Applications of Microscale XAS and XAS Imaging

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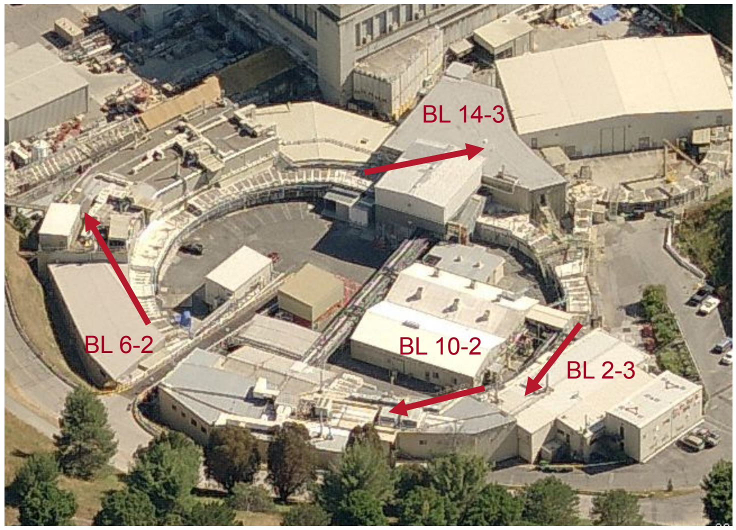
SMB XAS
SUMMER SCHOOL 2010

Outline

- SSRL Imaging Facilities
- What is micro-XAS?
  - Examples
- What is XAS-Imaging?
  - Examples
- Practical Aspects…

SSRL



SSRL Microfocus Beam Lines

Beam Line	Type	Optics	Spot Size	Energy (keV)	Flux (ph s^{-1})
2-3	μprobe	K-B	2 μm	5-23	$4x10^{8}$
6-2	TXM	Cap, ZP	40 nm	5-14	$\sim 10^{12}$
10-2	μprobe	Cap	10 μm	5-35	$6x10^{10}$
14-3	μprobe	K-B	2 μm	2-5	$\sim 5x10^{9}$

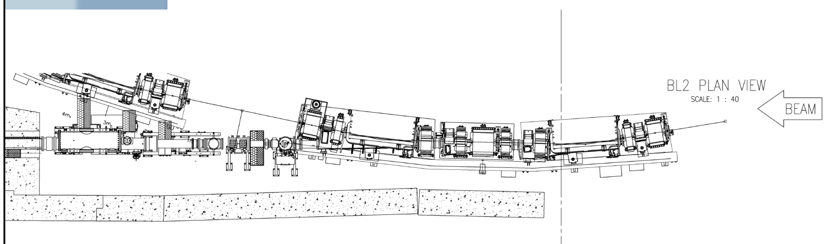
Microfocus Needs

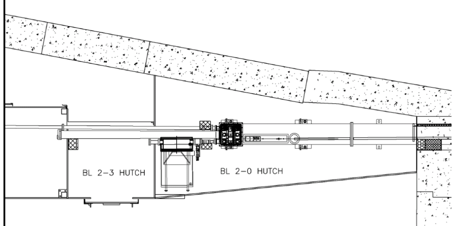
- As a facility, need to address the users of the Biological, Environmental, Material Science communities…
  - Small beam size
  - Large format – rapid mapping
  - High resolution mapping
  - High energy (10 keV +)
  - Low energy (2-5 keV)
  - Stability for spectroscopy and diffraction

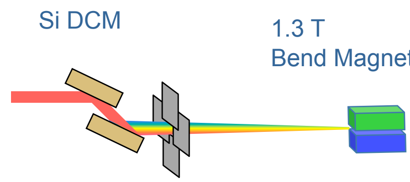
Microfocus Plan

1) High spatial resolution, good spectroscopy/diffraction (BL 2-3)
2) Moderate resolution, high flux, rapid scanning, spectroscopy, ideal diffraction (BL 10-2)
3) Low energy, high spatial resolution, good spectroscopy (BL 14-3)

BL2

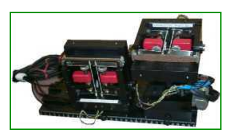


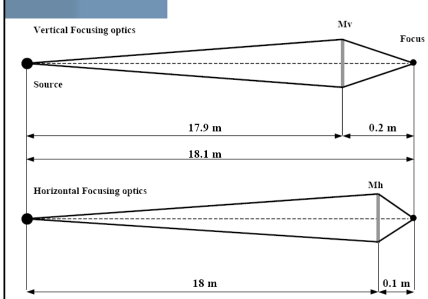


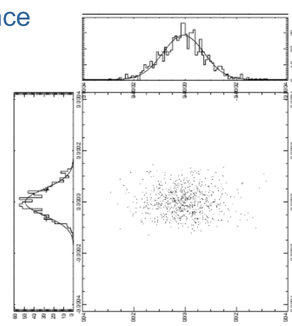


BL 2-3 Focusing Optics

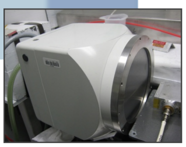
- The use of K-B optics, imaging the SPEAR source, was chosen to meet needs
  - Achromatic for spectroscopy
  - “Reasonable” working distance







Beam Line



CCD:

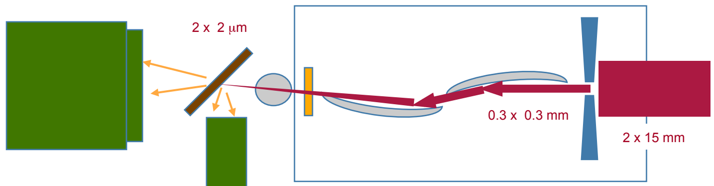
Area detector to measure micro-diffraction patterns at each sample spot. Data collection is integrated into scanning software.

Camera:

Sample camera mounted above sample using a Mylar mirror to get true view of sample – no parallax effects.

Gasbox:

Optic hardware enclosed in He filled box to increase mirror coating lifetime and reduce gas absorption effects.



Sample stage has X-Y-Z capability and 50nm repeatability. Motion of stage is programmable to enable correlated axis moves and digital programmable output to gate detectors for each pixel element moved. Range of motion ± 25 mm. Working distance from gasbox to sample is ~30 mm

Fluorescence:

3-element monolith detector with small snout in order to get close to sample + 1-element Si for low Z detection

KBs:

Horizontal and vertical focusing mirrors (Pt or Rd coated) focus beam at optimal position to 2 x 2 μm. Micro ion chamber in design developed to measure true I0 after mirrors.

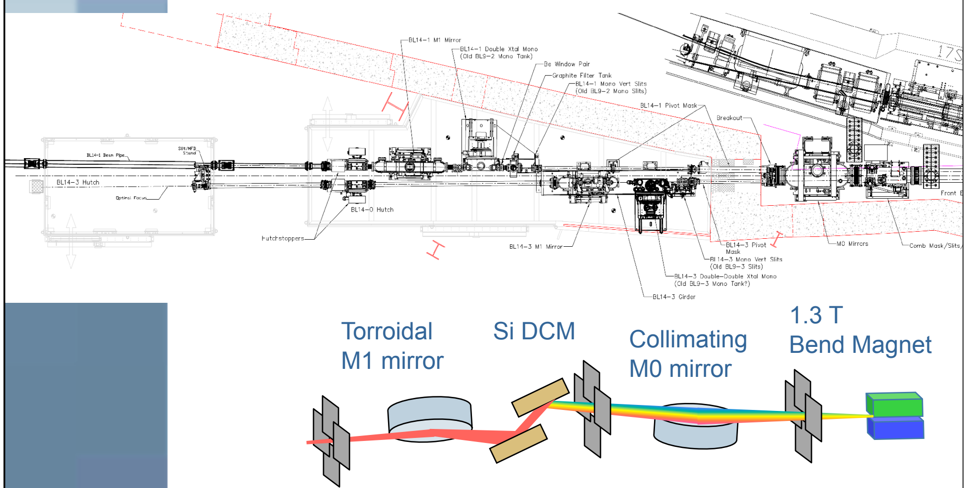
Slits:

Entrance slits define entrance aperture at ~ 0.3 x 0.3 mm

14-3 Design Parameters

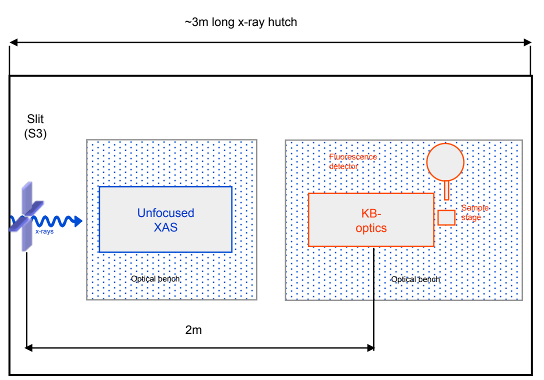
- Small beam (~2 μm)
- Low energy (S & P edge)
- XRF
- Need to be able to do S/P spectroscopy
- Sample mount interchangeability with BL 2-3
- Same software/hardware as BL 2-3

BL14



BL 14-3 Layout

- The KB optics will be a permanent installation in the back of the hutch with a temperature controlled enclosure, precision sample stages, solid-state detector, etc.
- Virtual source with KB optics. By slitting down virtual source, flux is traded for spot size - capable of sub-micron spots
- The front table will be used for bulk XAS and possibly single-crystal polarized XAS



What is microXAS?

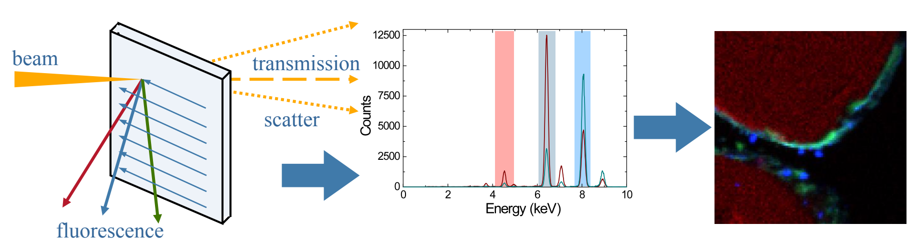
- MicroXAS is “simply” doing XAS measurements on a micron-size spatial scale using focusing optics to obtain a small beam size as opposed to “big” beams that give you bulk XAS.

Why use a microprobe?

- The environment (chemistry, biology, geology, etc.) is inhomogenous at nearly all length scales
- For every system, there is an optimal length scale for the information you want:
  - Too small: Unrepresentative sampling
  - Too big : Miss details, small objects
- This scale is often between 1 and 100 microns for environmental samples
- Want to gather chemical and spatial information on these scales…

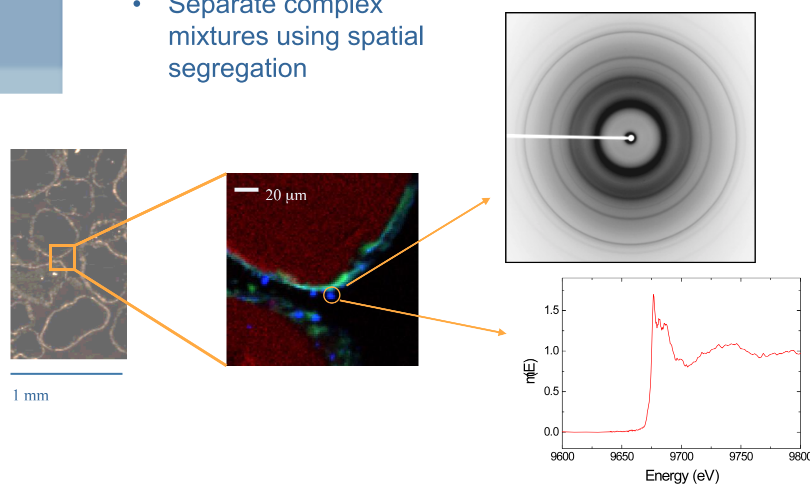
X-ray Microprobe (μXRF, μXAS)

- Raster a focused x-ray beam over sample
- Map intensity of x-ray fluorescence over various parts of sample
- Characterize interesting spots with XAS



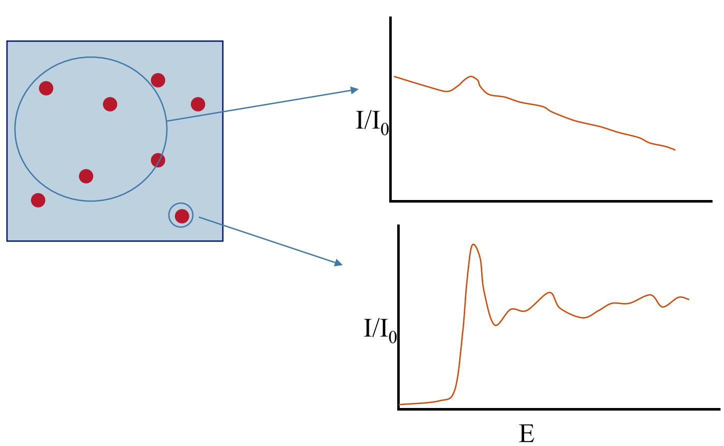
Microprobe Advantages

- Separate complex mixtures using spatial segregation



Microprobe Advantages

- Better signal to noise ratios on small particles

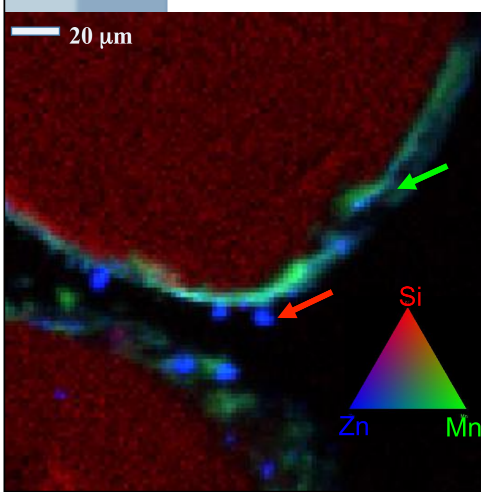


Micro-XAS and Imaging

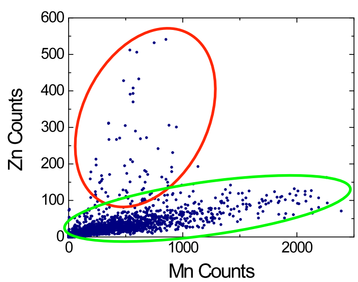
- On small, discrete points:
  - XANES
  - EXAFS
- On "larger" maps:
  - Fluorescence composition maps
  - Elemental correlations

Microscale Zn XAS

- Quartz grains incubated in Zn-Mn contaminated stream bed (Pinal Creek)

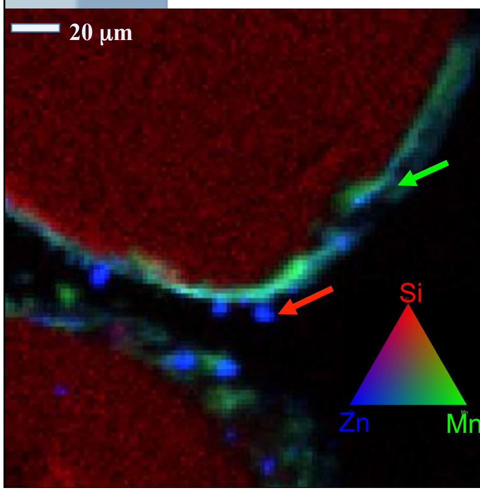


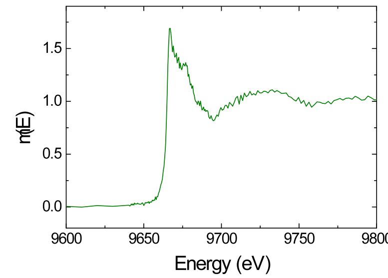
- Biogenic Mn oxides show significant uptake of Zn
  - Bulk EXAFS shows Zn sorbed to birnessite
- Not all uptake is reversible



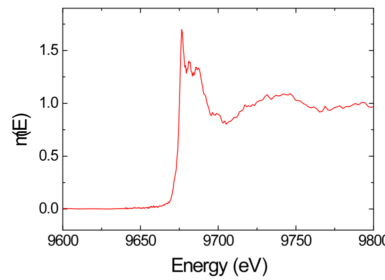
Microscale Zn XANES

Zn in biogenic Mn oxides

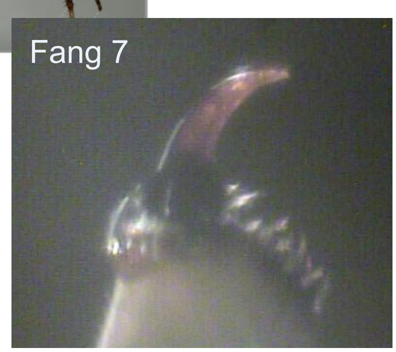




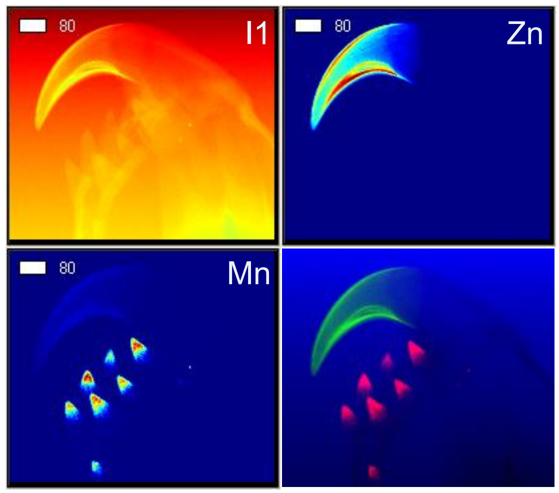
Zn in hetaerolite ($ZnMn_2O_4$)



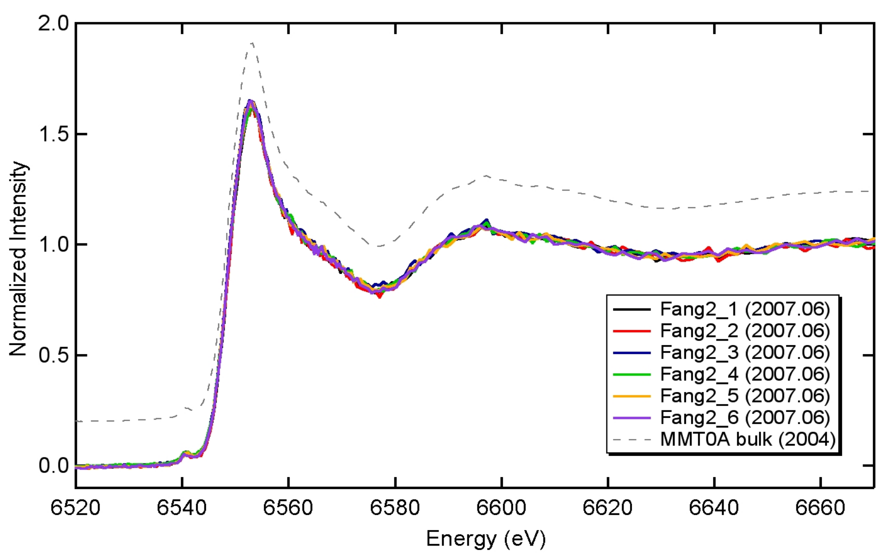
Araneus diadematus Fangs and Marginal Teeth

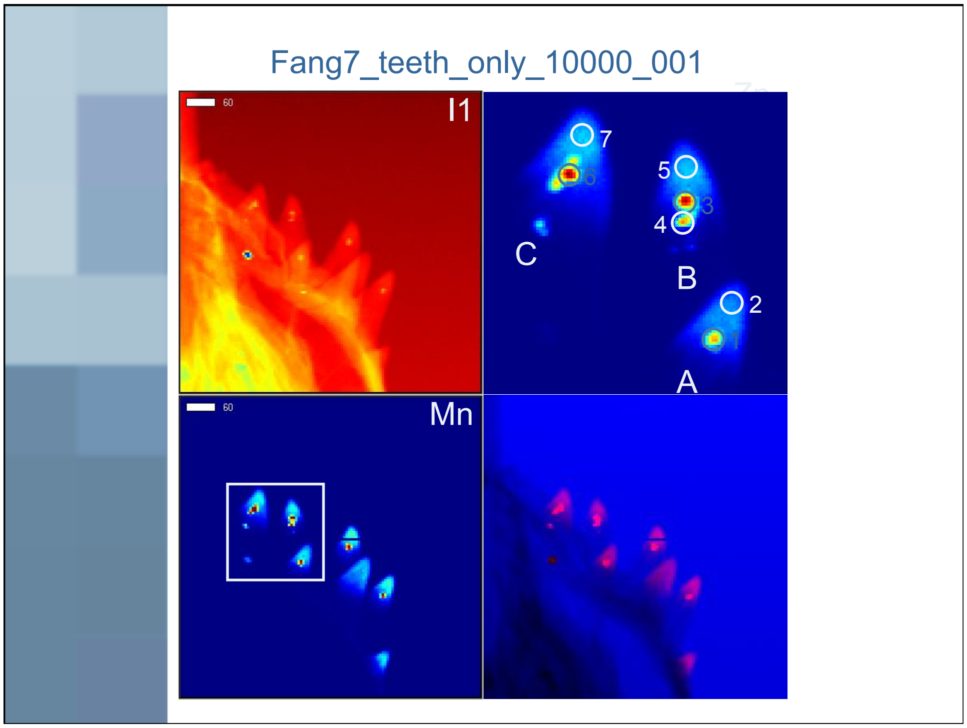


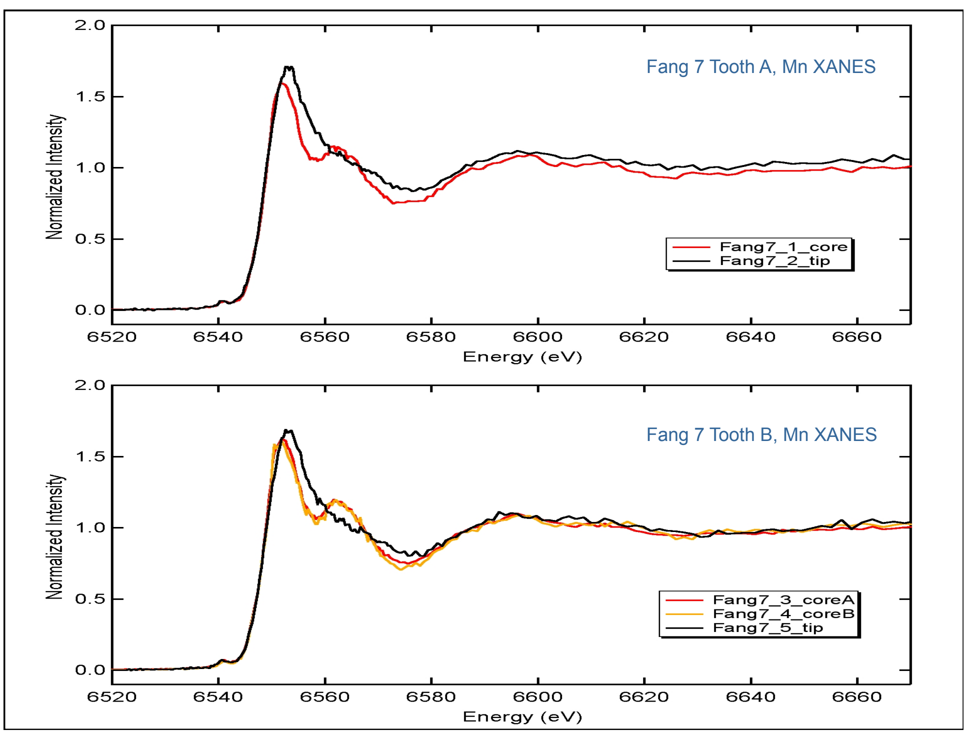
Fang2_init_14000_001



Fang 2 Teeth, Mn XANES




Fang7_teeth_only_10000_001
I1
Mn
7
5
4
3
C
B
2
A

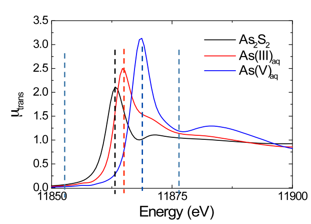

Fang 7 Tooth A, Mn XANES
Normalized Intensity
Energy (eV)
Fang7_1_core
Fang7_2_tip
Fang 7 Tooth B, Mn XANES
Fang7_3_coreA
Fang7_4_coreB
Fang7_5_tip

Micro-XAS and Imaging

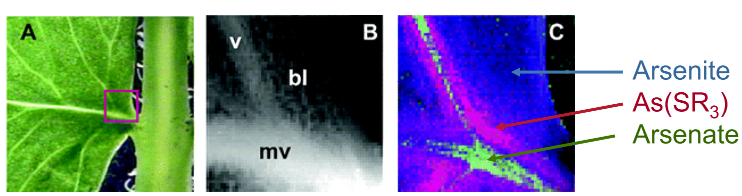
- On small, discrete points:
  - XANES
  - EXAFS
- On "larger" maps:
  - Fluorescence composition maps
  - Elemental correlations
  - ***XANES oxidation state/species maps***

What is XAS Imaging?

- XAS Imaging is taking several XRF maps at various excitation energies across and absorption edge.



- Examining the fluorescence yield at these energies can differentiate the oxidation state or species at every pixel in the image.

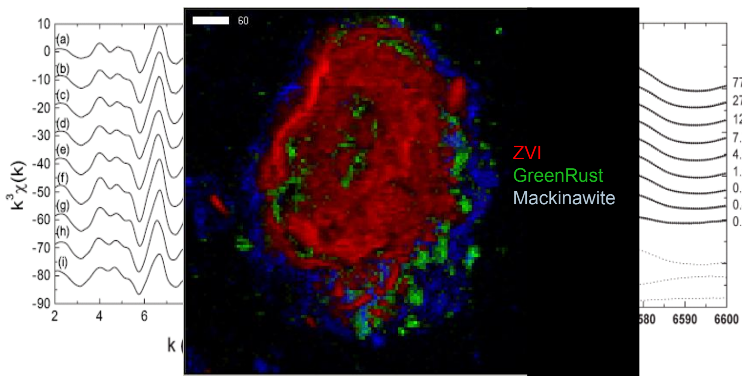


Pickering, et al. (2006) *ES&T*, **40**, 5010-5014.

Why do XAS Imaging???

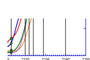
- A picture is worth a approximately 13,477 squiggly lines…

When you could have this!



XAS Image Fitting

- N species to calculate
- Need N+1 mapped energies to have statistical weight



FHY	**2-line ferrihydrite**
MACK	**Mackinawite (FeS)**
ZVI_NR	**Unreacted ZVI (Fe°, FeO)**
SID	**Siderite ($FeCO_3$)**
GRCO3	**Carbonate Green Rust**

XAS Image Fitting

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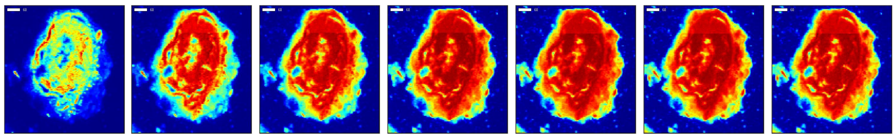
- Need N+1 mapped energies to have statistical weight



7113 7120 7122 7124 7126 7129 7140

- Do least squares fitting at each pixel
  - *n* energies and *m* components

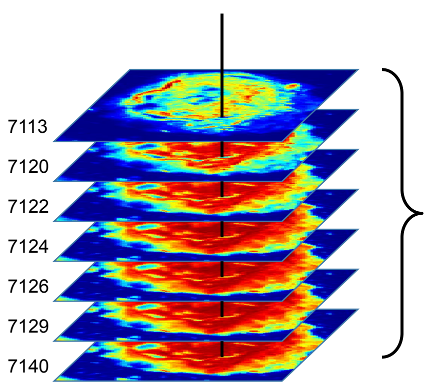
Find *f* such that you minimize:

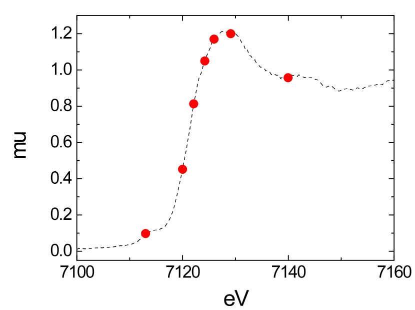
$$\|\mathbf{Mf}-\mathbf{D}\|^2$$

$$M=\begin{bmatrix}\mu_{1,\lambda 1} & \mu_{2,\lambda 1} & \cdots & \mu_{m,\lambda 1}\\ \mu_{1,\lambda 2} & \mu_{2,\lambda 2} & & \\ \vdots & & \ddots & \\ \mu_{1,\lambda n} & & & \mu_{m,\lambda n}\end{bmatrix} \quad f=\begin{bmatrix}c_1\\ c_2\\ \vdots\\ c_m\end{bmatrix} \quad D=\begin{bmatrix}\mu_{1,obs}\\ \mu_{2,obs}\\ \vdots\\ \mu_{n,obs}\end{bmatrix}$$

XAS Image Fitting

- Essentially doing least square fitting on a shortened XANES spectrum





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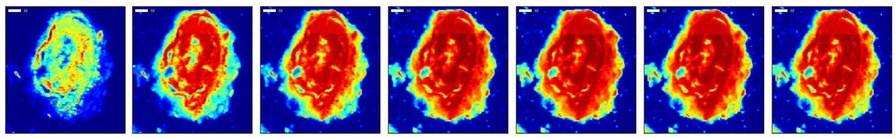
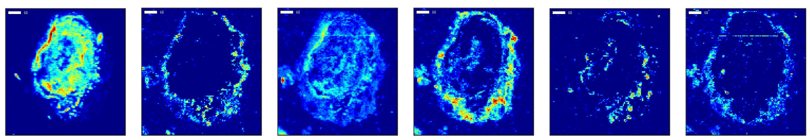


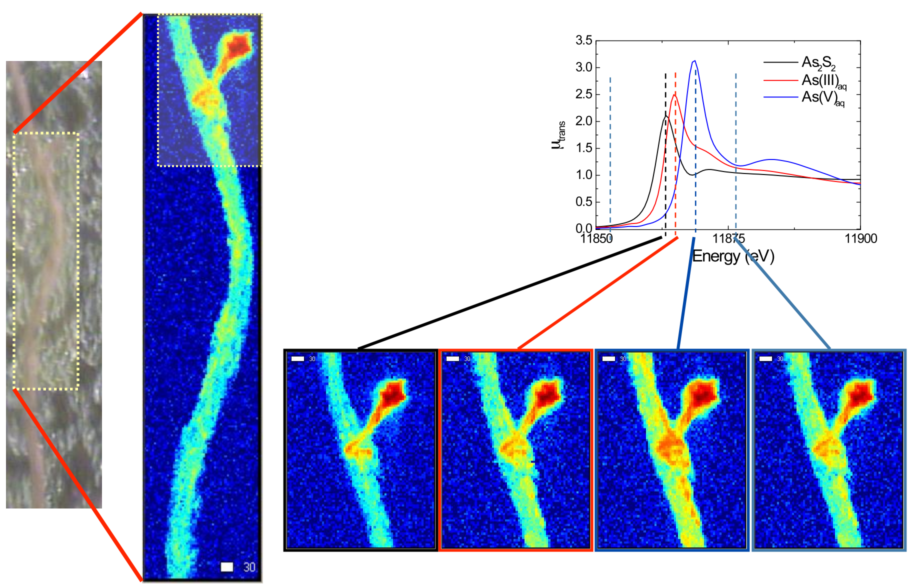
7113 7120 7122 7124 7126 7129 7140

- Do least squares fitting at each pixel

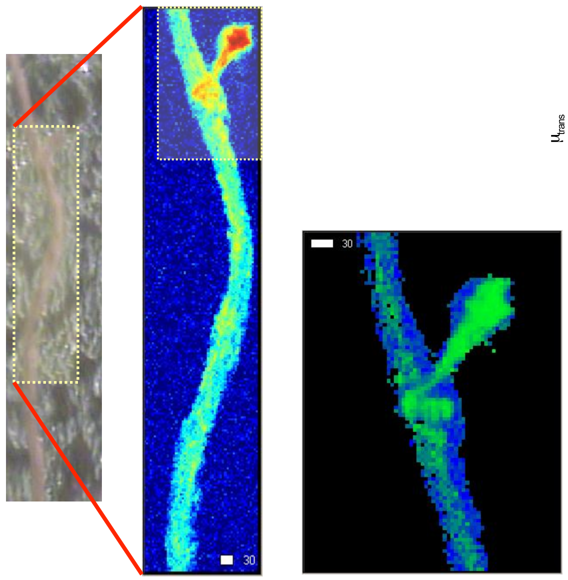


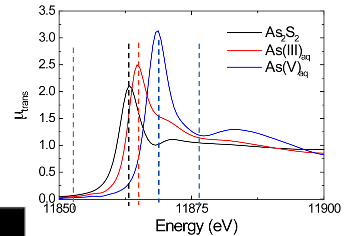
ZVI Mackinawite Ferihydrite Siderite Green Rust Vivianite

As in Bluegrass Roots

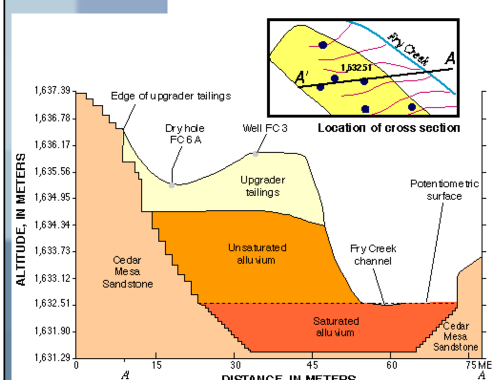


As in Bluegrass Roots

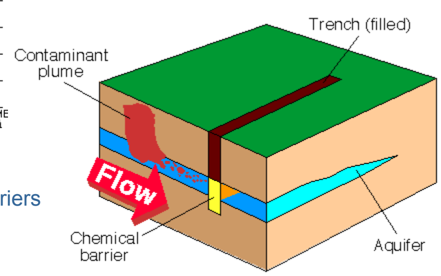




PRB Uranium Remediation

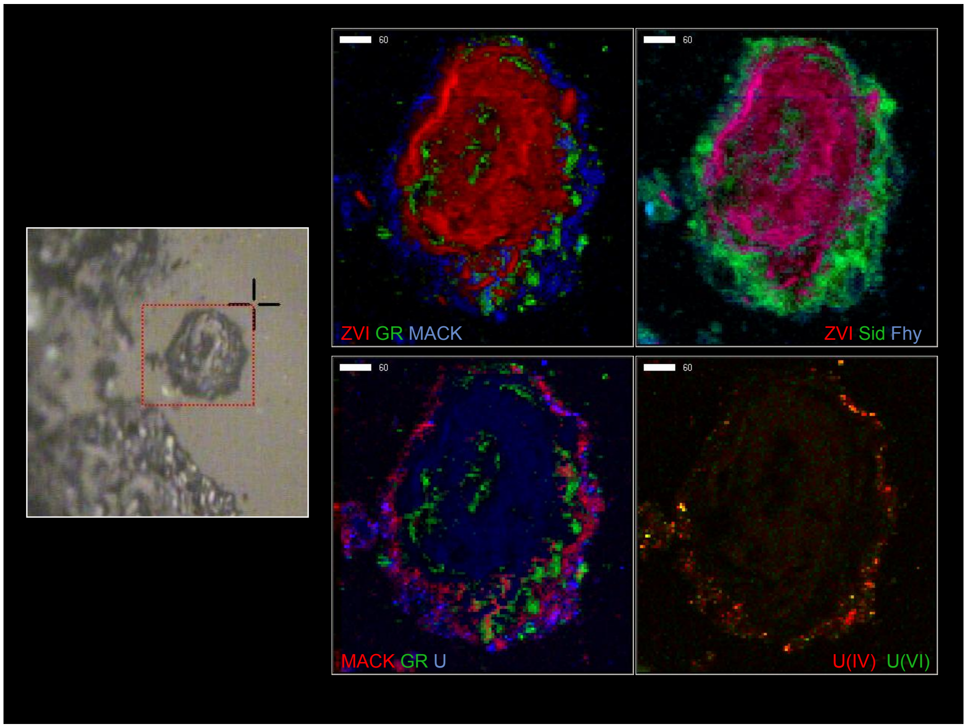


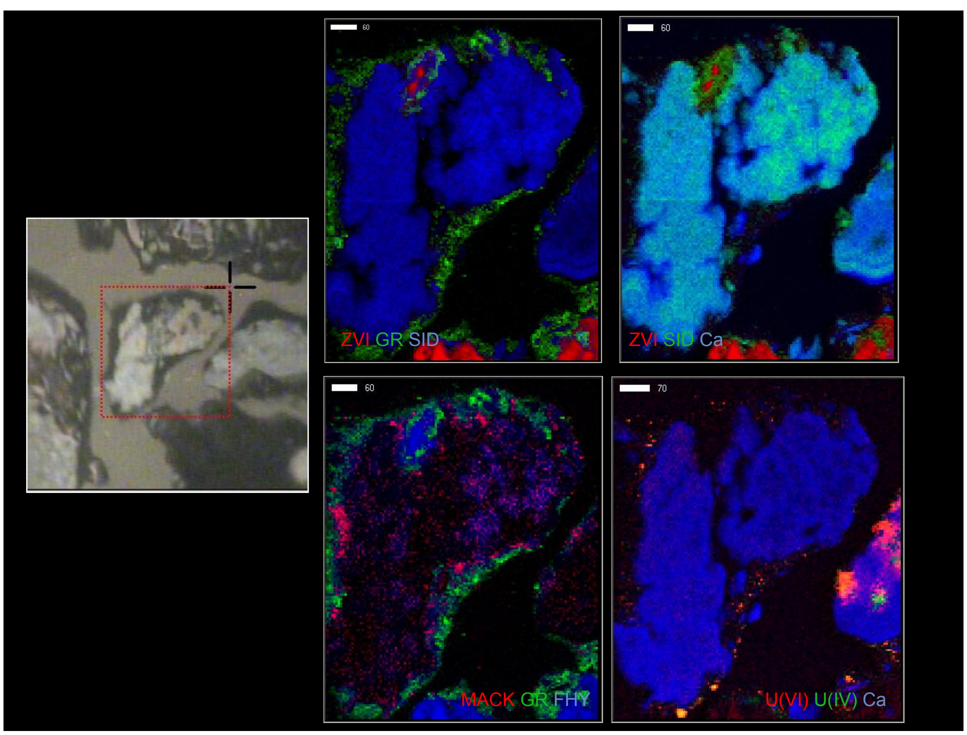
Hydrologic cross section A-A'.



Schematic diagram of a reactive barrier.
(Modified from Morrison and Spangler, 1992)

- 1997 Permeable reactive barriers consist of:
  - **Zero Valent Iron (ZVI)**
  - **Bone Char (PO4)**
  - **Amorphous Fe Oxides (AFO)**

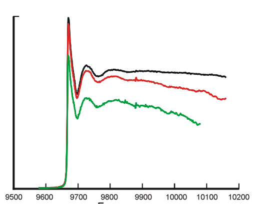

ZVI GR MACK
ZVI Sid Fhy
MACK GR U
U(IV) U(VI)

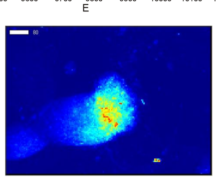

ZVI GR SID
ZVI SID Ca
MACK GR FHY
U(VI) U(IV) Ca

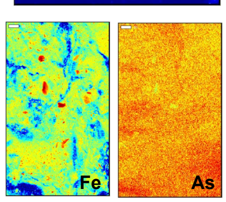
A Few Practical Aspects

- All of the principles of bulk XAS apply to microXAS
  - Thickness
  - Fluorescence self-absorption
  - Sample damage
  - Stability
- Sample prep, sample prep, sample prep…

Sample Design Considerations



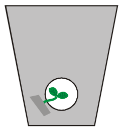




- Mechanical Stability
  - Will sample motion or drift cause problems
- Uniformity/Topography
  - Do you need a constant thickness?
  - Will shadows of topography create artifacts?
- Substrate/Background
  - Fluorescence from the substrate?
    - Glass microscope slides have major As & Co
- Transmission?
  - Need to have beam go through sample?
- Resins or fixatives
  - Important to use the right type
- Cooling for radiation damage?
  - Do you want to look at ice?

Sample Preparation

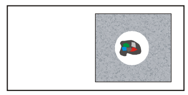
Intact specimen



\+ Simple, authentic

\- Topography
Need to fix
Easily damaged
Drifts
Not durable

Thin section



\+ Smooth surface
Good for quantitative
Avoid overabsorption
Avoid penetration effects
Images easy to interpret
Maintains spatial relationships
May be able to use in transmission

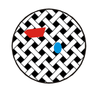
\- Resin effects on chemistry
Can accelerate rad damage
Requires work, time ($)
Careful about choice of substrates

Powder/sediment on tape

\+ Easy

\- Nonuniform thickness
Tends to drift
Kapton tape scatters
Not durable

Grid/filter



\+ Often only way to collect

\- Nonuniform thickness
Substrate scatter/fluorescence

Important Sample Preparation Methods to Conduct μ-XRF, -XAS, and –XRD

(Courtesy Y. Arai)

<u>Substrates (backing materials) for thin section prep:</u>

- Absolutely “no glass slides”!
- Quartz slides are recommended.
- Lexan or Delrin
  - -Very low trace metal (e.g., Zn and Cu) impurity, but abundant in Br.
  - -Transmit the beam so that the energy calibration can be done without talking out the sample.
  - - does not scatter as much as glass, so that it is suited for trans. micro-XRD measurements.

*each batch of lexan sheet must be checked with BL scientist for the trace metal impurity.

<u>Ideal resin medium:</u>

Important criteria:
-Must produce a certain hardness so that the surface can be polished down less than 30 micron. Over absorption issues when the thickness of sample is too thick (e.g., entrapped grains in kapton films)

- <u>3M electrical resin</u> (Lowest trace metal impurity in the market)

(cures well about 70°C , but it can be cured at room temp for several days)

- For redox sensitive sample, <u>Epotek 301</u> (cures at room temp.)

Warning for the low viscous medium!
-LR white resin <u>is not recommended</u> due to the redox changes in chemical Properties
-Spurr's resin (Spurr, 1969) and polymerized at 70°C for 24 h. It is not clean media

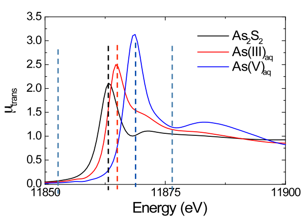
<u>Bonding adhesive:</u>

-Superglue is highly recommended due to its low trace metal impurity.

Requirements for XAS Imaging

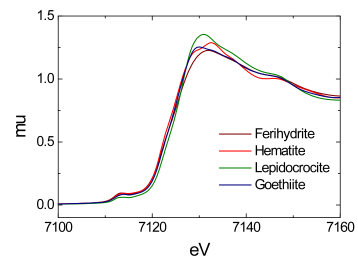
- Differentiable species!
  - XAS Imaging uses N+1 variables
  - Need to accurately determine N species with N+1 variables
  - Need variation, ideally within the absorption edge

Ideal



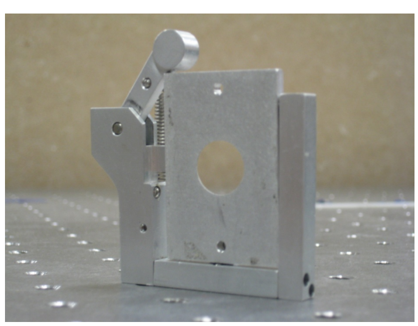
Good

Non-Ideal / Impossible



Sample Holders

- How things mount?
- Standard, thin section, films

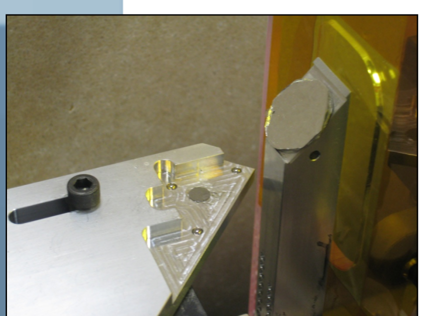


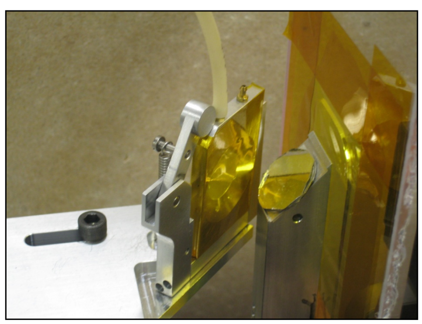
Sample Holders

- How things mount?
- Standard, thin section, films

Sample Holders

- Stage and sample holder have magnetic mounts
- Keeps sample repositioning accurate within approximately 10-20 microns
- Not a lot of room in sample area!





SSRL Microfocus Beam Lines

Beam Line	Type	Optics	Spot Size	Energy (keV)	Flux (ph s^{-1})
2-3	μprobe	K-B	2 μm	5-23	4×10^{8}
6-2	TXM	Cap, ZP	40 nm	5-14	$\sim 10^{12}$
10-2	μprobe	Cap	10 μm	5-35	6×10^{10}
14-3	μprobe	K-B	2 μm	2-5	$\sim 5 \times 10^{9}$

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