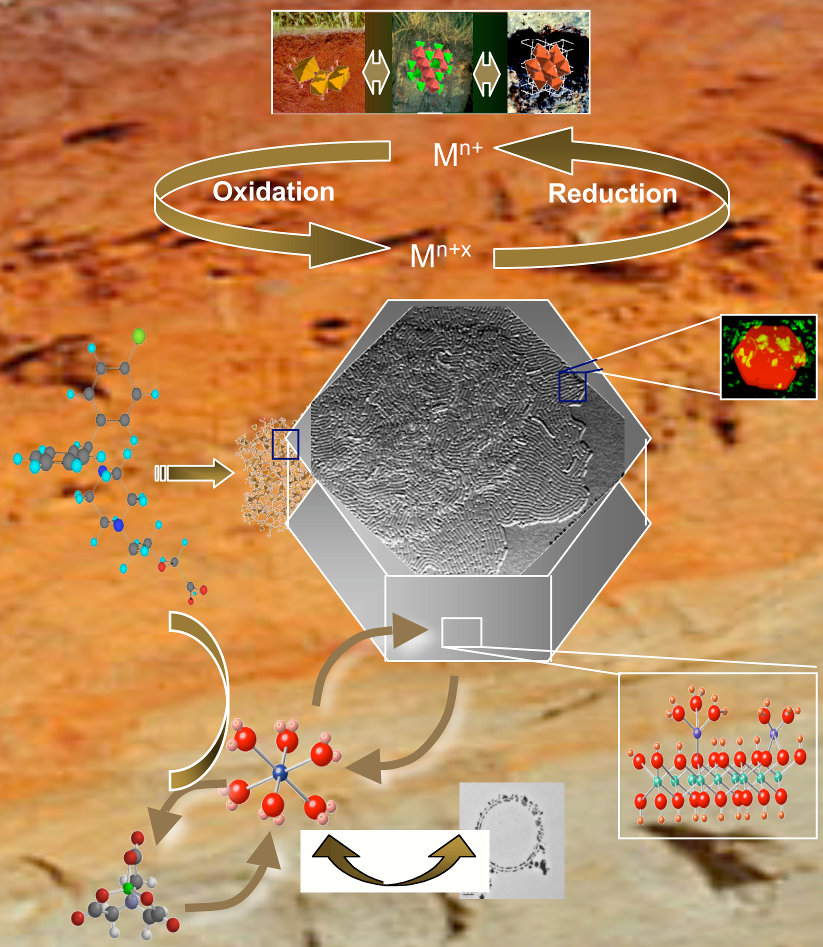
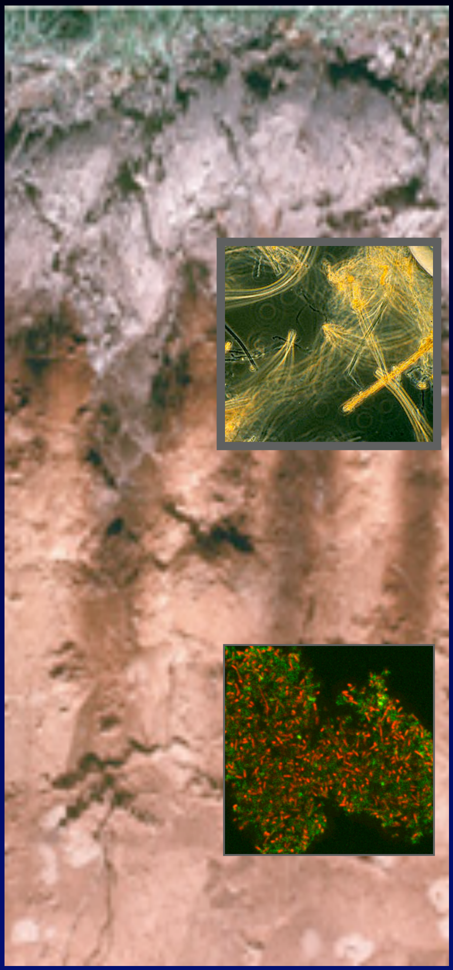
Biogeochemical Process Heterogeneity Impacting Contaminant Dynamics in Subsurface Environments



Scott Fendorf
Stanford University

CONTRIBUTORS

- Celine Pallud, Stanford University
- Peter Nico, LBNL
- Brandy Stewart, Stanford University
- Matt Ginder-Vogel, University of Delaware
- Jim Neiss, San Francisco State University
- Shawn Benner, Boise State University
- Colleen Hansel, Harvard University
- Thomas Borch, Colorado State University
- Kristin Revill, RHE
- Bruce Wielinga, MFG Incorp.

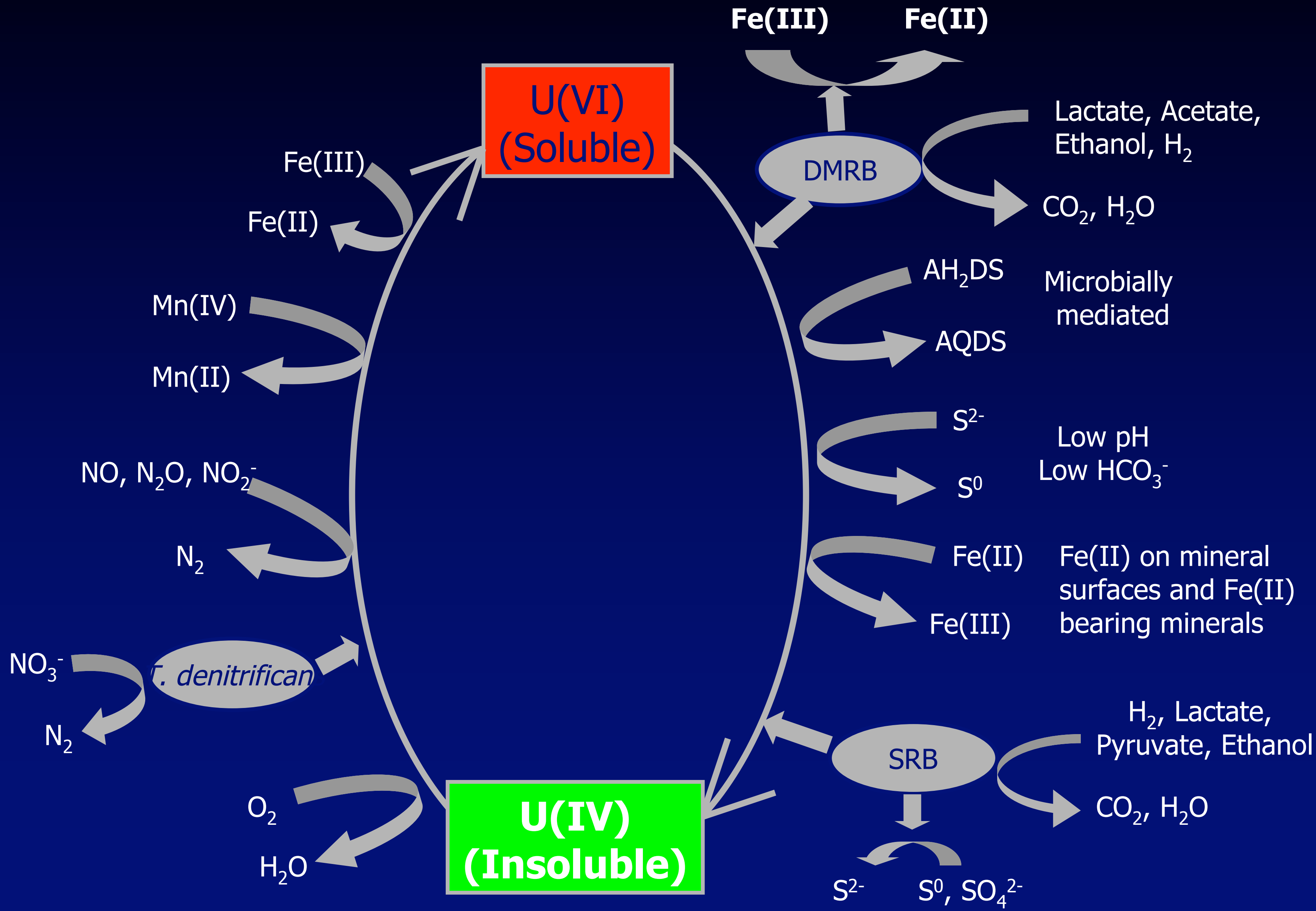


COLLABORATORS

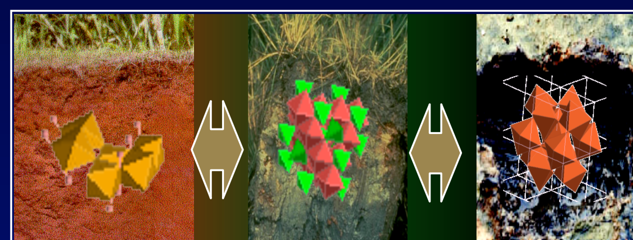
- Alice Dohnalkova, Ravi Kukaddapu   PNNL
- Phil Jardine   ORNL

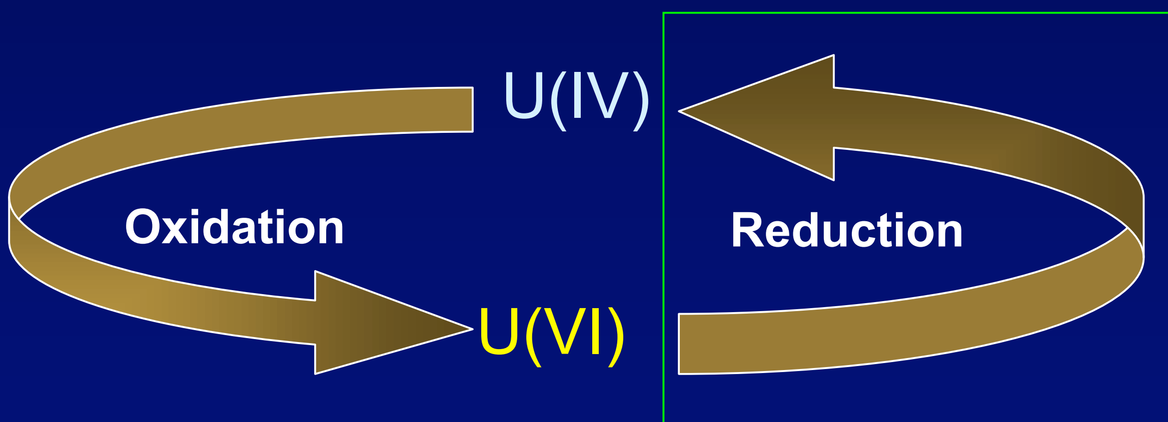
FUNDING: DOE-ERSP

Uranium Redox Cycle

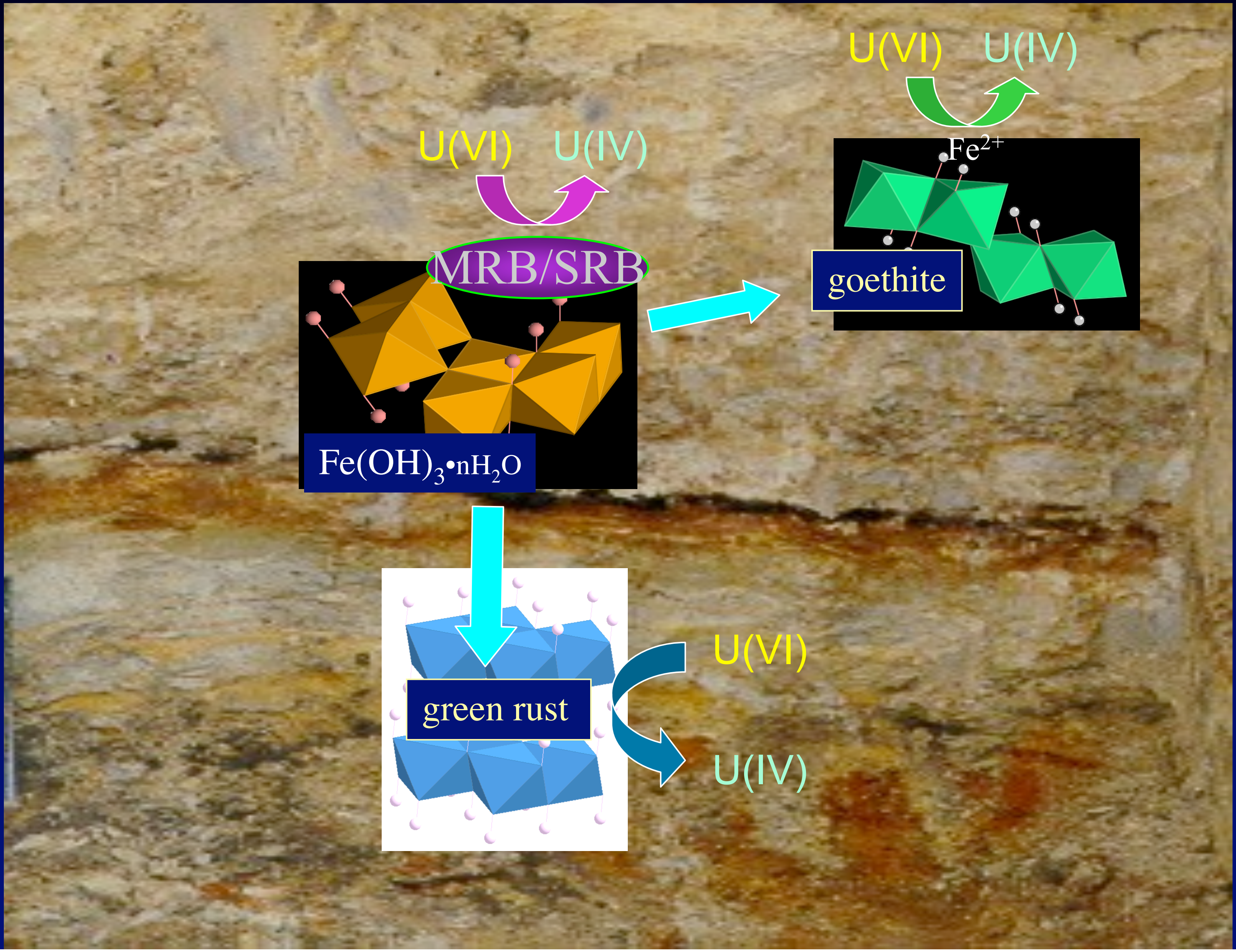


Reduction of Uranium



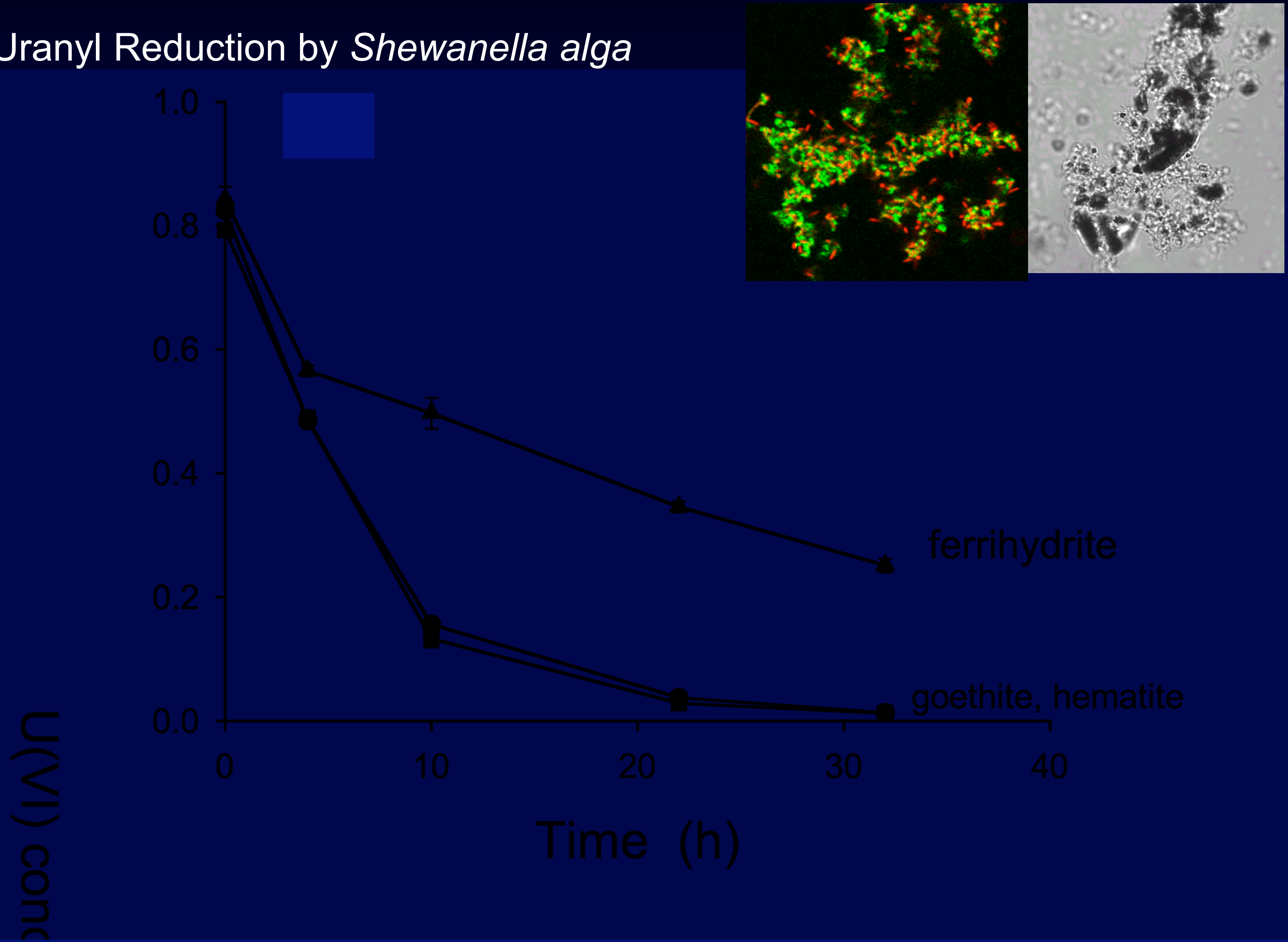


Uranium Reduction

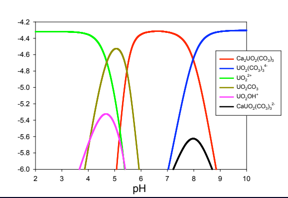


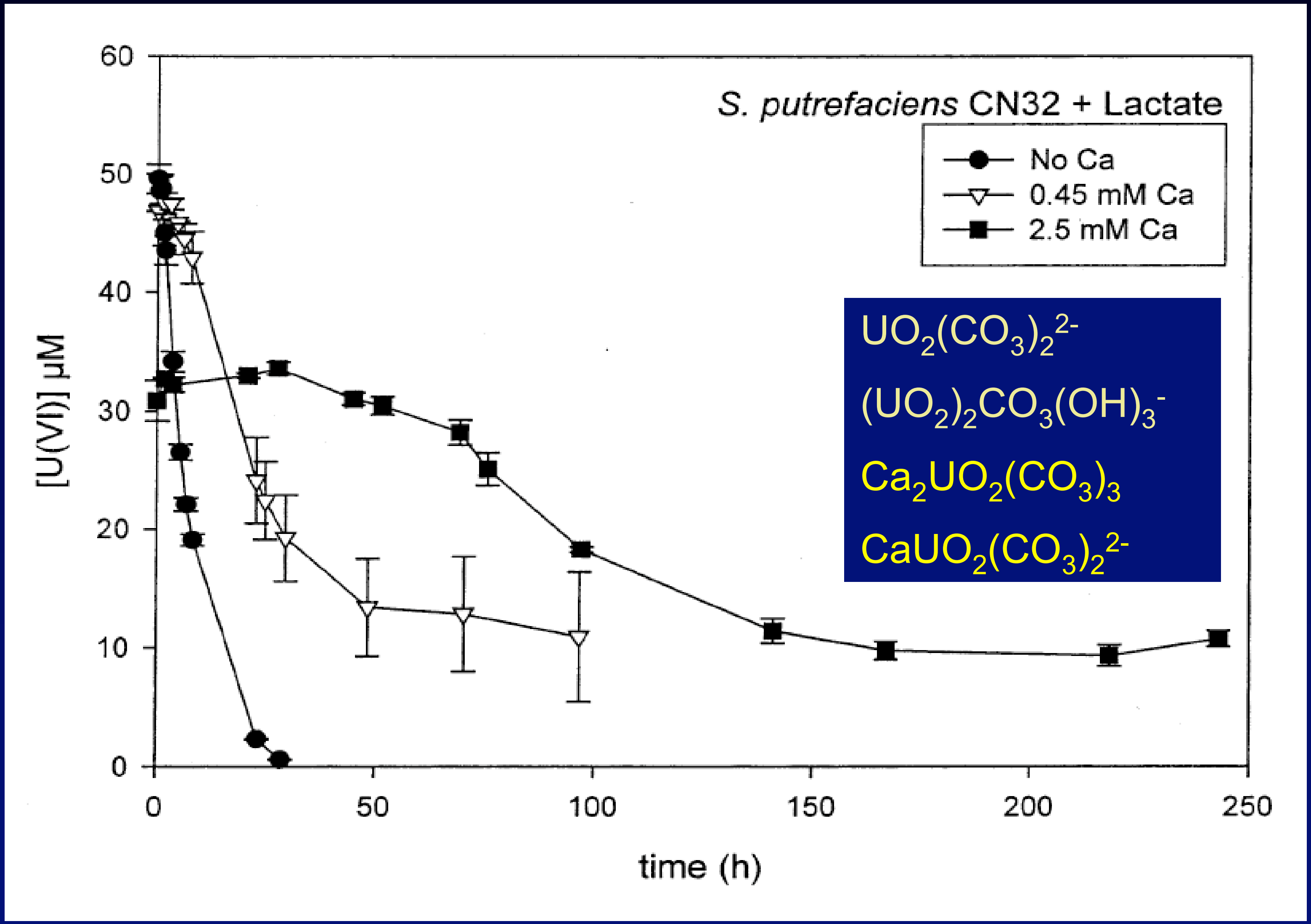
Geochemical Complexity: Impact of Iron

Uranyl Reduction by *Shewanella alga*



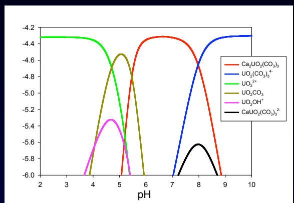
Geochemical Complexity: U Speciation





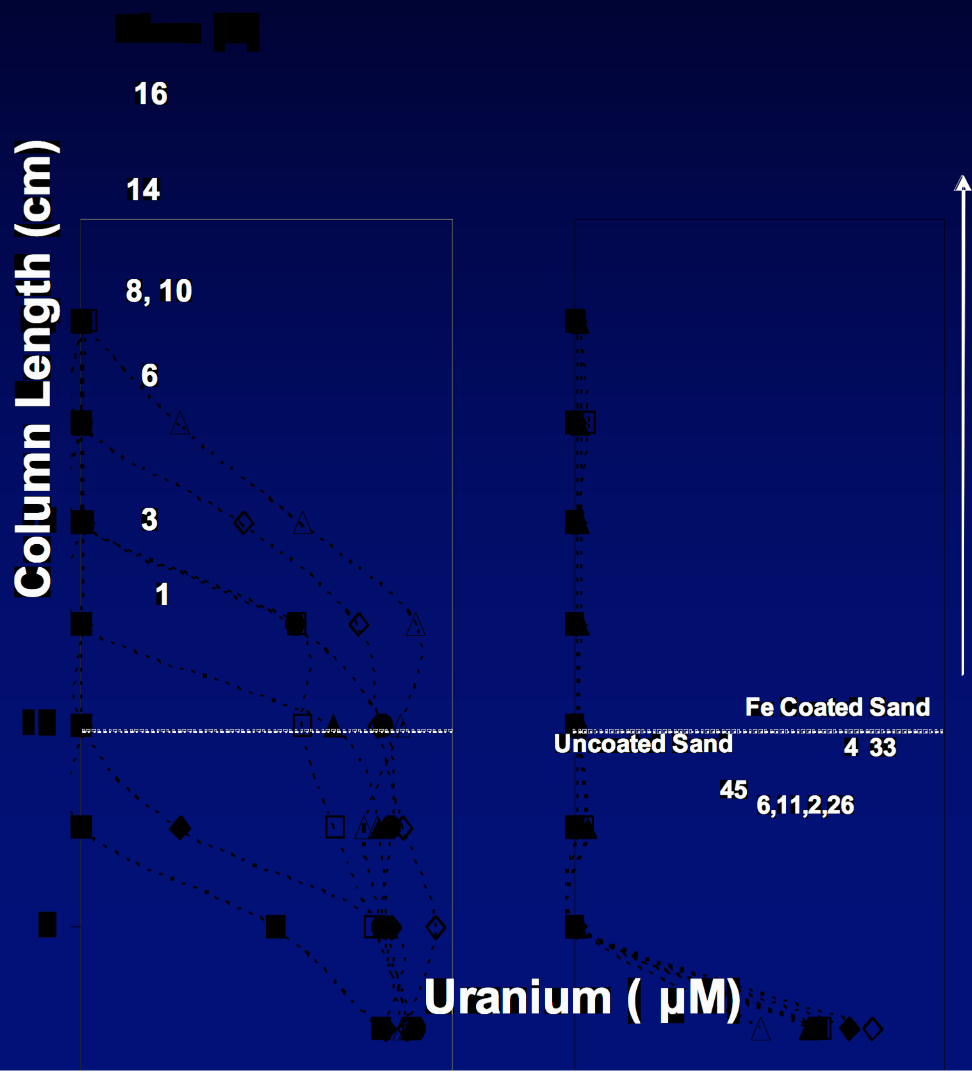
Brooks et al., 2003

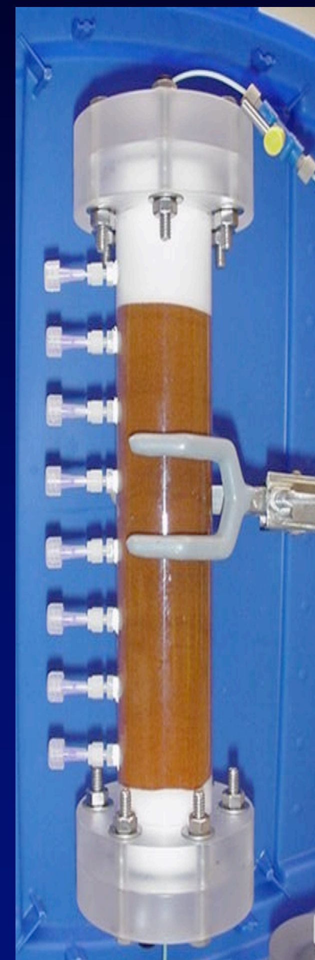
Uranium Speciation: Transport



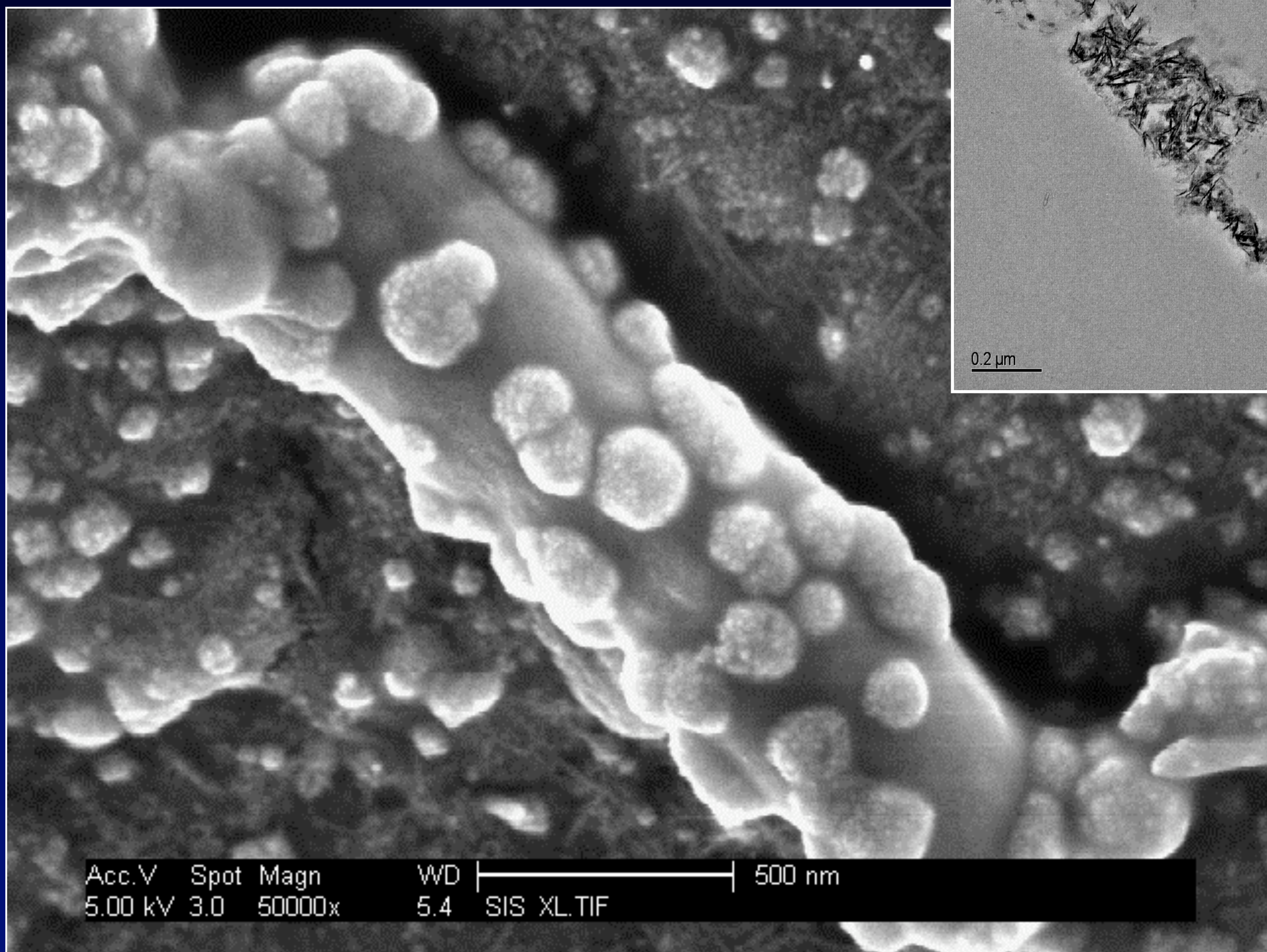
$Ca_2UO_2(CO_3)_3$ | $UO_2(CO_3)_2^{2-}$

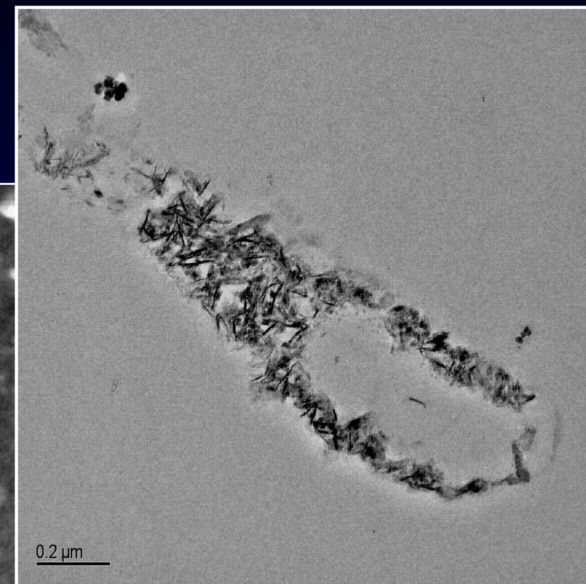
4 mM Ca | **0 mM Ca**



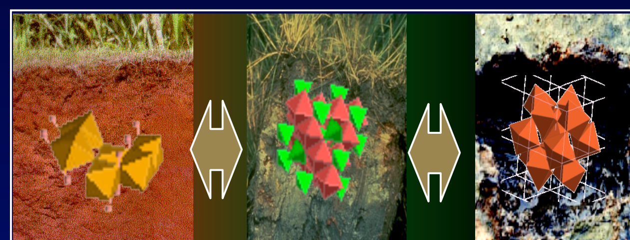


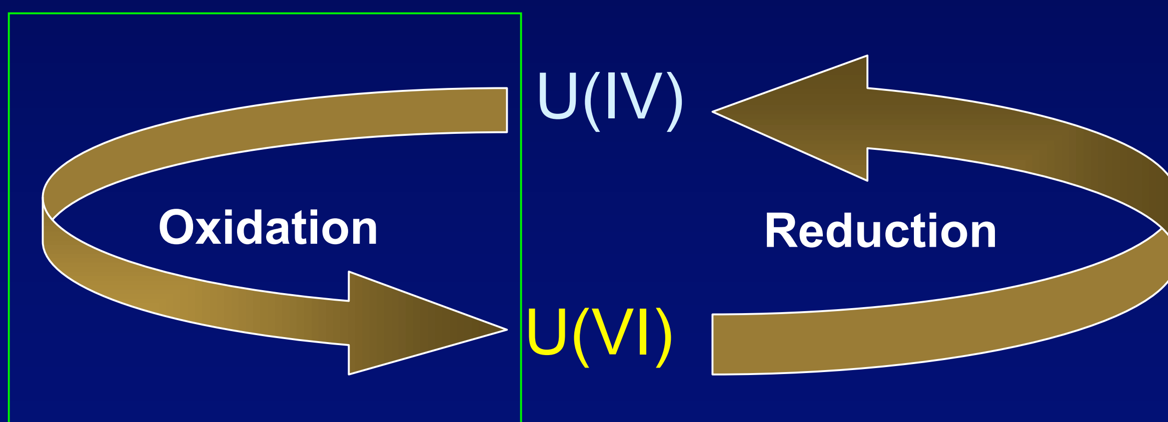
Uraninite Deposition

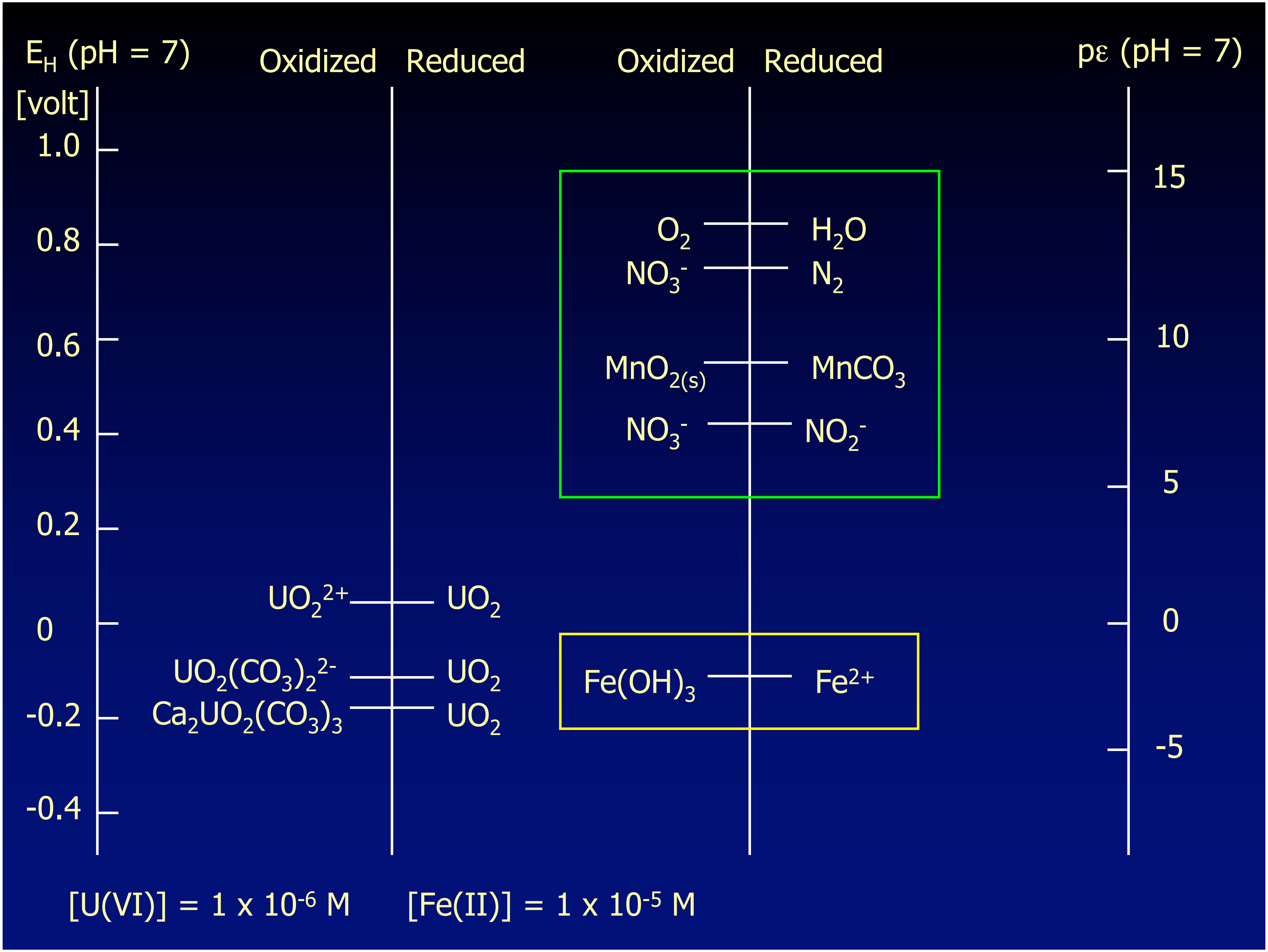




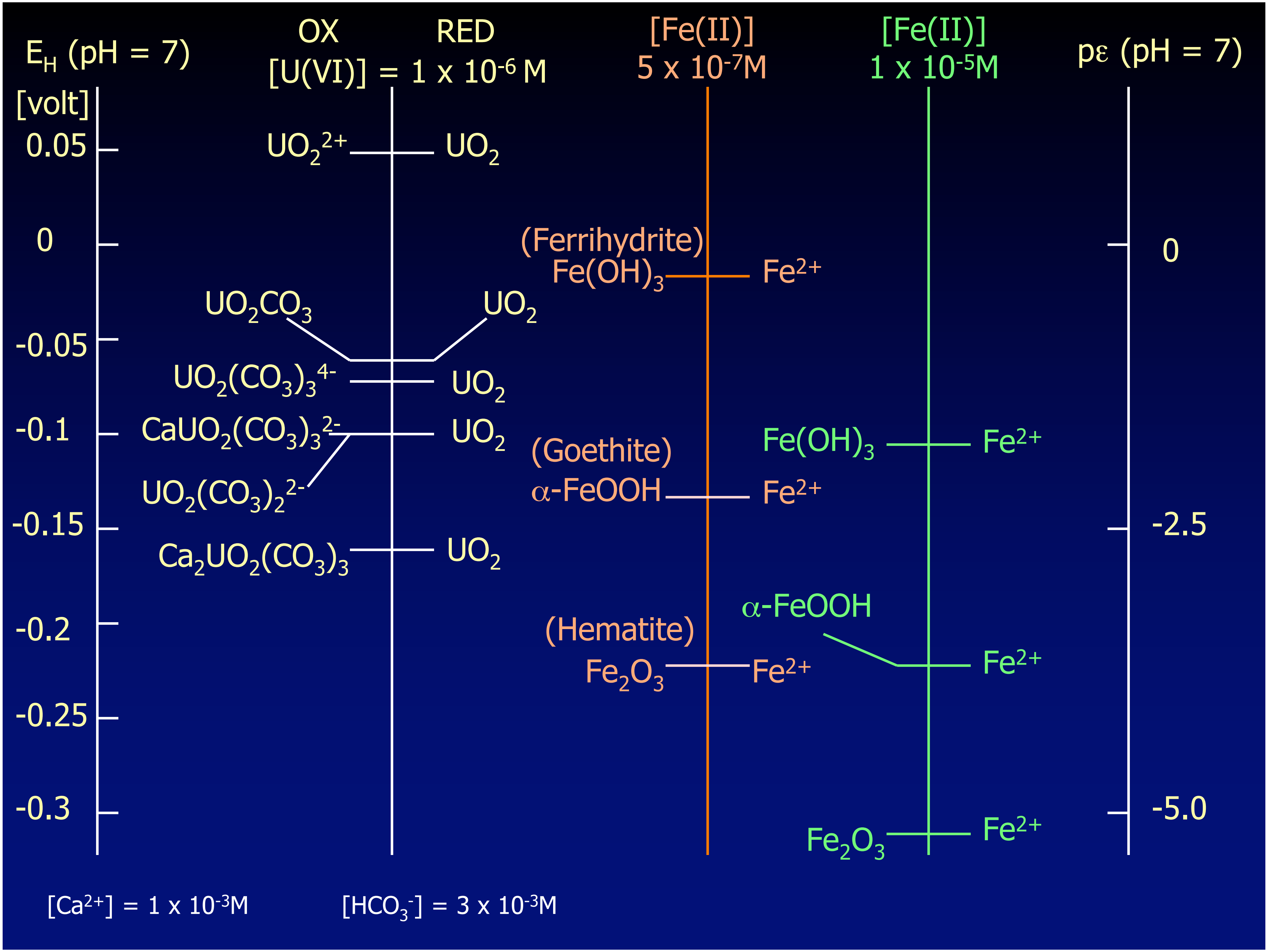
Redox Reactions of Uranium







E_H (pH = 7)
[volt]
Oxidized
Reduced
Oxidized
Reduced
pε (pH = 7)
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
15
10
5
0
-5
O_2
H_2O
NO_3^-
N_2
$MnO_{2(s)}$
$MnCO_3$
NO_3^-
NO_2^-
UO_2^{2+}
UO_2
$UO_2(CO_3)_2^{2-}$
UO_2
$Ca_2UO_2(CO_3)_3$
UO_2
$Fe(OH)_3$
Fe^{2+}
[U(VI)] = 1 x 10^{-6} M
[Fe(II)] = 1 x 10^{-5} M

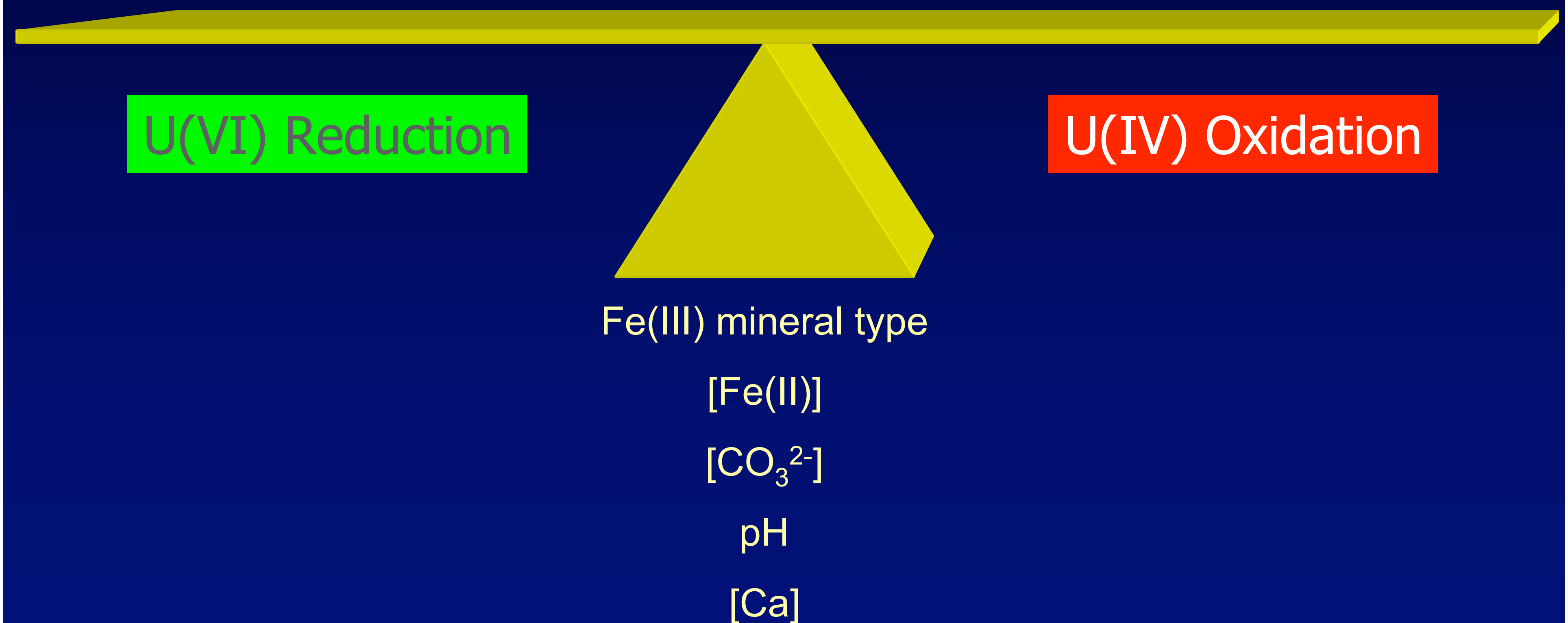


E_H (pH = 7)
[volt]
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
OX
RED
$[U(VI)] = 1 \times 10^{-6}$ M
UO_2^{2+}
UO_2
UO_2CO_3
UO_2
$UO_2(CO_3)_3^{4-}$
UO_2
$CaUO_2(CO_3)_3^{2-}$
UO_2
$UO_2(CO_3)_2^{2-}$
$Ca_2UO_2(CO_3)_3$
UO_2
[Fe(II)]
5×10^{-7}M
(Ferrihydrite)
$Fe(OH)_3$
Fe^{2+}
(Goethite)
α-FeOOH
Fe^{2+}
(Hematite)
Fe_2O_3
Fe^{2+}
[Fe(II)]
1×10^{-5}M
$Fe(OH)_3$
Fe^{2+}
α-FeOOH
Fe^{2+}
Fe_2O_3
Fe^{2+}
$p\varepsilon$ (pH = 7)
0
-2.5
-5.0
$[Ca^{2+}] = 1 \times 10^{-3}$M
$[HCO_3^-] = 3 \times 10^{-3}$M

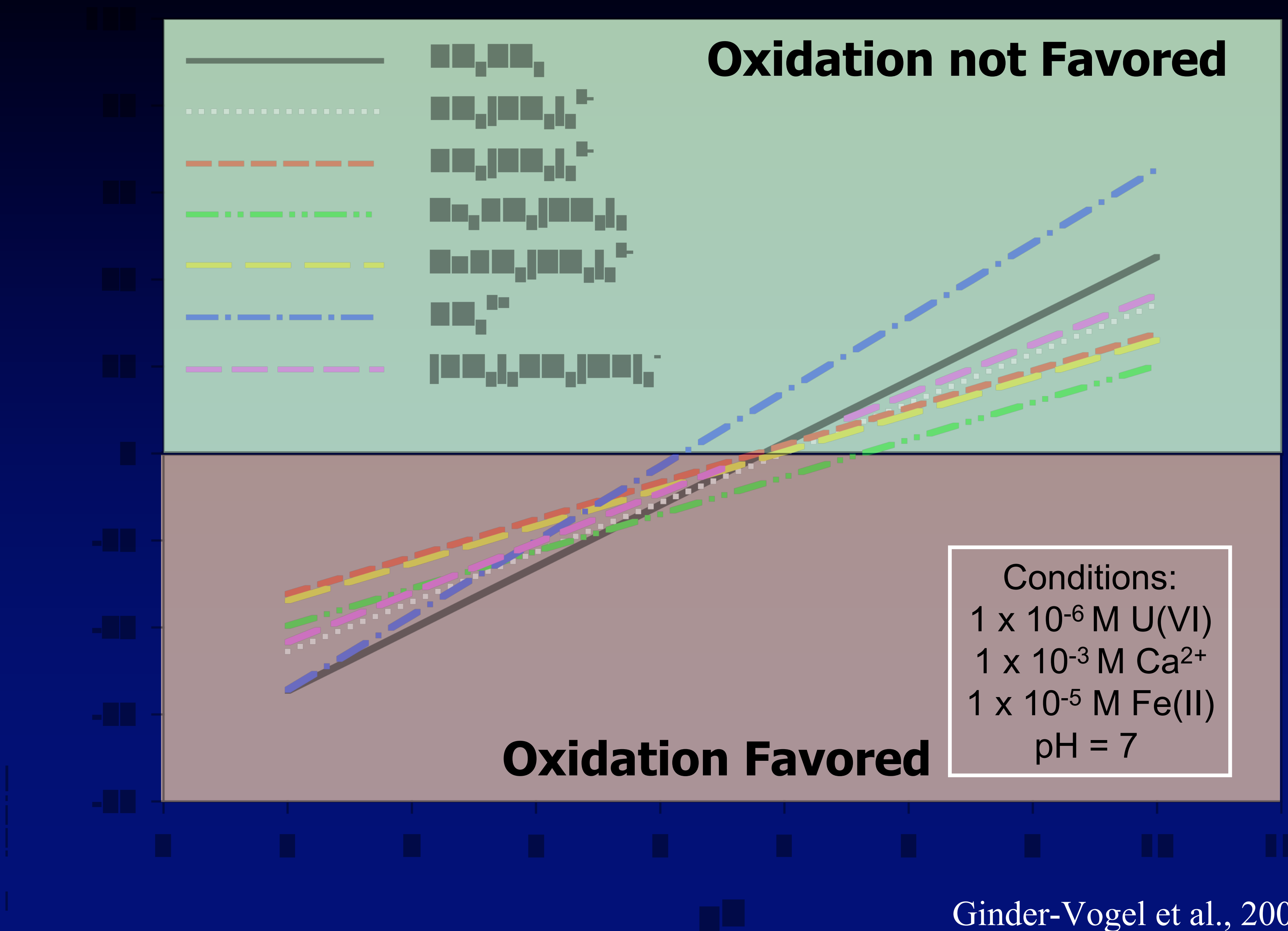
$$\text{Fe(III)-Oxide} + UO_2 + H^+ + HCO_3^- + Ca^{2+}$$

$$\rightleftharpoons$$

$$Fe^{2+}_{(aq)} + \text{Soluble U(VI)} + H_2O$$

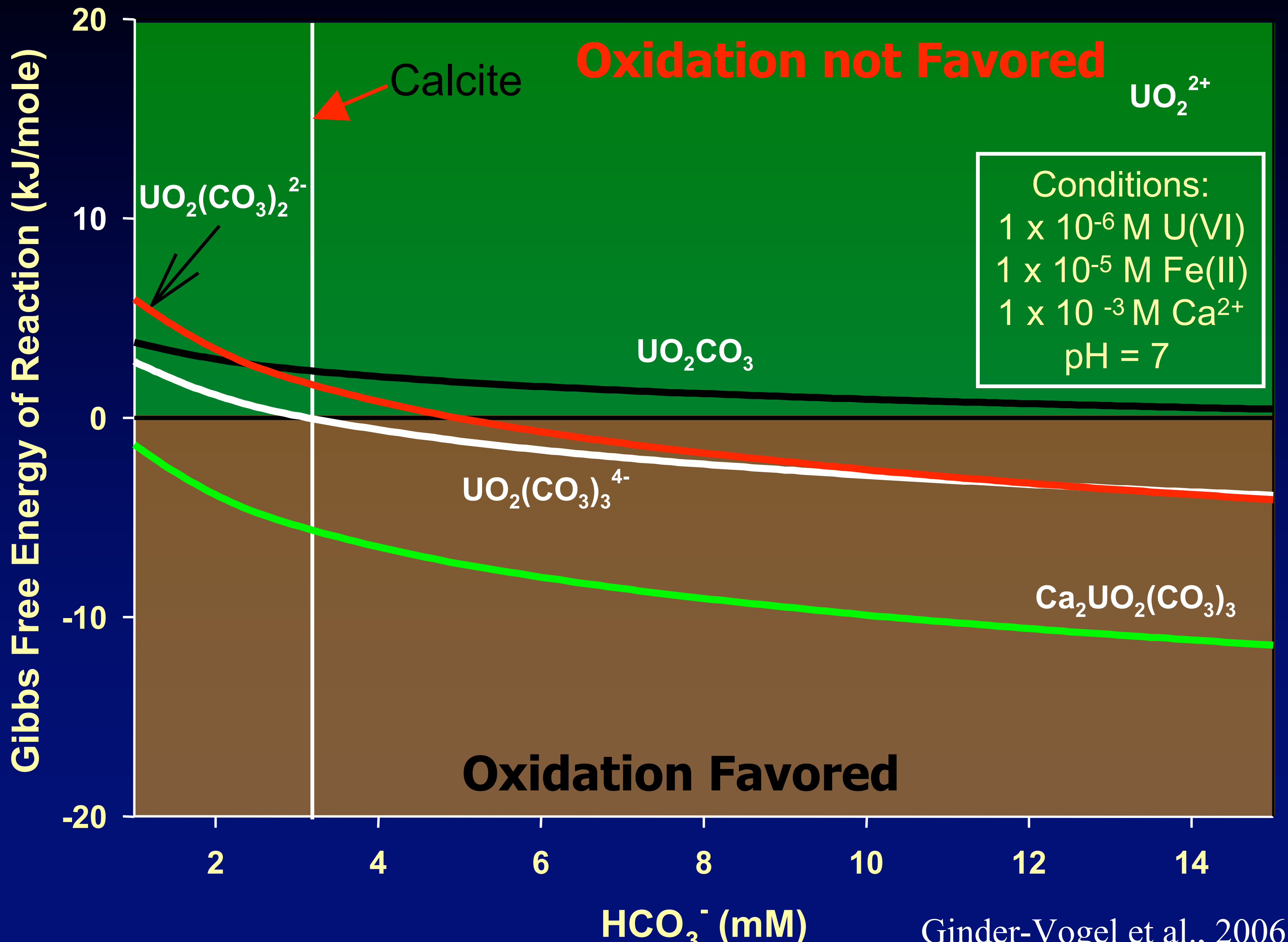


Favorability of UO_2 Oxidation by Ferrihydrite: pH Effects



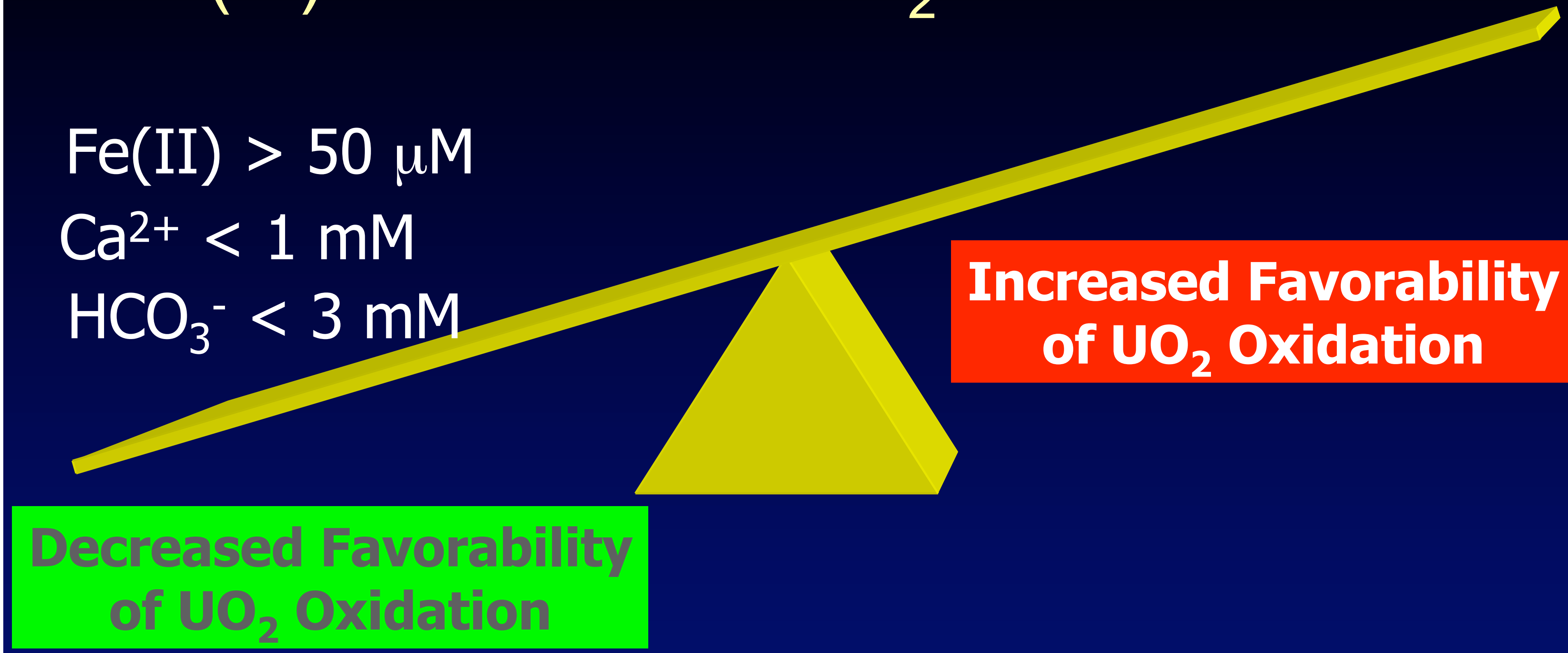
Ginder-Vogel et al., 2006

Favorability of UO_2 Oxidation by Ferrihydrite: Effect of $[HCO_3^-]$



Ginder-Vogel et al., 2006

Iron(III) Oxidation of UO_2



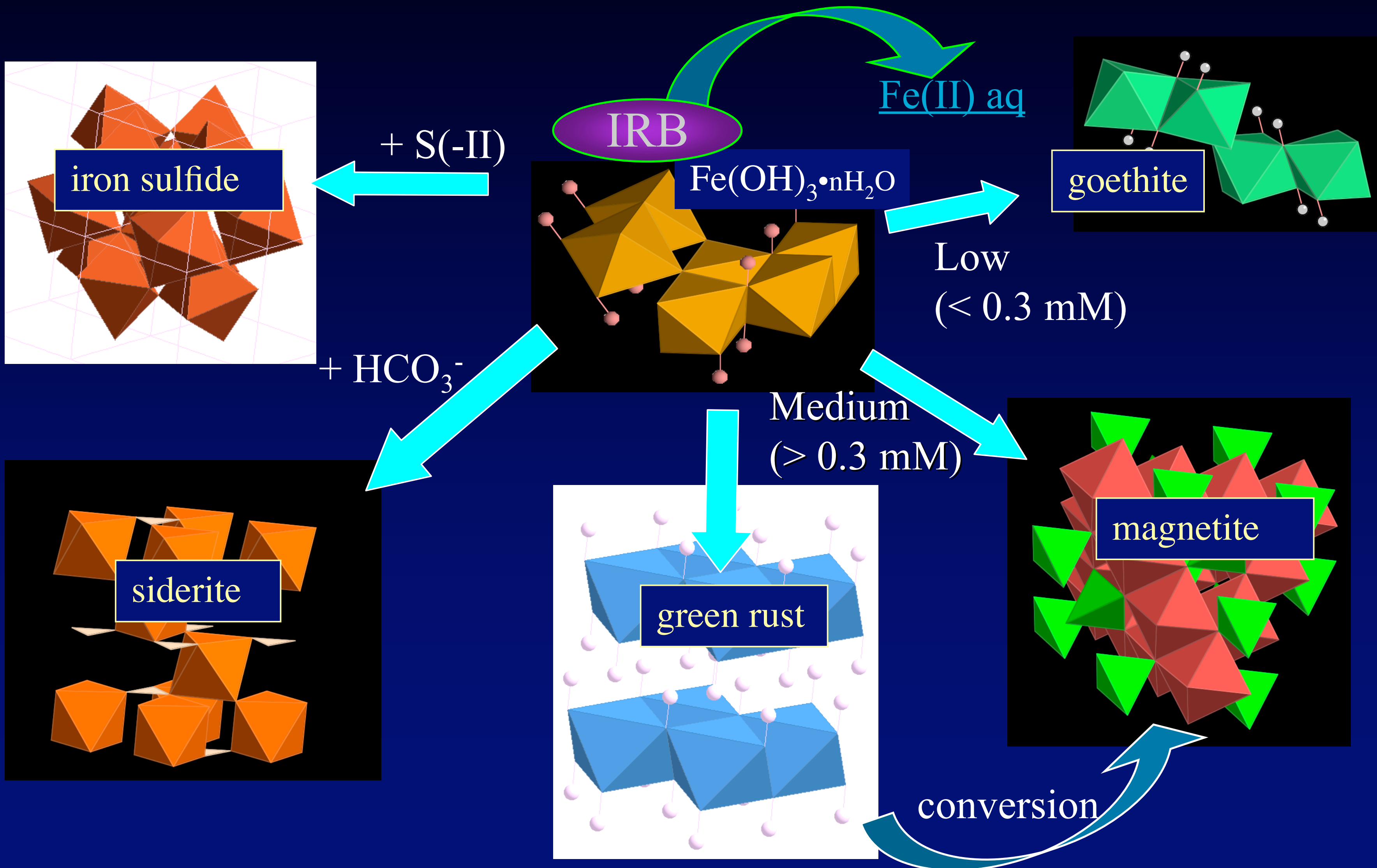
Favorability of UO_2 oxidation by ferric (hydr)oxides is highly variable

- May limit uranium sequestration under mildly reducing conditions

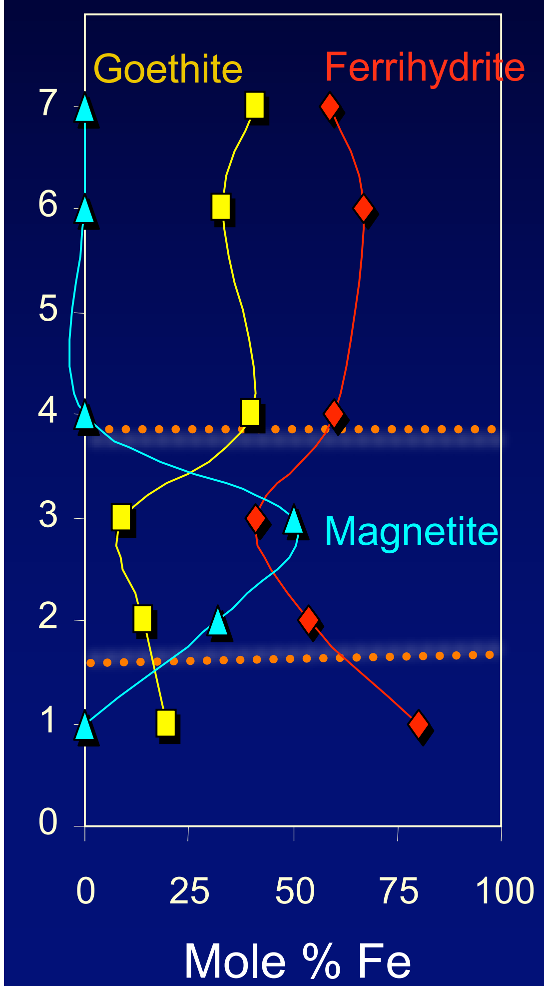
Physical-Biogeochemical Linkage

Biogeochemical Heterogeneity

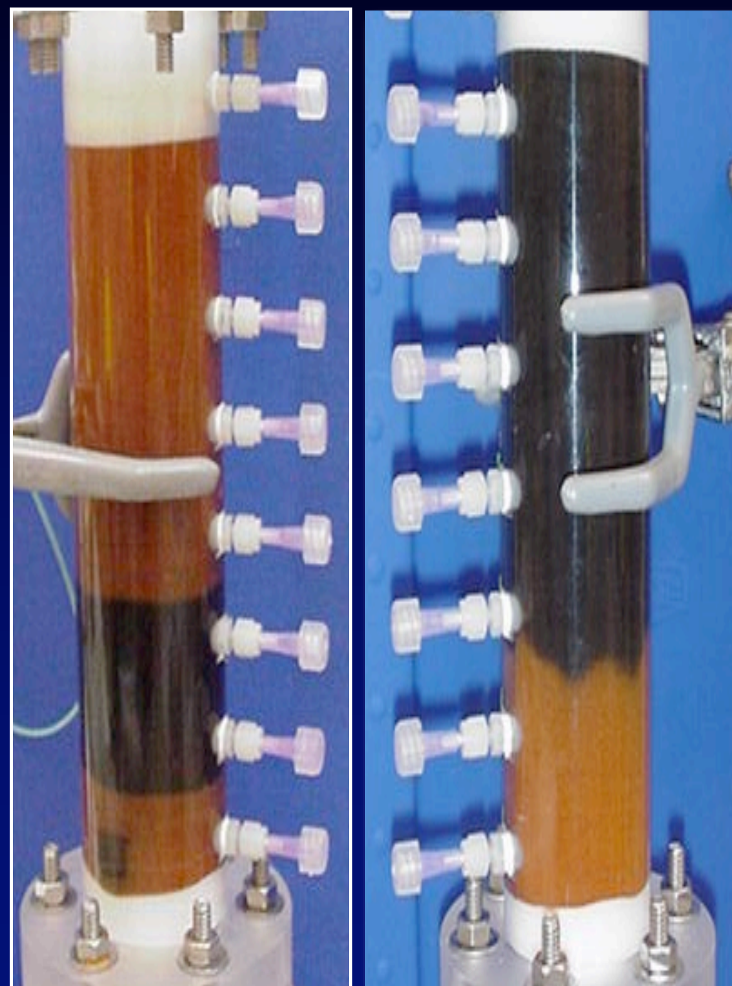
Iron Biomineralization



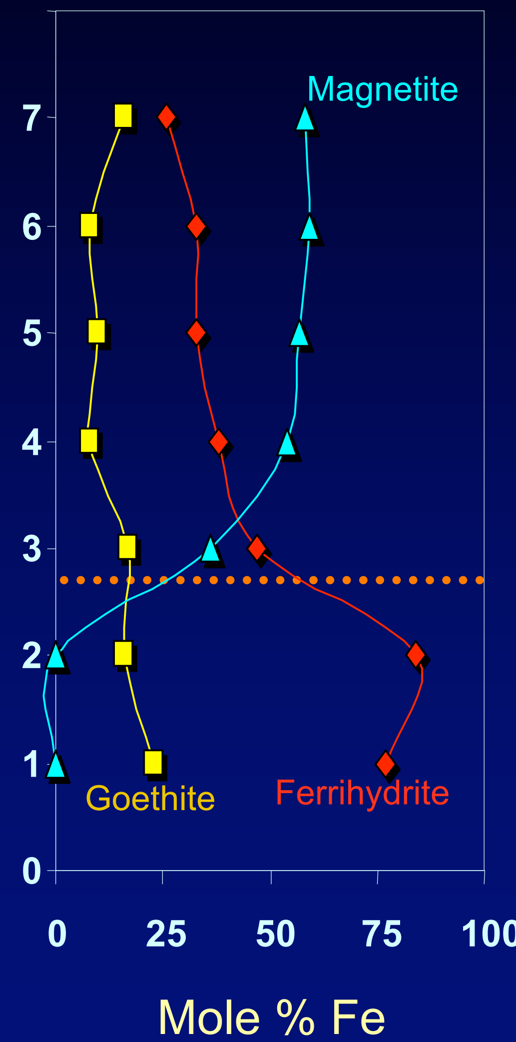
Flow Control on Solid-phase Distribution



q = 0.1 m/d q = 0.6 m/d



3 mM lactate, pH 7

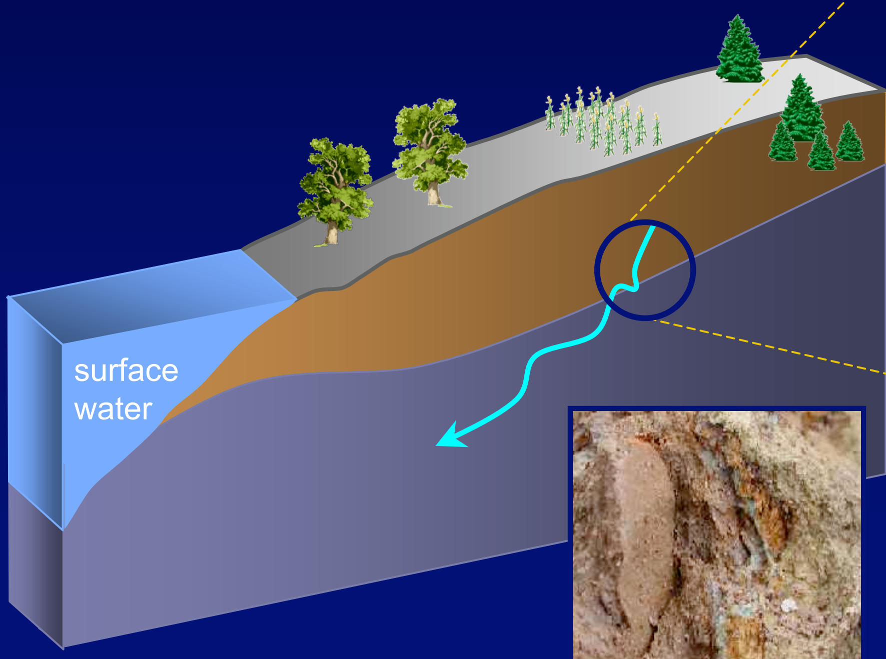


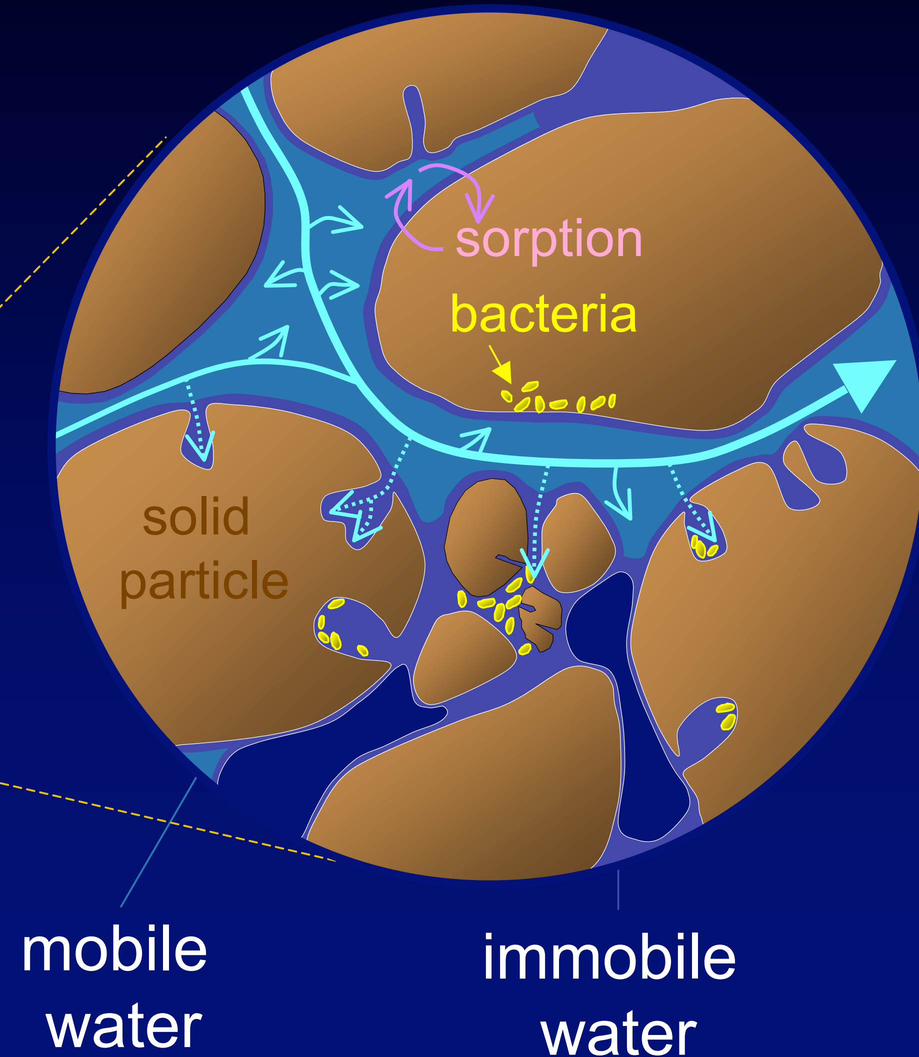
Hansel et al., 2003

Pore-scale Heterogeneity

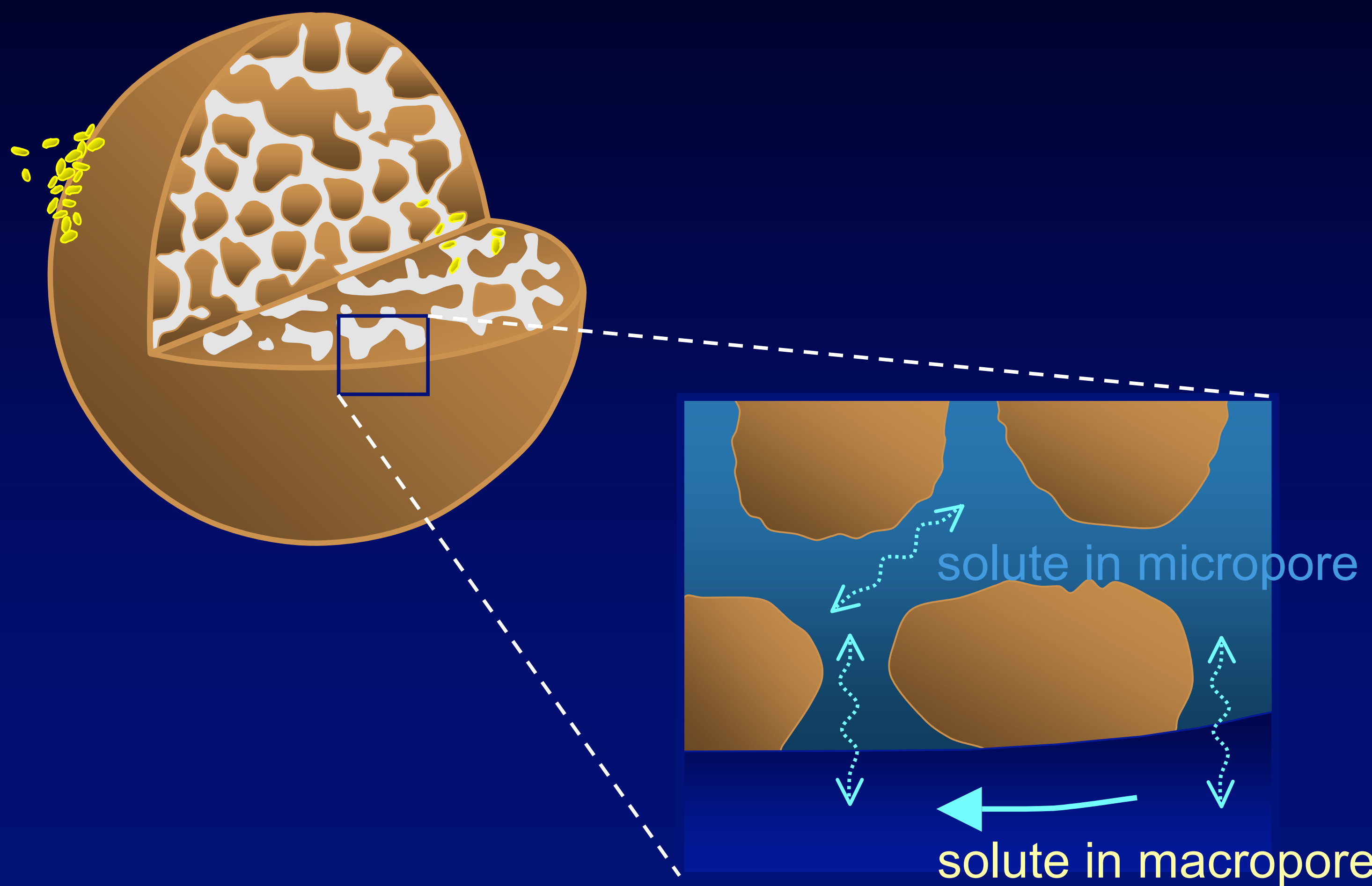
- advection
- dispersion
- diffusion with kinetics

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha \, (C_m - C_{im})$$

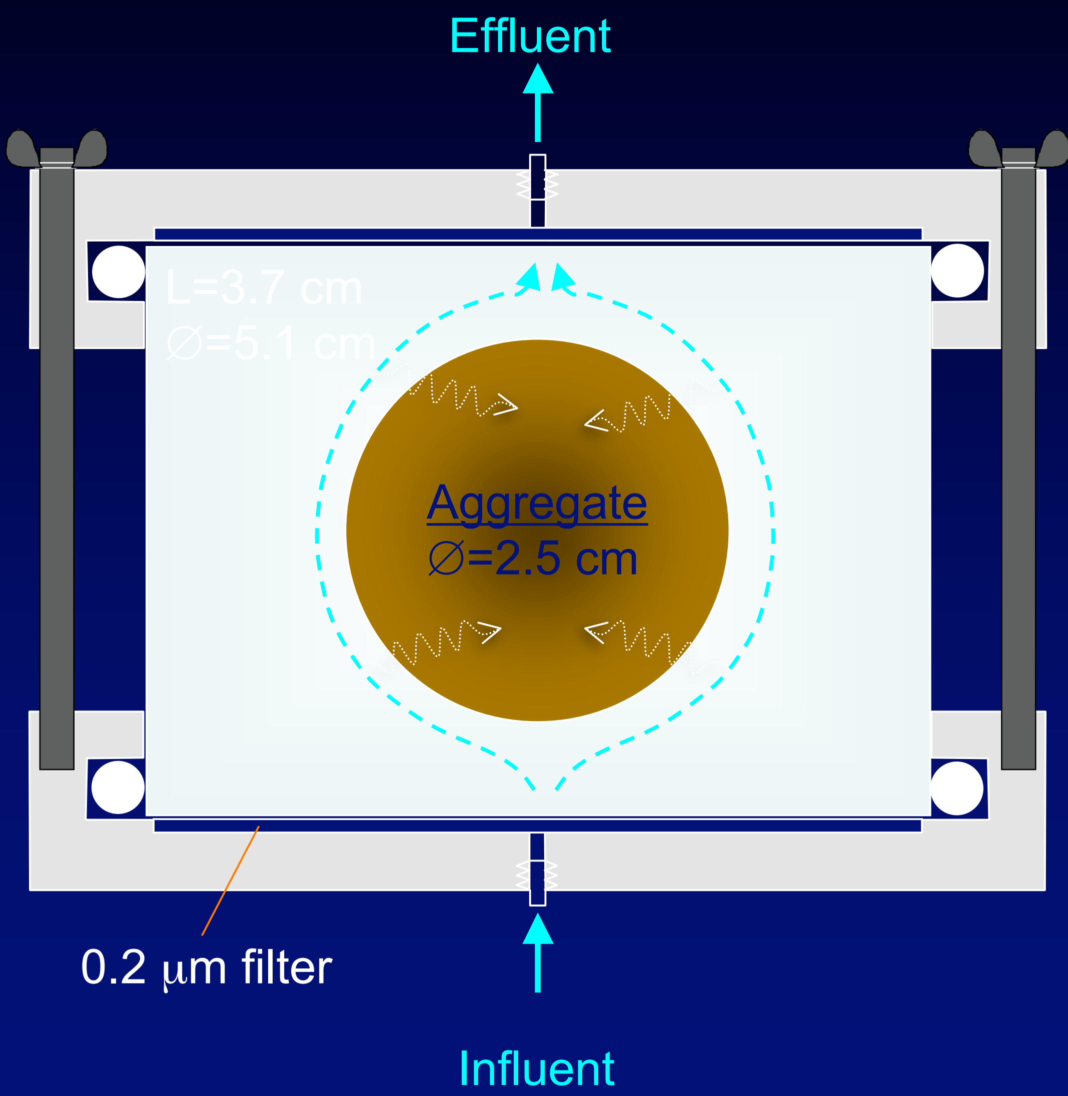


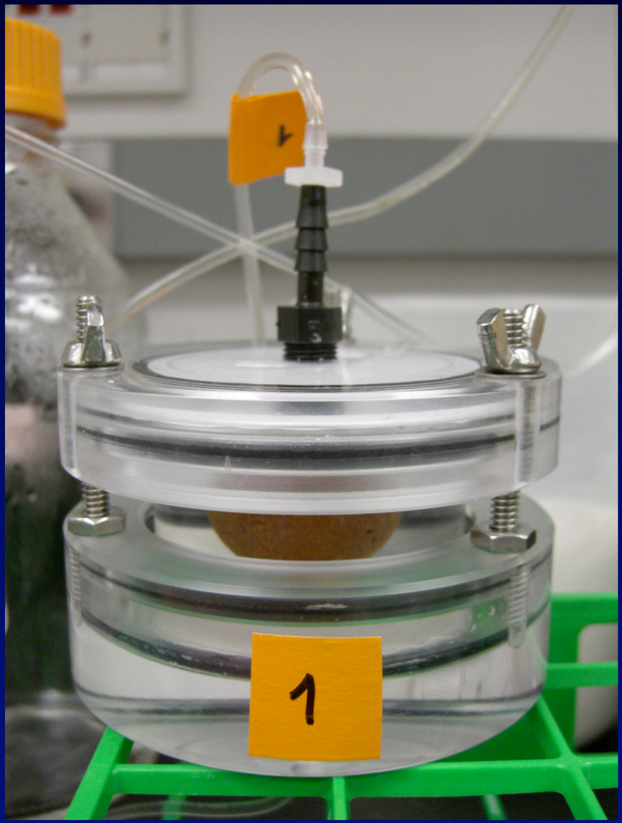


Aggregates Solute Domains

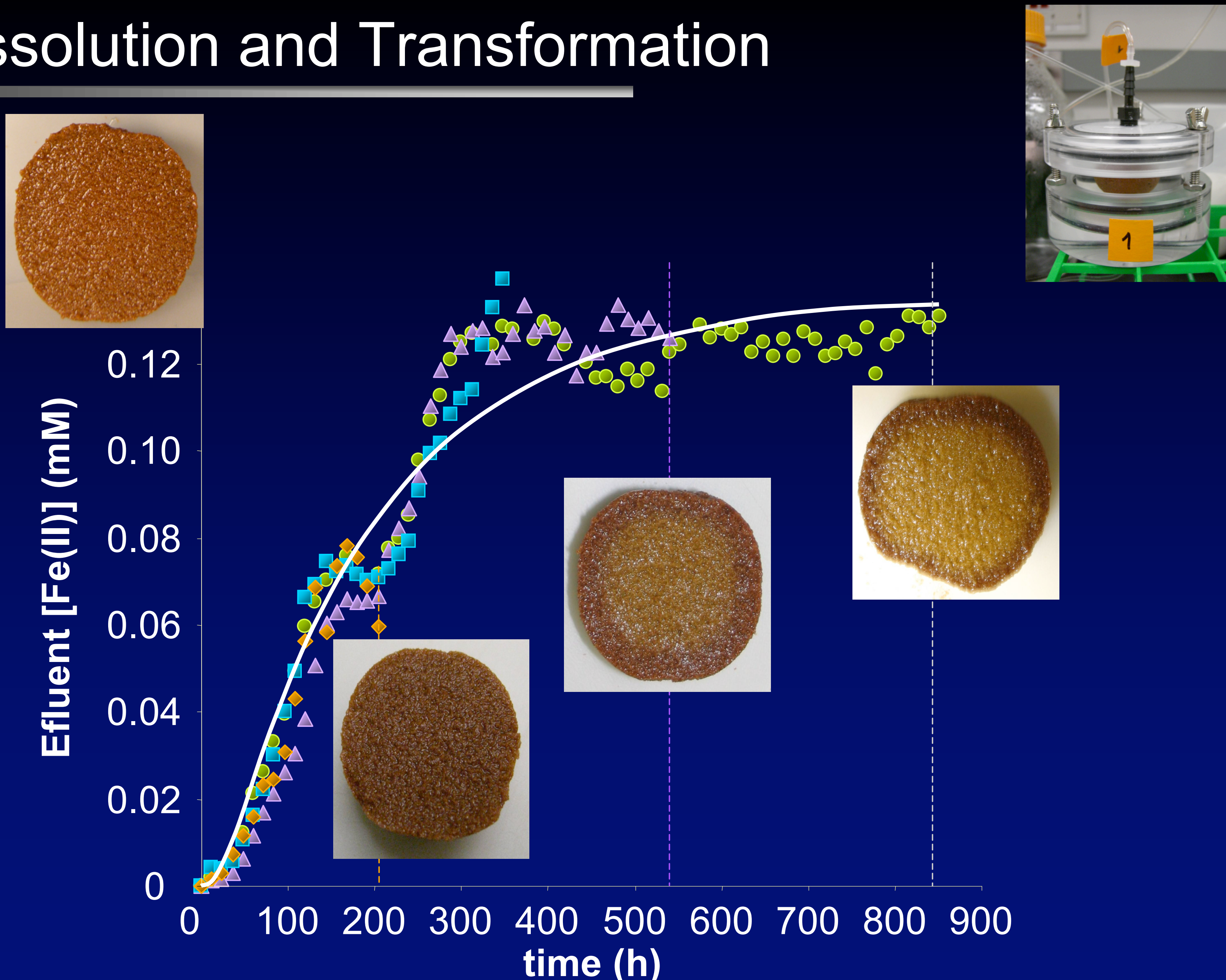


Synthetic Aggregates

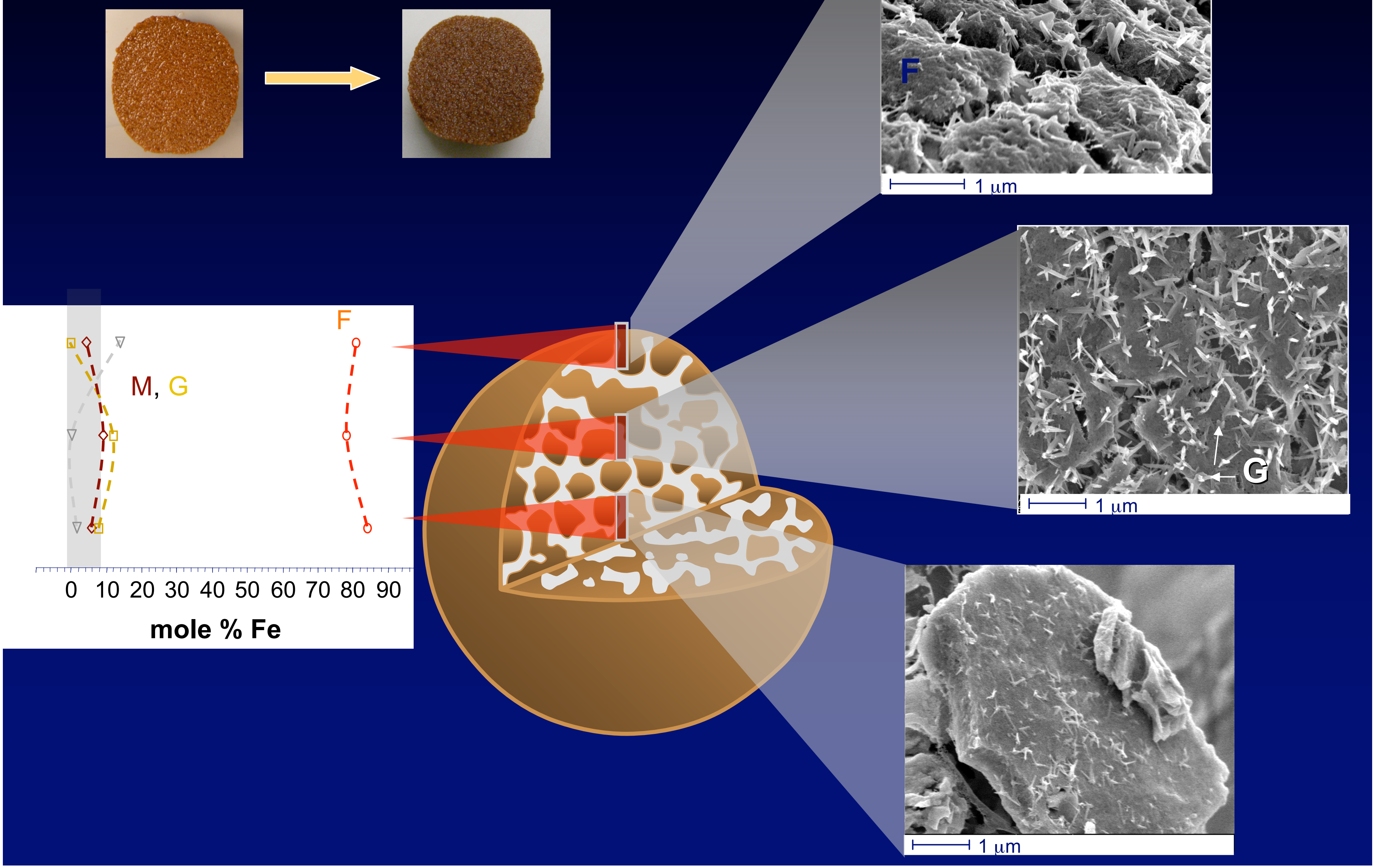




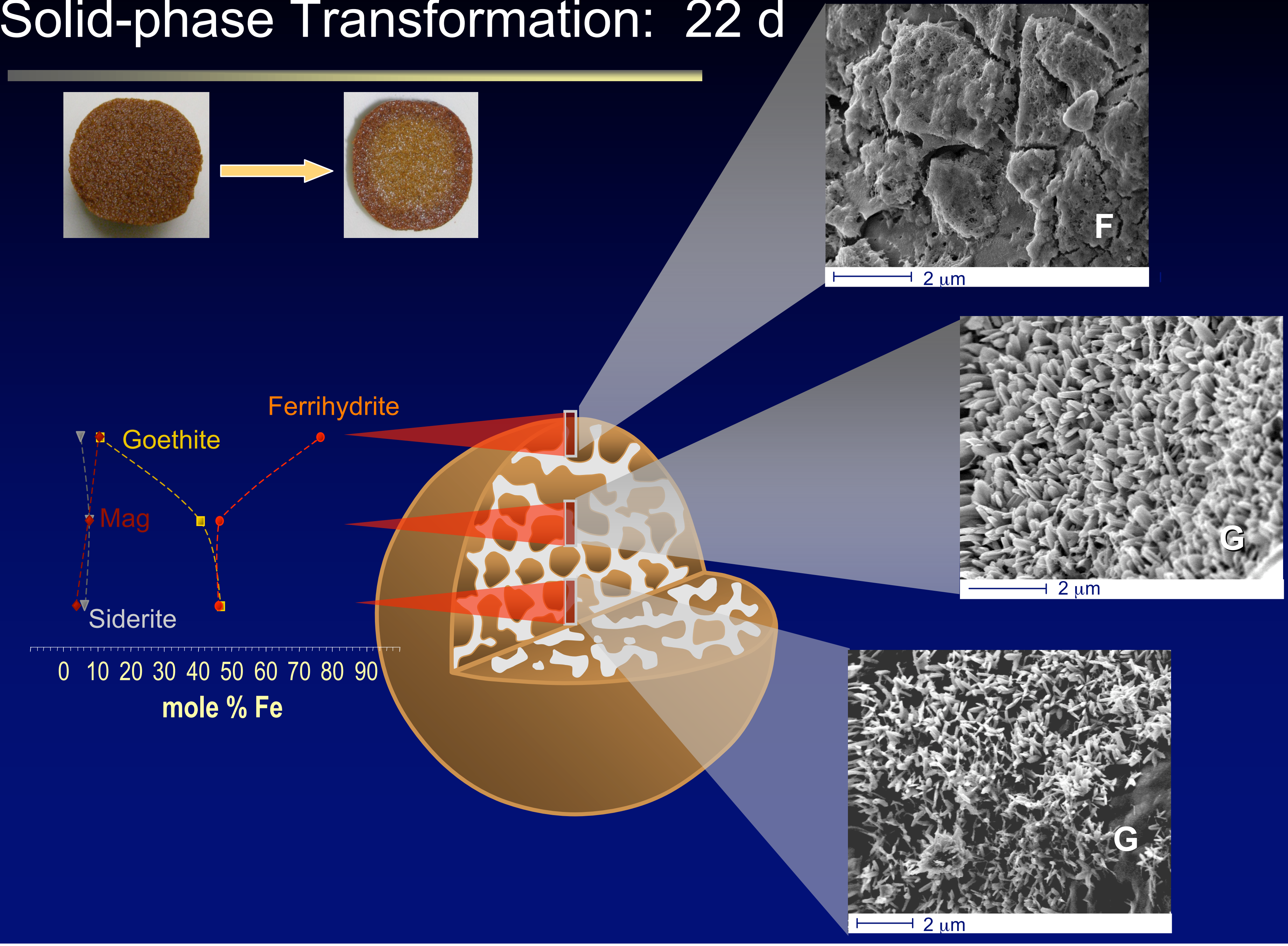
Dissolution and Transformation



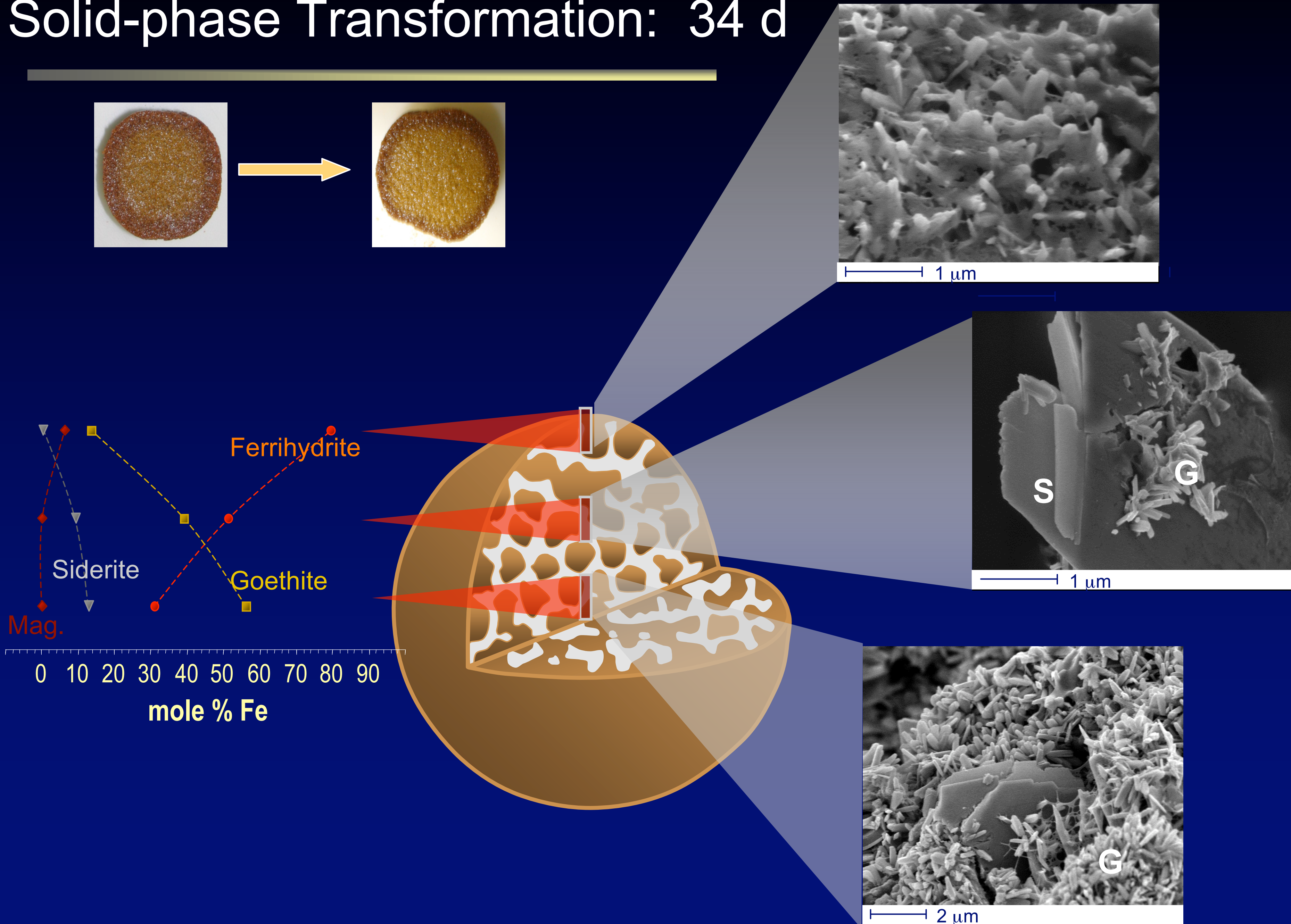
Solid-phase Transformation: 9d



Solid-phase Transformation: 22 d



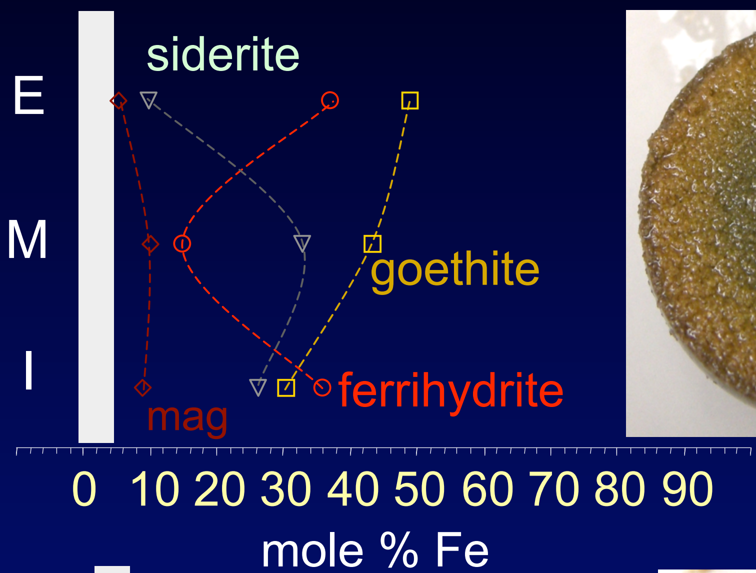
Solid-phase Transformation: 34 d



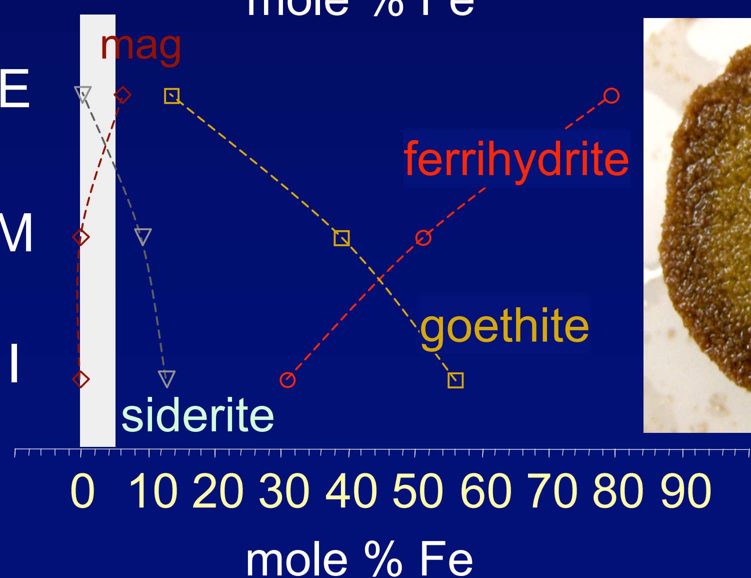
Transport Controls on Product Distribution

Macropore Flow

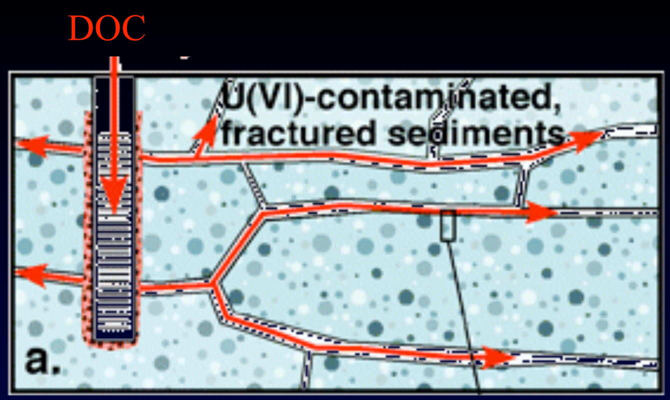
Q = 0

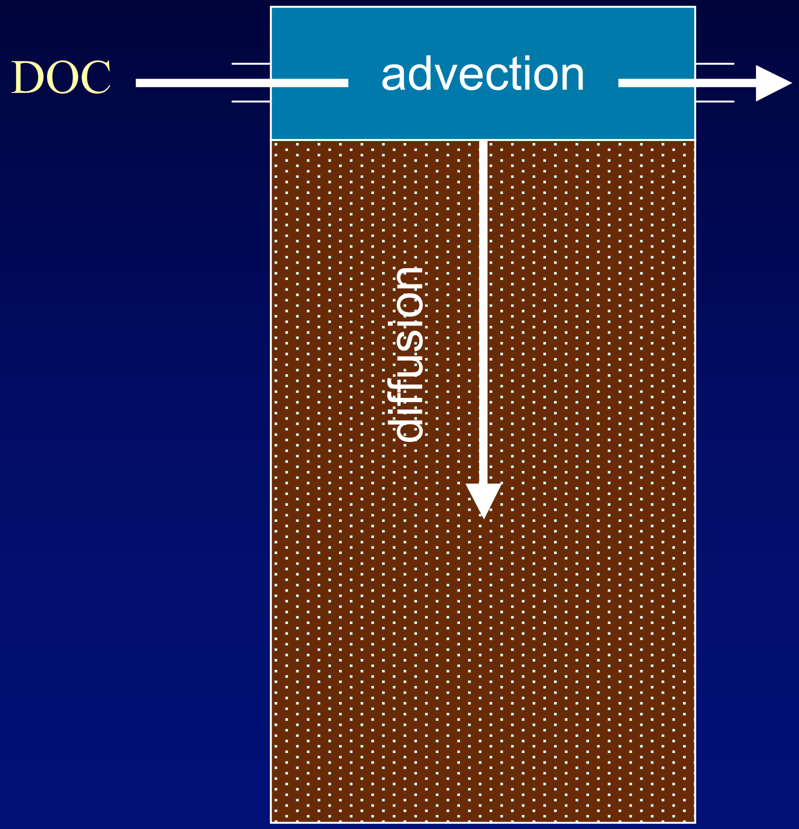


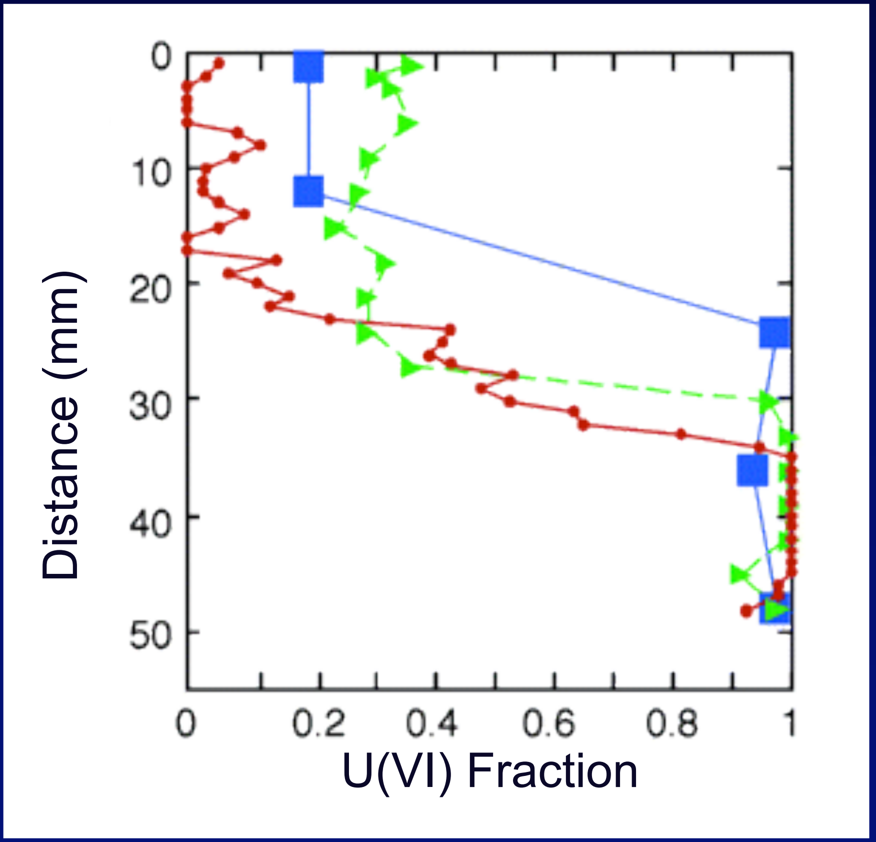
Q = 0.8 mL h^{-1}



Pore-scale Uranium Reduction

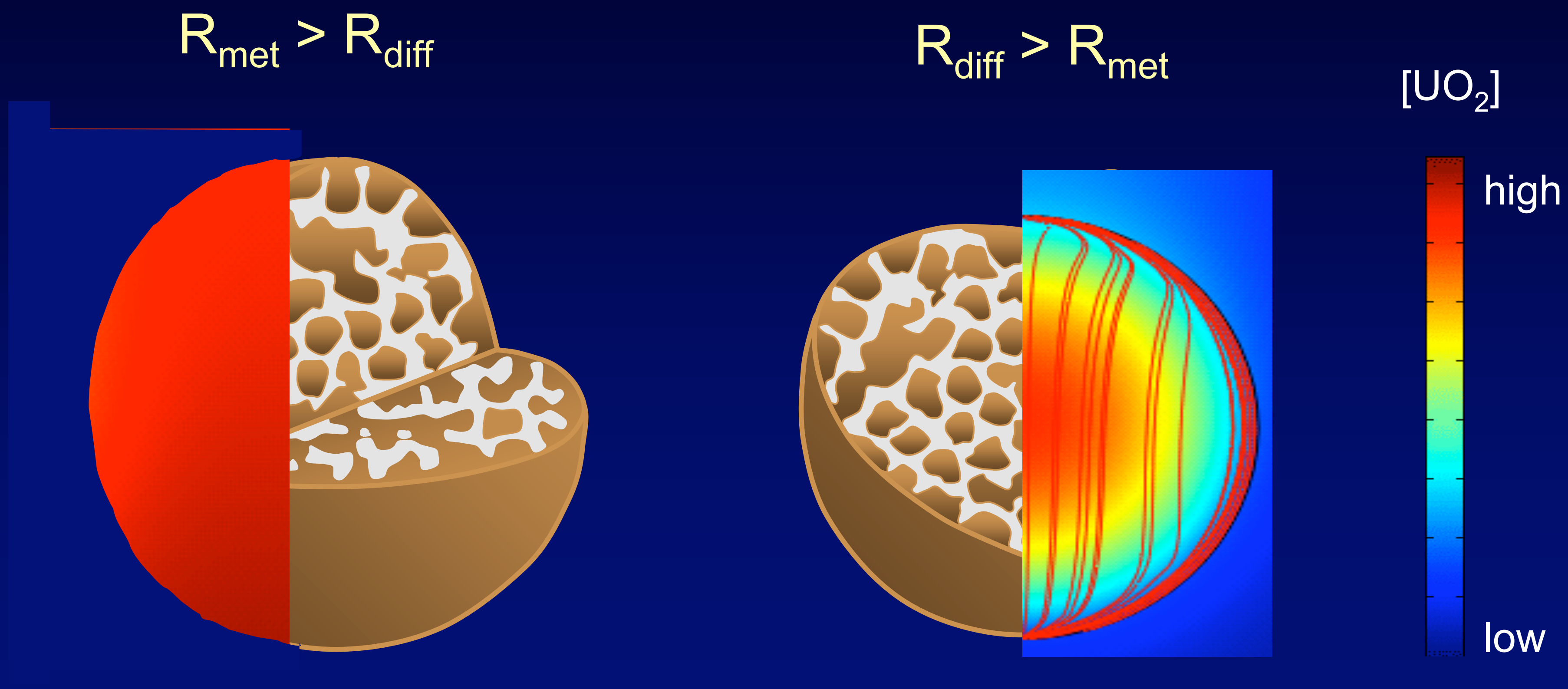


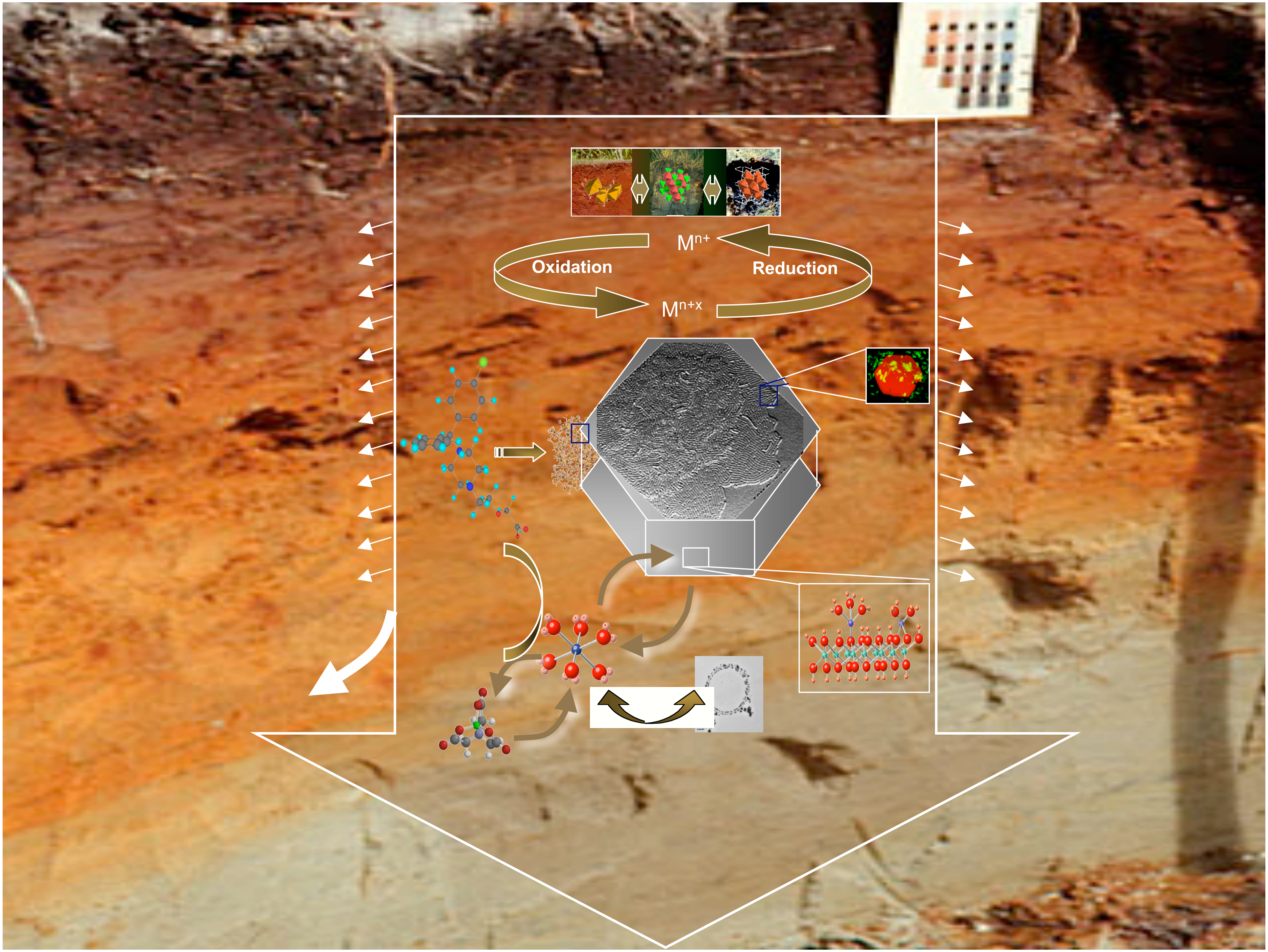




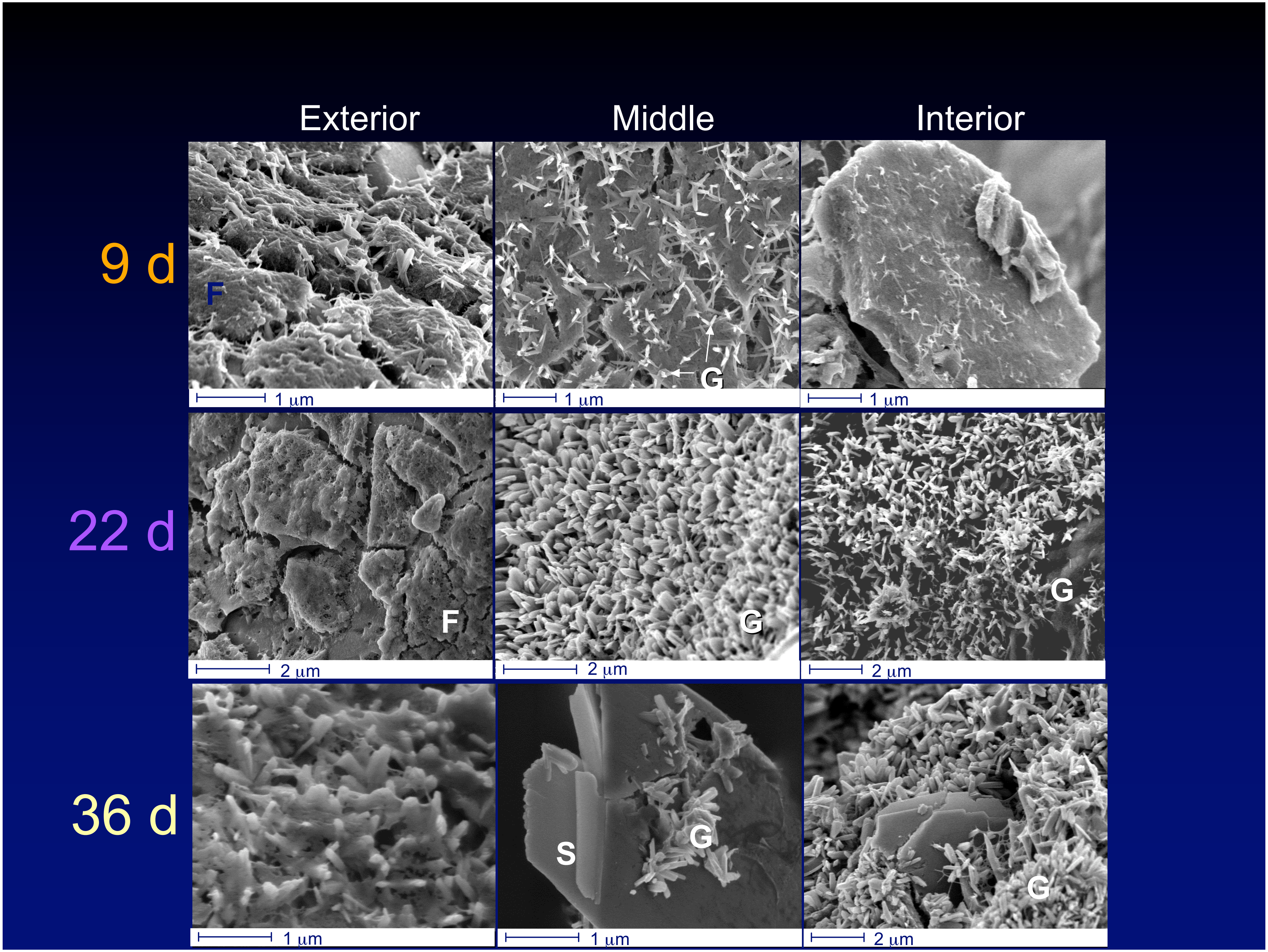
after Tokunaga et al., 2005

Projected Uraninite Deposition

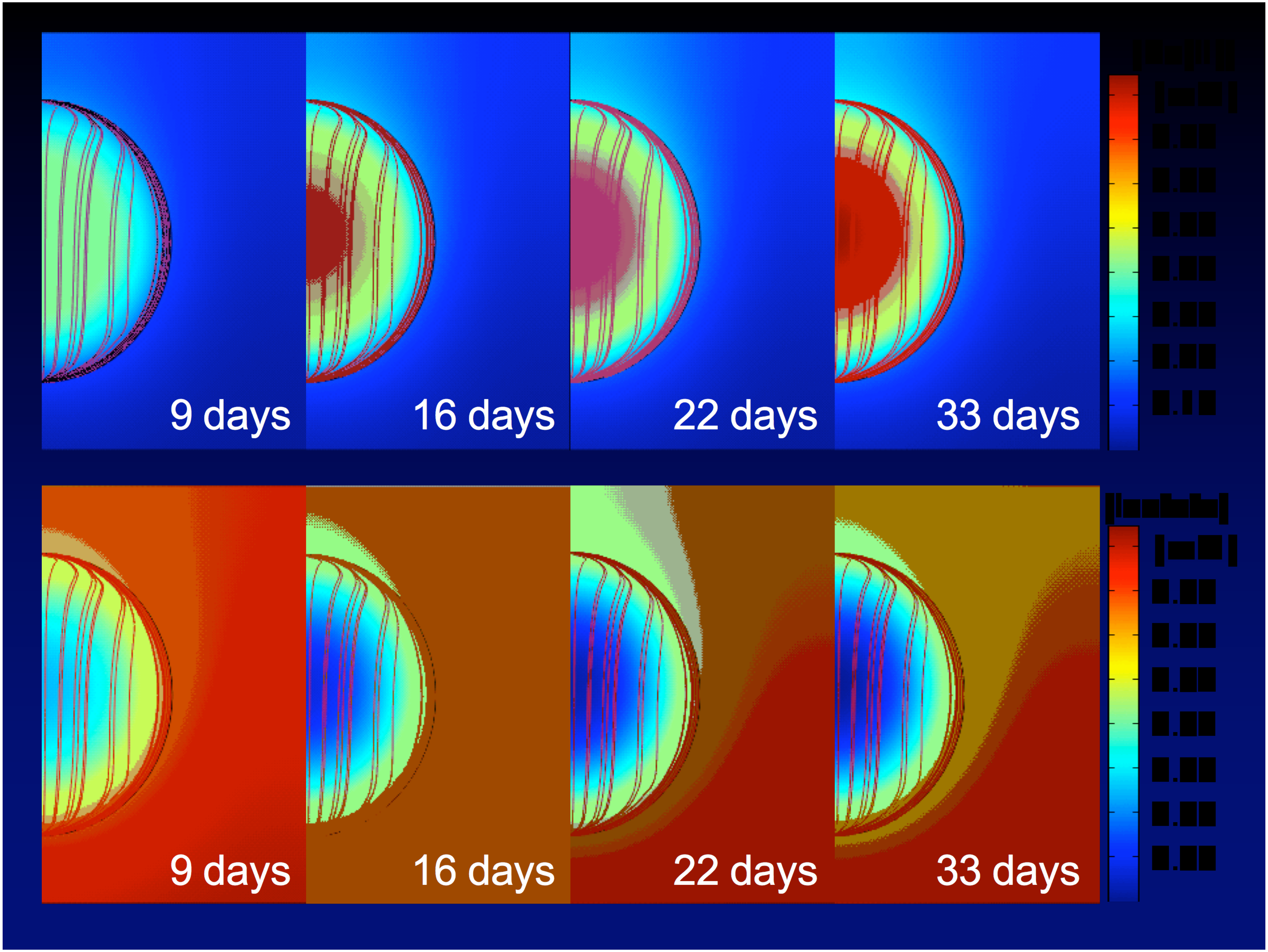




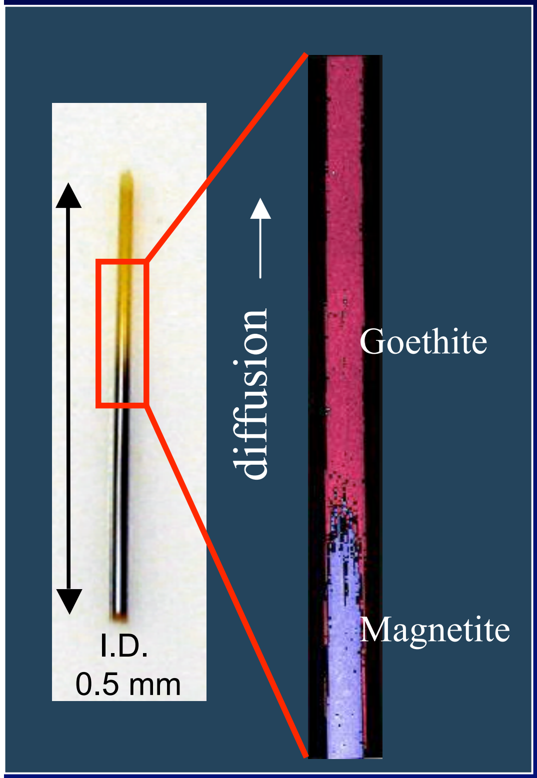
M^{n+}
Oxidation
Reduction
M^{n+x}

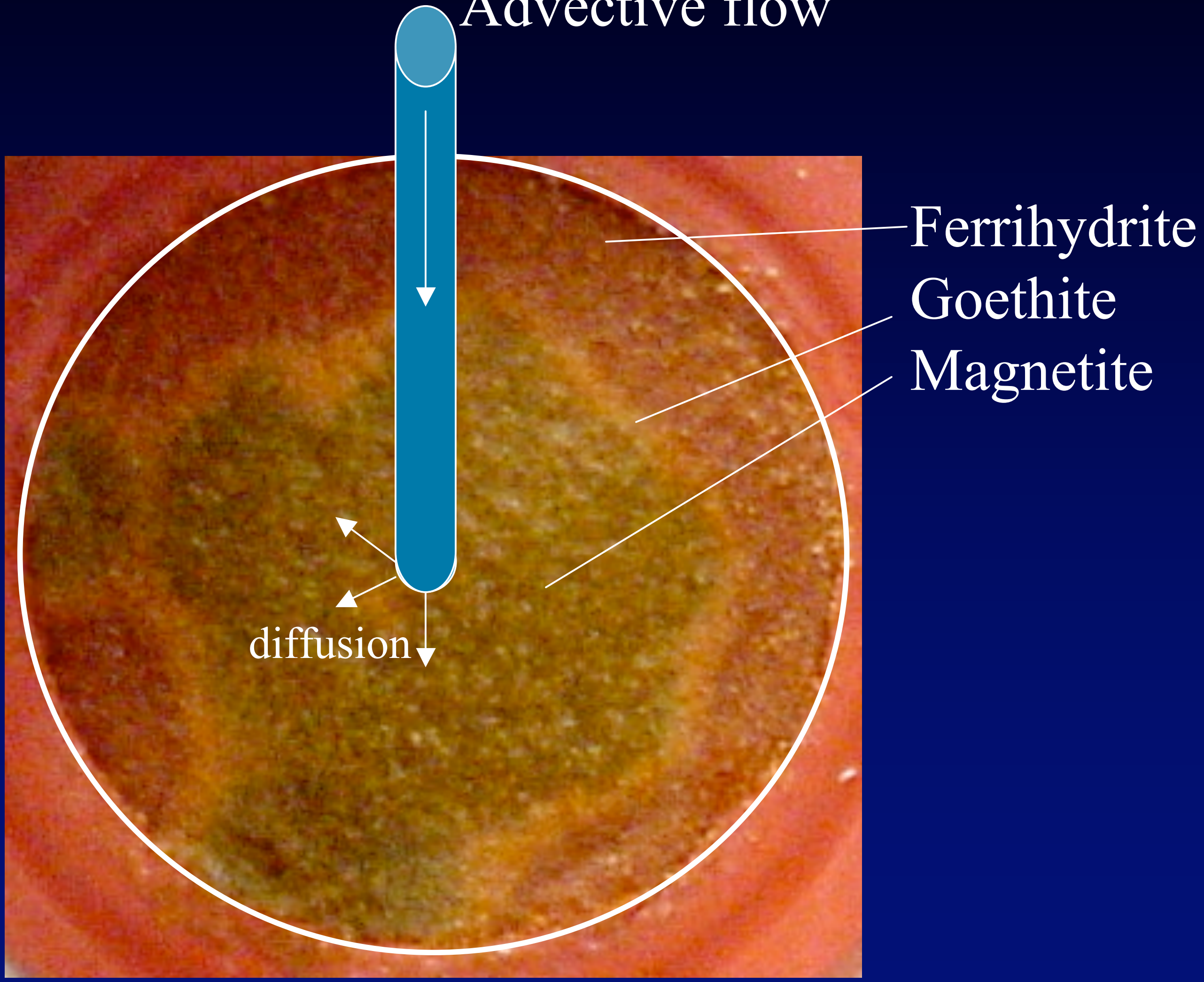


Exterior
Middle
Interior
9 d
22 d
36 d
F
G
1 µm
1 µm
1 µm
F
G
G
2 µm
2 µm
2 µm
S
G
G
1 µm
1 µm
2 µm

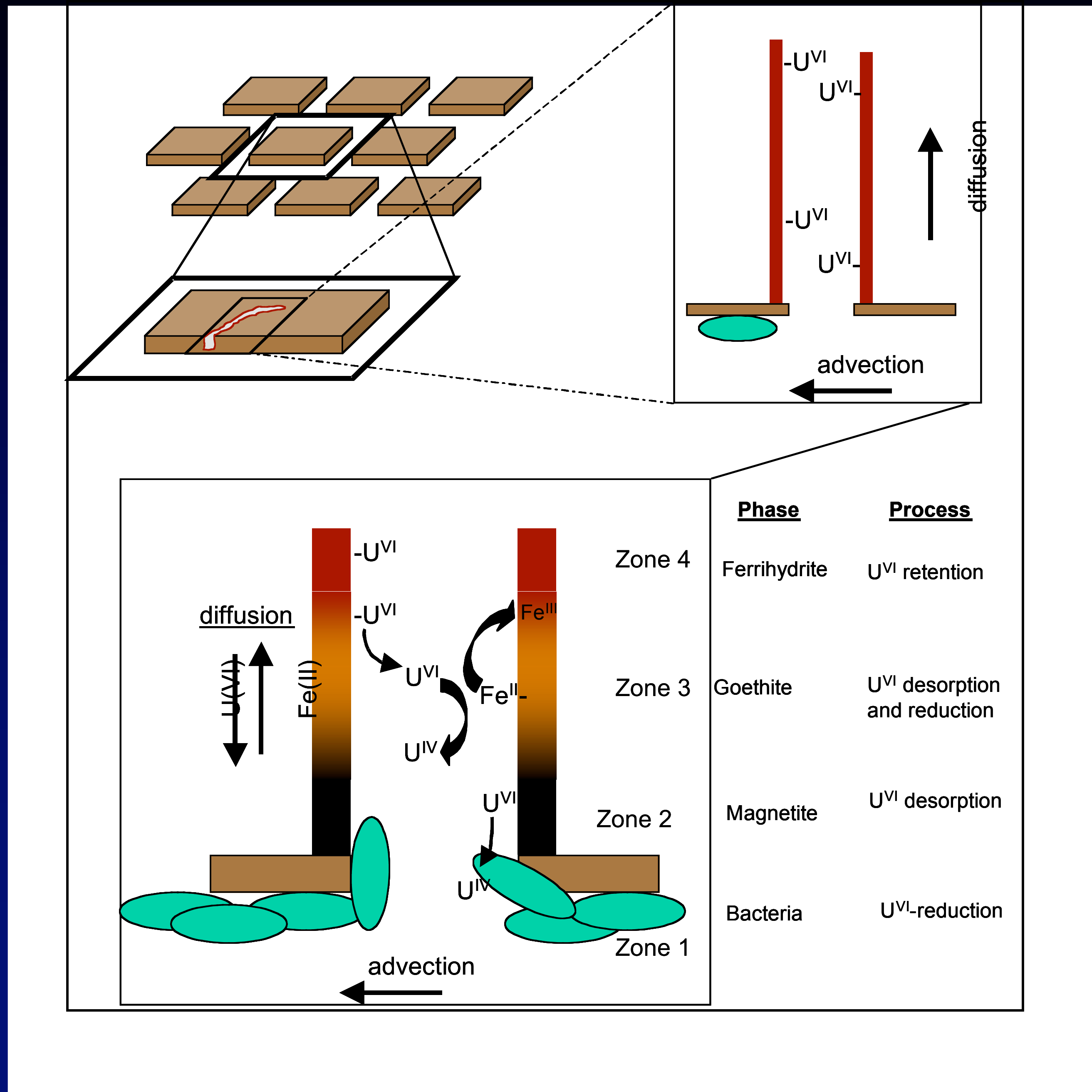

9 days
16 days
22 days
33 days
9 days
16 days
22 days
33 days

Biomineralization within Physically Complex Media

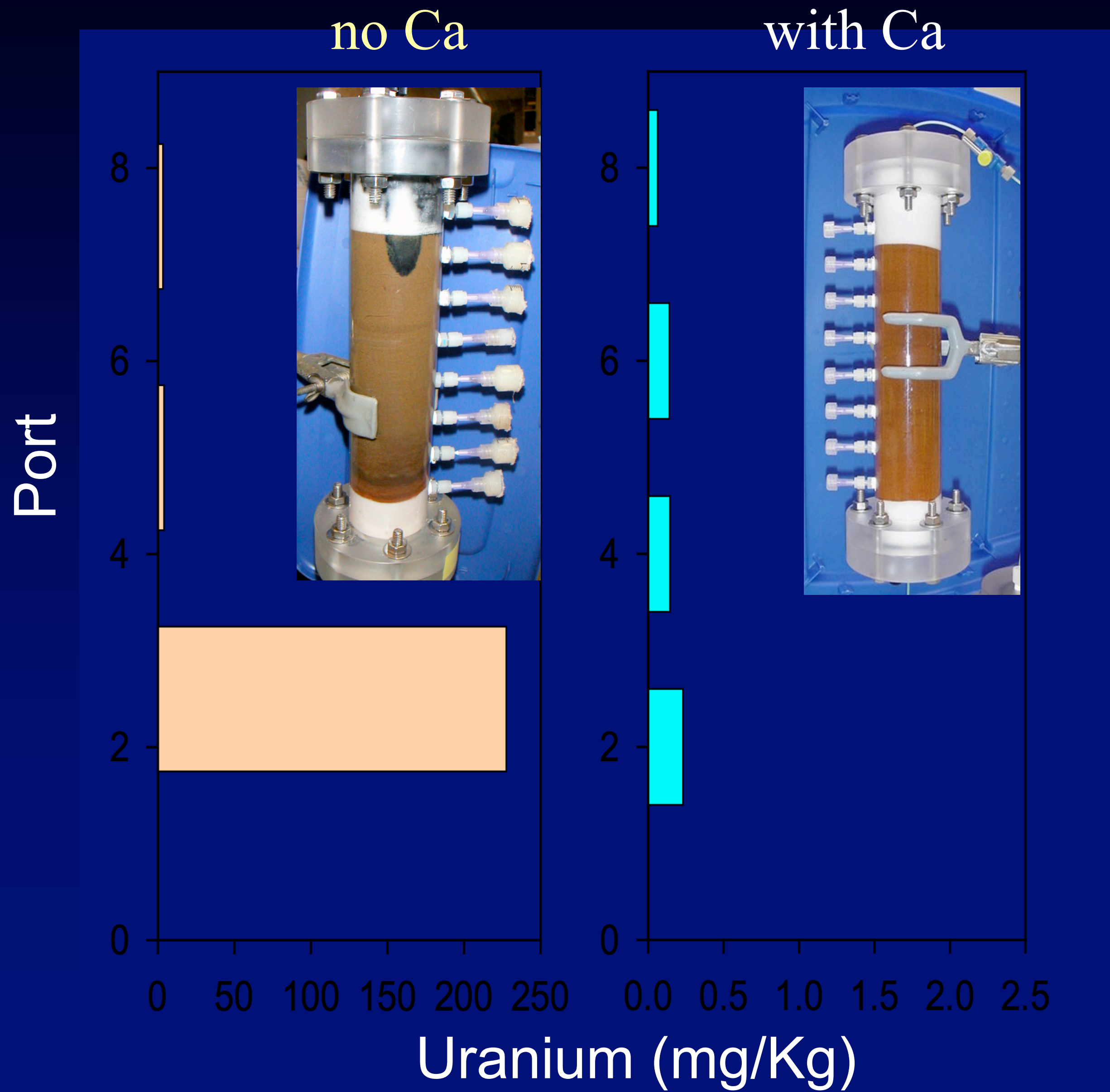


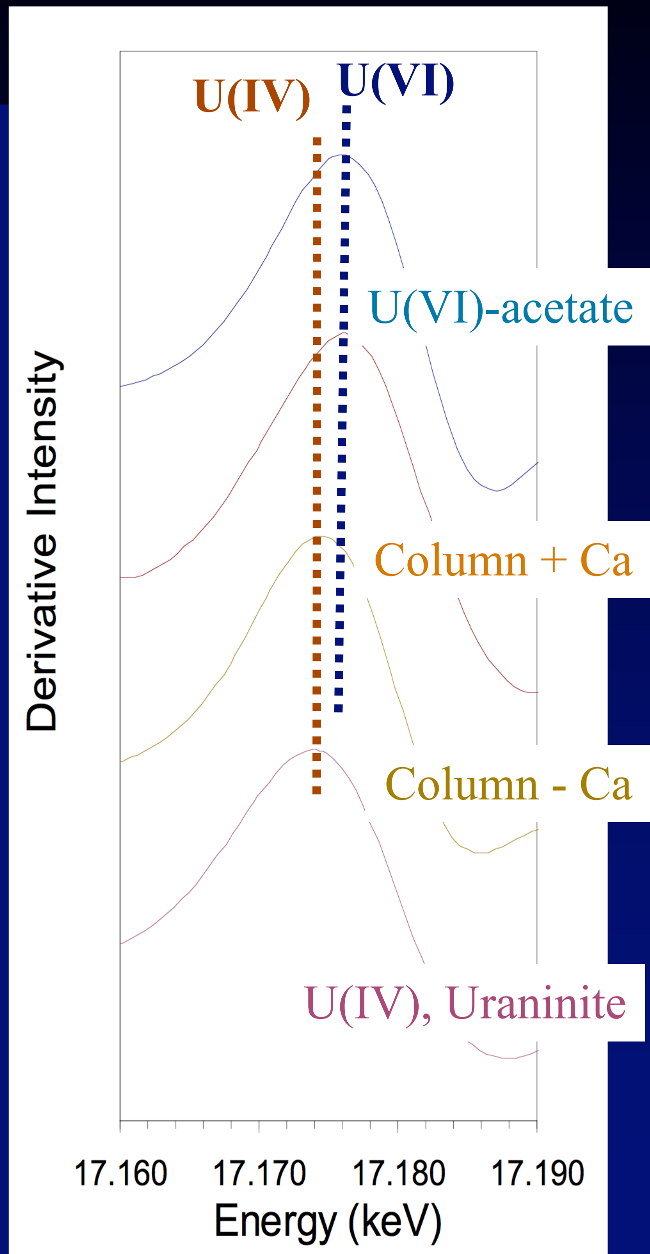


Pore-scale Heterogeneity in Uranium Dynamics



Uranium Speciation: Sequestration





- 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

Localized Biogeochemical Processes