Dealing with radiation damage in Biogeochemical systems

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NSLS/NSLS-II & CFN Joint Users' Meeting
Brookhaven National Laboratory
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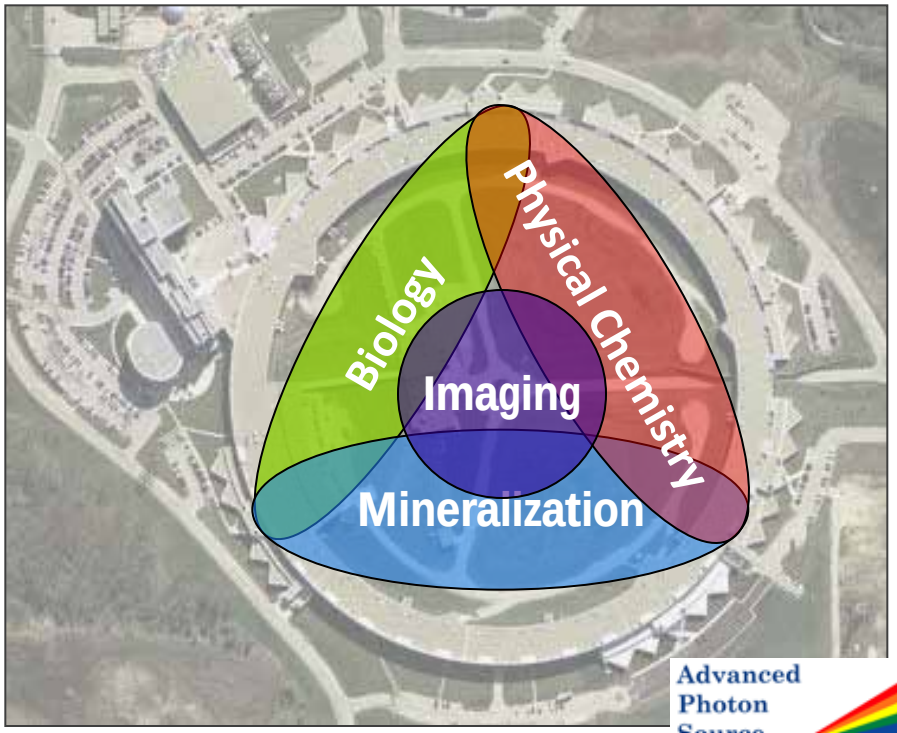
Molecular Environmental Science @ANL



Advanced Photon Source
Argonne National Laboratory

U. S. Department of Energy Office of Science
Subsurface Biogeochemical Research

U.S. DEPARTMENT OF ENERGY

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Baohua Gu, Scott Brooks, Dave Watson

Funding:
Argonne Subsurface Science Scientific Focus Area

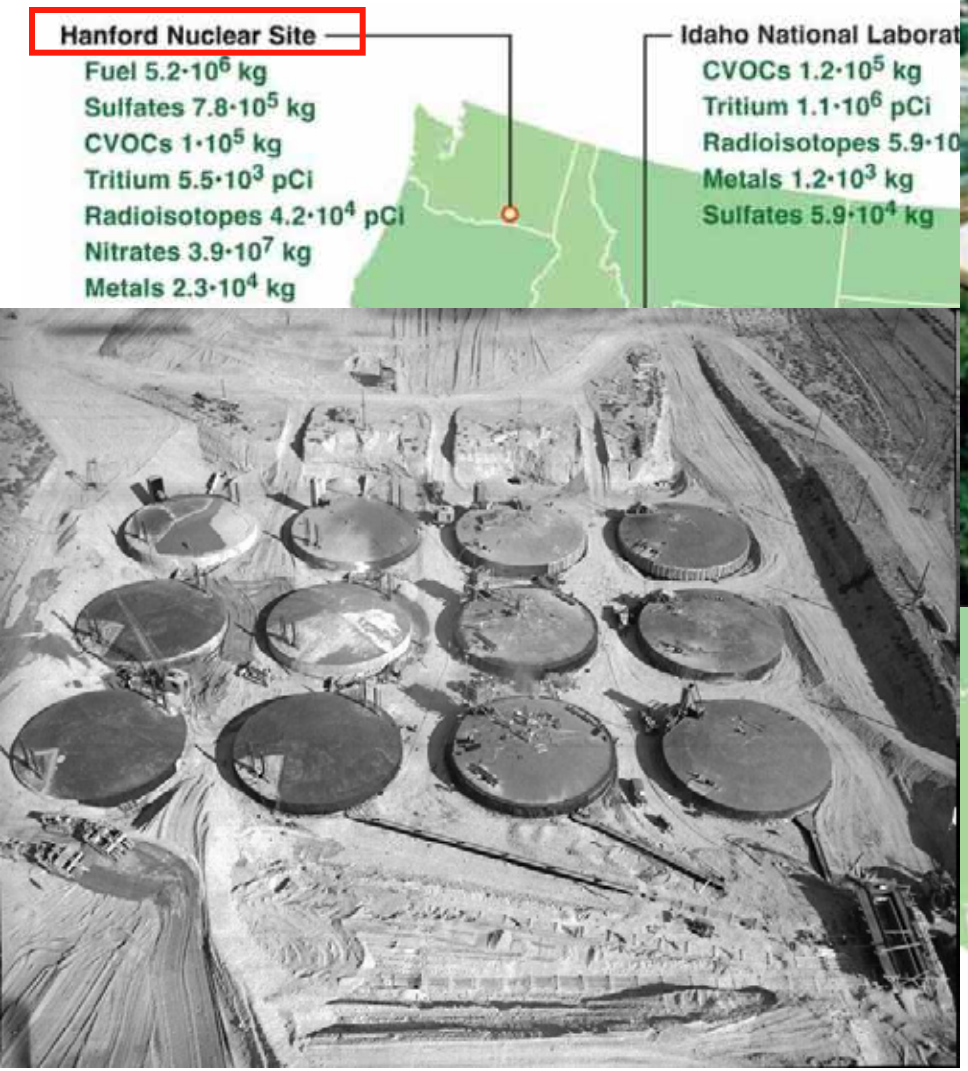
U. S. Department of Energy Office of Science
Subsurface Biogeochemical Research

Outline

- Argonne Subsurface Biogeochemistry Program
  - Hg and U contamination
- The need for intense synchrotron radiation
- Flux densities at the Advanced Photon Source
- XAS and XRF experiments
- Summary

Funding:
Argonne Subsurface Science Scientific Focus Area

Contamination, DOE



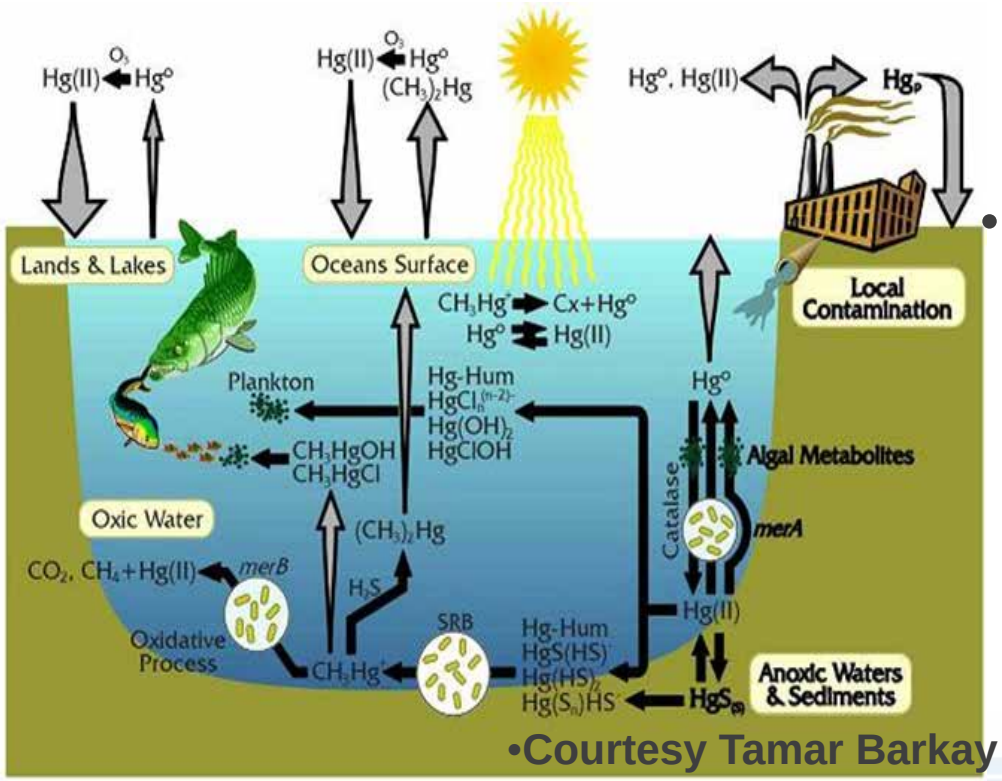
Terry Hazen, 2009 ERSP Meeting presentation

Cold War Legacy of Hg contamination at Oak Ridge

On May 17, 1983 Department of Energy released declassified version of 1977 report on mercury losses, revealing that *2.4 million pounds of mercury had been lost, discharged, or were otherwise unaccounted for at Oak Ridge's Y-12 plant between 1950 and 1963.* Mercury was used for processing Li isotope separation required for producing hydrogen bombs.

Abiotic Redox Transformations of Hg

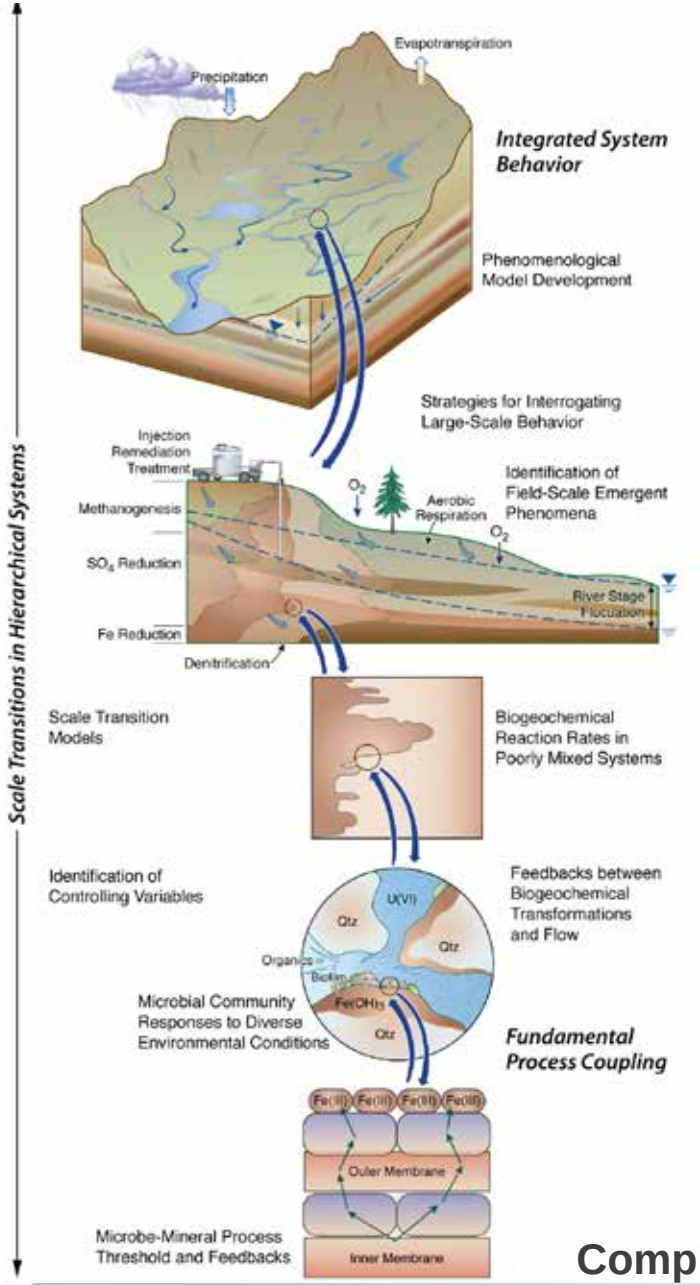
An overlooked component of Hg cycle



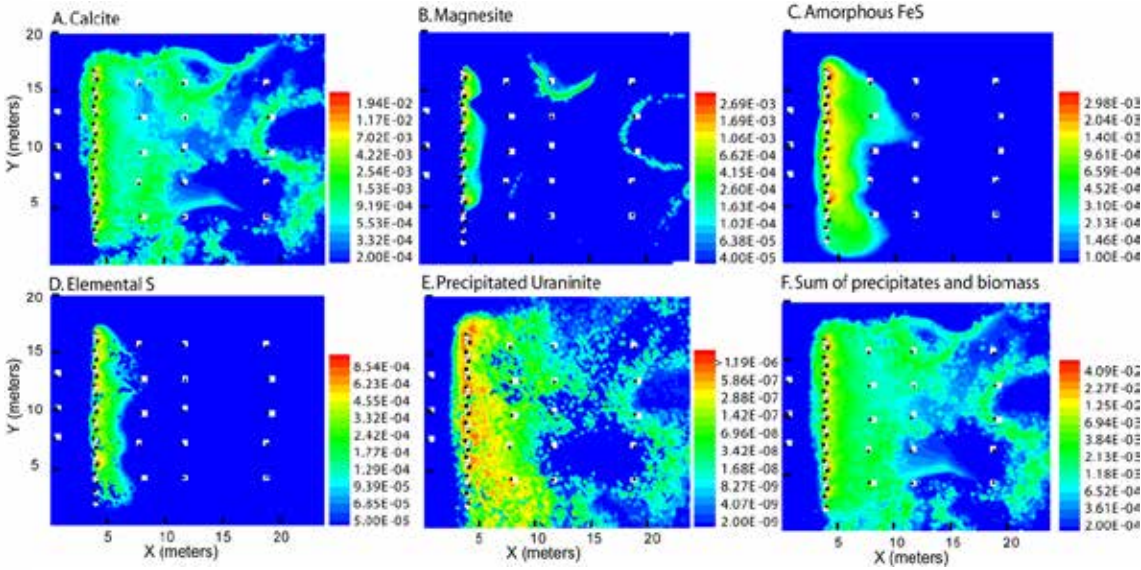
•Courtesy Tamar Barkay

- Fe^{II}-bearing phases such as magnetite and green rust reduce Hg^{II} to Hg^{0}
- O'Loughlin et al. 2003 (green rust)
- Wiatrowski et al., 2009 (magnetite)
- Mishra et al., 2011 (green rust and magnetite)
- Remy et al., 2012 (synthetic and biogenic green rust)
- Pasakarnis et al., 2013 (non-stoichiometric magnetite)

Multi-scale description of environmental processes



Field-scale transport modeling

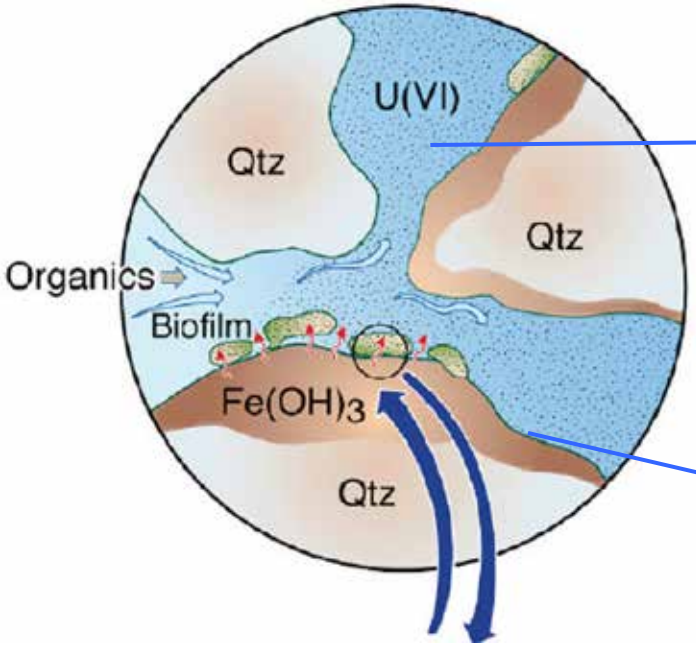


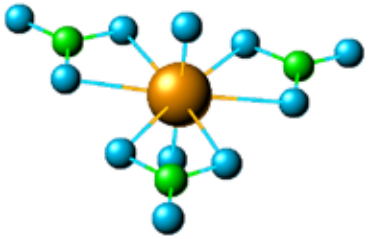
Li et al., J. Contaminant Hydrology 2010
Li et al., ES&T 2009

- reactions
- reaction rates
- mass transfer

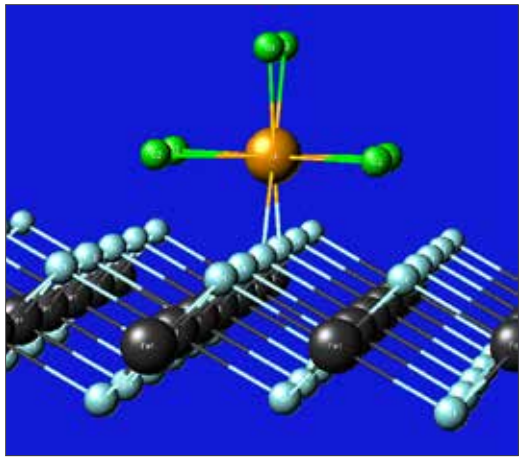
Complex system science report, SBR program, DOE, 2009

Molecular-scale processes

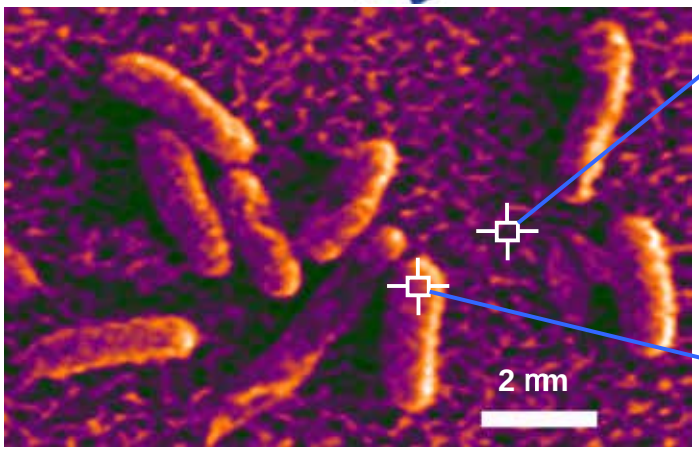




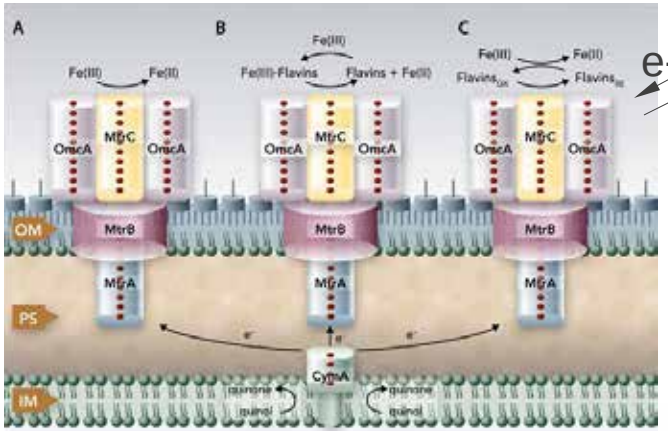
Aqueous complexes



Adsorption mechanisms, electron transfer, incorporation in minerals



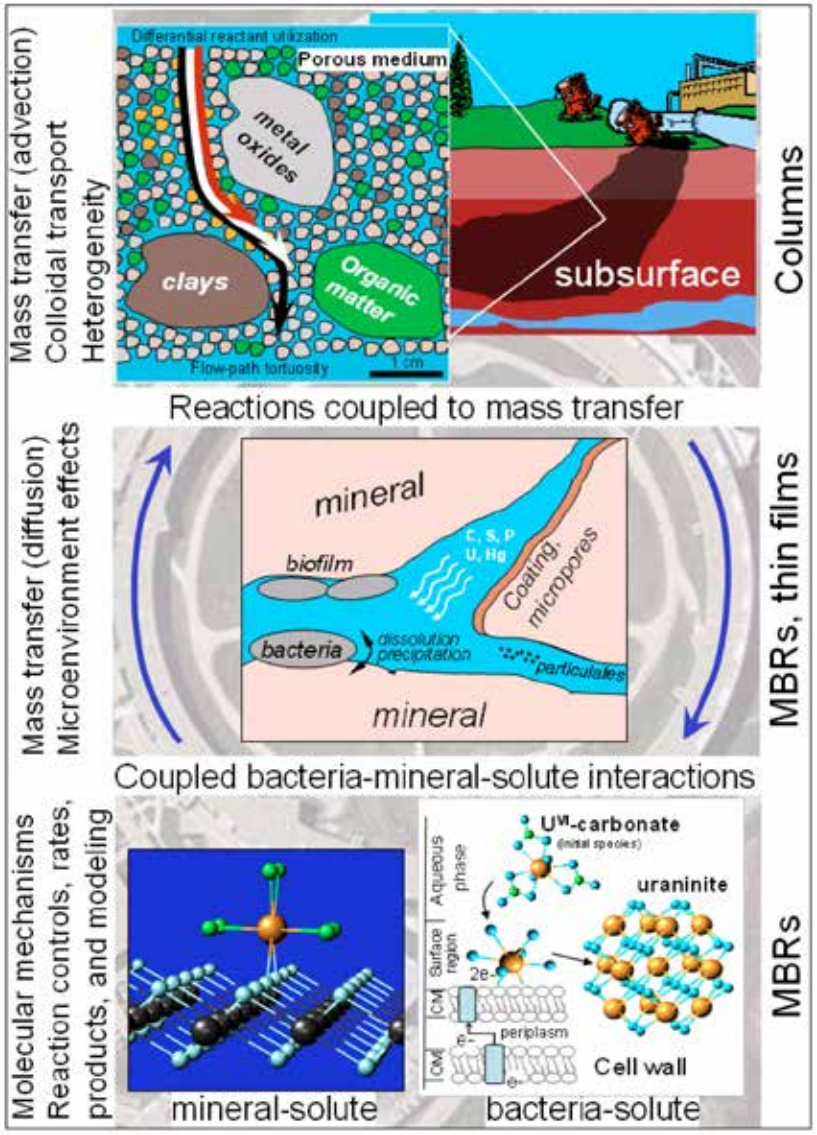
Shewanella MR-1 cells on a thin Lepidocrocite film (SEM image)

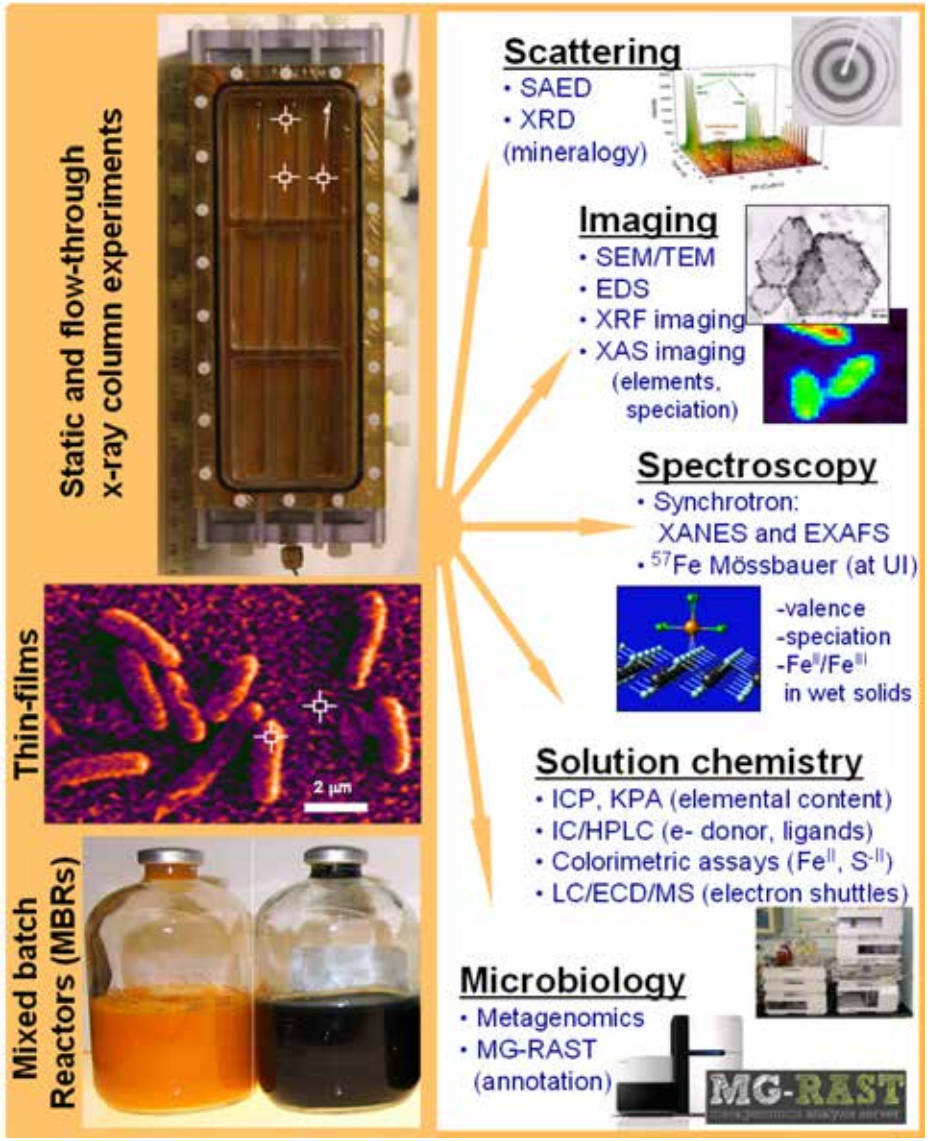


Electron transfer at cell walls, adsorption

Complex system science report, SBR program, DOE 2009

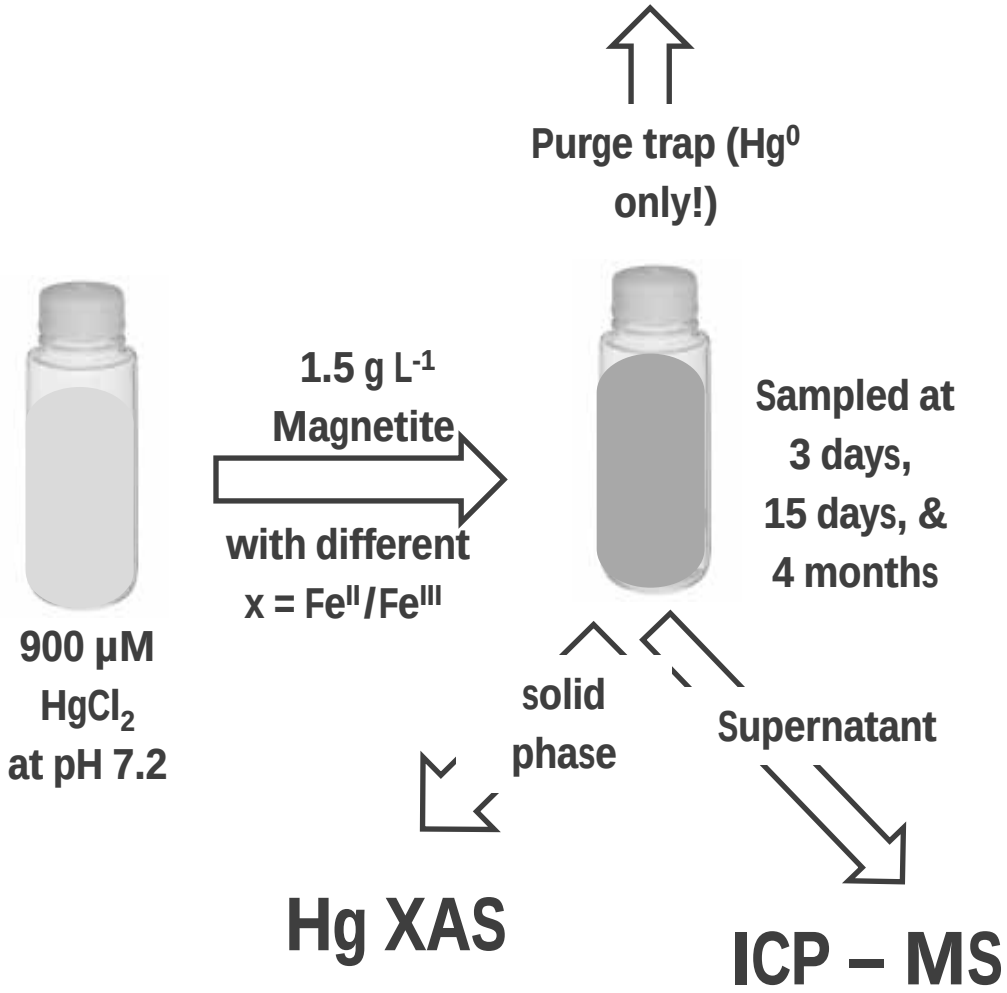
Integrating imaging with experimental systems to do science



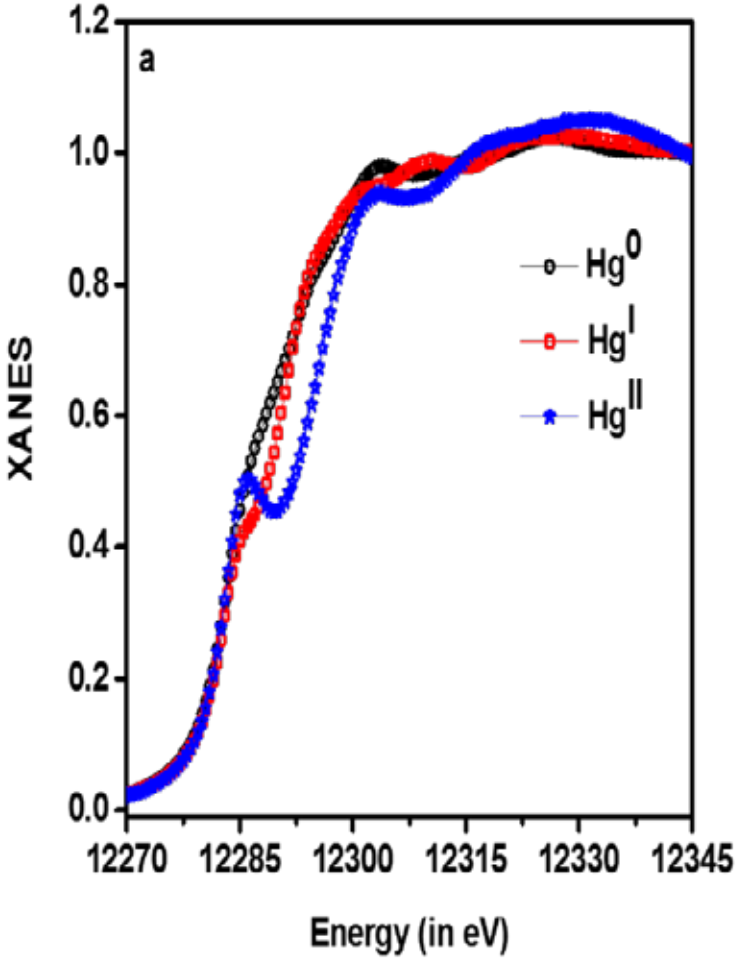


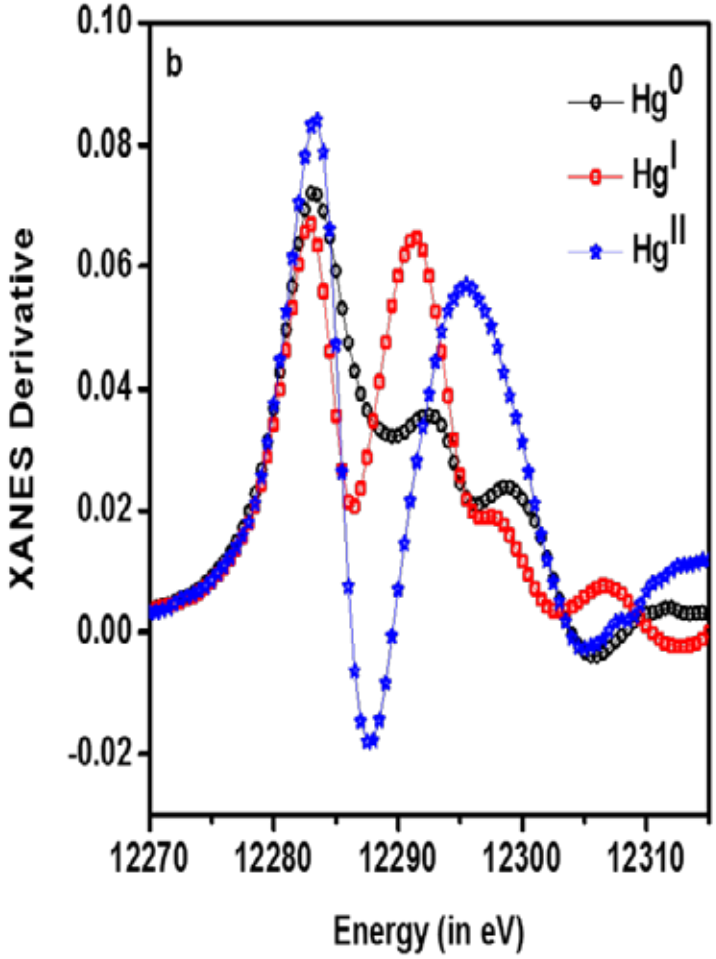
Let the scientific question and length scale determine the experimental setup and the methods to probe it.

Experimental Setup – Effect of Cl^- on the reduction of Hg^{II} by Magnetite



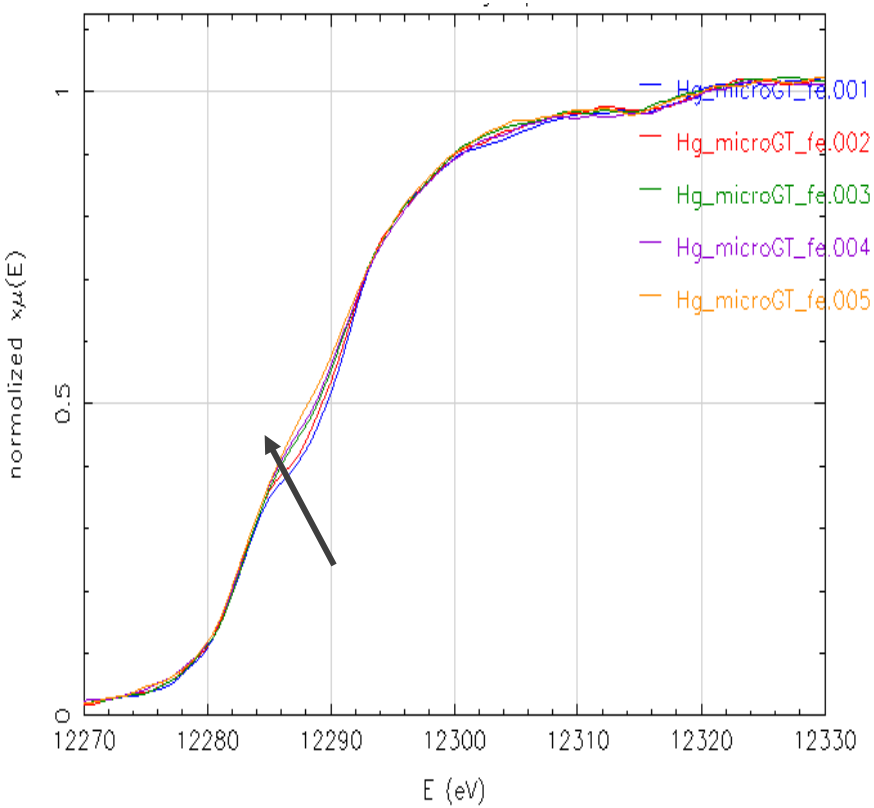
Hg Standards at Room Temperature





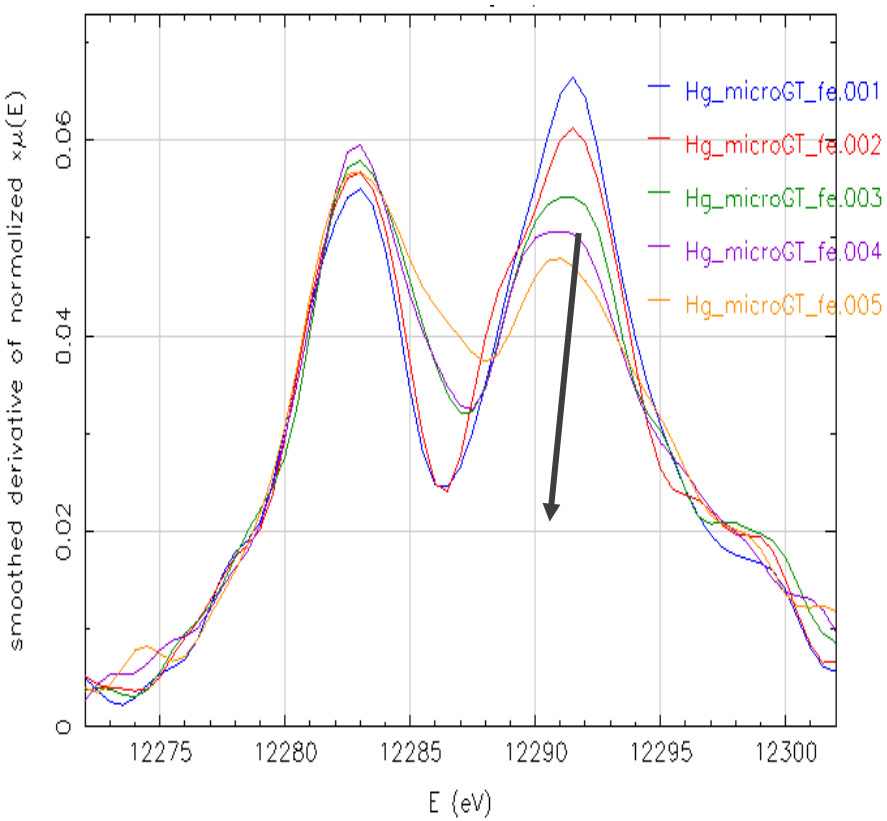
Hg XANES is not very informative due to lack of features. 1st derivative of Hg XANES provides better understanding of Hg oxidation state. Hg is sensitive to beam induced chemistry. It is recommended to make measurements at low temperatures (if possible).

Room Temperature data



Photon Flux = 1 x 10^{13}

Beam size = 1 x 1 mm^2



Fluorescence mode XAS

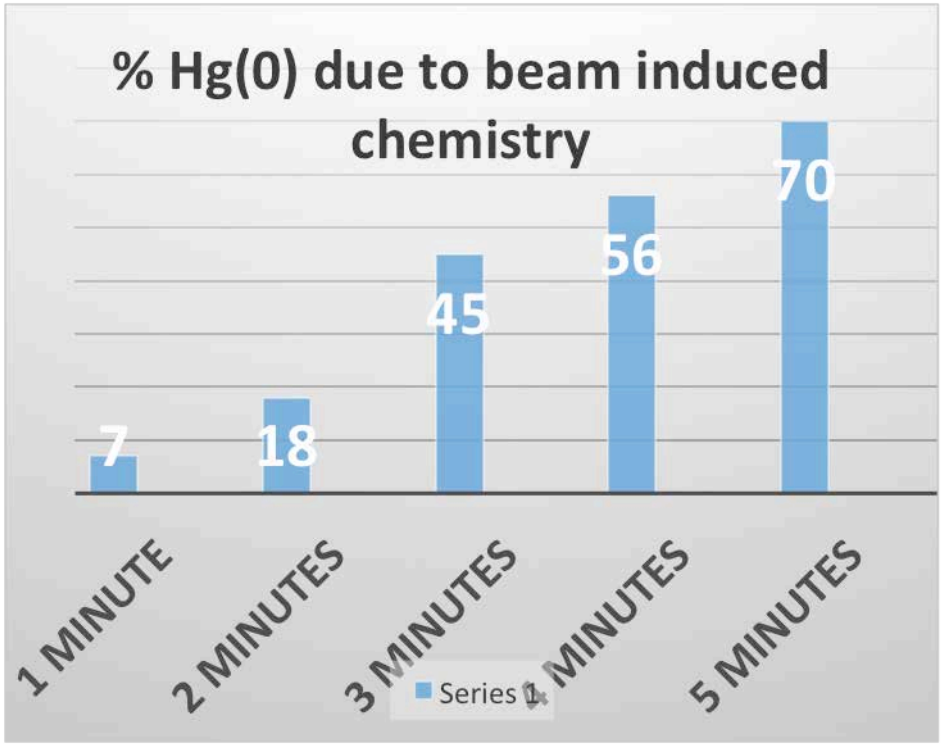
Stern-Heald Geometry

Quick-scan; 1 minute XANES

2nd Harmonic Undulator setting with 3.0 KeV taper

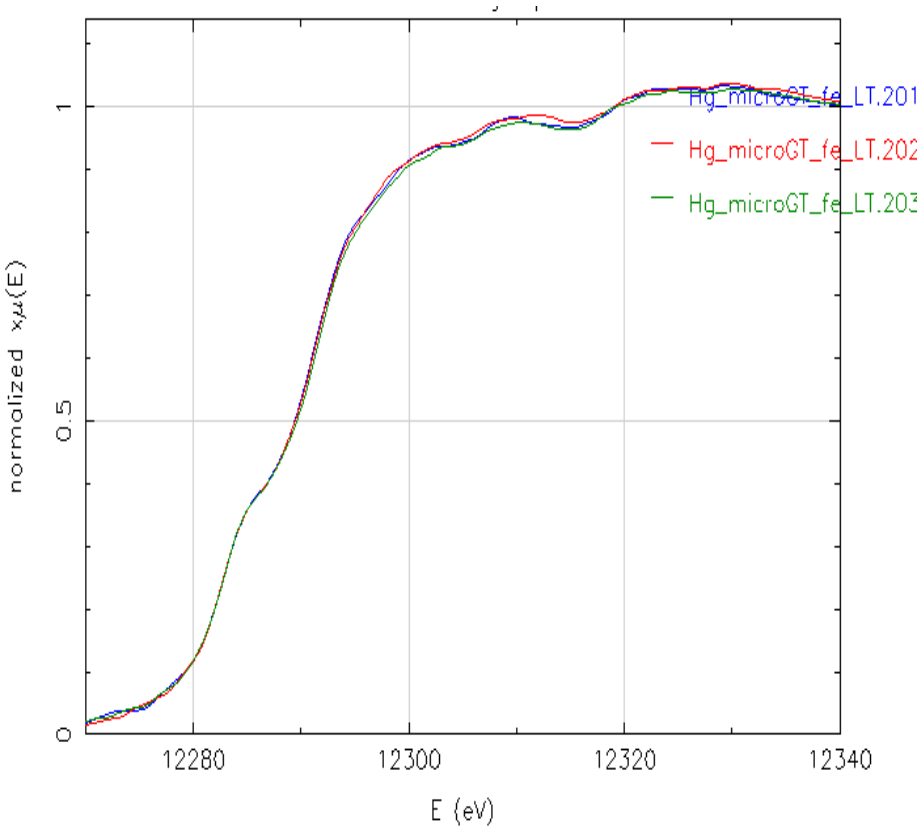
Rapid reduction of Hg during *Room Temperature* measurements

Time	% Hg(0)
1 minute	7%
2 minutes	18%
3 minutes	45%
4 minutes	56%
5 minutes	70%

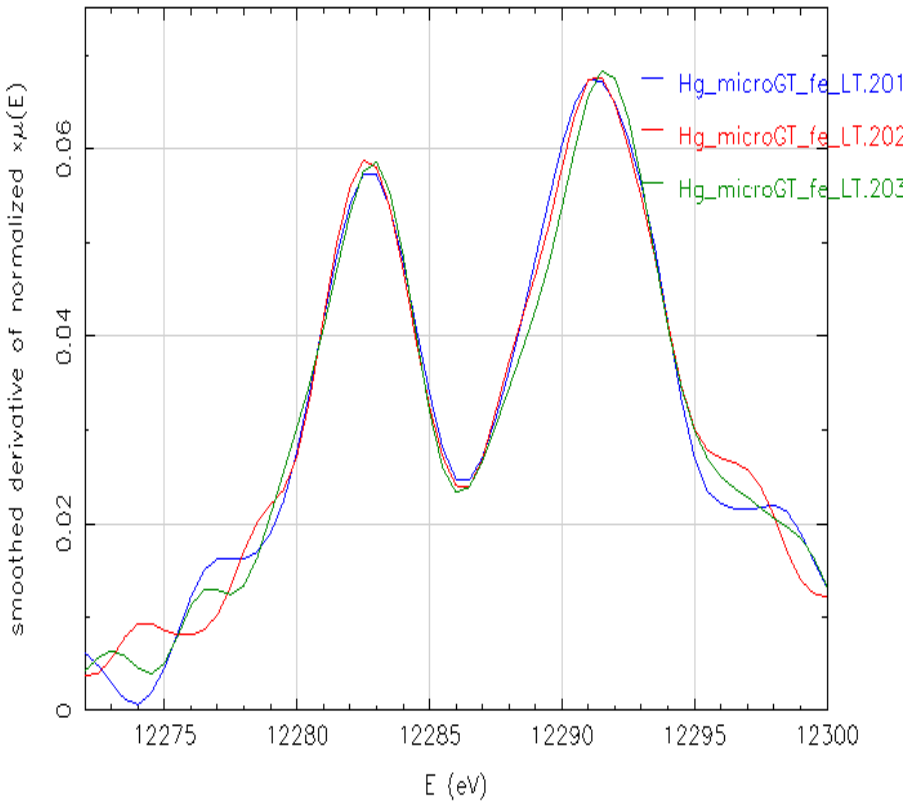


In contrast to the rapid reduction of Hg during room temperature measurement, reduction of Hg(II) and Hg(I) to Hg(0) was not observed during low temperature (-180 °C) measurements.

Low Temperature (-180 °C) data



- Photon Flux = 1 x 10^{13}
- Beam size = 1 x 1 mm^2

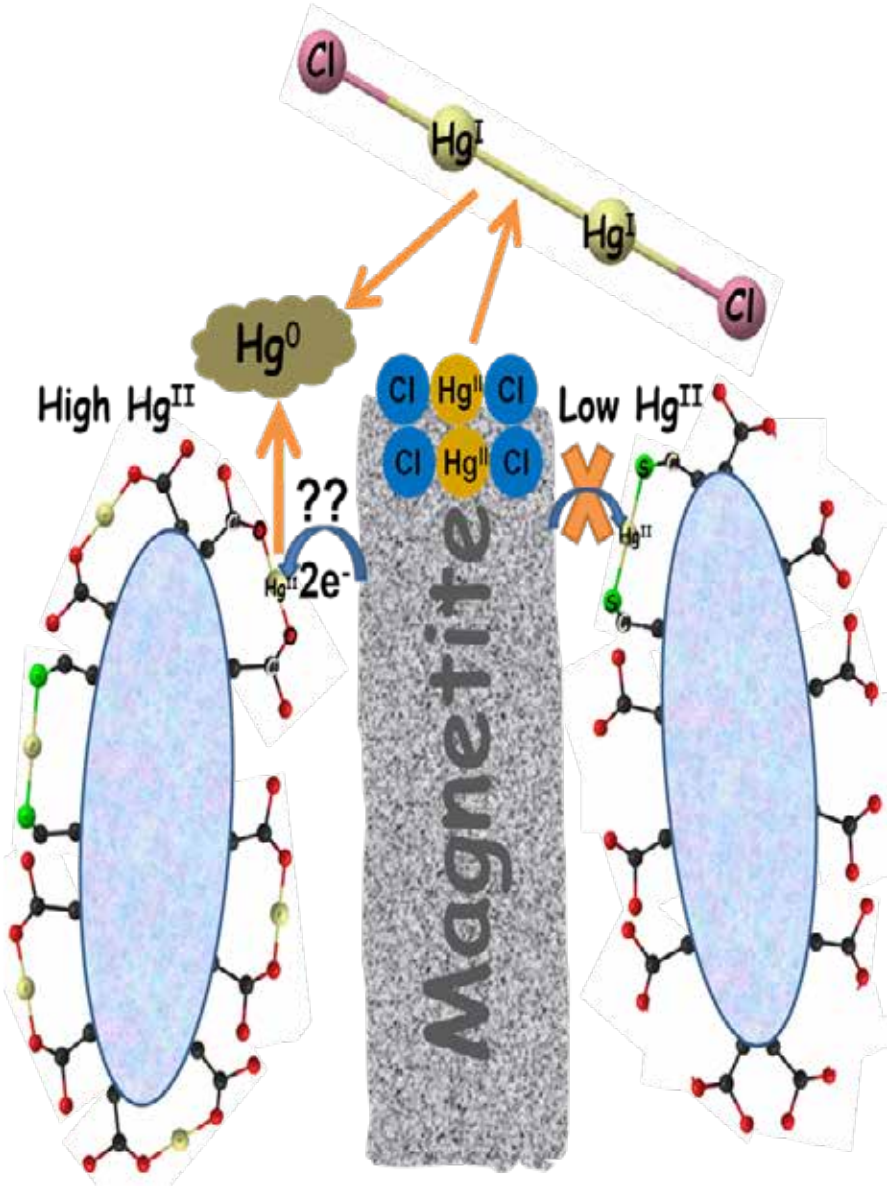


Fluorescence mode XAS

Stern-Heald Geometry

Quick-scan; 1 minute XANES

2nd Harmonic Undulator setting with 3.0 taper

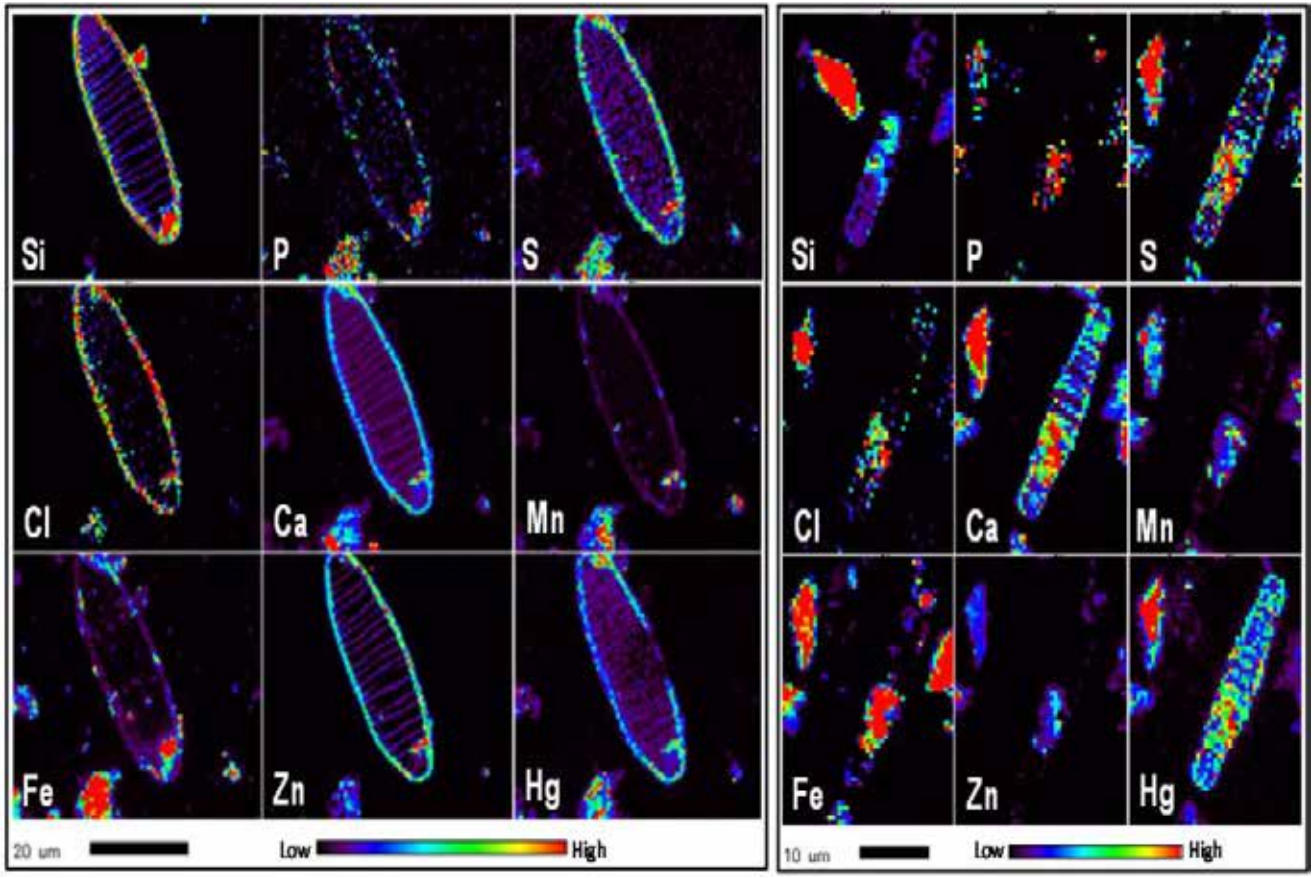


- In the presence of Cl, reduction of Hg(II) by magnetite results in formation of meta-stable Hg(I) (Calomel) phase, which slowly gets reduced to Hg(0) over few months.
- At high Hg:biomass ratio, magnetite reduced 90% Hg(II) to Hg(0) within 2 hours.
- At low Hg:biomass ratio, magnetite could not reduce Hg(II) to Hg(0) even after 2 months.

•Mishra et al., ES&T (2011)
•Pasakarnis et al., ES&T (2013)

μXRF Mapping of Diatoms and Suspended Mineral Particles in Oak Ridge Creek

(*Room Temperature data*)



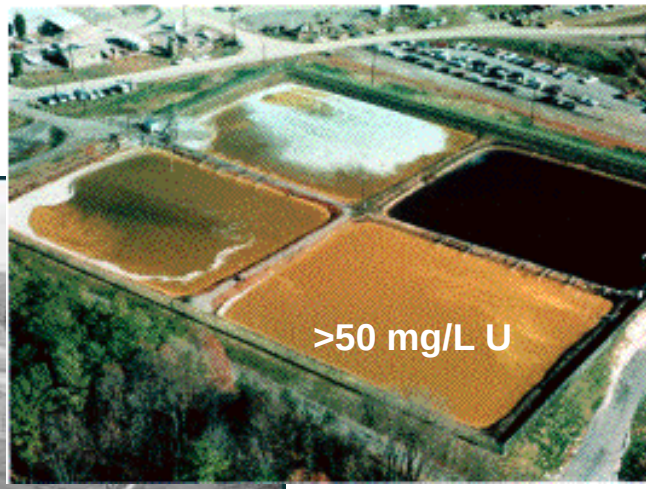
Gu, Mishra et al., Biogeosciences (2014)

- Organic/biomass coated Fe-oxides or clays are a big sink for Hg.
- Hg is associated with bio-signature.
- Could NOT "run away" from radiation damage fast enough to make XAS measurements.

Properties of Uranium

- Hazards:
  - Toxicity, Radioactivity

- Chemical properties:
  - U^{VI} forms the uranyl ion, UO_2^{2+}
    - **solubility ~10^{-4} M at pH 7**
  - UO_2^{2+} complexes with carbonate forming more soluble species, e.g. $UO_2(CO_3)$, $UO_2(CO_3)_2^{2-}$, etc.
  - UO_2^{2+} forms insoluble phosphate minerals, $(H,Na,Ca)(UO_2PO_4)_{1,2}$
    - **solubility ~10^{-6} M at pH 7**
  - Reduction to U^{IV} assumed to result in UO_2 (uraninite) formation
    - **solubility ~10^{-8} M at pH 7**

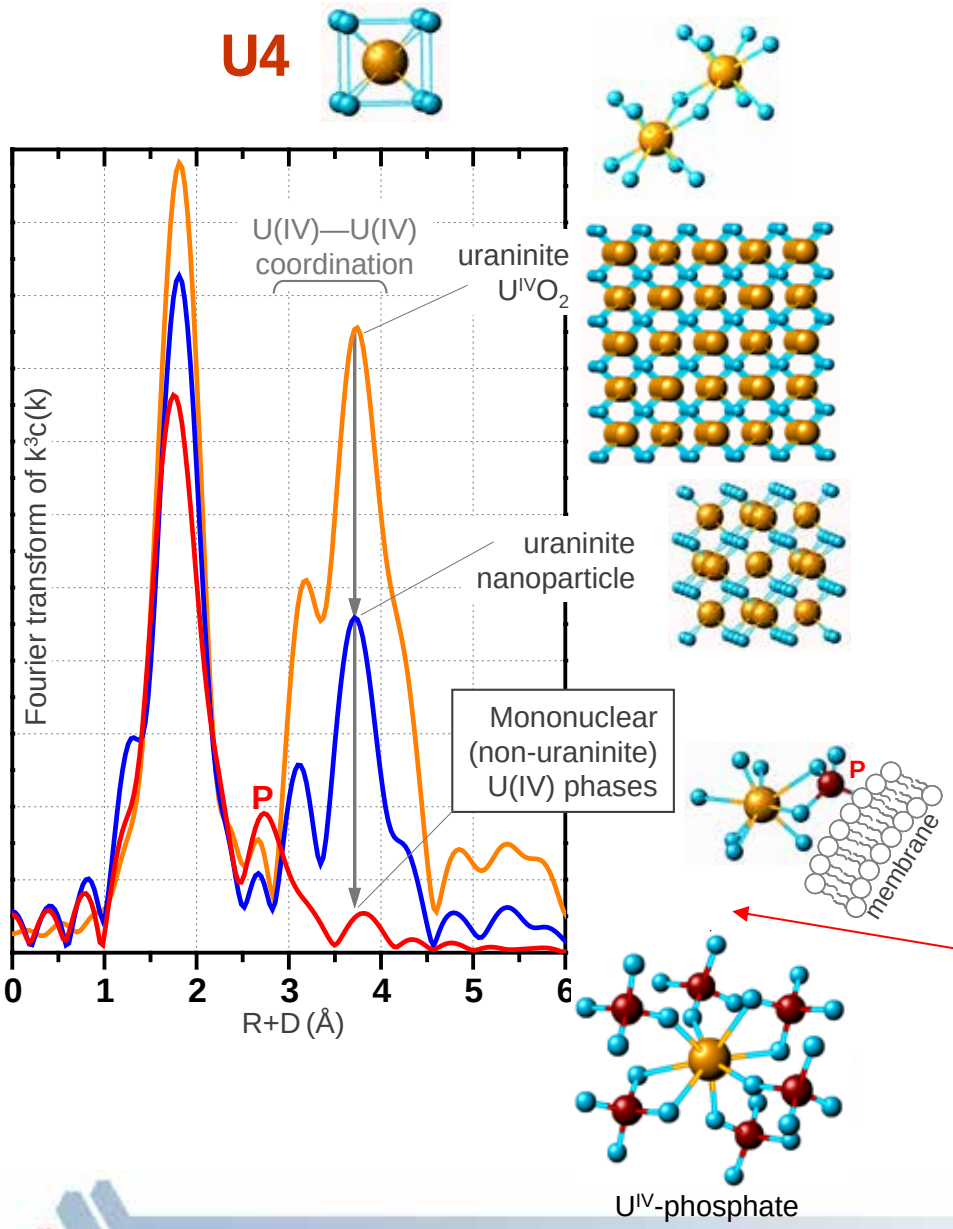


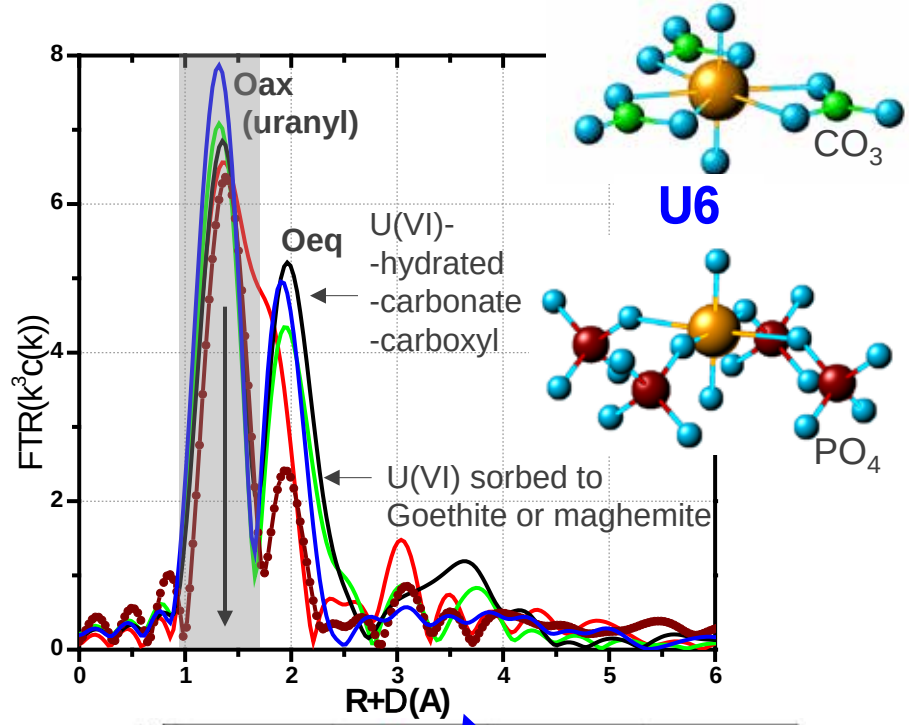
IFRC site,
Oak Ridge National
Laboratory

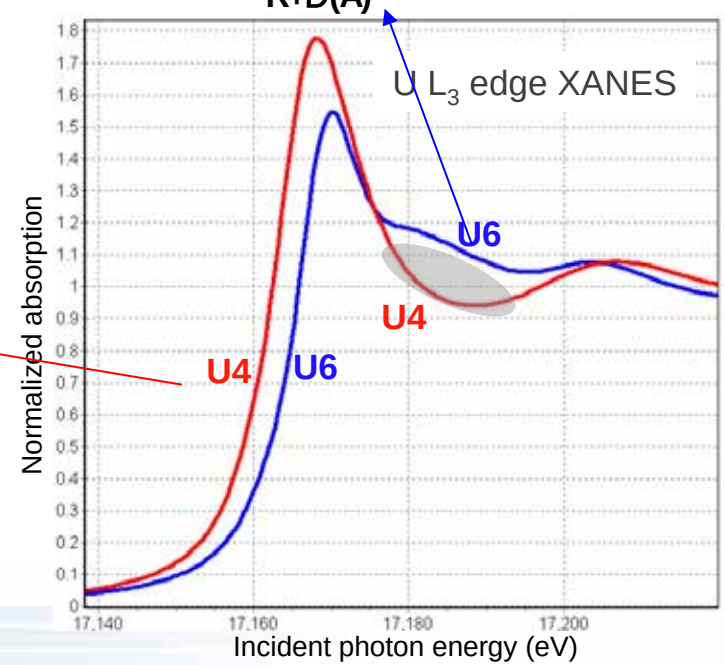
Hanford site, Pacific
Northwest National
Laboratory

- US EPA limits on U:
  - Drinking water: < 30µg/l, ~**10^{-7} M**

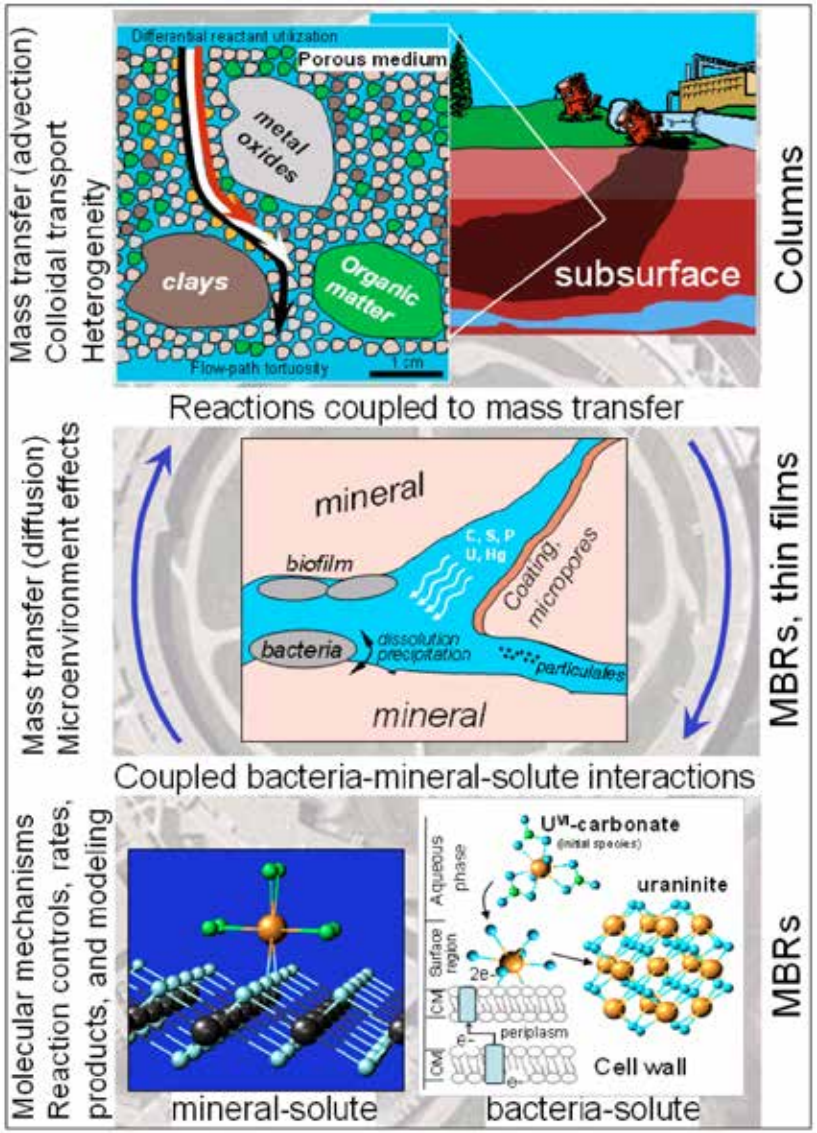
U4/U6 XAFS "101"

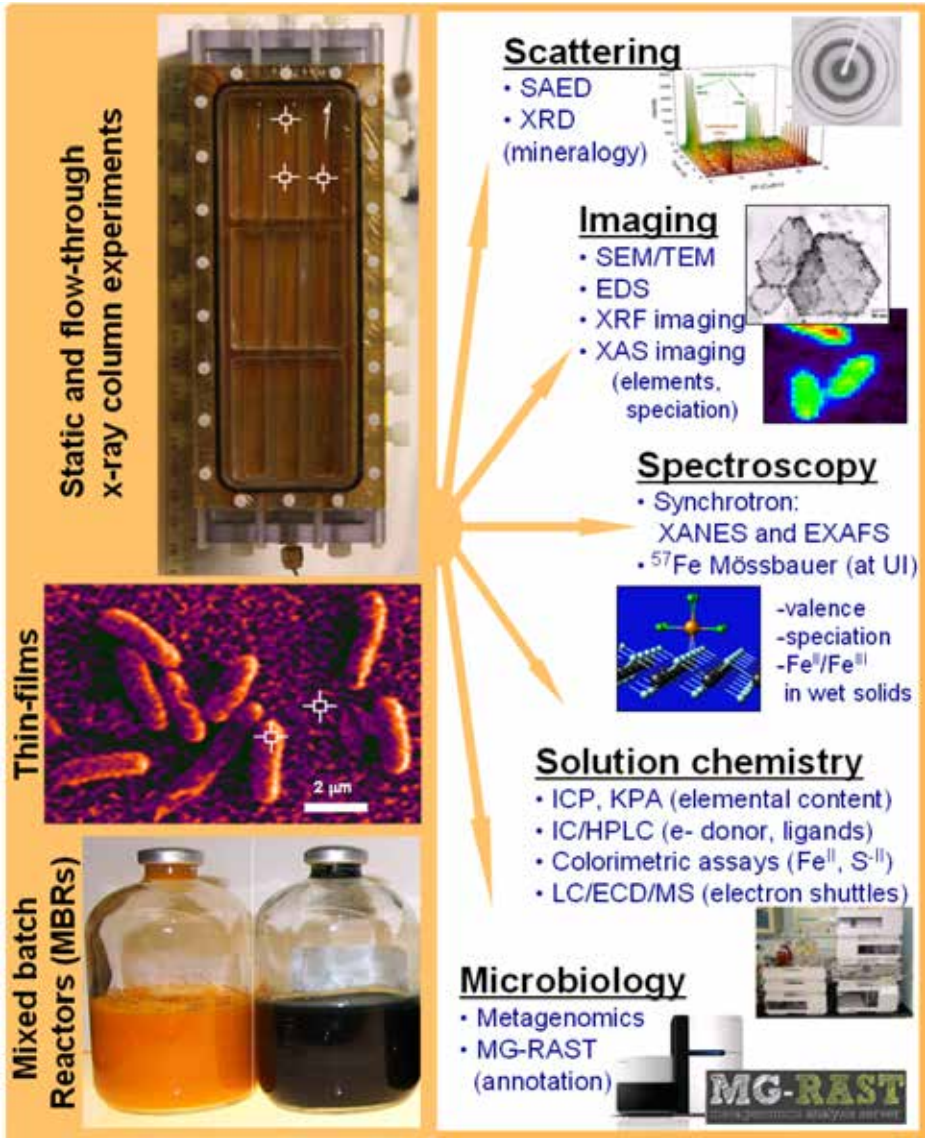






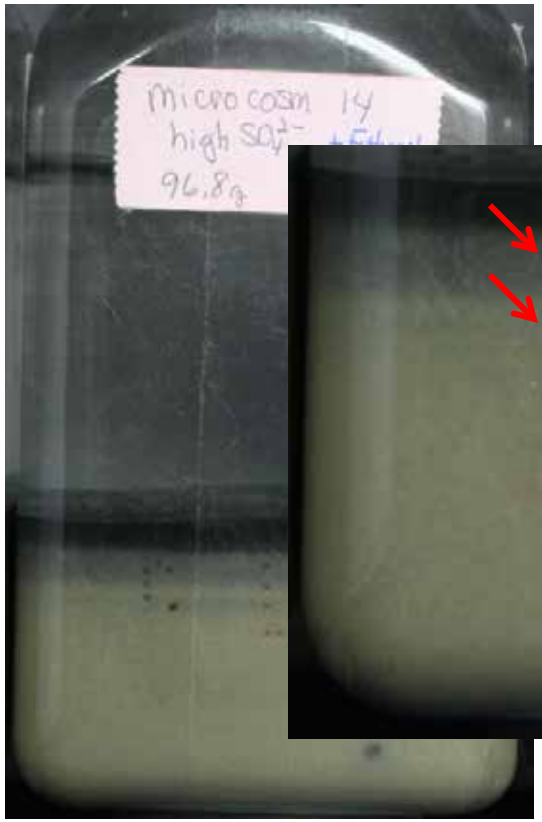
Integrating imaging with experimental systems to do science

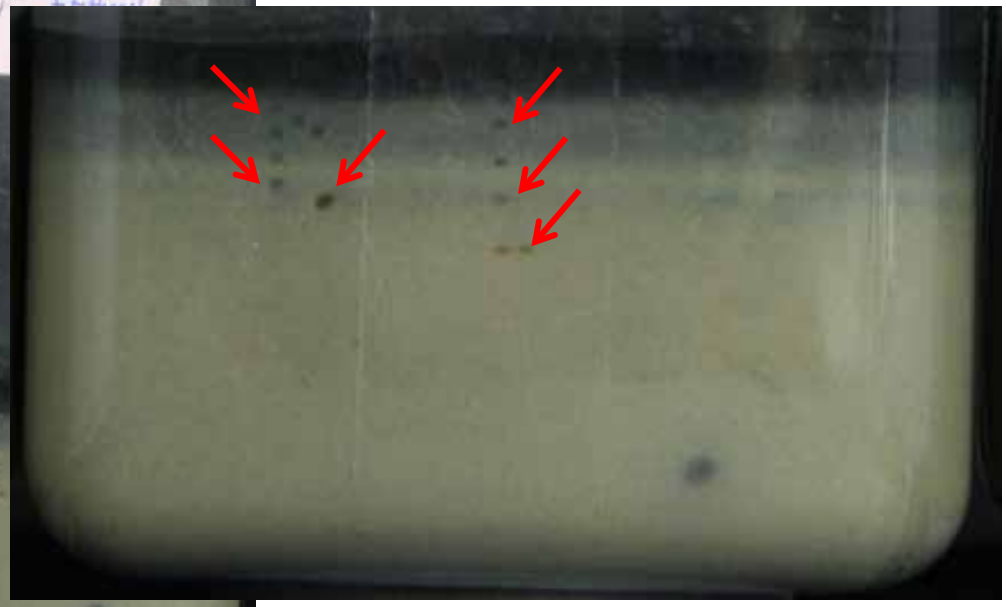




Let the scientific question and length scale determine the experimental setup and the methods to probe it.

Visible burn-marks from radiation exposure





Before radiation exposure

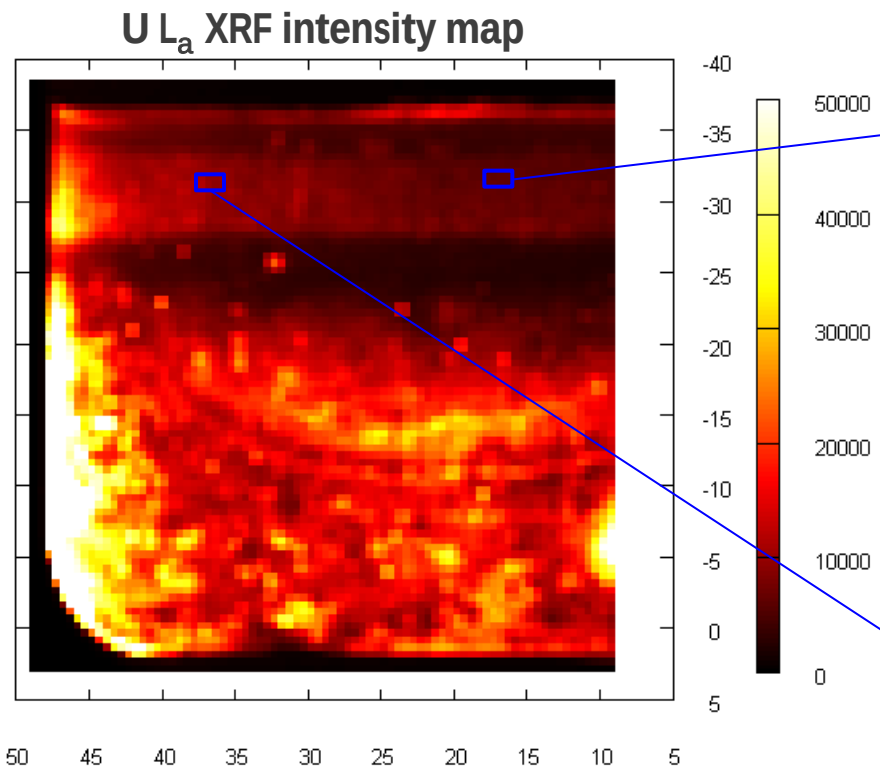
The system consists of U-containing fine-grain sediment overlaid by biostimulated groundwater. Container is a 1mm thick plastic bottle.

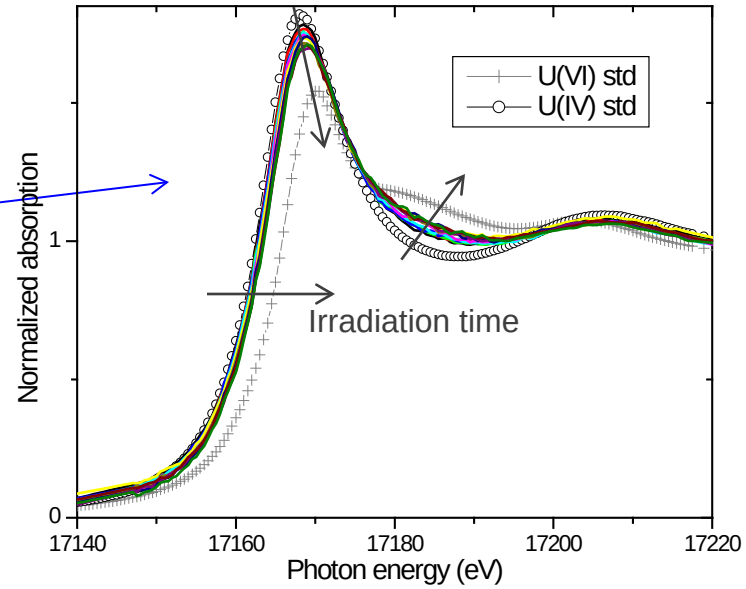
After radiation exposure

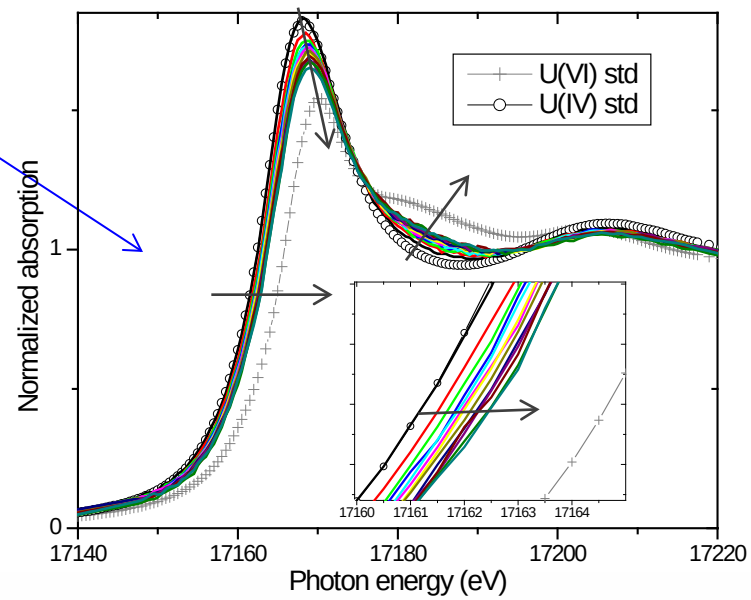
Visible burn-marks are left in the sediment at the location of beam exposure.

Beam parameters: 17.5 keV energy, ~10^{11} photons/s in a 700x700 micron beam. Burn marks appear in <1hour of scanning.

Spectral evolution with irradiation



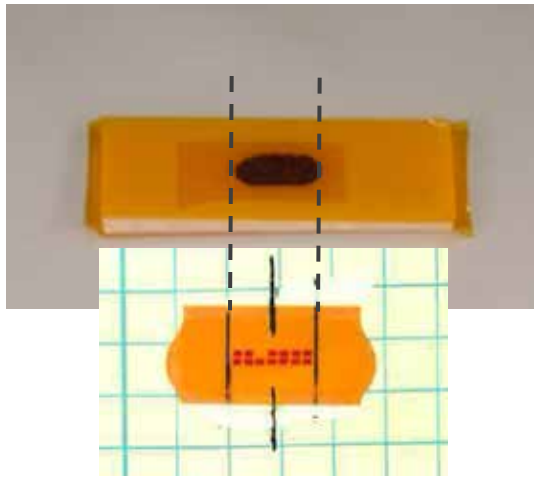




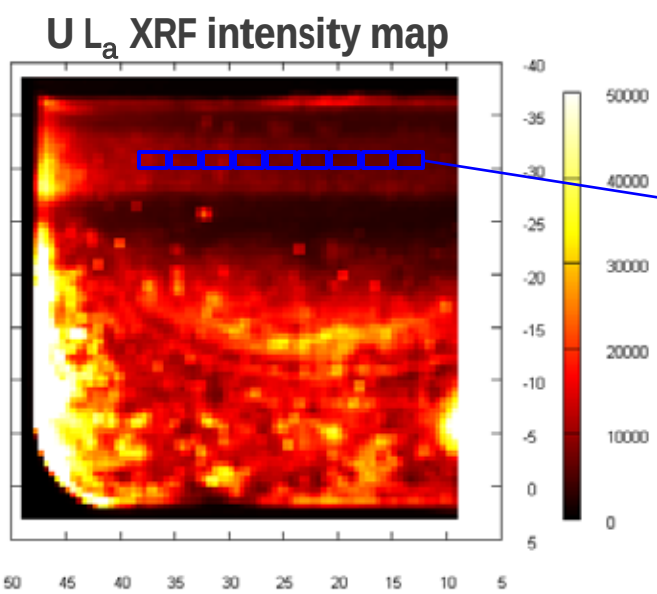
Beam exposure causes U oxidation in this sample.

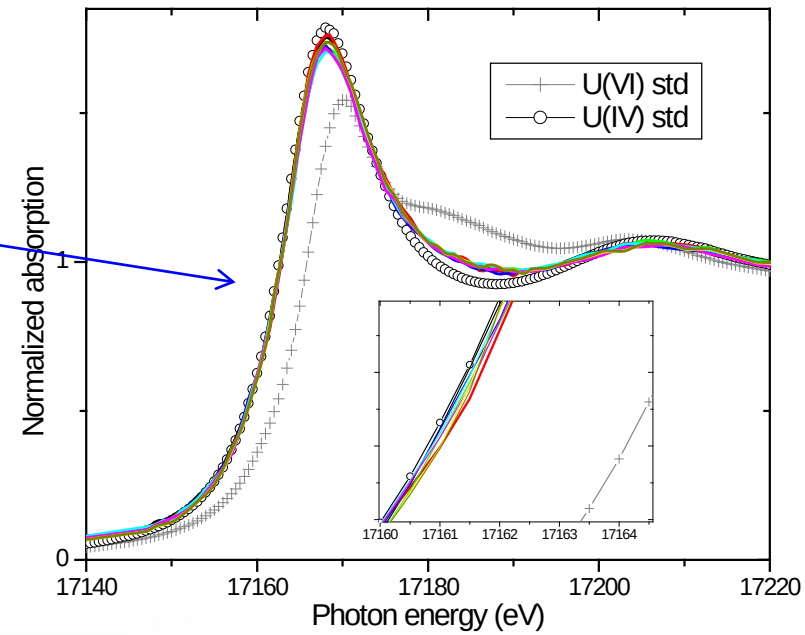
Changing to a fresh location results in a spectrum that starts from more reduced U and oxidizes with time.

Mitigation by movement of the beam



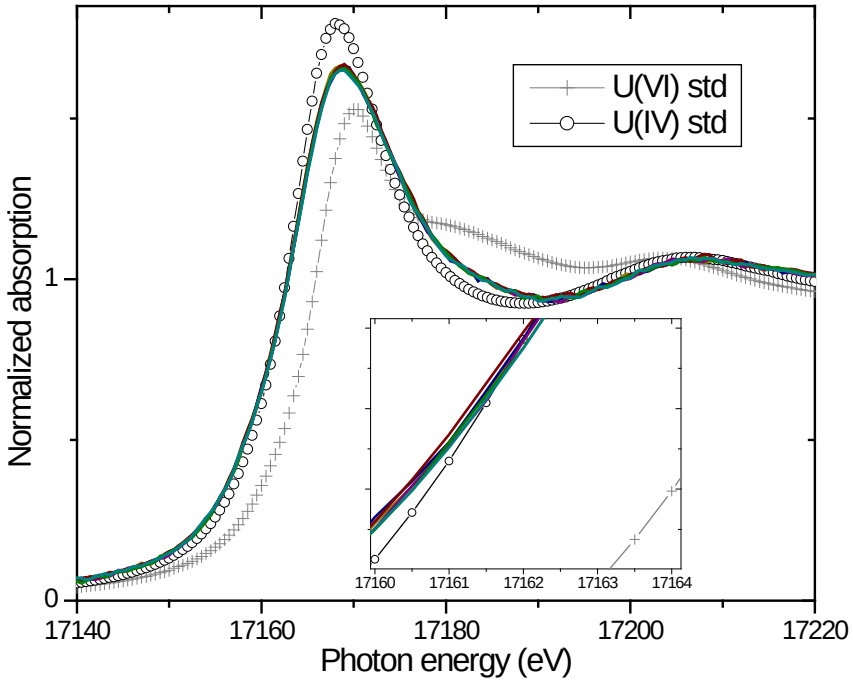
- Collect several scans at a single location to determine the rate of radiation-induced changes. **Determine the number of scans N that cause less than 10-20% change in the speciation of the analyte**.
- N can depend on x-ray intensity and x-ray density, the analyte itself, the solution matrix, and the underlying solid matrix.
- **Collect less than N scans at each fresh location, merge.**



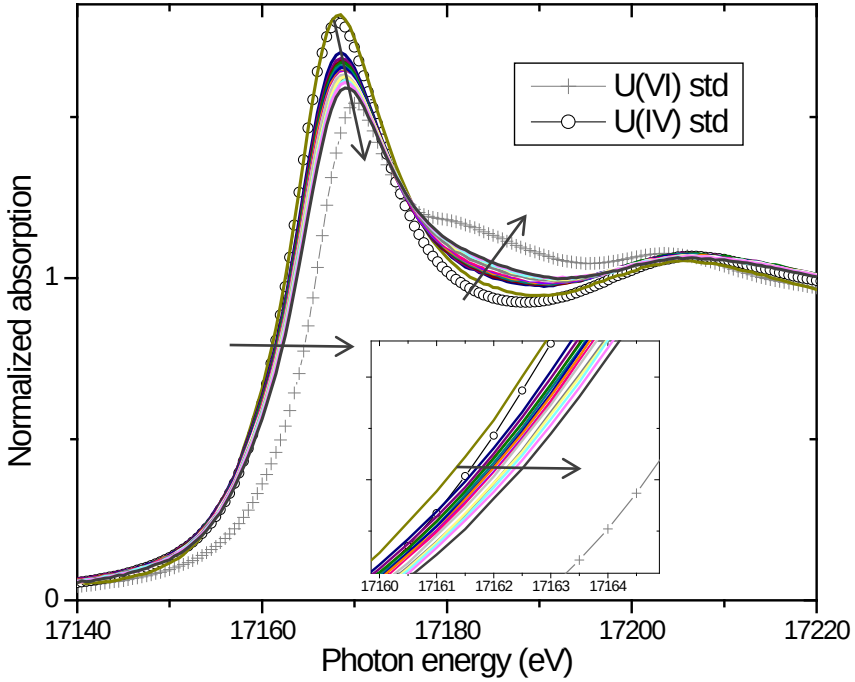


Spectral evolution in a Ti-containing sample

Pure magnetite (no Ti)



Magnetite with some Ti^{4+} for Fe^{3+} substitution



Magnetite without Ti:

Consecutive scans overlie each other Þ no change in valence state with irradiation time.

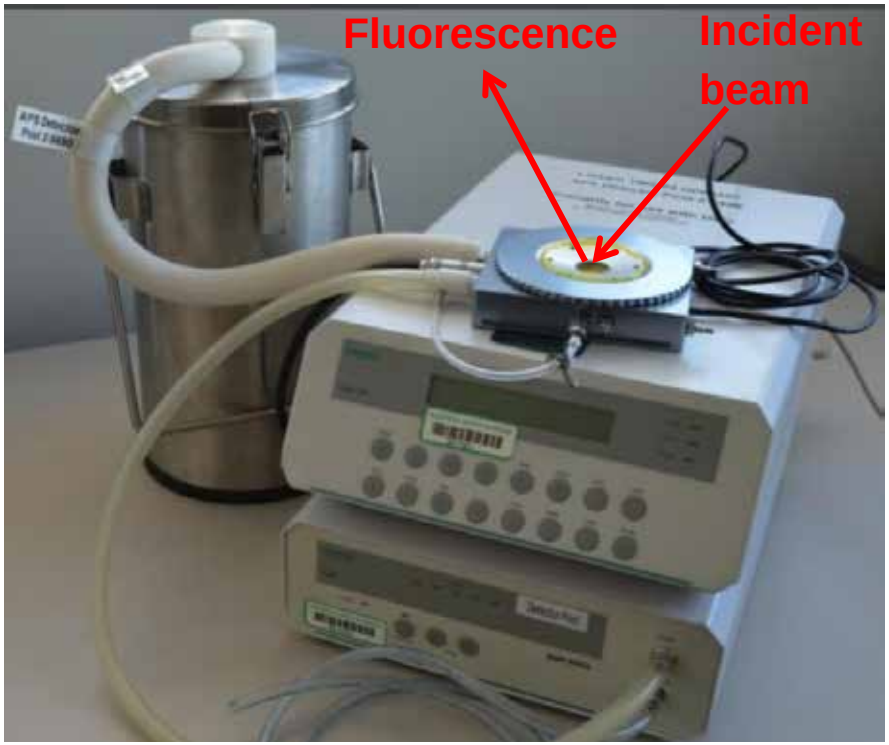
Data collected in fluorescence- not even the surface layer is transforming.

Ti: a more extreme case of photochemistry

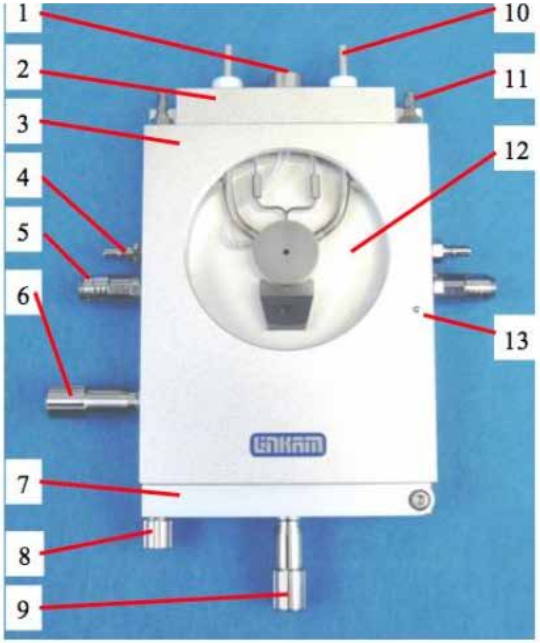
After first scan, white line intensity decreases dramatically, edge position shifts, uranyl resonance features become more pronounced Þ **rapid U oxidation is occurring.**

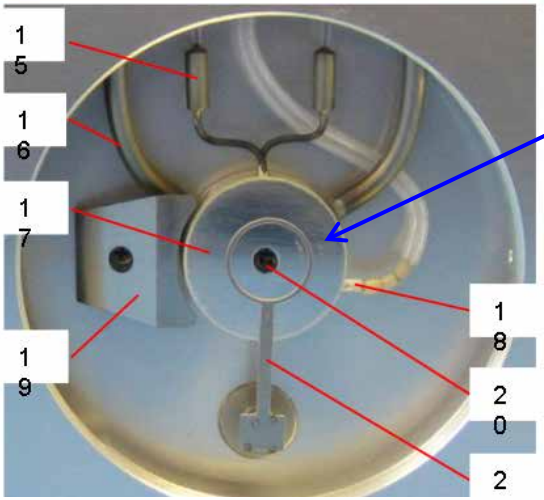
Data collected in transmission- transformation happening throughout entire sample volume.

Mitigation by freezing of the sample



Temperature controlled sample stage (Linkam®)

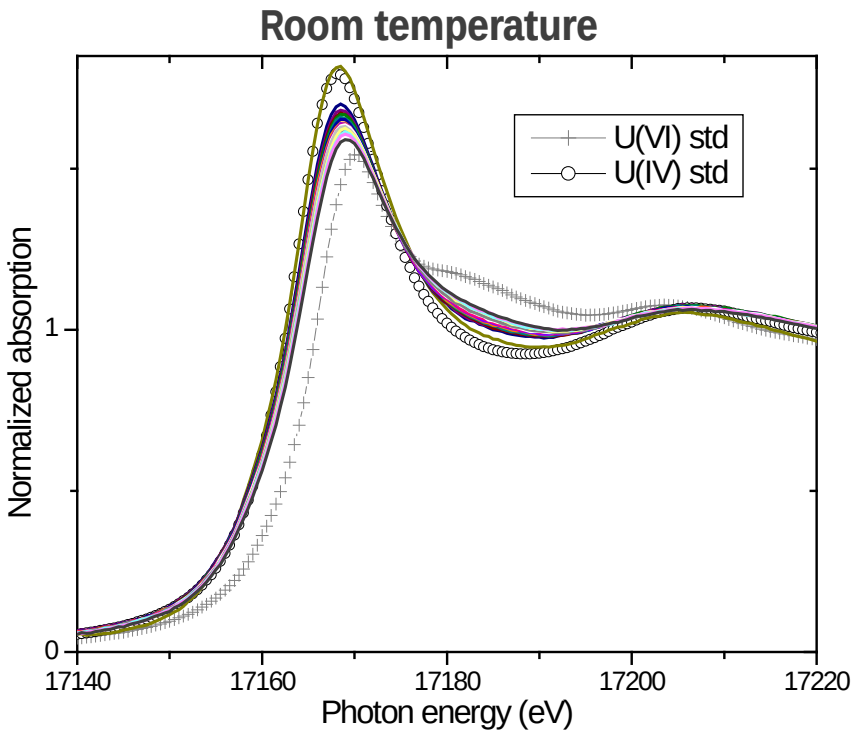


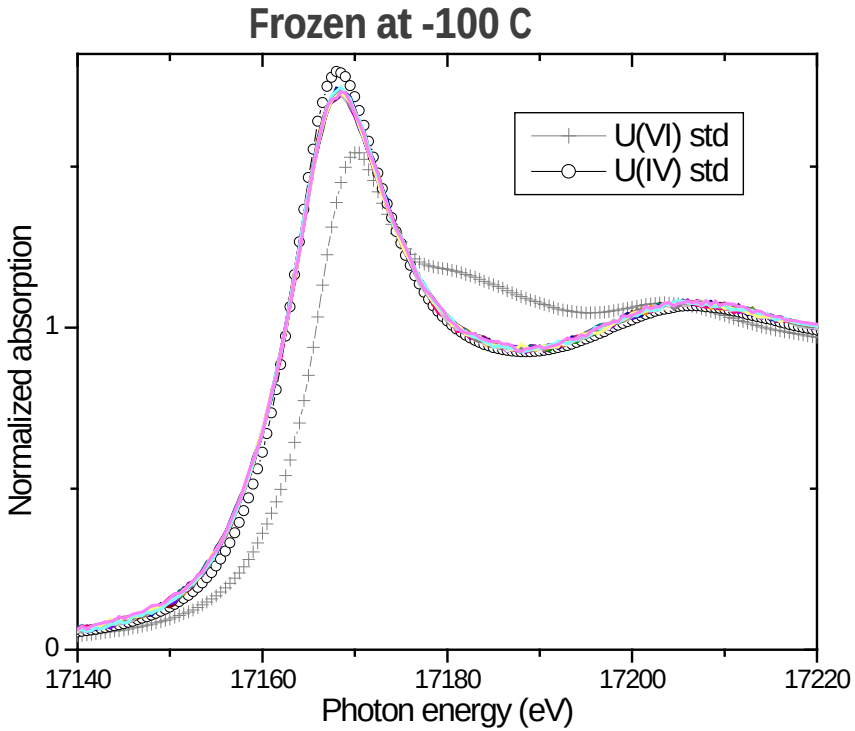


Consists of a beam-accessible sample stage, LN2 Dewar, pump, and controller. Automated stabilization of the temperature within 0.5 deg.

Temperature range: -180 C to +600 C.

Ti-doped magnetite, with and without freezing





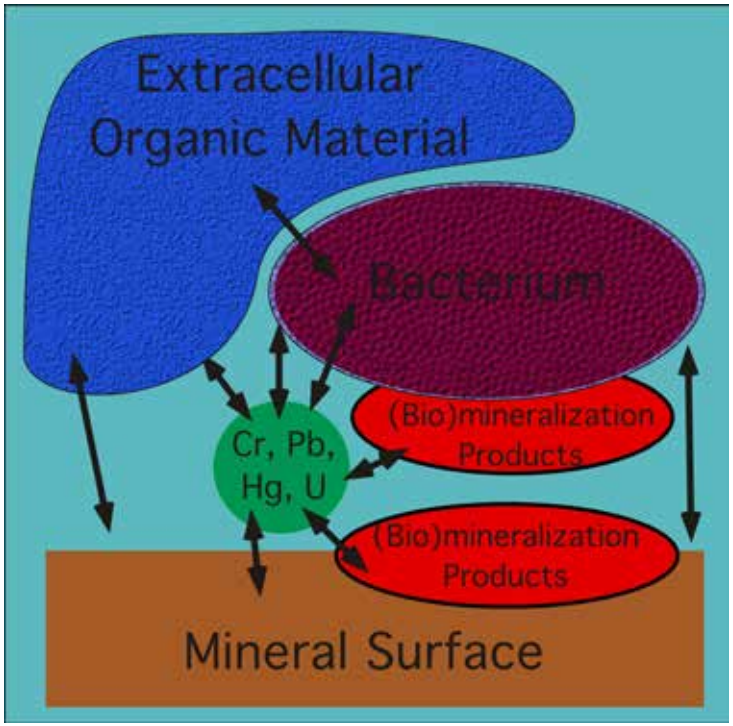
Choice of temperature when freezing:

The speciation of the analyte or the other components in the sample must be representative of those at room temperature.

For magnetite, in particular, the known Verwey (charge ordering) transition necessitates the use of temperatures higher than -150 C for freezing.

Transformations at the mineral-microbe interface microenvironment

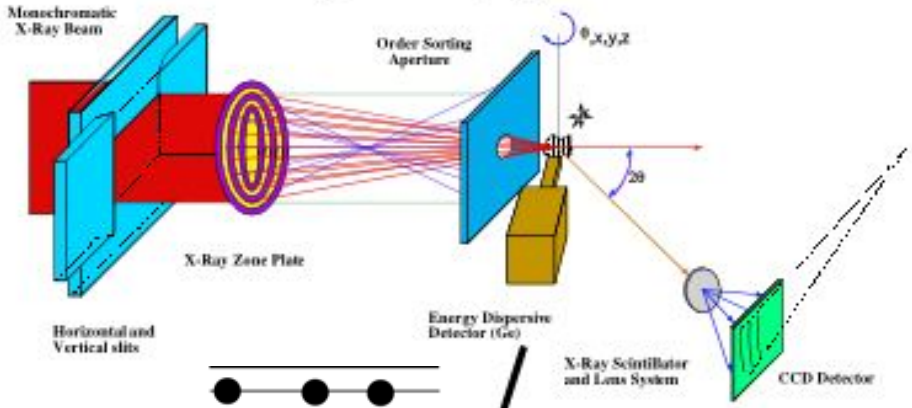
- Dissimilatory metal reducing bacteria (DSMR) and biomineralized Fe(II) minerals have been shown to be capable of reducing U(VI) to U(IV).
- Characteristics of microenvironments at and adjacent to cell surfaces can be significantly different from measurements averaged across larger spatial scales.
- The location/mechanism of U sorption, reduction, and precipitation processes, relative to cells attached to iron hydroxides is not well understood, partly because the chemistry of the mineral-microbe interface microenvironment is very difficult to define.
- An understanding of the spatial distribution of U and its valence state within and near the mineral-microbe interface microenvironment can provide key insights into the coupled biotic-abiotic processes that contribute to the chemical transformations of U.

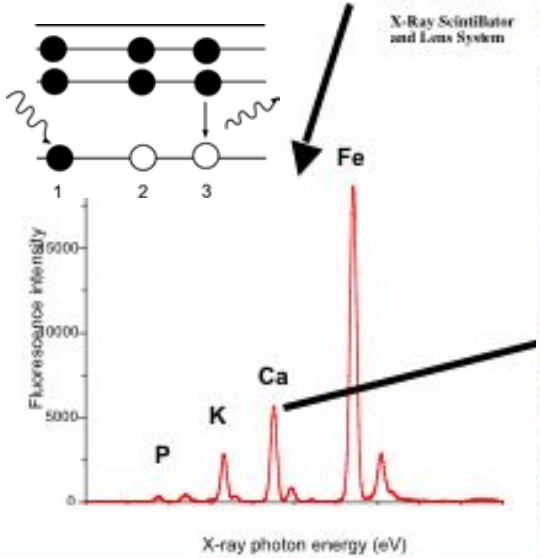


Kemner, O'Loughlin, Kelly, Boyanov, "Synchrotron x-ray investigations of mineral-microbe-metal interactions," *Elements* August 2005.

XRM with Fresnel zone plates:

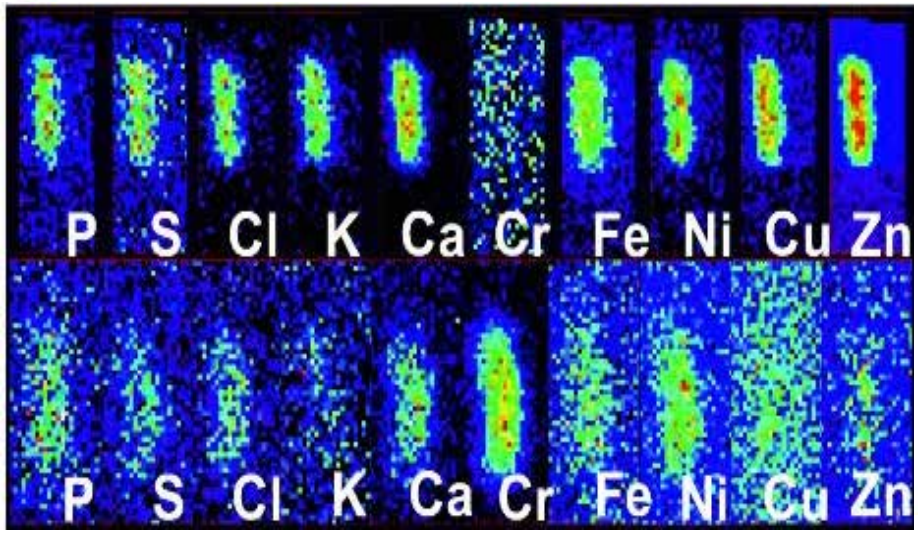
X-RAY MICROPROBE BEAMLINE AT APS (2-ID-D/E)





Resolution is dependent on the size of the x-ray probe - (~100nm).

Spatially resolve information provided by x-rays - (elements, chemical speciation).



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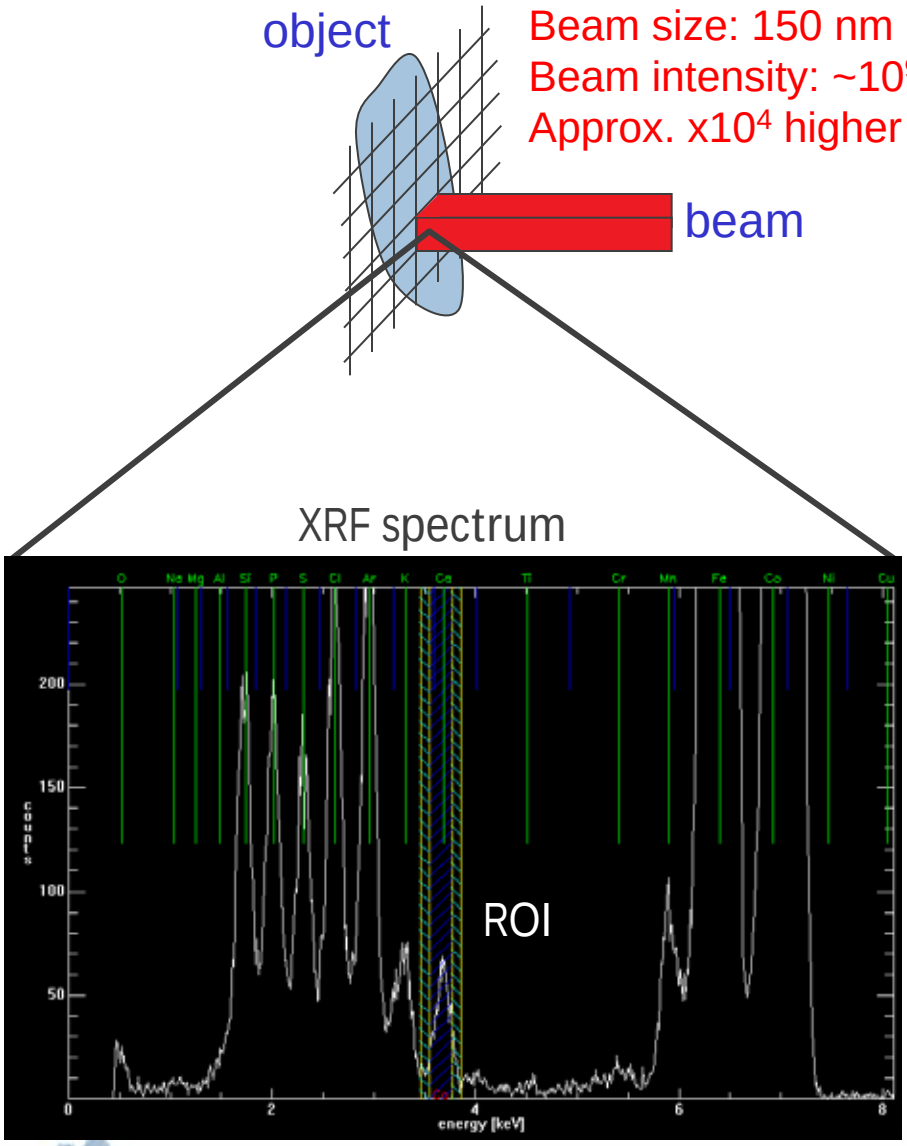
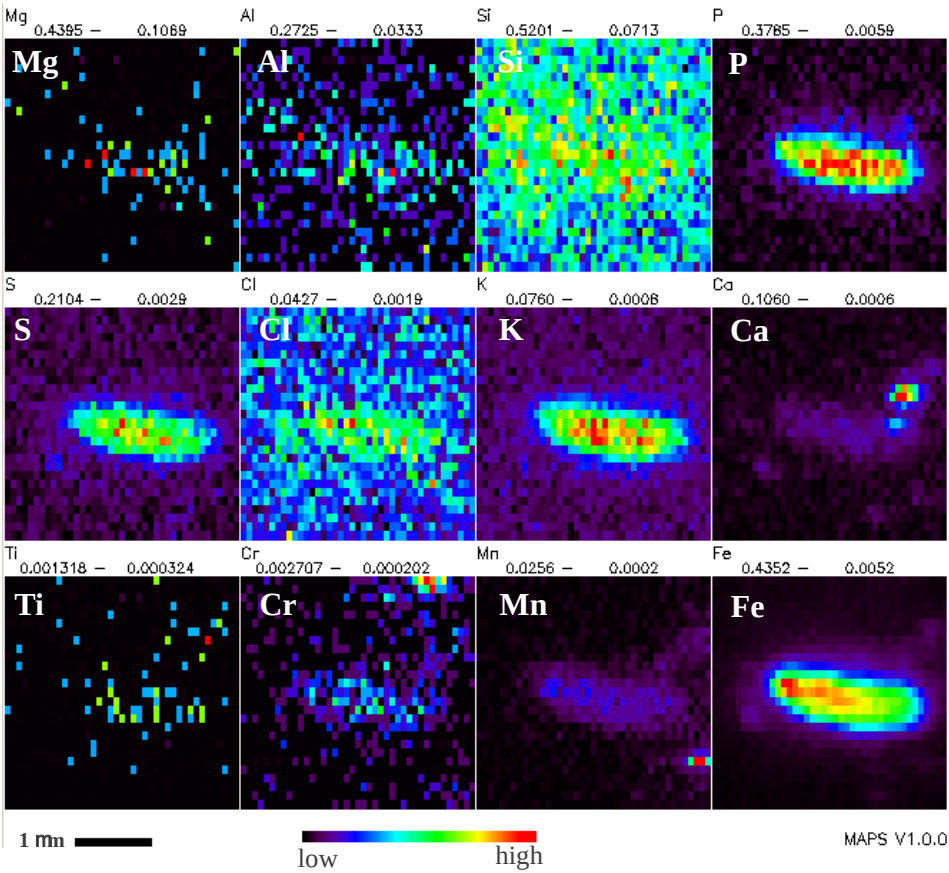
Kemner et al., *Science* 306 686-687, 2004.

Effects with higher photon density beams

Beam size: 150 nm FWHM
Beam intensity: ~10^9 photons/s
Approx. x10^4 higher density than unfocused beam

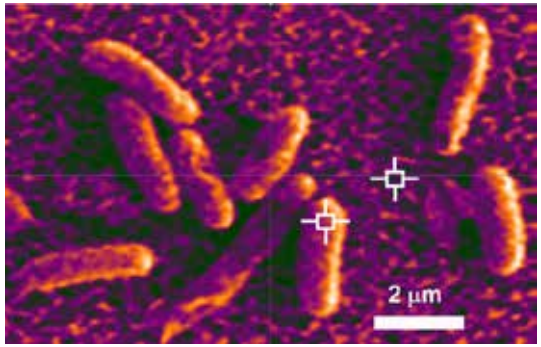


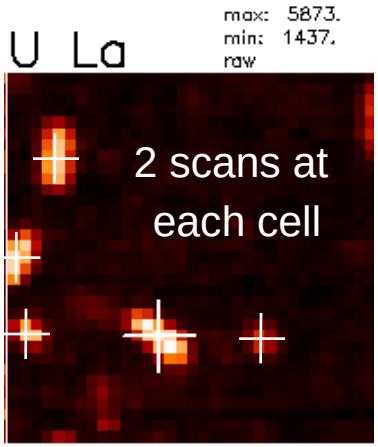


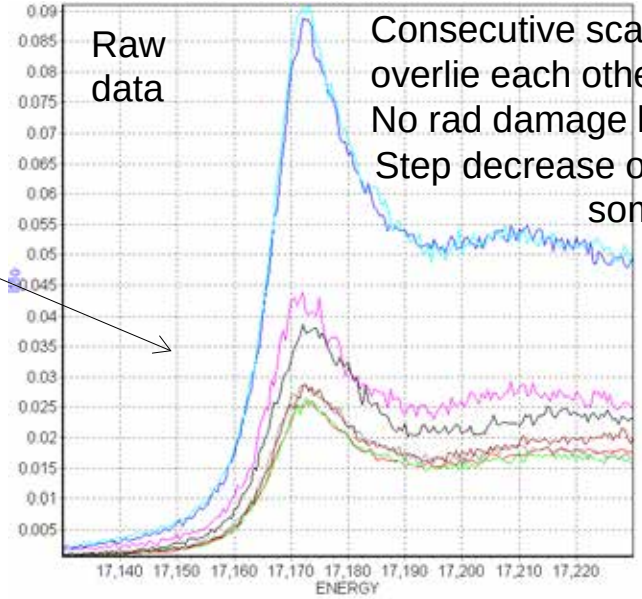
Raster XRF scanning is typically done for short residence times at each point Þ no rad damage issue.

Spectroscopy with higher photon density beams

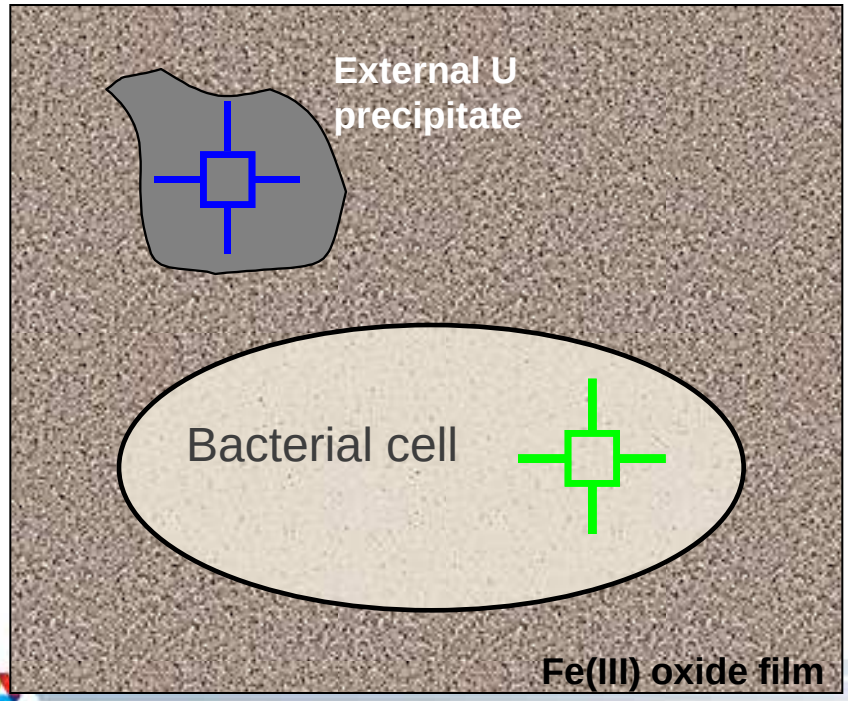
SEM

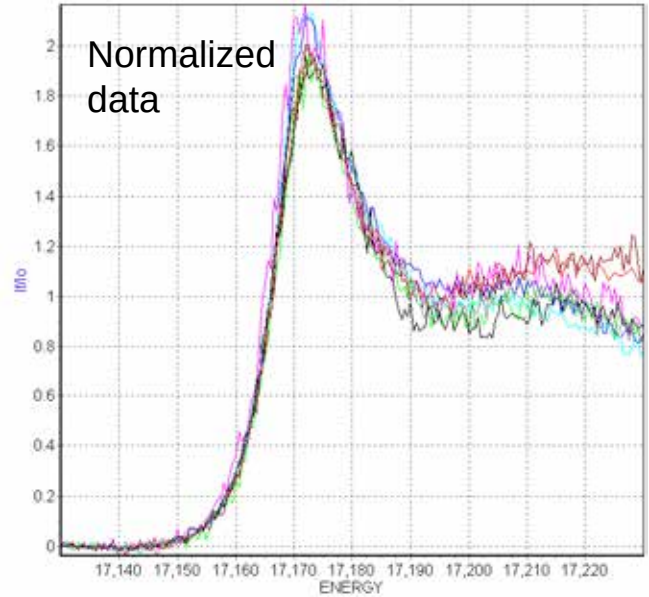






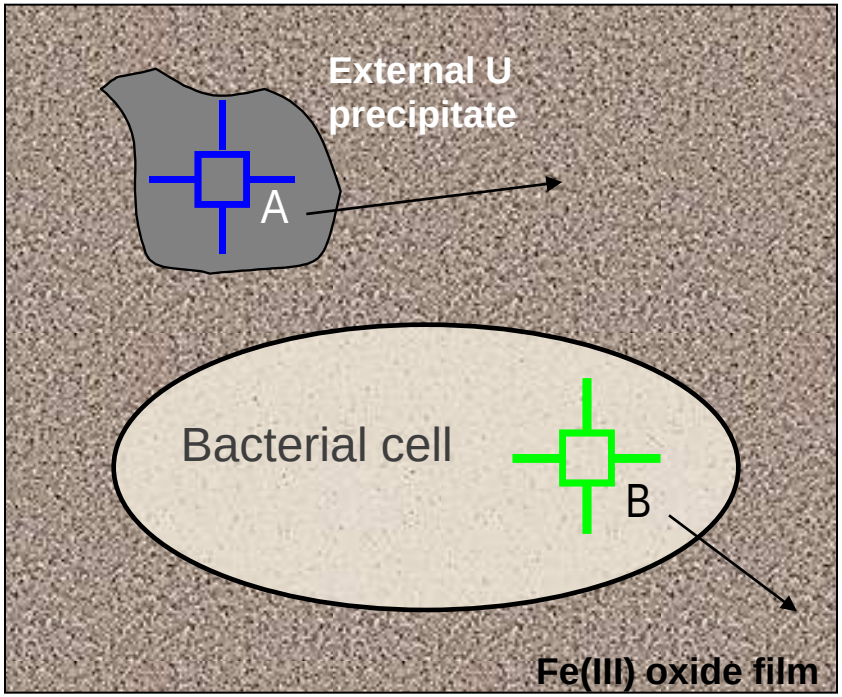
U + *Shewanella* MR1 on thin iron oxide film

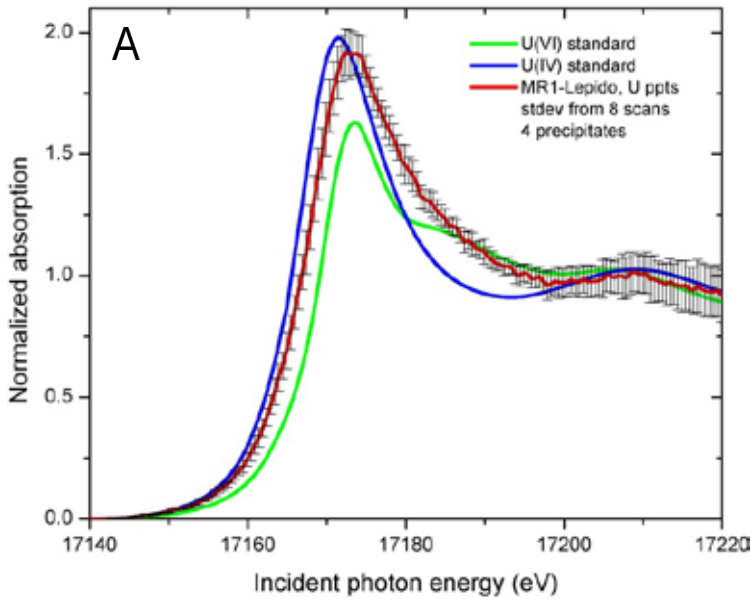


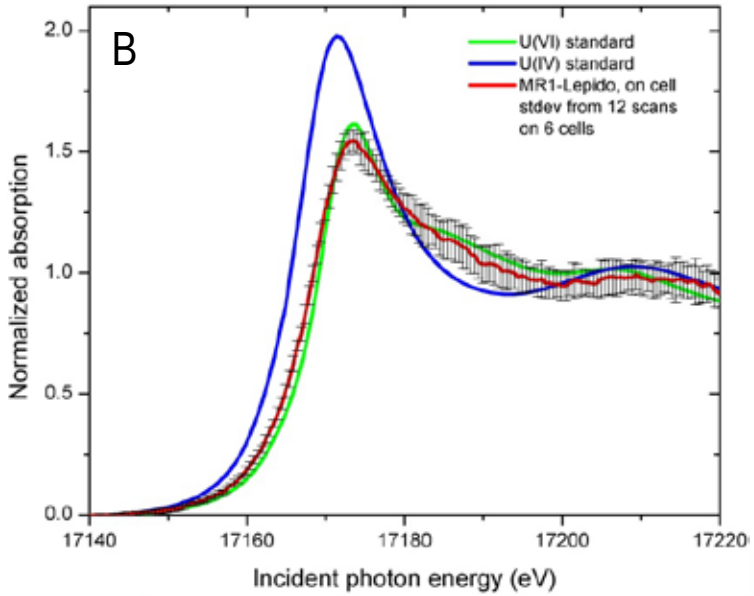


Kemner et al., in preparation

Spectroscopy with higher photon density beams





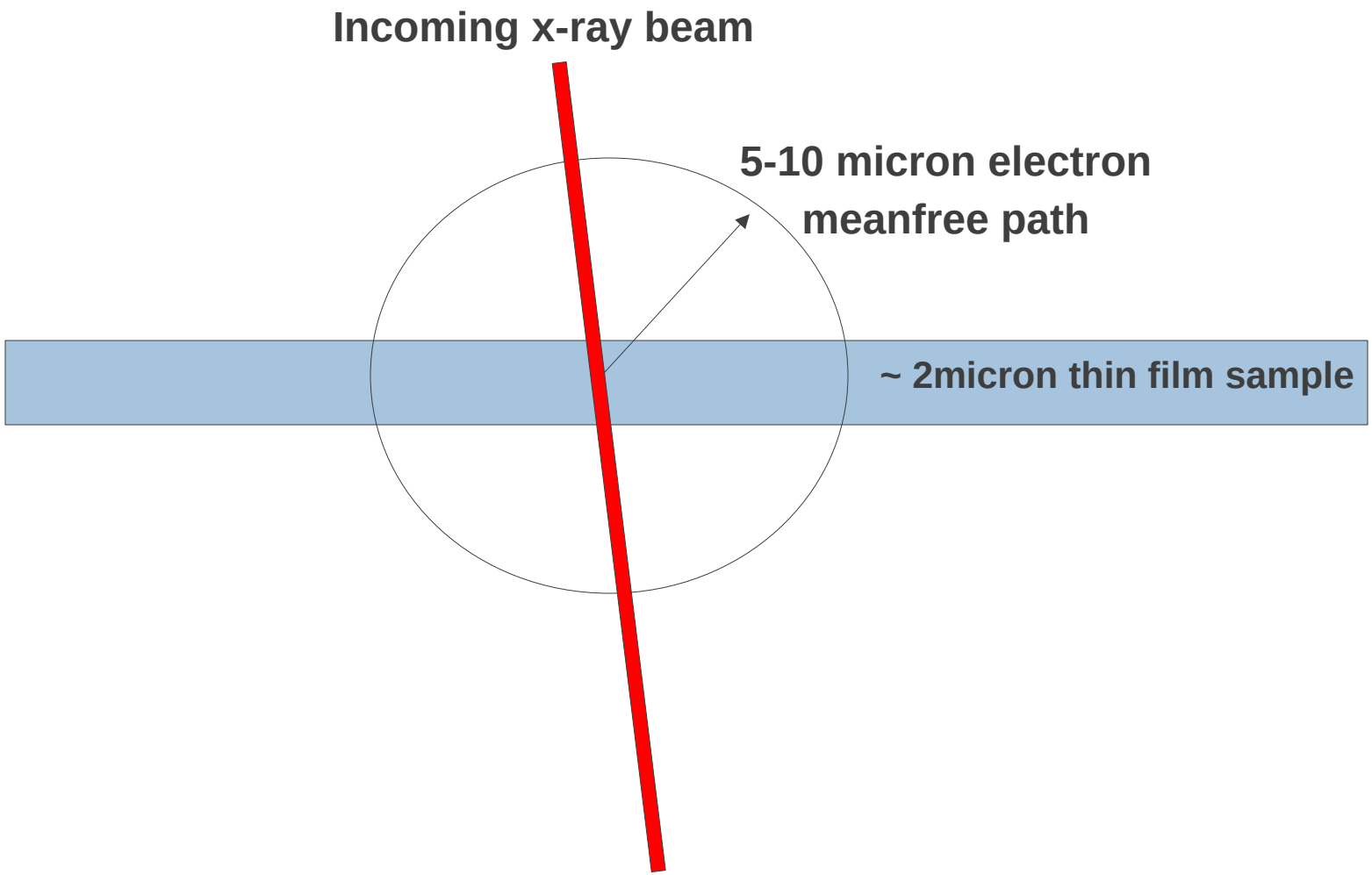


Only 2 scans at each spot are used.

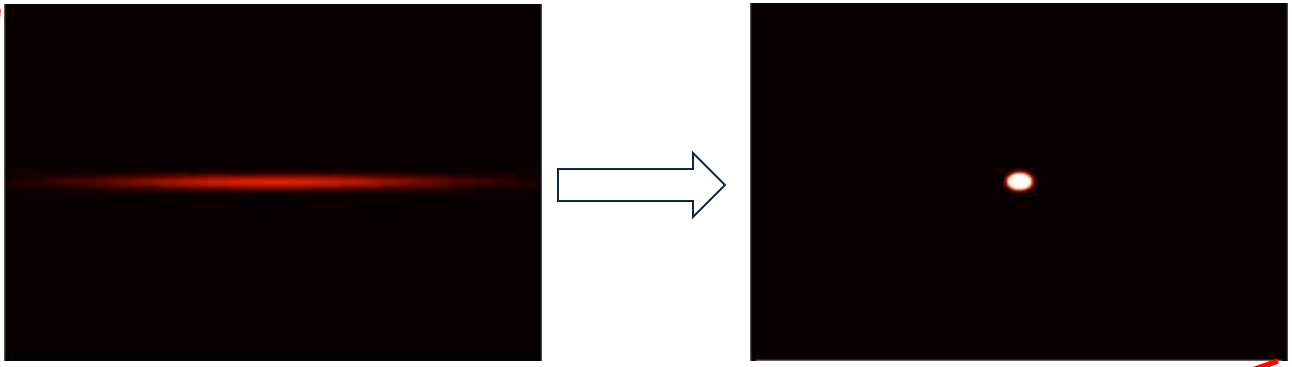
Averaging over several cells or precipitates results in analyzable XANES spectra.

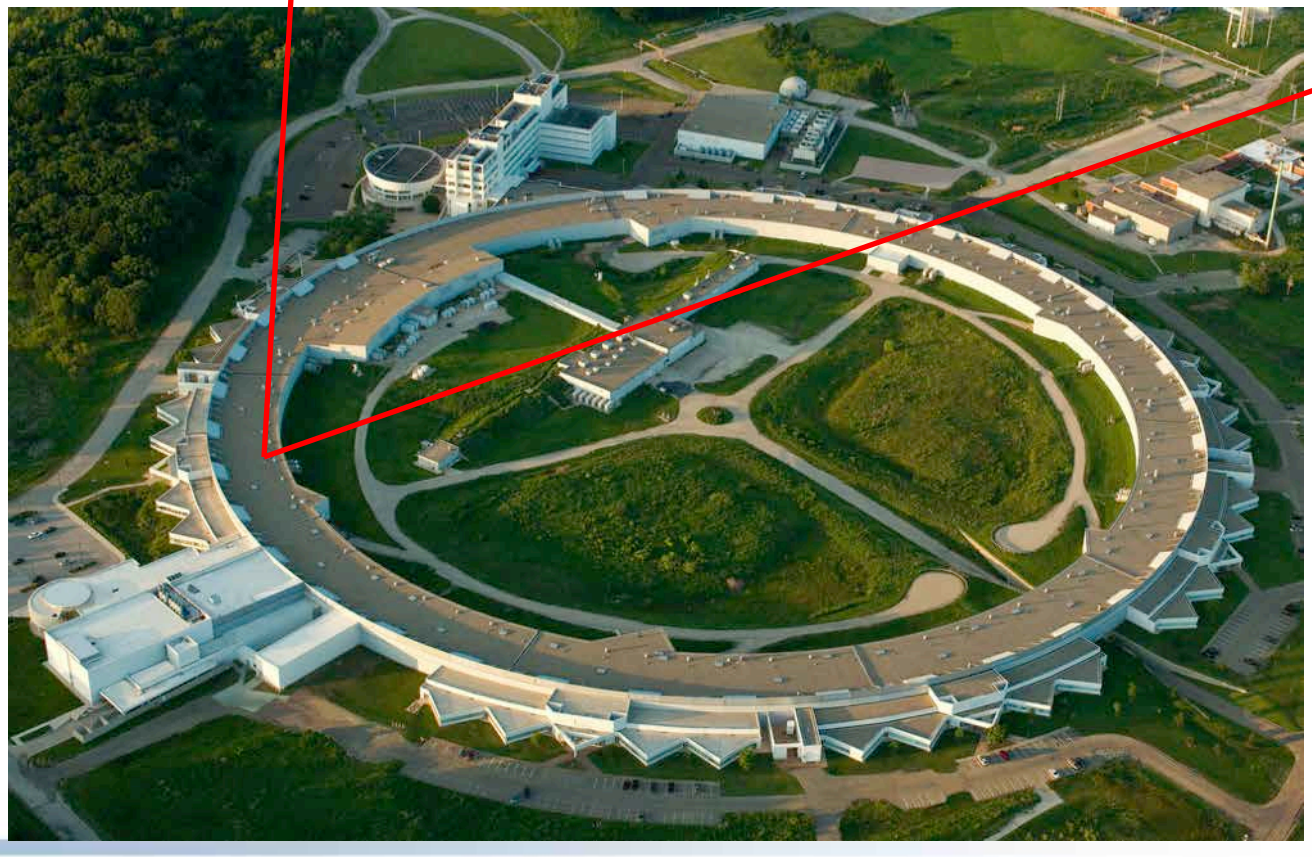
Kemner et al., in preparation

Why don’t we see catastrophic radiation damage at U LIII edge?



An MBA lattice at APS: a new generation





Summary

- Third generation synchrotron x-ray sources provide an opportunity to obtain critical information concerning environmental and biogoechemical systems.
- Radiation damage can be an unfortunate consequence of these intense radiation sources.
- Not all samples respond the same way to radiation damage.
- Ways to deal with damage (measure before damage overwhelms your measurement)
  - “run away” from it
  - Freeze samples
  - Thin samples with small beams