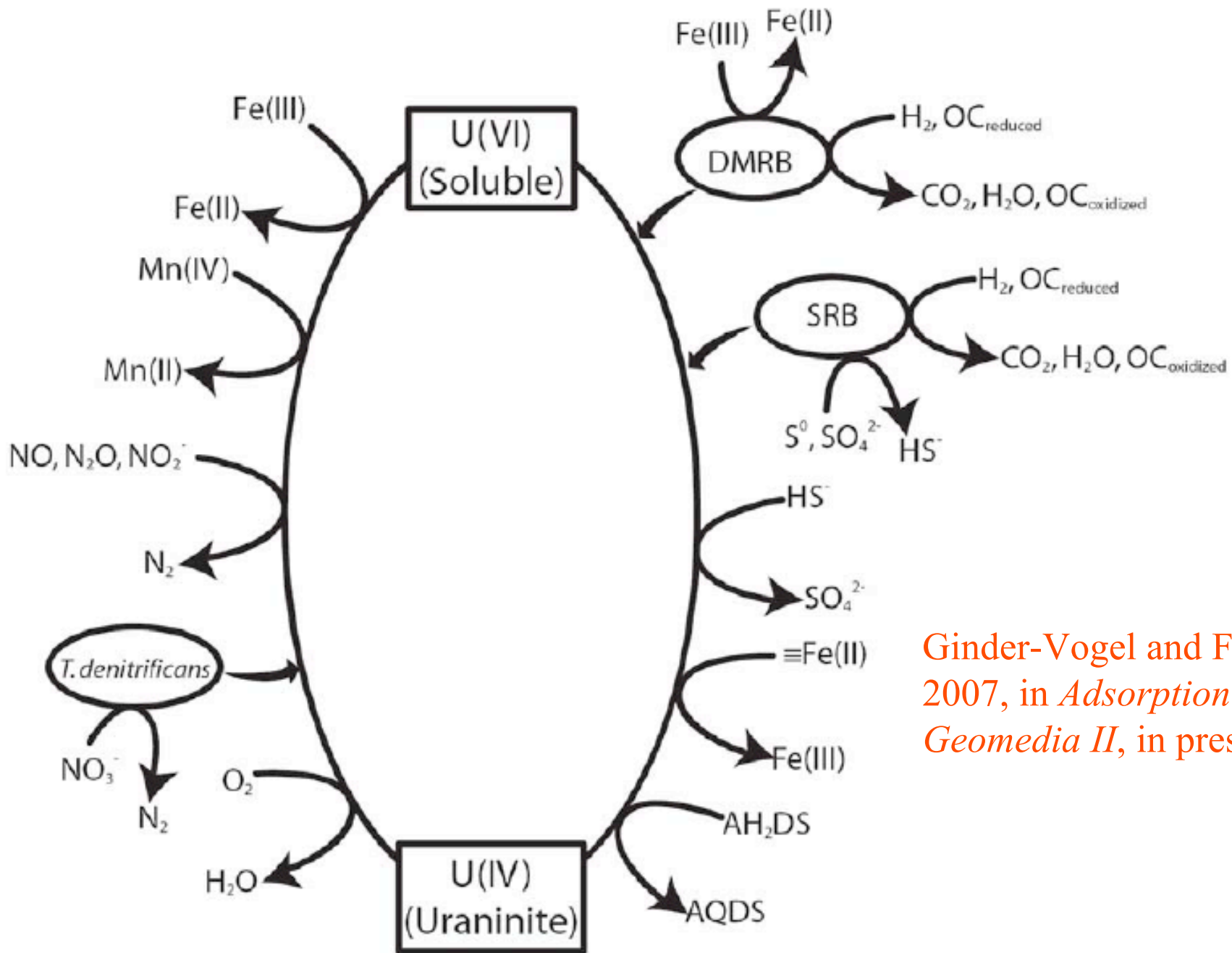

Rifle geochemistry and abiotic U(VI) reactions under Fe-reducing conditions
James A. Davis, USGS, Menlo Park, CA



Rifle Science (Geochemical) Issues

(Davis, Jaffe, Kukkadapu, Steefel, Banfield, Williams)

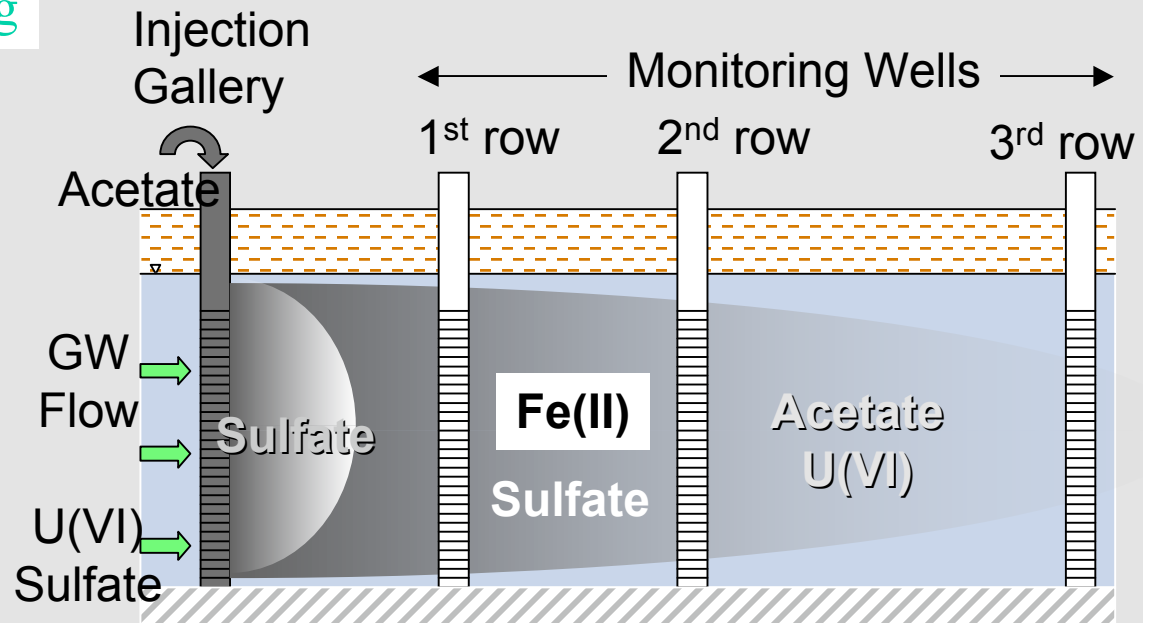
- Questions
 - Are there other microorganisms consuming acetate?
 - Is the Rittman-McCarty stoichiometry of the acetate conversion for the TEAP reactions appropriate?
 - What factors control the microbial reaction rates?
 - nutrient limitations?
 - water chemistry?
 - mineral form? (e.g., iron oxides vs. structural iron; metastable phases)
 - What factors control the onset of sulfate reduction?
 - “bioavailable” iron? (e.g., poorly crystalline iron)
 - metabolic lag?
 - What is the role of biomass in controlling U mobility?
 - production/consumption/decay
 - attachment/detachment
 - contribution to microbial reaction rates
 - effect on reactivity of mineral surfaces
 - sorption effects
 - What is the role of U(VI) adsorption during biostimulation?



Ginder-Vogel and Fendorf, 2007, in *Adsorption in Geomedia II*, in press.

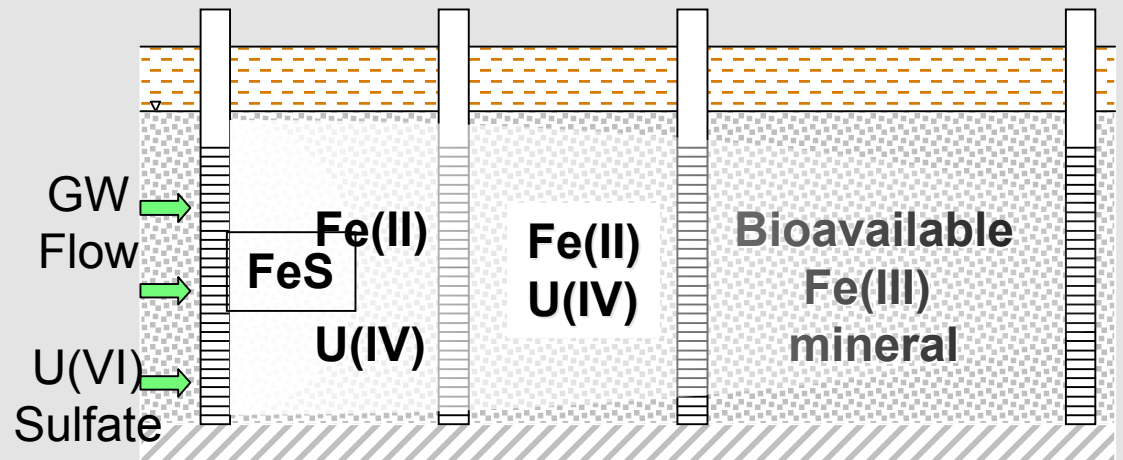
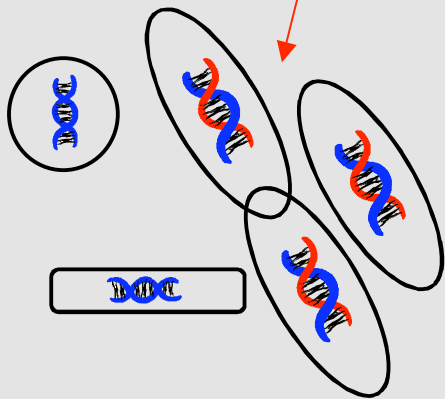
Goal 1: Reactive transport modeling

AQUEOUS PHASE



Goal 2: Contributions to protein expression studies

SOLID PHASE



Reaction Network

- Expanded Biogeochemical Reactions

- Aqueous

- U(VI), U(IV), Ca^{2+} , Fe^{2+} , K^+ , Mg^{2+} , Na^+ , H^+ , NH_4^+ , Cl^- , HCO_3^- , HS^- , SO_4^{2-} , NO_3^- , $\text{PO}_4(?)$

- Mineral

- CaCO_3 and $\text{Fe}(\text{OH})_3$ (U co-ppt), FeOOH , Fe(II)-bearing minerals (siderite, GR, Fe-clays), FeS , UO_2 , redox-inert adsorbents

- Sorption

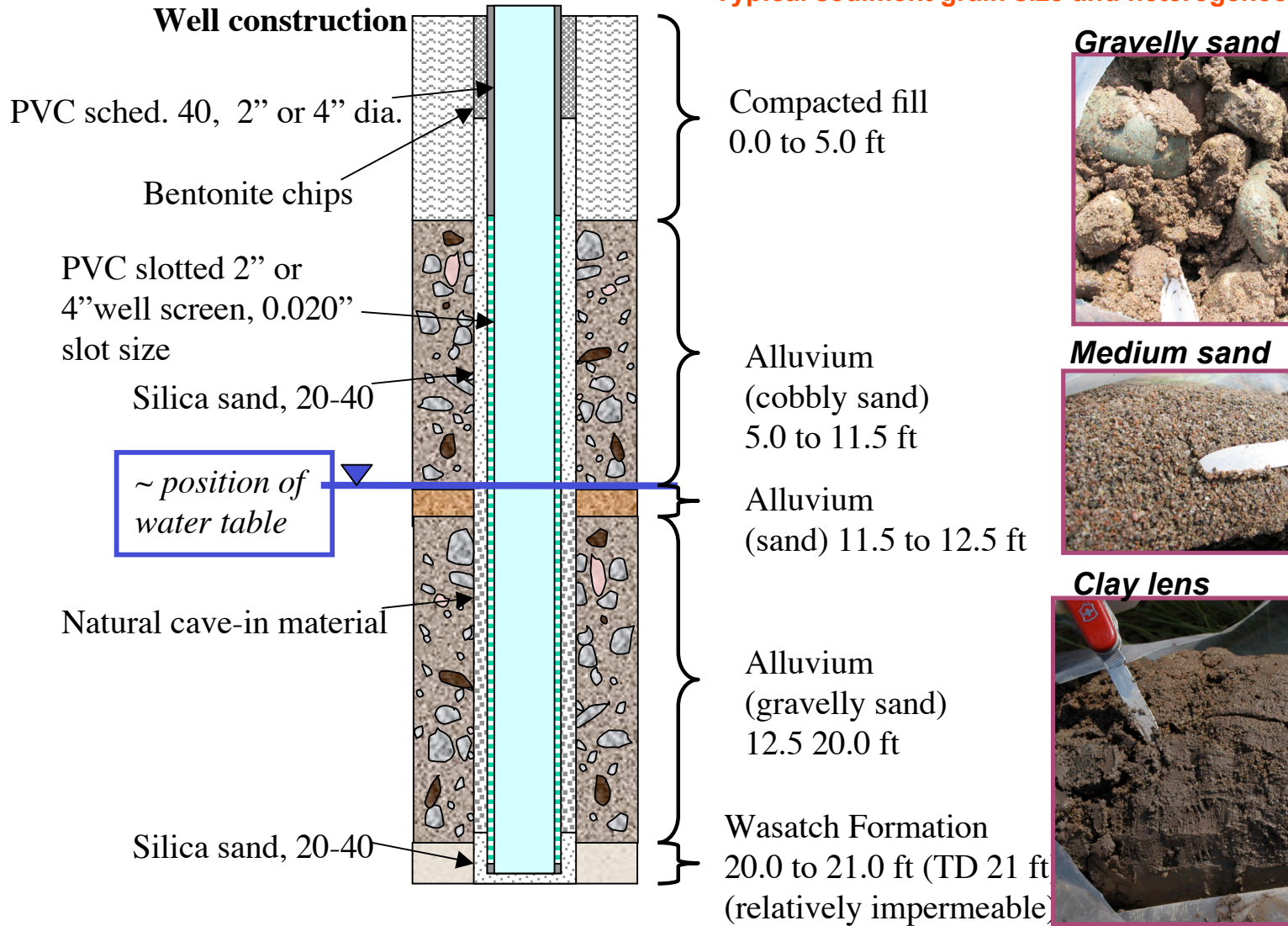
- U(VI), Fe(II), Ca and Mg (IX)

- Biologically-mediated (acetate)

- Fe(III), U(VI), sulfate TEAPs

Heterogeneity in Alluvial Sediment & Associated Permeability Structure

Typical sediment grain size and heterogeneous layering





RABS
Sampling
Location



Experiment
Plot



Image © 2007 DigitalGlobe

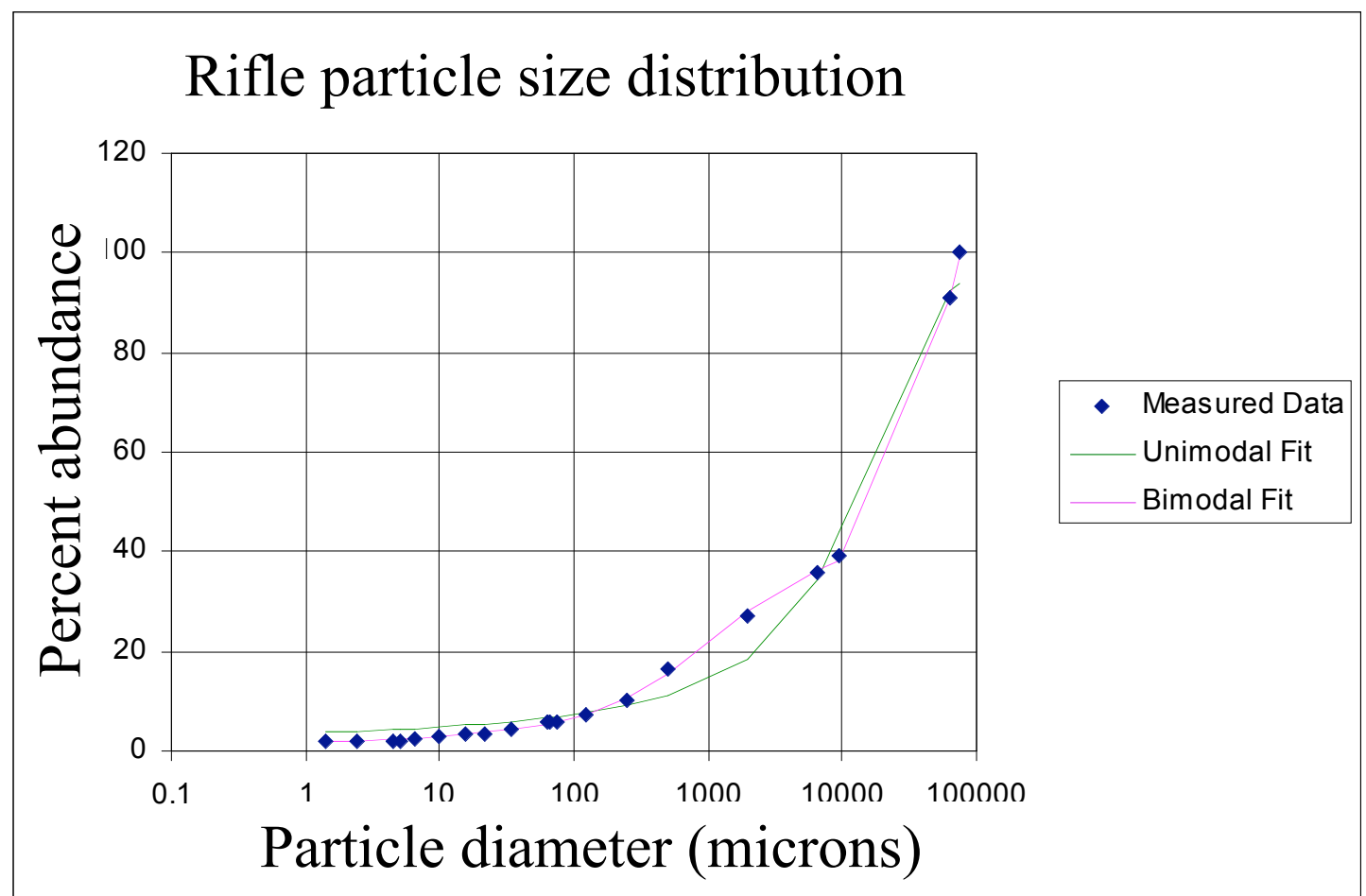
Streaming ||||| 100%

500 ft

Pointer 39°31'45.62" N 107°46'17.54" W elev 5327 ft

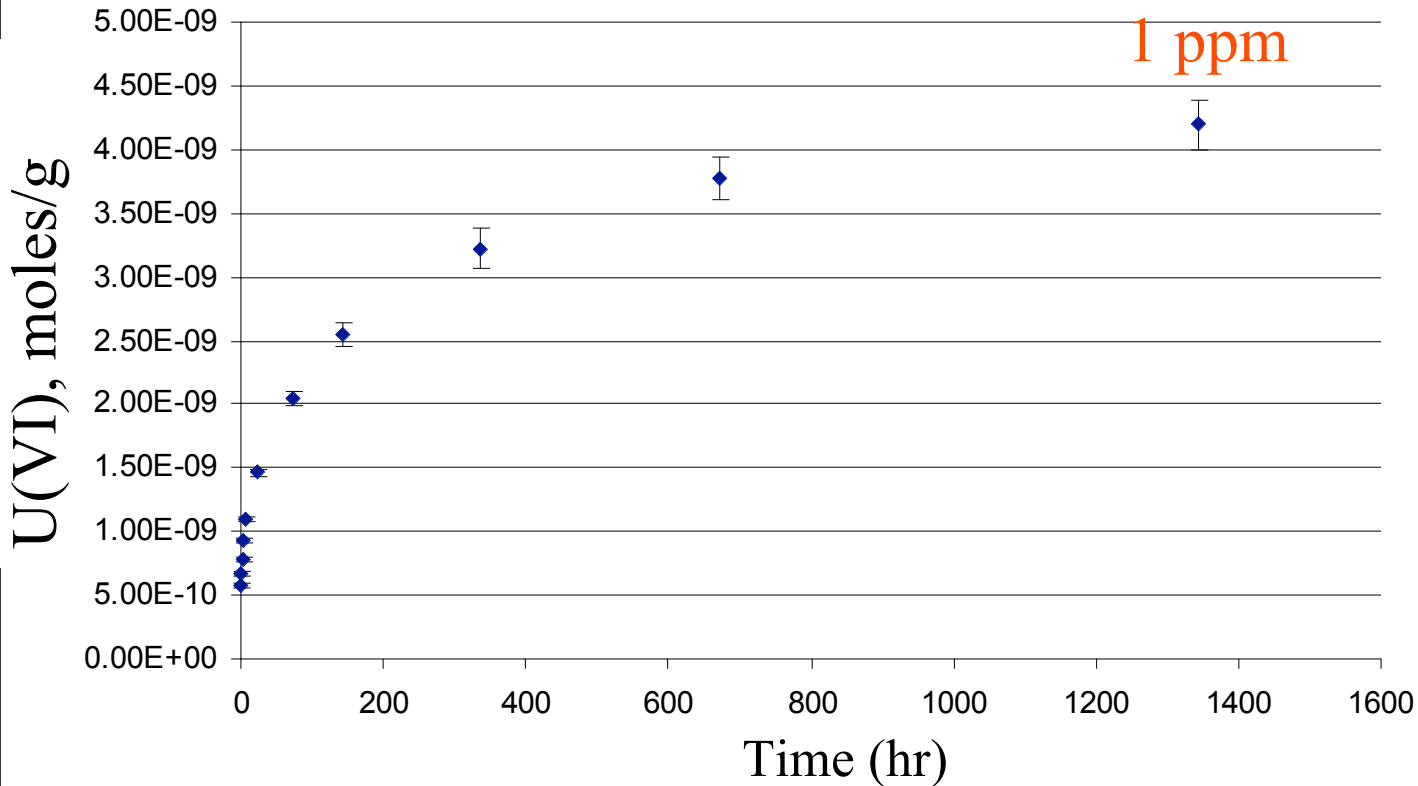
Rifle Aquifer Background Sediment (RABS)

- Backhoe sample collected on December 1, 2004
- Depth between 11.5 and 12.5 feet
- Sediment screened in field with 64 mm sieve; air-dried < 2 mm homogenized in lab



Rifle Aquifer Background Sediment (RABS)

RABS Carbonate Extraction (<2 mm fraction)



XRD and Mossbauer:

Iron oxides:

Magnetite

Hematite

Al-goethite?

Clays:

Muscovite

Clinochlore

Montmorillonite

Kaolinite

Micromoles/g

Total Fe	533
AAO Fe	5.2
HH Fe	9.5
DCB Fe	77.9

Total Mn	5
AAO Mn	0.2
HH Mn	0.6
DCB Mn	1.8

Carbonate extraction (Kohler et al. 2004)

14.4 mM NaHCO₃; 2.8 mM Na₂CO₃; pH 9.39

Surface area (<2 mm fraction):
4.3 m²/g

Rifle: U(VI) Adsorption Kinetics

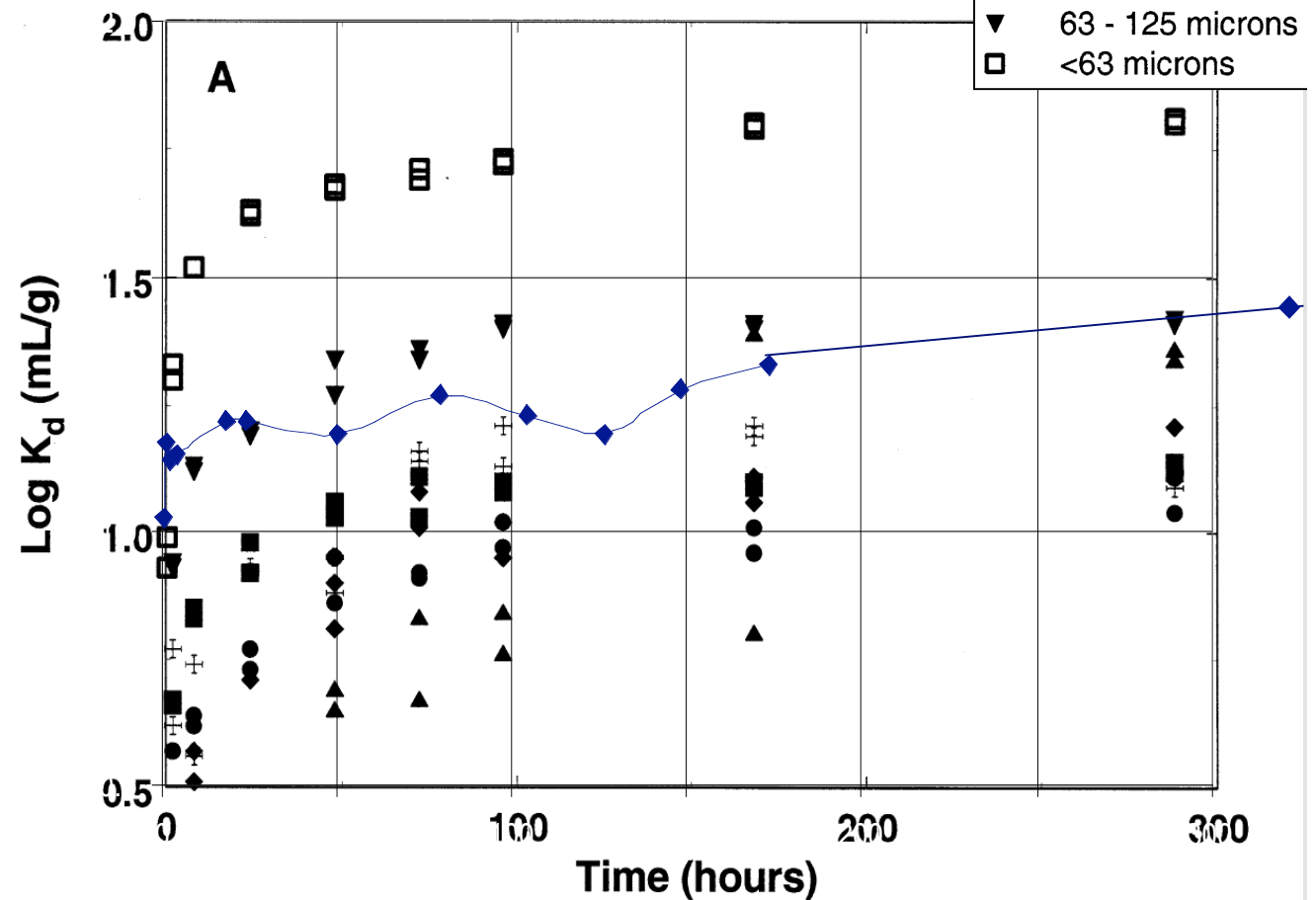
- Preliminary experiments with RABS and AGW-3 (Morrison et al.)
 - 25 g/L, 1 μ M U(VI) added

AGW-3

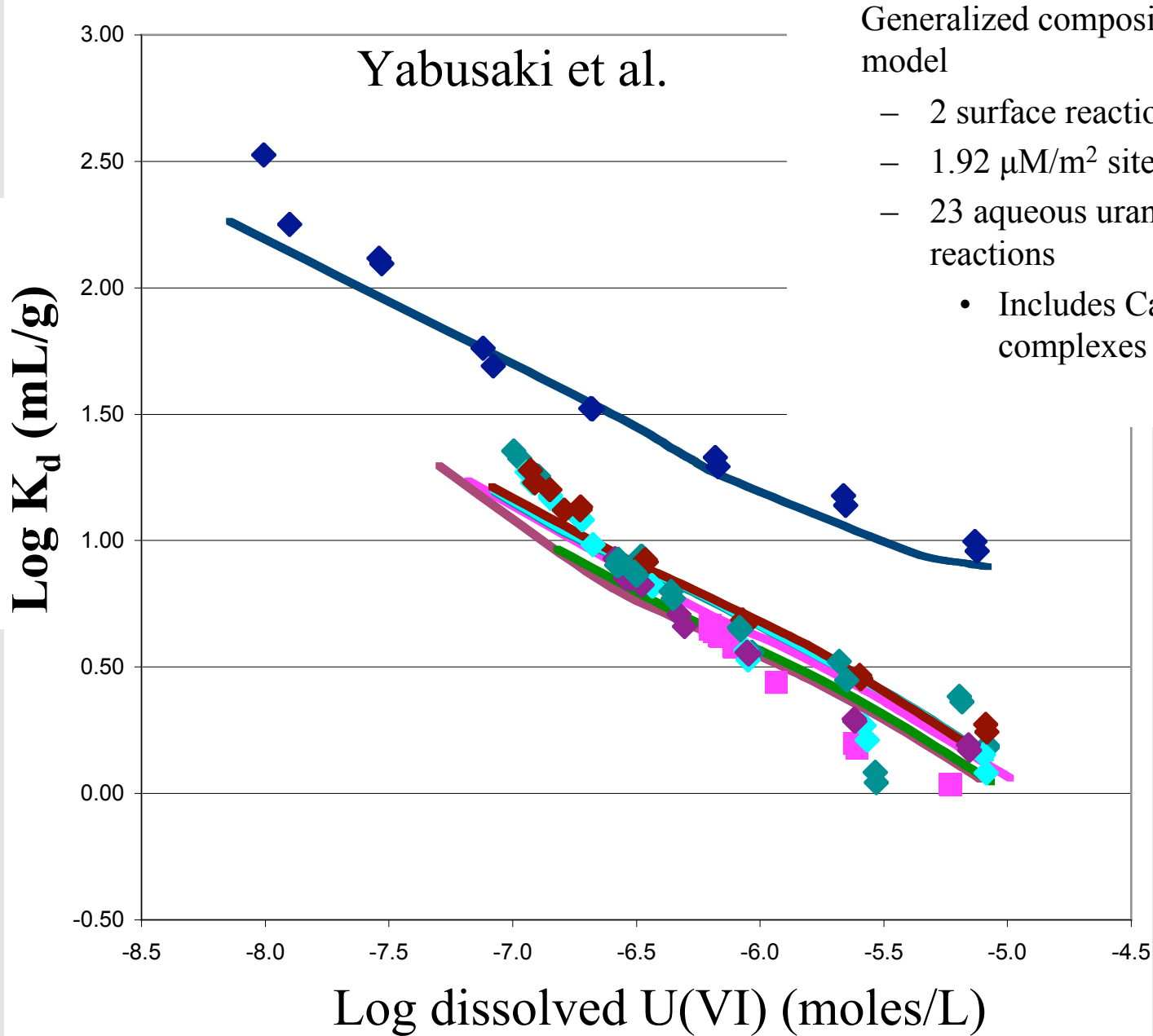
in air at 0.8547 atm
 pH 7.79
 pCO₂ 0.06%

CaSO ₄	$2.33 \cdot 10^{-3}$
MgSO ₄	$1.52 \cdot 10^{-3}$
Na ₂ SO ₄	$9.38 \cdot 10^{-4}$
CaCl ₂	$2.38 \cdot 10^{-3}$
KCl	$6.40 \cdot 10^{-5}$
NaHCO ₃	$5.38 \cdot 10^{-4}$

Adsorption Kinetics



Preliminary Uranium Surface Complexation Modeling



Plans:

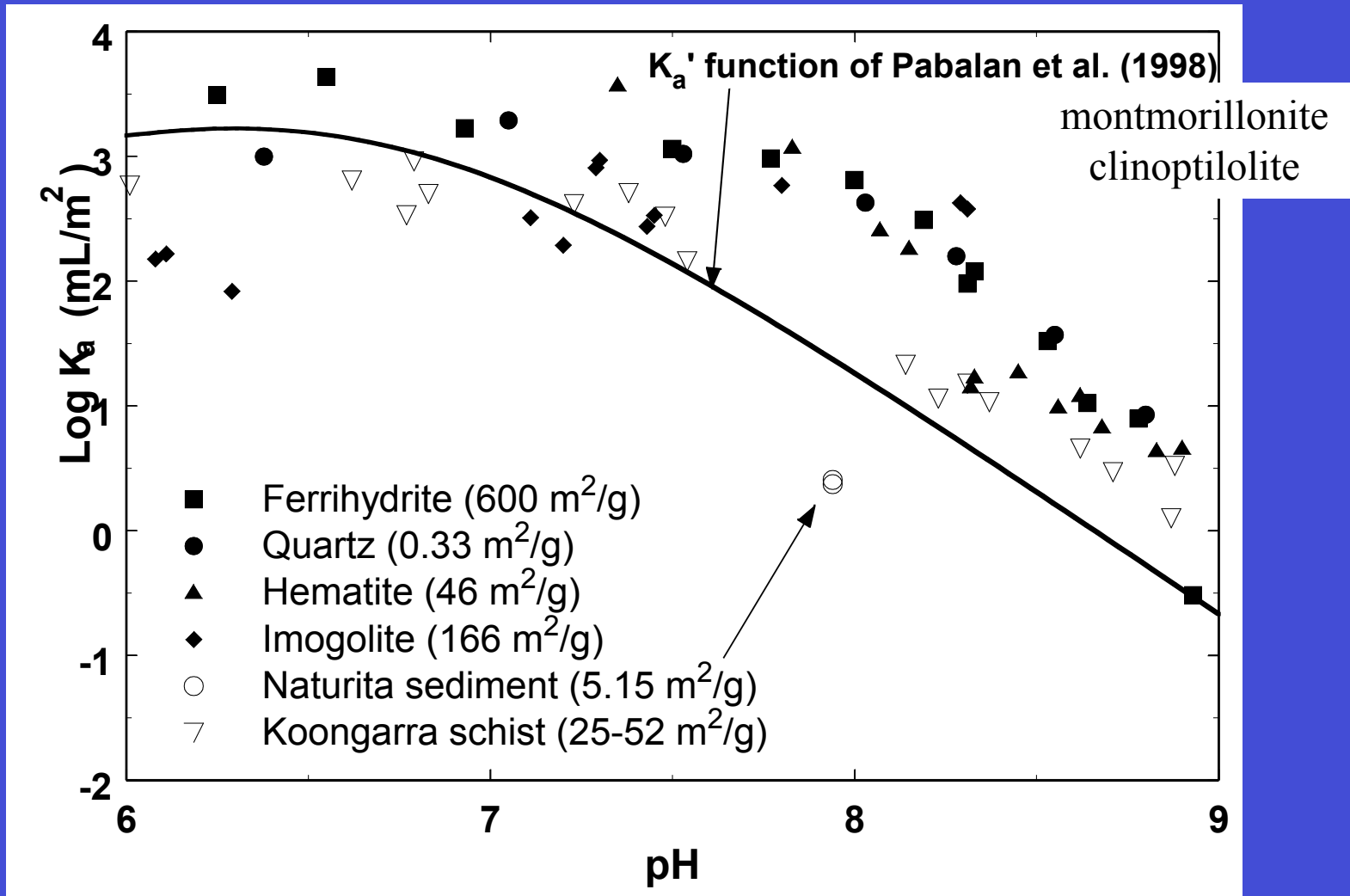
- More conditions
- Mg
- SO₄
- calcite removed
- Fe(OH)₃ added

U(VI) sorption under Fe-reducing conditions

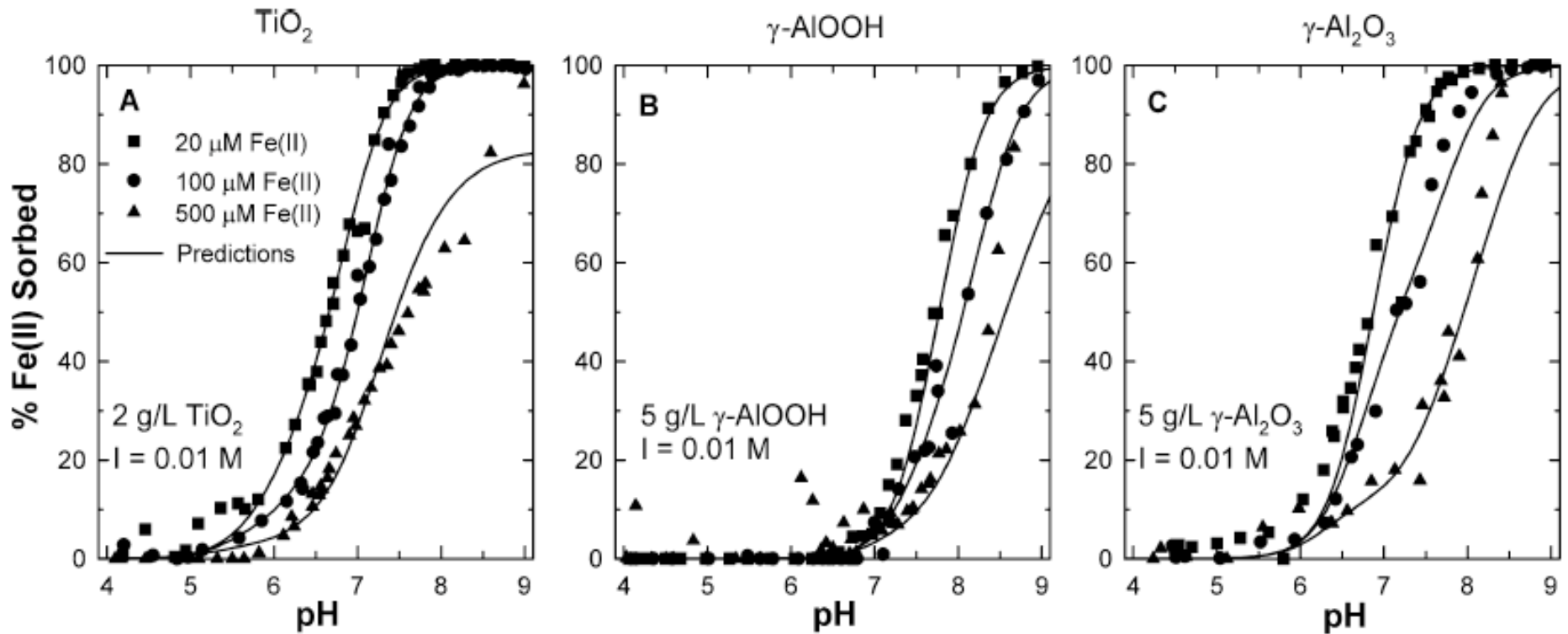
What's different?

- Fe(II) adsorbs and competes for sorption sites
- Sediment has less Fe(III) adsorbent phases
- U(VI) is (possibly) abiotically reduced by sorbed Fe(II) or Fe(II)-bearing mineral phases (FeCO₃, GR, Fe(II)-clays)
- Dissolved Mn(II) and Fe(II) exchange with Ca and Mg in clays and affect U(VI) aqueous speciation
- U(VI) co-precipitates during rapid calcite precipitation events

**U(VI) adsorbs on many minerals similarly
if scaled by BET surface area;
Fe(III) oxides not needed for U(VI) adsorption**



Fe(II) sorbs strongly at pH 7-8 on many minerals

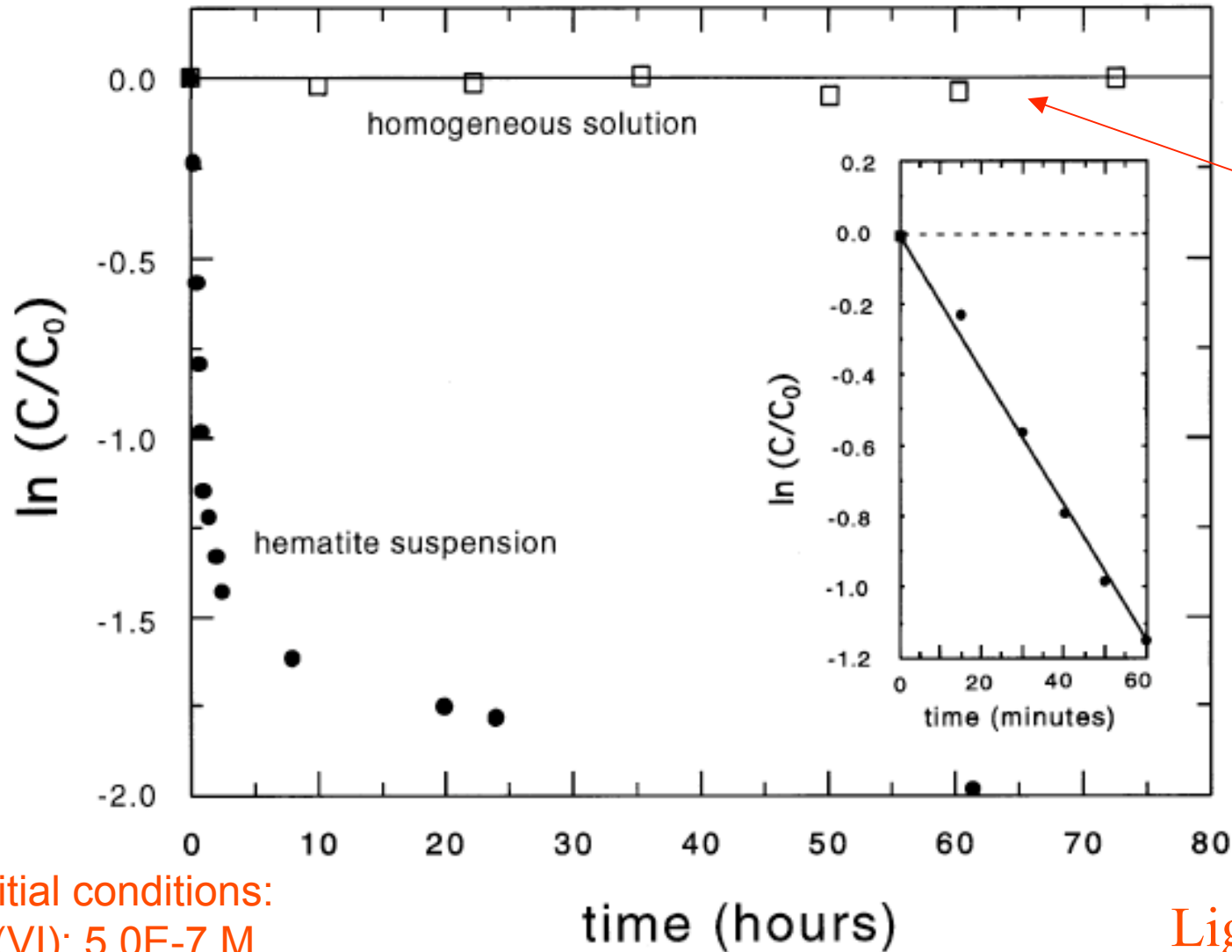


Nano and Strathmann, JCIS, 2006, 297, 443

Does Fe(II) at mM concentrations compete with U(VI) at μM concentrations for adsorption sites?

Abiotic U(VI) reduction by sorbed Fe(II)

pH 7.5
I = 0.1M

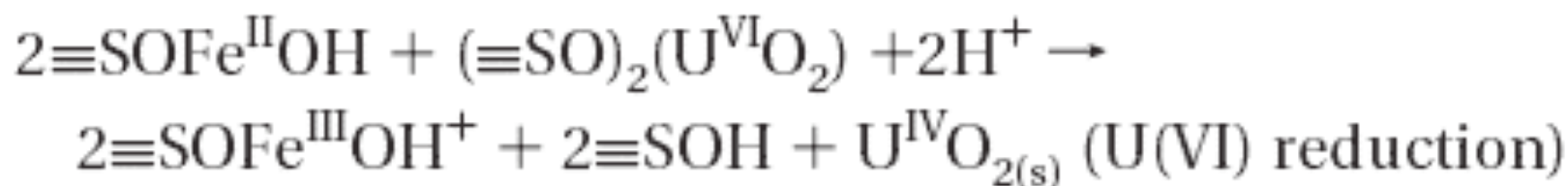
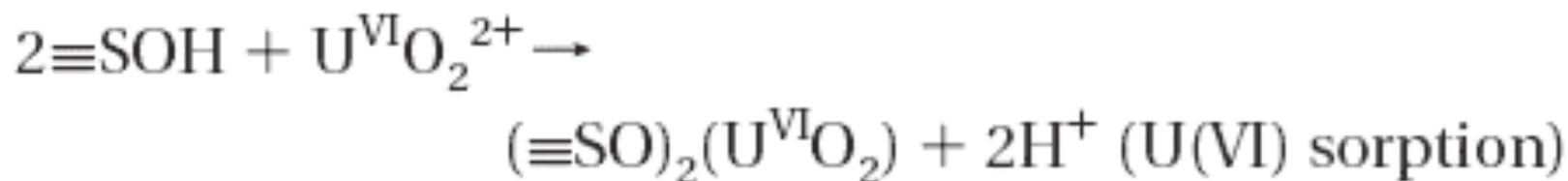
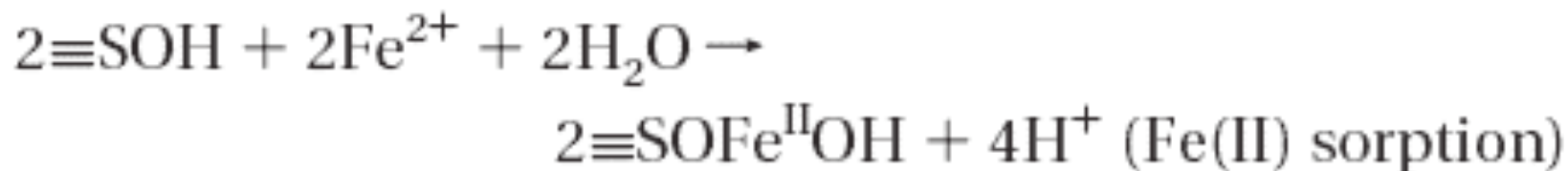


No U(VI)
reduction
in 3 days

Initial conditions:
U(VI): $5.0E-7$ M
Fe(II): $1.6E-4$ M

Liger et al. (1999)

Abiotic U(VI) reduction by sorbed Fe(II)



Jeon et al., 2005: magnetite, hematite, goethite, smectite, (**sediments with sorbed Fe(II) – more effective with sediments of high Fe(III)-oxide content**) – pH 6.8; initial Ca 0.6 mM; 10 mM added HCO_3^-

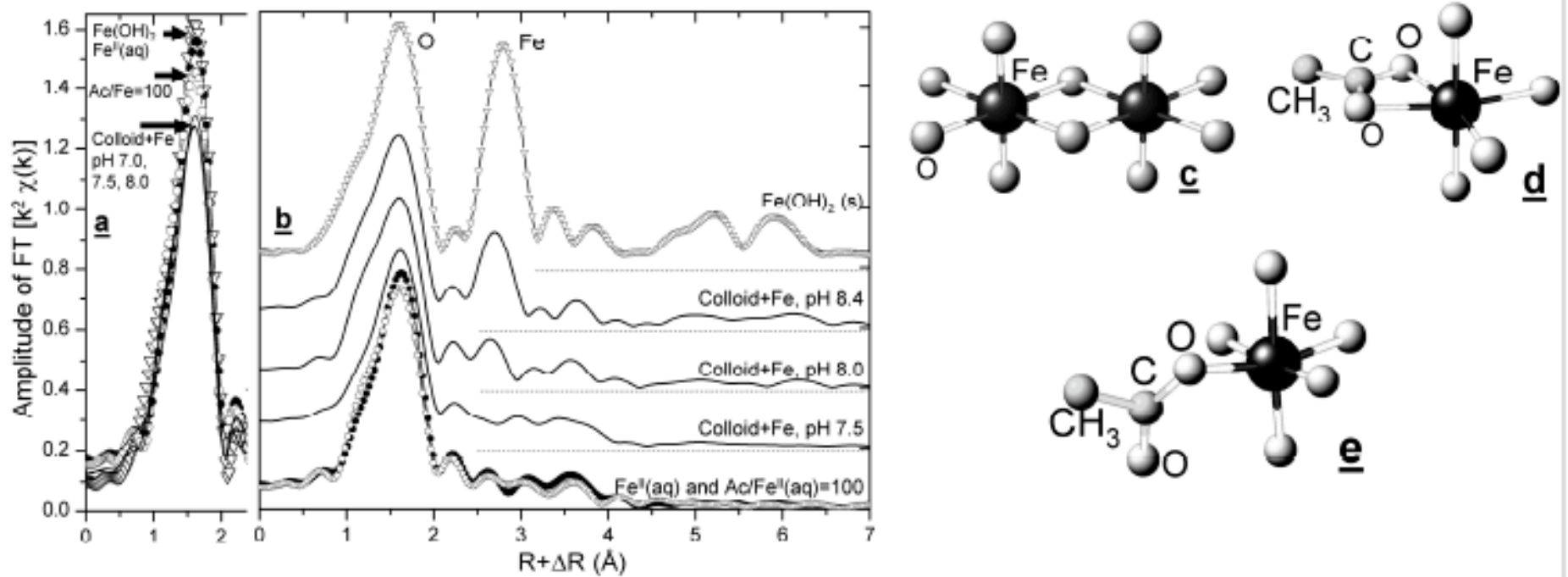
O'Loughlin et al., 2003: green rust – pH 6 – 7.5, absence of CO_3

Fredrickson et al., 2000: goethite – pH 7; added HCO_3^- (?), PIPES

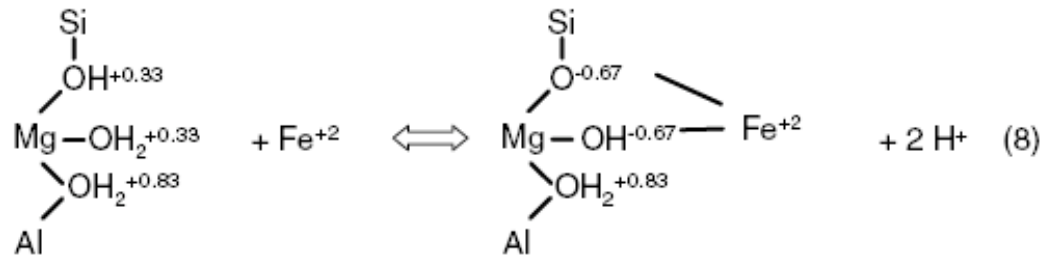
Ilton et al., 2006: Fe(II)-bearing micas – pH 4.5-6, 9.5; no Ca, absence of CO_3

Fe(II) and U(VI) abiotic reactions with carboxylated polystyrene microspheres

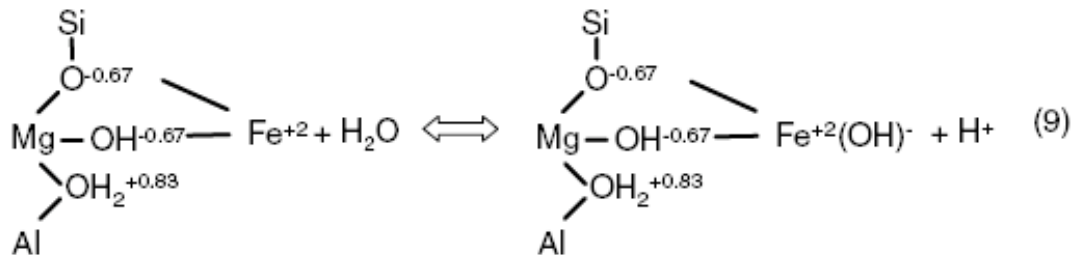
Transition from Fe(II) monomer to dimer occurred between pH 7.5 and 8.4. Over 4 month period, no U(VI) at pH 7.4. Complete U(VI) reduction at 8.4. U(IV) stable under anoxic conditions for 4 months



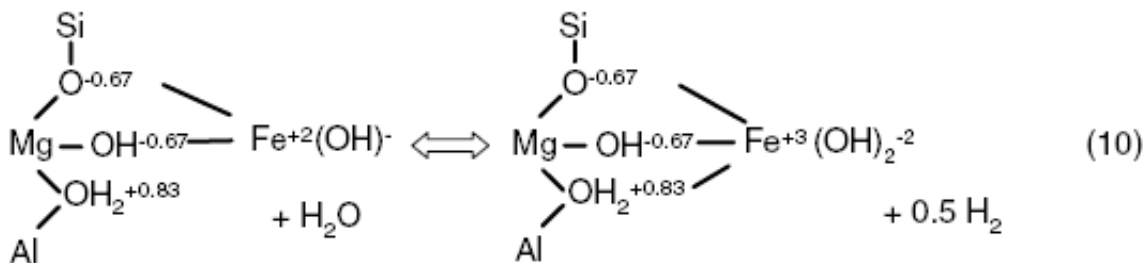
Boyanov et al., GCA, in press



Reversible electron transfer of Fe(II) in the interlayer of Ca-saturated montmorillonite

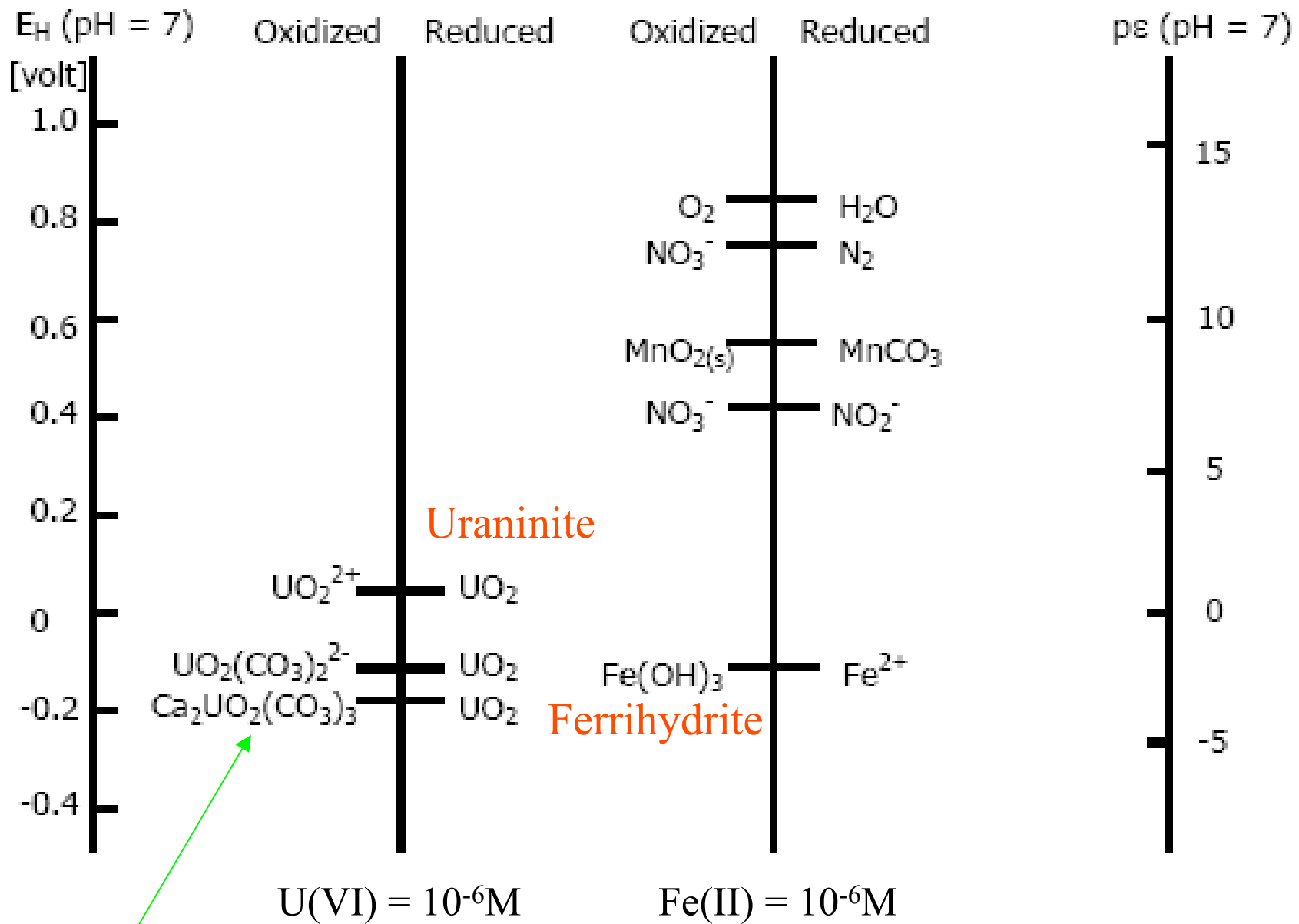


Electron transferred to the clay mineral structure; Fe(III) preferentially found at pH 7



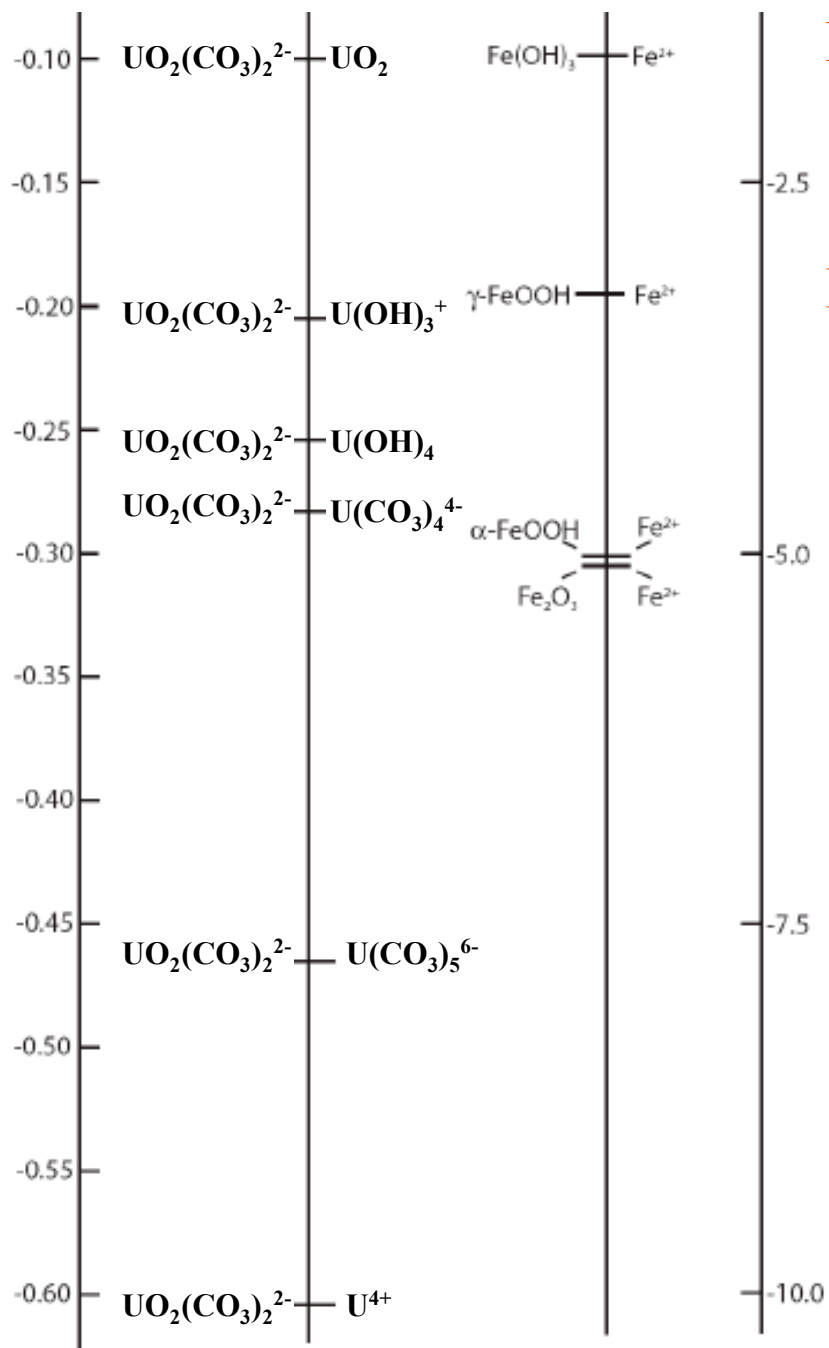
Reaction can be reversed by lowering the pH

Gehin et al., 2007, GCA, 71, 863



U(VI) speciation affects favorability for reduction

Ginder-Vogel and Fendorf, 2007, in *Adsorption in Geomedia II*, in press.



Ferrihydrite

Lepidocrocite

Goethite
Hematite

Ginder-Vogel and Fendorf,
2007, in *Adsorption in
Geomeia II*, in press.

U(IV) speciation and Fe(III)
oxide affect favorability for
reduction

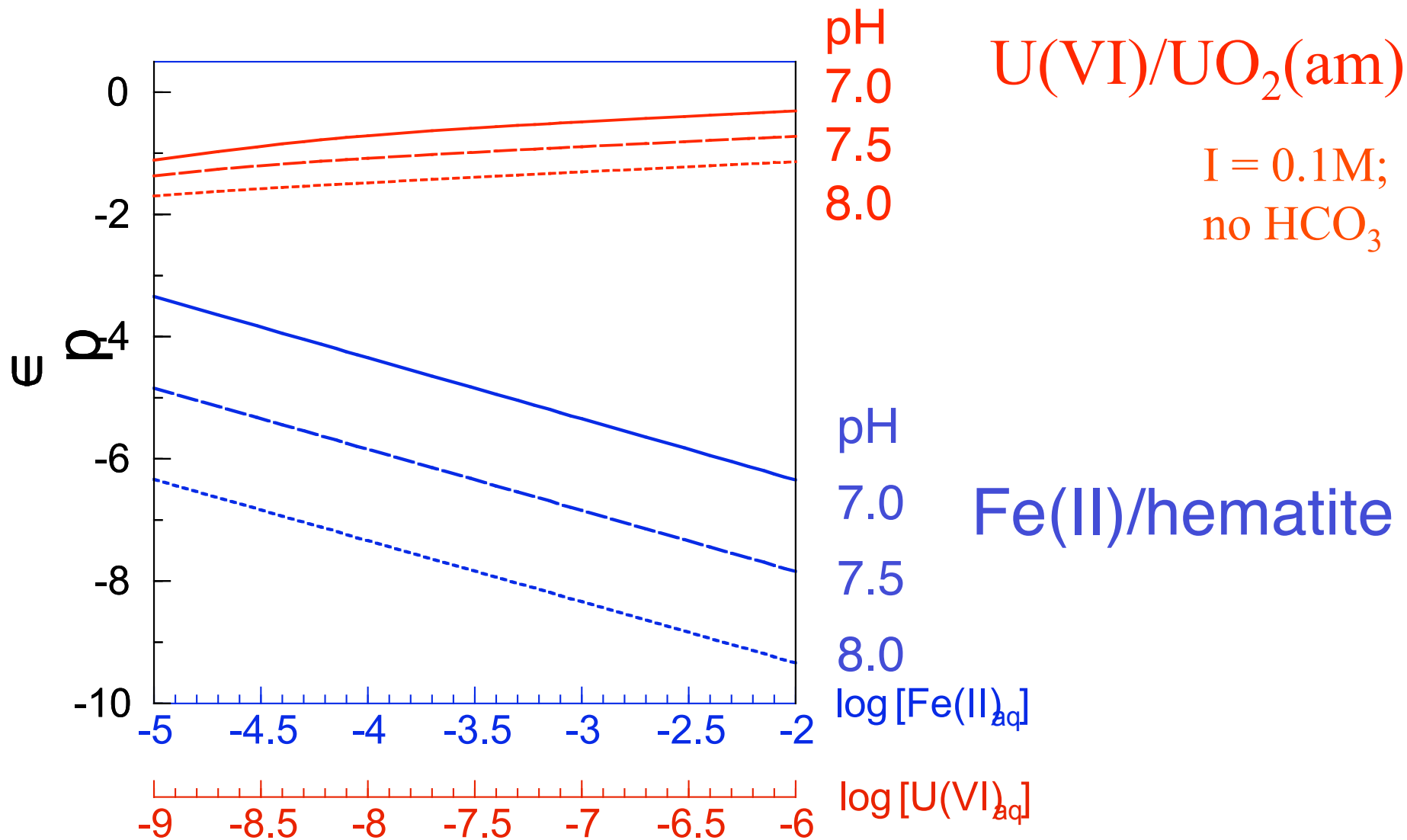
$U(VI) = 10^{-6}M$

$U(IV) = 10^{-9}M$

$Fe(II) = 10^{-5}M$

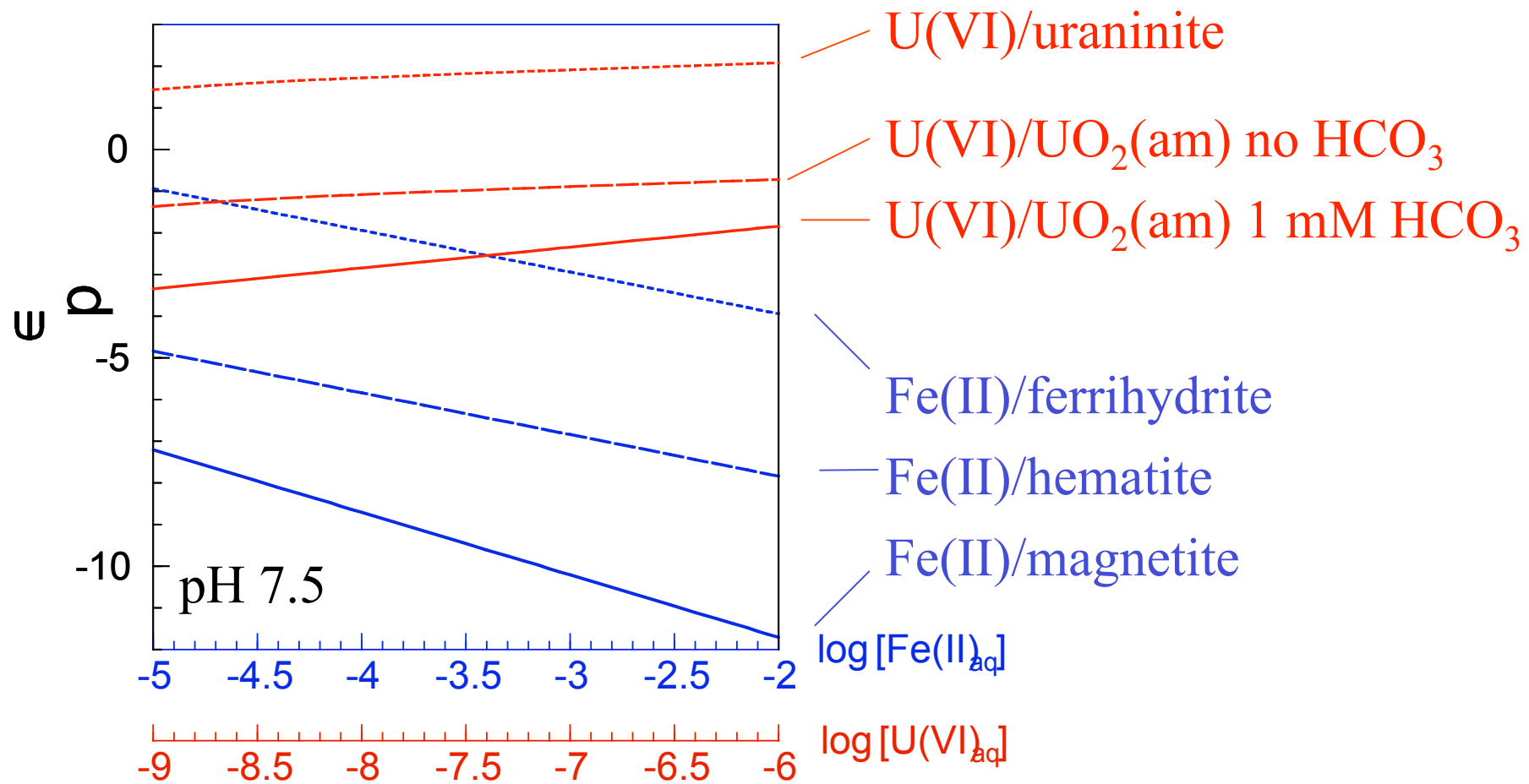
$HCO_3^- = 3 \text{ mM}$

$pH = 7$



Behrends and van Cappellen, 2007

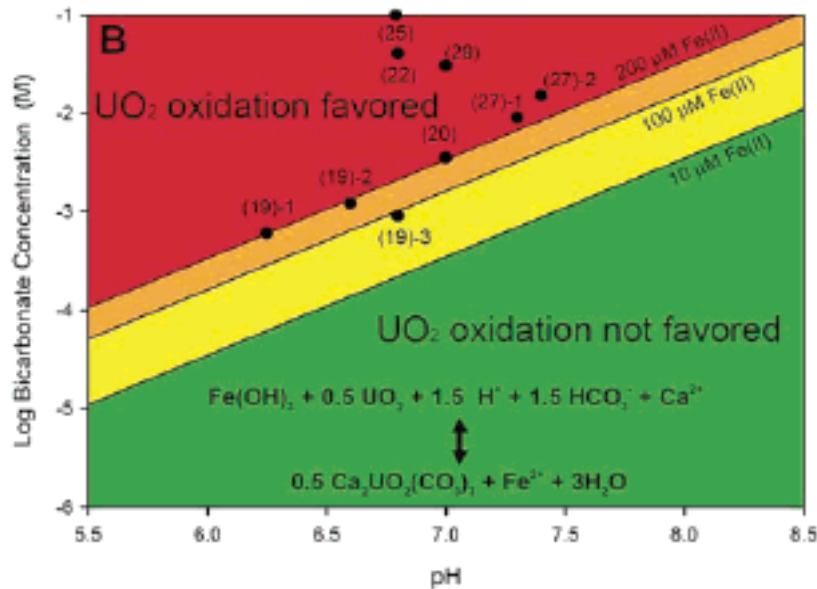
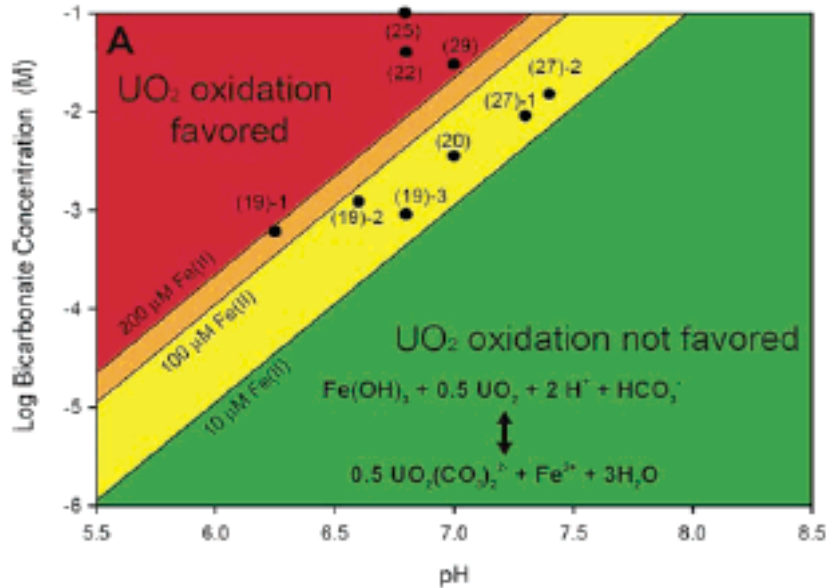
pH and concentrations affect favorability for reduction



Behrends and van Cappellen, 2007

Ginder-Vogel et al. (2006)

Effect of U(VI) aqueous speciation on thermodynamic free energies for oxidation of biogenic UO_2 by ferrihydrite



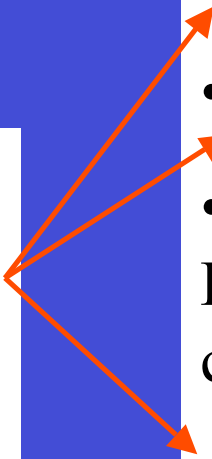
0.13 μM U(VI)
1 mM Ca^{2+}

U(VI) sorption under Fe-reducing conditions

What's different?

- Fe(II) adsorbs and competes for sorption sites
- Sediment has less Fe(III) adsorbent phases
- U(VI) is abiotically reduced by sorbed Fe(II) or Fe(II)-bearing mineral phases (FeCO₃, GR, Fe(II)-clays)
- Dissolved Mn(II) and Fe(II) exchange with Ca and Mg in clays and affect U(VI) aqueous speciation
- U(VI) co-precipitates during rapid calcite precipitation events

Use Ni(II)
and Zn(II)
for
comparison
with Fe(II)



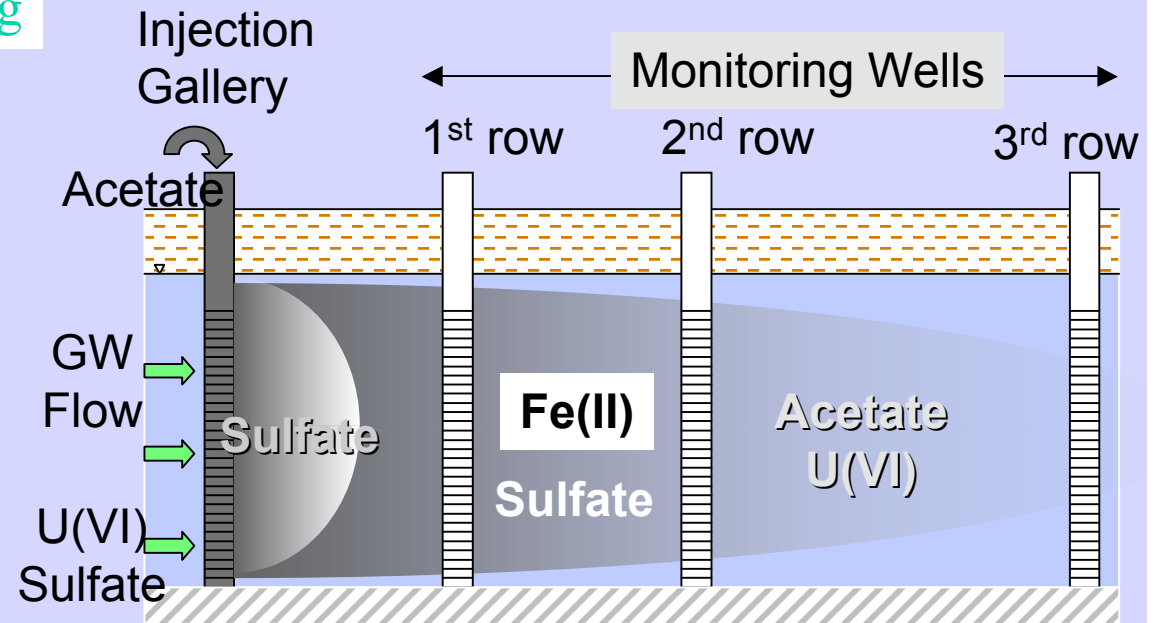
Experimental program U(VI) sorption and reduction under abiotic, Fe-reducing conditions

1. Study Fe(II), Zn(II), and Ni(II) sorption – Variables: pH, Ca, HCO_3 and metal concentrations, Mg, SO_4 , (competitive metal sorption, bioreduced sediment with some Fe(III) oxides removed)
2. Study U(VI), Zn(II) and Ni(II) sorption – Variables: As above (competitive metal sorption, bioreduced sediment with some Fe(III) oxides removed)
3. Study U(VI) sorption and reduction in the presence of Fe(II) - Variables: time, pH, Fe(II), Ca, U(VI) and HCO_3 concentrations, aging before U(VI) addition (U(VI) aqueous speciation and thus sorbed U(VI) concentration)
4. Are U(VI)-calcite interactions important at Rifle?

Minerals: Rifle sediments, Rifle sediments – carbonates, Rifle bioreduced sediments, mineral separates (magnetically susceptible, others?), Al-goethite, muscovite, ferrihydrite, clay?

Goal 1: Reactive transport modeling

AQUEOUS PHASE



Goal 2: Contributions to protein expression studies

SOLID PHASE

