

Influence of Mass Transfer on U(VI) Microbial Reduction

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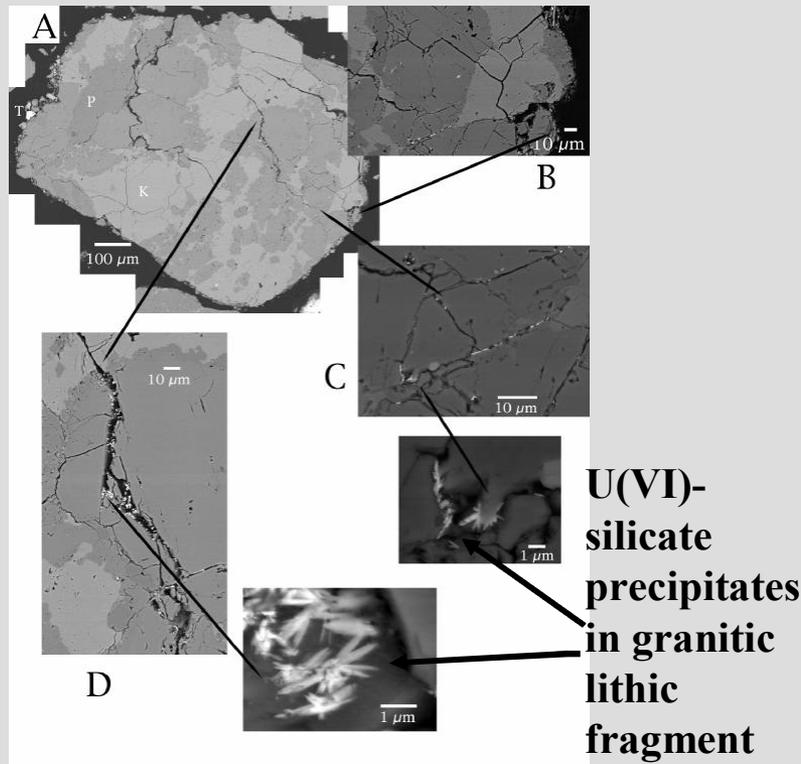
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DOE Environmental Remediation Sciences Division 2006 Meeting

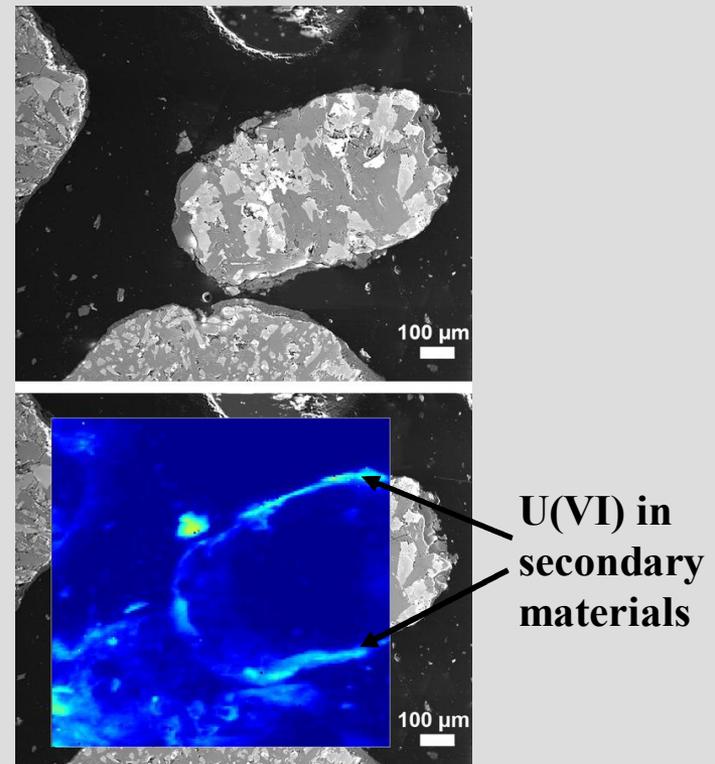
Uranium Physical Location in Contaminated Sediments

- At Hanford site, sorbed U exists as U(VI) with complex speciation, physical location, and mineral association.

Hanford 200 Area Sediments

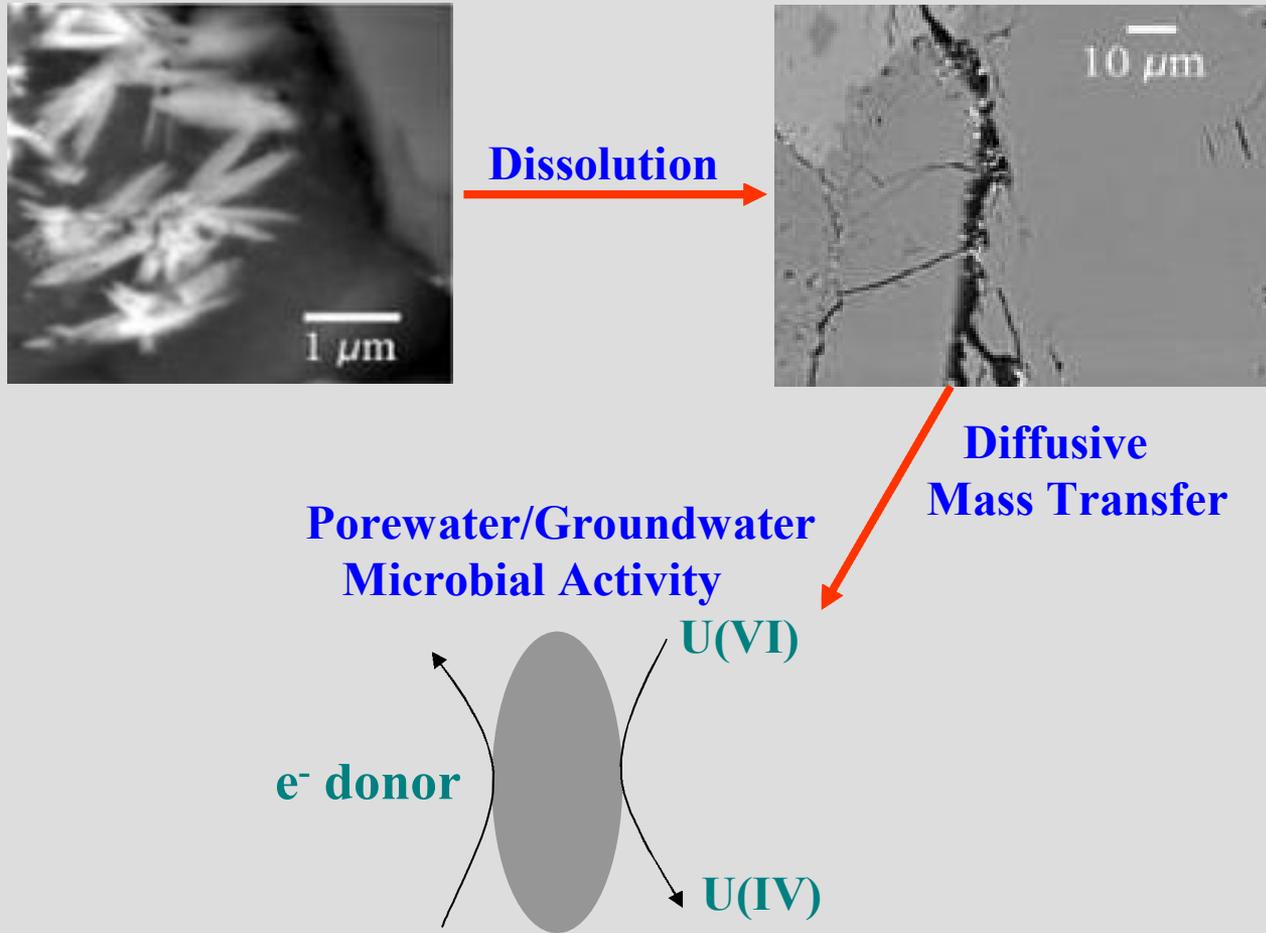


Hanford 300 Area Sediments



- Sorbed U is commonly associated with intragrain regions.

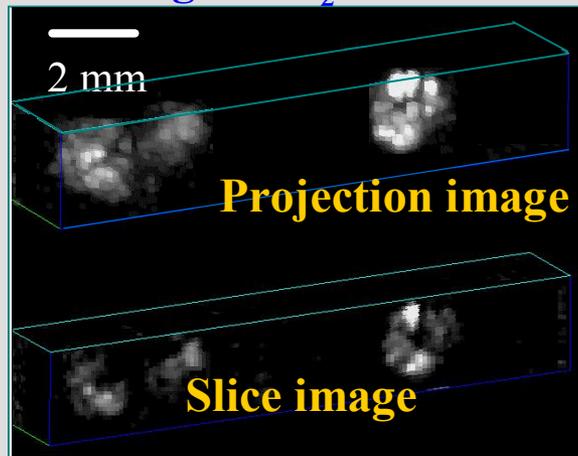
Conceptual Model



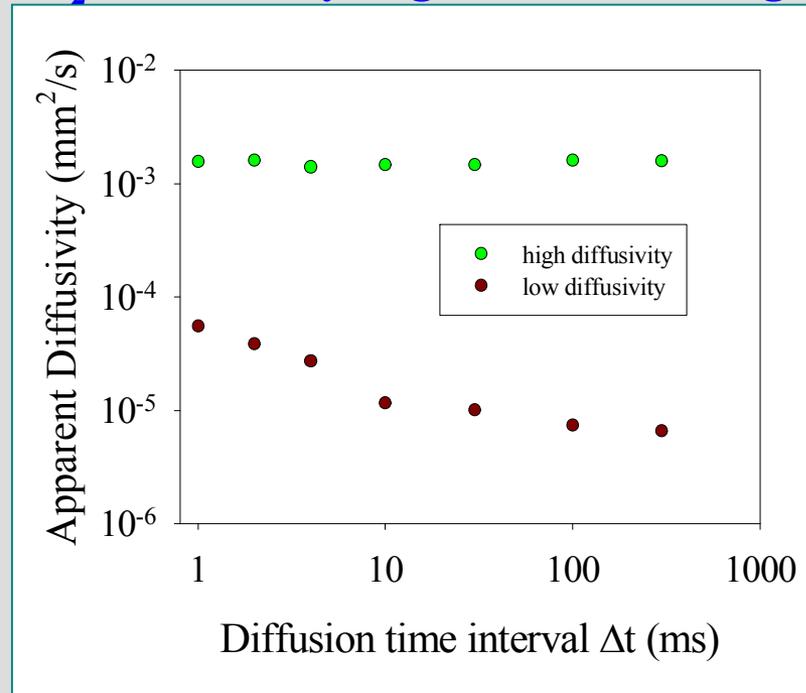
Characterization of Intragrain Diffusion

A ^1H nuclear magnetic resonance, pulse-field gradient spin echo (NMR-PGSE) approach was developed to measure intragrain diffusion properties using H_2O as a tracer.

NMR image of H_2O distribution



H_2O diffusivity in granitic lithic fragment



➤ Tortuosity factor ($D_p/D_{\text{H}_2\text{O}}$):

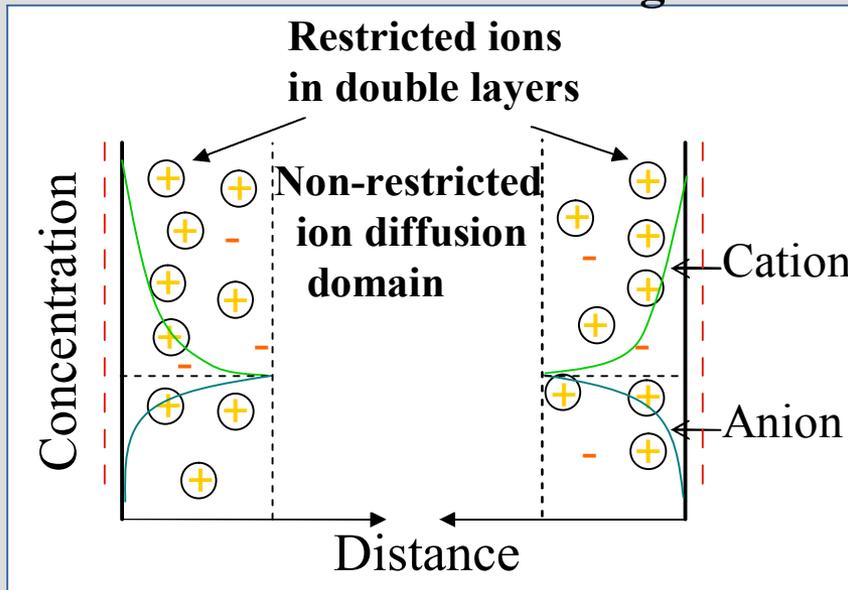
0.66	fast region
0.006	slow region

Models of Ion Diffusion Coefficients

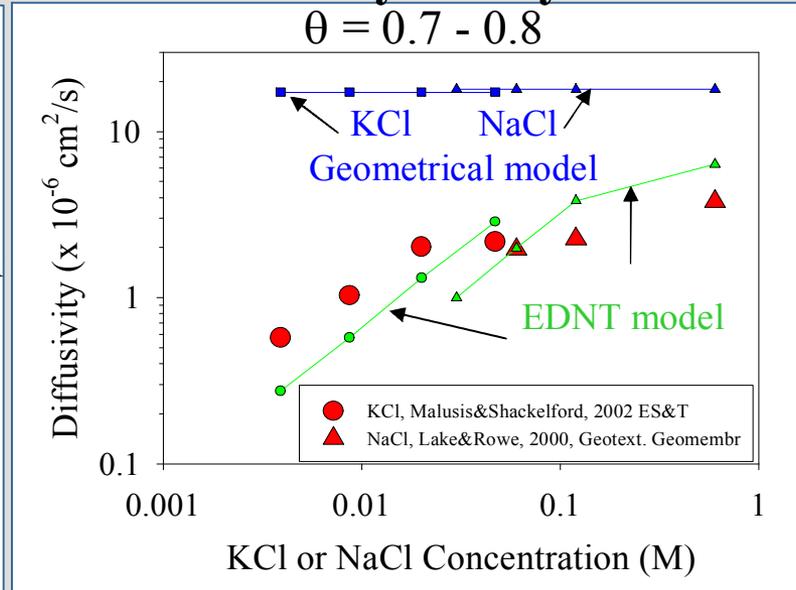
Geometrical model: $D_p^i = \tau D_w^i$

D_p^i : pore diffusivity, τ : tortuosity; D_w^i : diffusivity in water,

Schematic ion diffusion regions



Ion diffusivity in clay matrix



Coupled electrodynamics-nonequilibrium thermodynamics

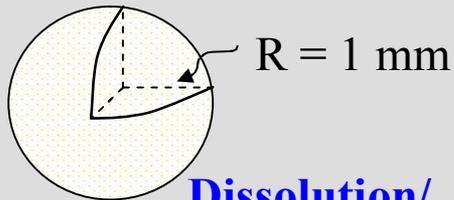
(EDNT) model: $D_p^i = f(\tau, \rho_c, D_p^j, C_j)$

ρ_c : surface charge density, D_p^j and C_j : diffusivity and concentration of ion j, respectively.

Microbial Reduction of Intragrain U(VI)

Coupling of Biogeochemical Processes: Synthetic System

Alginate beads with synthetic Na-boltwoodite



Dissolution/
diffusion

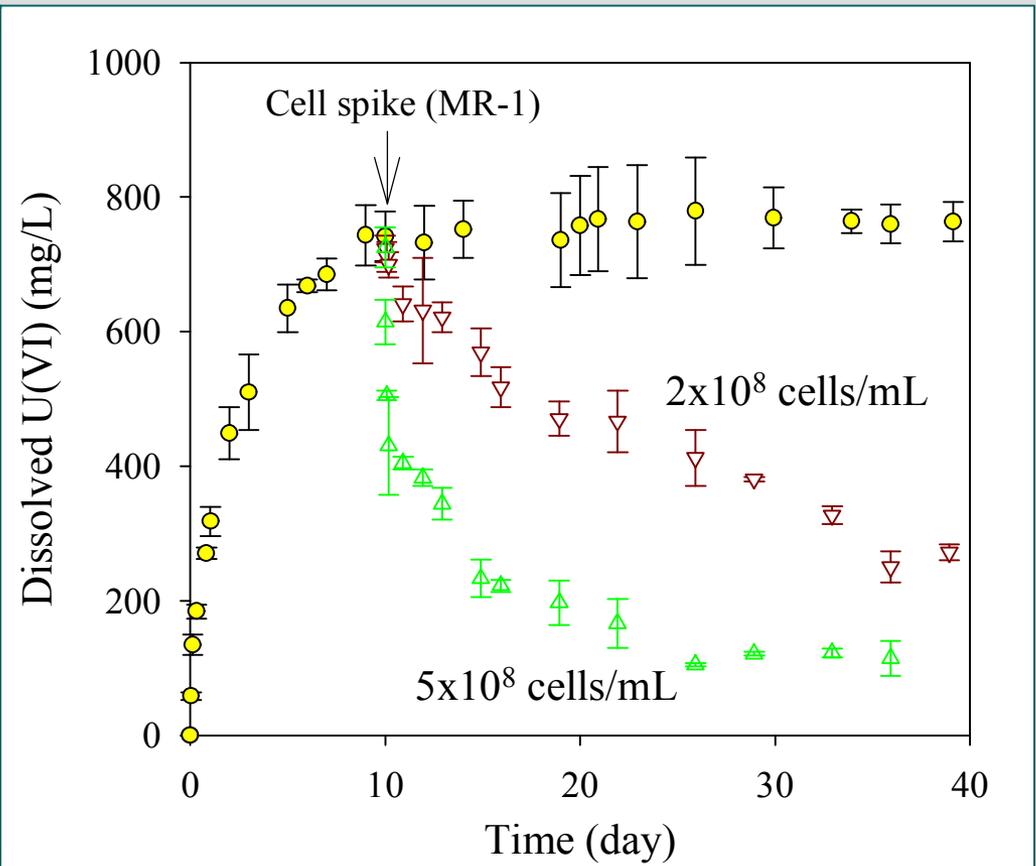
+

Dissolved U(VI)

Bioreduction

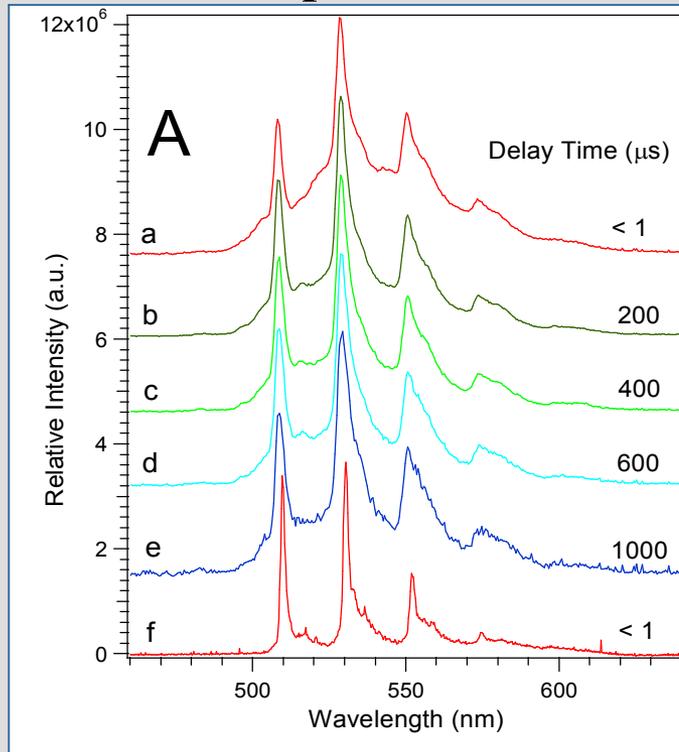
Cell

S. Oneidensis
MR-1

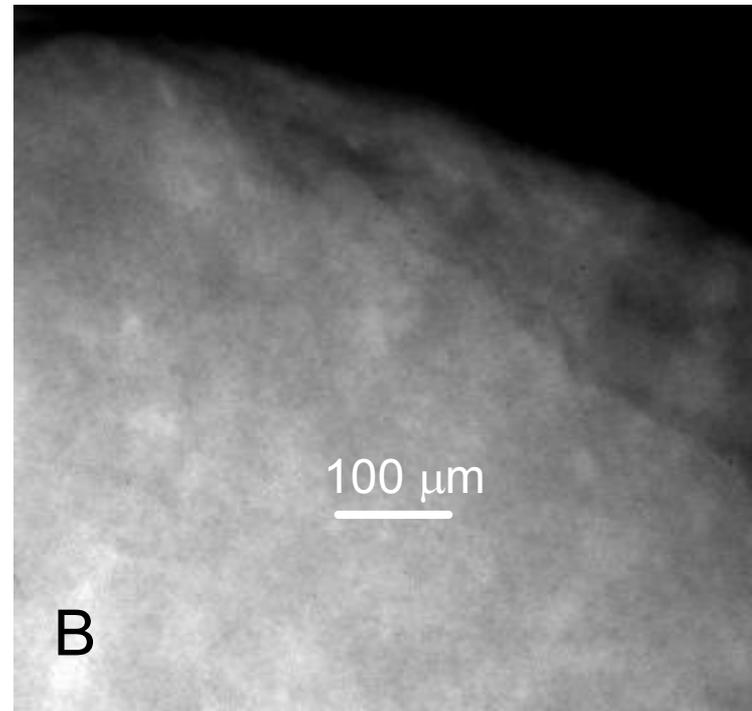


Intrabead U(VI) speciation and Distribution

LIFS spectra



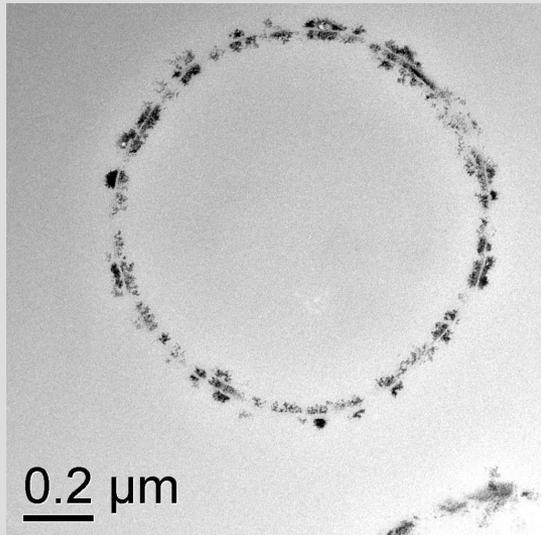
LIFS image



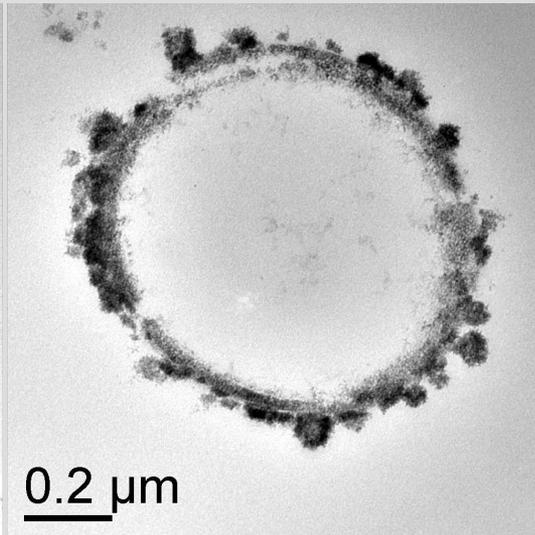
- No change of intrabead U(VI) speciation;
- U(VI) dissolved/diffused starting from bead edge to center.

U(IV) Precipitation on Bacterial Surface

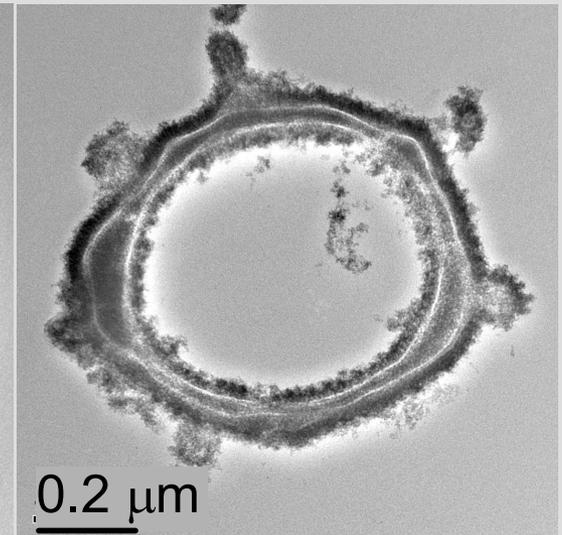
Time = 2 days



Time = 7 days



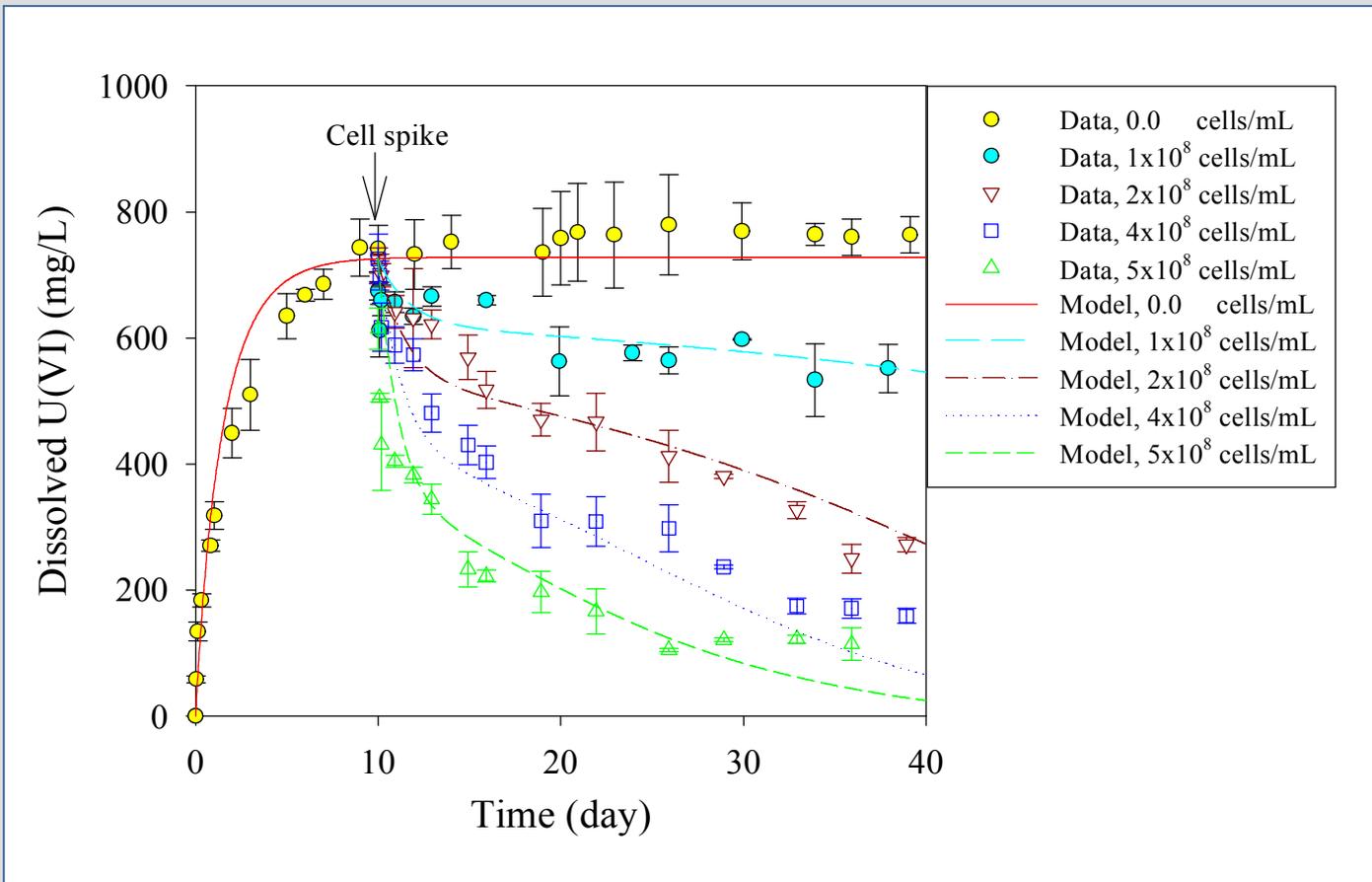
Time = 100 days



- U(IV) accumulation on bacterial surfaces and periplasm

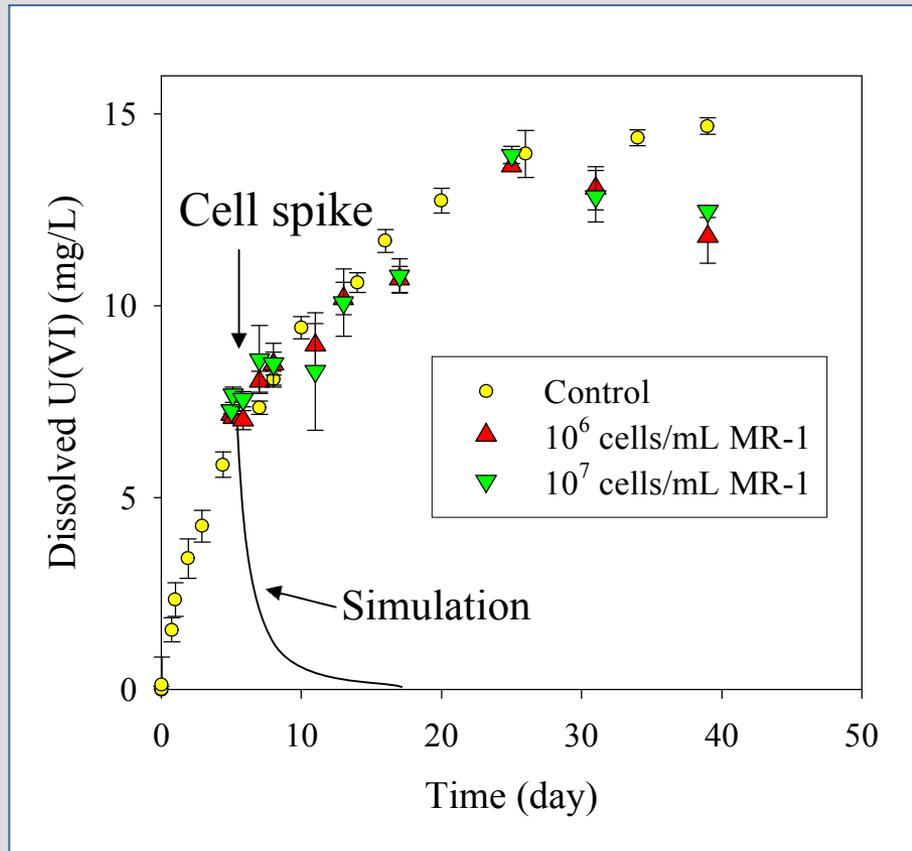
Modeling Coupled Biogeochemical Processes

Intragrain dissolution + Intragrain diffusion + Extragrain bioreduction

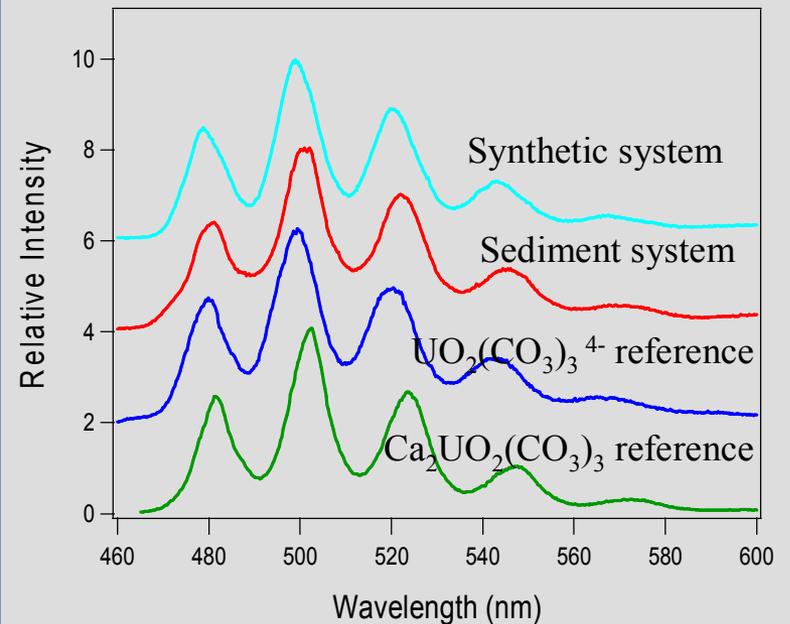


Microbial Reduction of Hanford Intragrain U(VI)

Effects of Calcite Dissolution

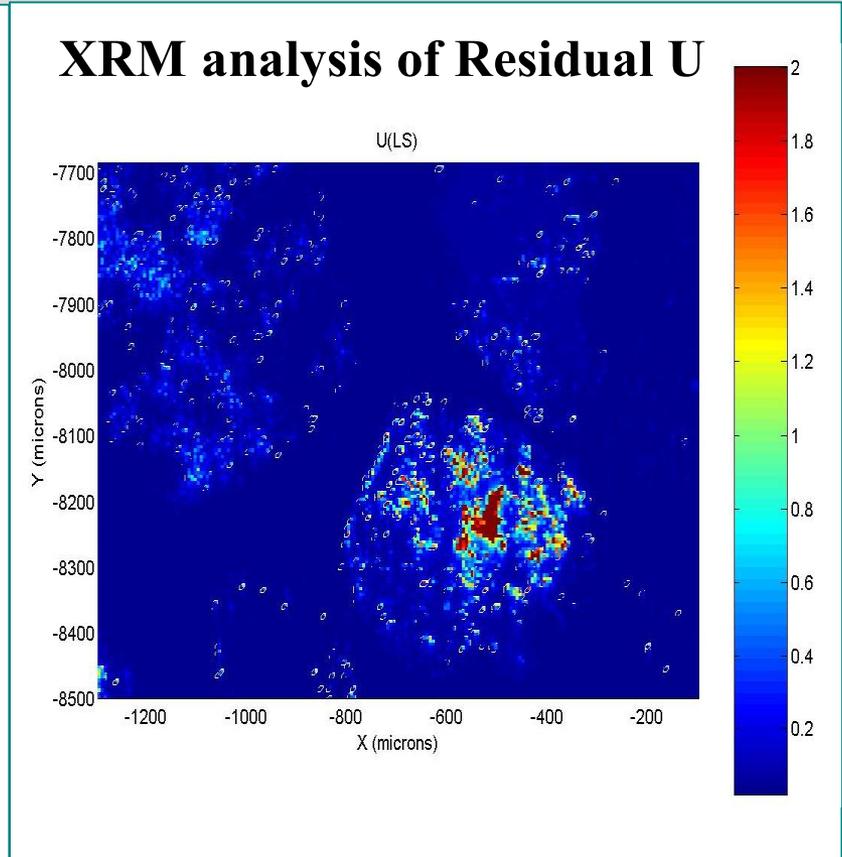
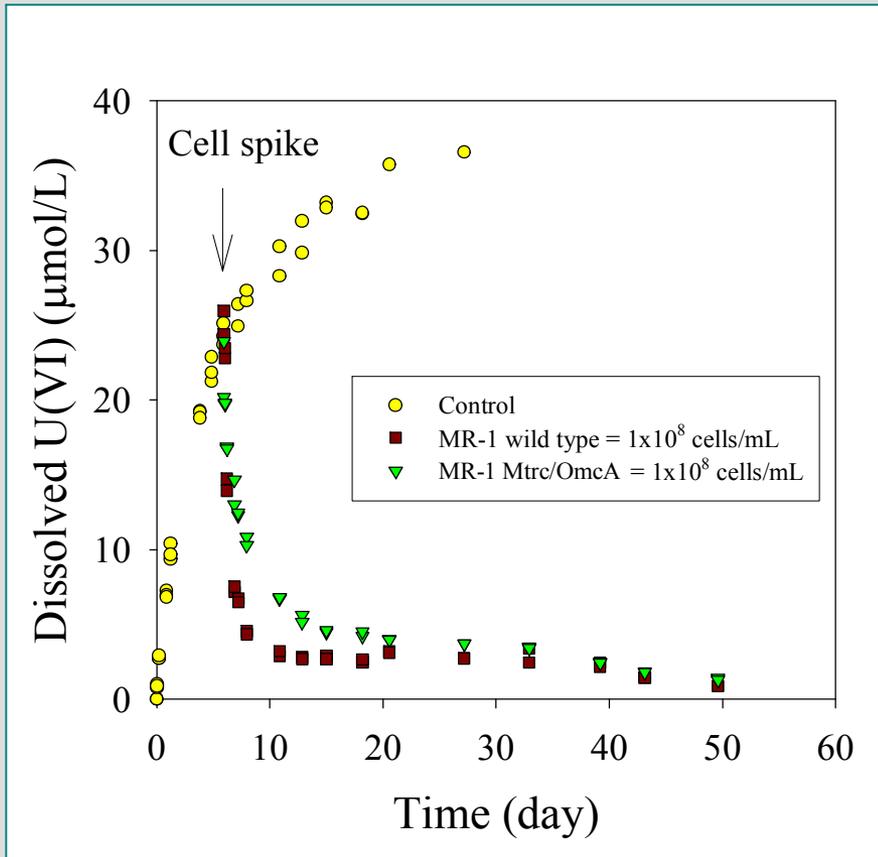


LIFS Spectra of Aqueous Solutions at liquid helium temperature



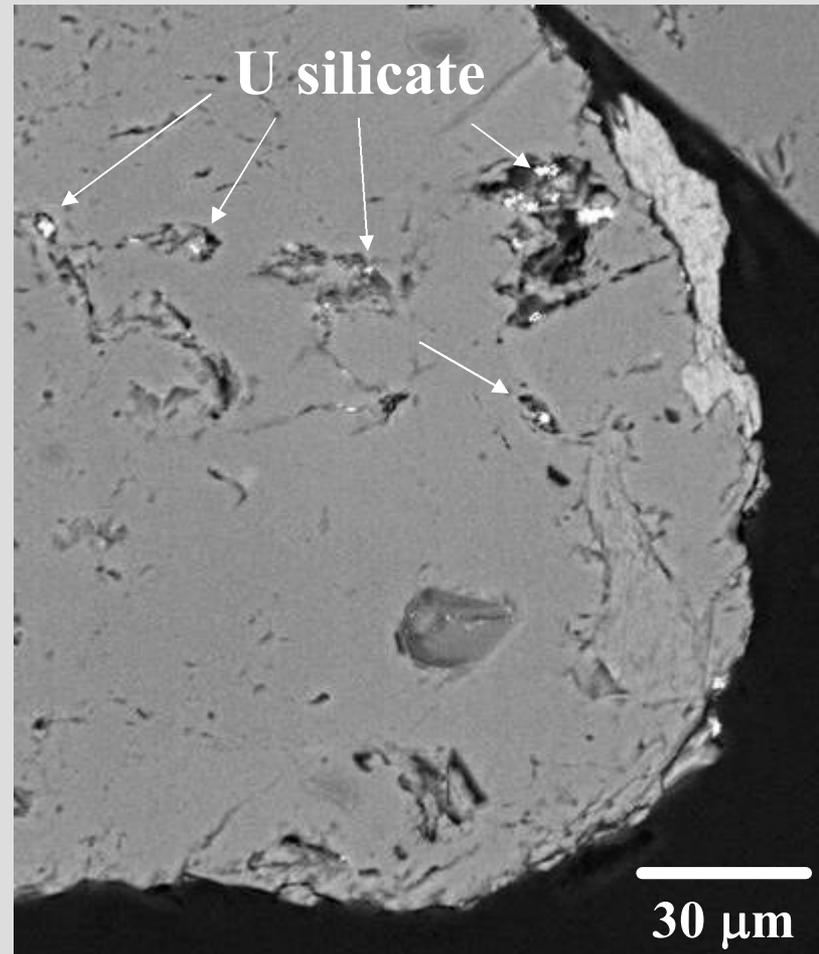
Microbial Reduction of Hanford Intragrain U(VI)

Coupling of Biogeochemical Processes



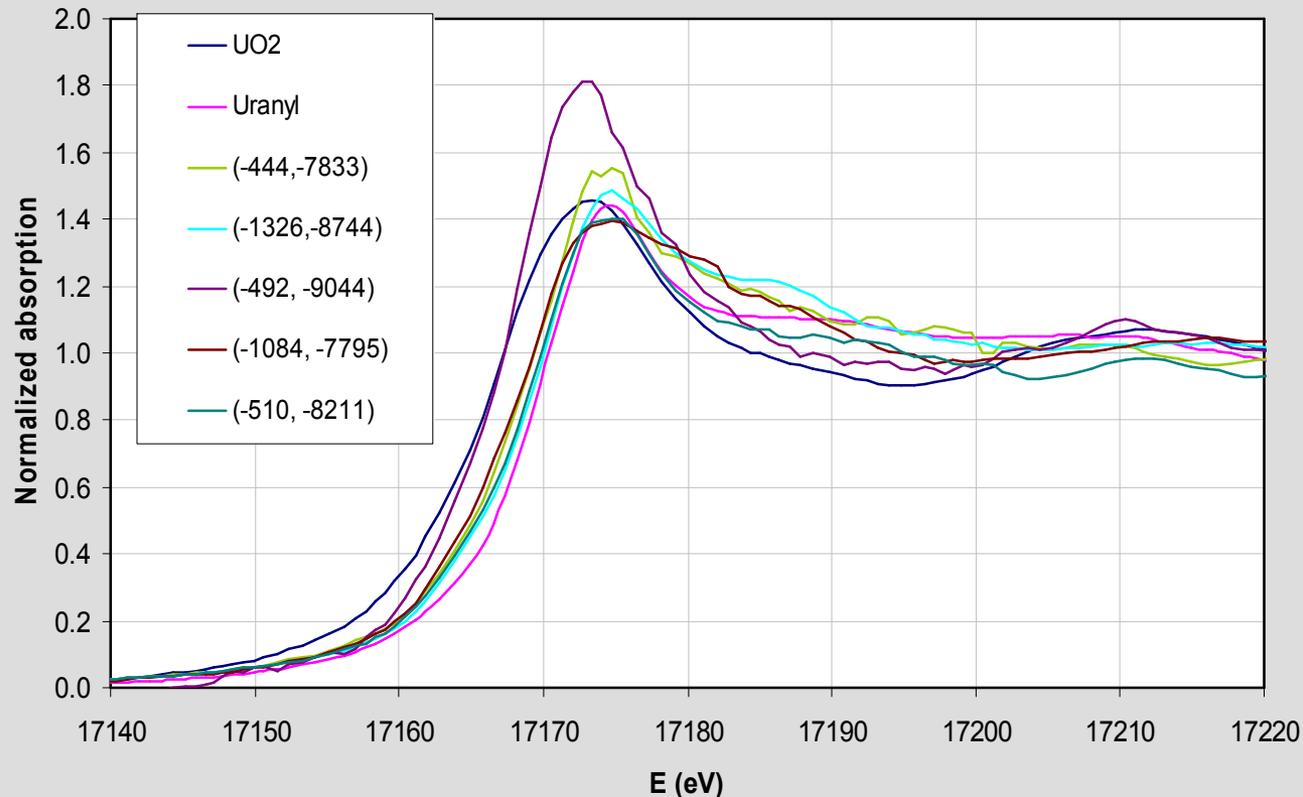
Microbial Reduction of Hanford Intragrain U(VI)

SEM analysis showed residual U silicate in occluded regions



Microbial Reduction of Hanford Intragrain U(VI)

XANES analysis found mixed valence distribution of U(IV) and U(VI) inside grains.



Other Reduction Process?

Conclusions

- ▶ **An NMR-PGSE technique indicated that a dual region diffusion model was required to simulate ion diffusion in the intragrain fractures of the granitic lithic fragment in Hanford sediment.**
- ▶ **Coupled electrodynamics and nonequilibrium thermodynamics (EDNT) model indicated that macroscopic ion diffusivity is a complex function of microscopic properties of mineral surface charges, ion exchange reactions, electrostatic double layers, and ion charge coupling.**
- ▶ **Macroscopic aqueous U(VI) concentration was determined by the microscopic coupling of biogeochemical processes of dissolution/desorption, diffusion and microbial activity.**
- ▶ **Microbial reduction of intragrain U(VI) in the contaminated Hanford sediment was complicated by the dissolution of calcite that released Ca to complex uranyl carbonates, which in turn slowed bioreduction rate and increased dissolution/diffusion rates. Some intragrain U(VI) in the contaminated Hanford 200 Area sediment was in occluded regions and might not be reactive due to mass transfer limitation.**