Coupled Biogeochemical Processes Governing the Stability of Bacteriogenic UO_2

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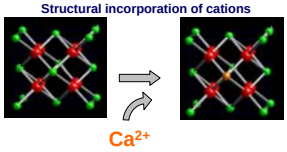
Background and Hypotheses

Introduction: The chemical stability of bacteriogenic UO_2 is the seminal issue governing its success as an "*in-situ* waste form" in the subsurface. The goals of this project are to identify key molecular-scale processes that mediate the stability and oxidation of bacteriogenic UO_2 in the subsurface and to measure their rates at the meter scale. We will eventually develop coupled (bio)geochemical conceptual process models describing the effects of these processes on U(VI) release from UO_2 in heterogeneous subsurface media.

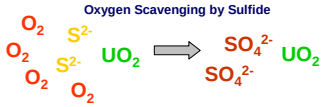
Hypotheses: We postulate that: (I) the stability of bacteriogenic UO_2 is enhanced by cation substitution into UO_2; (II) that sulfides may locally buffer the redox potential of ground water and protect UO_2 from oxidation; and (III) that subsurface bacterial Mn(II) oxidation may catalytically enhance UO_2 oxidation.

Processes that may stabilize bacteriogenic UO_2

Structural incorporation of cations

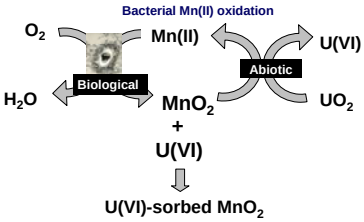


Oxygen Scavenging by Sulfide



Processes that may catalyze UO_2 oxidation

Bacterial Mn(II) oxidation



Production of Bacteriogenic UO_2 in the presence of divalent cations.

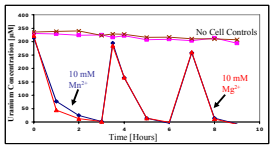
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Hypothesis:

The structure & stability of biogenic uraninite varies with the chemical and biological conditions under which it is formed.

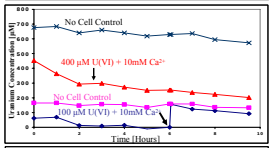
Approach:

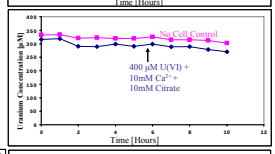
Biogenic uraninite was produced for structural analyses and the kinetics of its production were studied. Aerobically grown *Shewanella oneidensis MR-1* was used to reduce U(VI) anaerobically in the presence of various different divalent cation dopants (Mn^{2+}, Mg^{2+}, Fe^{2+}, Ca^{2+}) and the reduction kinetics were compared. 50 mM $NaHCO_3$ was used to keep U(VI) in solution, except in the case of Ca^{2+}, 10mM Citrate was used



Results & Conclusions:

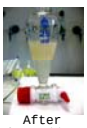
- U(VI) reduction kinetics are similar in the presence of 10mM Mn^{2+} or Mg^{2+}, but significantly slower in the presence of 10 mM Fe^{2+}
- U(VI) reduction in the presence of Ca^{2+} & HCO_3^- is known to be limited*, but that is also the case in the absence of HCO_3^-. An alternative complexing agent- citrate - was used. It maintained U(VI) in solution, but also inhibited reduction.
- A higher concentration (800 µM) of U(VI) is reduced efficiently providing a greater amount of UO_2 for further analysis.
- Attempts at separating UO_2 from biomass under anaerobic conditions - cell lysis followed by biphasic separation in hexane / water.





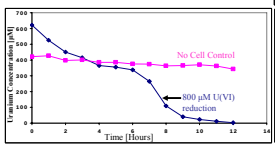
*Ref: Brooks et al. 2003. *Inhibition of Bacterial U(VI) reduction by Calcium*. Environ. Sci. Technol. 37:1850 - 1858

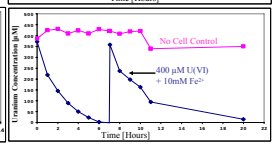
Before



After

Separation of biomass from Uraninite





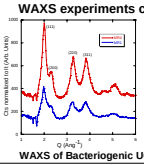
Team: H. Veeramani (Doctoral student), J. Sharp (Post Doc) & R. Bencheikh-Latmani.

Structural Chemistry of Bacteriogenic UO_2

SSRL

Wide Angle X-ray Scattering

WAXS experiments carried out on beamline 2-1 and 7-2



Q	d-spacing	(hkl)	FW HM	Particle size (nm)
2.00	3.142	(111)	0.18	5.69
2.29	2.744	(200)	0.20	6.03
3.26	1.927	(220)	0.21	5.36
3.81	1.649	(311)	0.19	5.02

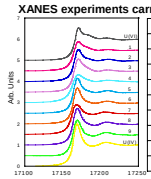
WAXS of Bacteriogenic UO_2 produced from MR1 and MR4 strains

Unit Cell of UO_{2+x}: fluorite structure (U, green; O, red).

- WAXS analysis carried out in transmission geometry
- Background subtracted using XRD-BS
- Peak positions & FWHM estimated in order to calculate the particle size using Scherrer equation
- Broad peaks associated with nanoparticulate UO_2
- Rietveld and PDF analysis will be carried out to obtain structural information

X-ray Absorption Near Edge Structure

XANES experiments carried out on beamline 11-2



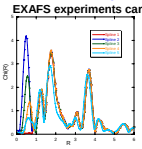
XANES Plot	Sample Description
1	Dry abiotic 1
2	Biotic; MR1; 100 mM Ca2+
3	Wet abiotic 1
4	Dry abiotic 2
5	Biotic; MR1; 1 mM Ca2+
6	Biotic; MR1; 10 mM Ca2+
7	Biotic; MR1
8	Wet abiotic 2
9	Biotic; MR4

To assess the fidelity of novel biotic synthesis and cleaning procedures (EPFL) and abiotic synthesis procedures (WUStL), XANES spectra (shown at left) were recorded from preliminary products. Key objective was to assess incomplete reduction of U(VI) or reoxidation of U(IV).

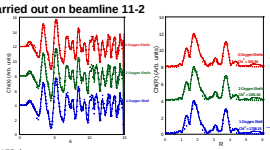
These measurements were instrumental in refining these processes.

Extended X-ray Absorption Fine Structure

EXAFS experiments carried out on beamline 11-2



R vs Chi(R) plot from U L_{III} edge EXAFS data - various spline fitting parameters in SIXPACK



EXAFS K and R plots for Bacteriogenic UO_2

Path	N	del R	Sig2
U-O(a)	0.754	1.926	0.004
U-O(b)	0.77	1.696	0.004
U-O(c)	8	2.365	0.015
U-U	6.397	3.859	0.008
U-O2	8	4.386	0.005

Path	N	del R	Sig2
U-O(b)	0.435	1.682	0.004
U-O(c)	8	2.357	0.014
U-U	7.261	3.851	0.008
U-O2	8	4.387	0.005

Path	N	del R	Sig2
U-O(c)	8	2.365	0.015
U-U	6.397	3.859	0.008
U-O2	8	4.386	0.005

- Fits to data support the presence of multiple U(VI)-O shells
- *Preliminary conclusion*: Bacteriogenic UO_2 contains non-stoichiometric U(VI)
- Consistent with Conradson model where a fraction of nonstoichiometric UO_2 was found to contain glassy U(VI) component.

Team: E. Schofield (Post Doc), J. Bargar, S. Webb, M. Toney, A. Mehta (Collaborators).

Equilibrium solubility and dissolution kinetics

Washington University in St. Louis
School of Engineering & Applied Science

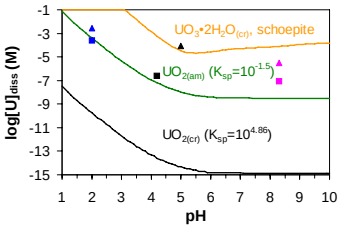
Hypothesis:

Equilibrium solubility and dissolution rates of bacteriogenic UO_2 are moderated by:

- solution composition (pH, pO_2, carbonate)
- cation substitution
- degree of crystallinity
- particle size

Approach:

Quantify dissolution rates in batch and flow-through reactors to determine rate constants as a function of pH and $[O_{2(aq)}]$. Synthesize abiotic UO_2 by reduction of U(VI) with H_2.



Measured and calculated uranium solubility

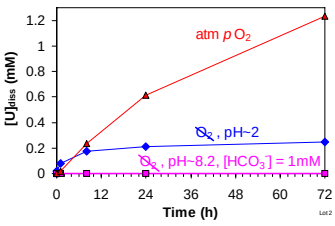
Results: Dissolution of U(IV)/U(VI) coprecipitate

In absence of O_2, low dissolution rates at pH~8.

At pH 2, faster U dissolution due to liberation of UO_2^{2+} bound in the solid.

At atmospheric pO_2, higher dissolution rates caused by oxidation of U(IV).

$[U]_{diss}$ data consistent with solubility of amorphous UO_2 and schoepite (upper right plot), using solubility and hydrolysis constants from [1].



Batch dissolution: $[U]_T$ = 5.6 mM, [solid] = 2 g/L

[1] Guillaumont R, et al. (2003) Chemical Thermodynamics Vol. 5, Elsevier.

Team: K.-U. Ulrich (Post Doc), A. Singh (Doctoral student), D.E. Giammar.

Role of Manganese(II)-oxidizing bacteria in UO_2 oxidation

OHSU

Hypothesis: Mn(II)-oxidizing bacteria may be abundant in U-contaminated environments and may accelerate the rate of UO_2 oxidation through the production of highly reactive MnO_2 phases. The rates of UO_2 oxidation are affected by:

- Mn(II) and O_2 concentration
- Properties of the bacteriogenic UO_2 (cations, crystallinity, particle size)

Approach:

- Assess the presence of Mn(II) oxidizing bacteria at the Rifle Field site. Obtain pure cultures.
- Use Rifle isolates and model systems in the laboratory to investigate UO_2 oxidation under different conditions

Results:

- Mn(II)-oxidizing bacteria are present in abundances of 10^3–10^5 per gram of soil but only represent minor components of the culturable bacteria at the Rifle Field site.
- 17 pure cultures have been isolated and are being characterized.
- One or two strong Mn(II) oxidizers representative of the Rifle site will be used in future studies, along with model laboratory isolates, to investigate the mechanisms and kinetics of UO_2 oxidation by Mn(II)-oxidizing bacteria.

In Progress:

- Kinetics experiments
- Microbial characterizations

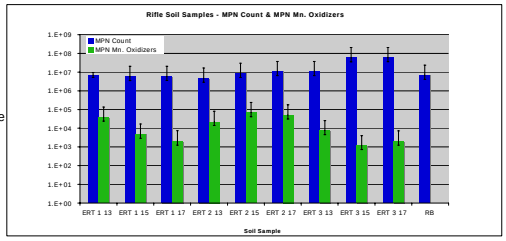


Figure: Mn(II)-oxidizing bacteria were present in all the well samples (ERT) but not the sample collected with the backhoe (RB). And represent only 0.001–1% of the total culturable bacteria

Team: C. Sheehan, C. Peterson (technicians), C. Anderson (Post Doc), B. Tebo.