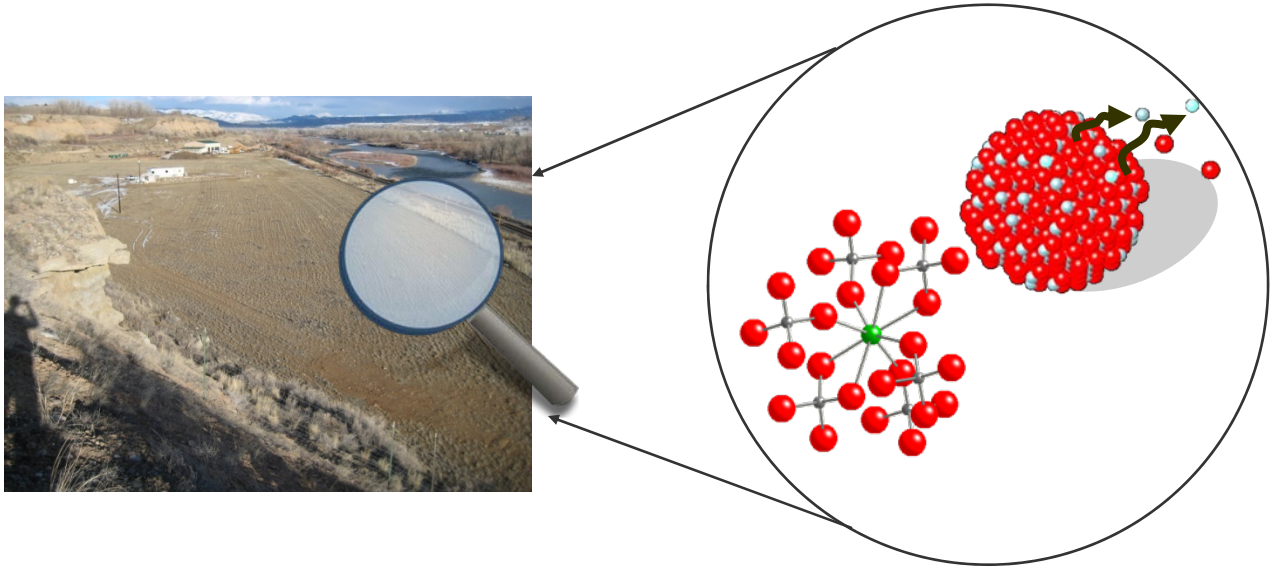
Stability of Biogeochemically Reduced Uranium Under in situ Conditions at the Old Rifle site

Collaborative Research by the SLAC-SFA and Rifle IFRC teams

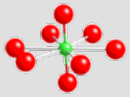


J.R. Bargar (SSRL)
K. Campbell (USGS), H. Veeramani, E. Suvorova, and R. Bernier-Latmani (EPFL), J.E. Stubbs, and J. Lezama (SSRL), K.-U. Ulrich, L.Y Blue, and D.E. Giammar (WUStL), P.E. Long, and S. Yabusaki (PNNL)

2010 Long-Term Surveillance and Monitoring Conference.
November 17, 2010. Grand Junction, Co

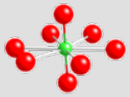
Dynamics of reduced U

State of our understanding

U(VI) 

Reduction ---------->

Naturally reduced sediments from the Rifle IFRC site, LQ Gallery

Oxidation ---------> U(VI) 

Dynamics of reduced U

State of our understanding

U(VI) --------> Reduction

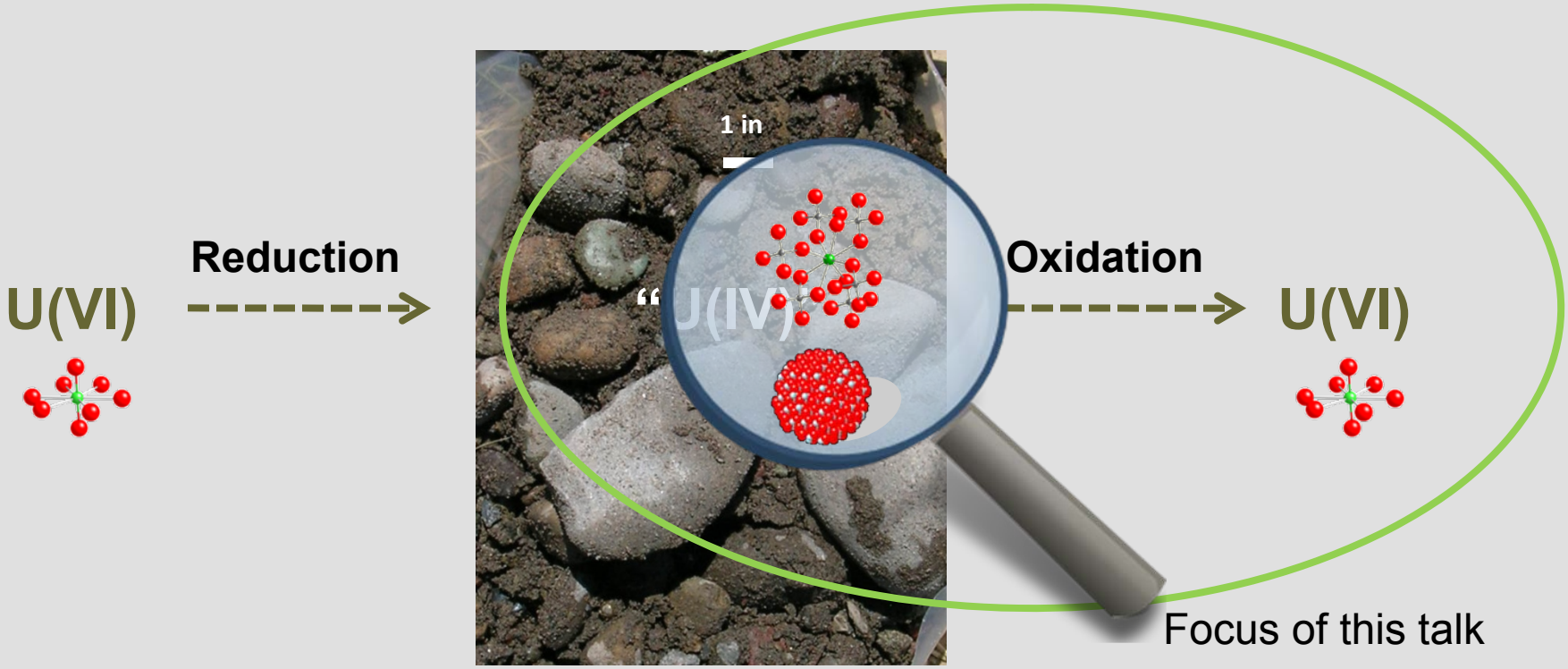
Naturally reduced sediments from the Rifle IFRC site, LQ Gallery

Oxidation --------> U(VI)

Focus of this talk

What are oxidation rates of reduced uranium?
What are the mechanisms and their products?

Dynamics of reduced U



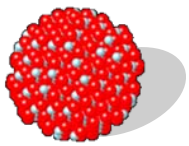
Naturally reduced sediments from the Rifle IFRC site, LQ Gallery

Goals:
- **Rates/mechanisms for *individual U(IV) species***
- **Under *aquifer conditions***

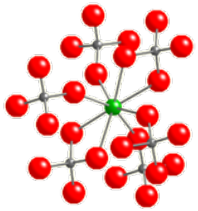
(*i.e.*, the parameters needed for biogeochem models)

Forms of reduced uranium

From literature and our group's work:



- uraninite ($UO_{2(s)}$)
- U(IV) sorbed to biomass
- U(IV) adsorbed to minerals
- U(IV) incorporated into Fe sulfides



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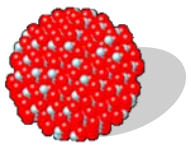

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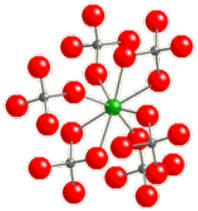


Biogenic uraninite

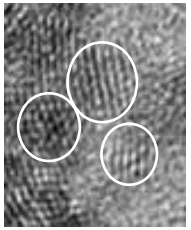
- Most well-studied of these materials
- *Only* form of U(IV) for which thermodynamic, kinetic parameters are known
- Can be used as a proxy to understand behavior of other forms of U(IV) in sediments
- Abundant in low-temp. sedimentary ore deposits
- Widely used sink term in biogeochemical models

How can we isolate individual U(IV) species & assess their reactivity under field conditions?

Capturing complexity

Simplest lab approach

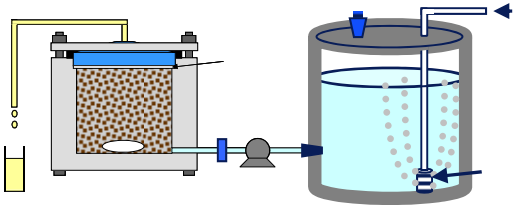
Stirred reactor: add soluble oxidants



Increasing complexity

The "real thing"

Solid-phase oxidants, in appropriate matrix



Ideal for studying individual species, but simplistic

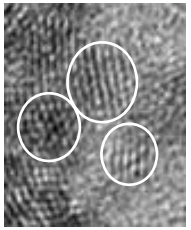
Highly complicated: difficult to isolate individual species

Capturing complexity

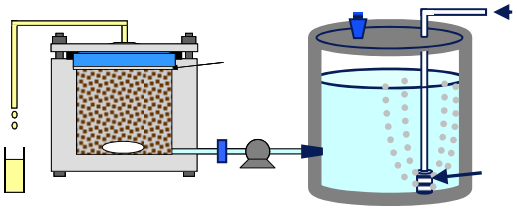
Add soluble oxidants

+ Artificial ground water

Solid-phase oxidants, in appropriate matrix



Increasing complexity

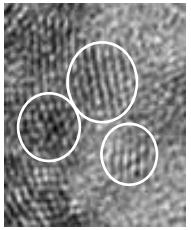


Capturing complexity

√ Add soluble oxidants

√ + Artificial ground water

Solid-phase oxidants, in appropriate matrix



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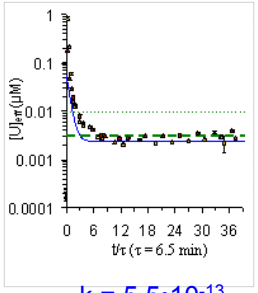
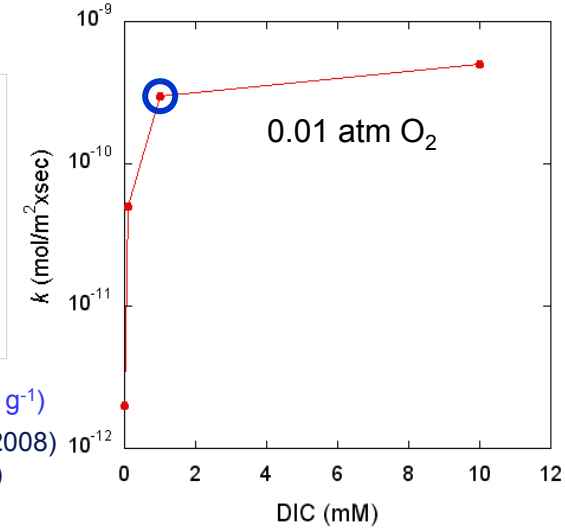


$k = 5.5 \cdot 10^{-13}$ mol m^{-2} s^{-1} (50.1 m^2 g^{-1})

Ulrich et al. *ES&T* (2008) and *GCA* (2009)

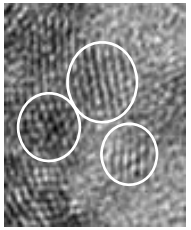


Capturing complexity

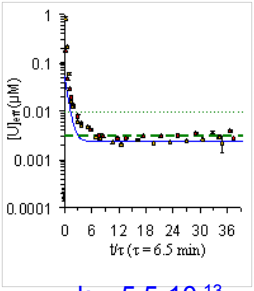
√ Add soluble oxidants

√ + Artificial ground water

Solid-phase oxidants, in appropriate matrix



Increasing complexity



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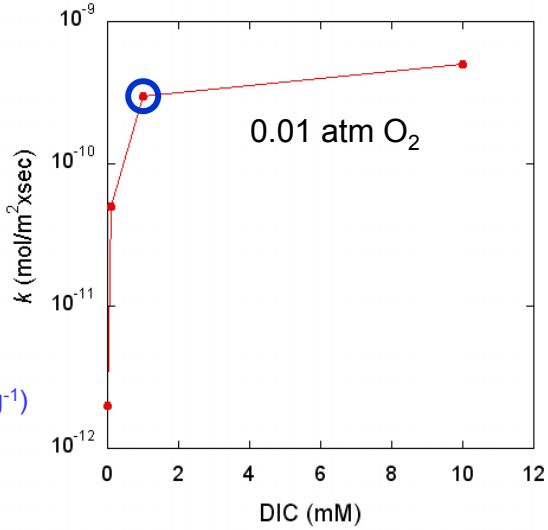


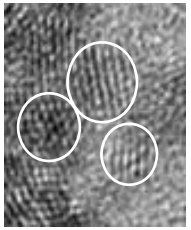
Problem is, this doesn't give us what we ultimately need to know……..

Capturing complexity

√ Add soluble oxidants

√ + Artificial ground water

Solid-phase oxidants, in appropriate matrix



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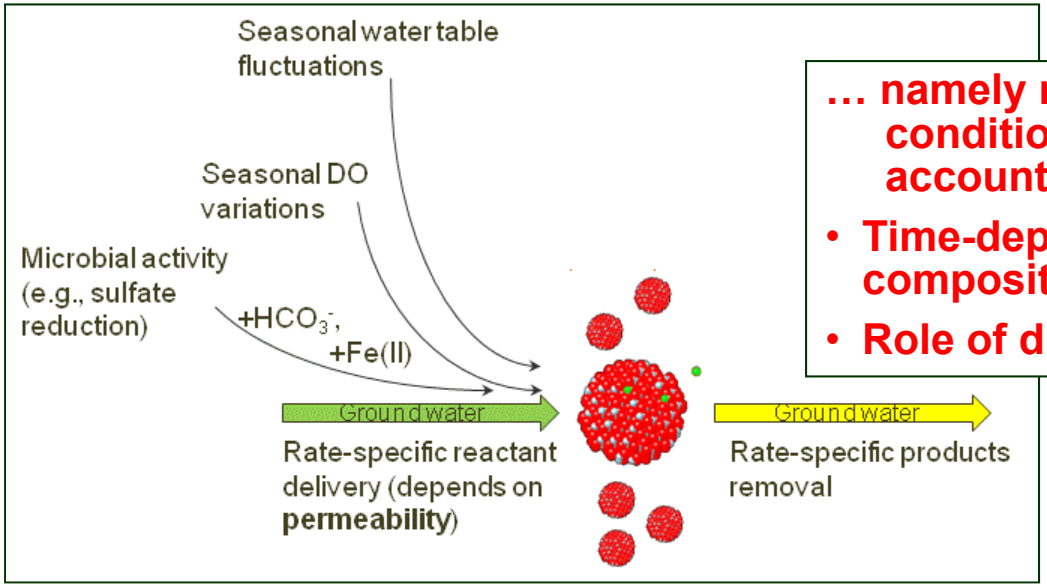


… namely rates under field conditions that take into account:

- Time-dependent ground water composition
- Role of diffusion

Approach: *in-situ* incubations in wells

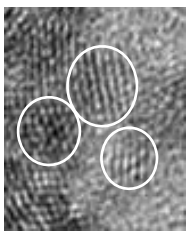
Add soluble oxidants

+ Artificial ground water

Conduct experiment in-well

In well, biomass present

Solid-phase oxidants, in appropriate matrix



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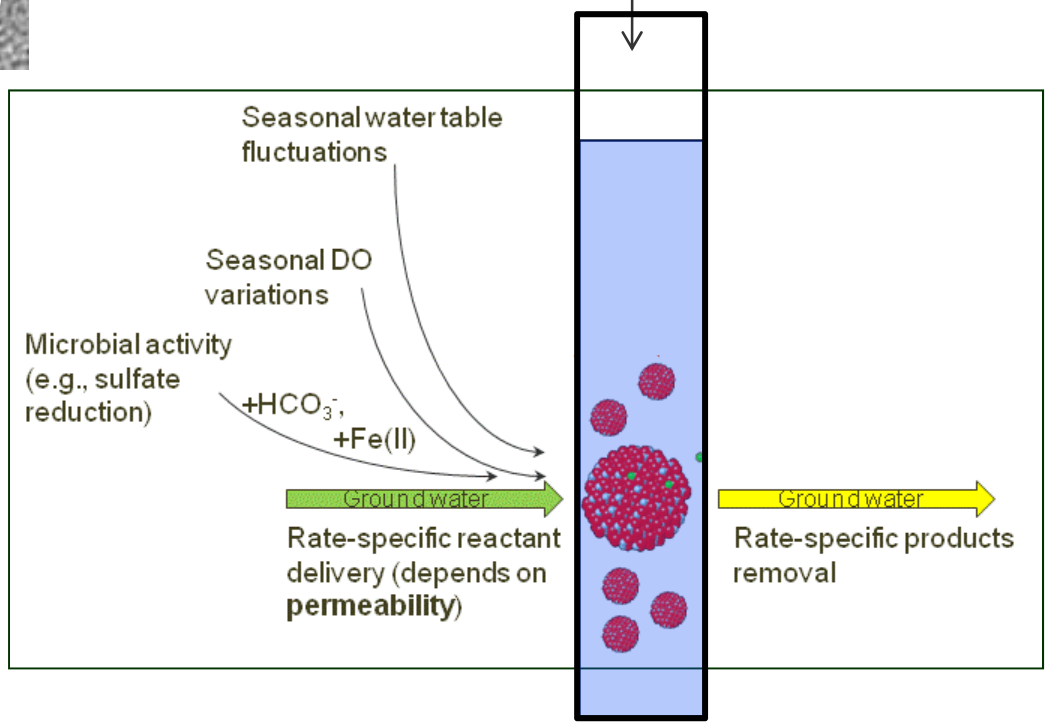
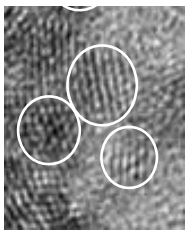


Approach: *in-situ* incubations in wells

This study

Add soluble oxidants → + Artificial ground water → Conduct experiment in-well → In well, biomass present → Solid-phase oxidants, in appropriate matrix



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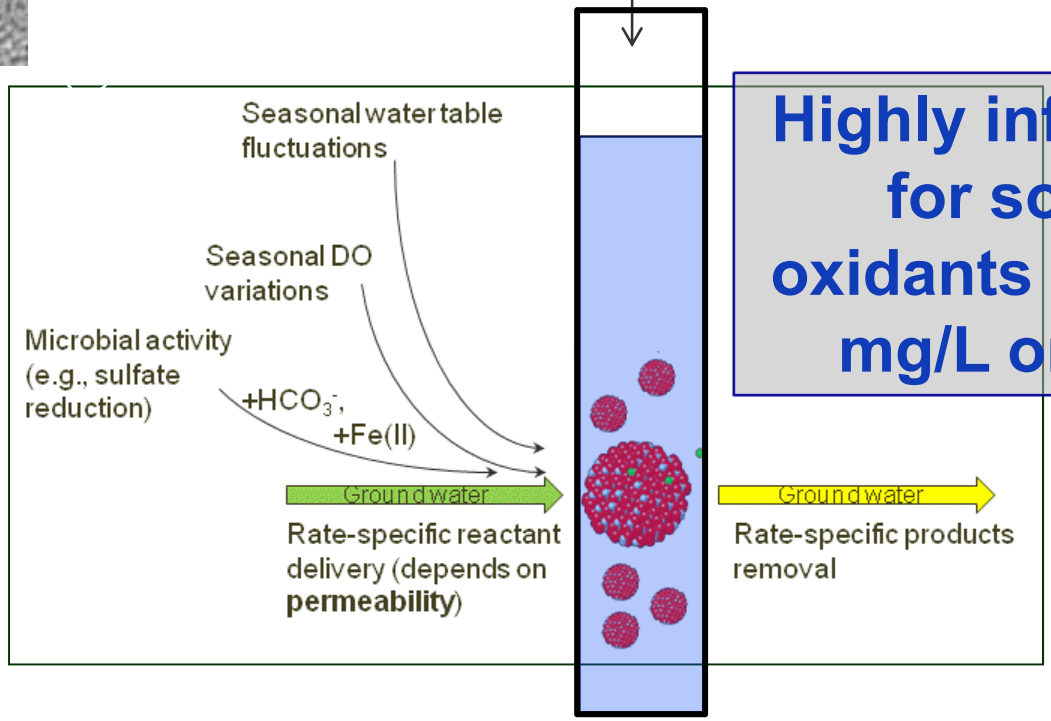
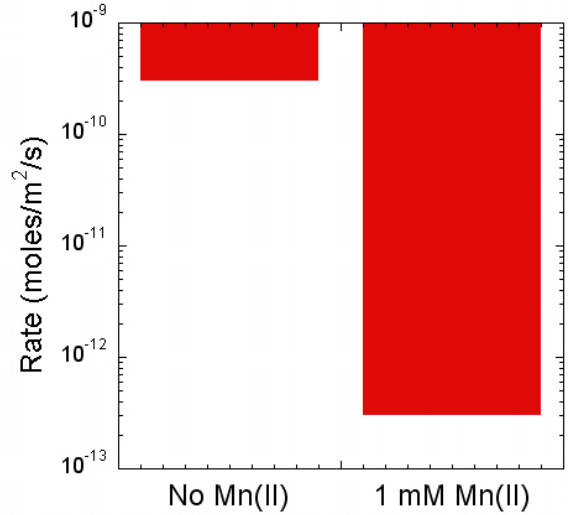


Highly informative for soluble oxidants (DO > 0.5 mg/L or NO_3^-).

Biogenic uraninite

- Trace solutes moderate uraninite stability – dramatically so.
- Ground water is compositionally complex in space and time.
- Laboratory investigations: challenged to provide meaningful rates for field (but provide crucial information that links reactivity to structure).

Bio-UO_2 dissolution rates



Courtesy of D. Giammar, WUStL

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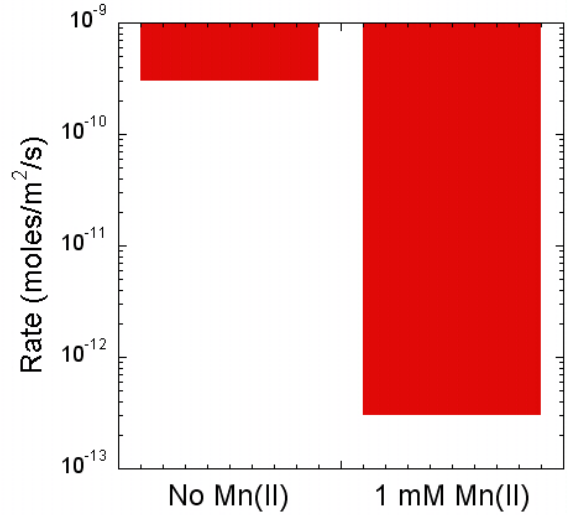


Courtesy of D. Giammar, WUStL

→ need for experiments that capture complex ground water behavior

To assess roles/function of molecular-scale processes at field scales

To obtain rate laws for biogeochemical models

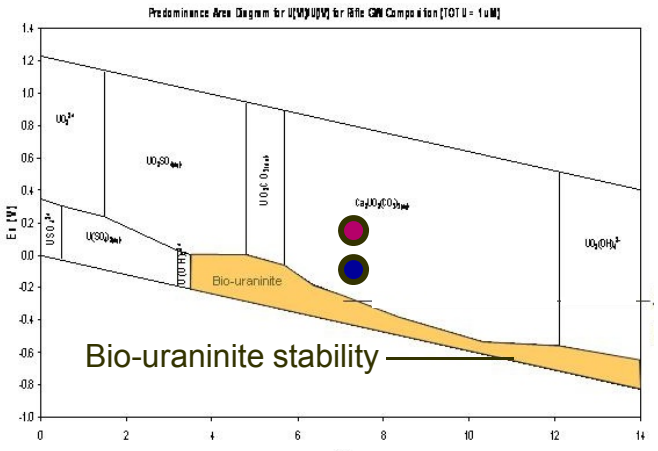
Rates and mechanisms of biogenic uraninite oxidation at the Rifle IFRC site

Approach: Rifle wells as *"in-situ* chemostats"

Model for contaminated DOE-LM sites in Co River basin

Approach: install bio-uraninite in ground water

- pre-characterize uraninite
- Install in wells in permeable reaction cells

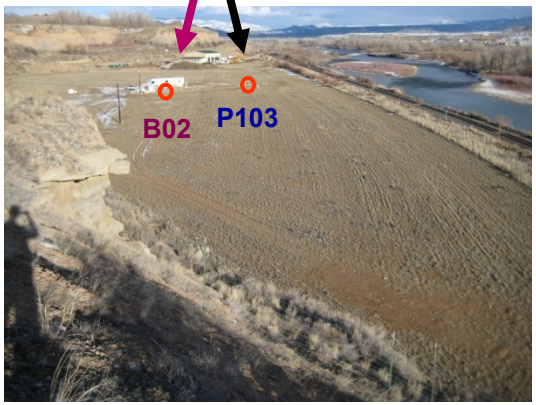


months to years

Choose wells w/ contrasting GW comp:

B-02: Oxic
D.O. 0.5-1.2 mg/L

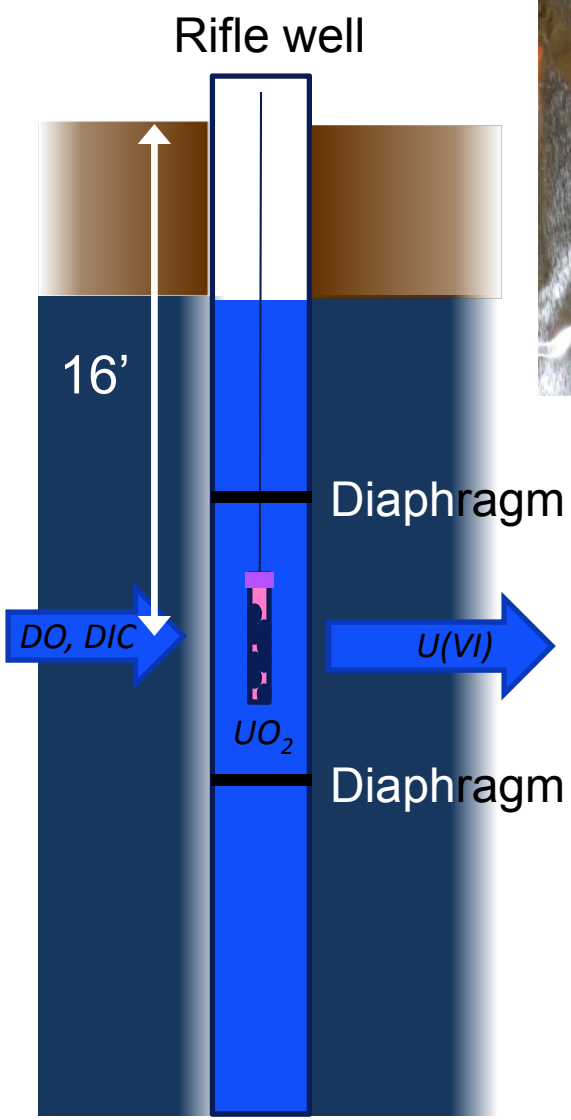
P-103: Suboxic
D.O. <0.1 mg/L

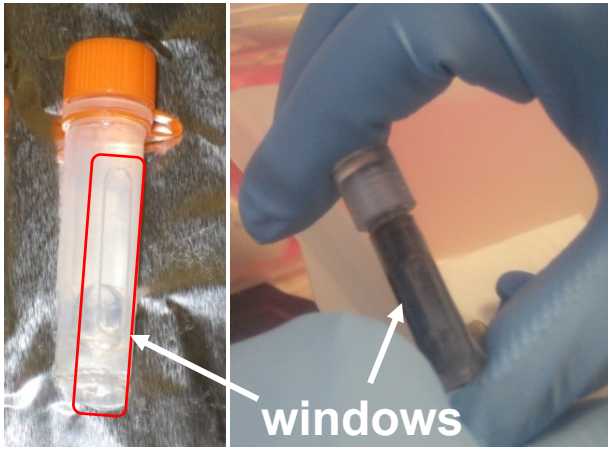


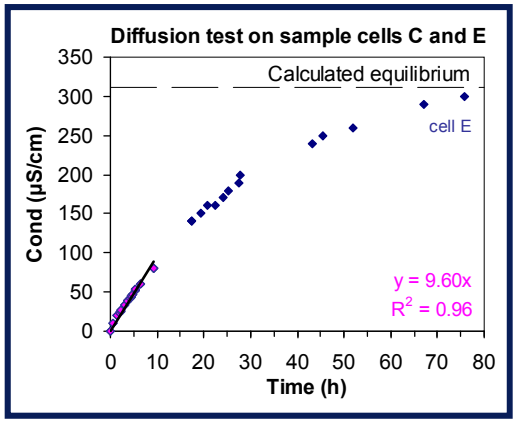
Remove & characterize:

- Structure (EXAFS/XANES, TEM)
- Composition (XPS, SR-PD)
- U loss rate (gel probes)
- Reactivity (CFR)

Permeable membrane cells:
Keep nanoparticles in/bacteria out



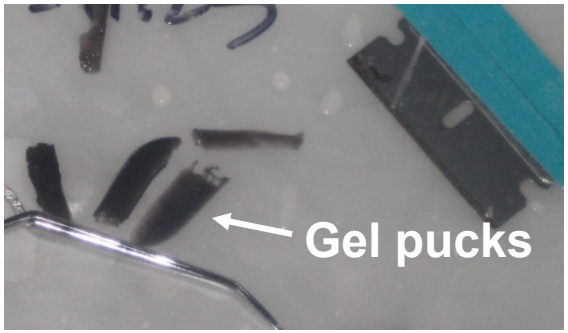




Cell diffusive half-equilib: ~20 hr.

Two types of samples:

- Uraninite-water suspensions
- Suspended in polyacrylamide gel pucks:

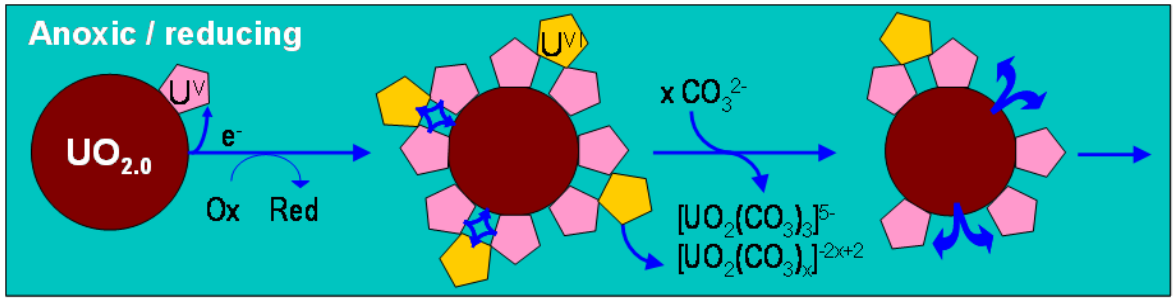


Diffusion time constant ~ few hr.

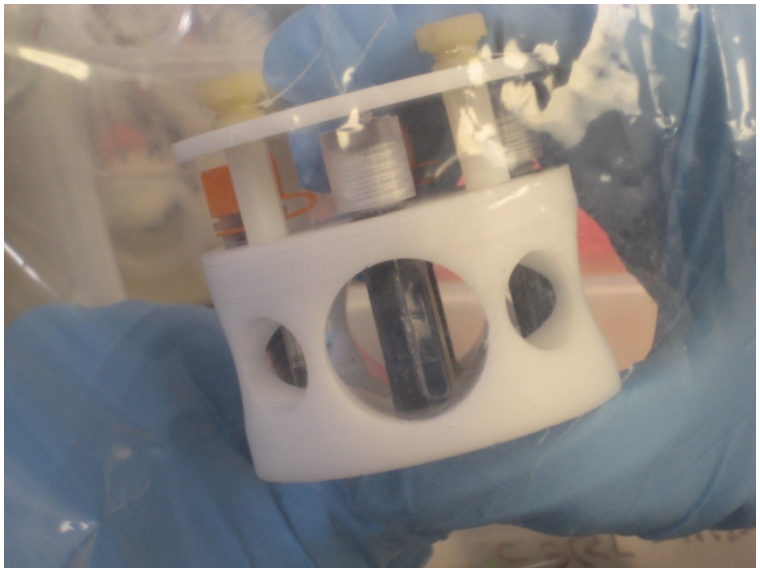
Predictions: 12 week reaction oxic well

RATE prediction:
complete
dissolution (B-02)

MECHANISM prediction:
Slow oxid. of surface U(IV) → Rapid removal by CO_3^-

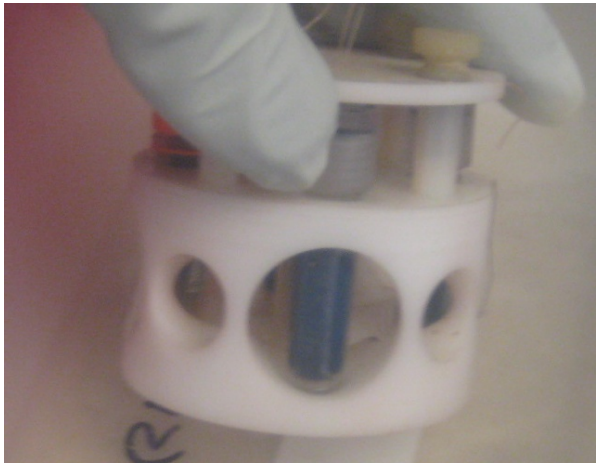


Observation ≠ Prediction

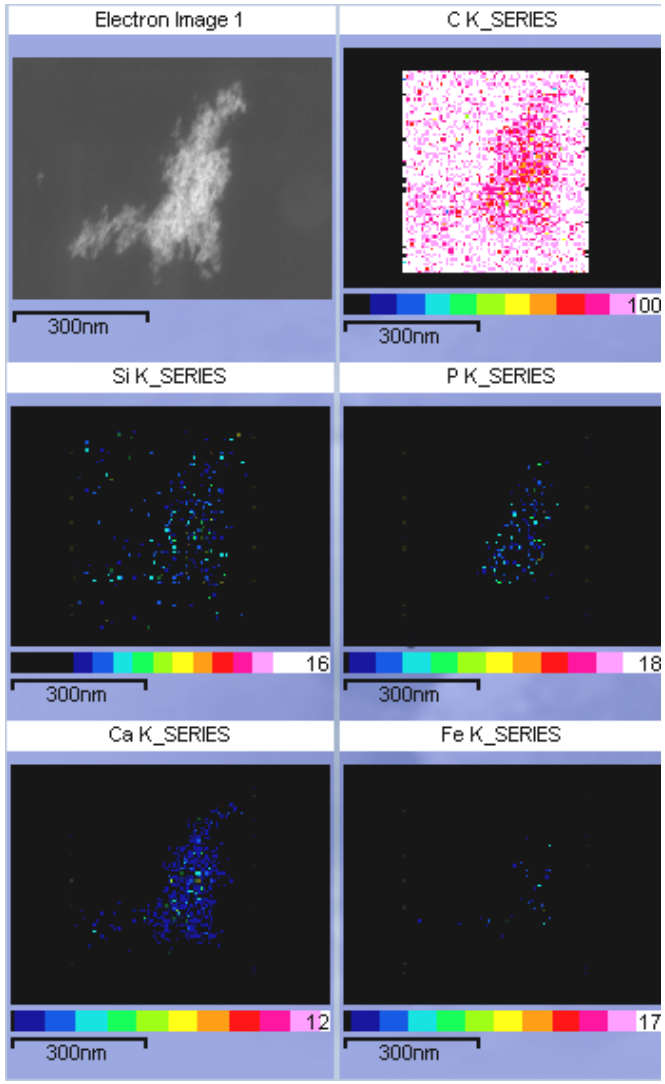


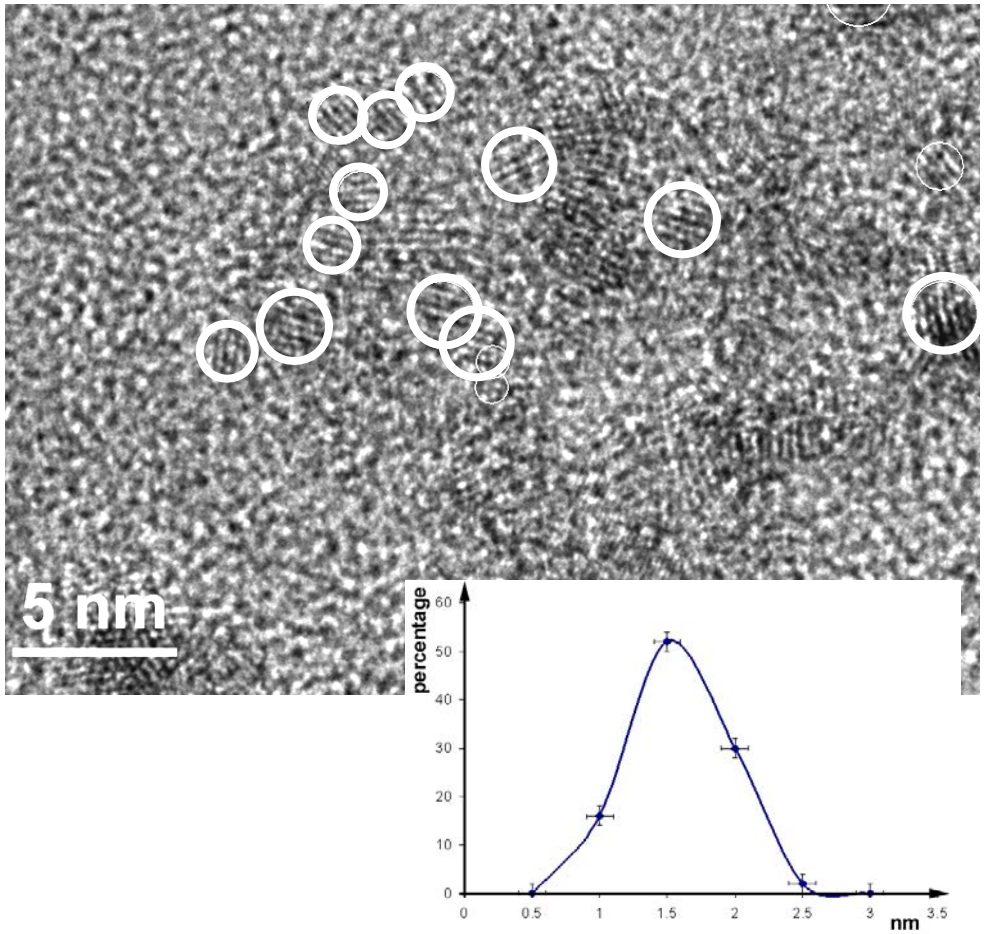
Before reaction

After 12 wk. reaction in oxic ground water



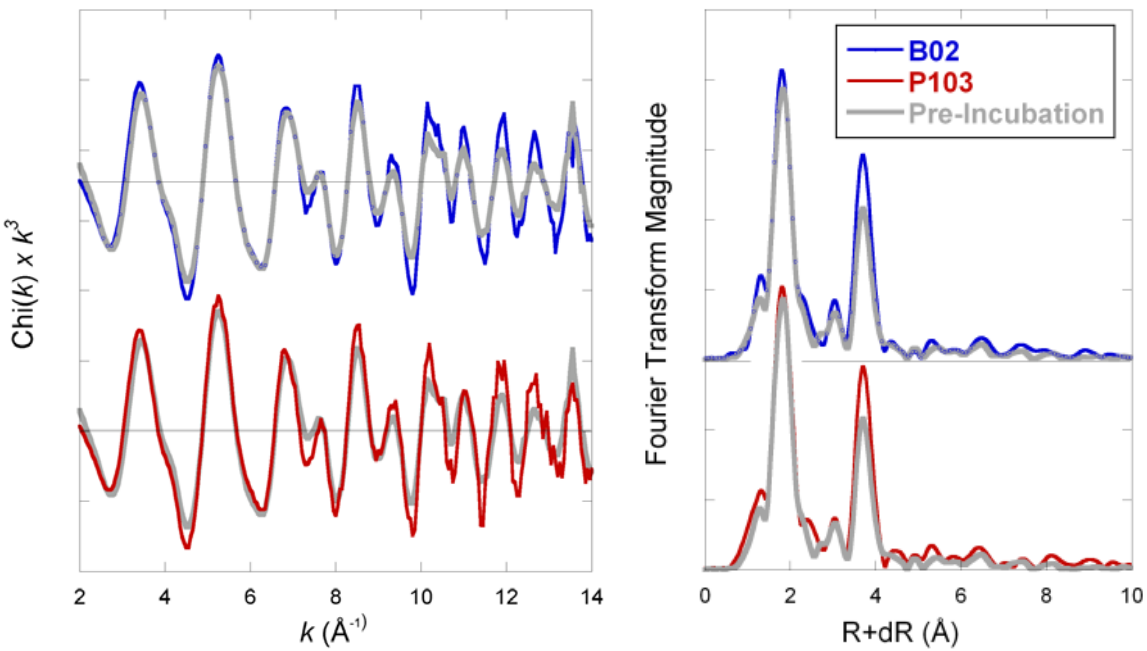
Electron Microscopy: after reaction



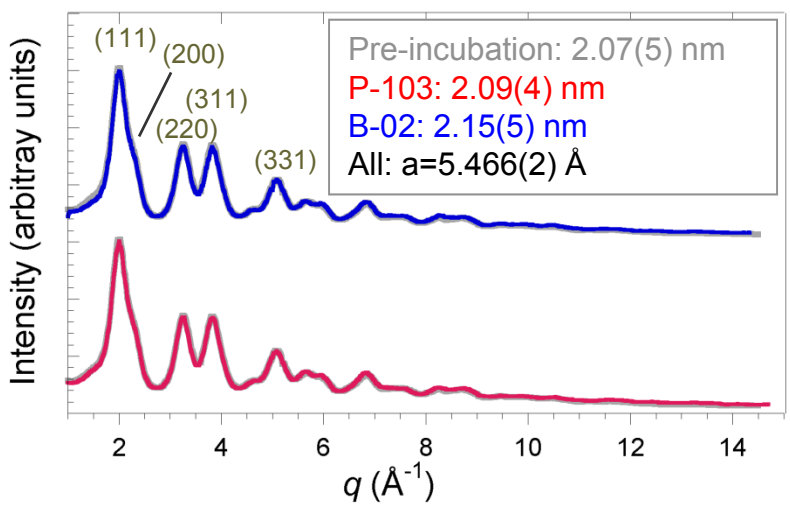


- UO_2 nanoparticles ~ 1.5 nm diam.
- No evidence for any crystalline secondary phases.
- Ca, Si associated with UO_2

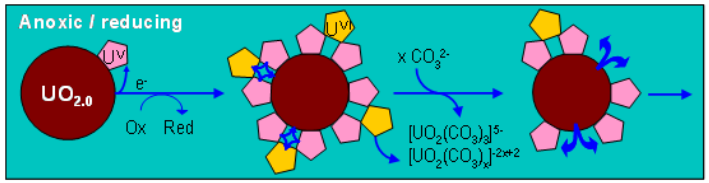
Corrosion mechanism



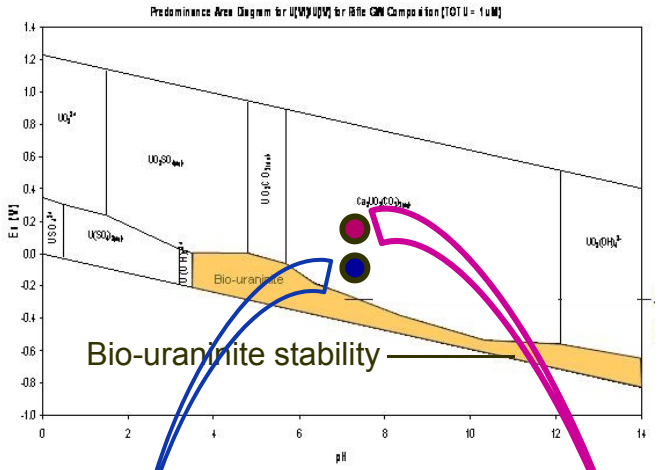
- No accumulation of UO_{2+X} or U(VI) solids.
- EXAFS: Local structural order similar before/after

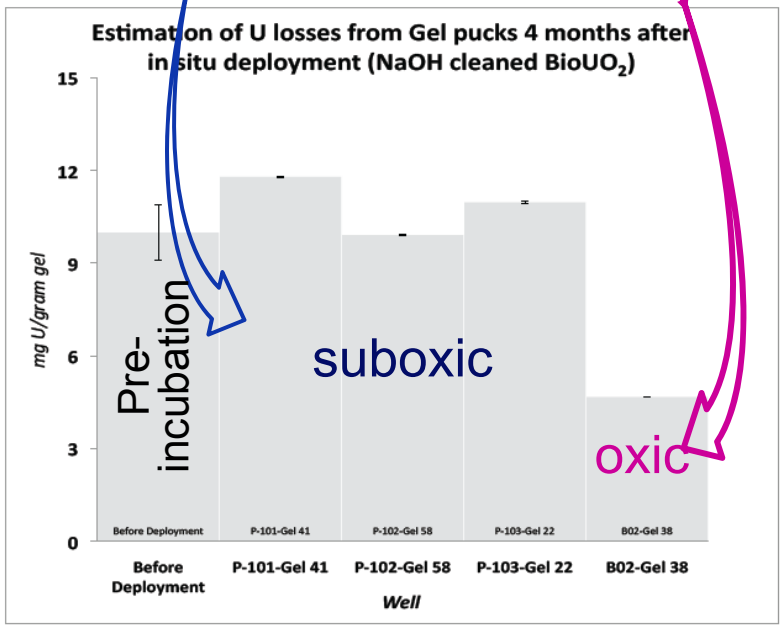


- Diffraction: no change in material, particle size.
- No UO_{2+x}, calcite, other phases.
- **Mechanism = prediction**



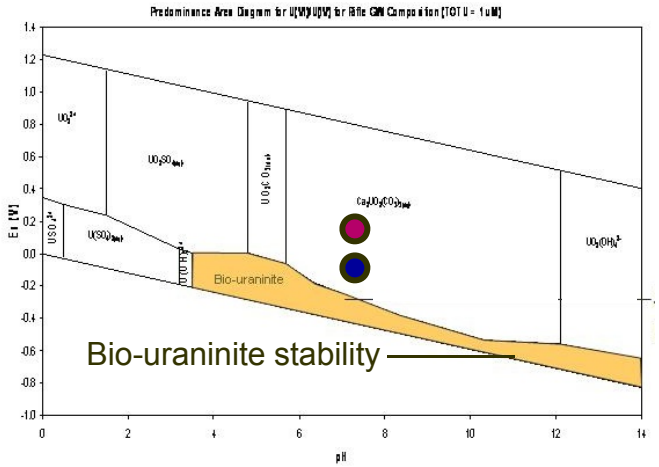
Uranium loss rates: gel puck measurements



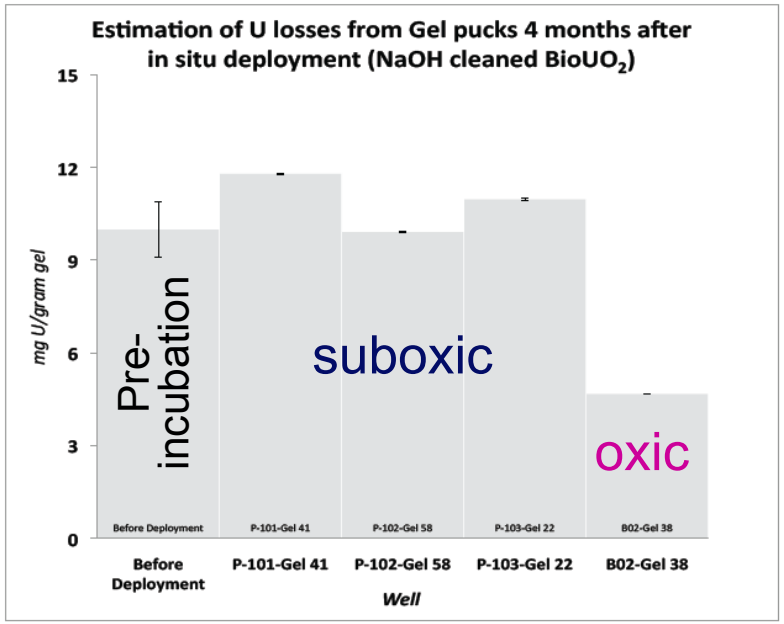


Cleaned uraninite

Uranium loss rates: gel puck measurements



Biomass retards U loss!



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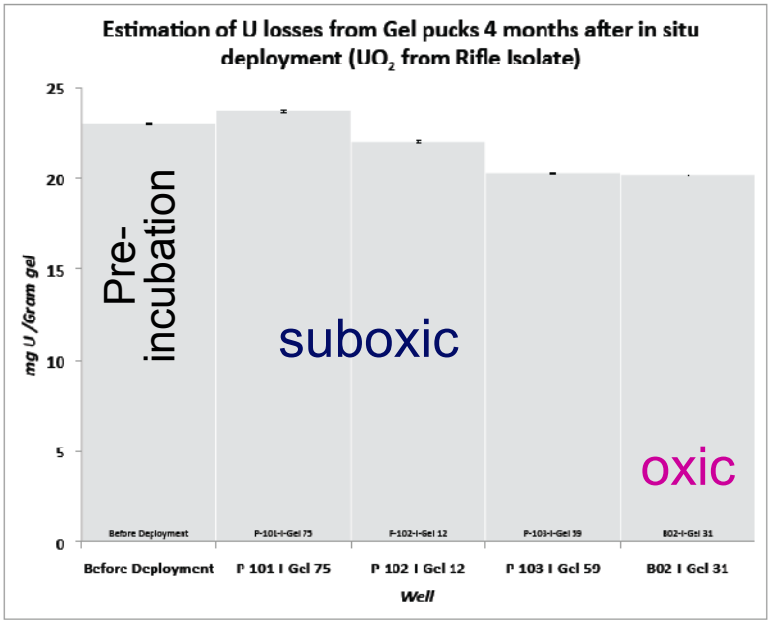
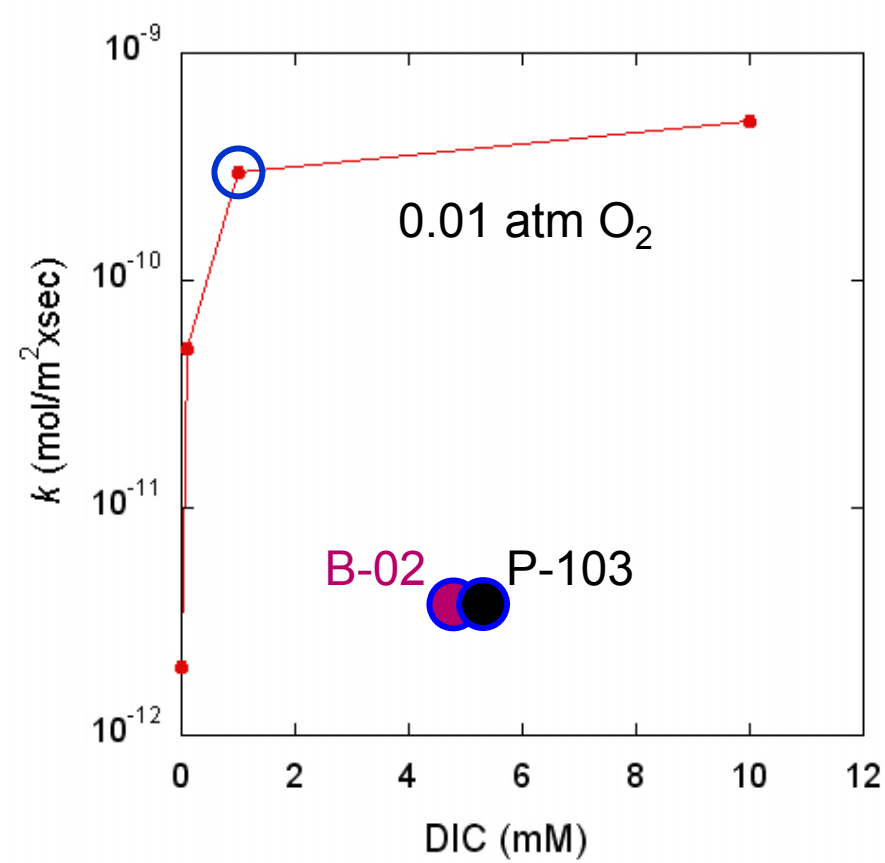


Uncleaned: cells + uraninite

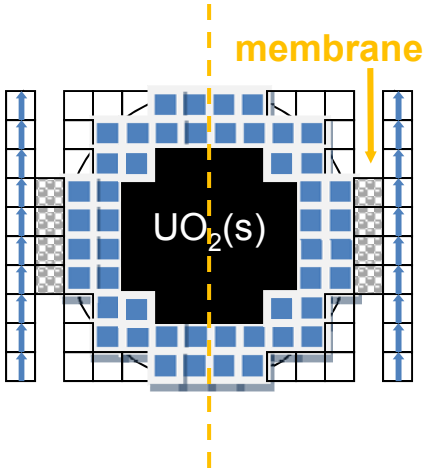
Mass Loss Rates in Rifle Wells

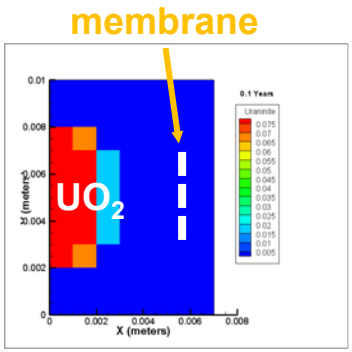


- Observed U loss rate is *slow*: $R \sim 2\times10^{-11}$
- 50 to100x slower than laboratory dissolution rate
- Ca is strongly associated with uraninite after retrieval

Why is U mass loss so slow?
Two possible explanations:

1. O_2 diffusion can account for rate (S. Yabusaki, PNNL)



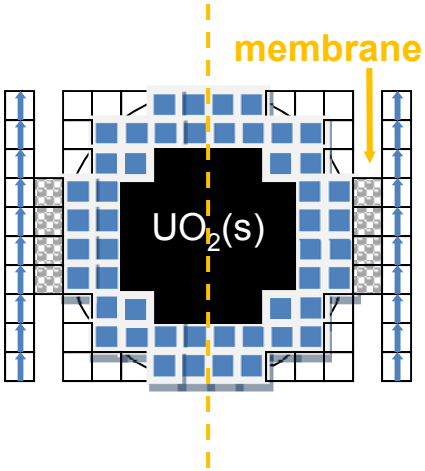


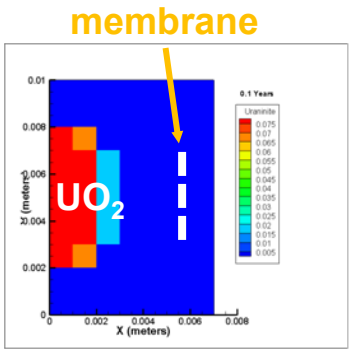
UO_2 distribution: 37d

4 month reaction: Predict 52% of uraninite is lost
Observe 55% of uraninite is lost

Why is U mass loss so slow?
Two possible explanations:

1. O_2 diffusion can account for rate (S. Yabusaki, PNNL)





UO_2 distribution: 37d

4 month reaction: Predict 52% of uraninite is lost
Observe 55% of uraninite is lost

2. Other possible explanation: dissolved trace solutes (*e.g.,* silicate, 0.5 mM, Ca^{2+}, 0.7 mM) retard U corrosion.

Conclusions

- Modest diffusion limitation causes large decrease in U loss rate
- Diffusive barriers in natural sediments are likely to be much higher: very slow U release, even in oxic ground water
- Presence of biomass *further* slows oxidation

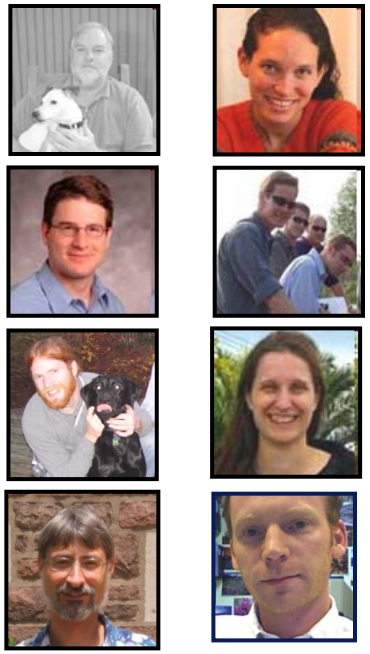
Conclusions

- Modest diffusion limitation causes large decrease in U loss rate
- Diffusive barriers in natural sediments are likely to be much higher: very slow U release, even in oxic ground water
- Presence of biomass *further* slows oxidation
- Suitable for bioremediation? Very good prospects
- Implications for other forms of U(IV):
  - O_2 diffusion limitation important for other forms of U(IV)
  - Establishes lower limit for U(IV) release rates.

Future directions

- Continue ongoing experiments for 21 months to establish rates over more realistic time scales
- Investigate stability of other forms of U(IV) (*in progress*):
  - Biomass-sorbed U(IV)
  - Mineral-sorbed U(IV)

Acknowledgements



SLAC-SFA team:

Dan Alessi
Juan Lezama
Mike Massey
Apurva Mehta
Marc Michel
Ellie Schofield
Joanne Stubbs
Kai-Uwe Ulrich
Harish Veeramani

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