

In-situ Recovery Uranium Mining Restoration Challenges

Darton Geological Society
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Please Note:

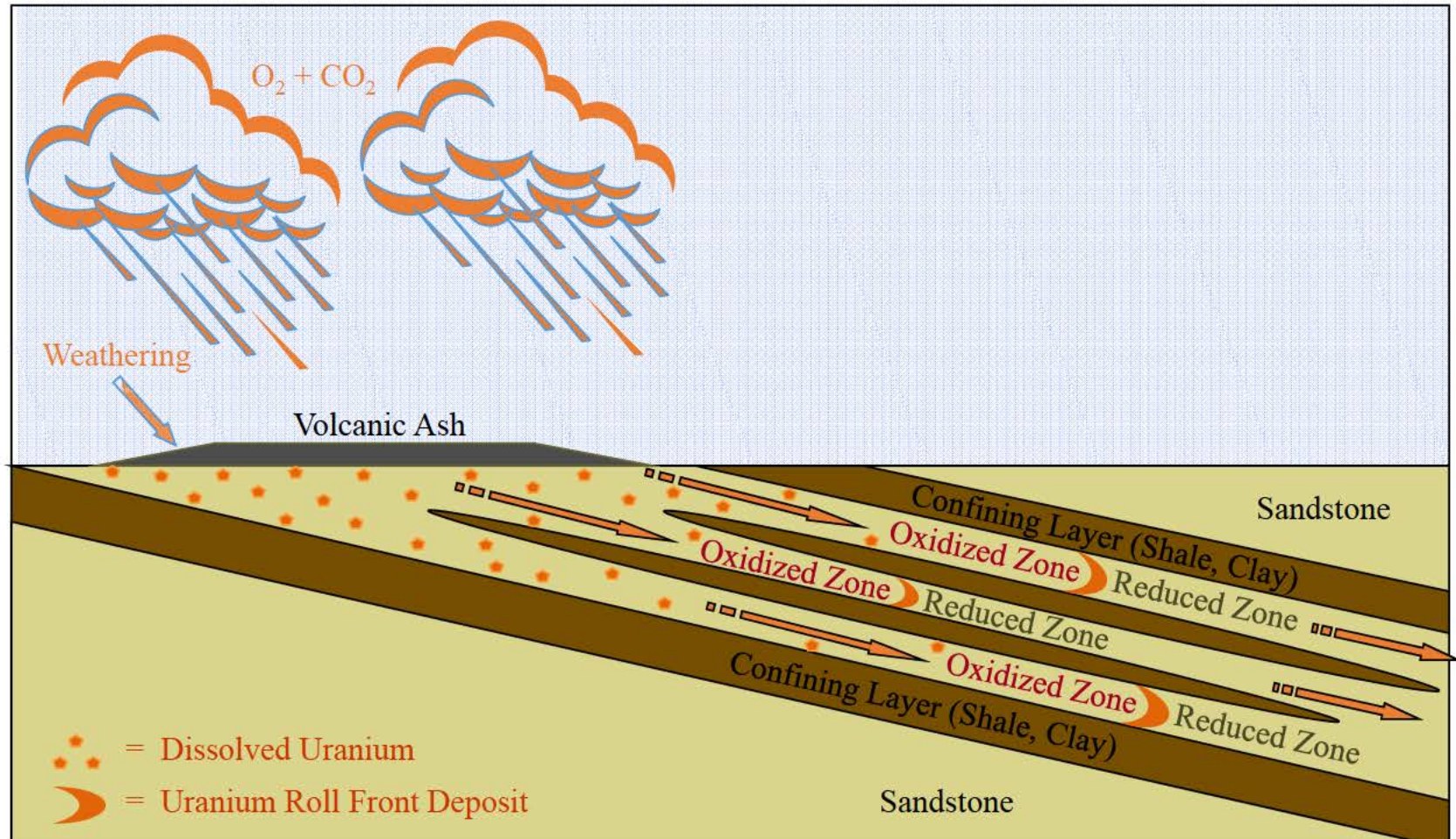
- On-going project is 'work in progress' – 1 yr remaining on project
- Non-Disclosure Agreement (NDA) with Cameco regarding site specific data
- Focus of talk will be on our approach (methods), and providing insight for other U ISR site restoration challenges

Major U.S. Uranium Reserves

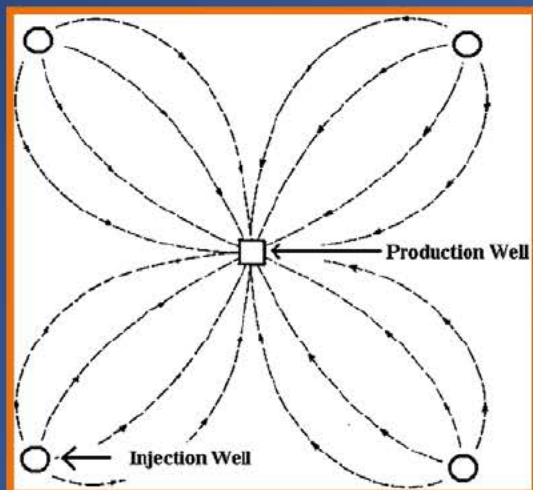


Sources: Based on U.S. Department of Energy, Grand Junction Project Office (GJPO). National Uranium Resources evaluation. Interim report (June 1979) Figure 3.2; and GJPO data files.

Uranium Roll-Front Formation

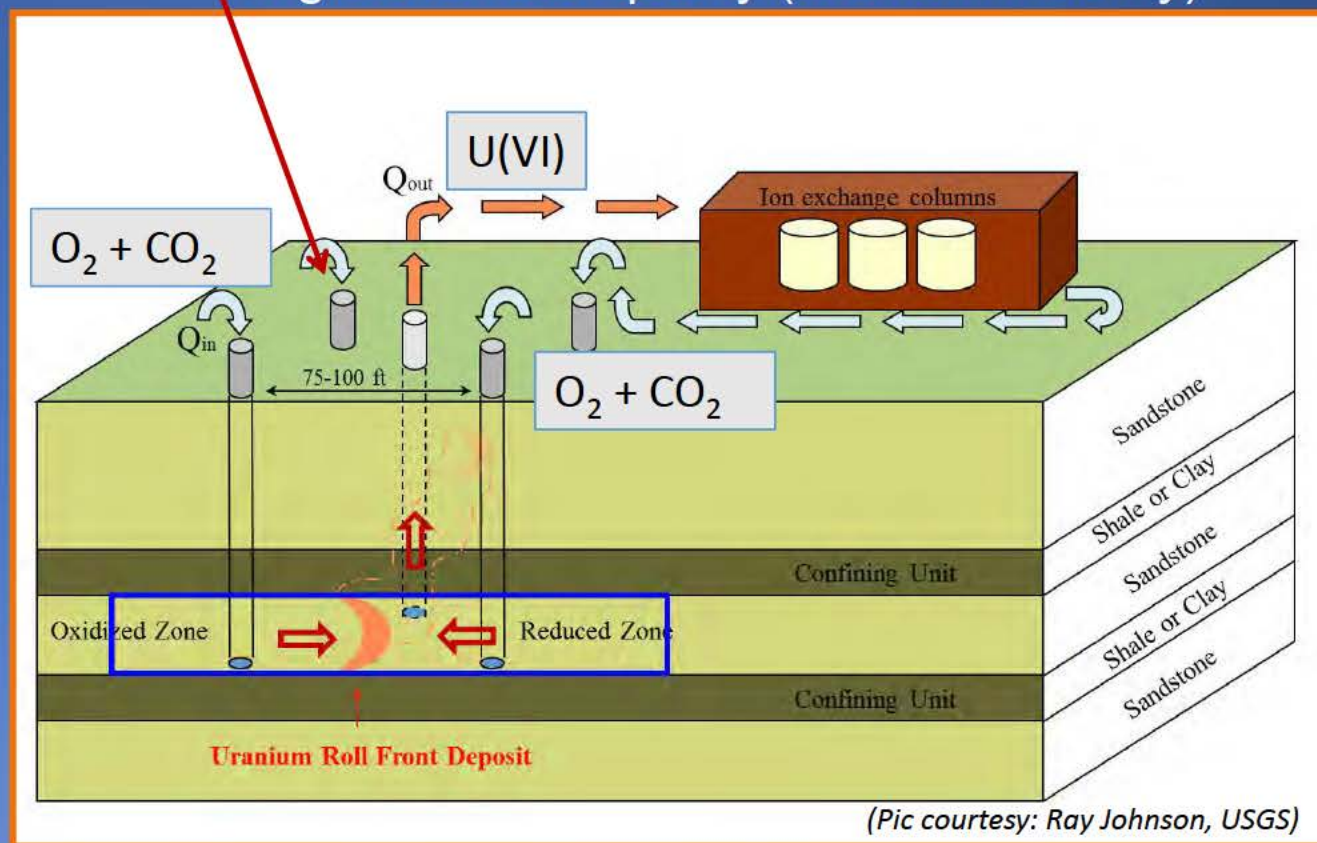


In-situ Recovery (ISR) Mining of U



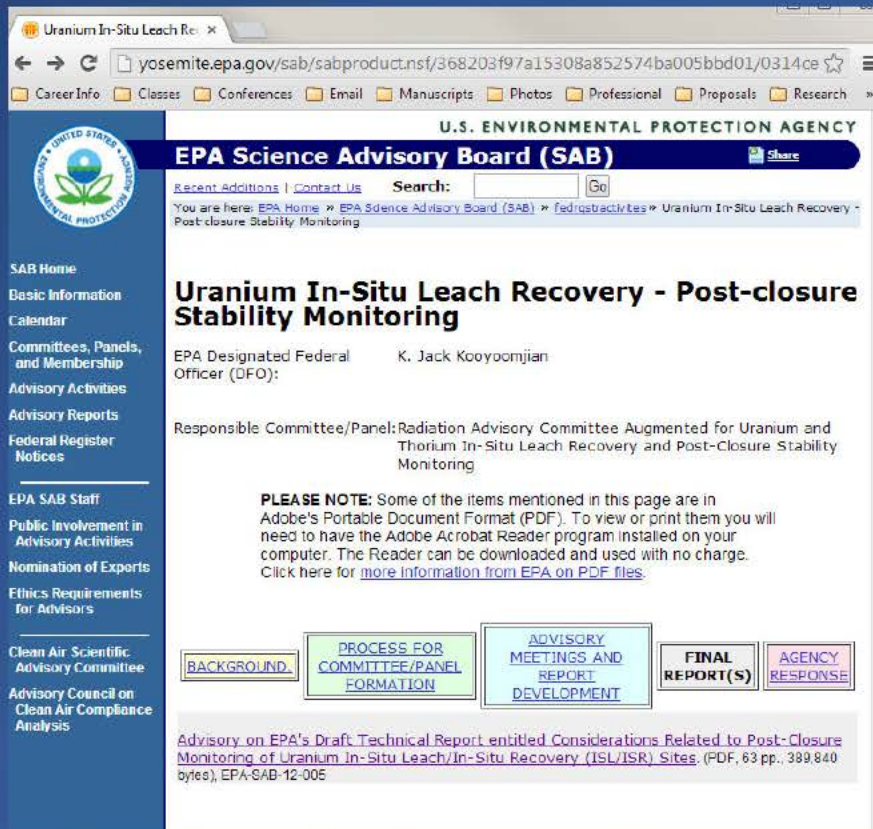
(Borch et al., 2012)

← Injection and Production wells
monitoring wells: emplaced to detect change in groundwater quality (uranium mobility)



• EPA SAB 2012 – ISR U Post- Closure

- Regulatory baseline condition requirements have **little scientific backing**
- Recommend applying environmental models to provide **realistic predictions** of the rates at which groundwater constituents approach stable conditions following the **cessation of mining operations**, for a range of realistic bounding conditions



Thomas Borch
ColoState U



Thomas Johnson
ColoState U



EPA

Underground Injection Control (UIC)

- Concern is protection of groundwater quality at the aquifer exemption boundary
- “UIC regulation 40 CFR 144.12 prohibits the movement of any contaminant into the underground source of drinking water located outside the aquifer exemption boundary” (NRC, 2012)
- Contaminant = “any physical, chemical, biological, or radiological substance or matter in water” (NRC, 2012 and 40 CFR 144.3)

Potential Risks Involved in ISR U mining

- Transport of contaminated water to regional aquifer
- Human, animal, crop exposure
- Potential for spill or accident (e.g., release of contaminated water)

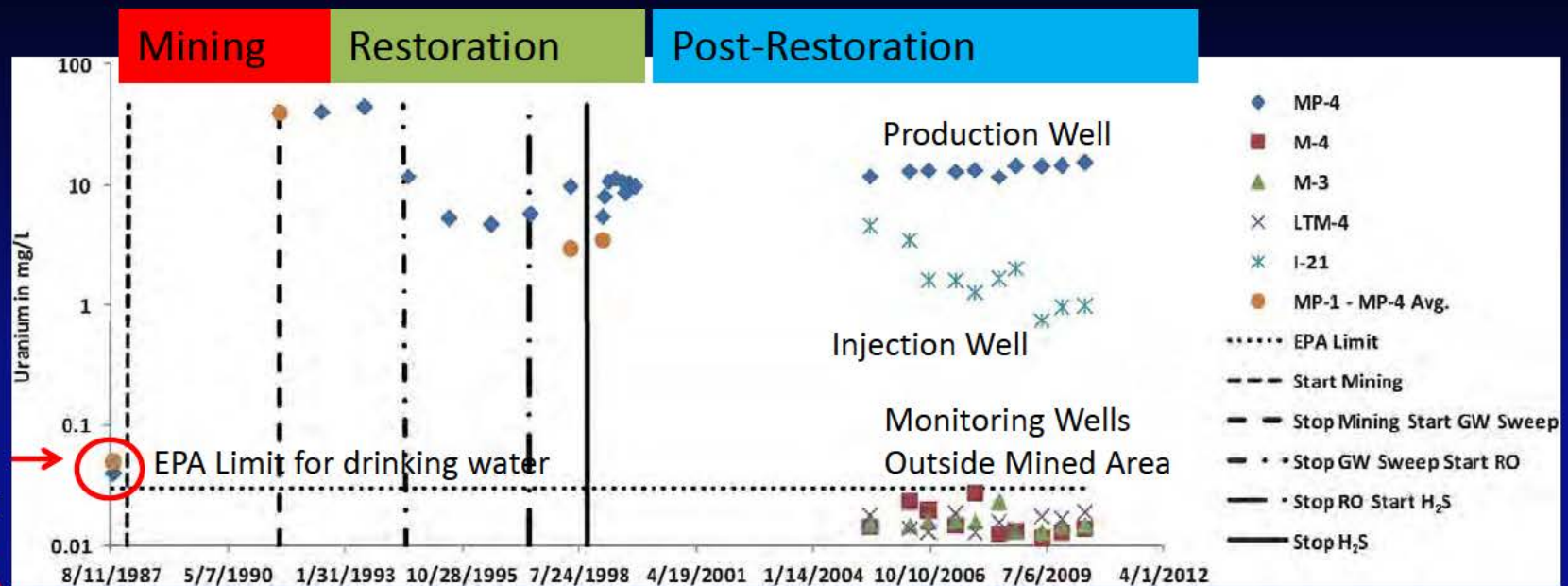
Mine Restoration Approach:

- Groundwater sweeping (high consumption of freshwater)
- Reverse osmosis, ion exchange (high cost & energy use)
- Injection of chemical reductants (HS^-) (not always efficient)

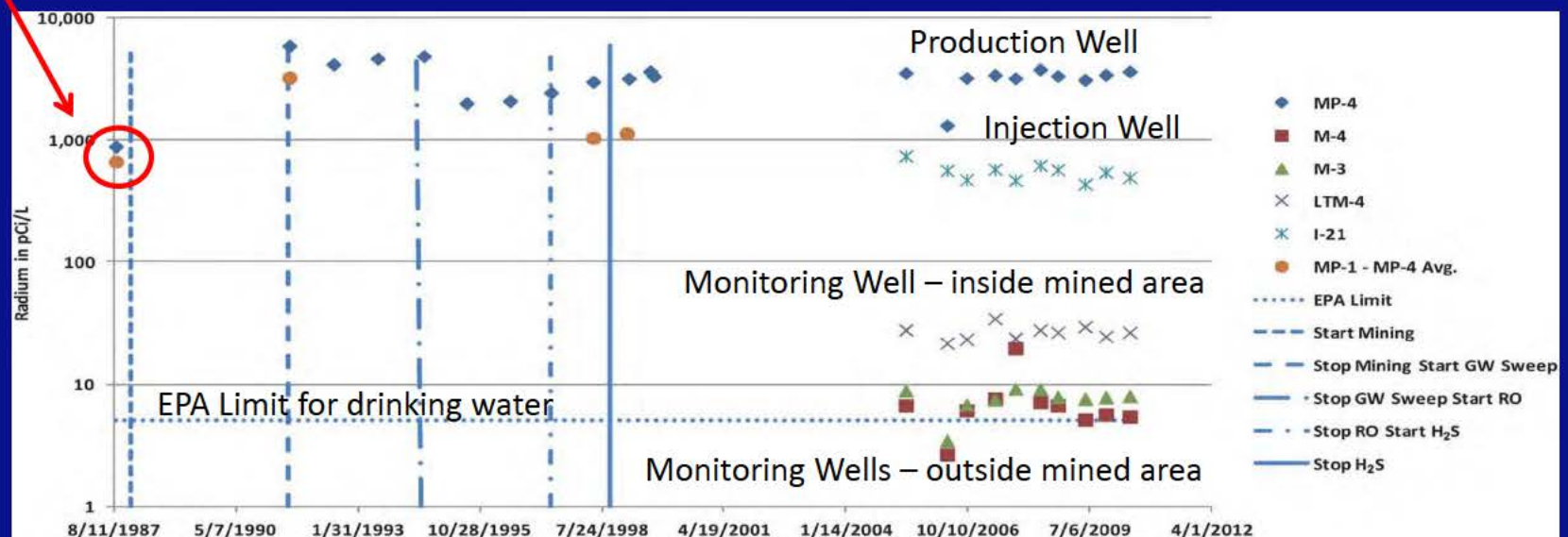
U and Ra at Smith Ranch ISR site (note: publicly avail. data)

U

Before mining



Ra



(Borch et al., Journal of Environmental Monitoring 2012)

USGS Texas review (Hall USGS OFR 2009-1143)

- Looked at 22 well fields in South Texas
- For uranium pre-recovery, 95% were above the EPA drinking water standards
- For radium pre-recovery, 100% were above the EPA drinking water standards
- For uranium, after restoration, 68% were still above pre-recovery baseline
- For radium, after restoration, 4% were still above pre-recovery baseline

How Baseline Characterization Should be Conducted at ISR U Mining Sites

Total elemental concentration is a poor indicator for restoration goal, bioavailability, mobility and toxicity.

Thus **its essential to carefully characterize the molecular nature and valence state** of key elements in order **to predict down gradient transport** of U, Ra, and toxic metal and **human health risks** in addition to **help determine reasonable restoration goals**:

Aqueous Phase

U(IV/VI), Fe(II/III), Mn(II/III/IV), S(-II/VI), As(III/V), Se, N, DOC, bicarbonate

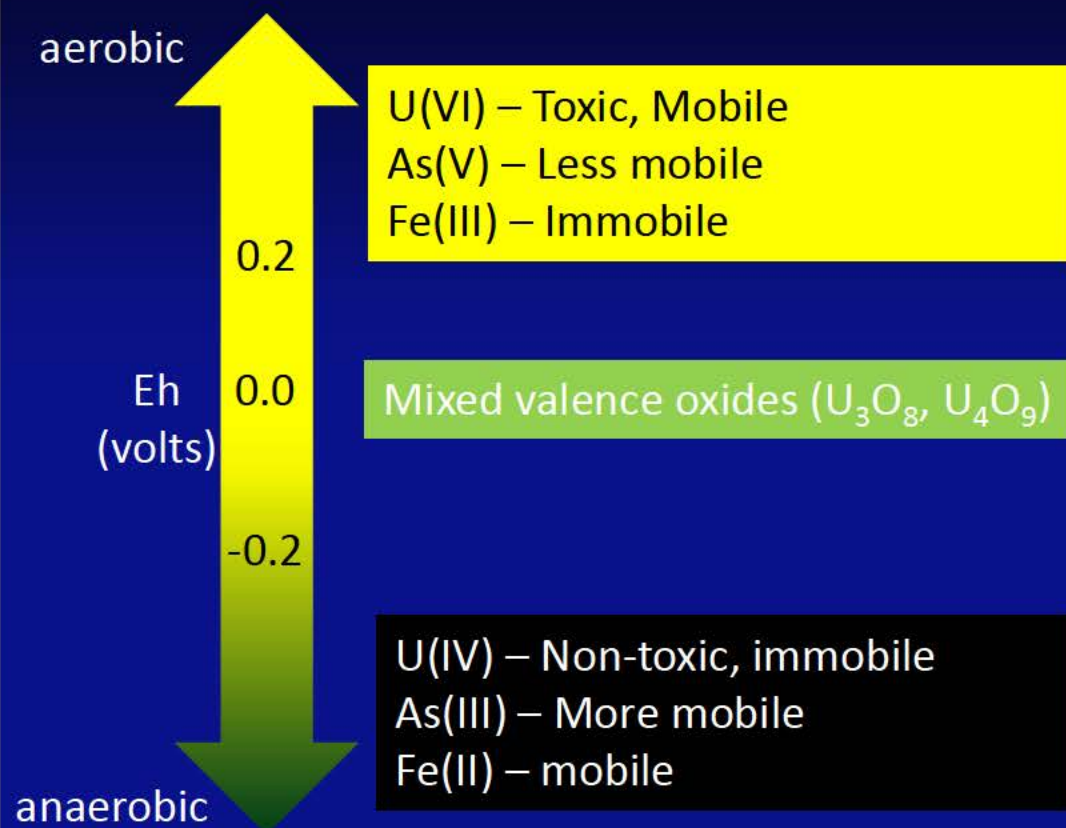
Mineral phases

Fe oxides, Mn oxides, Al oxides, carbonates, sulfates, sulfides, clays

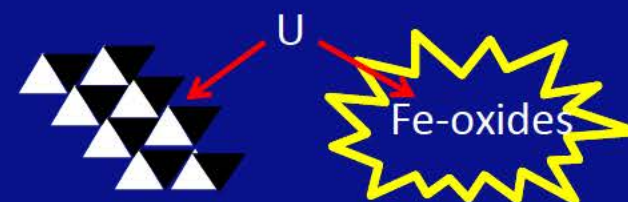
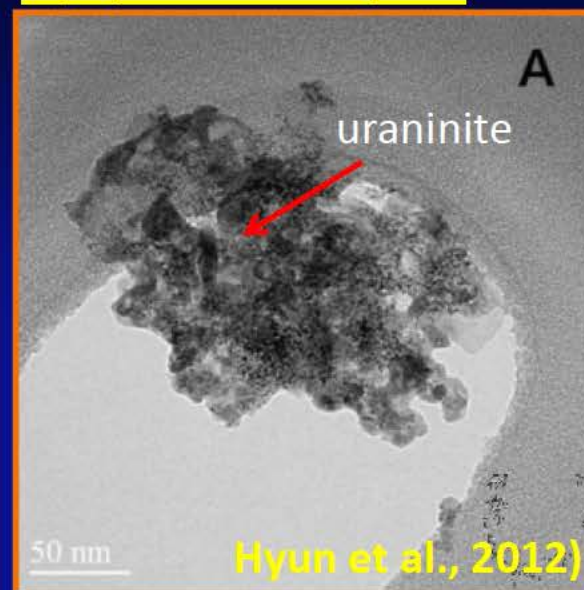
Soil/sediment Characterization

Sand/silt/clay fraction; CEC, AEC, SOM, porosity, surface area, zeta potential, redox potential, sorption capacity, “reduction capacity”

Impact of Redox Conditions on Mobility and Toxicity



U(VI) reduction by FeS



Co-precipitation of U

Aim for restoration processes: convert U(VI) to U(IV)

Borch et al., Biogeochemical Redox Processes and their Impact on Contaminant Dynamics. *Environmental Science & Technology* **44**, 15-23 (2010).

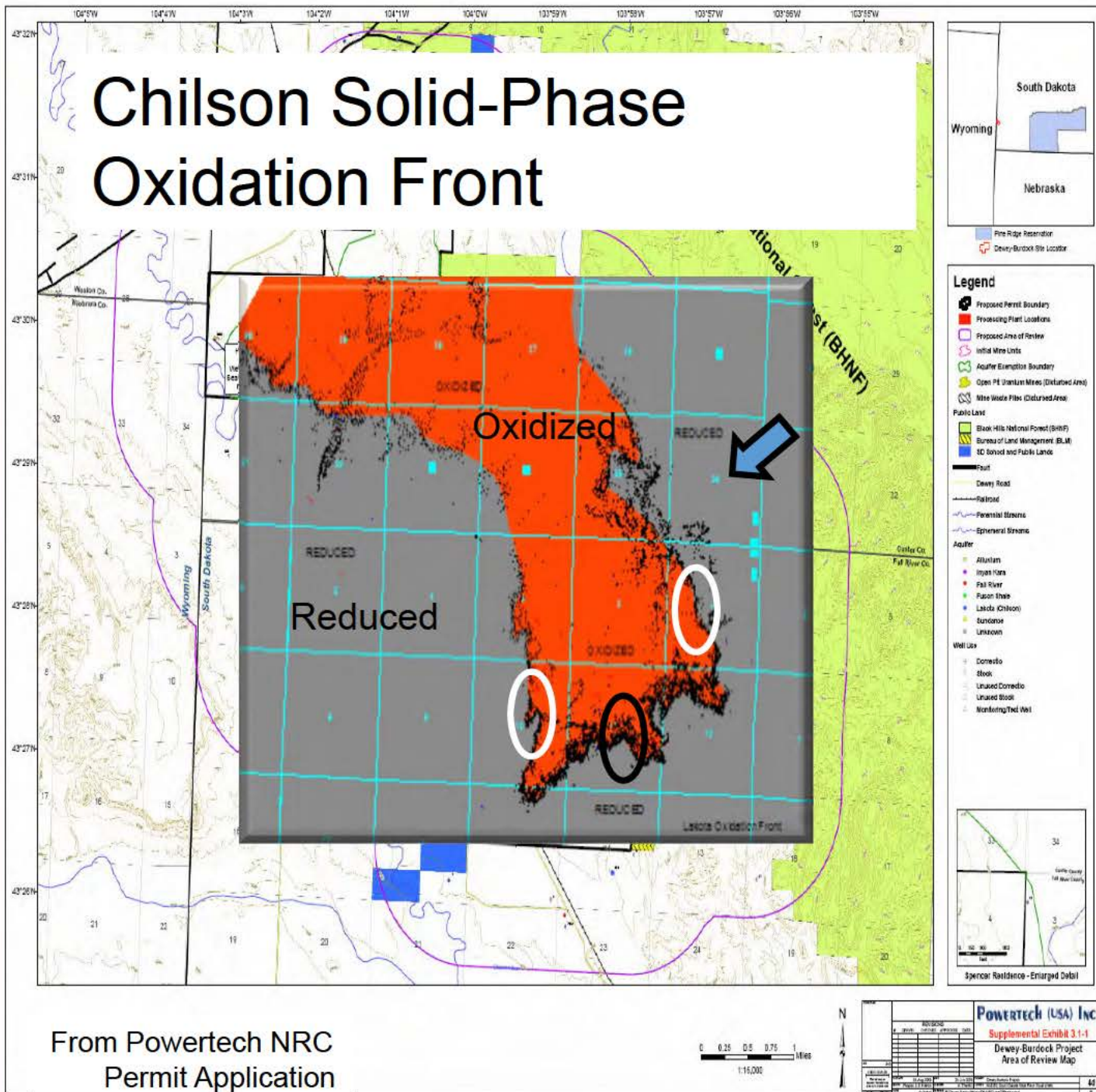
Importance of Determining the Biogeochemical Redox Conditions at ISR U Mining Sites

Here are a few examples of why we need to understand the redox conditions and element speciation:

1. Presence of REDUCED mineral phases and dissimilatory metal reducing bacteria are essential for **immobilization of uranium** down gradient (implication for reactive transport modeling and human health risk assessment)
2. Formation of **molecular-U(IV) instead of uraninite (UO_2)** will result in a less stable and more mobile U (implications for restoration)
3. Presence of **uranyl carbonato** complexes can **prevent reduction by sulfide** (thermodynamic issue; implications for restoration)

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Chilson Solid-Phase Oxidation Front



From Powertech NRC
Permit Application

- Funding from Legislature of the State of Wyoming In-Situ Recovery of Uranium Research Program
- \$1.6M appropriated in 2009 for activities related to ISR mining in WY.
- Several ~\$300k 2yr grants funded, including UWy, LANL, UC-Berkley, CSU-SDSM&T (2013)
- CSU-SDSM&T Project Goal:
 - Determine optimal restoration goals based on human and environmental risks at the Highlands-Smith Ranch ISR U mine site near Douglas WY



Geochemical Characterization

Thomas Borch
Amrita Bhattacharyya
Colorado State
University



PHREEQC Interactive
Version 3.0.4.7711
Implements PHREEQC 3.0.4
Released: May 13, 2013

Modeling Analysis

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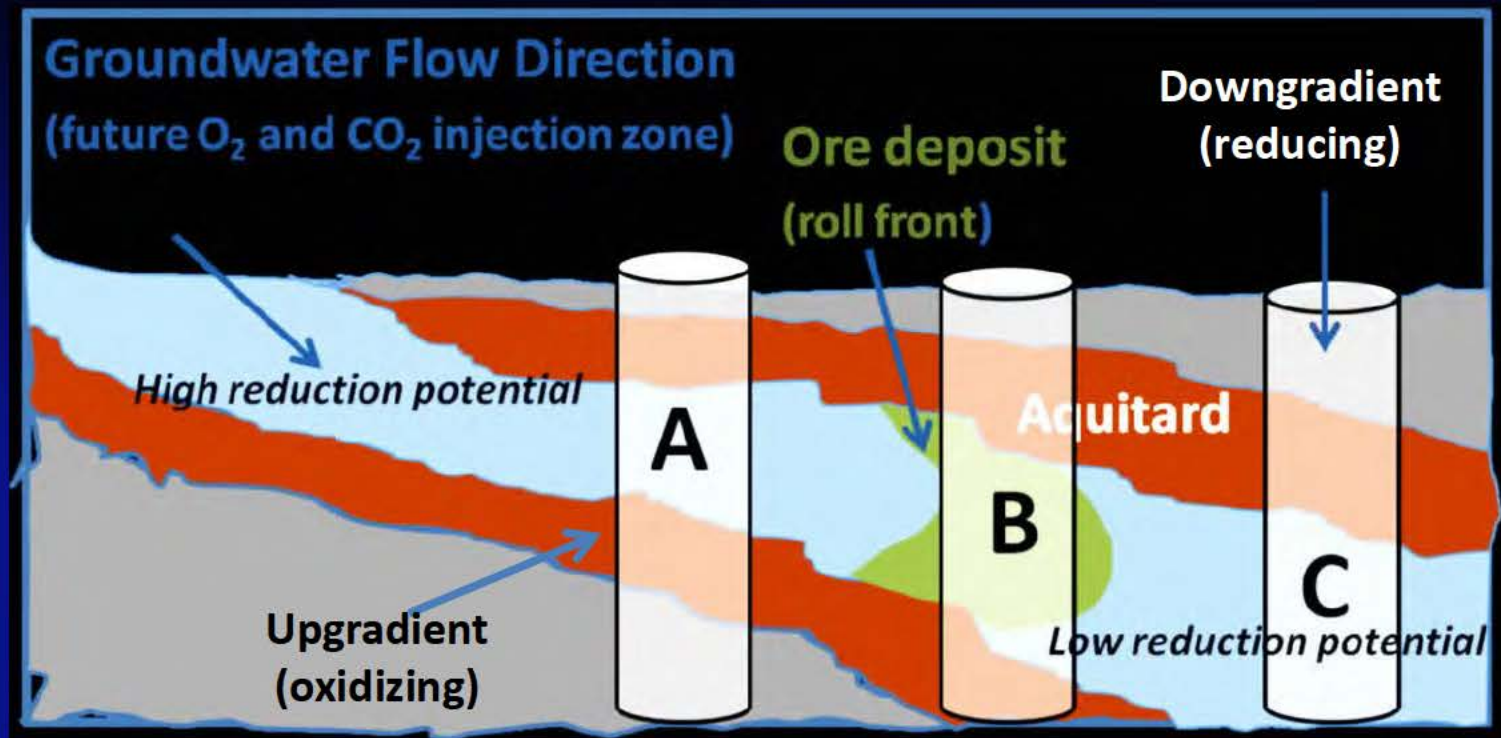


Human Health Determination

Thomas Johnson
Elizabeth Ruedig
Colorado State
University



Baseline Characterization Study: Experimental Set-up



2 sites; different mining stages

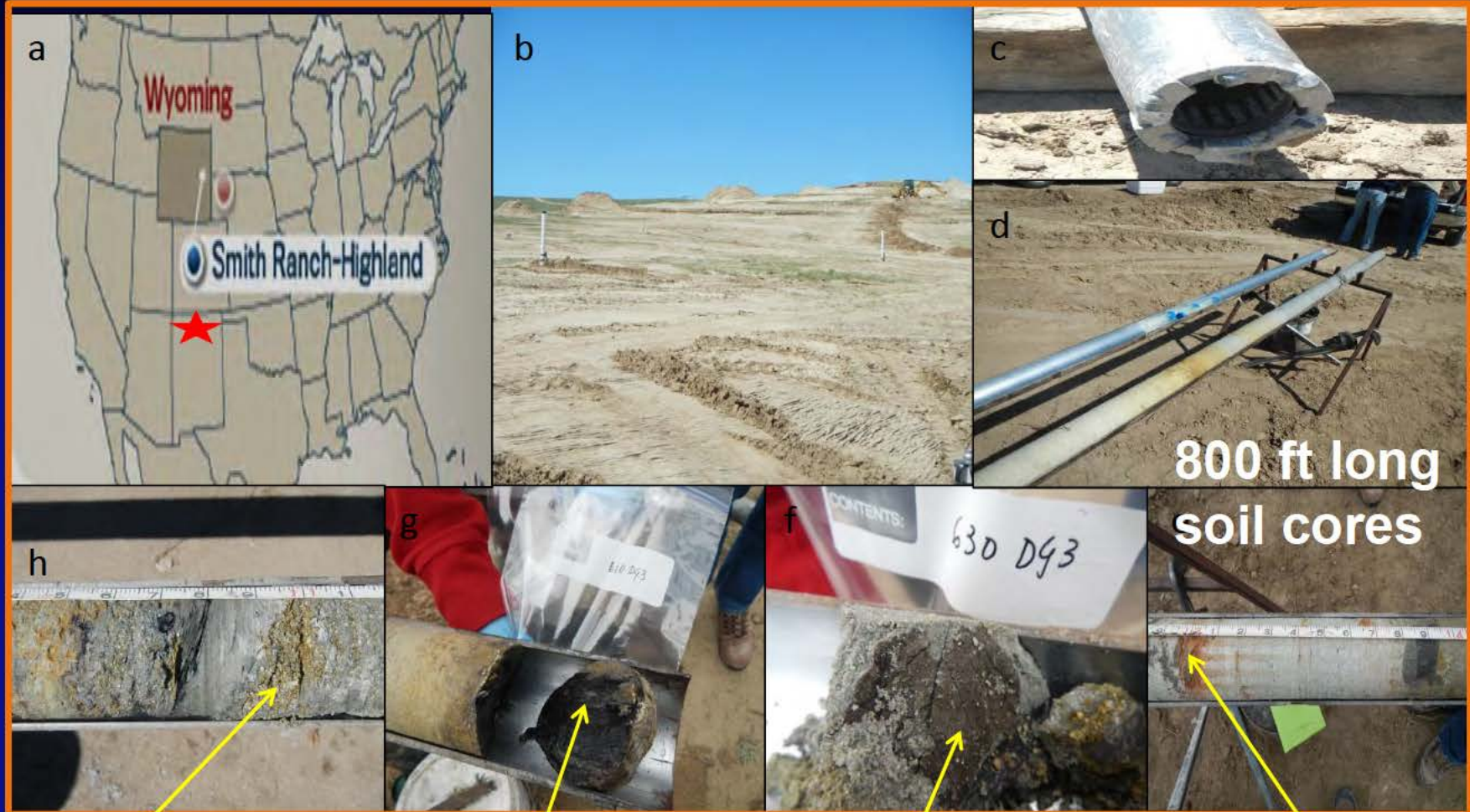
3 core positions

- pre-mining (upgradient, orezone, downgradient)
- post-mining and post restoration (upgradient, orezone, downgradient)

Biogeochemistry: Experimental Approach

1. **HF digests of solids** to determine the total elemental concentrations using ICP-MS and ICP-OES
2. Colorimetric analysis of Fe speciation (Fe(II), Fe(III), Fe_{total})
3. **Aqueous speciation** (valence states; redox couples); e.g., U(VI) vs U(IV) or As(III) vs As(V) or sulfide / sulfate ratio, etc
4. **Synchrotron X-ray Absorption Spectroscopy** (EXAFS and XANES) to determine bulk mineralogy and speciation (valence state)
5. **Synchrotron micro-XAS and micro-XRF** imaging to determine elements/minerals responsible for sorption/reduction of U etc.
6. **Pyrosequencing** to determine microbial communities with potential for metal and U immobilization

Study Site: Highlands-Smith



Complex heterogeneous matrix

Lignite

U with organic C

Redox-imorphic features

Sample collection and handling in the field



a. Intact core



b. Measuring 1 ft sections



c. Splitting the core into 1 ft sections



f. Vacuum packing the cores



e. Preserving each section in a vacuum sealed bag on ice



d. Saving sample for "microbiology" work in sterile tubes

Heterogeneity makes site characterization challenging (how many replicates are needed)



Homogenized samples stored in sealed serum bottles for experiments



Splitting open the core inside the anaerobic glove bag

Anoxic water sampling: Baseline/Pre-mining



Sampling Location	pH	Alkalinity (mg/L as CaCO ₃)	TDS (mg/L)	HCO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	U (mg/L)	Fe (mg/L)	As (mg/L)	Mn (mg/L)	Ra-226 (pCi/L)	Ra-228 (pCi/L)
Up-gradient	7.5	152.0	577	204	263	0.02	0.21	0.002	0.02	52	2.4
Orezone	7.2	146.5	578	205	261	<u>0.11</u>	0.05	0.005	0.01	<u>206</u>	5.4
Down-gradient	7.4	154.5	562	230	254	0.05	0.03	0.008	0.01	17	2.2

*USEPA-established Maximum Contaminant Level (MCL) in drinking water:

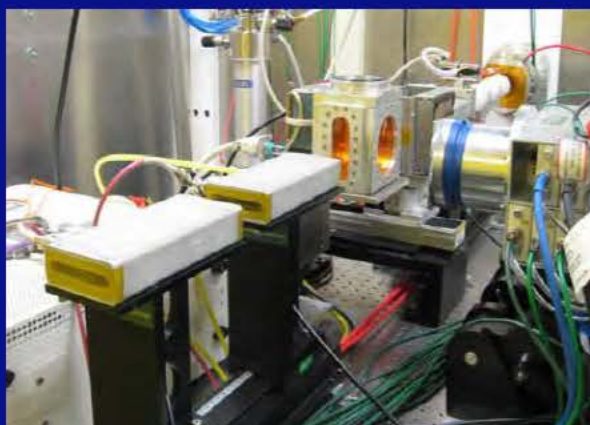
U = 0.03 mg/L

226 and 228 Ra = 5 pCi/L

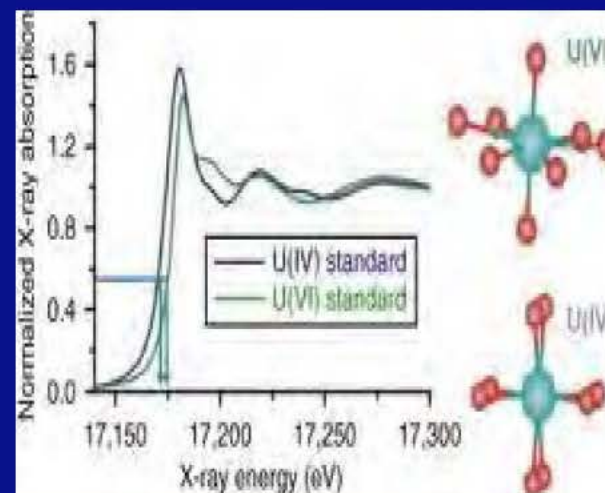
U speciation in solids: Synchrotron X-ray absorption spectroscopy



- Element-specific
- Oxidation states (U(IV) vs U(VI))
- Coordination environment (identity, distance and number of the ligand atoms to the central atom)
- Ratios of U species present
- Minimal sample preparation

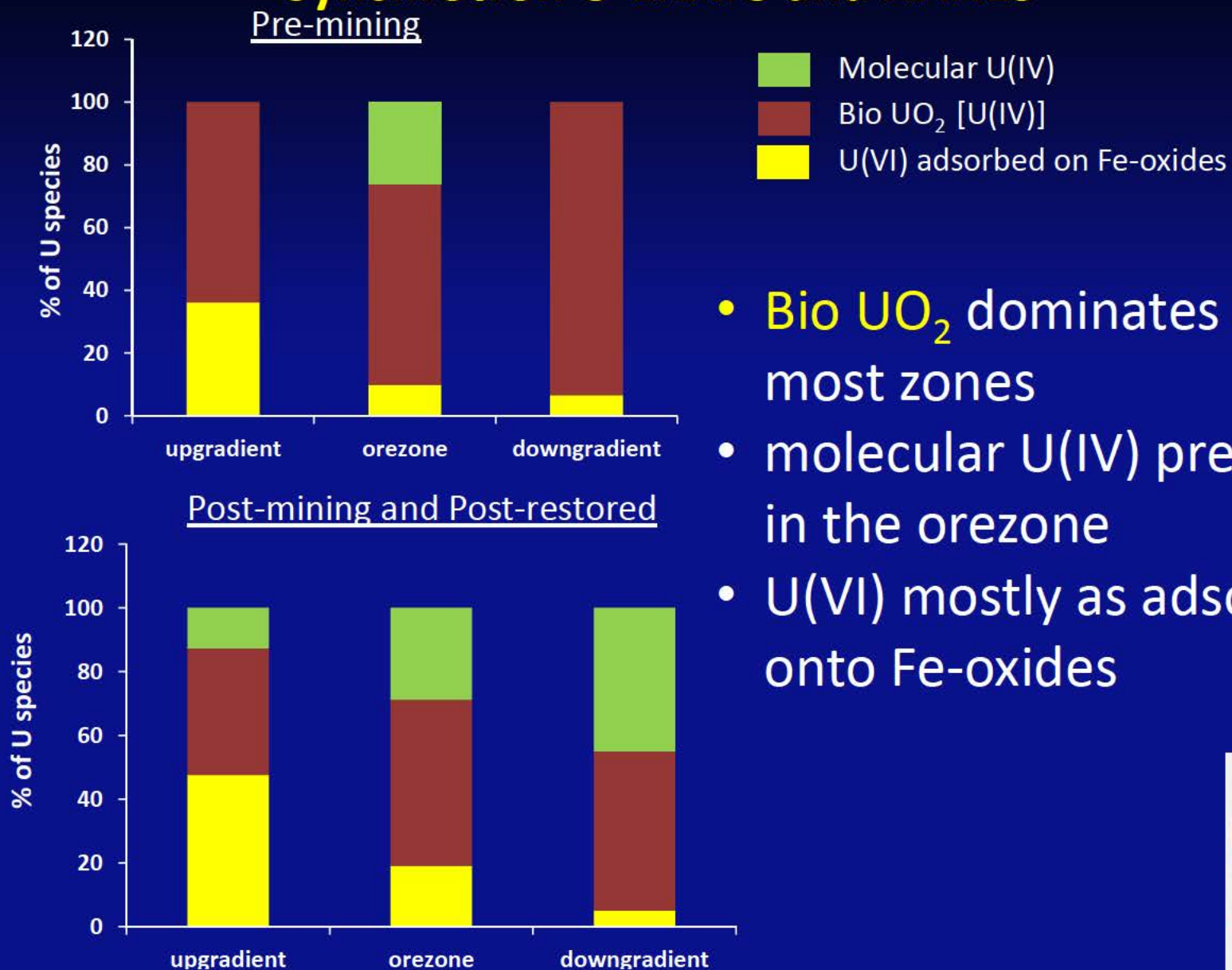


Beamline 11-2 at the Stanford Synchrotron Radiation Lightsource



Uranium XANES spectra

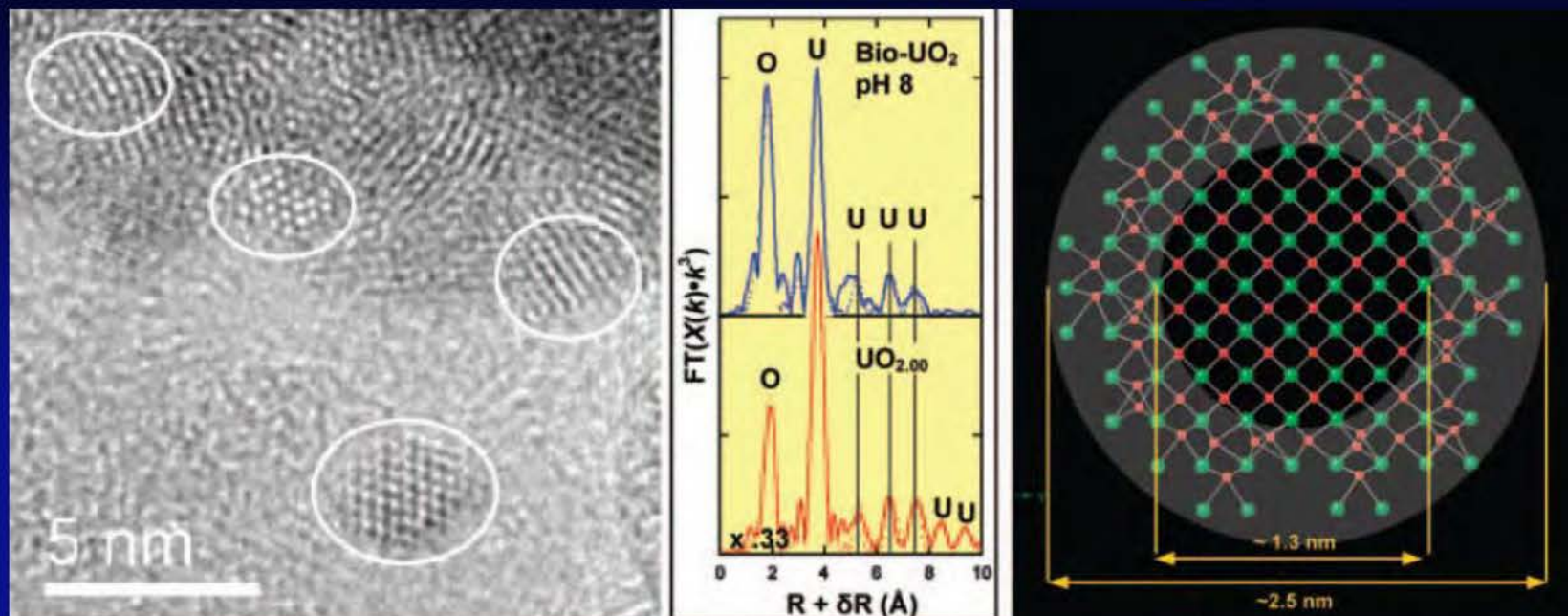
Presence of U(IV) and U(VI) species: Synchrotron U-EXAFS and XANES



- Bio UO_2 dominates in most zones
- molecular U(IV) present in the orezone
- U(VI) mostly as adsorbed onto Fe-oxides



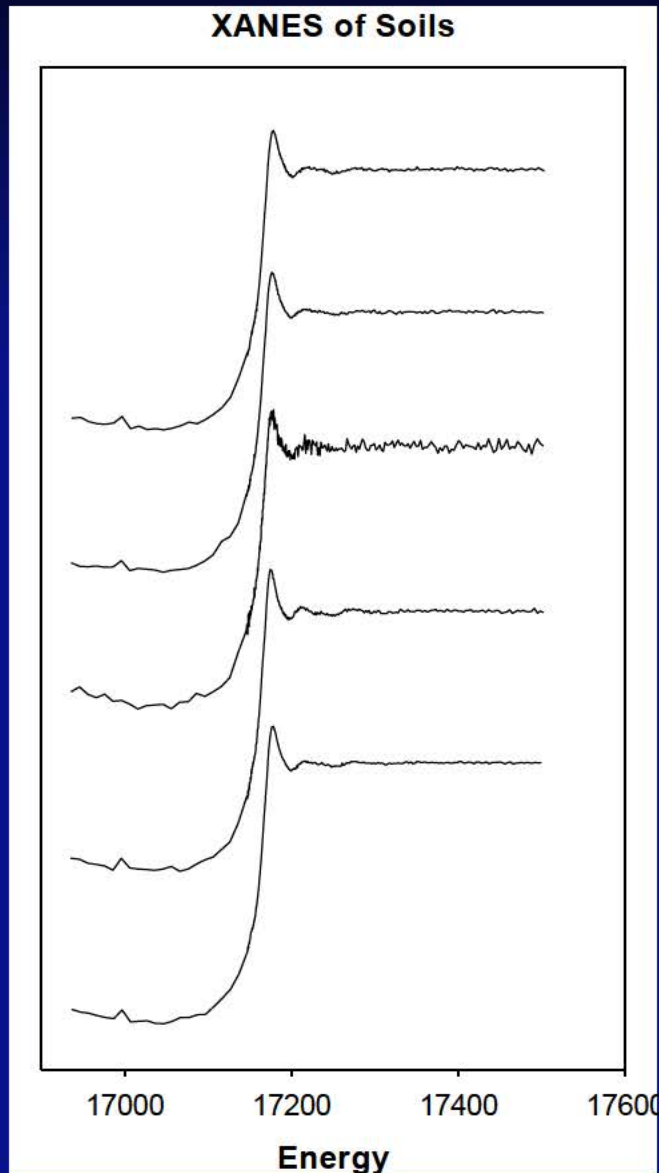
Bio-molecular UO_2



Barger Elements 2009, Schofield EST 2008

- Interfacial chemistry of biogenic uraninite ('non-uranite') is much different (Barger Elements 2009)
- Differing reoxidation pathways and transformation processes, especially in silicate and gypsum (calcium sulfate) matrix (Stylo EST 2013)

micro-XANES U imaging data



(Bio UO₂= 80%, U adsorbed on Fhy=20%)

(Bio UO₂= 83%, U adsorbed on Fhy=17%)

(Bio UO₂= 78%, U adsorbed on Fhy=22%)

(Bio UO₂= 36.7%, U adsorbed on Fhy=63.3%)

(Bio UO₂= 78.6%, U adsorbed on Fhy=21.4%)

Geochemical Modeling

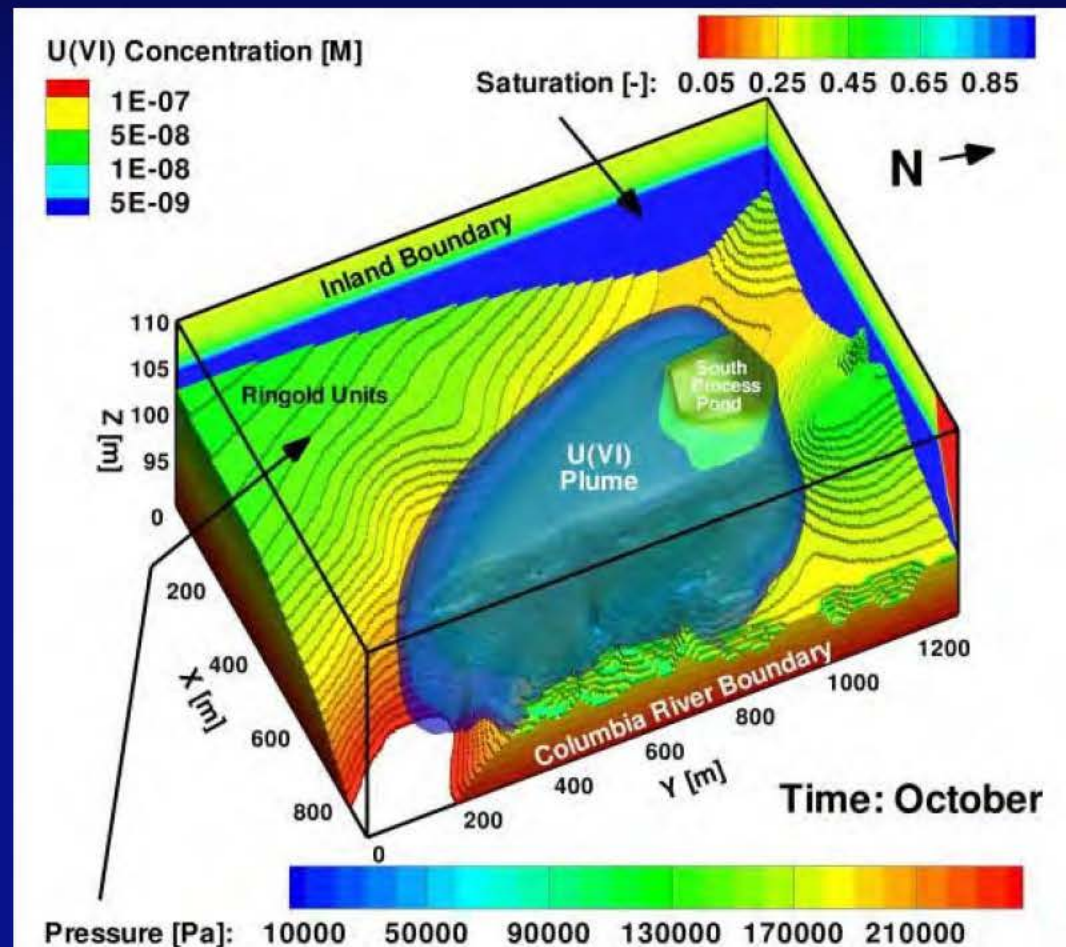


Figure courtesy PNNL.gov

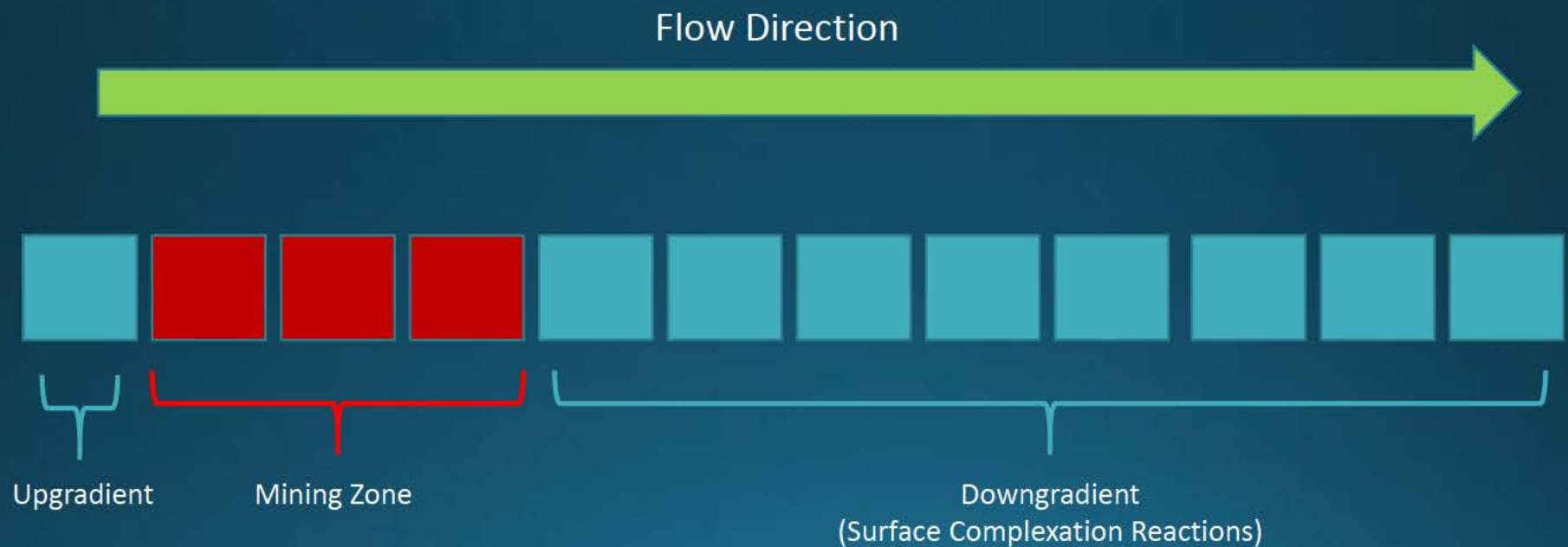
Geochemical Modeling



- Create a predictive geochemical model of 1-D uranium transport through porous media
- Software
 - **PHREEQC** (Version 3)--A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations
 - **PEST**: Model-Independent Parameter Estimation and Uncertainty Analysis
- Natural attenuation rates vary dramatically based on individual site characteristics

General Example

- 1-Dimensional transport represented via cells



Define Conditions and Reactions for Each Cell



Upgradient Gw
Composition



Remediation Zone
Comp.



Downgradient Gw
Composition



Downgradient Surface
Complexation Reactions
(Dzombak and Morel 2 layer
model HFO)



1-D Advective transport
calculations



```

SOLUTION_SPREAD
-units      mg/l
Description  Number      pH    pe    Temp  O(0)      Alkalinity      As      B      Ba      Ca      Cl
              mg/l      mg/l  mg/l  mg/l  mg/l as CaCO3      ug/l      mg/l      mg/l      mg/l      mg/l
Upgradient      0      6.78  1.2   12.8  1.2      269      4.72  0.143      0.012      365  9.67

SOLUTION_SPREAD
-units      mg/l
Description  Number      pH    pe    Temp  O(0)      Alkalinity      As      B      Ba      Ca      Cl
              mg/l      mg/l  mg/l  mg/l  mg/l as CaCO3      ug/l      mg/l      mg/l      mg/l      mg/l
Remediation Zone  1-8      6.78  1.2   12.8  8      269      4.72  0.143      0.012      365  9.67

SOLUTION_SPREAD
-units      mg/l
Description  Number      pH    pe    Temp  O(0)      Alkalinity      As      B      Ba      Ca      Cl
              mg/l      mg/l  mg/l  mg/l  mg/l as CaCO3      ug/l      mg/l      mg/l      mg/l      mg/l
Downgradient    9-40      6.78  1.2   12.8  1.2      269      4.72  0.143      0.012      365  9.67

SURFACE 9-40 Add HFO sorption in oxidized zone
Hfo_s      0.0041073421      600      8.89
Hfo_w      0.010101378

TRANSPORT
-cells      40
-shifts     40
-time_step   31536000 # seconds = 1 year
-lengths     40*5
-diffusion_coefficient 0
-thermal_diffusion 1 0
-print_cells 1-40
-punch_cells 1-40
-multi_d     false

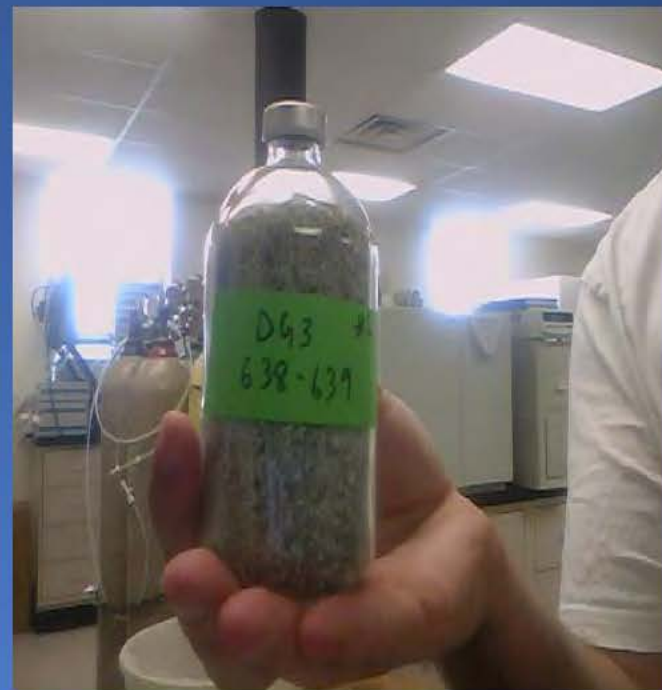
END
    
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Adsorption Isotherms for Surface Complexation Estimates

- establish site/condition specific thermodynamic K_d values
- Focusing on downgradient geochemical condition for our various mine status conditions (pre,post,post)



Differing sediments, CO_2 , U_{aq} , Ca, OC, biotic/abiotic, redox





PEST Interface



1. Assume Sorption Equations based on expected reactions at the site.

Gc_{ss} = super strong sorption site

Gc_s = strong sorption site

Gc_w = weak sorption site

2. However, equilibrium constants or sorption sites of core material is unknown. PEST helps estimate this parameters by determining a best-fit solution between experimental data (**isotherms**) and model calculations.

```
SURFACE_SPECIES
Gc_ssoH = Gc_ssoH

Gc_ssoH + UO2+2 = Gc_ssoUO2+ + H+

Gc_ssoH + H2O + UO2+2 = Gc_ssoUO2OH + 2H+

Gc_sOH = Gc_sOH

Gc_sOH + UO2+2 = Gc_sOHUO2+ + H+

Gc_sOH + H2O + UO2+2 = Gc_sOHUO2OH + 2H+

Gc_wOH = Gc_wOH

Gc_wOH + UO2+2 = Gc_wOHUO2+ + H+

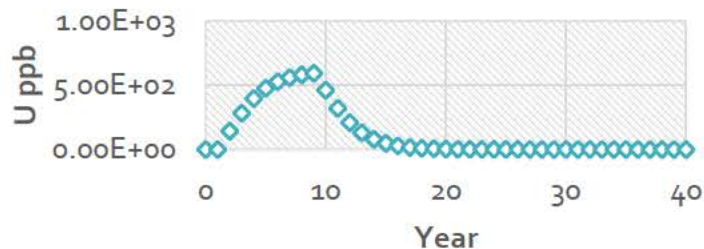
Gc_wOH + H2O + UO2+2 = Gc_wOHUO2OH + 2H+
```



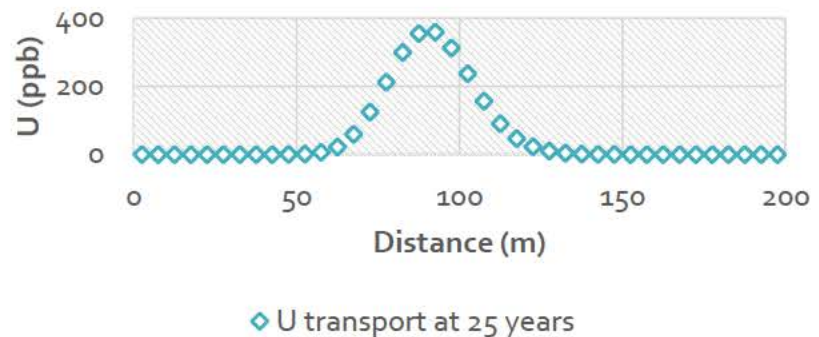
Downgradient U Plume Estimates

- Can simulate a uranium plume at either a fixed distance or time.

50 meters from start of remediation zone

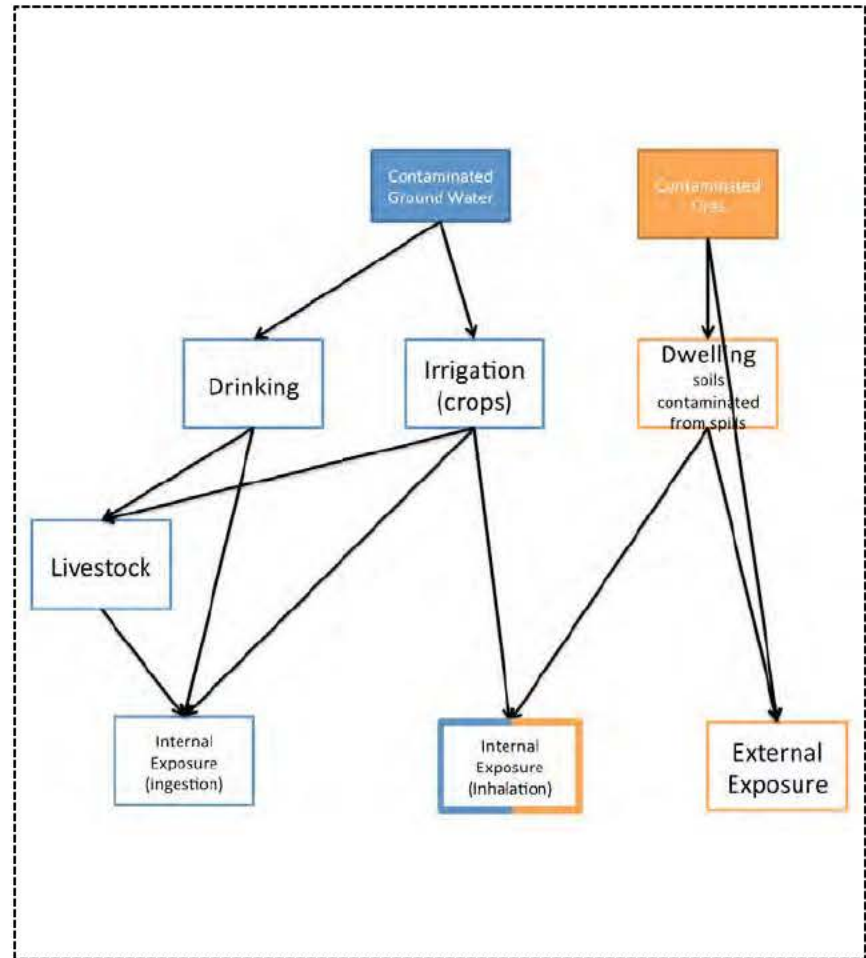


U transport at 25 years



Human Health Risk Assessment

- Similar model to that used for Yucca Mountain
- Adapted for local conditions and agricultural products;
- 3 cases considered:
 - High Exposure: subsistence farmer with no remediation technology
 - Middle Exposure: rancher with no remediation technology
 - Low Exposure: rancher with remediation technology



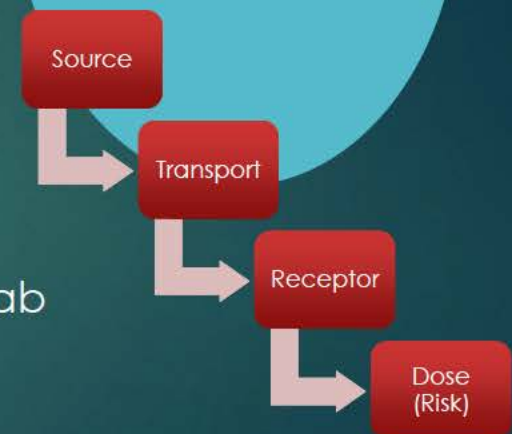
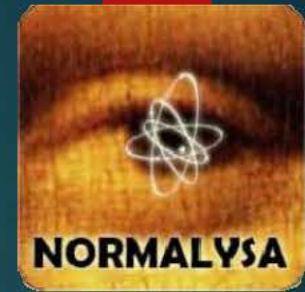
Pathways of exposure for high-exposure case.



Modeling Risk

- ▶ Benchmark two tools for modeling biospheric transport to compute risk.
- ▶ Based on source term equilibrium conditions calculated using PHREEQC
- ▶ **NORMALYSA** (NORM and Legacy Site Analysis)
<http://project.facilia.se/normalysa/software.html>
 - ▶ Tool currently under development by the International Atomic Energy Agency
 - ▶ Codes that have similar functionality: HYDRUS, RESRAD, ERICA
- ▶ **RESRAD-OFFSITE**
<http://web.ead.anl.gov/resrad/home2/offsite.cfm>
 - ▶ Tool developed and maintained by Argonne National Lab
 - ▶ 2D underground dispersion model

Will use robust source terms for pre-mining, post-mining, and post-restoration cases → using PHREEQC



Preliminary Conclusions

(again, work in progress....)

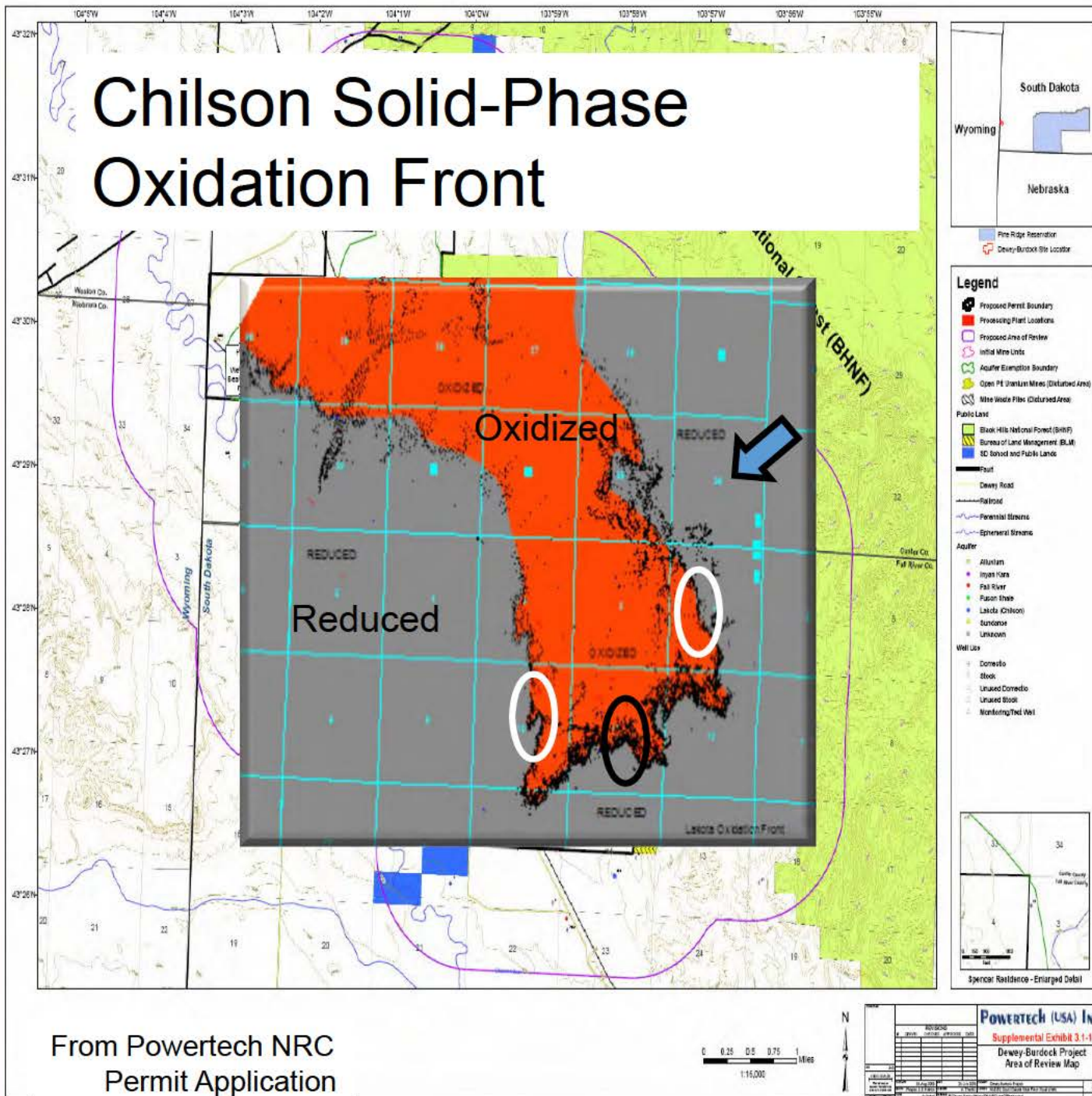
- Uranium sorption is a balance between true sorption strength (mainly **Fe hydroxides?**) and dissolved **carbonate complexes**
- Restoration of orezone U chemistry appears **successful** based on valence speciation
 - However, implications associated with **biogenic uraninite** (non-uraninite) are unknown
- Robust downgradient modeling efforts provide much needed insight towards meeting restoration goals
 - How far will plume travel?
 - Is site restoration needed?
 - Natural attenuation pathways?
 - What are the health and environmental risk?

Baseline Characterization is Needed at Every New ISR U Mining Site

How does Dewey-Burdock differ from Smith Ranch-Highland??

- Geology (e.g., sediment types; high V, variable Fe down-gradient – > 500-2500 ppm, ‘unpreserved’ cores)
- Water chemistry (e.g., high sulfate and bicarb)
- Microbial community influences?
- Influences of biogenic U(IV)?
- Potential ‘oxidized’ down-gradient zones, and subsequent natural attenuation capacities?
- Restoration strategy needs to be developed based on detailed baseline characterization – in order to protect the public, and help Power-Tech, and EPA develop scientifically sound restoration goals.
- **The CSU/SDSMT-Cameco project is a good example of how to develop best management strategies for ISR U mining (and a positive collaboration between academia and industry).**

Chilson Solid-Phase Oxidation Front





Thank you for your attention

Jim Stone

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