

GSECARS X-ray Microprobe for Earth and Environmental Science

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Objective for Earth and Environmental Sciences:

Determine chemical associations, speciation, and structure of heavy elements on heterogeneous samples: soils, sediments, aggregates, plant material, isolated inclusions, or contaminants.

X-ray Microprobe techniques:

X-ray Fluorescence (XRF), Fluorescence Mapping

abundance and spatial correlations of heavy elements

X-ray Absorption (XANES / EXAFS)

oxidation state of selected element

near-neighbor distances and coordination numbers



GSECARS XRF/XAFS Microprobe Station

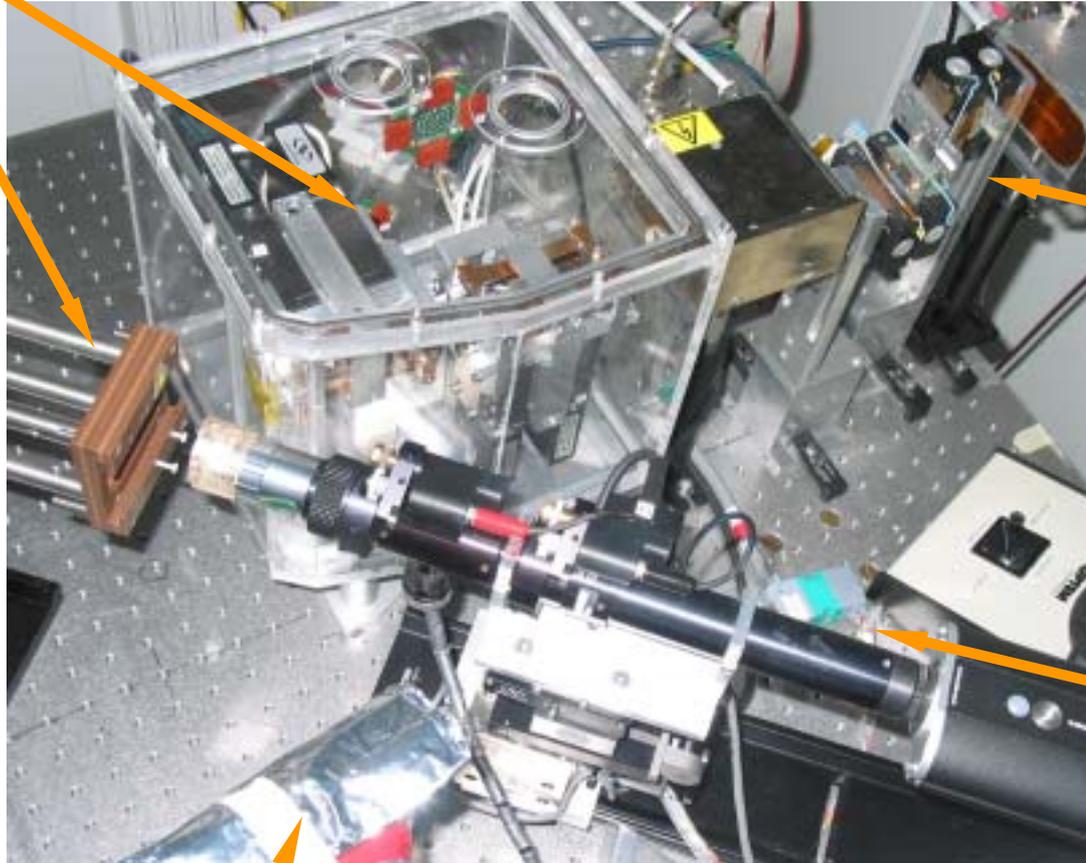
Focusing: Kirkpatrick-Baez mirrors: Rh-coated Si, typically using $3 \times 3 \mu\text{m}$ spot sizes, at 50mm from end of mirrors.

Incident Beam:
LN₂ cooled Si (111)

Sample Stage:
x-y-z stage,
 $1 \mu\text{m}$ resolution

Samples in air
or He, typically

Data Collection:
custom software
for XRF, mapping
and XAFS, based
on EPICS.



Slits: typically
200 to 300 μm ,
accepting ~20%
of undulator
beam at 50m
from source.

Optical Microscope:
5x to 50x objective
to external video
system.

Fluorescence detector: 16-element Ge detector / DXP electronics,
Lytle Detector, or Wavelength Dispersive Spectrometer

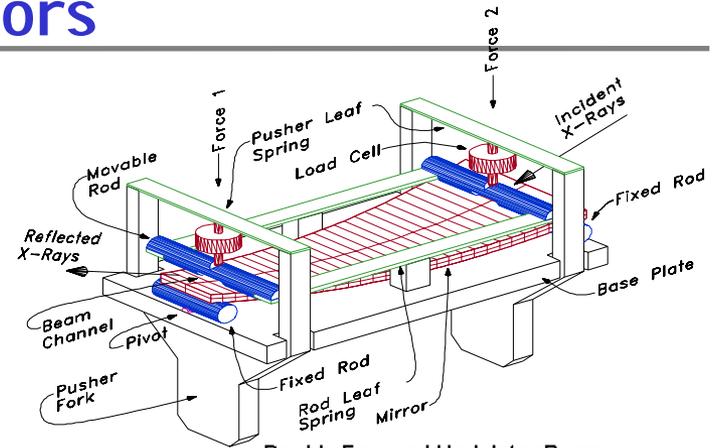


Kirkpatrick-Baez Focusing Mirrors

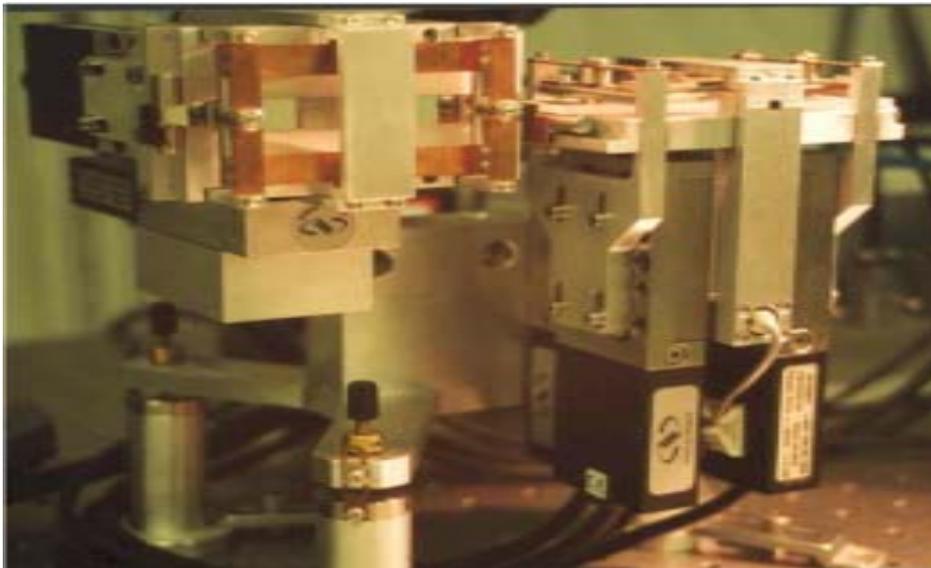
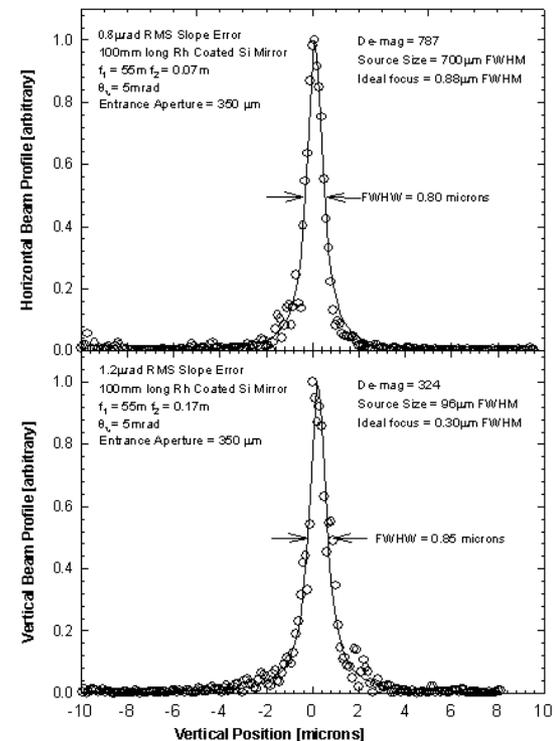
The table-top Kirkpatrick-Baez mirrors use four-point benders and flat, trapezoidal mirrors to dynamically form an ellipsis. They can focus a $300 \times 300 \mu\text{m}$ beam to $1 \times 1 \mu\text{m}$.

With a typical working distance of 100mm, and a **focal distance and spot-size independent of energy**, they are ideal for micro-XRF and micro-EXAFS.

We use Rh-coated silicon for horizontal and vertical mirrors to routinely produce $2 \times 3 \mu\text{m}$ beams for XRF, XANES, and EXAFS.



Double Focused Undulator Beam
Flux Density Gain = 113,000

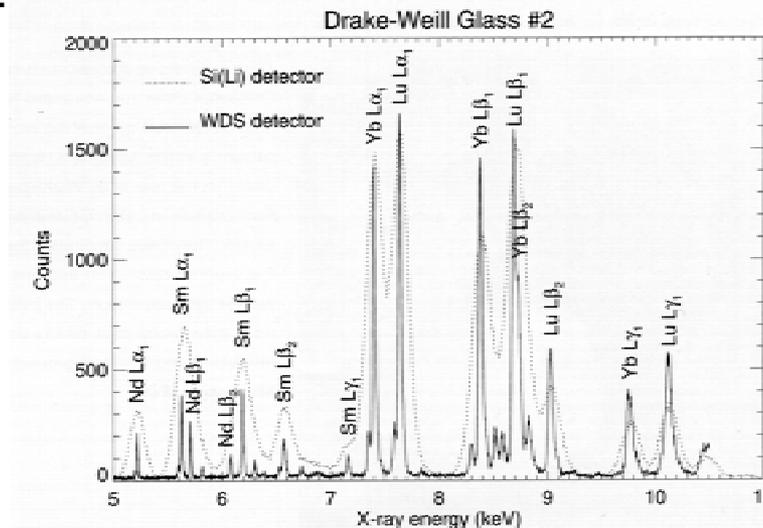


X-ray Fluorescence Detectors

Multi-Element Ge Detector: energy resolution ~ 250 eV, which separates most fluorescence lines, and allow a full XRF spectrum (or the windowed signal from several lines) to be collected in a second.

This is limited in **total count rate** (to ~ 250 KHz), so multiple elements (10 to 30) are used in parallel. Detection limits are at the ppm level for XRF. XANES and EXAFS can be measured on dilute species (~ 10 ppm) in heterogeneous environments.

Wavelength Dispersive Spectrometer: has higher resolution (~ 20 eV), and smaller solid angle. This can be used for XAS, and is able to separate fluorescence lines that cannot be resolved with a Ge detector.



Metal Speciation in Hydrothermal Fluid Inclusions

John Mavrogenes, Andrew Berry (Australian National University), GSECARS

Hydrothermal ore deposits are important sources of Cu, Au, Ag, Pb, Zn, and U.

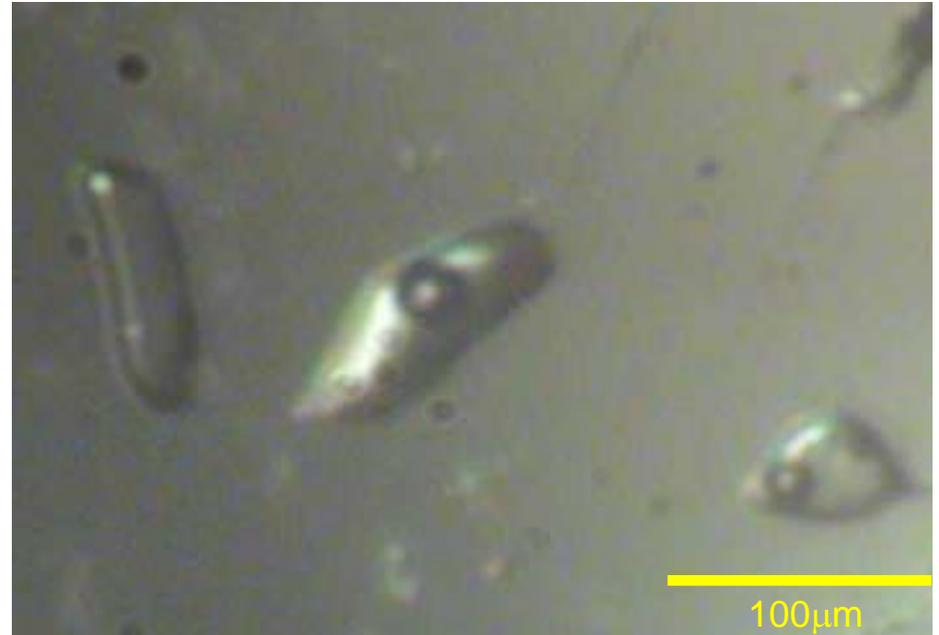
Metal complexes in high-temperature, high-pressure solutions are transported until cooling, decompression, or chemical reaction cause precipitation and concentration in deposits.

To further understand the formation of these deposits, the nature of the starting metal complexes need to be determined.

XRF and XAFS are important spectroscopic tools for studying the chemical speciation and form of these metal complexes in solution.

This is challenging to do at and above the critical point of water (22MPa, 375°C).

Fluid inclusions from hydrothermal deposits can be re-heated and used as sample cells for high temperature spectroscopies.



Natural Cu and Fe-rich brine / fluid inclusions in quartz from Cu ore deposits from New South Wales, Australia were examined at room temperature and elevated temperatures by XRF mapping and XAFS.



Cu speciation in Hydrothermal Fluid Inclusions

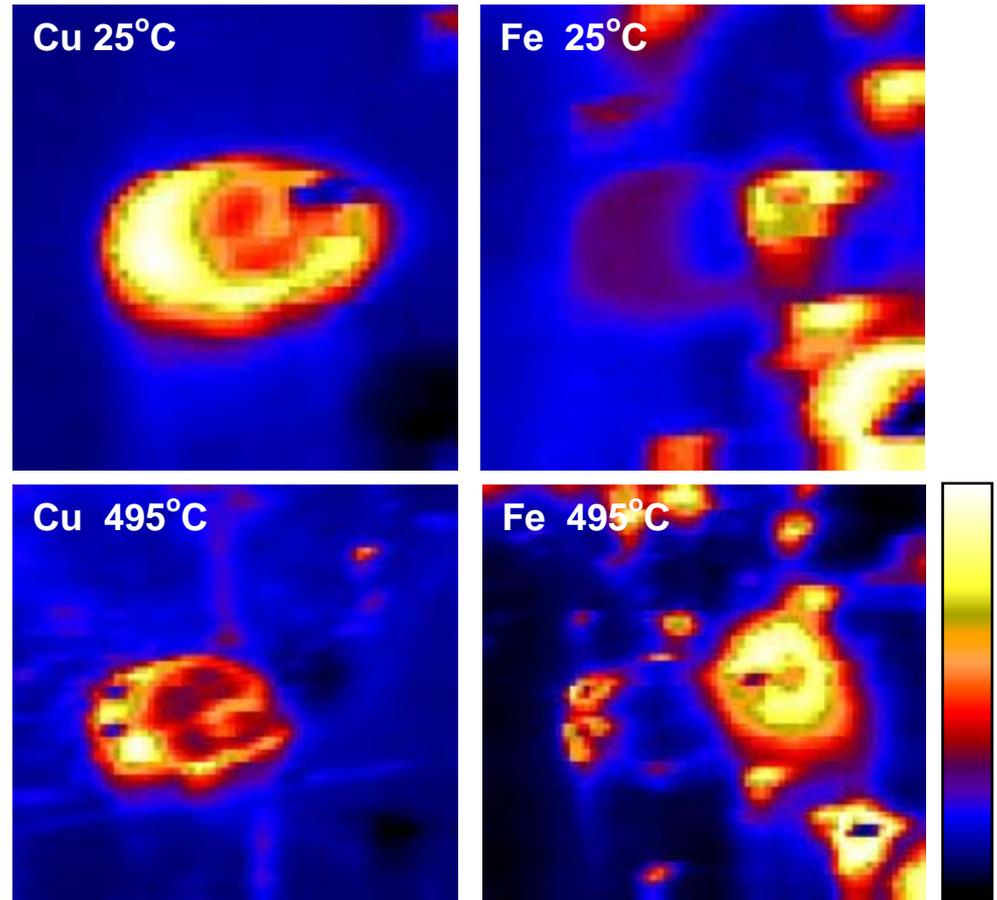
XRF Mapping

Understanding the metal complexes trapped in hydrothermal solutions in minerals is key to understanding the formation of ore deposits.

Natural Cu and Fe-rich brine and vapor-phase fluid inclusions in quartz from Cu ore deposits were examined at room temperature and elevated temperatures by XRF mapping and EXAFS.

Initial Expectation: chalcopyrite (CuFeS_2) would be precipitated out of solution at low temperature, and would dissolve into solution at high temperature. We would study the dissolved solution at temperature.

Result: XRF mapping ($2\mu\text{m}$ pixel size) showed that for large vapor-phase inclusions, a uniform distribution of Cu in solution at room temperature was becoming less uniform at temperature. This was reversible, and seen for multiple inclusions.



Cu XANES: Speciation in Fluid Inclusions

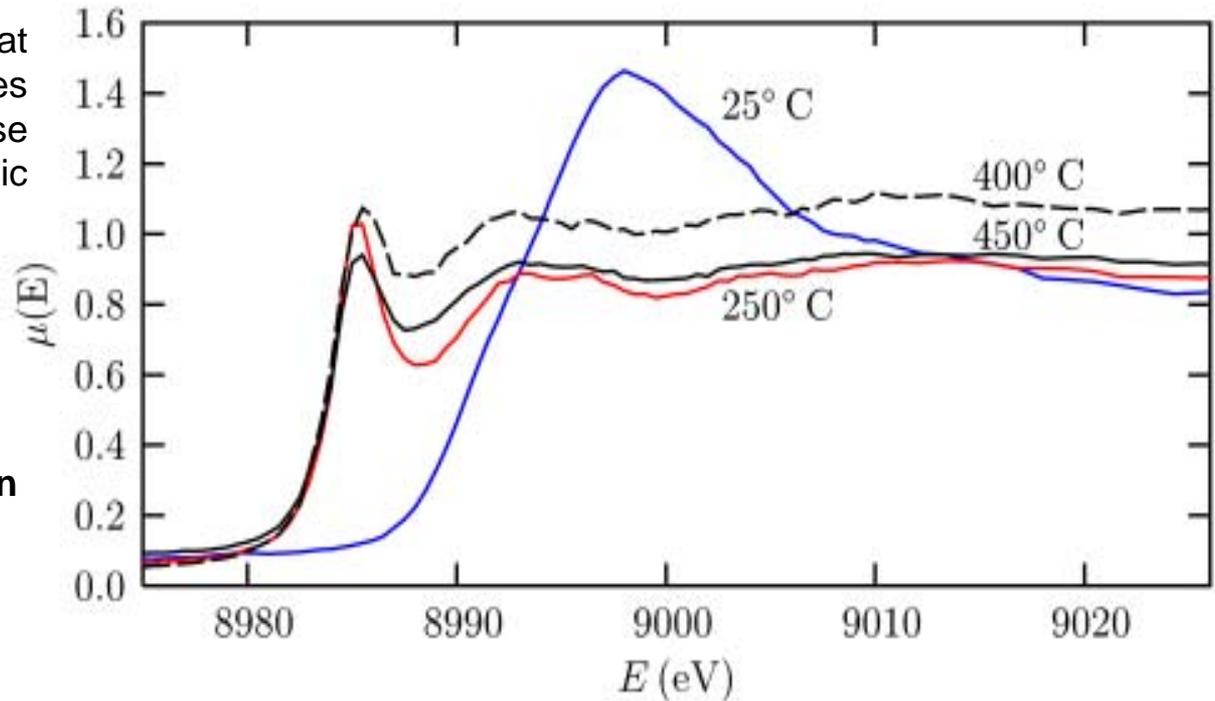
XANES measurements at low and high temperatures for the vapor-phase inclusions show dramatic differences:

Low temp:

Cu²⁺, aqueous solution

High temp:

Cu¹⁺, Cl or S ligand.

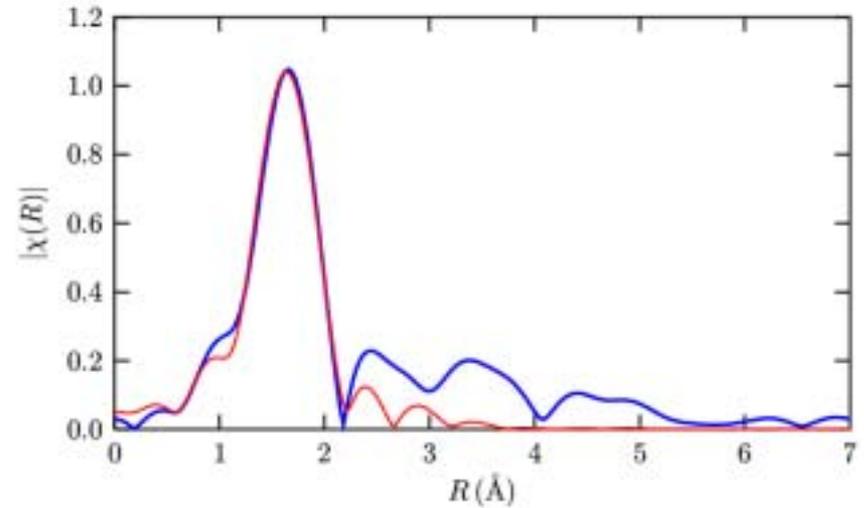
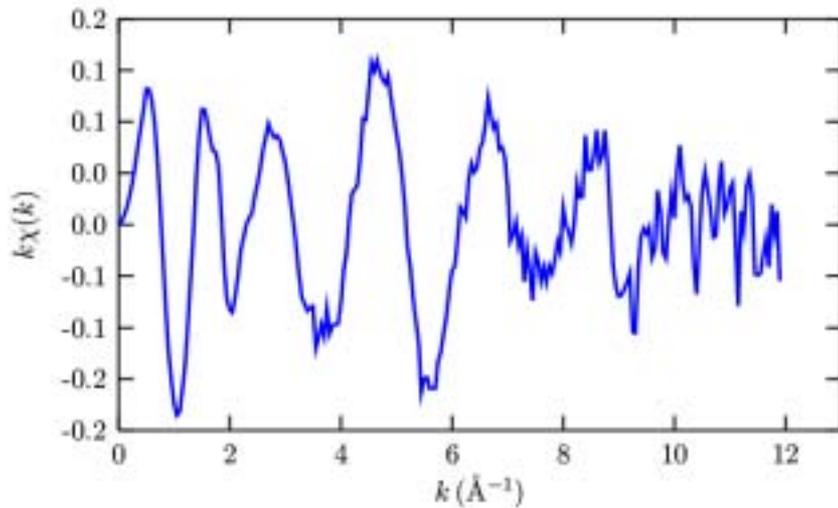


These results are consistent with Fulton et al [Chem Phys Lett. 330, p300 (2000)] study of Cu solutions near critical conditions: Cu²⁺ solution at low temperature, and Cu¹⁺ associated with Cl at high temperatures.



Cu XAFS in Fluid Inclusions

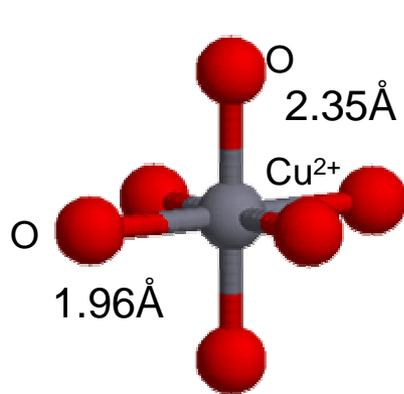
EXAFS from the high temperature phase:



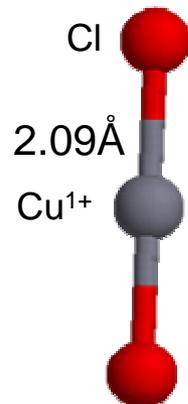
Fit (red) to 450C Cu solution XAFS in vapor-phase fluid inclusion (blue). Good fits can be obtained with

- 1 Cl at $\sim 2.09\text{\AA}$ and 1 O at $\sim 2.00\text{\AA}$,
- or 2 Cl at $\sim 2.08\text{\AA}$.

These findings are consistent with the model of for aqueous Cu^{1+} of Fulton et al.



Low temp

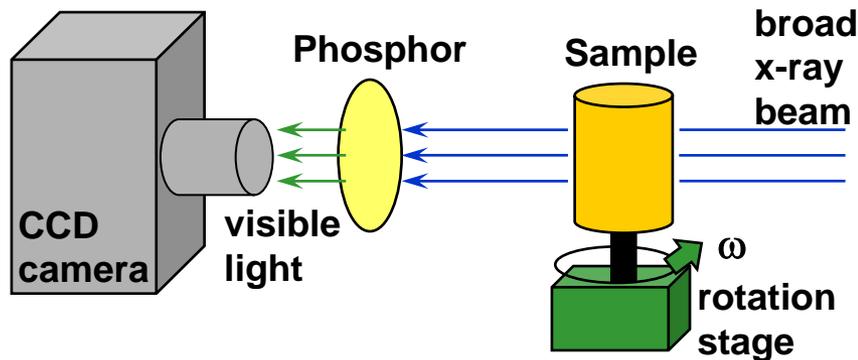


High temp



J. A. Mavrogenes, A. J. Berry, M. Newville, S. R. Sutton, *Am. Mineralogist* 87, p1360 (2002)

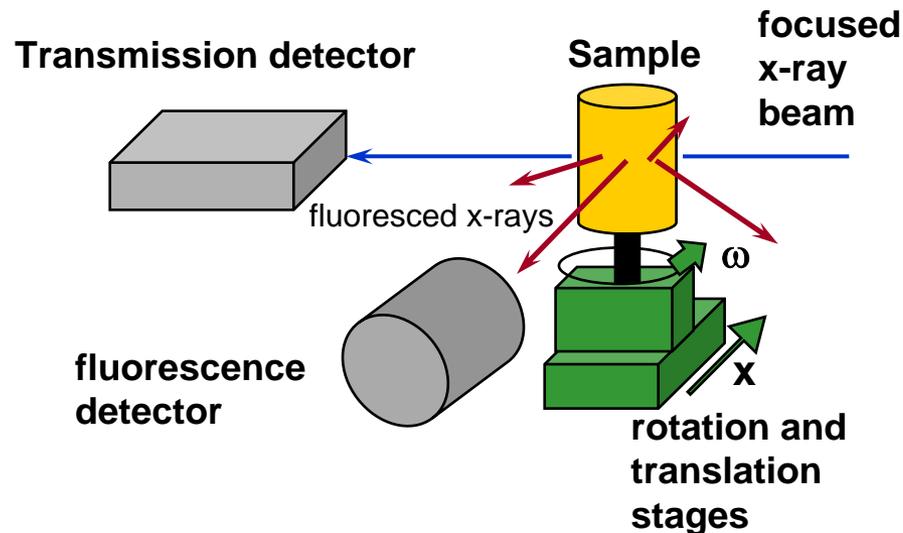
X-ray Fluorescence Tomography: Overview



X-ray computed microtomography (CMT) gives 3D images of the x-ray absorption coefficient.

An absorption image is collected as the angle ω is rotated through 180° , and the 3D image is reconstructed in software.

In some cases, element-specific images can be made by tuning the x-ray energy above and below an absorption edge.



Fluorescence x-ray tomography use a focused beam, scanned across the sample. The sample is rotated around ω and translated in x .

Fluorescence x-rays are collected as for XRF maps. Transmission x-rays are measured as well to give an overall density tomograph.

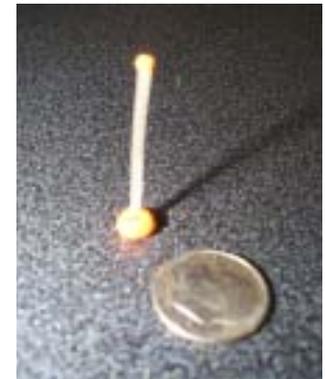
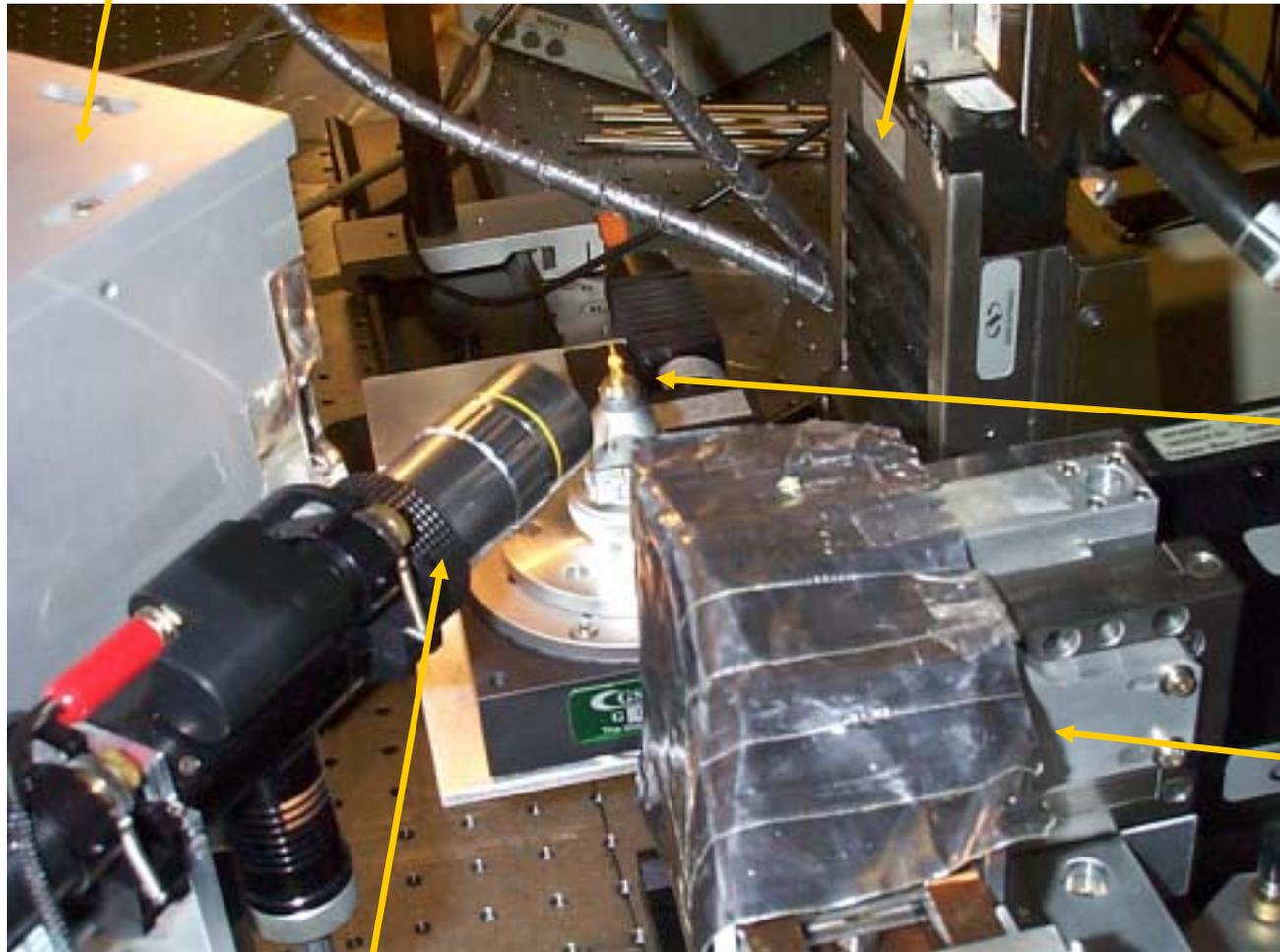
- can collect multiple fluorescence lines.
- data collection is relatively slow – one slice can be made at a time.
- can be complicated by self-absorption.



Fluorescence Tomography: Experimental Setup

Fluorescence detector:
multi-element Ge detector

Sample stage:
x-y-z- θ



Sample, mounted
on silica fiber, or
in 'shrink-wrap'
tube, on a
goniometer head

KB mirrors,
with Pb tape
shield

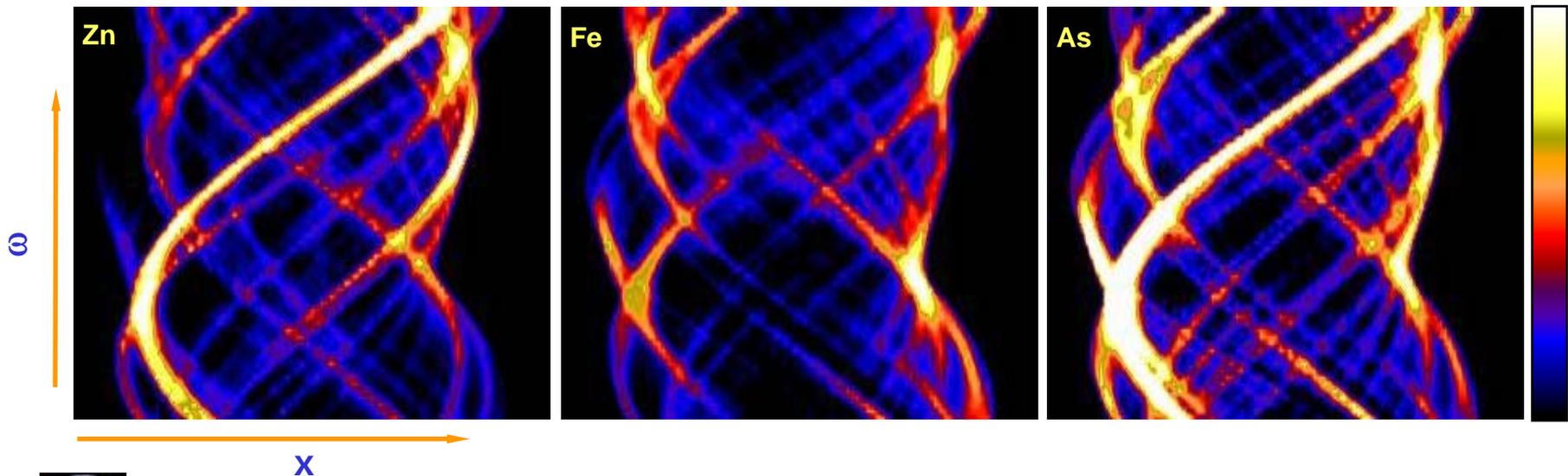
Optical microscope



Fluorescence Tomography: Sinograms

The raw fluorescence tomography data consists of elemental fluorescence (uncorrected for self-absorption) as a function of position and angle: a **sinogram**. This data is reconstructed as a virtual **slice** through the sample by a coordinate transformation of $(x, \omega) \rightarrow (x, y)$. The process can be repeated at different z positions to give three-dimensional information.

Fluorescence sinograms collected simultaneously for Zn, Fe, and As for a cross-section of As-contaminated cattail root (photo, right): x : 1100 μm in 10 μm steps ω : 180 $^\circ$ in 3 $^\circ$ steps



Arsenic Distribution in Cattail Roots

Nicole Keon, Daniel Brabander, Harold Hemond (MIT), GSECARS

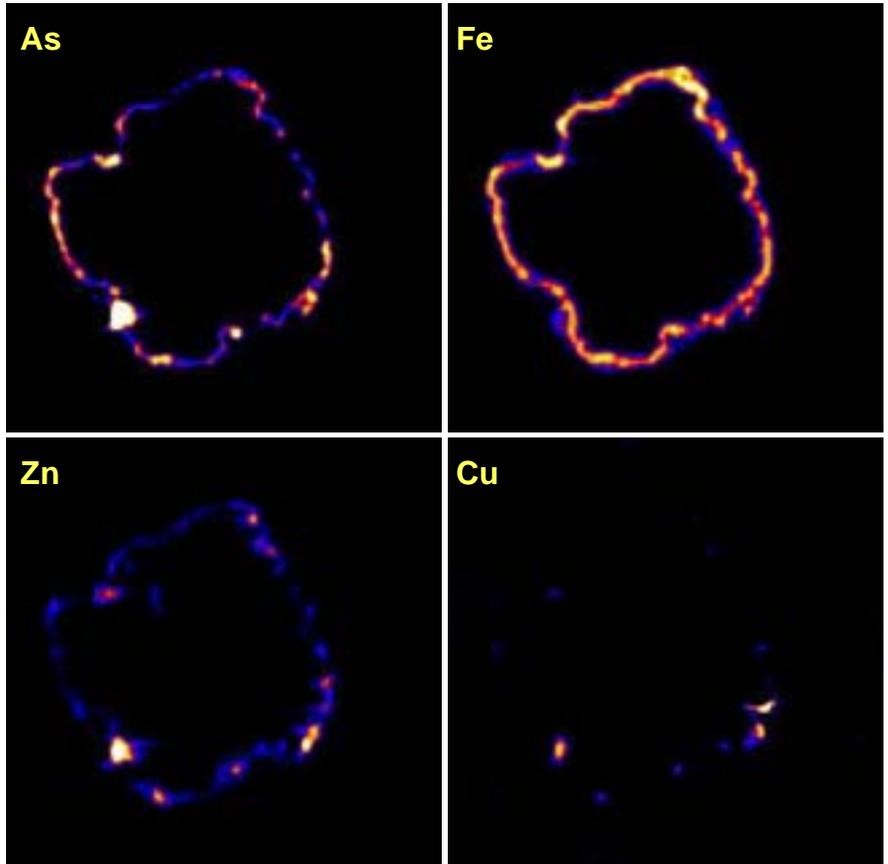
Studying a Superfund site (Wells G+H wetland, which gained notoriety in *A Civil Action*), a reservoir with ~10 tons of arsenic within the upper 50cm of the sediment. Most of the arsenic is sequestered in the wetland peat sediments with relatively As concentration in the groundwater.

In contrast, riverbed sediments in the wetland have higher concentrations of aqueous arsenic, despite lower solid phase concentrations.

Can the metabolic activity of wetland plants, such as *Typha latifolia* (cattail) explain the sequestration of arsenic in the wetland?

- Where is As in the wetland plants?
- What elements are associated with As?
- What is the As oxidation state?

Slicing the root would cause enough damage that 2D elemental maps would be compromised. Tomography can be used to make a virtual slice of the root.



Wells G&H *Typha latifolia* root: reconstructed slices from fluorescence μ -tomography, showing As concentrated on the root exterior, associated with Fe and Zn.

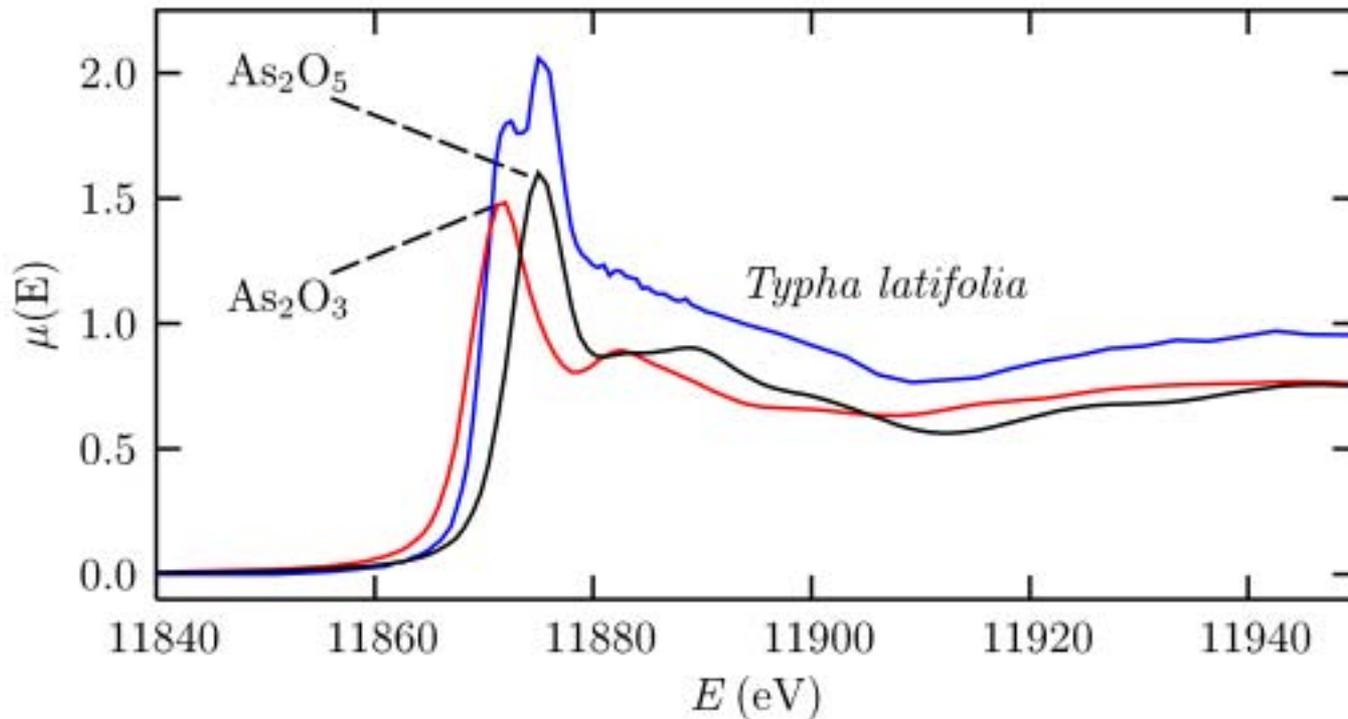


As XANES

XANES measurements on the *Typha latifolia* cattail roots show mixed As oxidation state – roughly equal portions As^{3+} and As^{5+} .

The As^{3+} fraction did vary between different root samples, and even along a single root.

Is there a spatial dependence to the As oxidation state?



As XANES, Oxidation State Tomograms

XANES measurements on the *Typha latifolia* cattail roots show mixed As oxidation state – roughly equal portions As^{3+} and As^{5+} .

The As^{3+} fraction did vary between different root samples, and even along a single root.

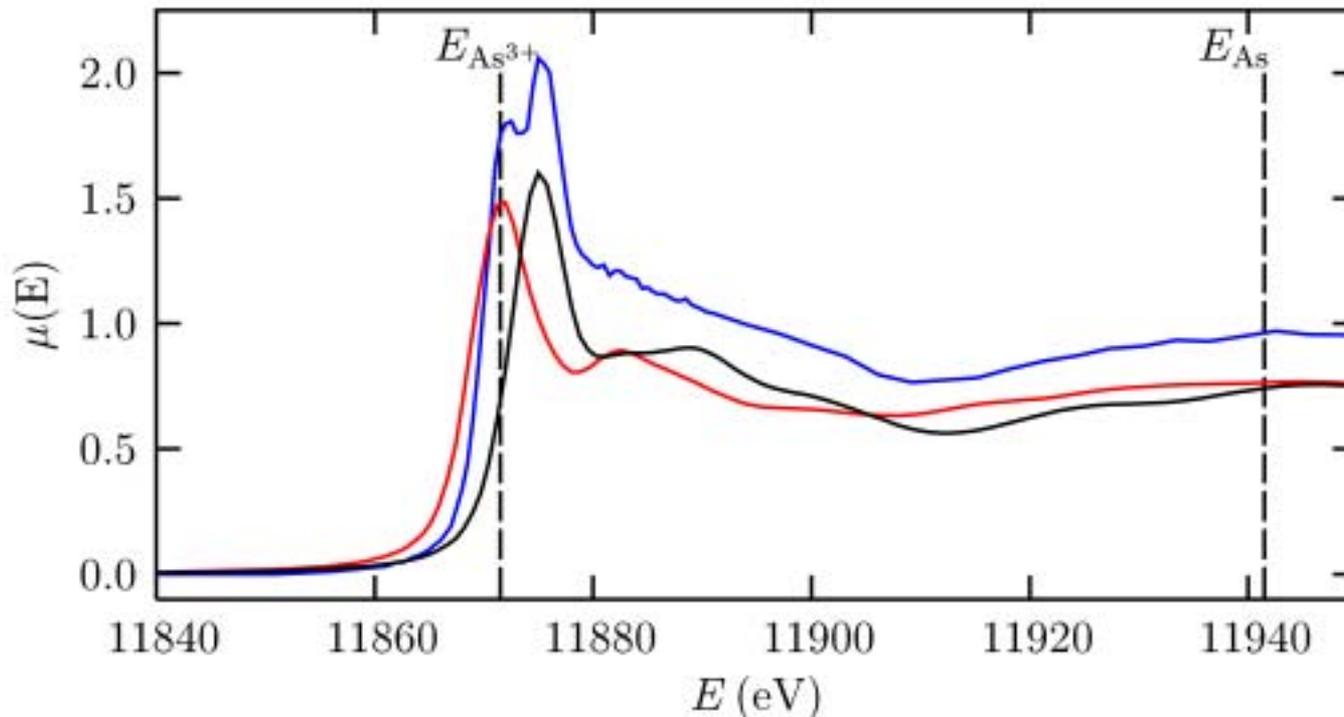
Is there a spatial dependence to the As oxidation state?

Fluorescence tomograms made at 2 different energies:

E_{As} total As concentration

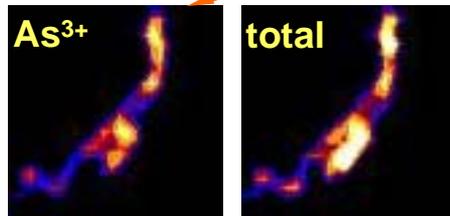
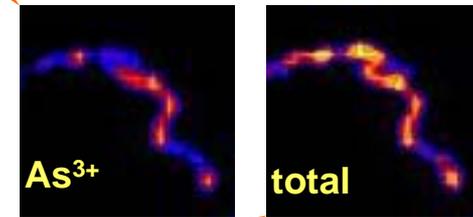
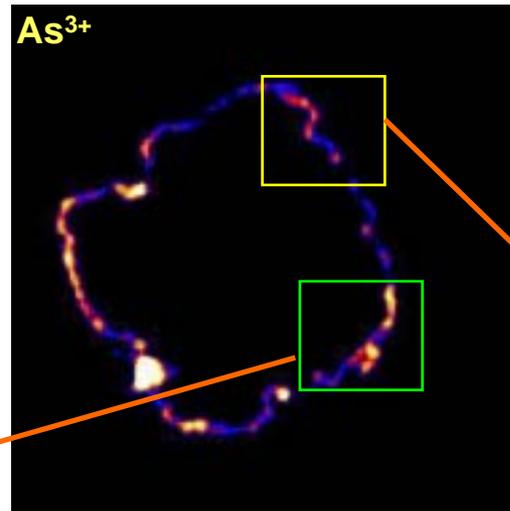
$E_{\text{As}^{3+}}$ As^{3+} concentration

would show spatial dependence of the As oxidation state.

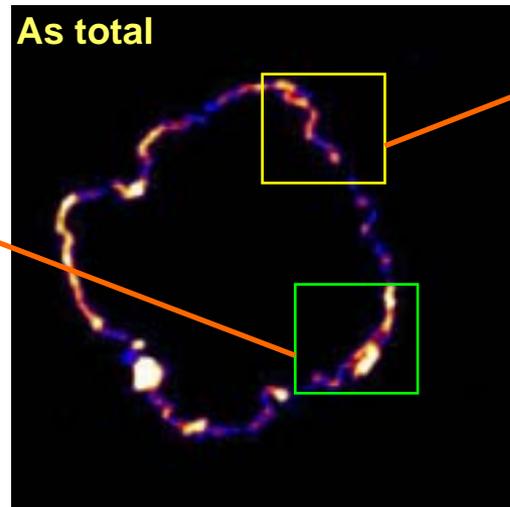


As oxidation tomograms for Cattail Roots

The $\text{As}^{3+} / \text{As}$ ratio is heterogeneous (boxed areas). As^{5+} appears correlated with metals (Fe, Cu, Zn).



As^{5+} appears at location with high Cu and Zn.



As^{5+} appears at location with high Fe.

More detailed spatial and oxidation state information would need faster data collection rates.



Future Directions and Microprobe Improvements

The GSECARS microprobe station is running well and productively, combining μ XRF, mapping, XANES, and EXAFS for a wide range of problems in geological, soil, and environmental sciences.

Areas for Improvement:

Beam positional stability, especially during XAFS scans
Ease of focus to below $2\mu\text{m}$

Using new x-ray beam position monitor with fast feedback, our 1-m long beamline KB mirrors can be used to stabilize the beam position at the $\sim 200\mu\text{m}$ slit in front of the small KB mirrors.

Data collection speed / efficiency

Even using DXP electronics for the multi-element detector, the detector is the rate limiting step for maps and XAFS. Being able to read out the detector faster will help speed up mapping and XAFS collection.

