50th Anniversary Symposium
Stanford Synchrotron Radiation Lightsource
SLAC National Accelerator Laboratory
Stanford University
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The Development and Growth of Molecular Environmental Science at SSRL

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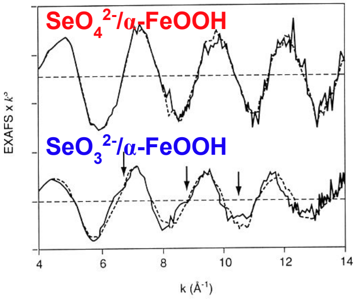
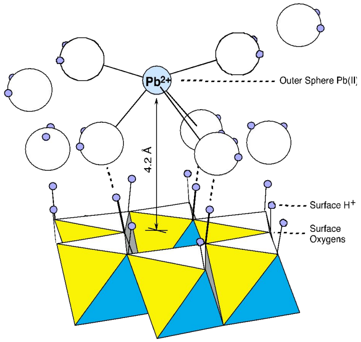
XAS of Se on FeOOH



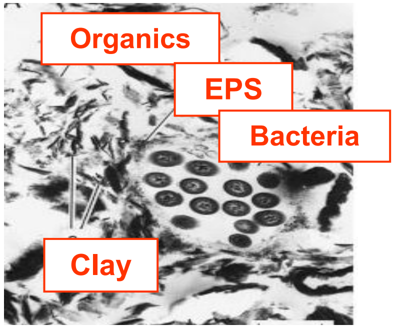
(Hayes *et al.*, *Science* 1987, *238*, 783)

Outer-sphere Pb Sorption



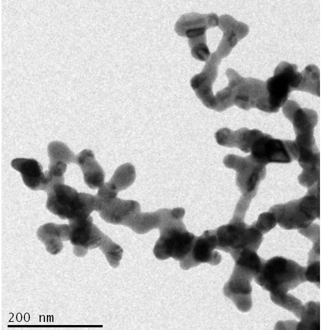
(Bargar *et al.*, *GCA*, 1996, *60*, 3541)

Complex Interfaces



(Ransom *et al.*, *Marine Geology*, 1999)

Nano-Oxide Interfaces

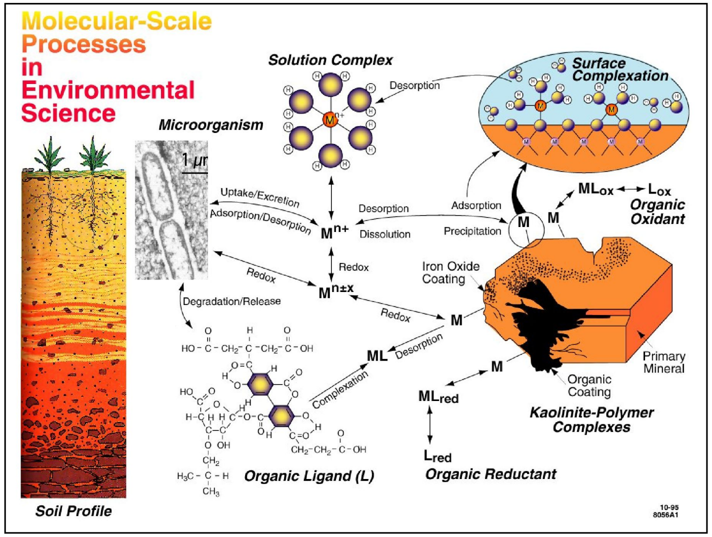


(Levard *et al.*, *ES&T*, 2012, *46*, 6900)

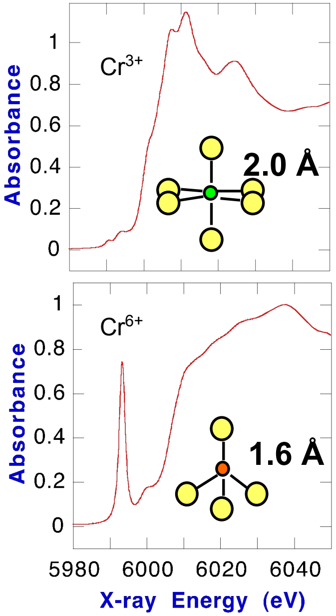
Some Key Issues in Molecular Environmental Science

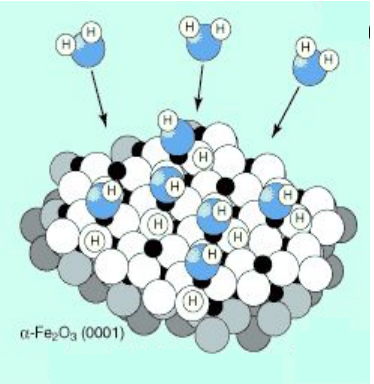
Water and Interfaces

Complexity

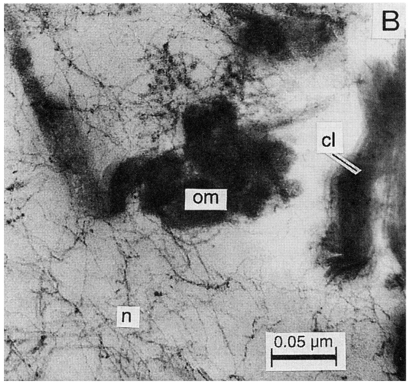


Speciation

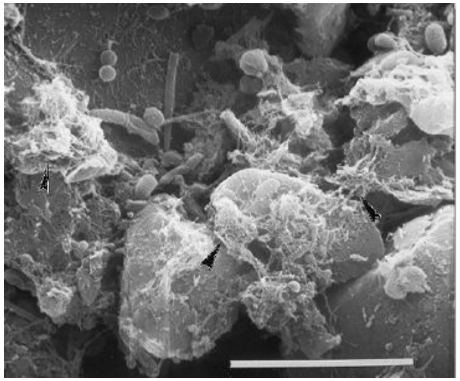




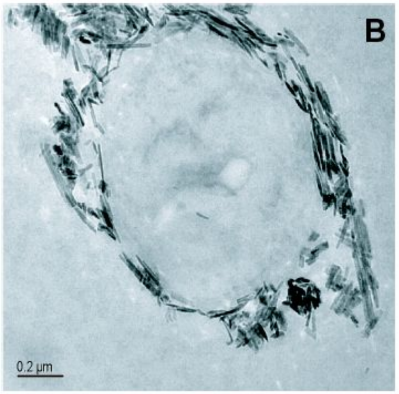
Interfacial Reactions



Natural Organic Matter

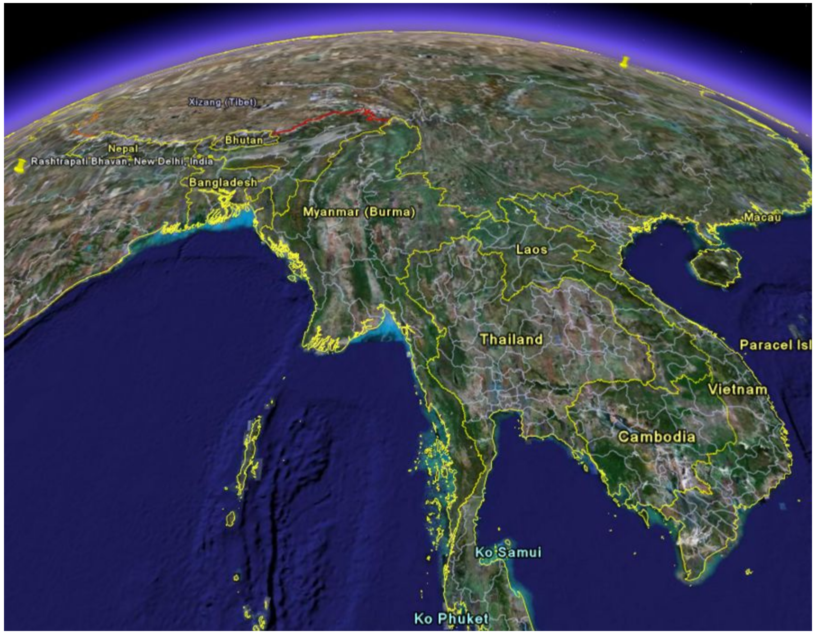


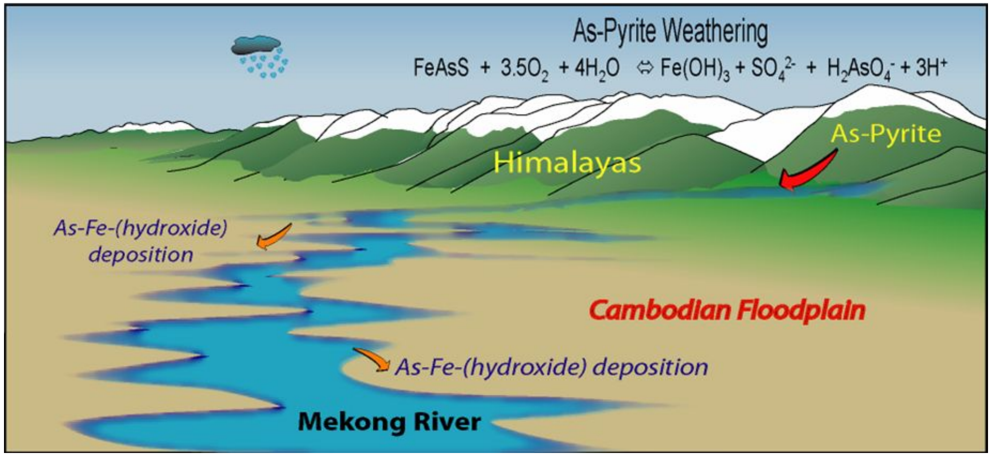
Microorganisms & Microbial Biofilms



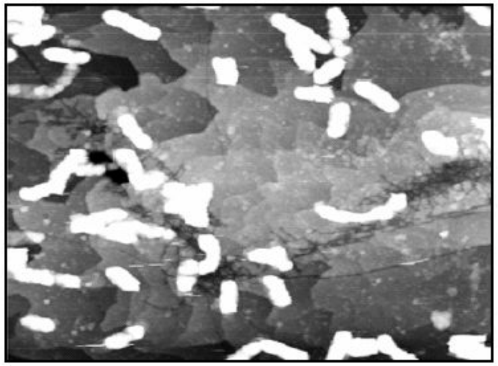
Nanoparticles & Nanopores

The Surface Chemistry Associated with the Largest Mass Poisoning in History

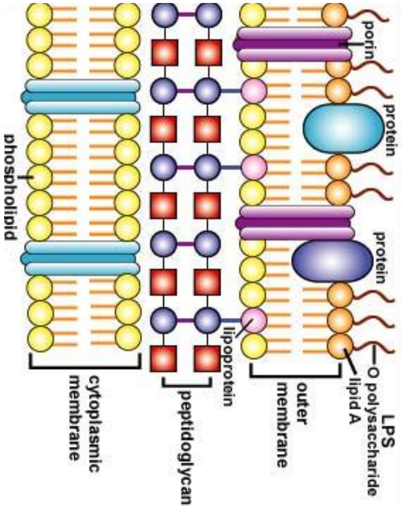


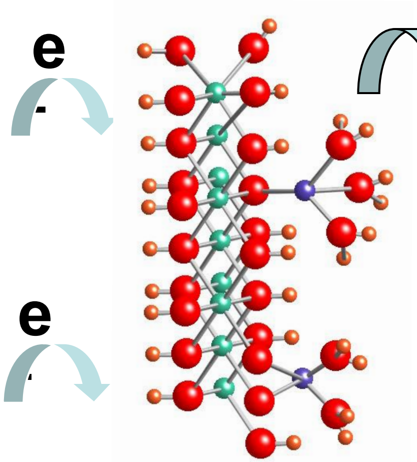


Bacteria Can Reductively Dissolve Fe(III) Oxides and Release Adsorbed As

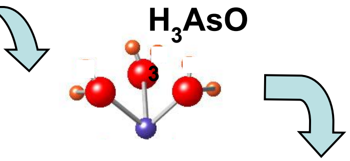


(Rosso, PNNL, STM Image)



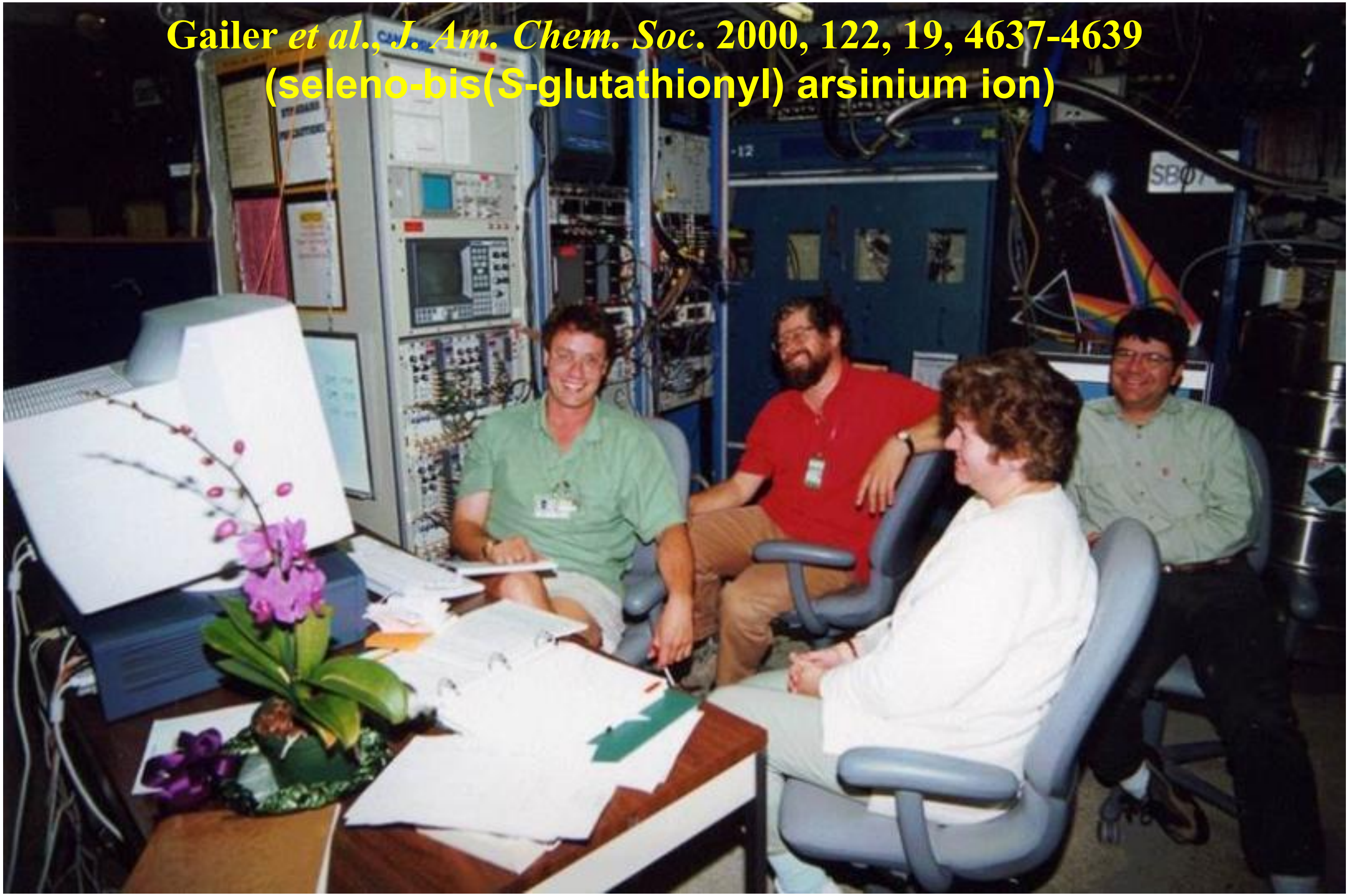


As-Fe-hydroxide



$$H_xAsO_4\text{-}Fe(OH)_3(s) + 5H^+ + 3e^- = Fe^{2+} + H_3AsO_3 + 4H_2O$$

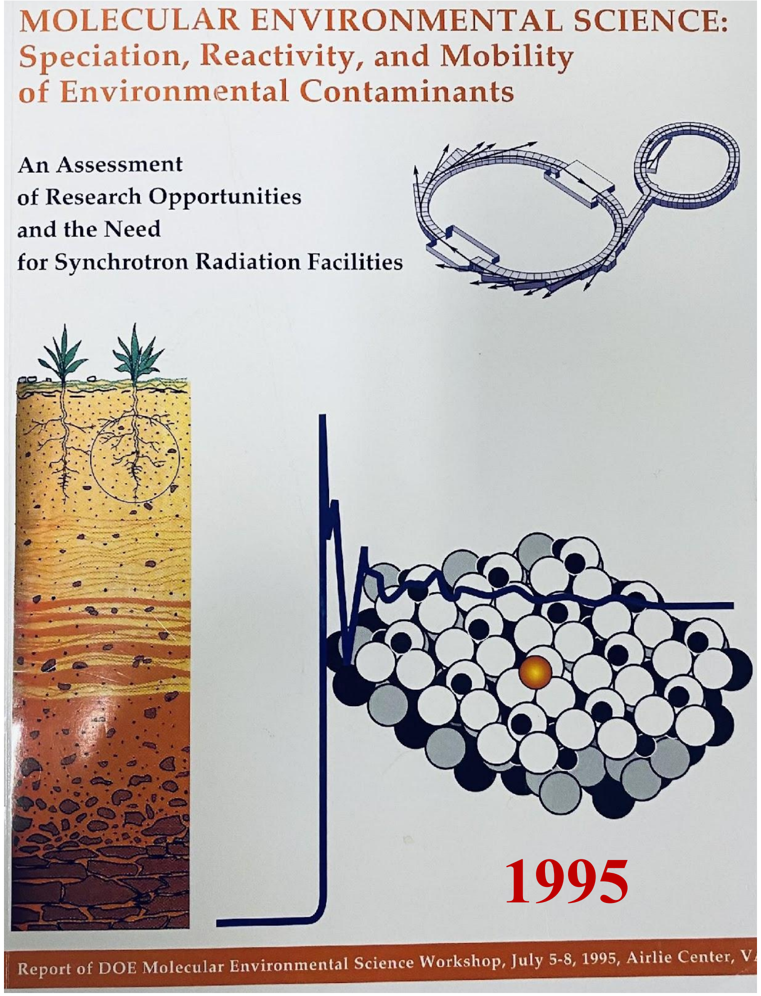
Graham George (left), Roger Prince (center), Ingrid Pickering, and Jurgen Gailer (right) collecting XAS data on As and Se at SSRL to determine the antagonistic effects of these two pollutants in the bile of rabbits ingested with aqueous selenite and arsenite solutions



Gailer *et al.*, *J. Am. Chem. Soc.* 2000, 122, 19, 4637-4639

(seleno-bis(*S*-glutathionyl) arsinium ion)

Assessment of Research Opportunities and the Need for Synchrotron Radiation Facilities Relevant to Molecular Environmental Science

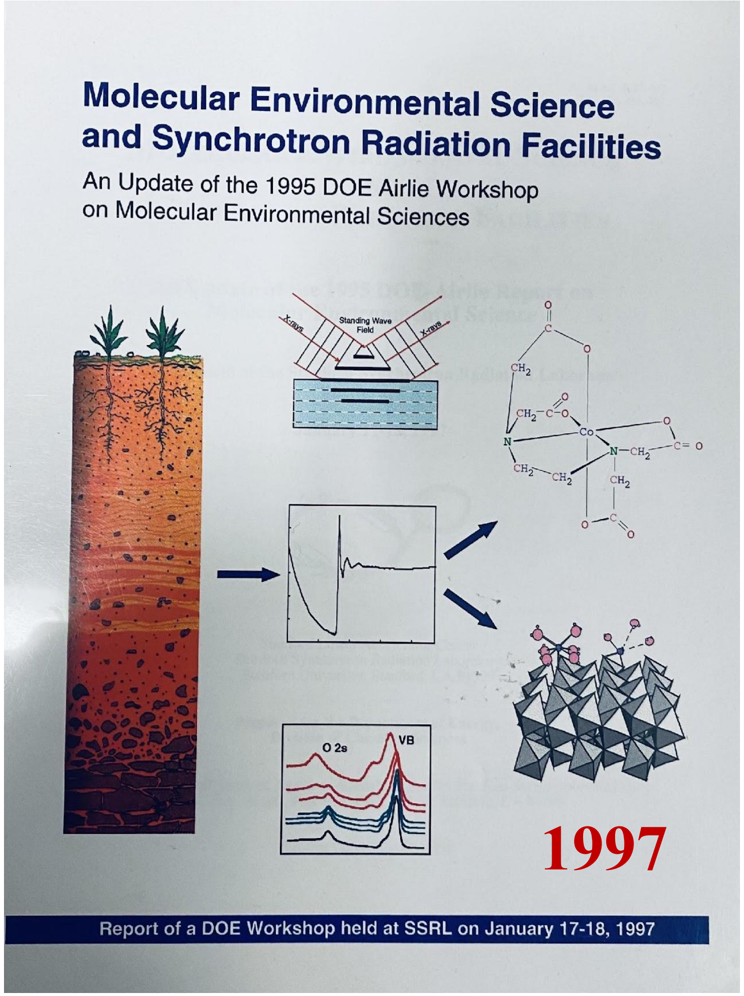


MOLECULAR ENVIRONMENTAL SCIENCE:
Speciation, Reactivity, and Mobility
of Environmental Contaminants

An Assessment
of Research Opportunities
and the Need
for Synchrotron Radiation Facilities

Report of DOE Molecular Environmental Science Workshop, July 5-8, 1995, Airlie Center, V

1995



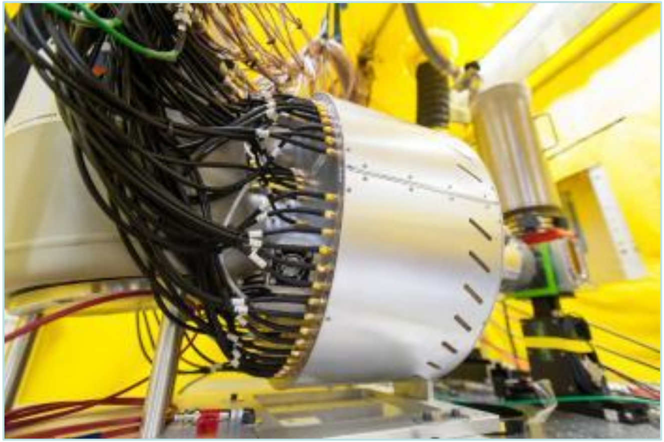
Molecular Environmental Science
and Synchrotron Radiation Facilities

An Update of the 1995 DOE Airlie Workshop
on Molecular Environmental Sciences

Report of a DOE Workshop held at SSRL on January 17-18, 1997

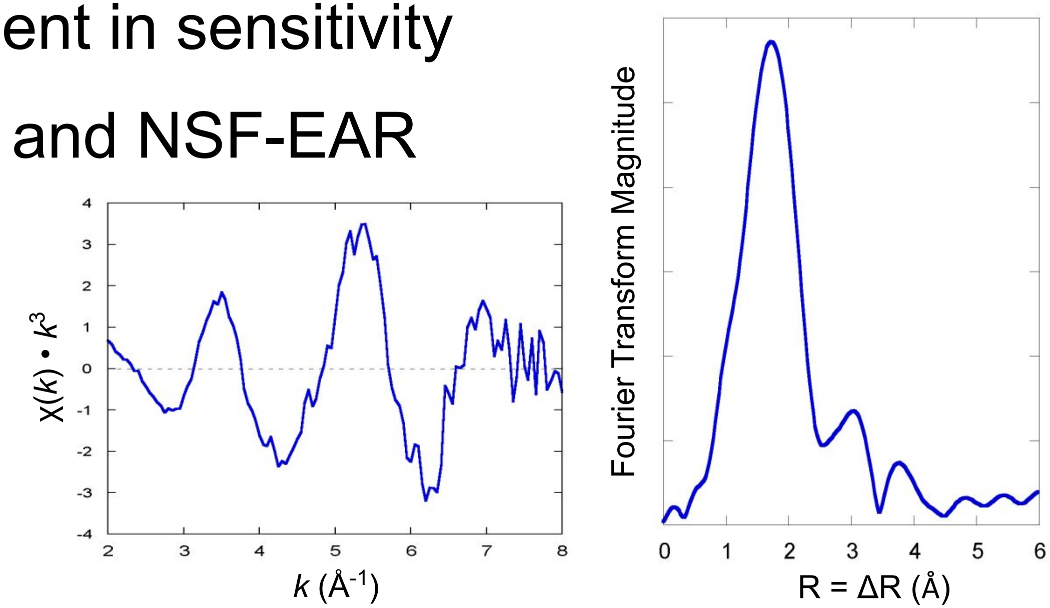
1997

BL11-2 – MEIS XAS – Special Capabilities



- 100-element Ge detector for BL11-2 delivered and commissioned – 2nd at SSRL (SMB BL9-3)
  - ~20 mm^2 active area/element
  - Thin Ti grid mask - minimize cross beam effects
- XIA XMap digital electronics
- 5- to 10-fold improvement in sensitivity
- DOE-BER, DOE-BES, and NSF-EAR

XAS data from 11 ppm U(IV) in sediments from Old Rifle, CO BER-CESD field site. The previous lower limit for U XAS analysis in such samples was 50 to 100 ppm



BL11-2 MEIS

Techniques: EXAFS/XANES, grazing-incidence EXAFS, X-ray standing-wave, reflectivity.
Instruments: Radionuclide enclosure, Grazing-incidence EXAFS spectrometer, 30-element Ge detector array, Liquid helium cryostat, Lytle-type detector, High-resolution fluorescence analyzer.

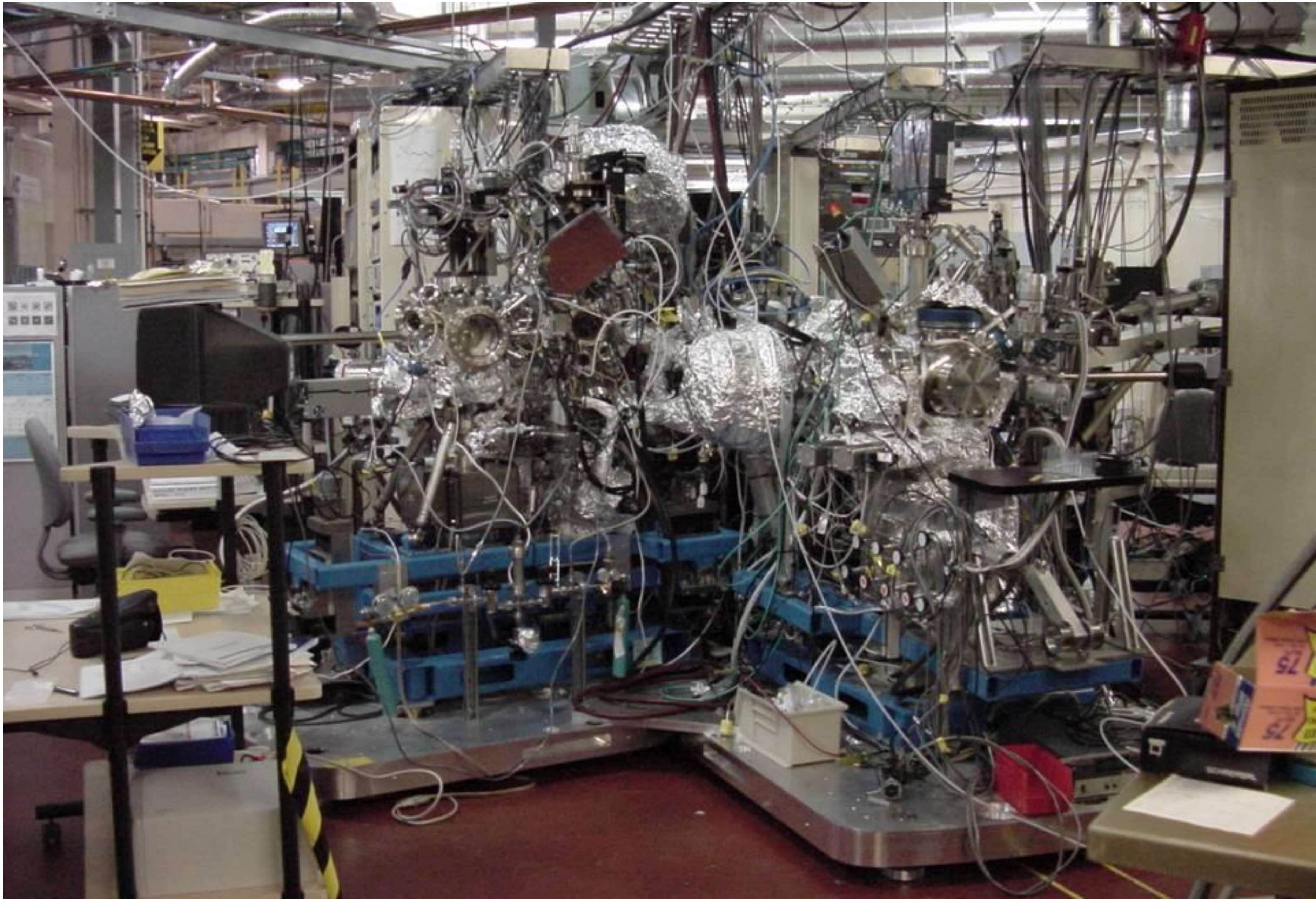
Remediation of Tc in Hanford tank wastes

Chromium speciation and mobility in a high level nuclear waste vadose zone plume

Remediation of Uranium-contaminated Water at Fry Canyon, Utah

Interaction of Toxic Metals with Complex Biofilm/Mineral/Solution Interfaces

Scanning Transmission X-ray Microscopy and *In-Situ* Ambient Pressure X-ray Photoelectron Spectroscopy on Beamline 11.0.2 at the Advanced Light Source



Two Leaders at DOE-Basic Energy Sciences Who Were Strong Supporters of the Development of Molecular Environmental Science at SSRL and Other National Labs

Dr. Patricia Dehmer,
Head of DOE-BES

Dr. Robert Marianelli,
Director, DOE-Chemical
Sciences Division

Early Scientific Contributors to the Development of Molecular Environmental Science at SSRL

- Gordon Brown (SSRL and Stanford University)** and grad students/postdocs
- Kim Hayes (Stanford University and University of Michigan)
- Britt Hedman (SSRL)
- Keith Hodgson (SSRL and Stanford University)
- Artie Bienenstock (SSRL and Stanford University)
- Steve Conradson (LANL)
- David Clark (LANL)
- David Morris (LANL)
- David Shuh (LBNL)**
- Norman Edelstein (LBNL)
- George Parks (Stanford University)**
- Jim Leckie (Stanford University)**
- Georges Calas, Guillaume Morin, and Karim Benzerara (Sorbonne University, Paris)**
- Glenn Waychunas (Stanford University and LBNL)
- Anders Nilsson (SSRL and University of Stockholm)**
- Alfred Spormann (Stanford University)**
- James Rytuba**, Jim Davis, and Chris Fuller (USGS – Menlo Park)
- Tetsu Tokunaga (LBNL)**
- Ingrid Pickering and Graham George (SSRL and University of Saskatchewan)
- Roger Prince (Exxon Mobil)
- John Bargar (SSRL and PNNL)
- Sam Webb, Adam Jew, Kristen Boye (SSRL)
- Scott Fendorf (Stanford University)**
- Greg Lowry (Carnegie Mellon University)**
- Clement Levard (University Marsailles)**
- John Zachara and Ann Chaka (PNNL)**
- Satish Myneni (LBNL and Princeton University)••

** Members of the NSF-DOE Stanford Molecular Environmental Science Institute (2004-2011) and/or the NSF-EPA Center for Environmental Implications for Nanotechnology (2008-2017)

Types of Chemical Reactions at Metal Oxide/Water Interface

(after Stumm and Morgan, *Aquatic Chemistry* (3rd Ed.), 1996)

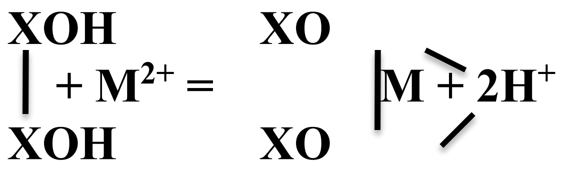
Hydrolysis (Acid-Base)

$XOH_2^+ = XOH + H^+$

$XOH = XO^- + H^+$

Adsorption

$XOH + M^{2+} = XOM^+ + H^+$



$$\begin{array}{l} XOH \\ | \\ XOH \end{array} + M^{2+} = \left.\begin{array}{l} XO \\ \\ XO \end{array}\right| \begin{array}{l} \diagdown \\ M \\ \diagup \end{array} + 2H^+$$

Ligand Exchange

$XOH + ROH = XOR + H_2O$

Electron Transfer

$H_3AsO_4\text{-}Fe(OH)_3 + 5H^+ + 3e^- = Fe^{2+} + H_3AsO_3 + 4H_2O$

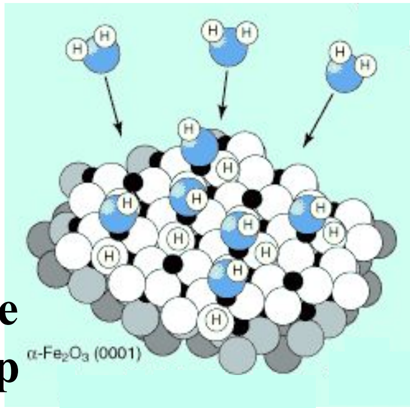
H-Bond Formation

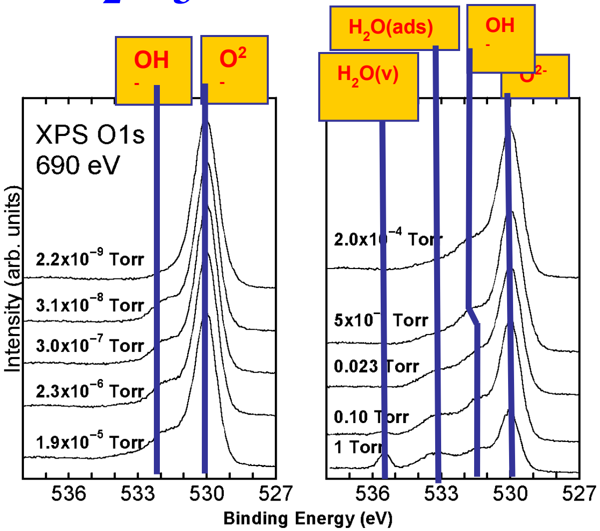
$XOH + M^{2+}(H_2O)_6 = XOH\cdots(H_2O)_6M^{2+}$

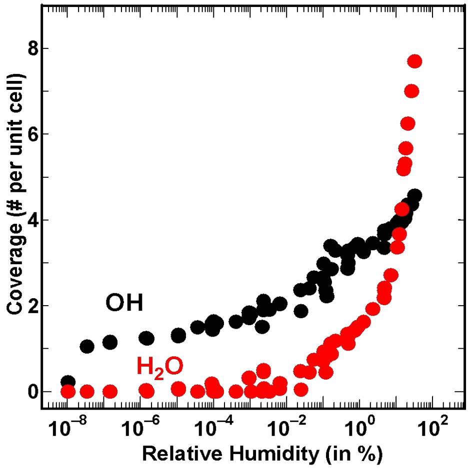
Reaction of H_2O with α-Fe_2O_3(0001) at T = 23°C

(Yamamoto *et al.*, *J. Phys. Chem. C* **20 10,** *114*, 2256)

Bridging the pressure gap







Hydroxylation (OH)

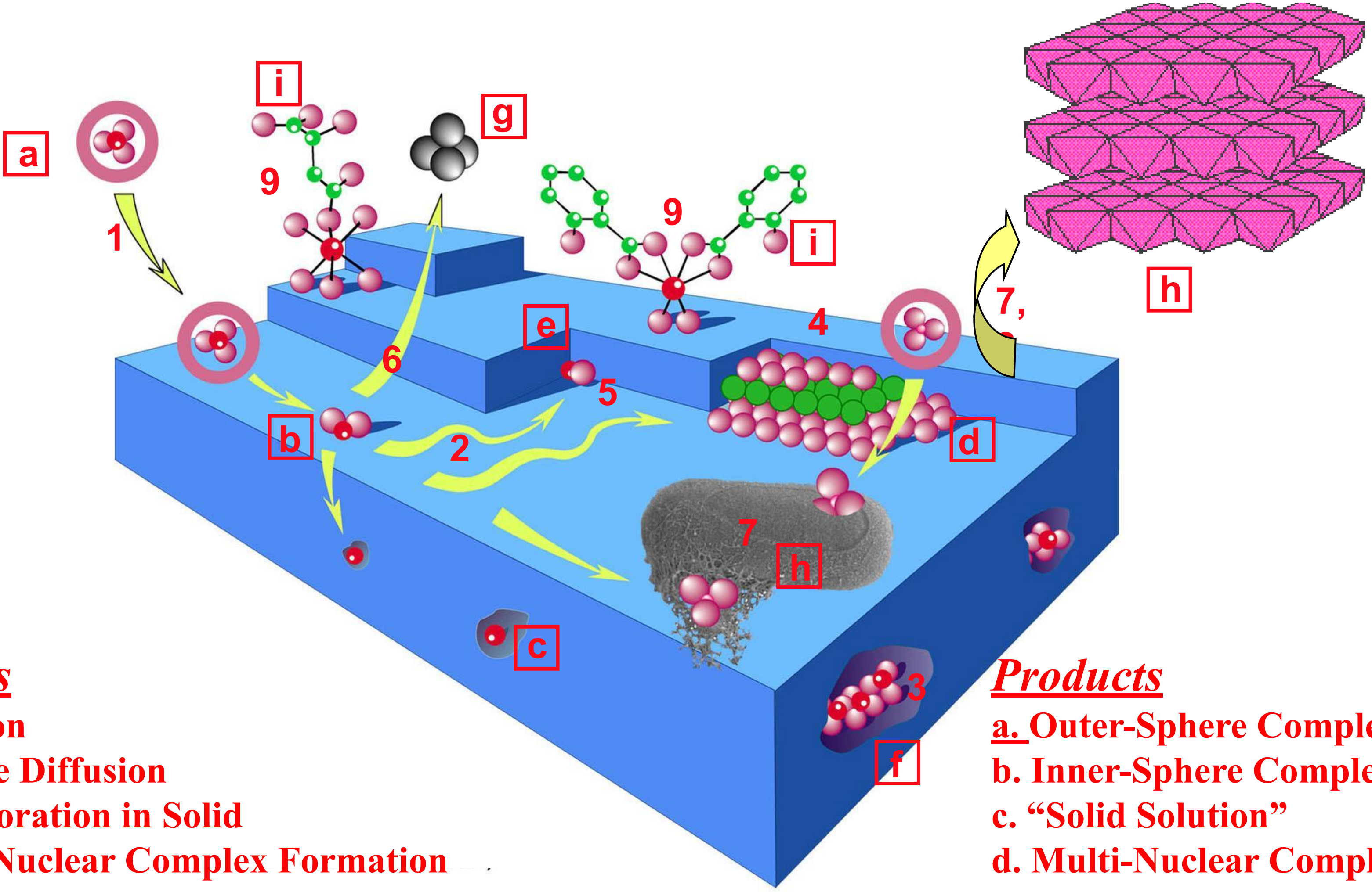
- Occurs rapidly even at RH < ~10^{-7} %
  - The rate of hydroxylation increases after the onset of water adsorption.

Hydration (H_2O)

- Onset is ~1x10^{-5} % RH at room temperature, changes (10^{-5}~10^{-2} % RH) with temperature
- Proceeds more rapidly at coverage of > ~2 water molecules per unit cell, suggesting cooperative effects

Sorption Processes at Solid/Aqueous Solution Interfaces

(after Manceau *et al.*, *Rev. Mineral.* **2002**, *49*, 341)



Processes

1. Sorption
2. Surface Diffusion
3. Incorporation in Solid
4. Multi-Nuclear Complex Formation
5. Diffusion to Step-Edge Defect
6. Desorption
7. Dissolution
8. Precipitation
9. Ternary Complex Formation

Products

a. Outer-Sphere Complex
b. Inner-Sphere Complex
c. "Solid Solution"
d. Multi-Nuclear Complex
e. Sorption at Step-Edge
f. "Solid Solution"
g. Solution Complex
h. Precipitate
i. Ternary Complex

How Can We Study Adsorbate Reactions at Aqueous Solution/Metal Oxide Interfaces at the Molecular Level?

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy

Electron Spin (Paramagnetic) Resonance (ESR/EPR) Spectroscopy

Nuclear Magnetic Resonance (NMR) Spectroscopy

Scanning Tunneling/Atomic Force Microscopy (STM/AFM)

X-ray Photoelectron (Photoemission) Spectroscopy (XPS)

X-ray Absorption Fine Structure (XAFS) Spectroscopy (EXAFS & XANES)

- 1900-1987: 4 XAFS studies of sorption complexes
- 1988-present: > 1,000 XAFS studies of sorption complexes at mineral/aqueous solution interfaces

Long-Period X-ray Standing Wave Fluorescence Yield (LP-XSW-FY) Spectroscopy

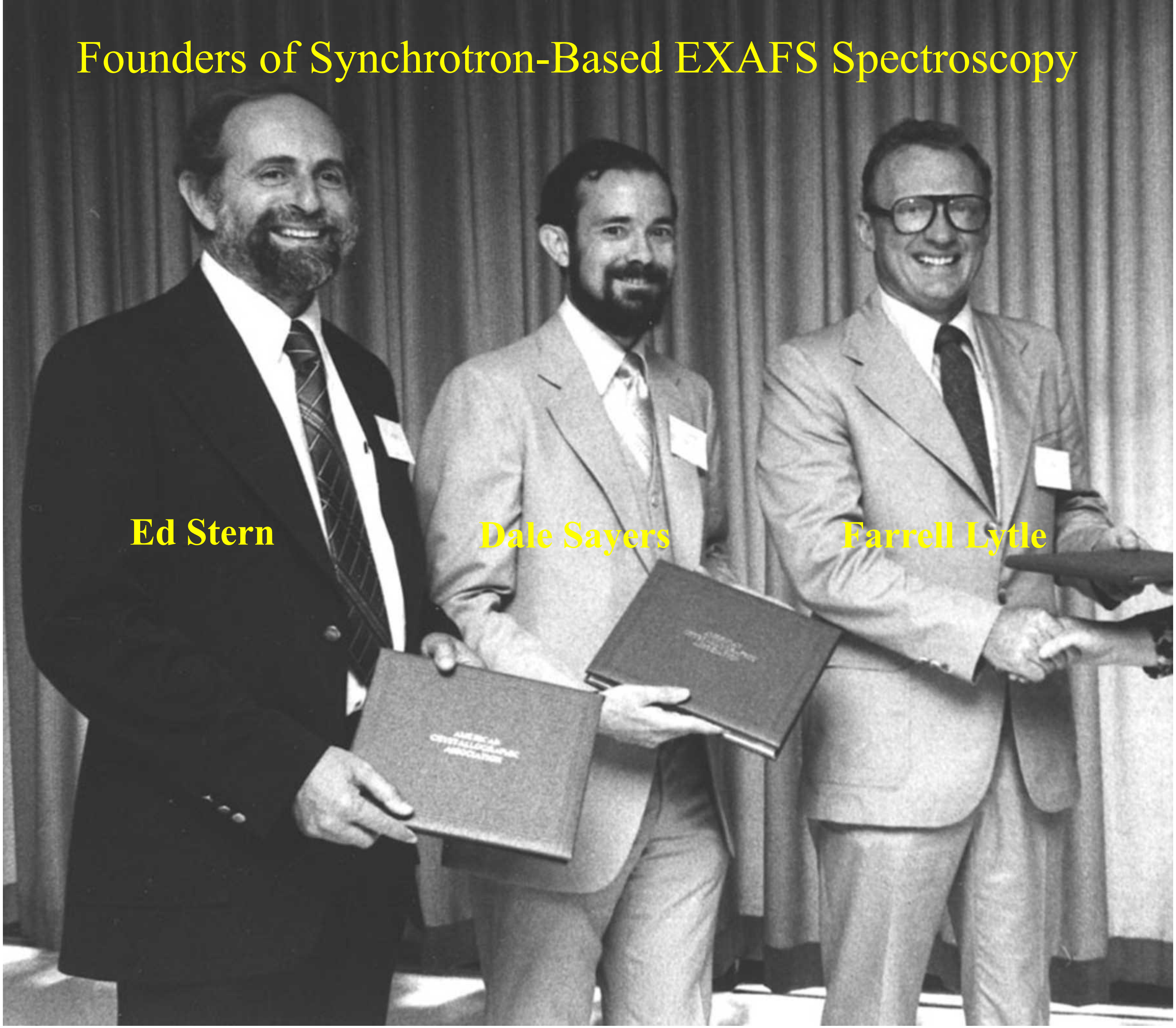
Bragg X-ray Standing Wave Spectroscopy

Crystal Truncation Rod (CTR) Diffraction

Resonant Anomalous X-ray Reflectivity (RAXR) and Related Reflectivity Methods

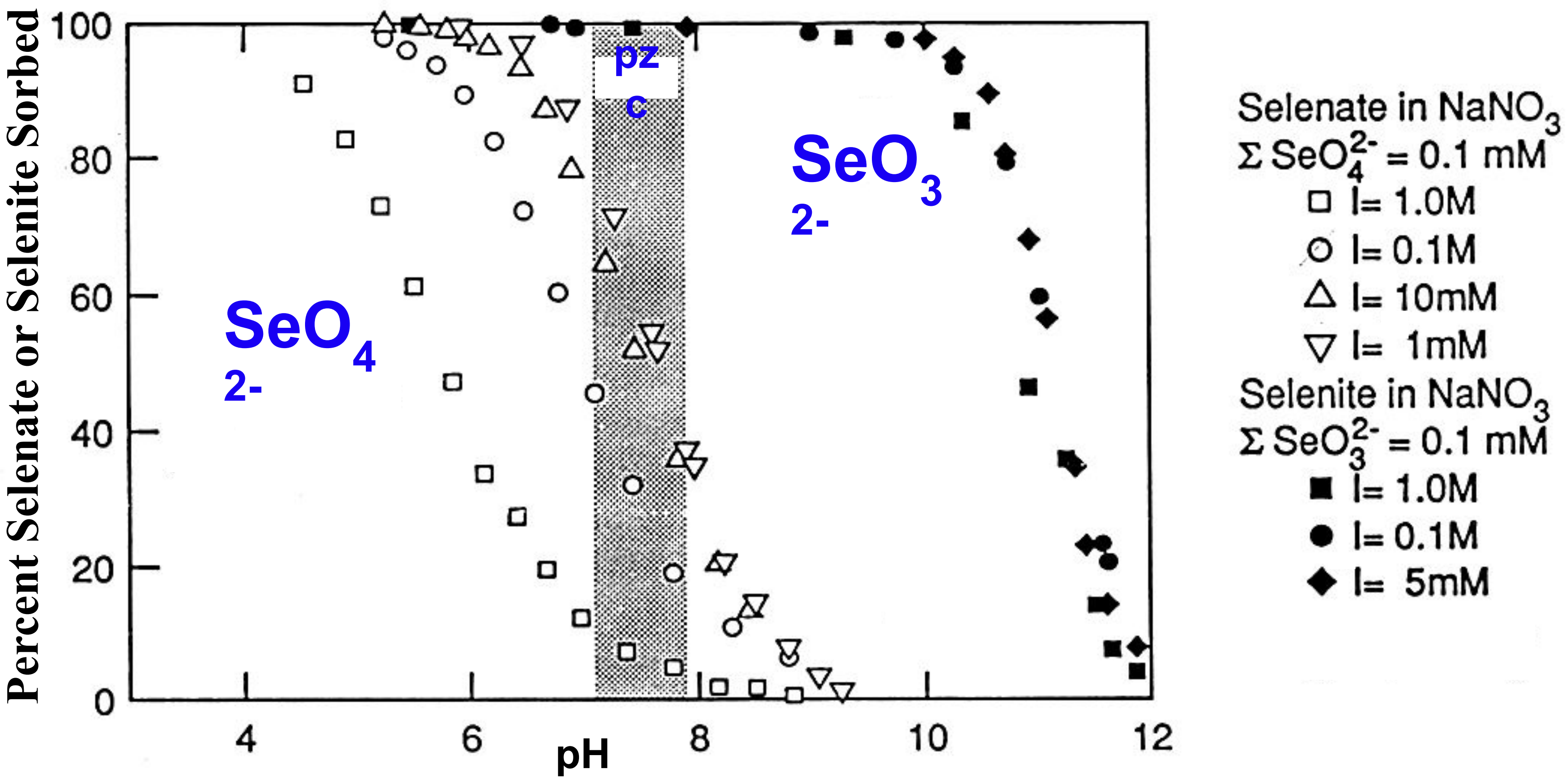
Non-Linear Optical Methods

Founders of Synchrotron-Based EXAFS Spectroscopy



Sorption of Selenate and Selenite on α-FeOOH

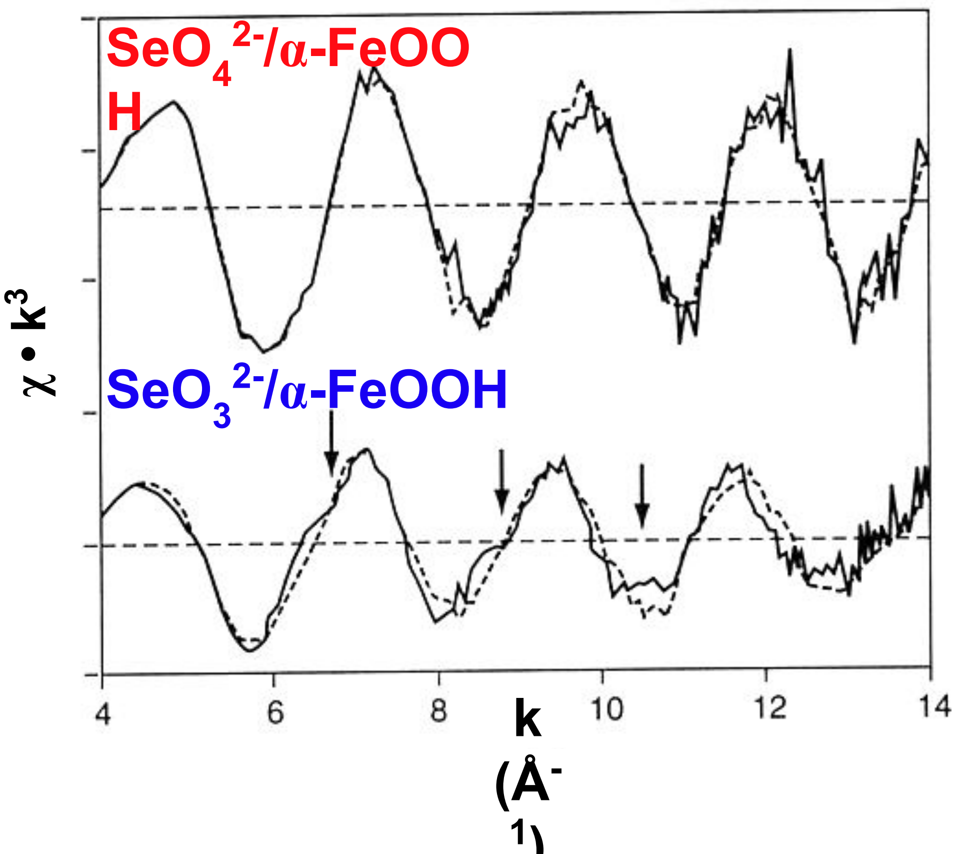
(Hayes *et al*., *J. Colloid Interface Sci*. 1988, *125*, 717-726)

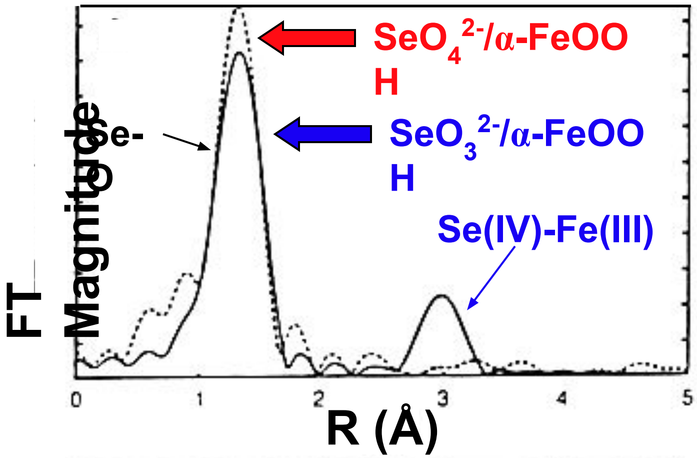


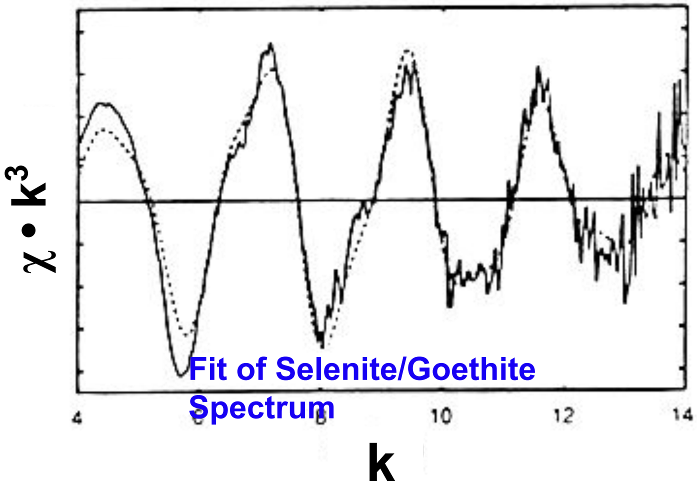
Conclusion: Ionic strength does not affect SeO_3^{2-} sorption, but it has a major effect on SeO_4^{2-} sorption, which implies that SeO_3^{2-} sorbs more strongly than SeO_4^{2-} on goethite.

Se K-edge EXAFS Spectra and FT's of Selenate and Selenite Sorbed on α-FeOOH

(Hayes *et al.*, *Science* 1987, *238*, 783-786)



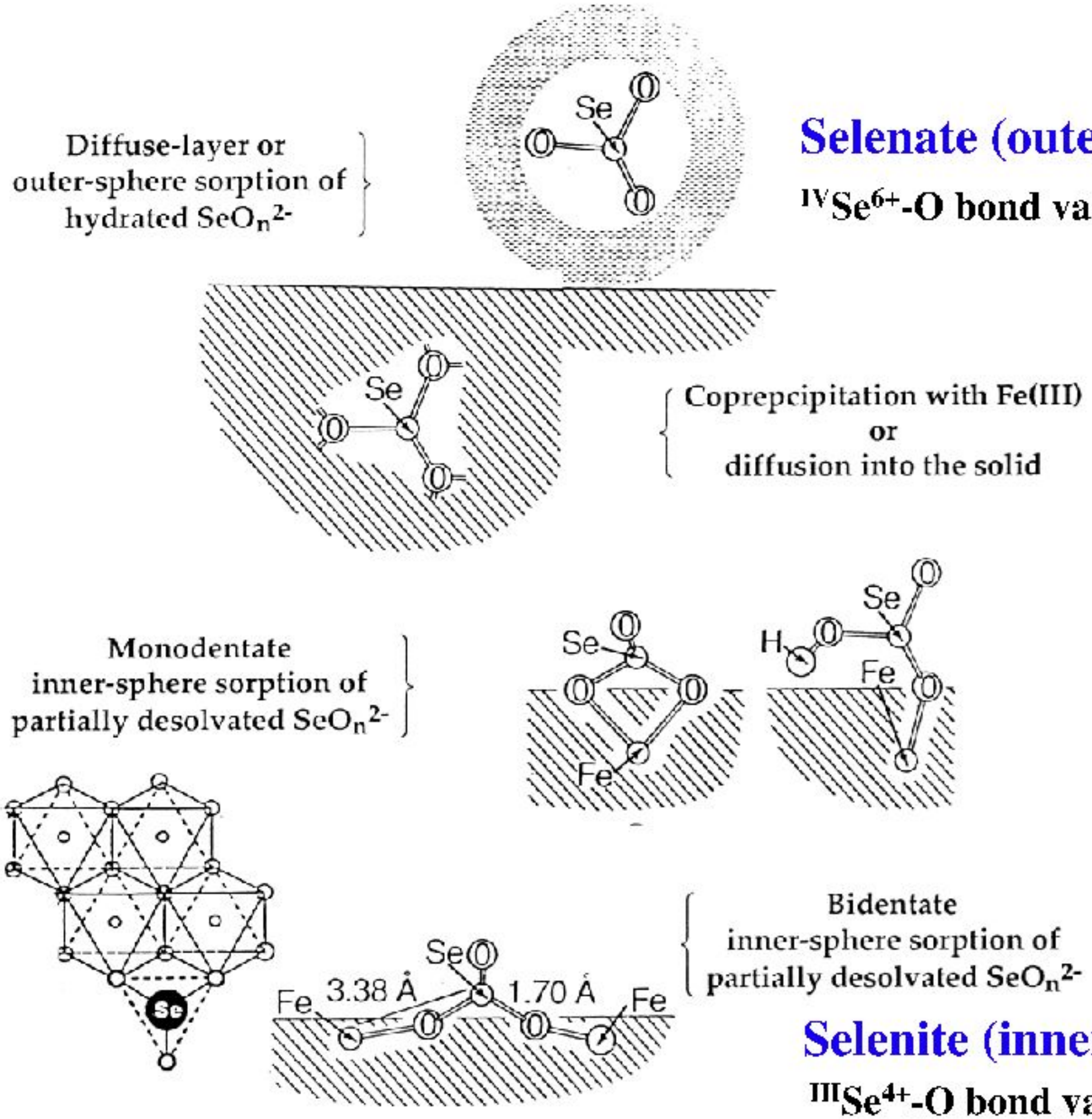




Conclusion: Selenite has 2nd-neighbor irons; Selenate has no 2nd-neighbor irons.

Modes of Sorption of Selenate and Selenite on α-FeOOH

(Hayes *et al.*, *Science* 1987, *238*, 783-786)



Selenate (outer-sphere)

$^{IV}Se^{6+}$-O bond valence = 1.5 v.u.

Selenite (inner-sphere)

$^{III}Se^{4+}$-O bond valence = 1.33 v.u.

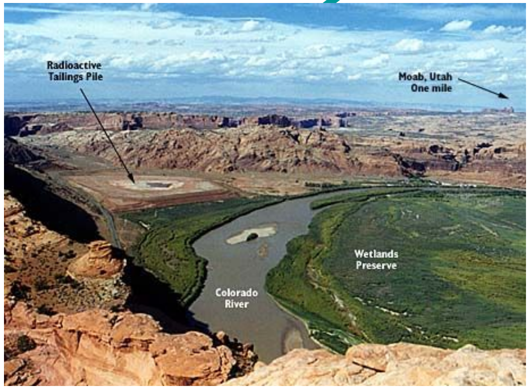
RADIOACTIVE WASTE: A major driver of molecular environmental science research: Speciation, Migration

Aerial View of Area 300 North Process Pond after 2001-2002 Remediation Effort

Examples of Radionuclide Pollution in the United States

Tank Farms
Hanford Site, WA

Waste Pits
Fernald, OH

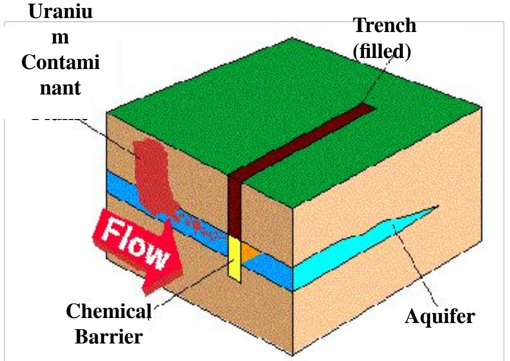


Uranium Tailings Pile
near Moab, UT

Plutonium Processing Facility
Rocky Flats, CO

Disposal Ponds
Oak Ridge, TN

In-situ Reactive Barrier at Fry Canyon, UT



Schematic Diagram of a Reactive Barrier
(modified after Morrison and Spangler, 1992)

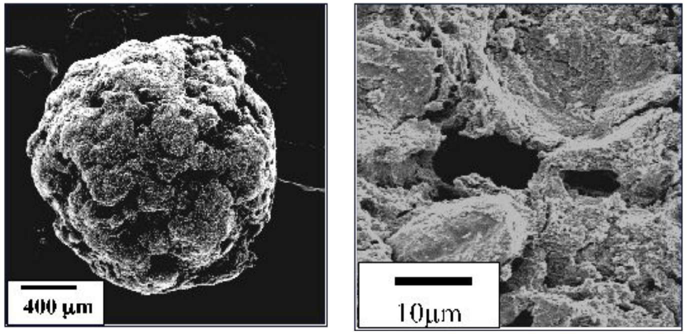
- U(VI)-contaminated groundwater
- Intercepted by reactive barrier
- Fill material (bone char) releases PO_4
- *Hypothesis: precipitation of U(VI)-phosphate (autunite) attenuates U(VI)*

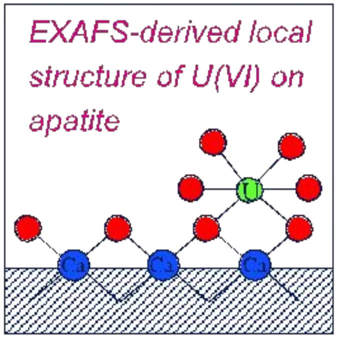
Synchrotron-based XAFS and XRD

- XAFS: inconsistent with local structure in apatite and U(VI)-phosphate
- XRD: No U-containing crystalline phases; U solid solution in apatite not observed
- TEM & Filtration: no colloidal U-phases
- *U(VI) attenuated by chemisorption on apatite surfaces*

Installation of Fry Canyon Trench

SEM Images of Bone-Char Pellets



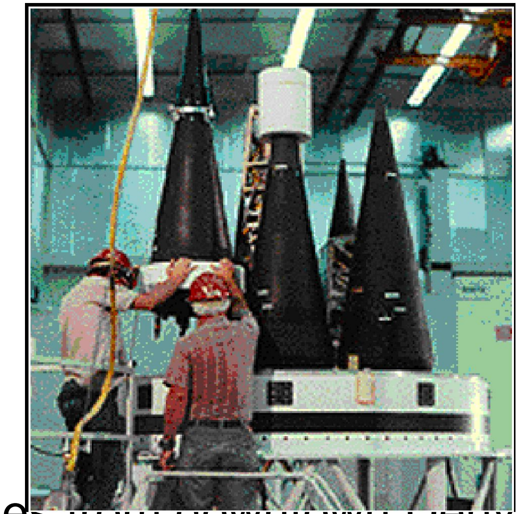

EXAFS-derived local structure of U(VI) on apatite

Impacts barrier design, cost, maintenance, life span

(Fuller *et al.*, *Environ. Sci. Technol. 36*, 158, 2002)

Environmental Stewardship - Rocky Flats Colorado

- From 1952 to 1989 the Rocky Flats Plant manufactured Pu pits for US nuclear weapons



- 16 miles from downtown Denver – 2.5 million people
- 300,000 live within Rocky Flats watershed
- A small city - 385 acre industrial area with 805 buildings surrounded by 6000 acres of controlled open space (buffer zone & security perimeter)

The Cost of Winning the Cold War

- Environmental contamination
  - Over 200 Pu fires, with major releases in 1957, 1965, and 1969 (media attention)
  - Illegal dumping & improper storage
- FBI/EPA raid shutdown Site in 1989

THE DENVER POST

June 7, 1989 *Voice of the Rocky Mountain Empire* ★★★★ 50 cents

Federal Agents Raid Rocky Flats

By Tom Graph, Peter G. Chronis, Mark Obmascik, Alan Gottlieb
Denver Post Staff
Copyright 1989, The Denver Post Corp.

JEFFERSON COUNTY – The Federal Bureau of Investigation raid Rocky Flats, the Energy Departments plutonium trigger plant near Denver.

- Sudden shutdown stranded 26 tons of Pu in various intermediate steps of processing
- 2 decades of monitoring revealed Pu/Am contamination from site operations
- EPA Superfund Site

1995: Impetus to understand Science of Pu migration

- Intense rainfall and increased Pu concentrations at surface water monitoring stations generated concern (Site personnel, regulators, citizens)
- Pu was assumed to be soluble – yet modeling efforts (K_d) predicted no transport
- Discord between data and models resulted in public mistrust / lack of confidence – concerned citizen's and antinuclear groups

Plutonium is an emotional issue - myth, mystery and misinformation

- Stakeholder and regulatory agencies could not reach consensus on cleanup
- DOE estimated cleanup to cost > $37 billion and take 70 years to complete

DOE Baseline Envir. Manage Report, **1995**

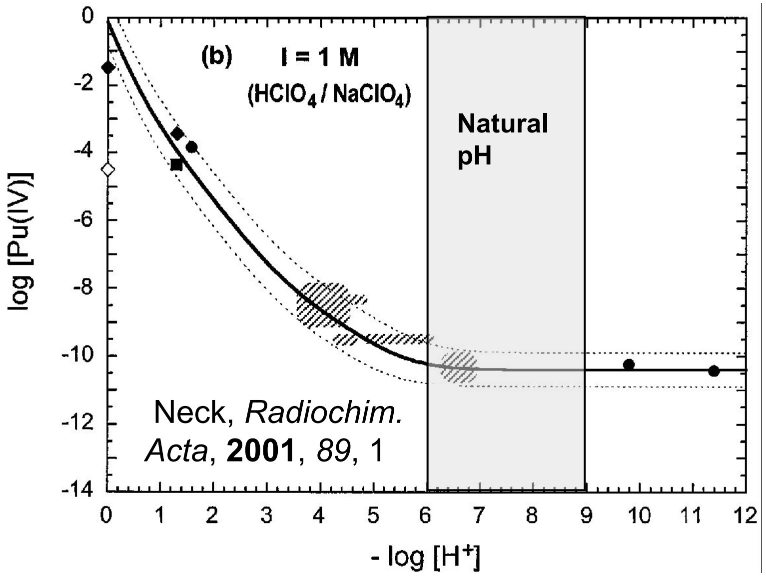
- Actinide Migration Evaluation (AME) group was formed to bring in independent expertise
- Brought scientific debate & stakeholder education to public forum

Leonard Lane **David Janecky** **David Clark** **Greg Choppin**

Expectations from Actinide Chemistry

- In nature, Pu(IV) and $PuO_2 \cdot nH_2O$ is the most stable chemical form – extremely insoluble
- Sorption on surfaces is a dominant and controlling geochemical feature of Pu
- Site-specific studies revealed Pu/Am Contamination in upper 12-20 cm of soil
- **Expert Judgment** – Pu is likely insoluble oxide form, migration occurs as colloids and particulates
  - took years of convincing
- Needed direct experimental proof of speciation to convince stakeholders
  - **Molecular Environmental Science approach - turned to XAFS**
  - SSRL system allowed rapid attempt under existing related proposals

Pu(IV) Solubility



Neck, *Radiochim. Acta*, **2001**, *89*, 1

Settling Ponds

A Paradigm Shift

- **XAFS** provided first definitive proof that Pu in RFETS environmental media predominantly in oxidation state **IV**, and chemical form $\mathbf{PuO_2 \cdot nH_2O}$
- **Cross-flow ultrafiltration**: Pu is associated with small particles (< 2µm, 10 – 20% colloidal)

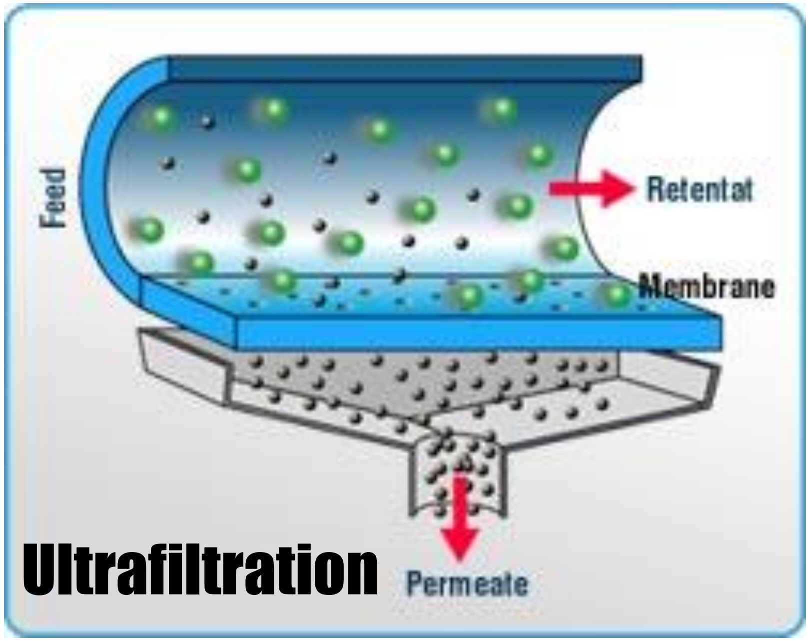
Santschi, *Environ. Sci. Technol*. **2002**, *36*, 3711-3719

- **Plutonium transport occurs by dispersal of particulates and colloids; not by soluble species migration**
- **Stakeholder epiphany:**

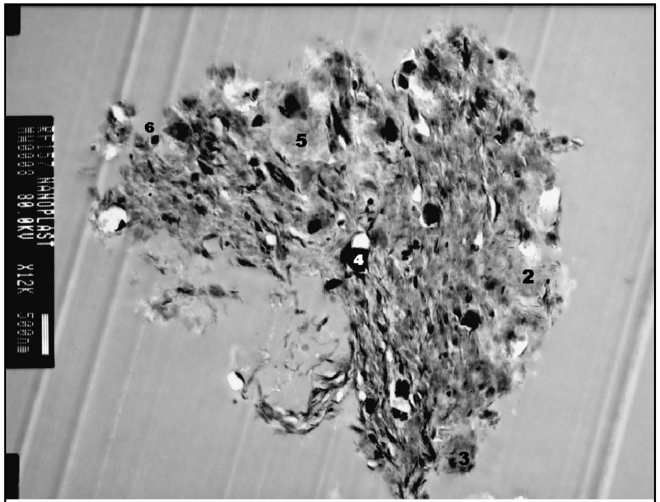
insolube ≠ immoble

- Soluble transport models were indefensible
- Wind & surface water erosion models developed

Physics Today, **2006**, *59*, 34-40



Ultrafiltration/SEM



TEM pictures of colloid samples. RF157N-2

Rocky Flats, CO 1995

Rocky Flats, CO 2005

Scientific Understanding Brought Clarity To Issues

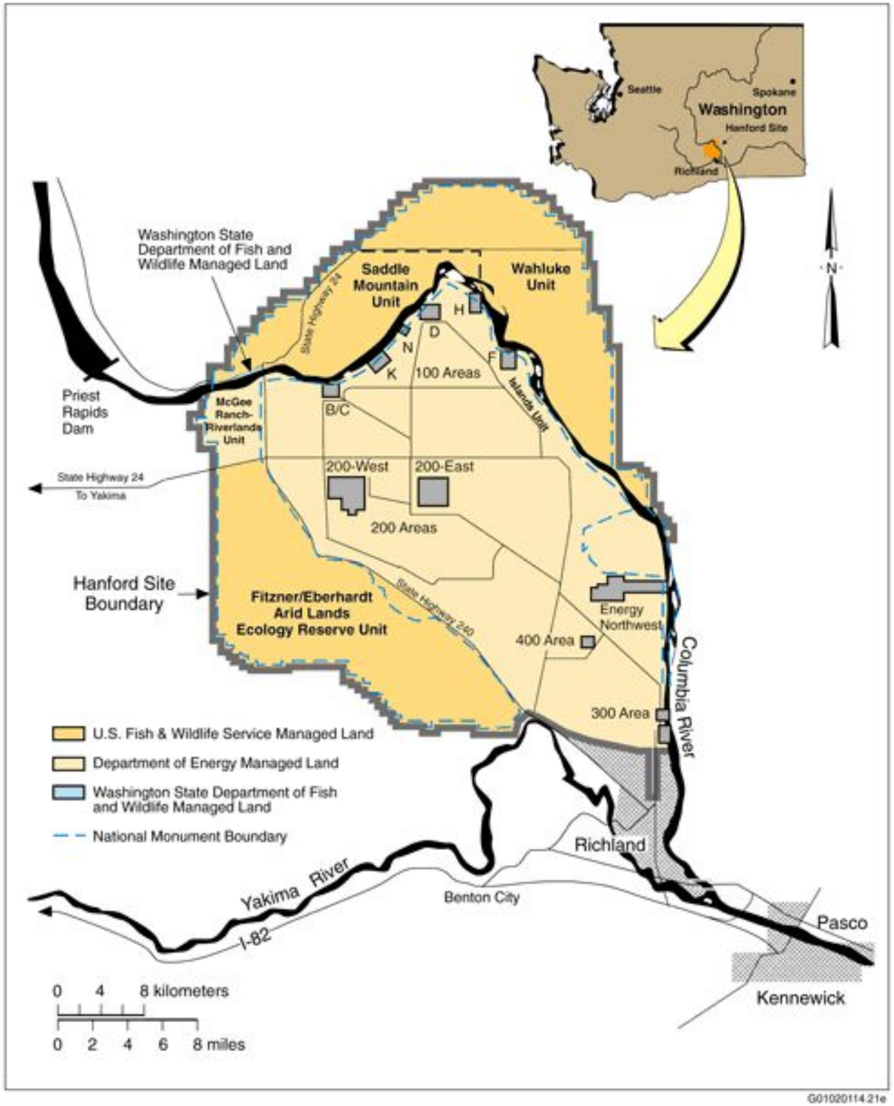
- The scientific case for particulate transport of Pu/Am established the dominance of physical mechanisms
  - SSRL played key role
- Good scientific understanding in public interest brought clarity and focus to real issues of migration
- Developed a more defined scope with clearer endpoint that allowed
  - Most extensive cleanup in history of Superfund legislation
  - Finished one year ahead of schedule
  - $billions in taxpayer savings
  - Removed $600-million plus annual liability from DOE budget forever

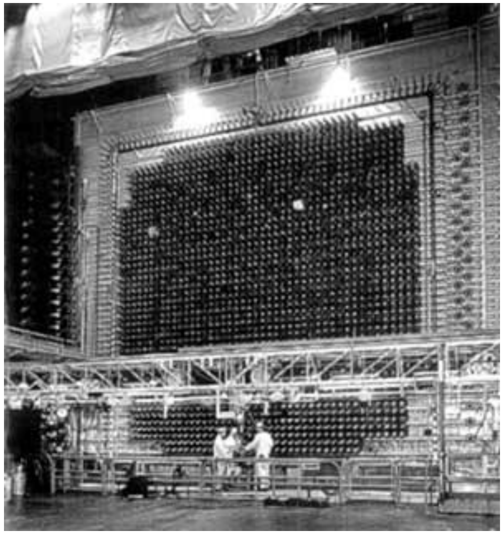
"This represents a historic milestone in closing Rocky Flats and the most significant cleanup accomplishment to date in the DOE complex,"

Secretary Abraham July 14, 2004

The Hanford Site

- WW II and Cold War sit of Pu production for nuclear weapons
- Reactors operated from 1944 to 1990



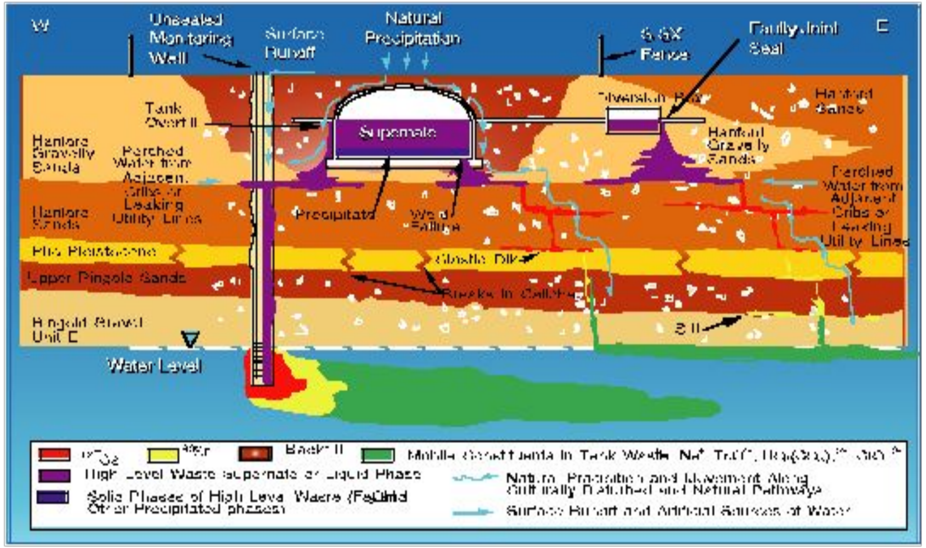


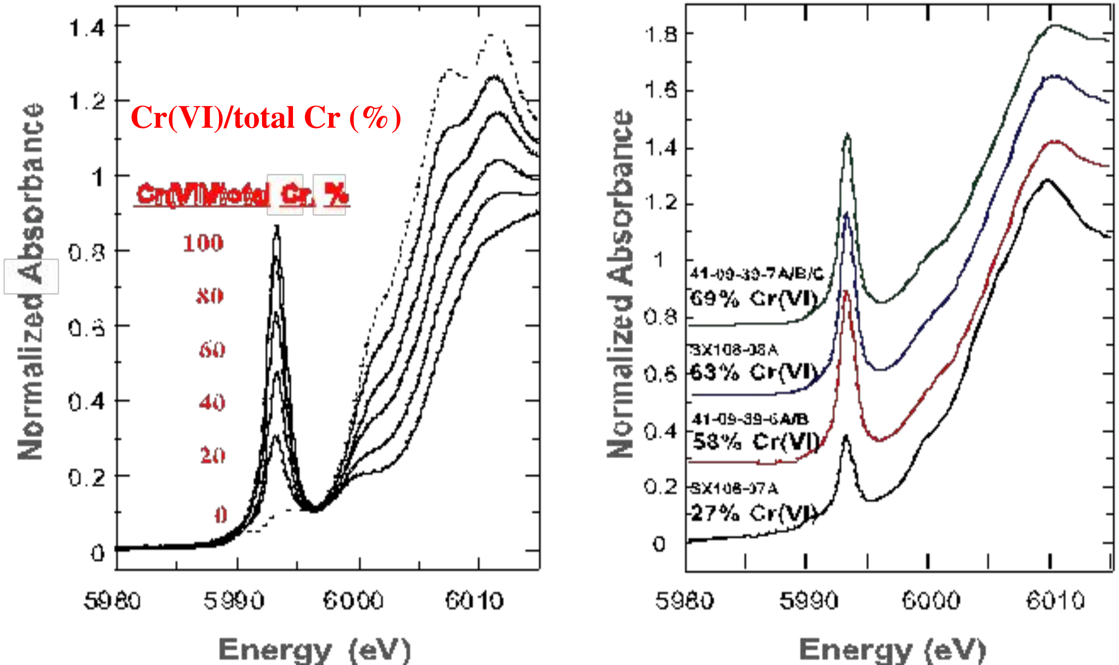
- Located on Columbia River
  - A source of cooling water

Hanford Tank Farm Under Construction

Cr Speciation in the Hanford Tank Farm Vadose Zone

(Zachara *et al*., *Geochim. Cosmochim. Acta* **68**, 13, 2004)

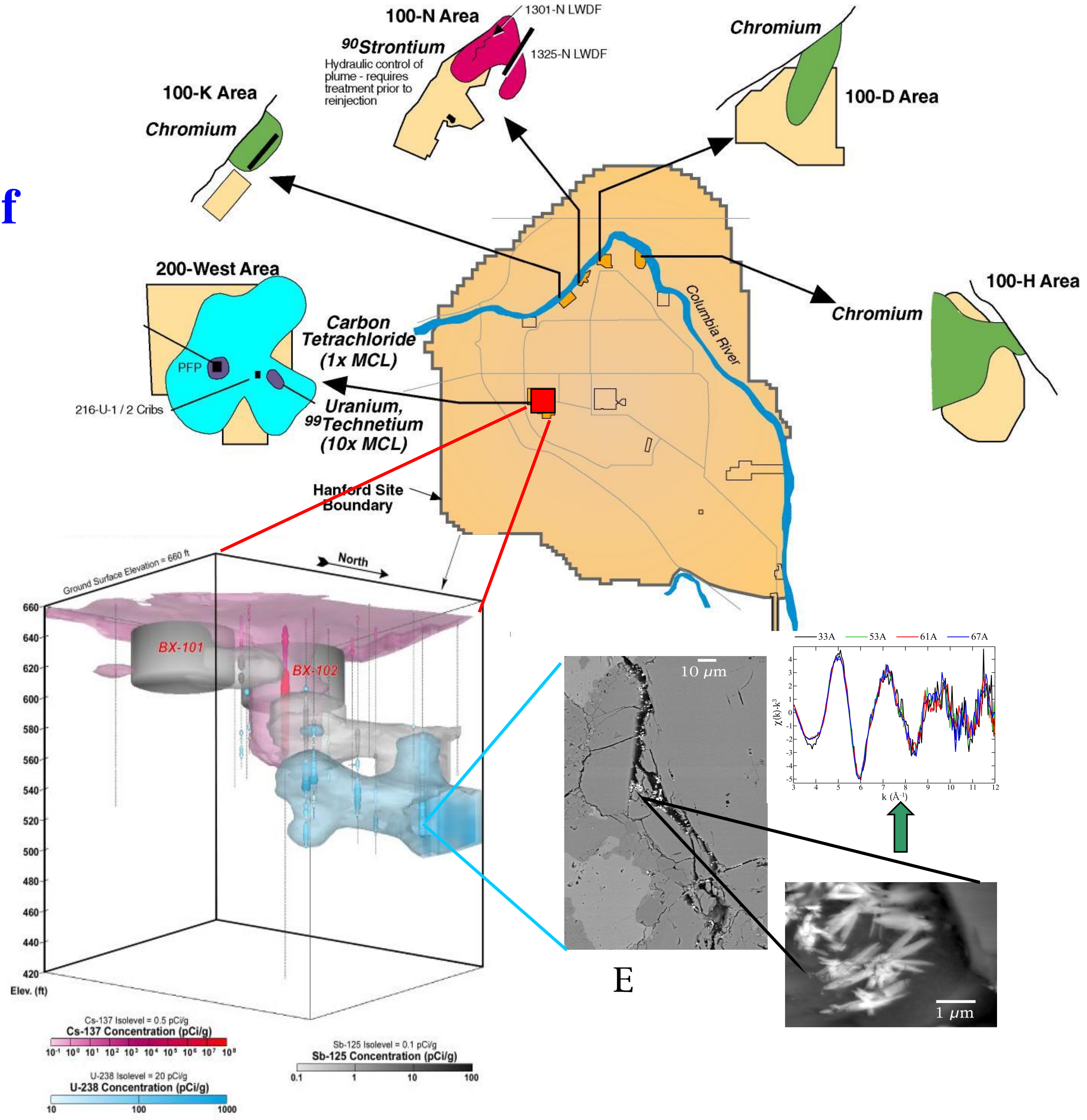




(SSRL)

Speciation of Uranium in Vadose Zone of Hanford Area 200

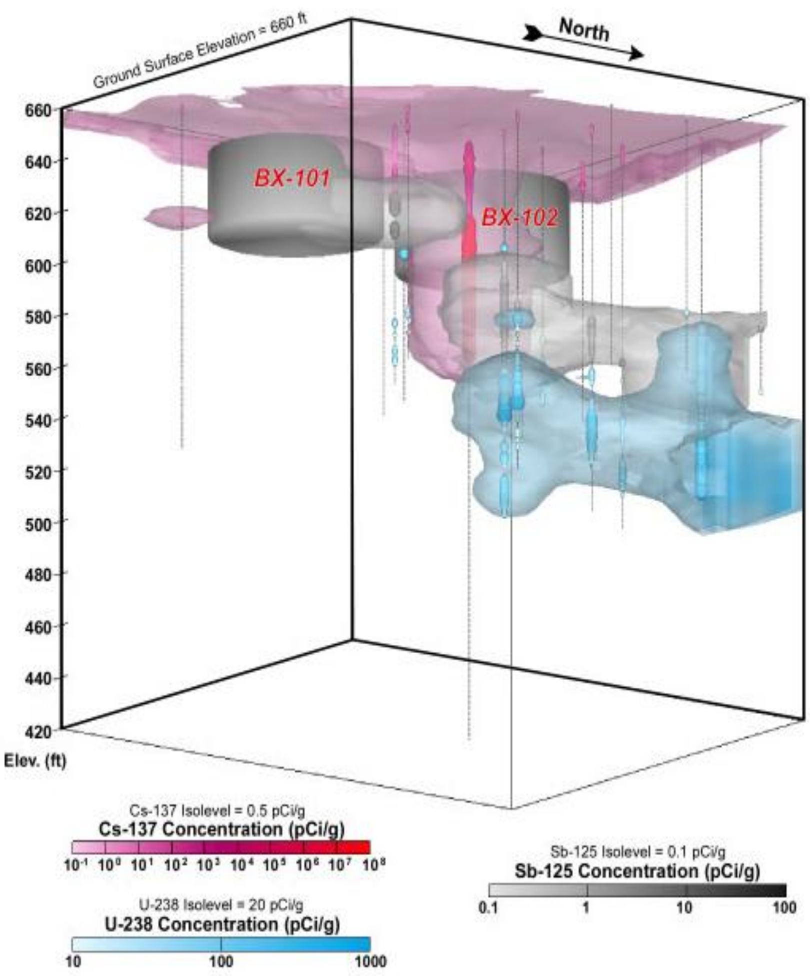
Catalano *et al.*,
Environ. Sci. Technol.
(2004)



Synchrotron-Based Studies of Uranium Speciation in Contaminated Sediments and Related Model System

Leakage at Tank BX-102

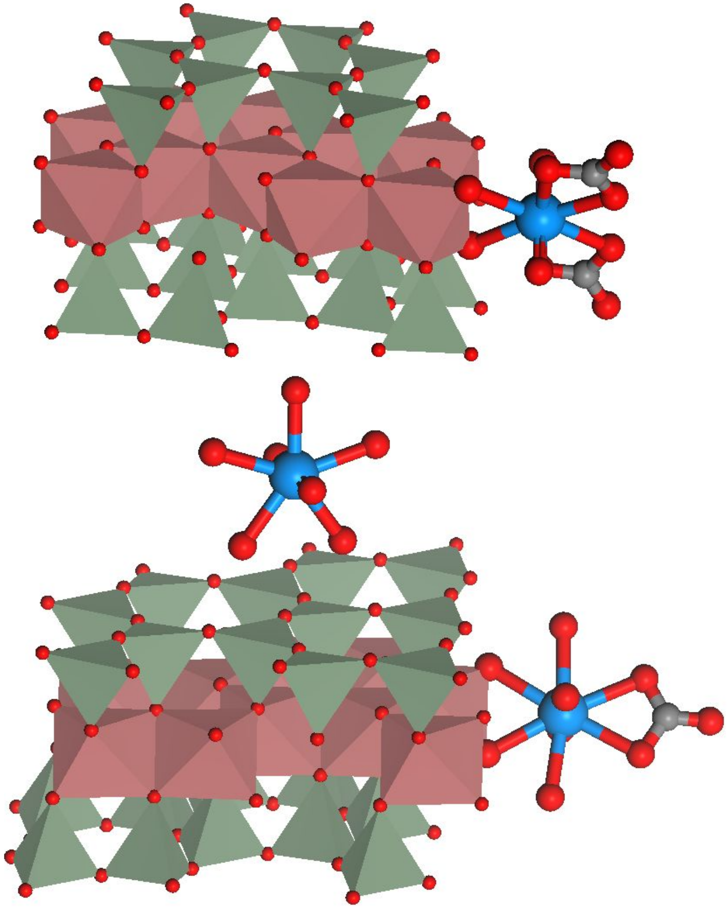
- **300,000 L of waste containing 7 to 8 metric tons of U spilled in 1951**
- **Waste composition**
  - **pH 10**
  - **0.5 M uranium**
  - **0.6 M carbonate**
  - **0.36 M phosphate**
  - **3.0 M sodium**
  - **Numerous fission products**
- **Extensive vadose zone plumes developed**



A.W. Pearsons (2000) *Hanford Tank Farms Vadose Zone Monitoring Project, BX Tank Farm Addendum.* U.S. Department of Energy GJO-98-40-TARA, GJO-HAN-19

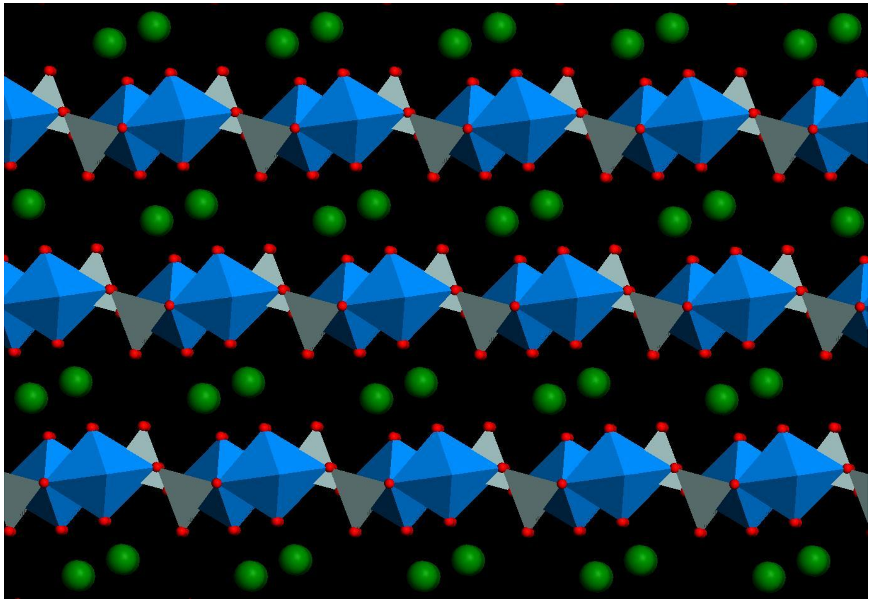
What is the speciation of uranium in the Hanford Vadose zone?

Adsorbed to Mineral Surfaces



Uranyl and uranyl carbonate complexes sorbed to clay

Precipitated as a Solid Phase (if so, how insoluble?)



Na-Boltwoodite ($NaUO_2SiO_3OH\cdot1.5H_2O$)

Overview of the Development of MES Over the Past 35 Years at SSRL

There has been an enormous increase in XAS and micro-XAS studies of the molecular-scale speciation, reactivity, and spatial distribution of environmental contaminants and pollutants in model systems and in complex environmental samples since 1987.

The realization that most chemical reactions involving environmental contaminants and pollutants take place at interfaces, particularly the interfaces between water and naturally occurring solids, has led to several thousand studies of environmental interfaces and the hydrolysis, adsorption, ligand exchange, and electron transfer reactions at these interfaces over the past 35 years.

The development of new beam lines at SSRL (BL 11-2) and ALS (BL 11.0.2) optimized for Molecular Environmental Science research in the mid- to late 1990's has resulted in a major increase in the interest in this growing multidisciplinary/interdisciplinary field, particularly at SSRL.

MES Beamline 11-2 and hutch were designed to perform safe XAS studies of samples containing radioactive pollutants, such as soils polluted by uranium, neptunium, and plutonium and the Pu pits in nuclear weapons. Since its commissioning in 1996, there has been no accidental release of radionuclides at SSRL.

XAS studies at SSRL of the speciation of U and Pu in contaminated soils, groundwater aquifers, and buildings, such as those at Rocky Flats, CO and Hanford, WA have revealed the molecular-level speciation of these radionuclides, leading to billions of dollars in taxpayer savings and the safe disposal of legacy nuclear materials used in nuclear weapons and spent nuclear fuels from civilian nuclear power. However, there is still much to do.

Thoughts on the Future of Molecular Environmental Science and Chemistry at Environmental Interfaces

As embodied in a quotation from
Sir Winston Churchill
from a speech he made in 1942:

"Now this is not the end. It is not even the beginning of the end. But it is perhaps the end of the beginning."

Anders Nilsson and Bride
Maria Timoshenko in Stockholm
Married on April 15, 2023