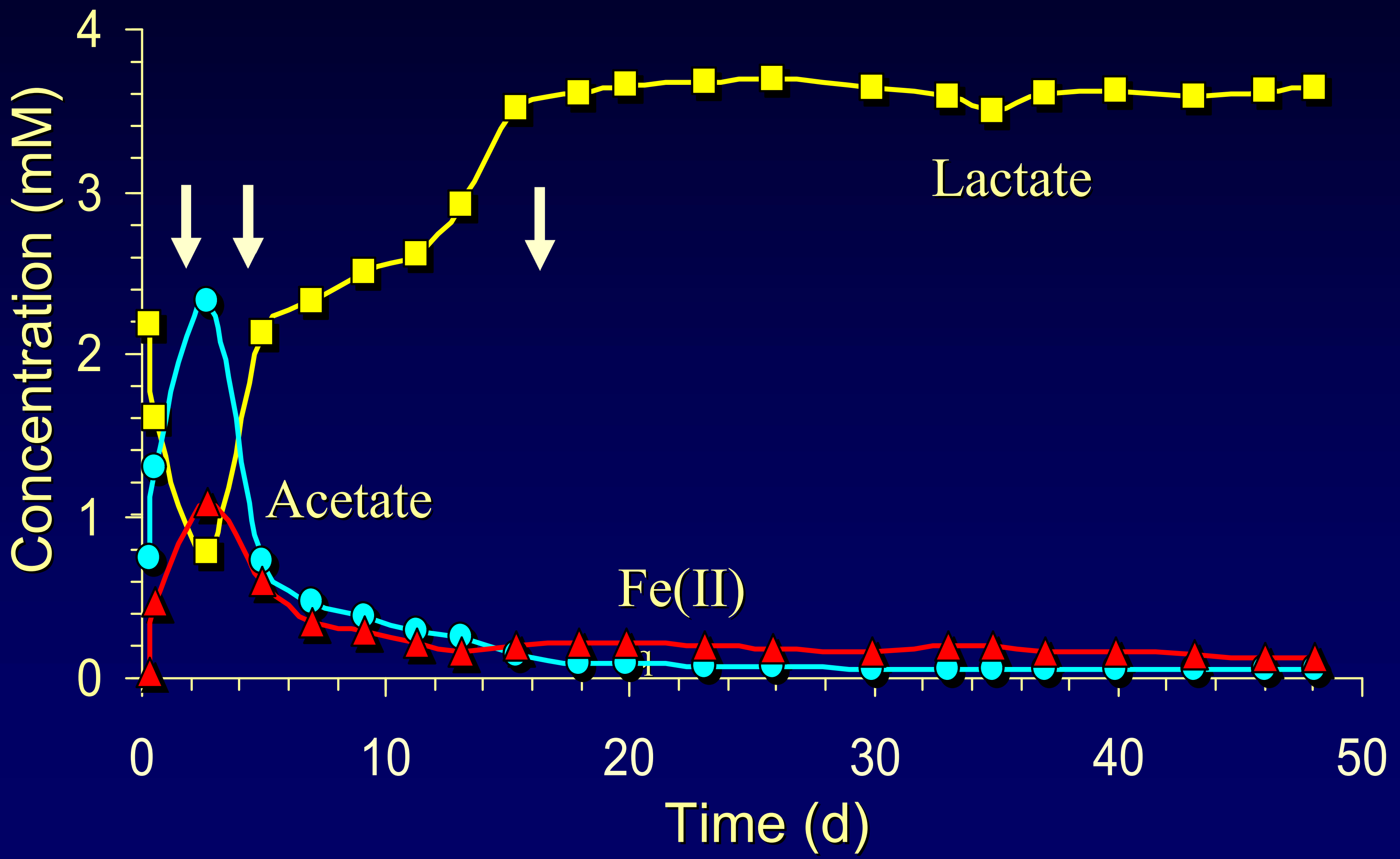


- Ferrihydrite transformation proceeds rapidly
  - Coupled biotic-abiotic reaction path
  - Generation of goethite and magnetite (lepidocrocite and green rust)
- Chromate reduction is dominated by Fe(II) (sorbed and aqueous) and green rust.
- Uranyl reduction is dependent on aqueous speciation and active metal reducing bacteria

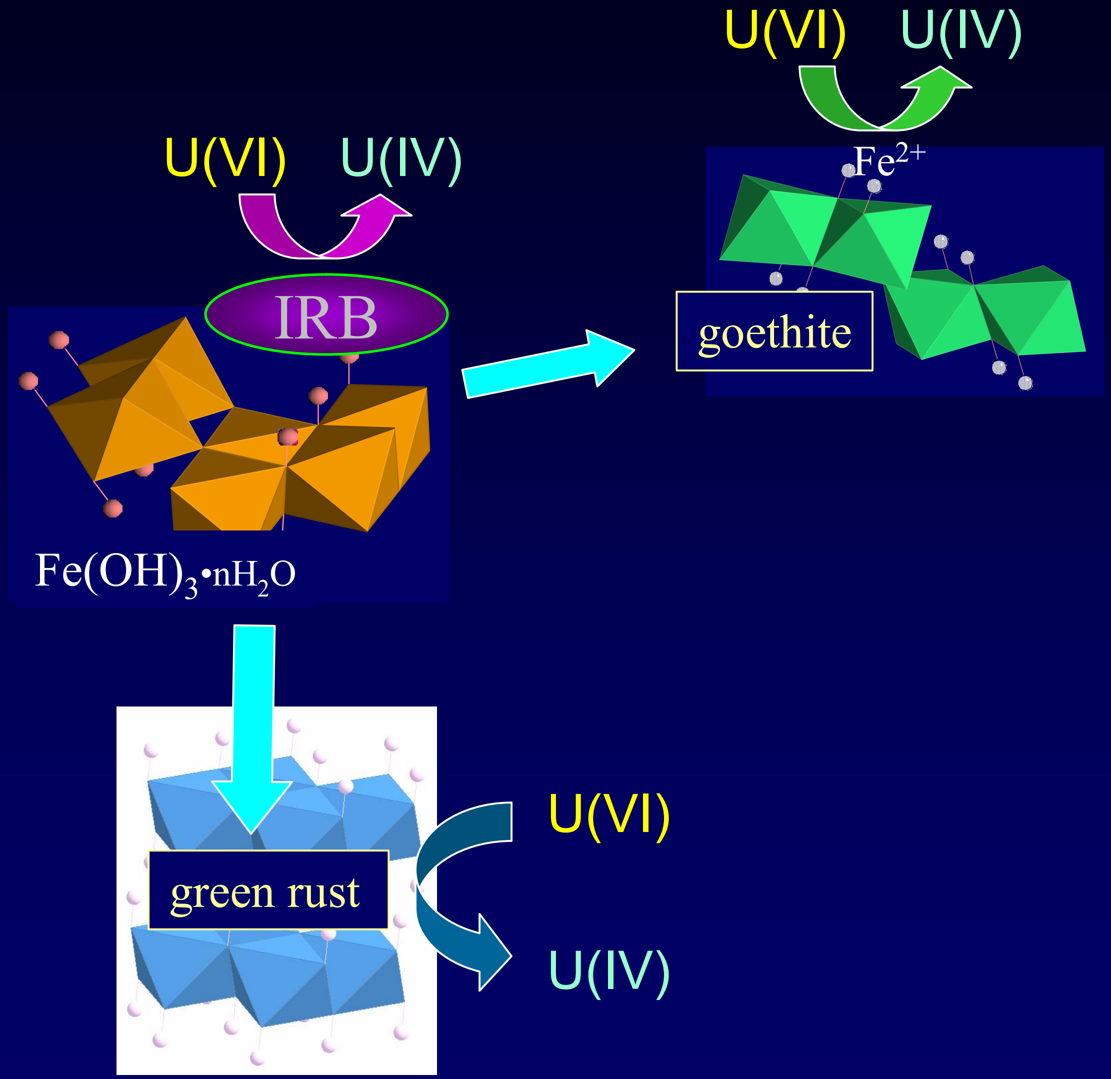
- Biomineralization of ferric hydroxide, a ubiquitous and reactive aerobic iron phase, results dominantly in goethite and magnetite
- Biomineralization occurs via a coupled, biotic-abiotic process that results in solids with constrained size and morphology
- Physical complexity will result in biomineralization heterogeneity
- Iron transformations in natural systems will impact contaminant dynamics and Fe availability
  - alter magnitude and retention strength of contaminants
  - impart reductive capacity

Reaction Progression

$\frac{1}{4}C_3H_5O_3^- + Fe(OH)_3 \rightarrow \frac{1}{4}C_2H_3O_2^- + Fe^{2+} + \frac{1}{4}HCO_3^- + 2/3H_2O + 7/4OH^-$



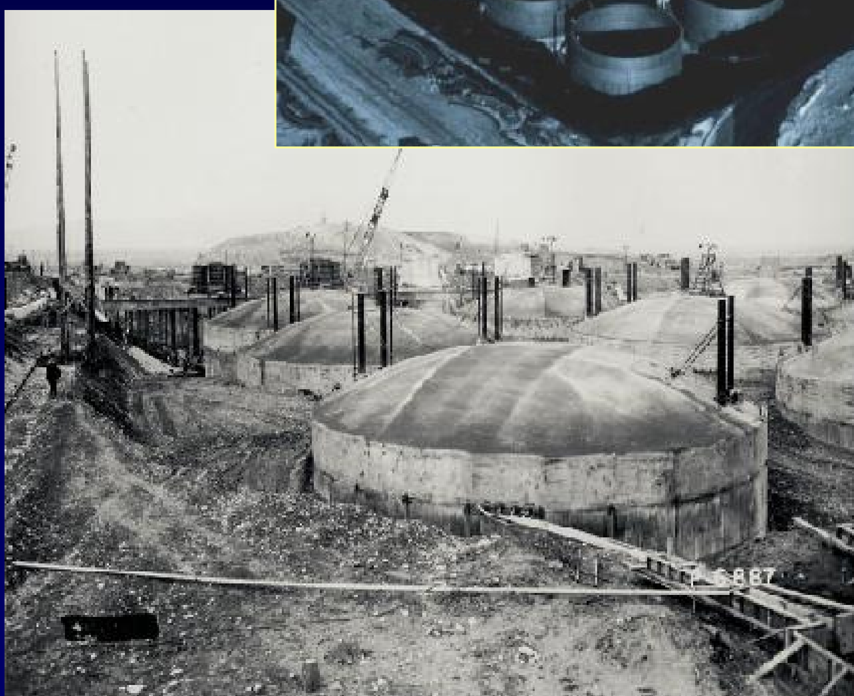
Processes Controlling Uranium Reduction

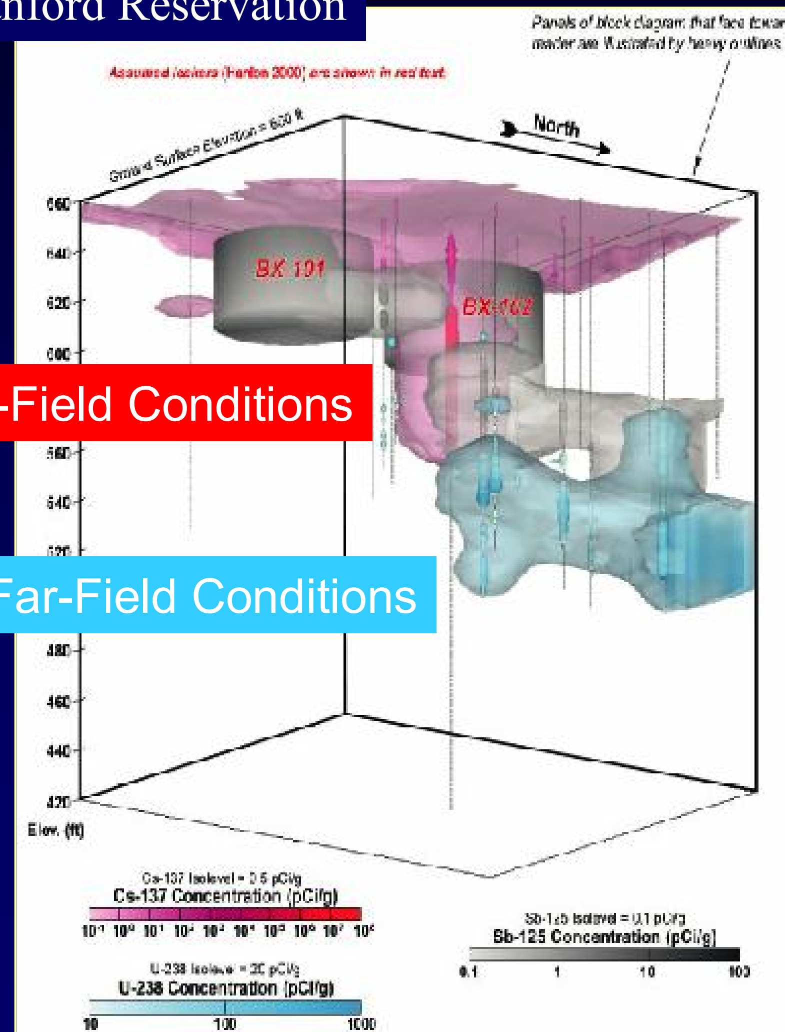


Physical-Chemical/Mineralogical Challenges

Defining reactive constituents within innately heterogeneous media

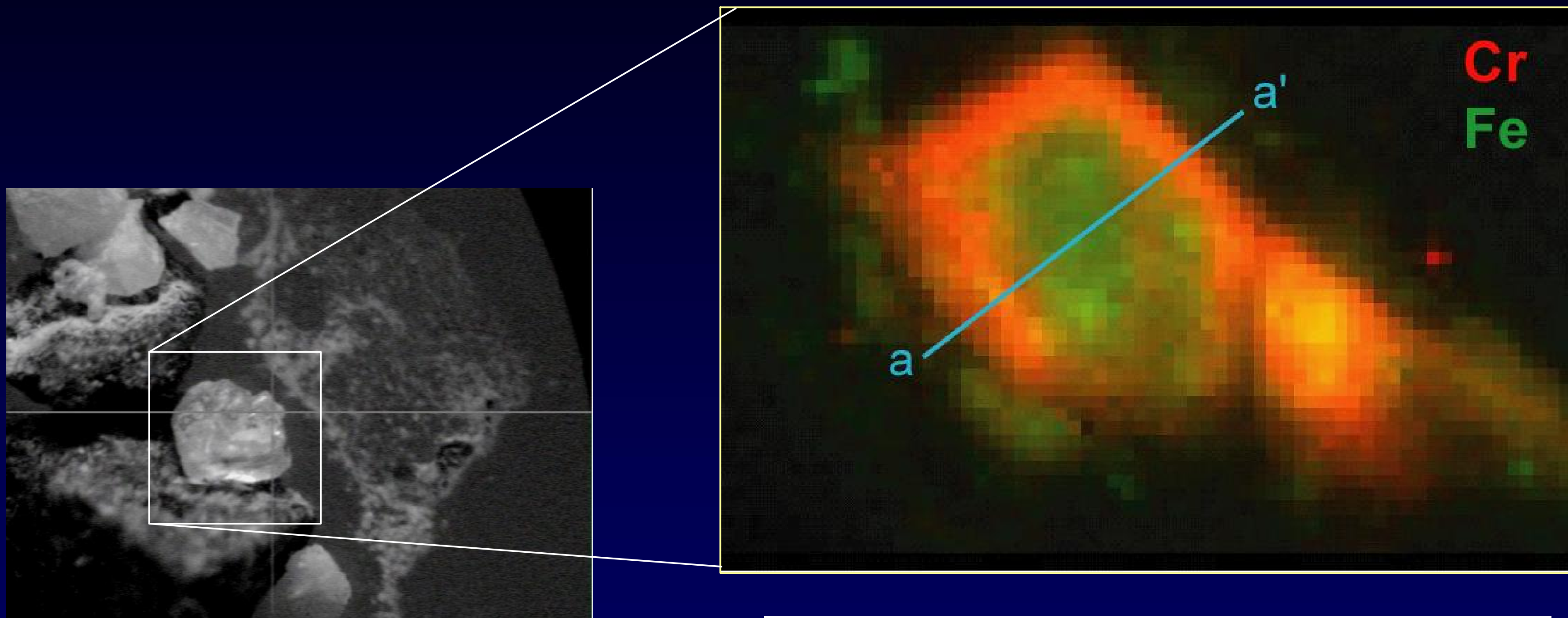
Chromium(VI) Transport at the Hanford Reservation

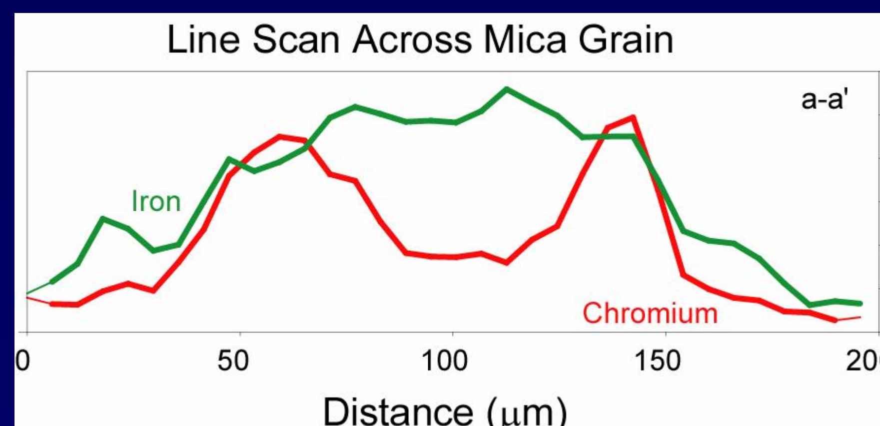


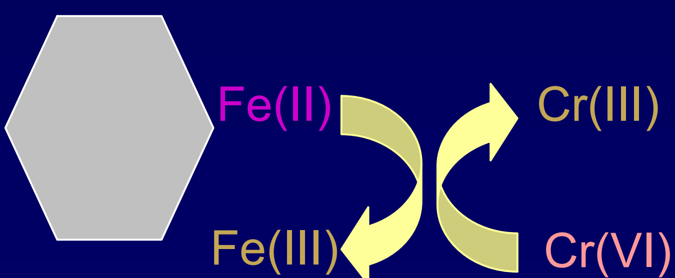


Cr(VI) Reactions within Hanford Sediments

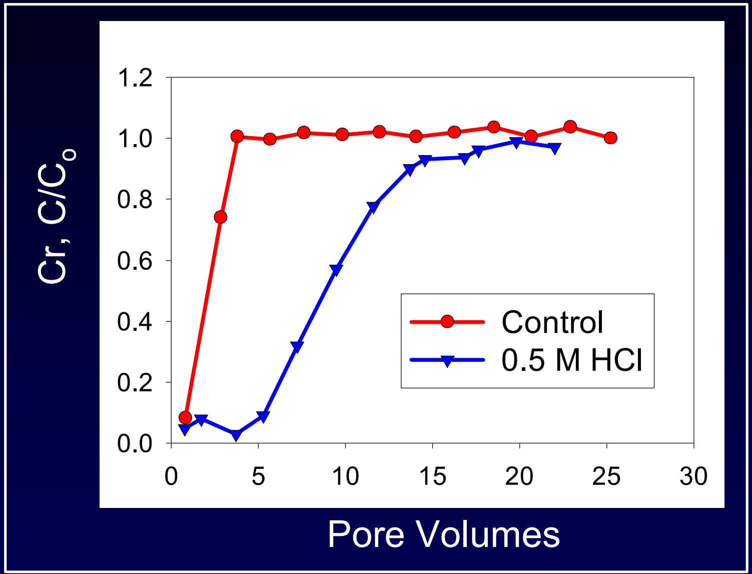
Defining reactive constituents within innately heterogeneous media





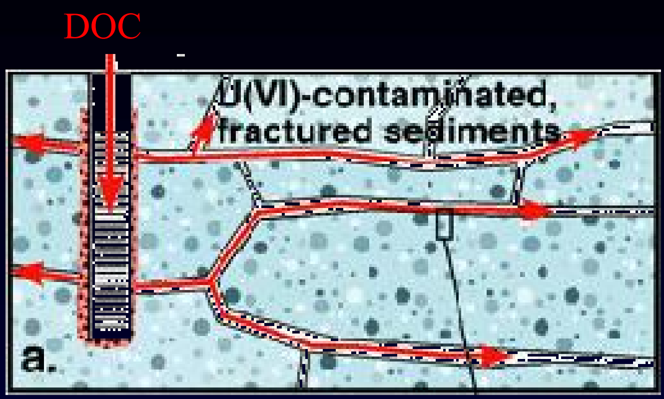


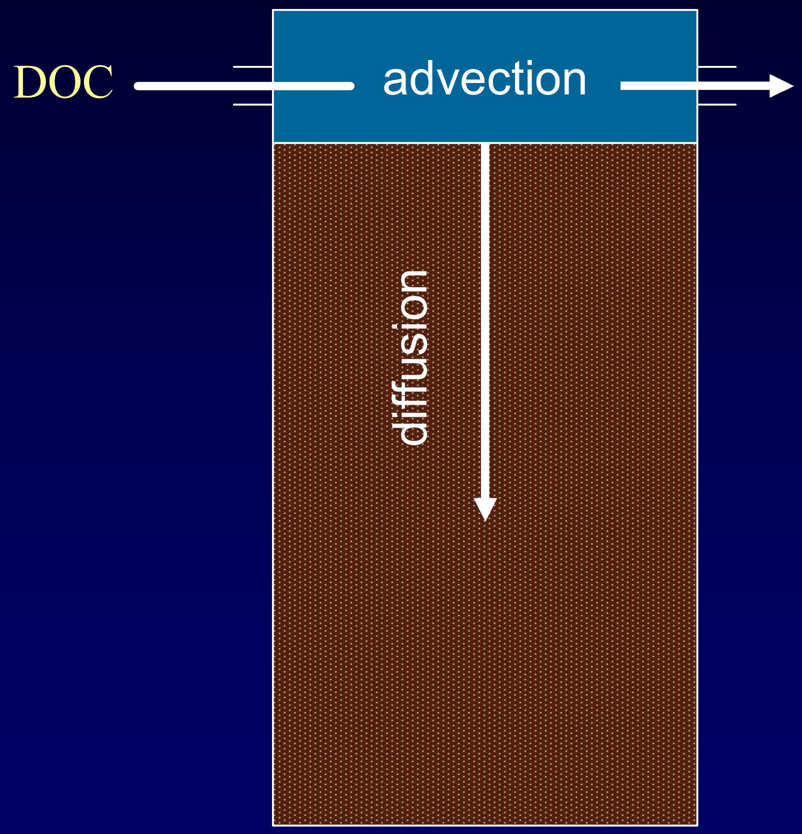
Reactive Transport of Cr(VI) within Hanford Sediments

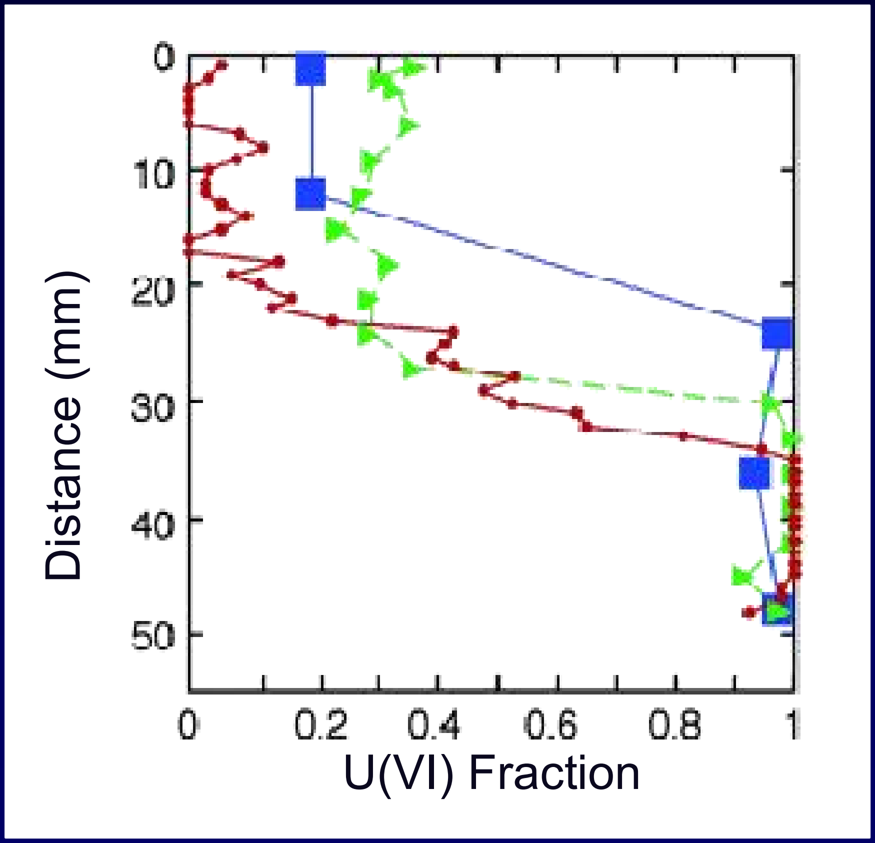


- Cr(VI) (0.2 mM, pH 8) was reacted with Hanford sediments
- Cr breakthrough was retarded in acid treated sediment
    - 300 mg/Kg Cr retained within sediment
- What are the specific reductants?

Pore-scale Uranium Reduction

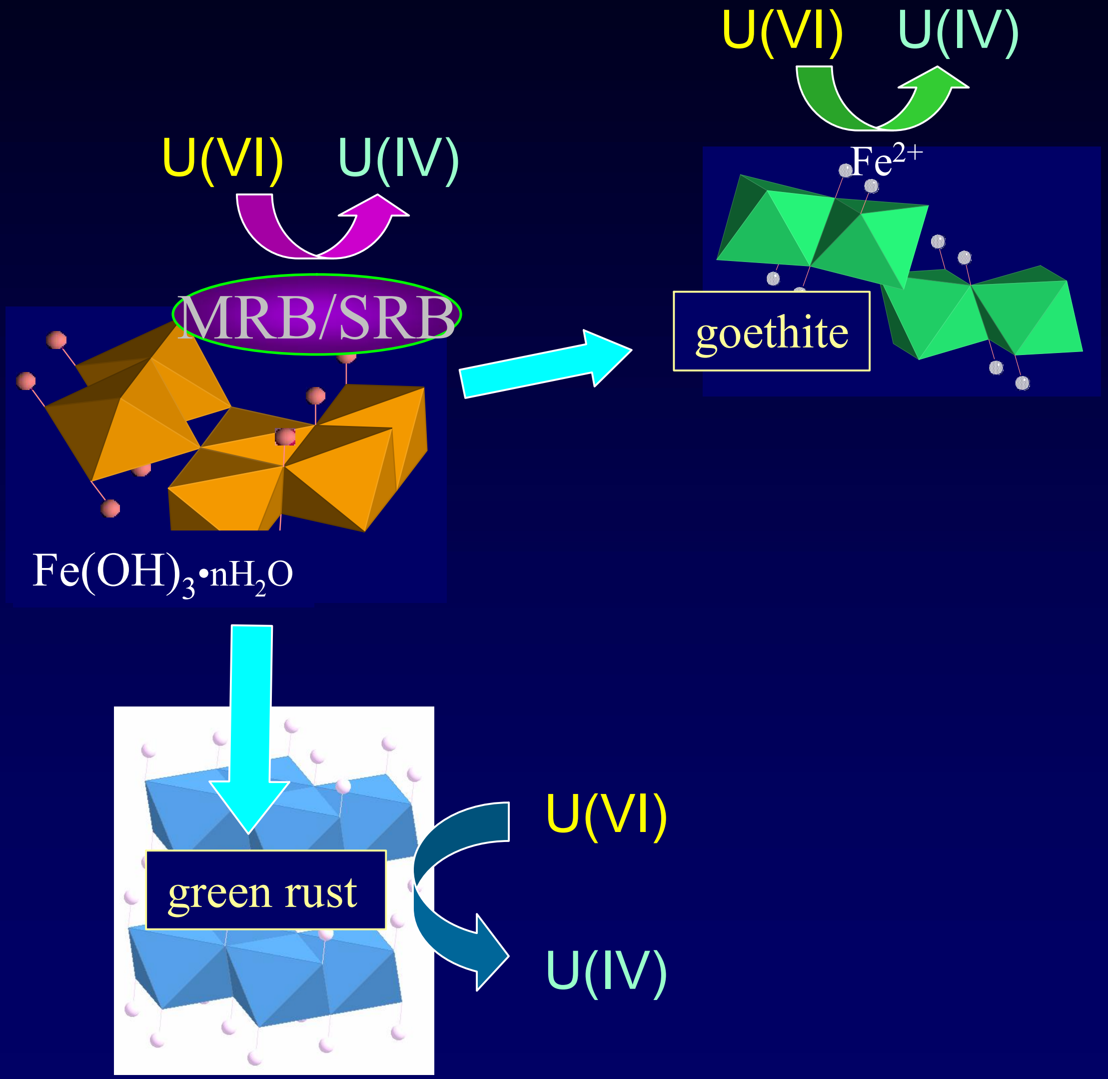




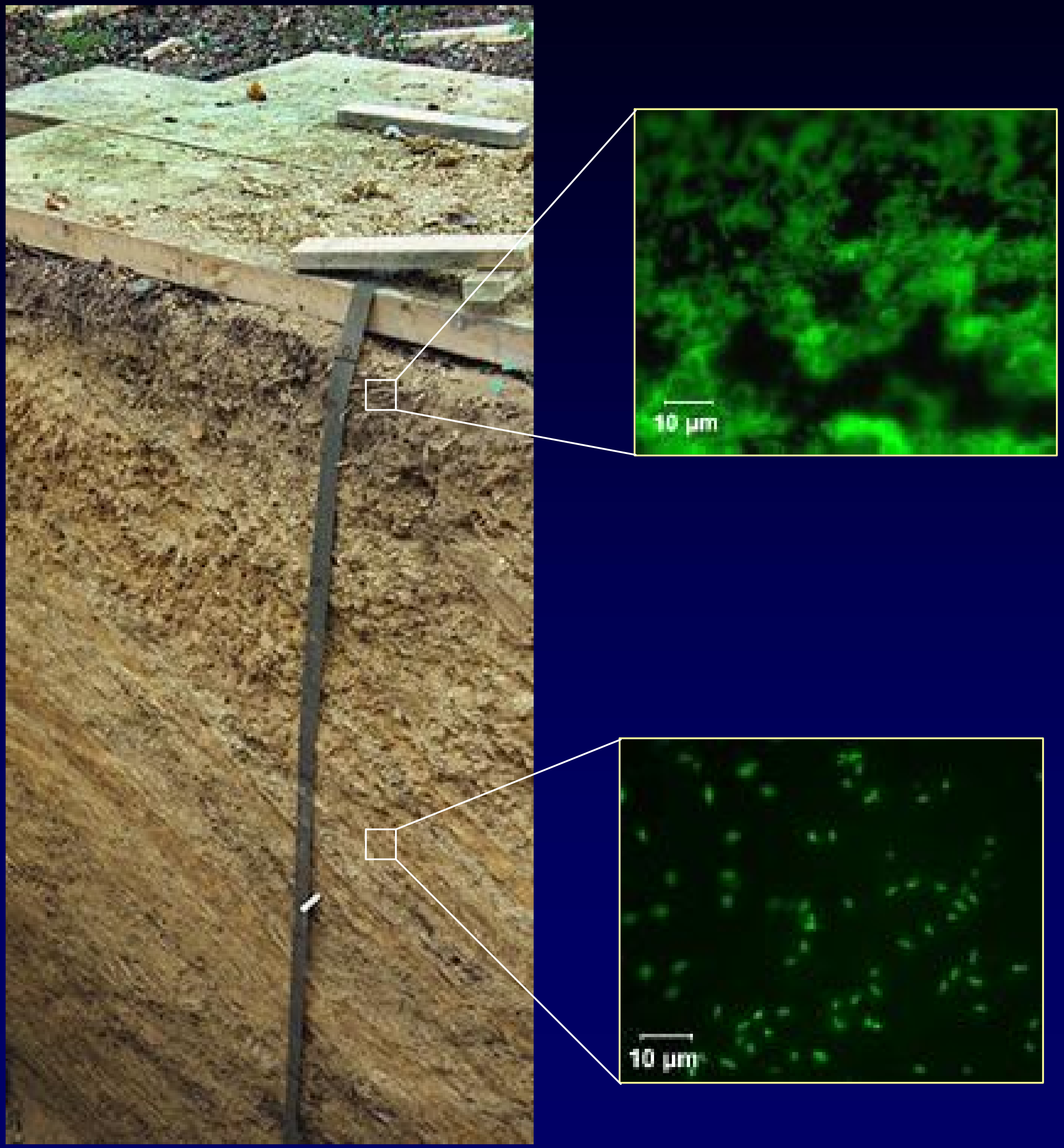


after Tokunaga et al., 2005

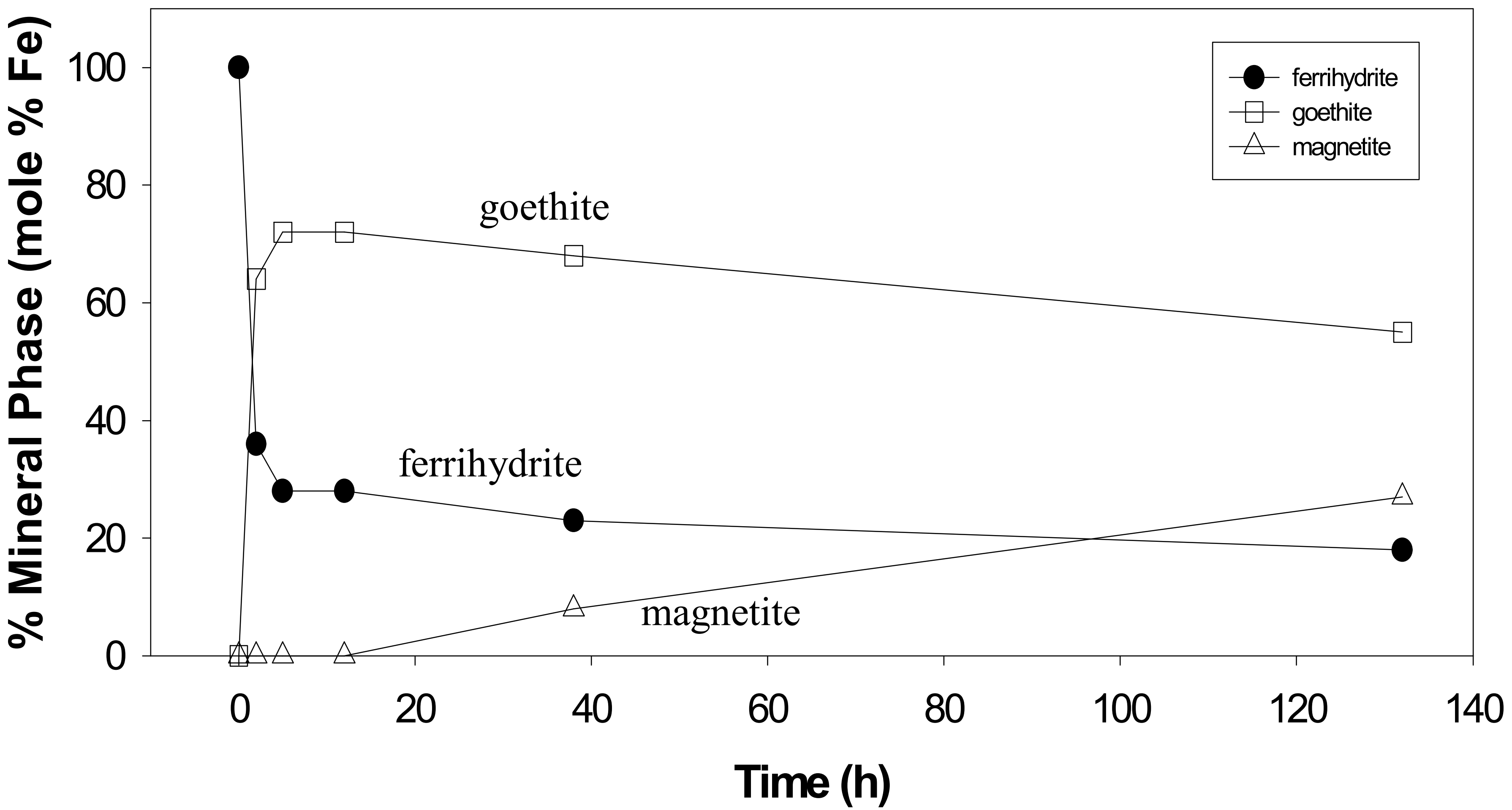
Reductants of Uranium



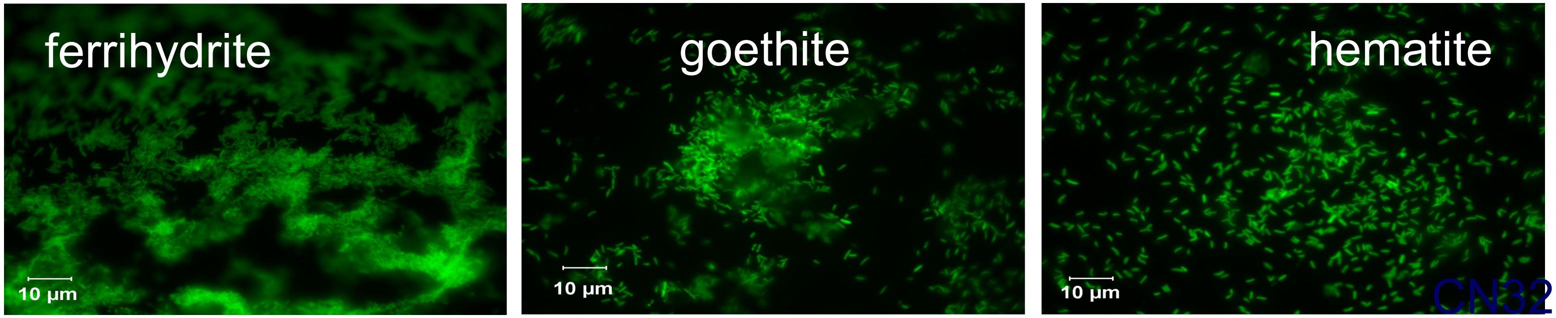
Localized Biogeochemical Processes



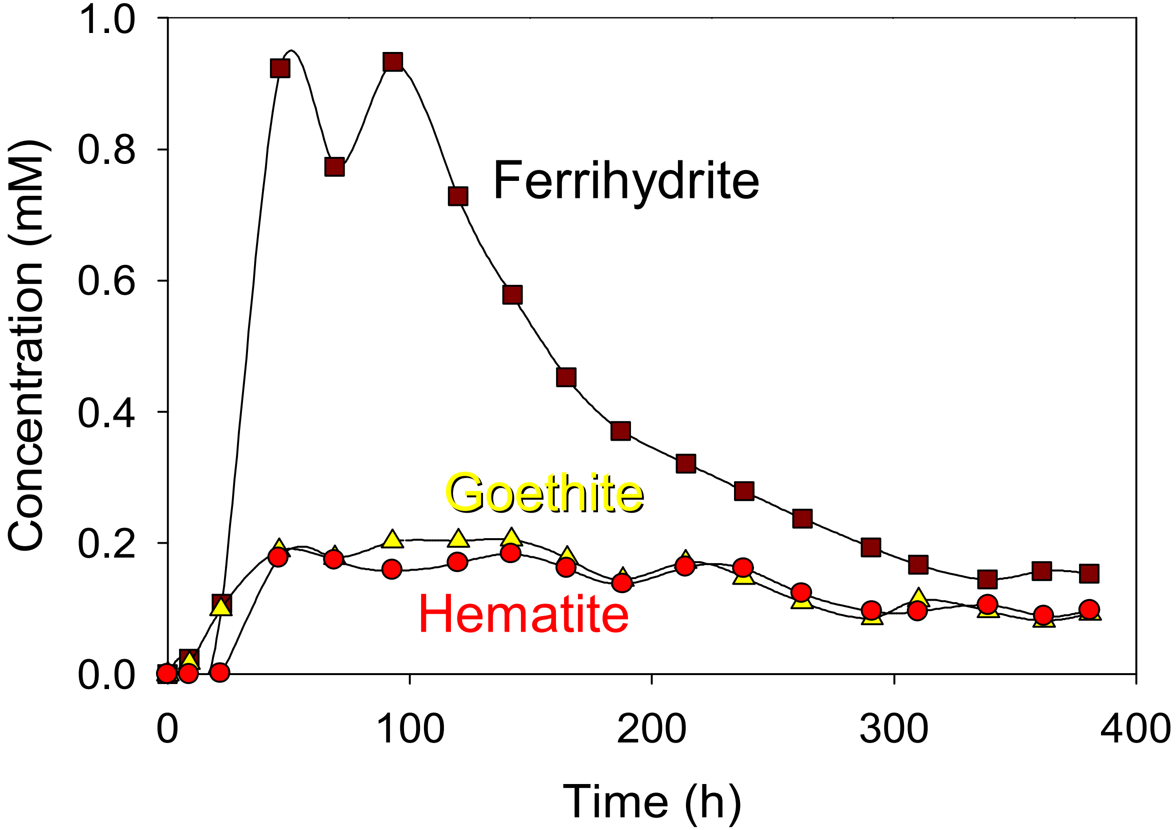
Ferrihydrite Transformation Upon Reaction with Fe(II)



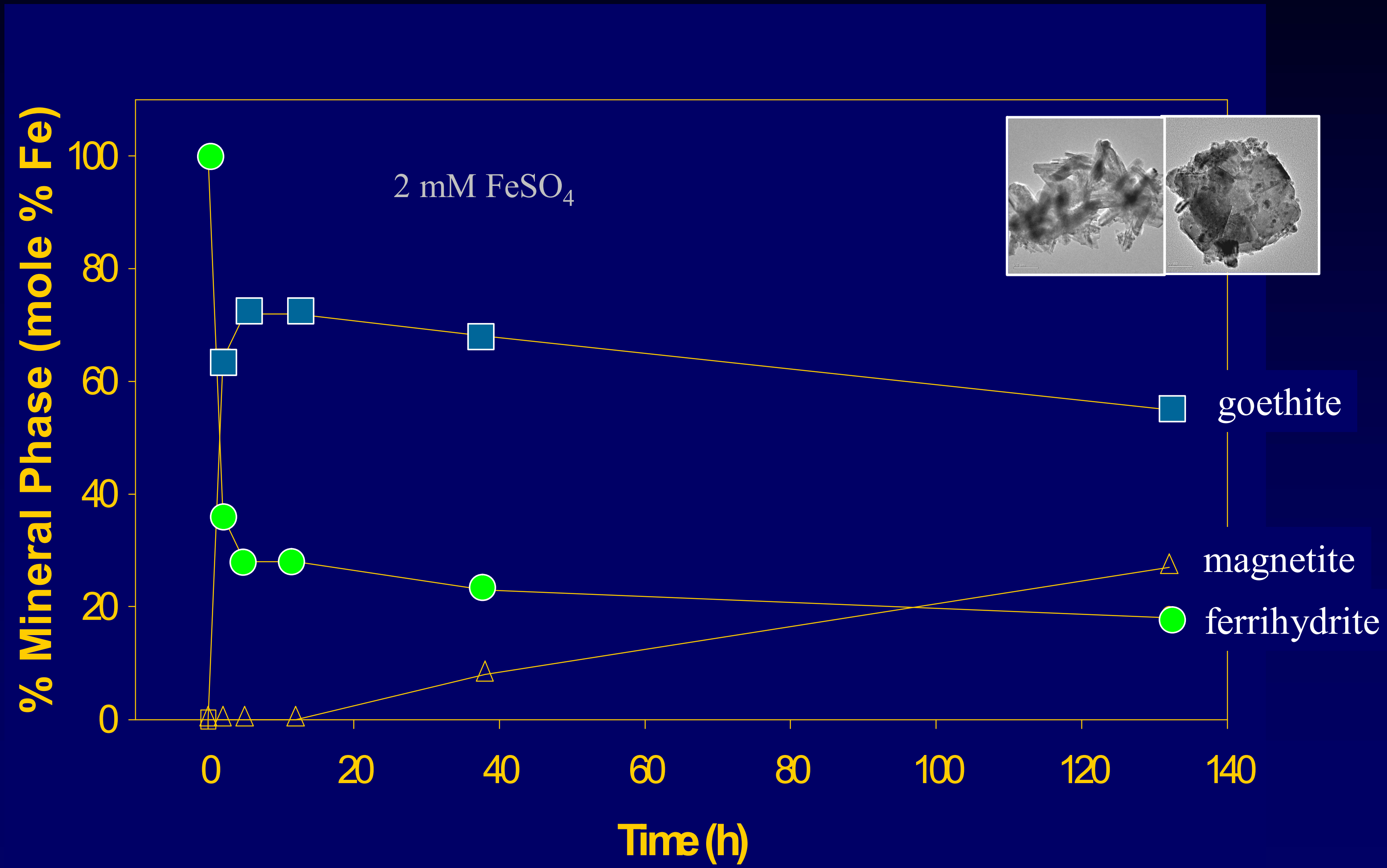
Changing Reactivity of Ferrihydrite



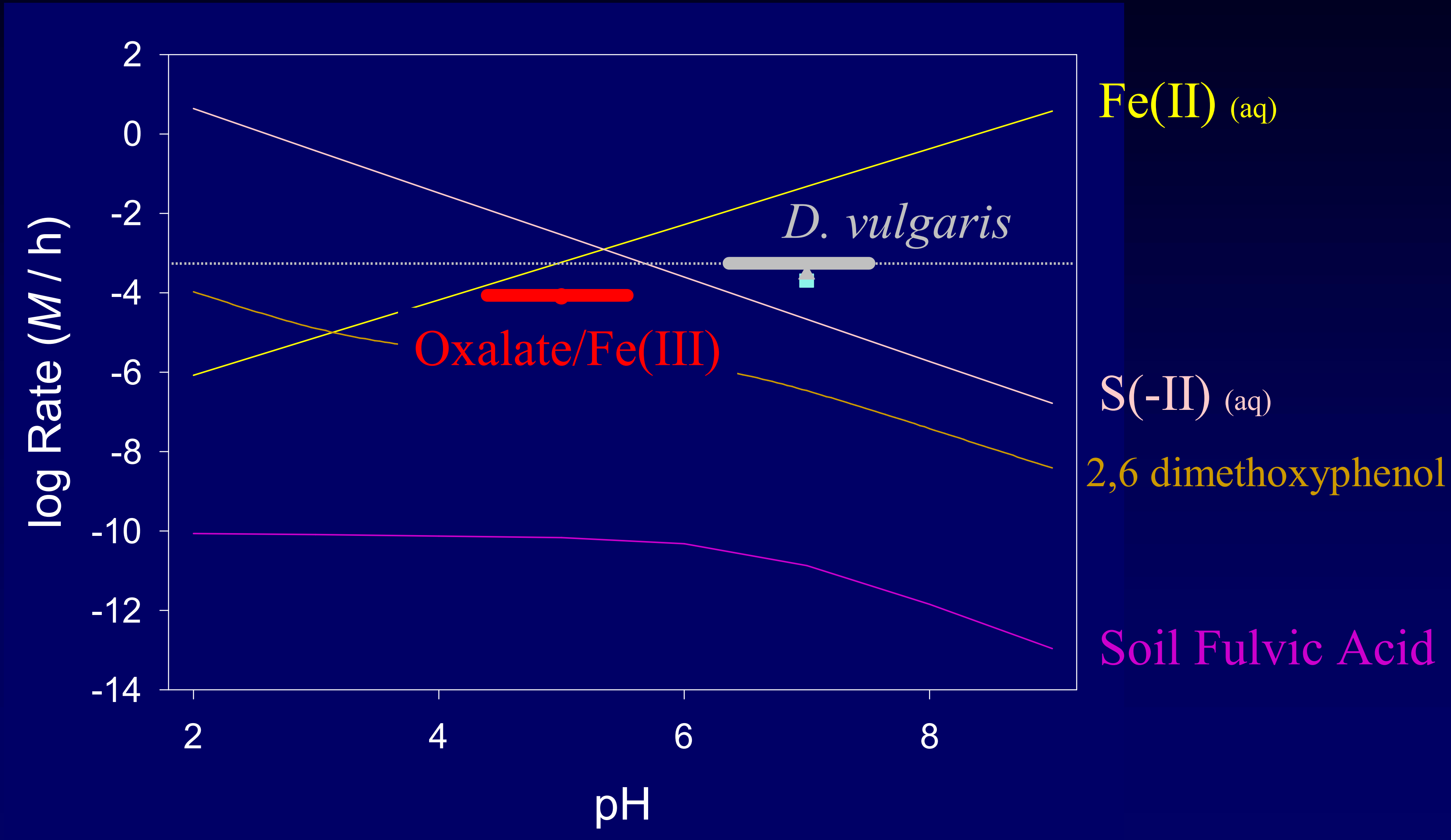
$C_3H_5O_3^- + 4Fe(OH)_3 \rightarrow C_2H_3O_2^- + 4Fe^{2+} + HCO_3^- + 8/3H_2O + 7OH^-$



Rate of Mineralogical Transformation



Comparative Rates of Chromate Reduction



Controlling Factor in U(VI) Reduction