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# Micro-beam X-ray absorption and fluorescence spectroscopies at GSECARS: APS beamline 13ID

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GeoSoilEnviroCARS, sector 13 of the Advanced Photon Source at Argonne National Laboratory, provides a micro-beam facility for XAFS, XANES, XRF, and x-ray diffraction studies. A Kirkpatrick-Baez mirror pair gives a focussed monochromatic undulator beam down to $1 \times 1\,\mu$m with sufficient intensity for x-ray fluorescence mapping and extended XAFS of dilute systems at energies above 4KeV. Special emphasis for these facilities has been given to environmental and earth science studies, including dilute contaminants in natural sediments. As an example, XRF maps and EXAFS data taken with a $4\mu$m by $7\mu$m spot size are shown for the Pu $L_{\rm III}$ edge of a natural tuff exposed to a dilute aqueous solution of Pu. In addition, x-ray diffraction and scattering capabilities allow the study of surfaces and surface adsorbates with micron-sized beams using x-ray reflectivity, x-ray standing-waves, and grazing-incidence XAFS.

**Keywords: micro-beam; XAFS; Kirkpatrick-Baez mirrors.**

## 1. Introduction

Non-destructive measurements of local structural and chemical speciation using synchrotron-based x-ray absorption and fluorescence spectroscopies on natural systems with minor and trace elements give important information for the earth and environmental sciences. An important requirement for these studies is the ability to focus x-rays so that fluxes with sufficient intensity for XANES and EXAFS measurements on low concentration elements can be performed on natural samples, with grain sizes of 10 microns or less. The Geology, Soil, and Environmental Science group of the Consortium for Advanced Radiation Sources at the University of Chicago (GeoSoilEnviroCARS) is dedicated to providing these x-ray spectroscopy capabilities to the earth science community by operating sector 13 at the Advanced Photon Source (APS) at Argonne National Laboratory. We describe the facilities and give an example of their application.

## 2. Beamline Optics and Microprobe Configuration

The high brilliance from APS undulator A beamlines offer extraordinary x-ray focusing capabilities. There has been significant effort made in the field of x-ray focusing at the APS, using Fresnel zone plates (Lai *et al.*, 1995), capillaries (Heald *et al.*, 1996), and Kirkpatrick-Baez mirrors. Because the design goals of our sector are influenced by the need for high flux over a wide energy range, a fairly large working distance, and focal spots of 1 to 10 $\mu$m, the Kirkpatrick-Baez geometry is a very attractive option. The achromatic focus and large working distance of this configuration make it convenient for x-ray fluorescence, XANES, and EXAFS microprobe work on natural samples, as well as diffraction experiments requiring high flux and high energy x-ray beams.

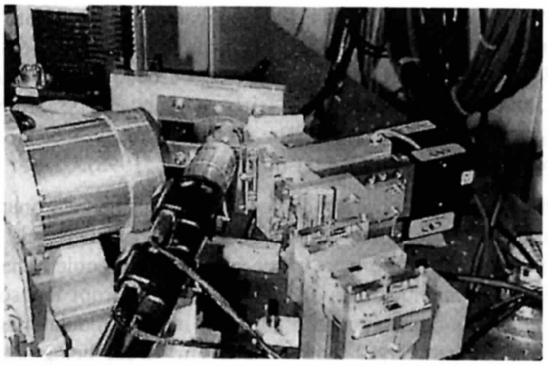

**Figure 1**
The microprobe station at GSECARS. Shown is a photograph of the optical table in the end-station of the undulator beamline, $\sim 55$ m from the APS storage ring. The x-ray beam comes from the lower right-hand corner, through the horizontal and vertical Kirkpatrick-Baez mirrors (shown on the left of the photograph) and to the sample position (illuminated spot on sample stage). The fluorescence is detected using a 13-element detector (large cylinder at left), and an optical microscope (thinner tube from lower left to sample position) is used for visual alignment of the x-ray beam on the sample.

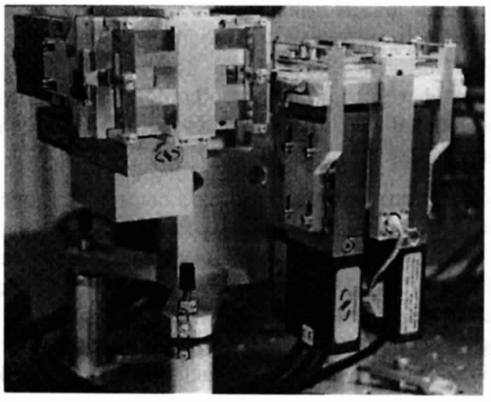

**Figure 2**
Table-top Kirkpatrick-Baez mirror pair. Each mirror has 4 motorized degrees of freedom: translation normal to the mirror plane, rotation around the axis perpendicular to the surface normal and to the beam direction, upstream bending force, and downstream bending force on the mirrors.

The focusing optics used at the GSECARS microprobe station are small Kirkpatrick-Baez mirrors (Eng *et al.*, 1998) that sit on the same table as the sample, detector, and optical microscope, as

shown in Figure 1. The compact mirror pair uses 100mm trapezoidal mirrors and four-point benders for each mirror to approximate an ellipse with one focus at the source ($\sim$ 55 m upstream) and one focus at the sample point ($\sim$ 70 mm from the center of the second mirror). A close-up view of the mirror pair mounted on the table is shown in Figure 2. To match the source characteristics of the APS, the vertical mirror is placed upstream of the horizontal mirror. This geometry gives a working distance of $\sim$ 20 mm from the end of the second mirror and a demagnification of the source of $\sim$ 780 in the horizontal and $\sim$ 320 in the vertical. Focusing, alignment, and use of these mirrors is fairly easy, and can be automated. Using Si mirrors coated with Rh, a focal spot of $0.80 \times 0.85\ \mu$m has been achieved with this set-up (Eng *et al.*, 1998).

Though a liquid-nitrogen-cooled, fixed-exit, monochromator is expected to be installed as this paper goes to press, the measurements shown here were made with a water-cooled channel-cut Si (220) monochromator, placed at 45 m from the source. Heating of the monochromator from the intense undulator source prevents a beam larger than $\sim$ 300 $\mu$m$^2$ from being incident on this monochromator, which accepts about 5% of the incident monochromatic intensity. The Kirkpatrick-Baez mirrors are used to reject the higher harmonics as well as focus the beam.

## 3. Example microprobe use: Pu sorbed on Yucca Mountain Tuff

As an example use of the GSECARS microprobe station, we show micro-XRF and micro-XAFS measured at the Pu $L_{III}$ edge for a core rock sample (or "tuff") taken from 450m below the surface of the Yucca Mountain site in Nevada, USA. The sample was exposed to a synthetic groundwater solution with a millimolar concentration of Pu (Duff *et al.*, 1999). Using float-glass Kirkpatrick-Baez mirrors coated with Pt, a $300 \times 300\ \mu$m$^2$ monochromatic x-ray beam was focused down spot size of $4 \times 7\ \mu$m$^2$ (full-width at half-maximum) on this sample.

Two-dimensional x-ray-fluorescence maps were made with a step size of 5 $\mu$m by simultaneously collecting the fluorescence signals from several metals using a single-element Si/Li detector. Elemental signals for Pb, Zn, Y, Mn, Sr, and Pu in the vicinity of a Mn-rich mineral are shown in Figure 3. It was observed that the Pu is highly concentrated at the Mn-rich minerals, and not in the surrounding quartz and zeolites, which made up the bulk of the sample.

Identifying two spots of relatively high Pu concentration as "A1" and "A2" in Figure 3, XAFS measurements were made at these two spots, with the same $4 \times 7\ \mu$m$^2$ beam and Si/Li detector used for the elemental mapping. The top panel of Figure 4 shows the averaged $\mu(E)$ data for the two spots, each representing about 6 hours of XAFS data collection. The XAFS $\chi(k)$ data was isolated from $\mu(E)$ (Newville *et al.*, 1993), and extended to $\sim 9$ Å$^{-1}$ before being dominated by random noise, as shown in the middle panel of Figure 4. The Fourier Transforms of the data for the two spots are shown in the bottom panels of Figure 4.

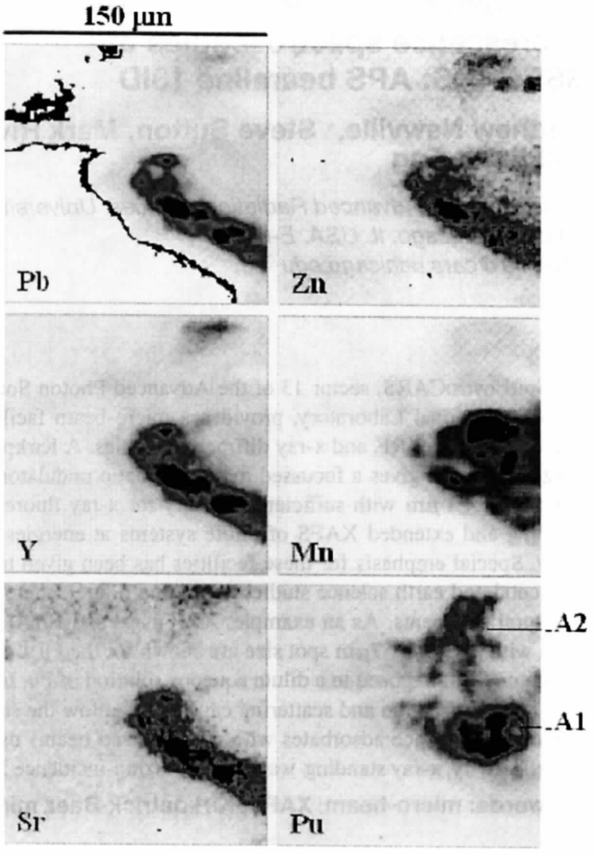


**Figure 3**
Two-dimensional x-ray fluorescence maps of a Pu-dosed piece of Yucca Mountain tuff. Shown are the intensities of the fluorescence lines for Pb, Zn, Y, Mn, Sr, and Pu in the region of a Mn-rich mineral phase. Each map is $150 \times 150\ \mu$m. The two spots marked "A1" and "A2" on the Pu map (lower right) were further analyzed by XAFS.

Also shown in the middle and bottom panels of Figure 4 are preliminary fits to the Pu-O first shell. As is discussed in more detail elsewhere (Duff *et al.*, in progress), both the XANES and first shell EXAFS results are consistent with Pu-O coordination at $\sim$ 2.25 Å and with no short axial Pu-O bonds as might be expected in a Pu hydrate system. Reliable fits to the "second shell" could not be found for these data. This may indicate a highly disordered Pu distribution in the Mn-rich mineral phase, though the $k$-range and data quality might make it difficult to see anything but a very highly ordered second shell.

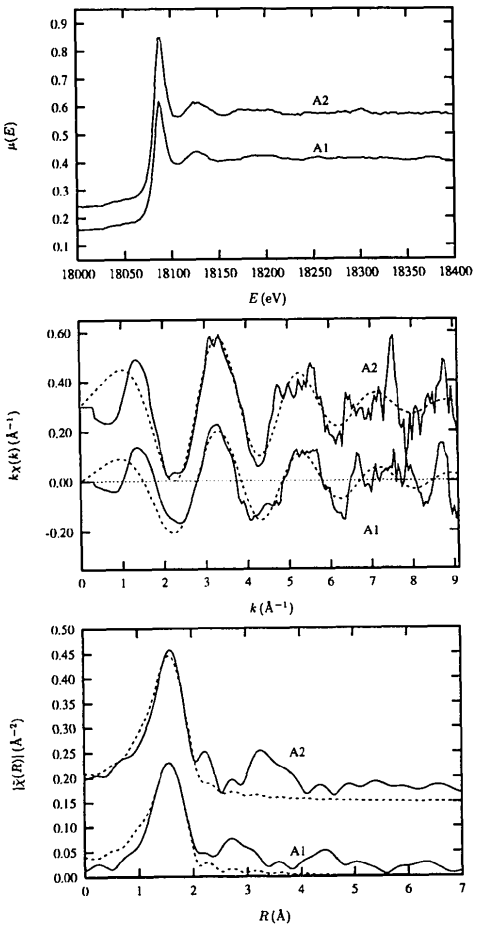


**Figure 4**
XAFS scans at the two Pu-rich sites "A1" and "A2" shown in Figure 3. The top panel shows the $\mu(E)$ data, after averaging 9 scans for spot A1 and 10 scans for spot A2. The middle panel shows $k\chi(k)$ data for the two spots (solid), and fits to the Pu-O first shell (dashed). The bottom panel shows $|\chi(R)|$ for the two spots (solid) and the first shell fits (dashed).

## 4. Conclusion

The GeoSoilEnviroCARS x-ray microprobe station at the APS provides a facility to study heterogeneous and low concentration samples for earth and environmental sciences. We have demonstrated the ability to use micro-focusing optics to achieve beam sizes of 1 $\mu m^2$, and the use of a $4 \times 7$ $\mu$m beam for XRF mapping and XAS on selected portions of dilute and heterogenous natural systems. As an example, XRF maps made on a core sample from Yucca Mountain dosed with a dilute Pu solution show the Pu to be highly localized at Mn-rich mineral sites, and XANES and EXAFS measurements at these enriched spots show an oxygen coordination consistent with a lack of axial oxygens, and no clear demonstration of a well-ordered second shell environment.

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