Synchrotron Radiation Based Techniques for Nuclear Power Research

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Calgary, June 3, 2009

Why a talk about "synchrotron radiation"?

There are still a lot of open problems (regarding chemistry and material sciences) connected to the nuclear fuel cycle and to the operation of nuclear power plants (Lunch talk on Tuesday)!

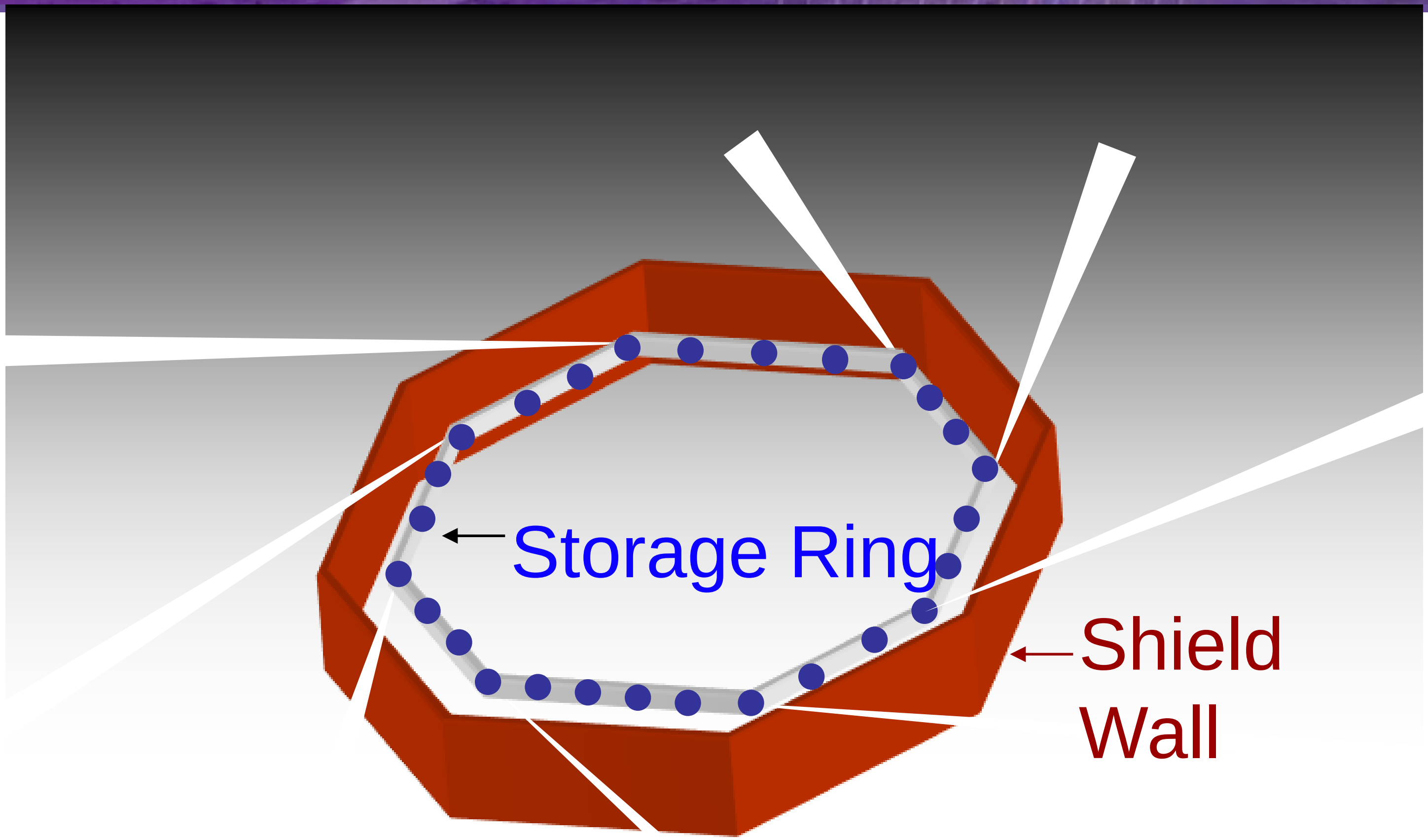
Synchrotron radiation based techniques can help to solve these problems!

Canada has a synchrotron radiation facility: Canadian Light Source (CLS inc.) in Saskatoon (Group for collaboration with industry!!)

“Typical” problems in Nuclear Power Research

- **Chemistry and Materials**
  - Stress corrosion cracking (SAXS, XRD, tomography)
  - Corrosion of carbon steel (XAS)
  - Lead induced stress corrosion (XAS, SAXS)
  - Gadolinium Chemistry in Moderator Water (XAS)
  - Crystal structure of Pure and Dy-Doped Urania (XRD)
  - Magnetic moment of Nb in Zirconia (XAS)
- **Environment and Waste Management**
  - Spent Nuclear Fuel Disposal Containment (XAS, SAXS)
  - Removal of Radionuclides and Metal contaminants from liquid effluents (XAS)
  - Concrete Spent Fuel Dry Storage Module (SAXS, XRD)

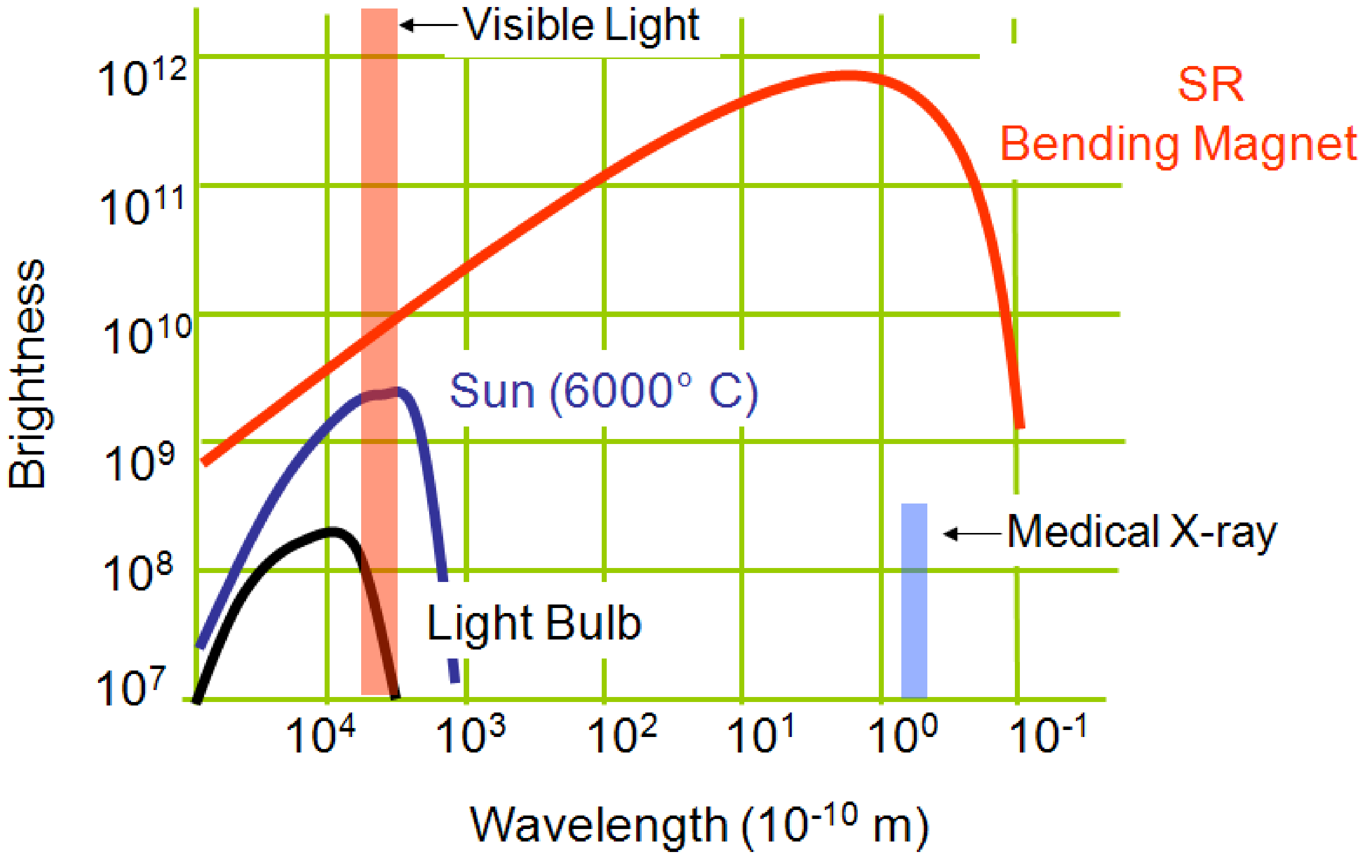
What is Synchrotron Radiation (SR)?



Synchrotron radiation is “light” (electro-magnetic radiation) emitted from electrons moving with about the speed of light on macroscopic circular orbits (synchrotrons, storage rings)

The properties of synchrotron radiation

SR is the most intense light source in the VUV and X-ray spectral regions



The properties of synchrotron radiation

- Continuous spectrum

  (1 eV – 100 keV, most intense spectrum in the VUV and X-ray region)

- Collimation **(1 mrad)**

  - **New X-ray techniques (XAS, element specific tomography)**
  - **Improvement of “standard” techniques (spatial/time resolution, detection limits)**

Why are X-rays so important?

- X-ray have high energies (keV)
  - "Looking through matter"

    (in situ investigations!)
  - Fabrication of tall structures (microfabrication) →

    LiGA = X-ray lithography

- X-ray have short wavelengths (Å)
  - Investigation of small particles (cells, molecules, atoms)
  - Fabrication of small structures microelectronics)

Why are X-rays so important?

Wilhelm Conrad Röntgen
1845 - 1923

X-ray image 1895
Hand of Röntgen's wife

Analytical X-ray Techniques

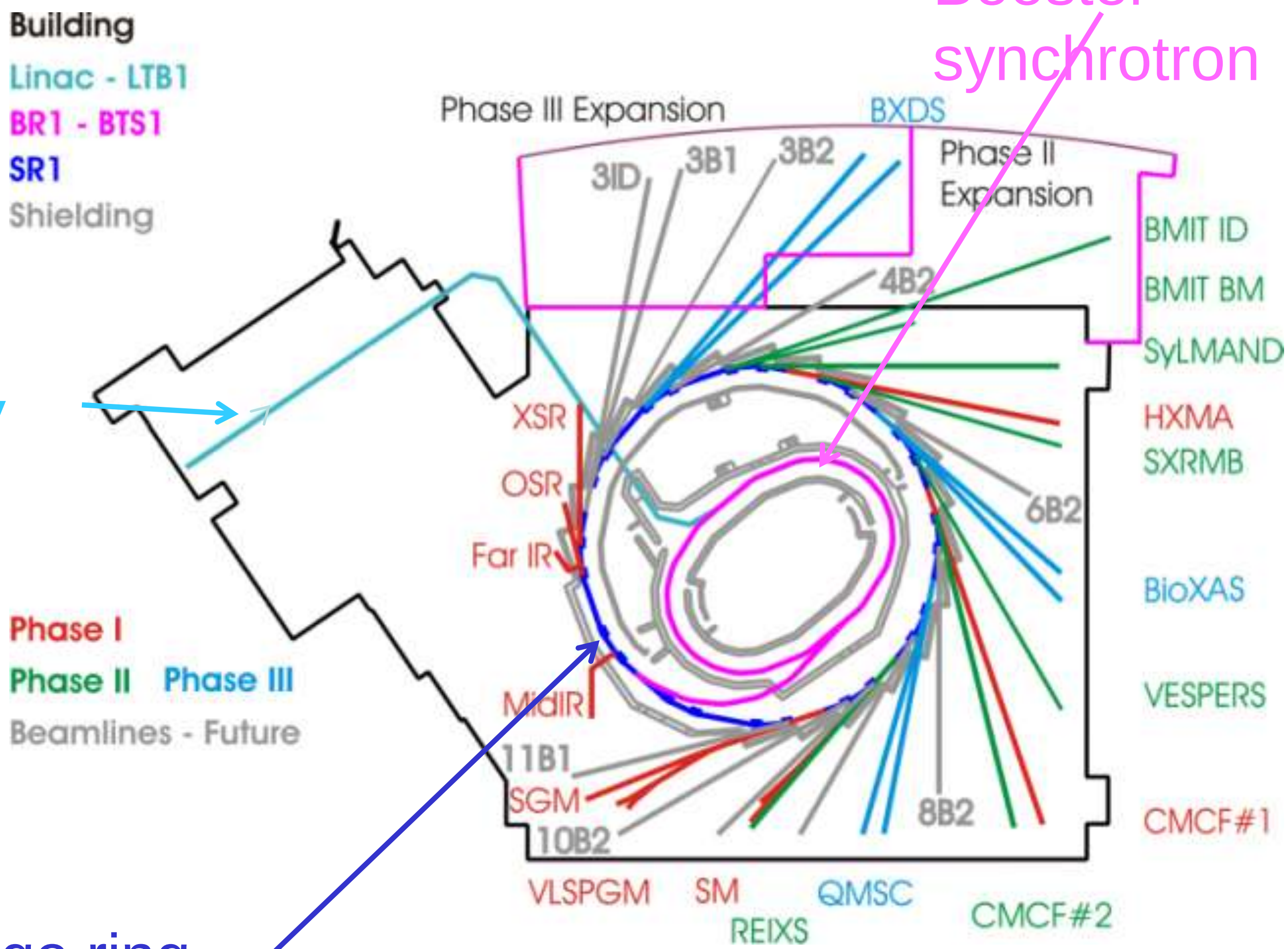
- X-ray fluorescence (Type of element and concentration in the sample)
- X-ray diffraction (Crystallographic structure of the sample, minerals)
- Small angle X-ray scattering (Structural inhomogeneities in the sample, 0.001–1 mm)
- X-ray absorption spectroscopy (Speciation of elements; geometric structure around a specific element)
- X-ray tomography (3-dim images (element – specific))

The Canadian Light Source in Saskatoon I

Canadian Light Source: the floor plan:

Booster synchrotron

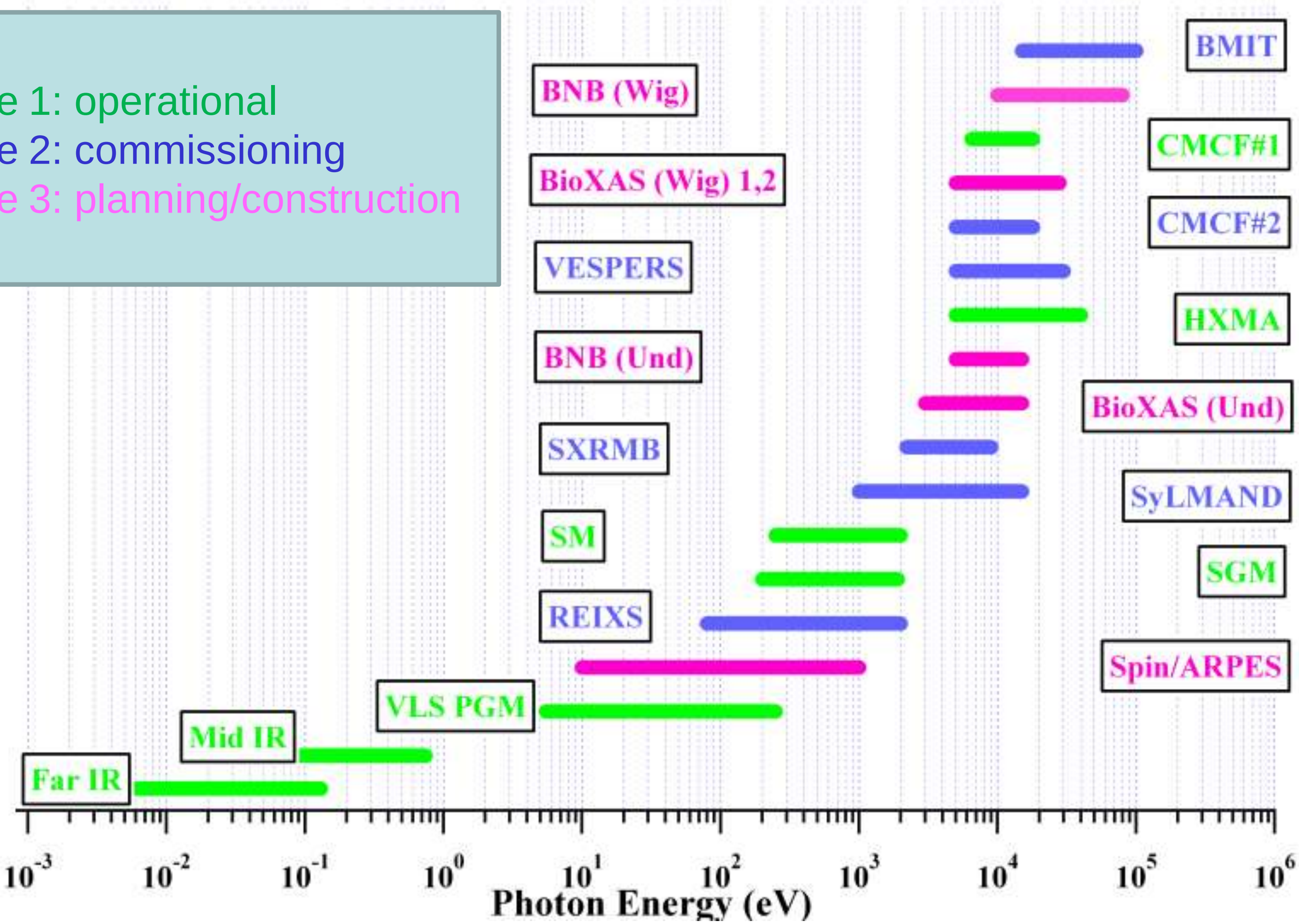
250 MeV Linac



Storage ring

CLS: beamlines phase I, II and III

Phase 1: operational
Phase 2: commissioning
Phase 3: planning/construction

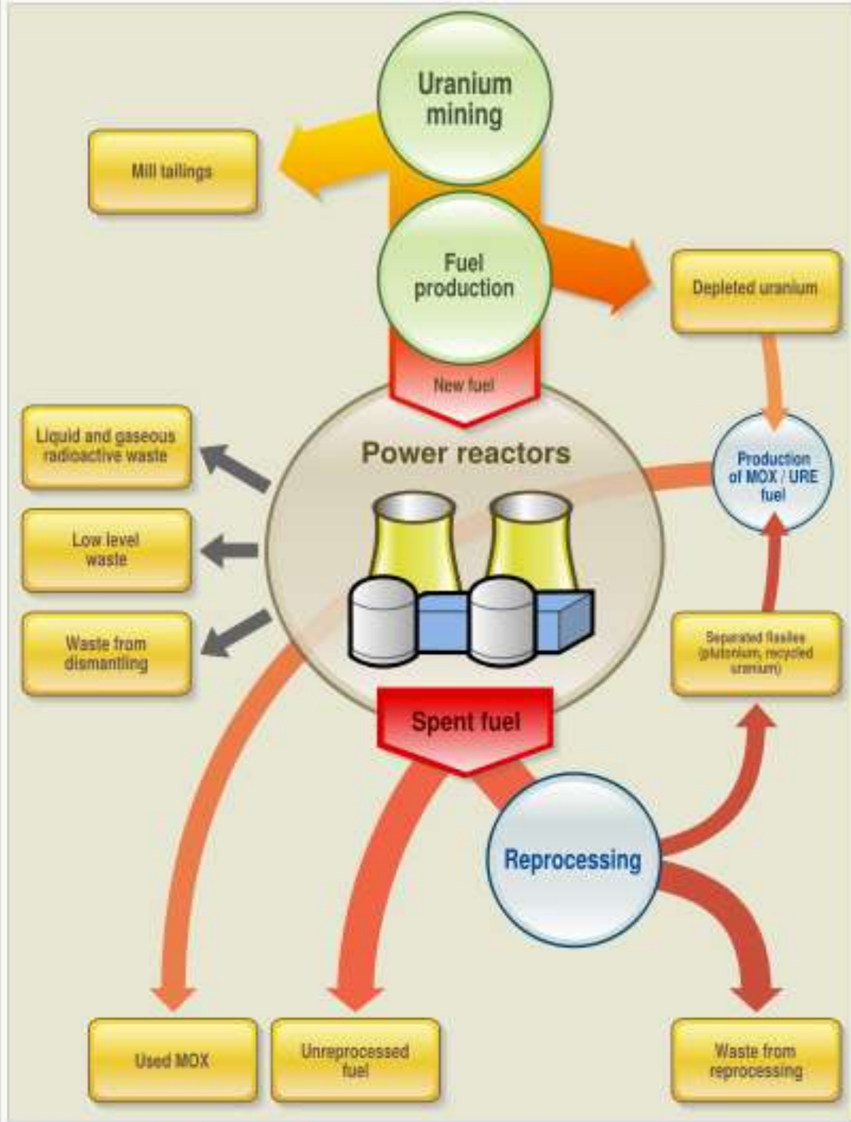


Some Problems in Nuclear Fuel Processes

Mining
Complexation/Reactivity
(Canada – Arsenic)

Geologic Storage
- Stability?
- Phases, Reactions?
- Subsurface character?

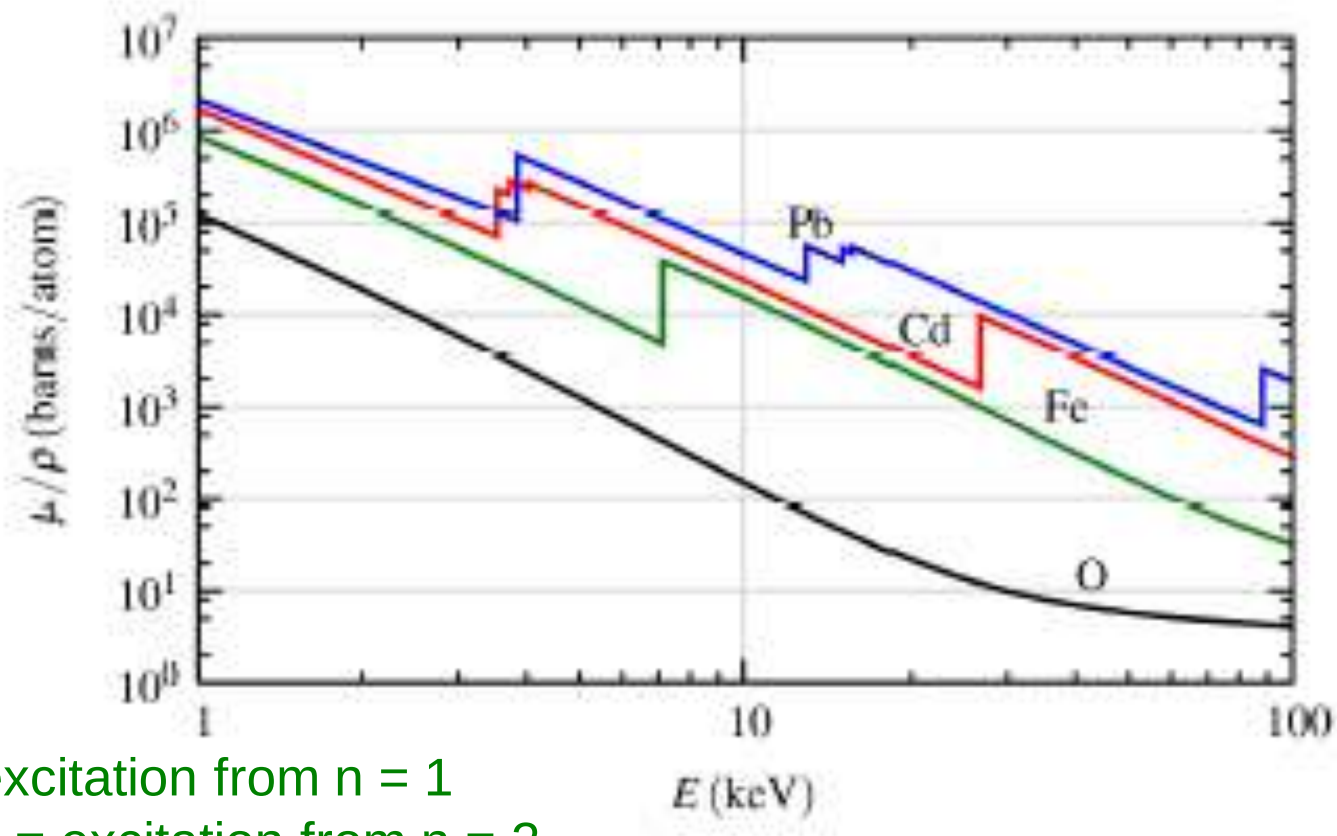
Safety/Security
- Environmental Concerns
  - (hot particles)
- Nuclear Forensics
  - (Spent Fuel – Origins?)



Nuclear Fuel Process

X-ray absorption spectroscopy :

X-ray absorption "edges" are characteristic for each element

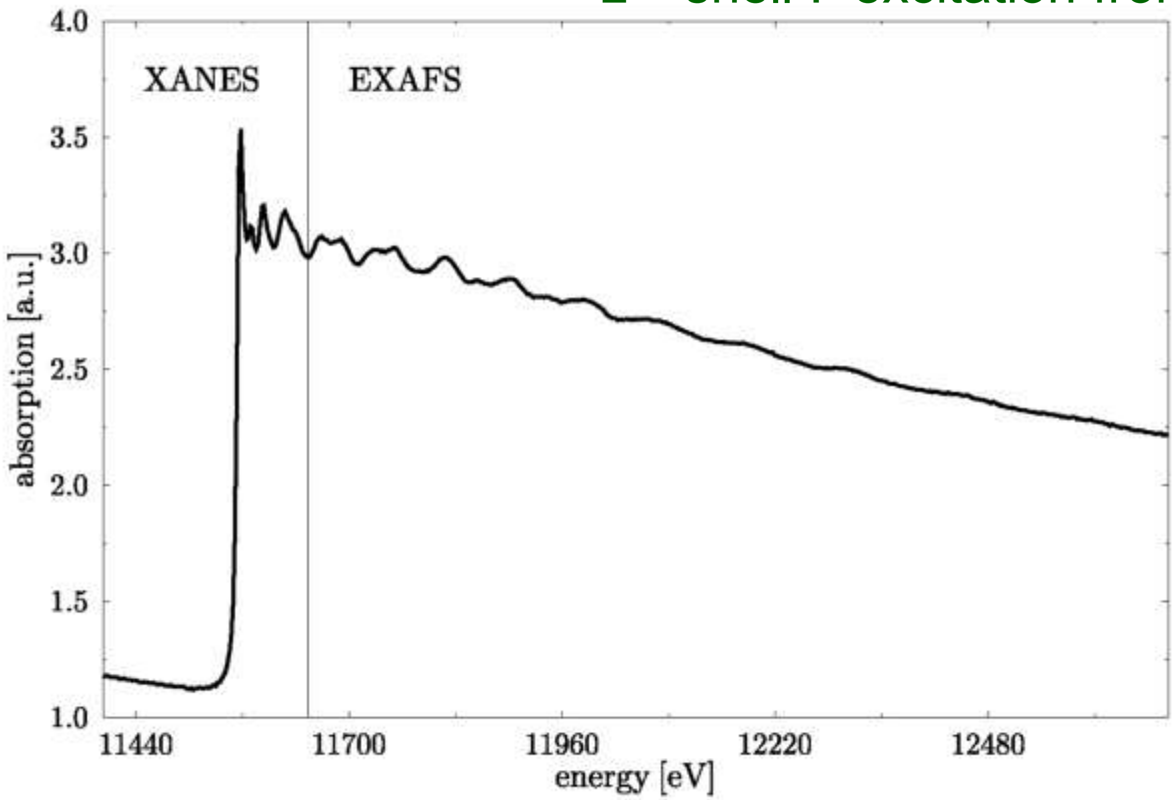


K –edge = excitation from n = 1

L $_{I,II,III}$ –edge = excitation from n = 2

X-ray absorption spectrum Pt-L-III-edge of Pt-metal

K – shell : excitation from n=1→∞
L – shell : excitation from n=2 →∞

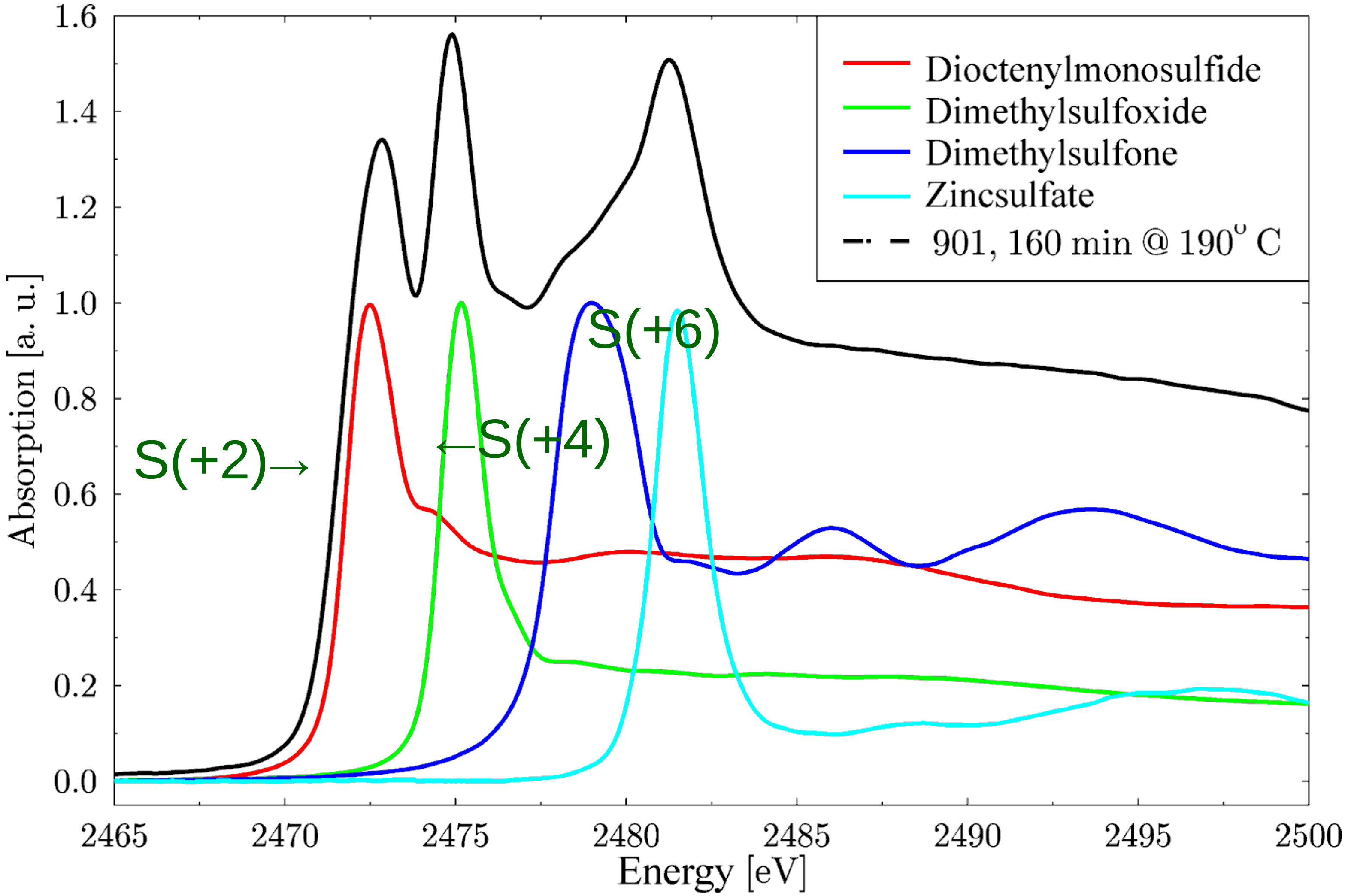


XANES = X-ray absorption near edge structure
EXAFS = Extended X-ray absorption fine structure

What can be learned from X-ray absorption spectra?

- Valency of the excited atom
- Symmetry of unoccupied electronic levels
- Electronegativity of neighboring atoms
- Radial distances between the excited atom and the neighboring atoms in the “first” coordination shells (± 0,005Å → ± 0.01Å)
- Coordination number (± 25%)
- “Type” of neighboring atoms Z (±5)

Influence of "valency" on S-K-XANES spectra (I)



Advantages of X-ray absorption spectroscopy as analytical technique:

- Element specific
- Non-destructive
- No long range order required
- Extremely sensitive (ppm – range?)
- No special requirements for the samples
- Quantitative analysis of spectra is possible
- “No vacuum” required
- Time resolved “in situ” experiments are possible

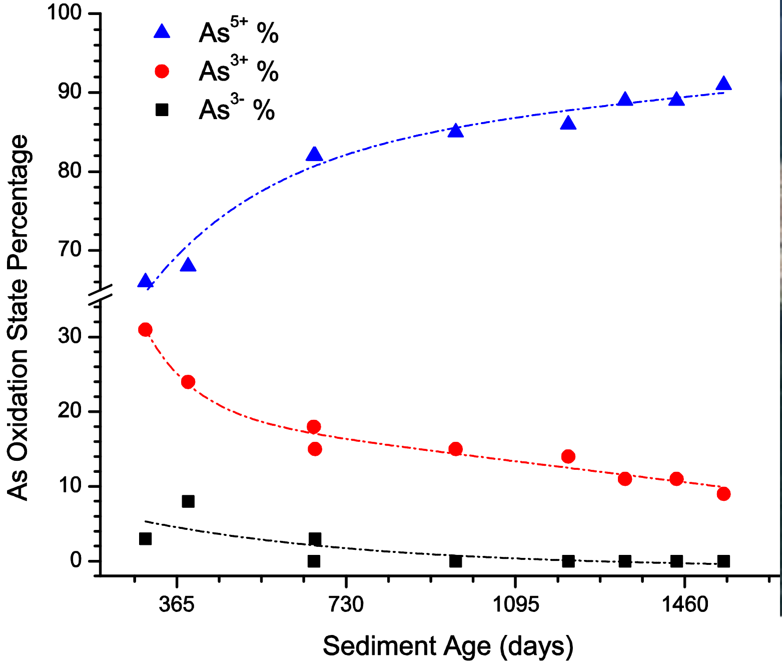
Arsenic in Mining

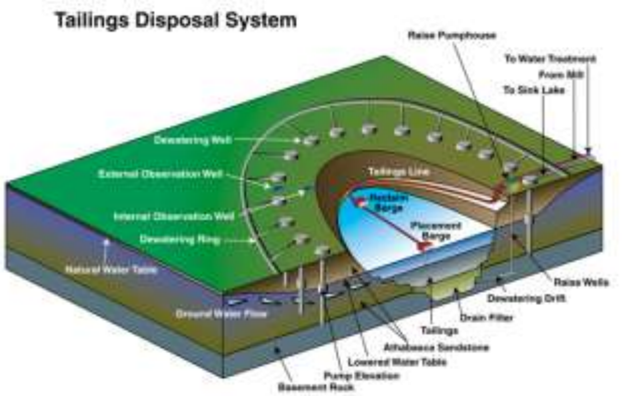
Arsenic is a common component in tailings impoundments

Some of the open questions:

- how arsenic is retained and released, i.e. binding processes, and how this affects long term stability
- microbial transformation of arsenic, chemical mobility and chemical speciation
- the long term stability of arsenic in submerged tailings and other reducing conditions
- need to know more about the fate and behaviour of arsenic during mill processing and waste treatment

Arsenic in Mill Tailings





Understanding the stability and long term fate of mill tailings

Arsenic in Mining

American Mineralogist, Volume 83, pages 553–568, 1998

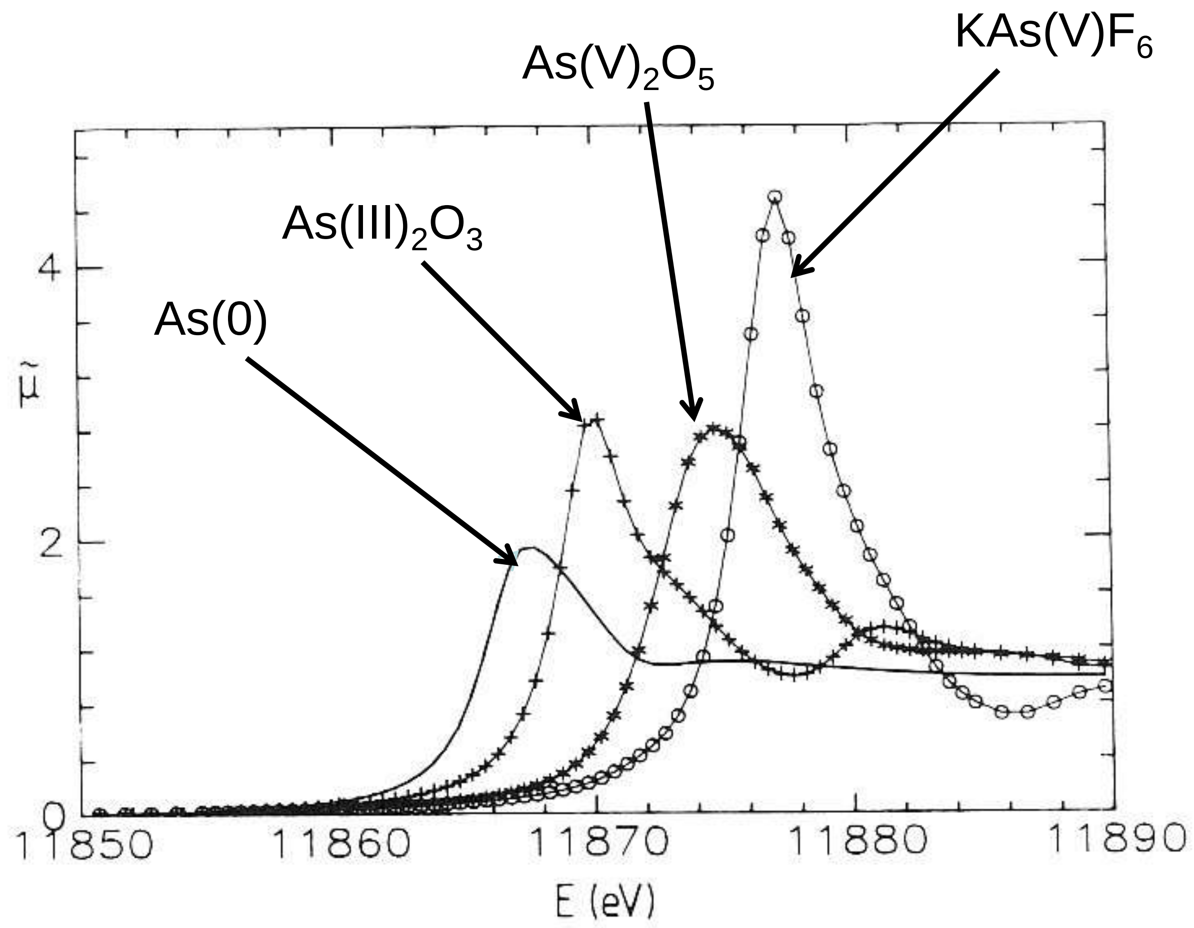
Quantitative arsenic speciation in mine tailings using X-ray absorption spectroscopy

ANDREA L. FOSTER,[1,*] GORDON E. BROWN JR.,[1,2]
TRACY N. TINGLE,[1,3†] AND GEORGE A. PARKS[1]

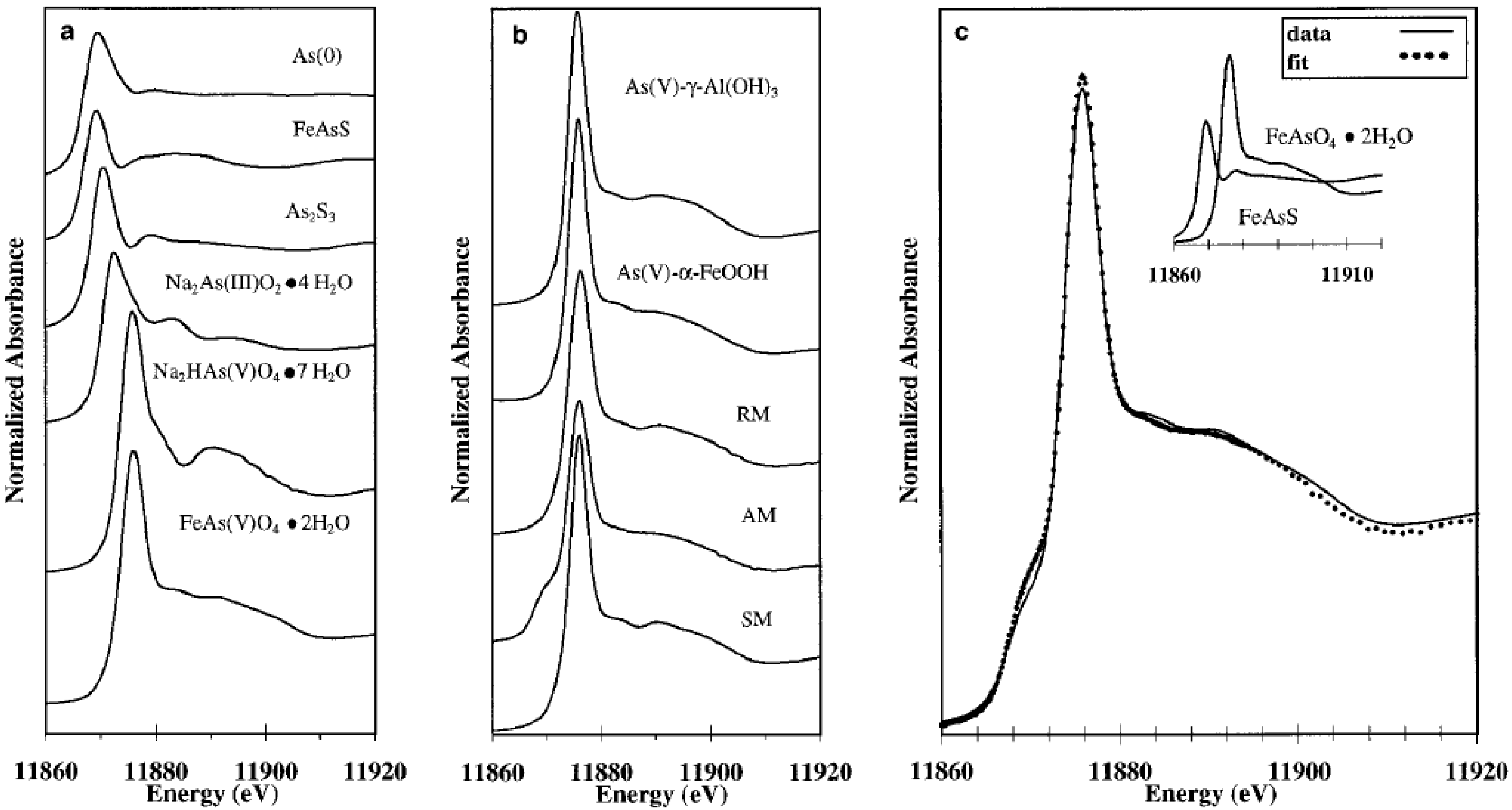
three California mine wastes were investigated:

- fully oxidized tailings (Ruth Mine),
- partially oxidized tailings (Argonaut Mine), and
- Roasted sulfide ore (Spenceville Mine).

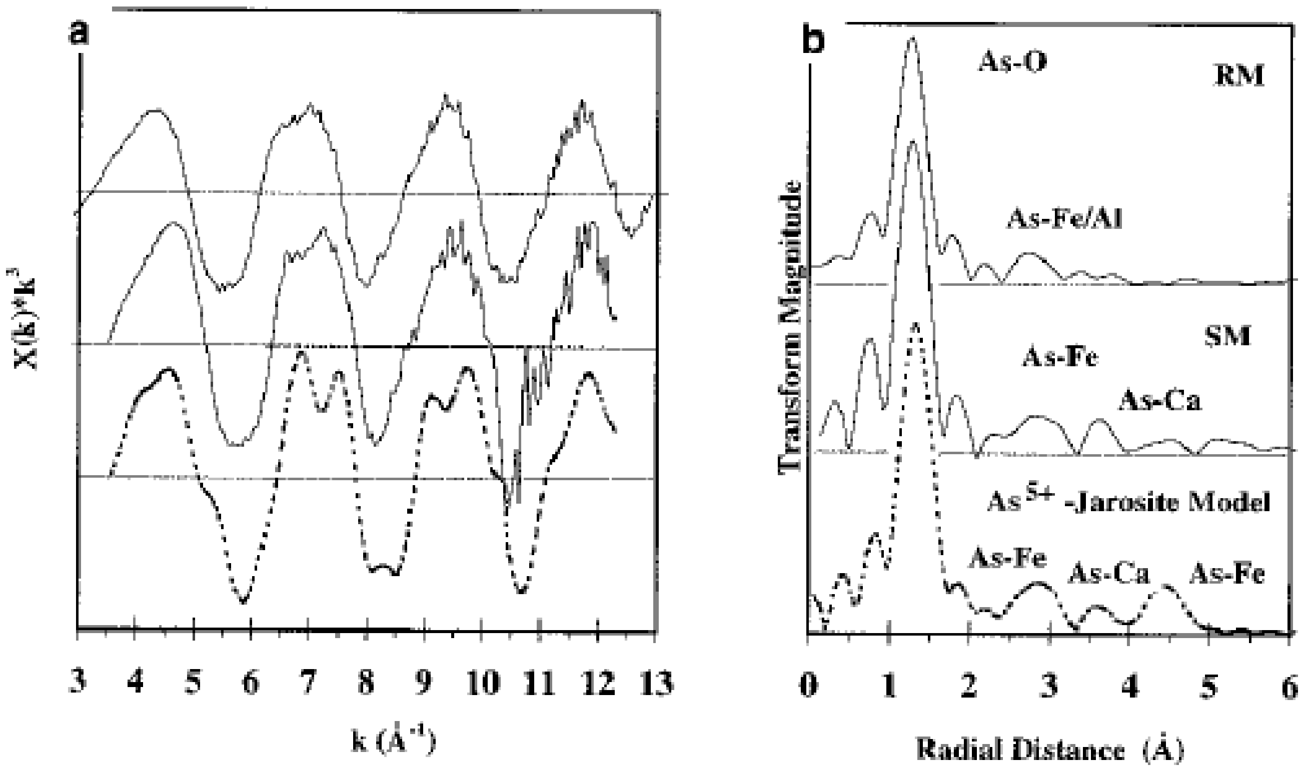
Arsenic K-XANES Spectra



Arsenic in Mining



Arsenic in Mining



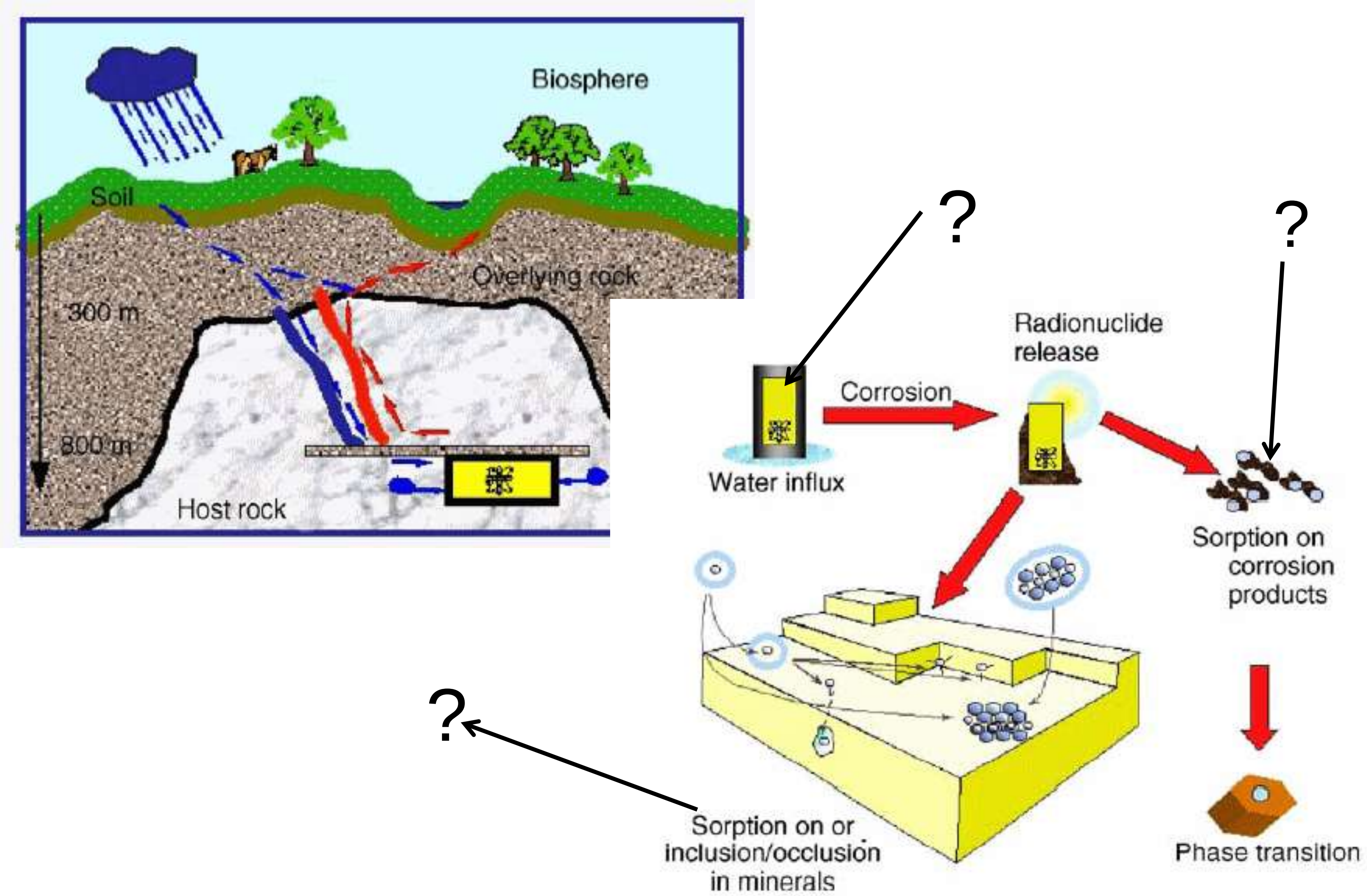
Dominant valency is As(V)

Ruth mine: sorbed on ferric oxyhydroxides + aluminosilicates

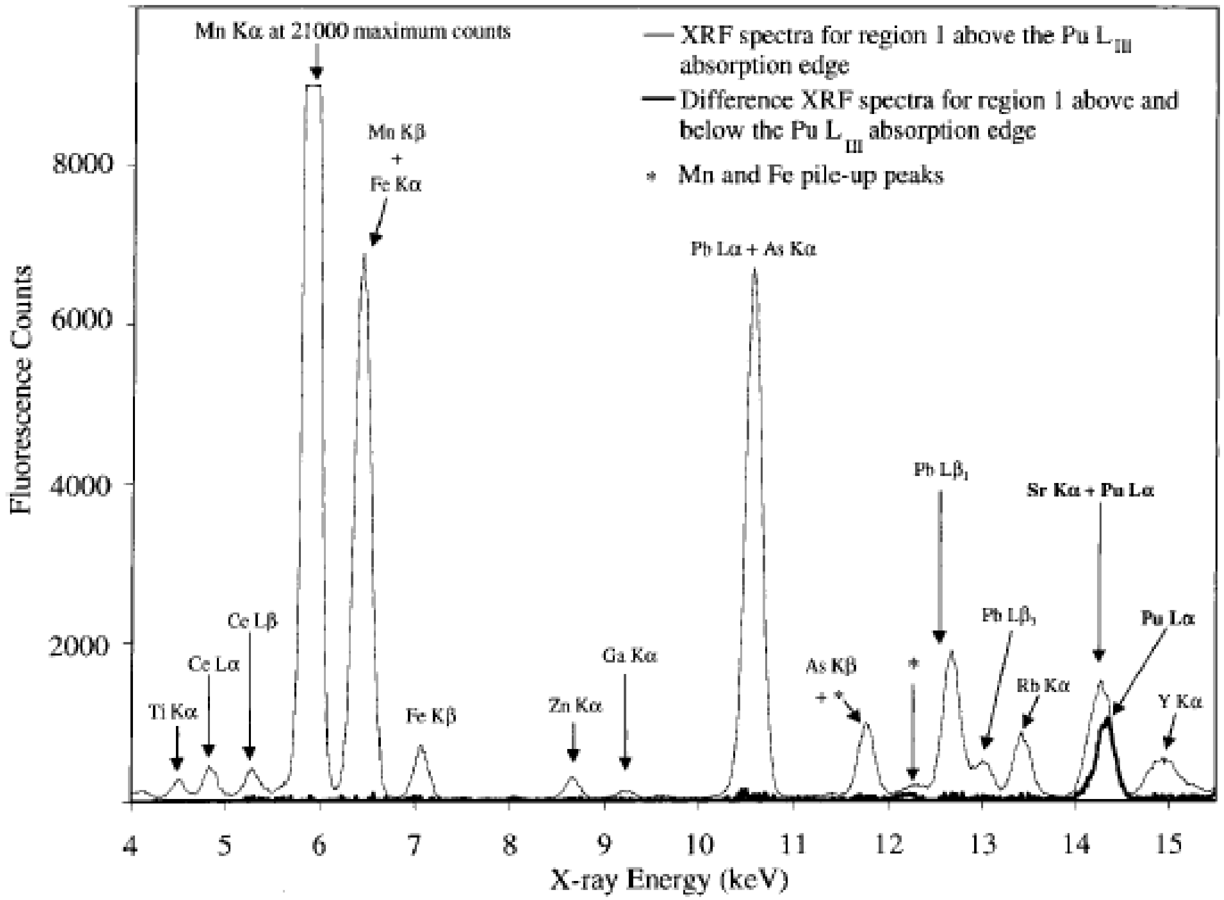
Argonaut mine: 20% arsenopyrite (FeAsS) + 80% in a precipitate

Spenceville mine: in jarosite (KFe3(SO4)2(OH)6 + sorbed on hematite

Geological storage of high level nuclear waste

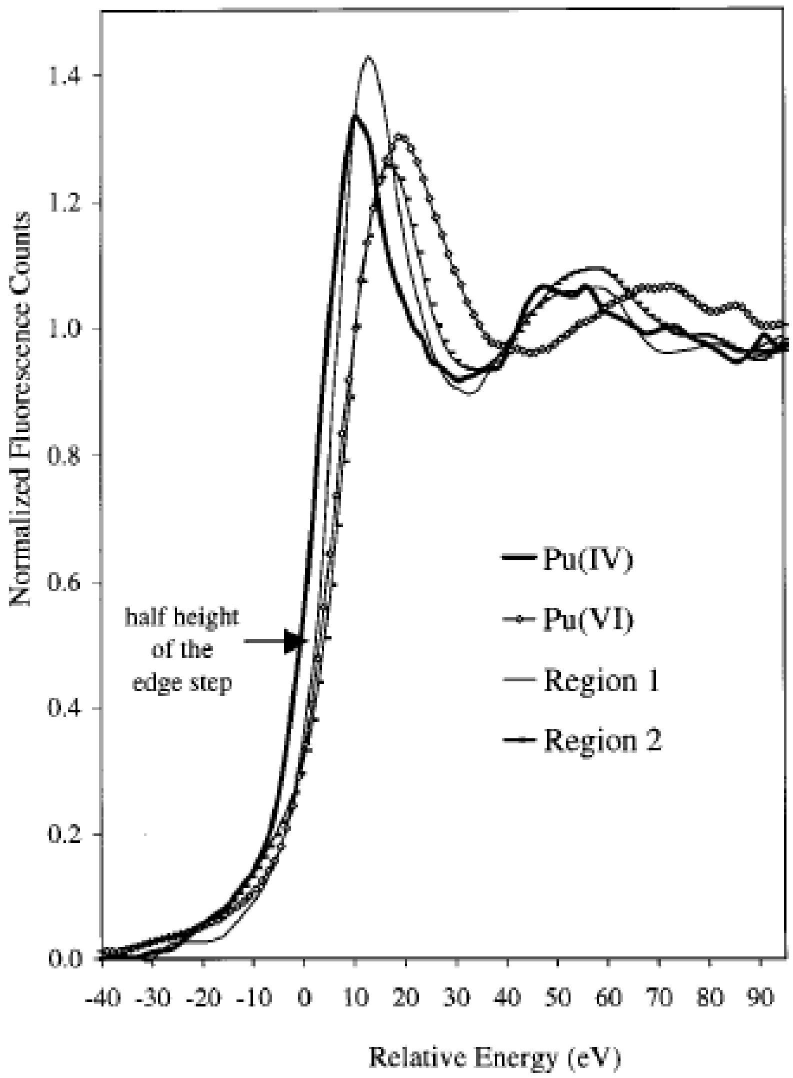


Mineral Associations and Average Oxidation States of Sorbed Pu on Tuff: I



- M.C. Duff et al. Environ. Sci. Technol. 1999, 33, 2163-2169

Mineral Associations and Average Oxidation States of Sorbed Pu on Tuff: II

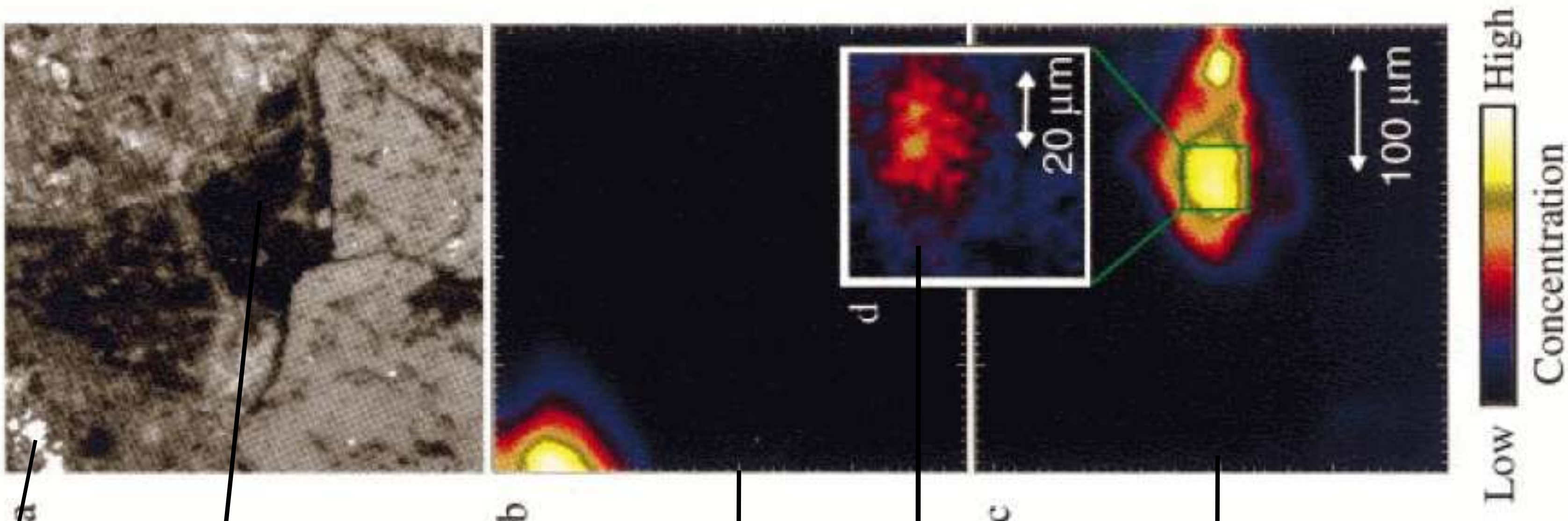


Spatially resolved Pu L-III XANES spectra

In different regions of the material Pu has different valencies (different speciation!)!

Mineral Associations and Average Oxidation States of Sorbed Pu on Tuff: III

Spatially resolved X-ray fluorescence (10 x 15 µm^2



hematite

Manganese oxide

XRF:FE

XRF: Pu

XRF : Mn

Sorption of Pu to tuff at manganese oxide!

XANES and microprobe experiments on *Hanford Sediments*

Cr and ^{137}Cs are a major component of leaking tanks

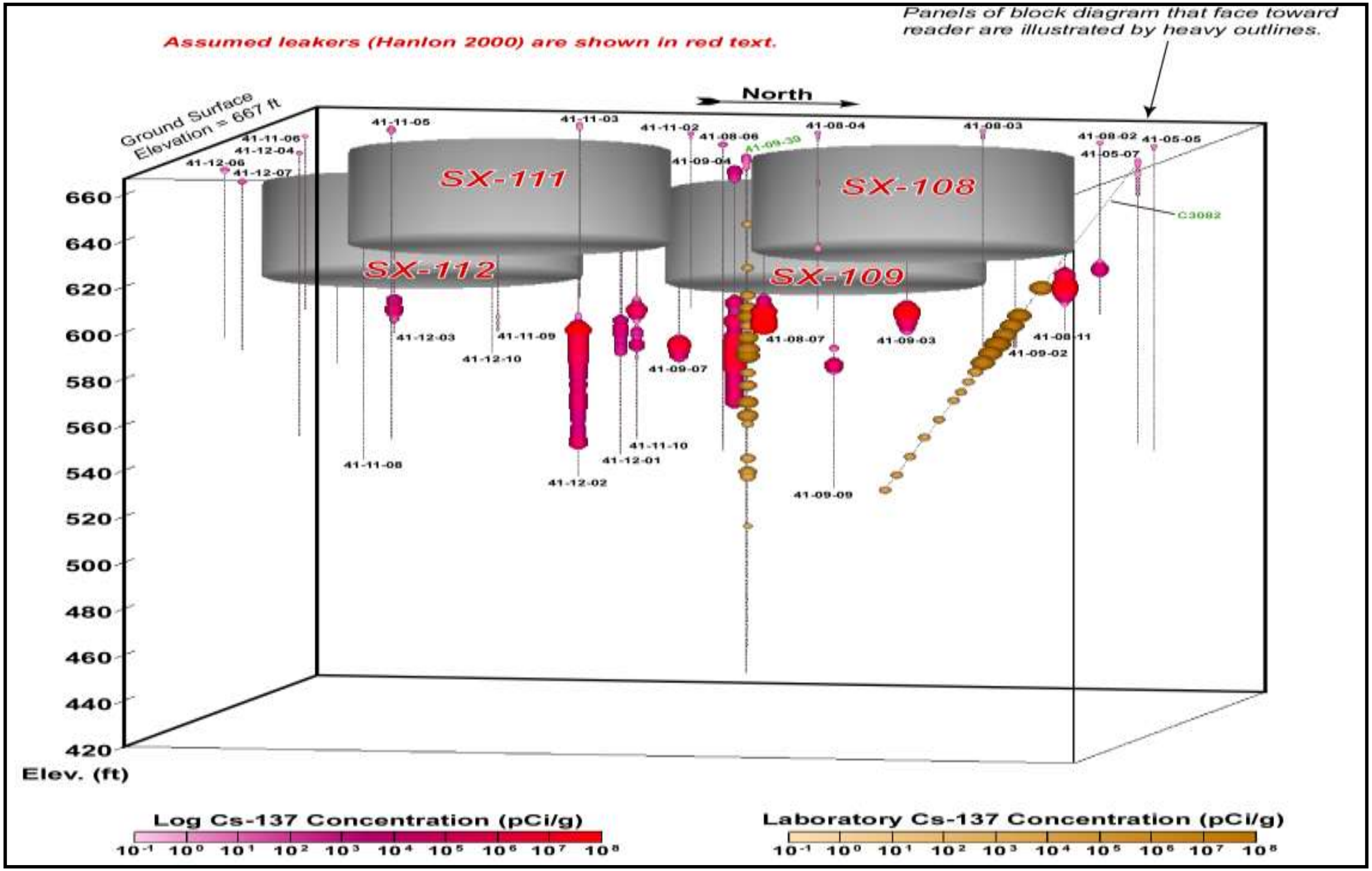
Example Courtesy of

S. M. Heald, J. McKinley and J. Zachara, PNNL, PNC-CAT/APS

Double shelled tanks under construction showing the scale of the problem. (156 tanks of similar size)

Boreholes and ^{137}Cs Distribution Near SX-108 and SX-109

Cr a major non-radioactive concern
Cs is a high yield fission product that partitions to supernatant, 100kCi released in S-SX tank farm

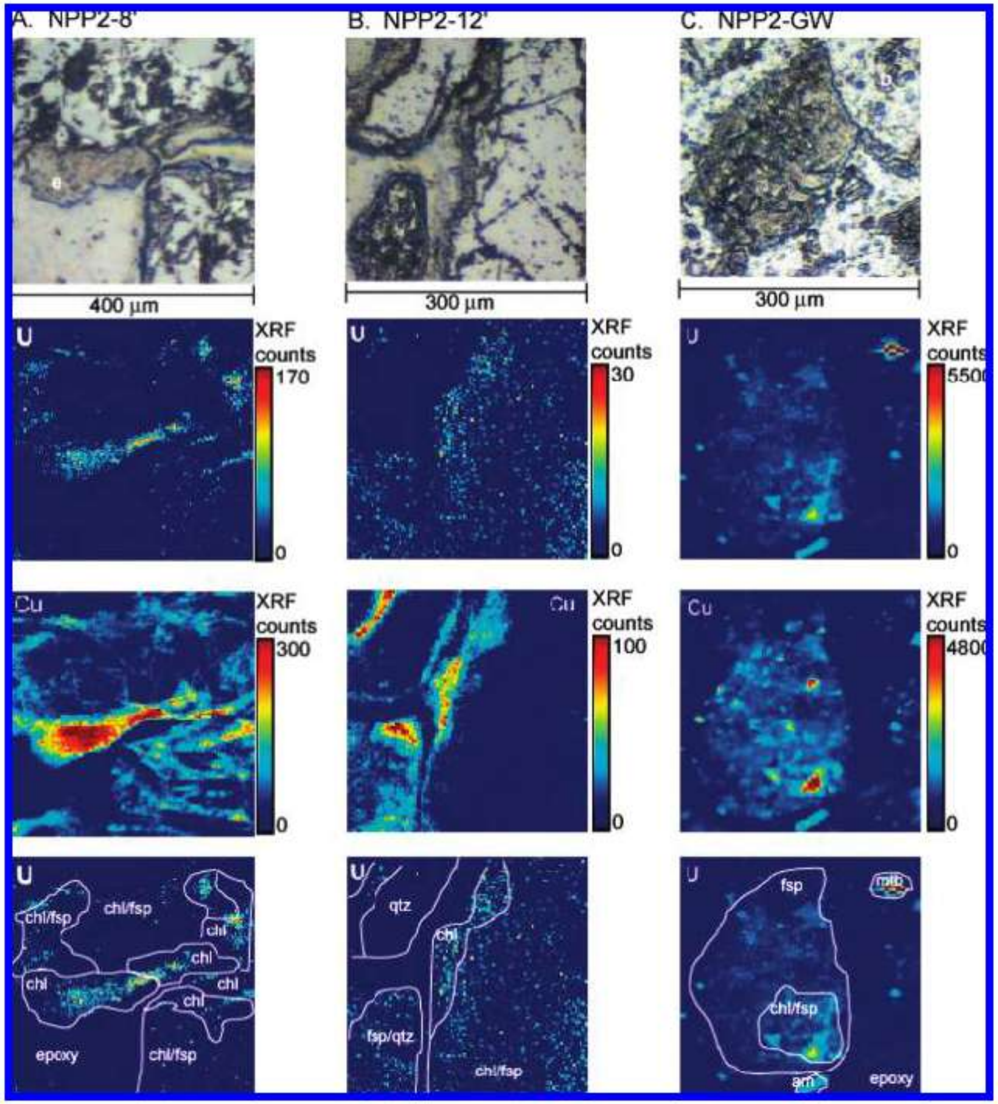


Courtesy of Heald, PNNL, PNC/APS

Uranium Speciation As a Function of Depth in Contaminated Hanford Sediments - A Micro-XRF, Micro-XRD, and Micro- And Bulk-XAFS Study

David M. Singer, John M. Zachara, and Gordon E. Brown Jr

Environ. Sci. Technol., **2009**, 43 (3), 630-636• DOI: 10.1021/es8021045 • Publication Date (Web): 05 January 2009



Micro-XRF U L_{α} and CuK_{α} maps

- **High U concentration spatially correlated with high Cu concentration!**
- **These U-Cu hot spots are X-ray amorphous!**

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chl = clinochlore; cps = cuprosklodowskite, mtb = metatorbernite

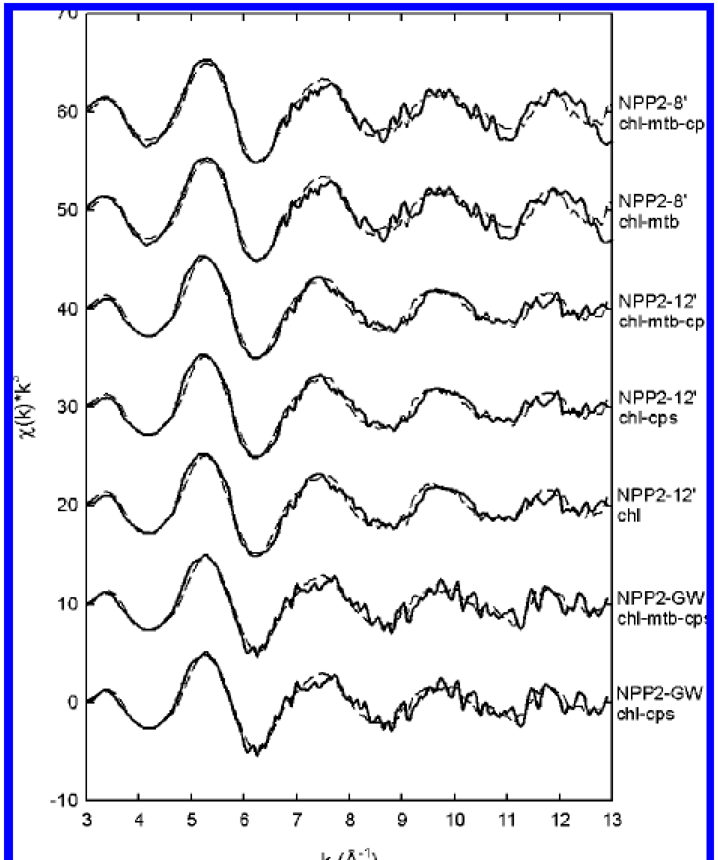
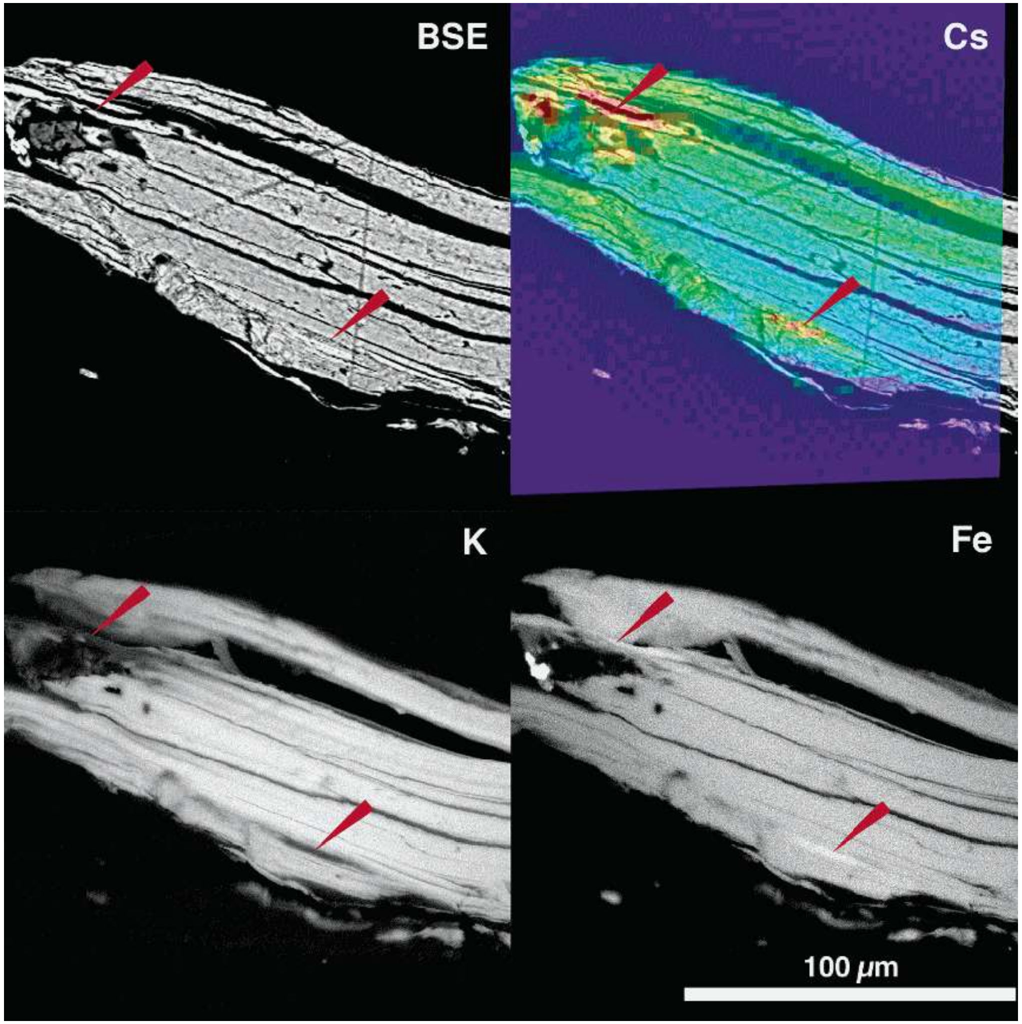


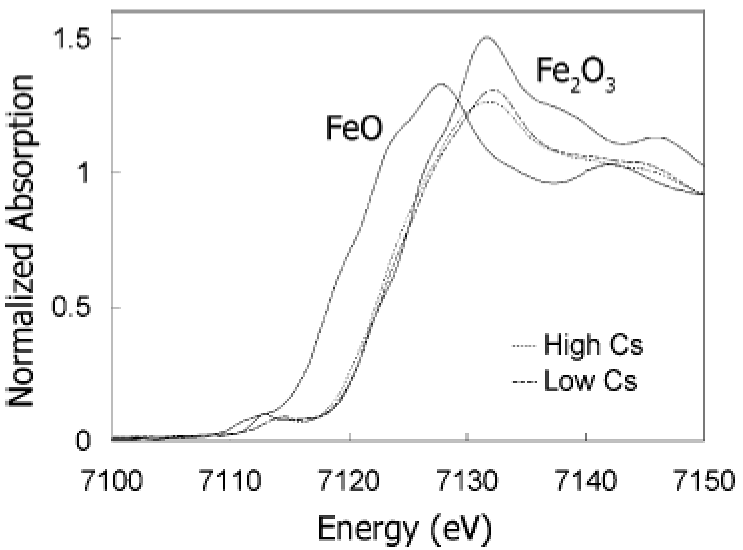
FIGURE 3. Best fit results (dashed lines) by least-squares linear combination Fitting of the bulk U L_{III}-edge EXAFS spectra (solid lines) of the Hanford 300 Area NPP2 sediments samples. The best-fit components are listed for each spectrum are uranyl sorbed to chlorite (chl), cuprosklodowskite (cps), and metatorbernite (mtb). Tabulated best fit results are presented in Table 2.

TABLE 2. Best Fit Results of the Bulk U L_{III}-edge EXAFS Spectra of the Hanford 300 Area NPP2 Sediments[a]

sample depth (ft)	component	component fraction (from fit)	component sum	reduced χ^2
8	chl mtb cps	0.68 0.25 0.06	0.99	0.67
8	chl mtb	0.74 0.25	0.99	0.70
12	chl mtb cps	0.78 0.16 0.07	1.01	0.35
12	chl cps	0.87 0.14	1.01	0.35
12	chl	0.99	0.99	0.38
GW	chl mtb cps	0.63 0.06 0.30	0.99	0.45
GW	chl cps	0.71 0.28	0.99	0.44

Microscale Distribution of Cesium Sorbed to Biotite and Muscovite

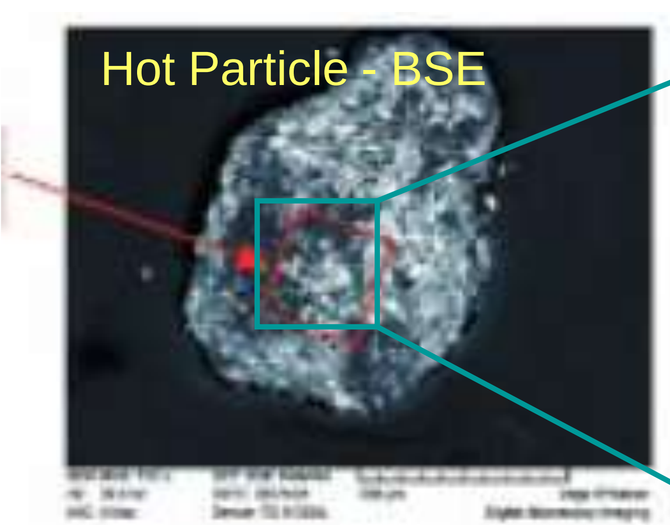




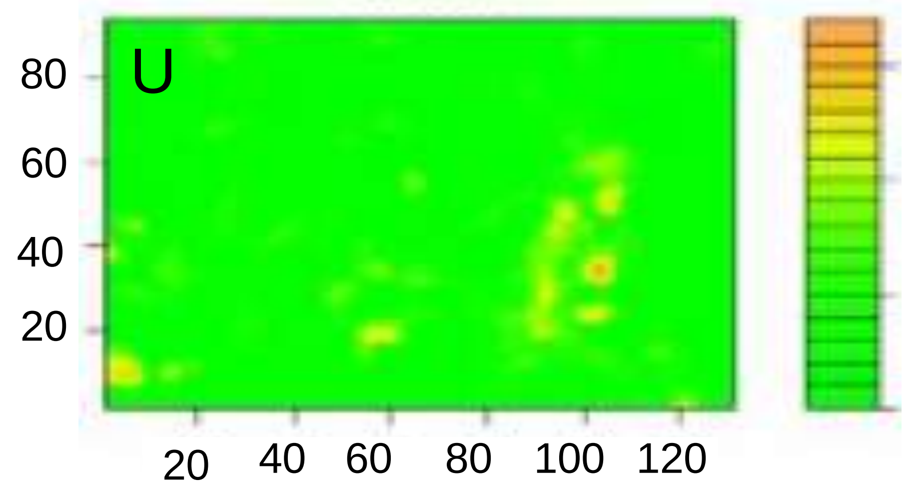
Cs sorbs at mica "edges" and zones where K is depleted and Fe concentration is high (all structural Fe is oxidized!)

Spatial resolution 6 μm detection limit 5 x 10^9 Cs atoms!)

Hot Particles in the Marine Environment – Synchrotron Characterization

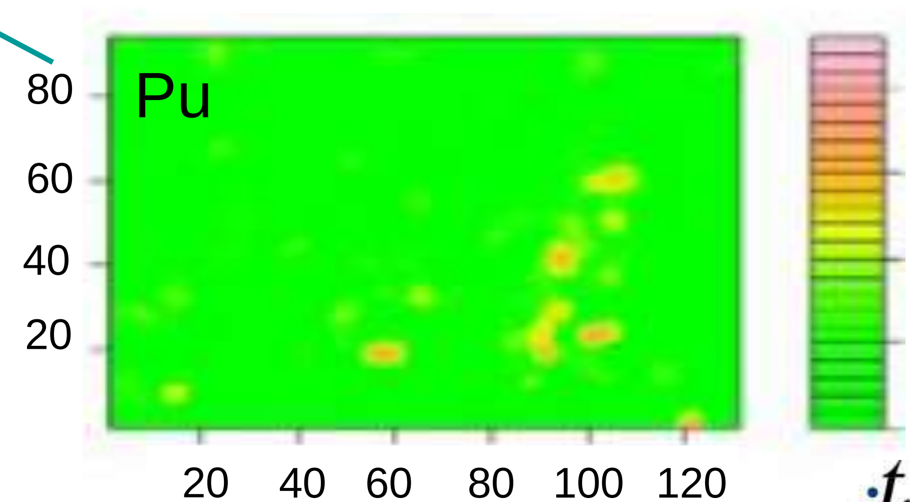


sXRF element mapping (2.5 um beam)



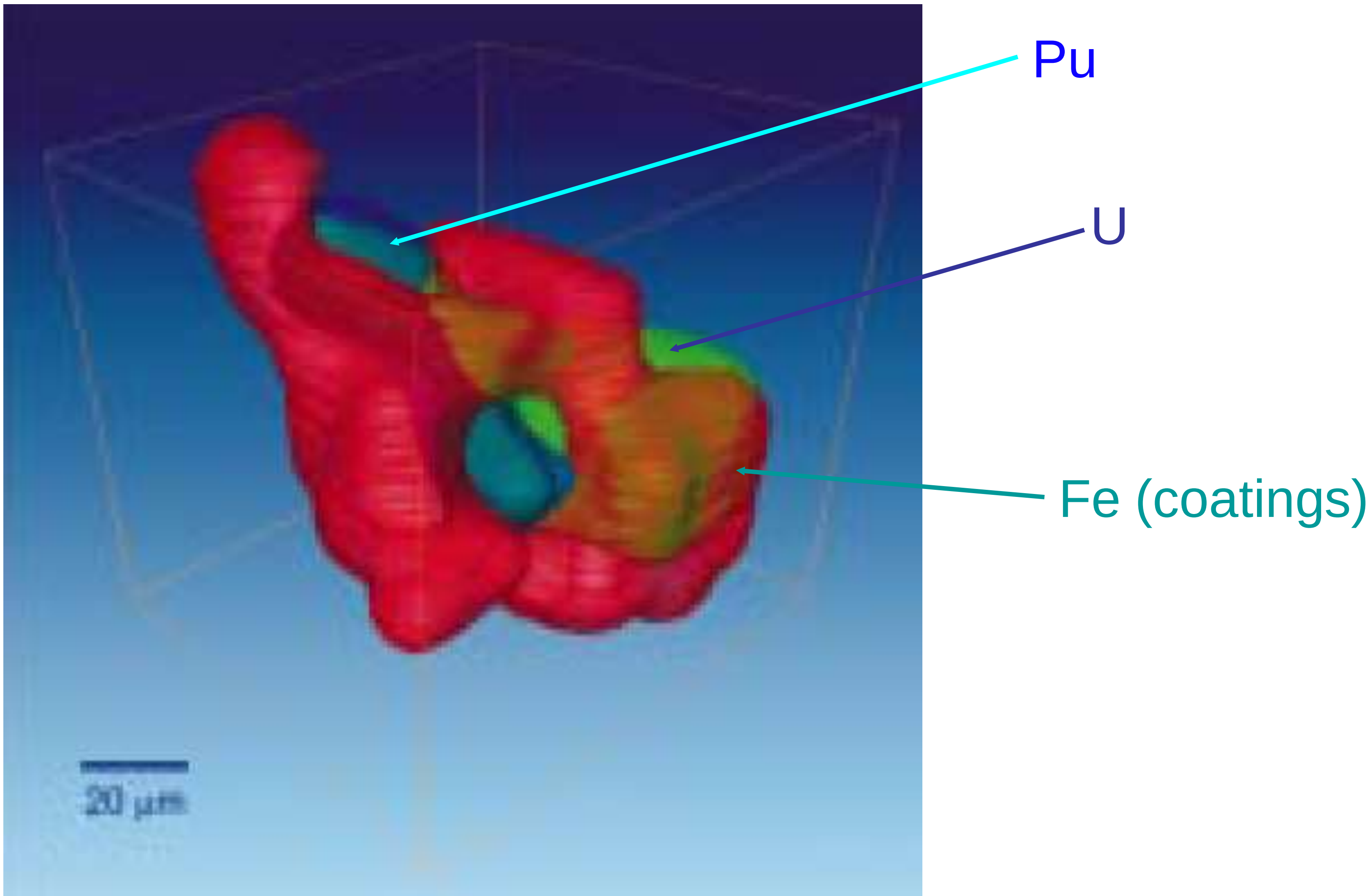
Micro-XANES

ID	U(IV) %	U(VI) %	Pu(IV) %	Pu(VI) %
3	90.9	9.1	92.0	8.0
5	90.9	9.1	97.0	3.0
6	100.0	0	25.0	75.0



(ITU Annual Report, 2004)

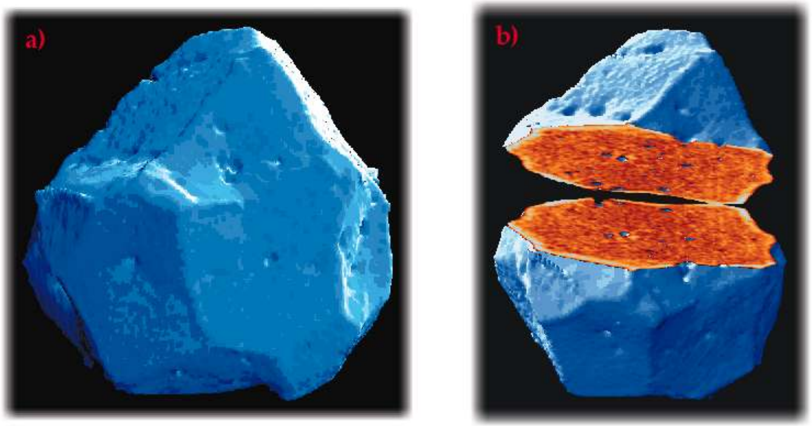
Hot Marine Particles: 3-D Distribution of Pu, U, Fe
(2-D sXRF and Absorption Micro-Tomography combined)



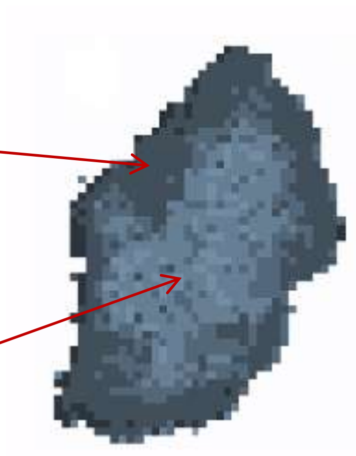
(ITU Annual Report, 2004)

Micro-Imaging and Tomography

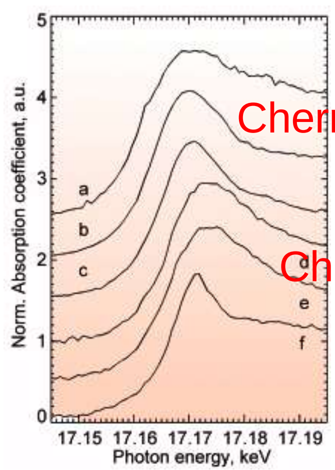
- Uranium fuel particle from Chernobyl



oxidized



reduced



Chernobyl West

Chernobyl North

Chernobyl West deposited during initial explosion – UO2

Chernobyl North deposited during reactor core fire - mostly U3O8

B. Salbu, 1999

ESRF

Investigation of highly radioactive samples

Physica Scripta. Vol. T115, 1001–1003, 2005

The INE-Beamline for Actinide Research at ANKA

Melissa A. Denecke[1*], Jörg Rothe[1], Kathy Dardenne[1], Hubert Blank[2] and Josef Hormes[2]

[1]Forschungzentrum Karlsruhe, Institut für Nukleare Entsorgung, P.O. Box 3640, D-76021 Karlsruhe
[2]Universität Bonn, Physikalisches Institut, Nußallee 12, D-53115 Bonn

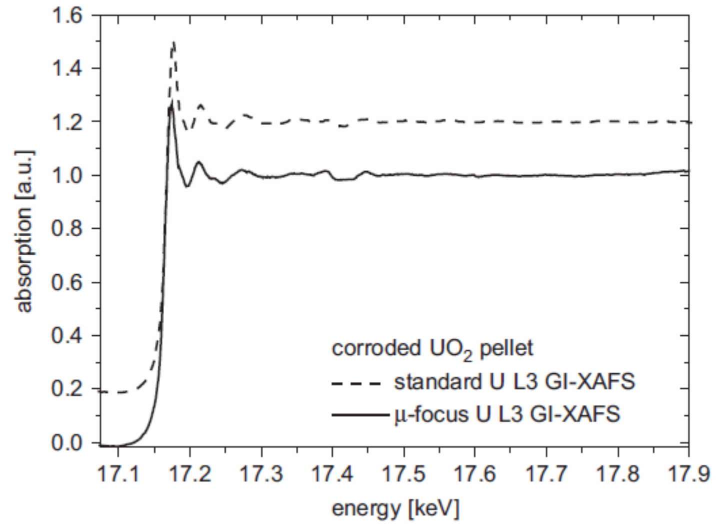


Fig. 1. Average of six U L3-edge EXAFS spectra of a corroded UO_2 pellet recorded using a 45 µm vertically focused beam, focused using CRLs as a virtual slit (solid line), compared to GI-XAFS data recorded using a standard 200 µm slit (dashed line, shifted for clarity).

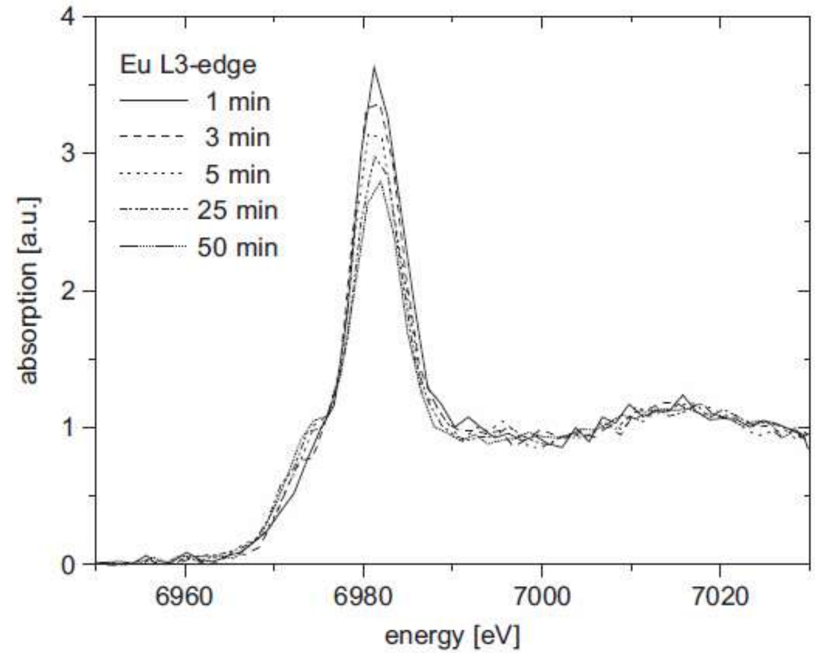


Fig. 2. Eu L3-edge Quick-XAFS of Eu incorporated in calcite. Partial reduction of Eu^{3+} to Eu^{2+} is indicated by the decrease in white line intensity and the accompanying pre-edge shoulder intensity increase.

Activities up to 10^6 times the limit of exemption

The uses of synchrotron light are as limitless as your imagination is!

If you are interested, contact:

Julie.Thompson@lightsource.ca
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Thank you for your attention!