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PROGRESS TOWARDS SUB-MICRON HARD X-RAY IMAGING USING ELLIPTICALLY BENT MIRRORS AND ITS APPLICATIONS

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Progress towards sub-micron hard x-ray imaging using elliptically bent mirrors and its applications

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ABSTRACT

We have developed an x-ray micro-probe facility utilizing mirror bending techniques that allow white light x-rays (4-12keV) from the Advanced Light Source Synchrotron to be focused down to spot sizes of micron spatial dimensions. We have installed a 4 crystal monochromator prior to the micro-focusing mirrors. The monochromator is designed such it can move out of the way of the input beam, and allows the same micron sized sample to be illuminated with either white or monochromatic radiation. Illumination of the sample with white light allows for elemental mapping and Laue X-ray diffraction, whilst illumination of the sample with monochromatic light allows for elemental mapping (with reduced background), micro-X-ray absorption spectroscopy and micro-diffraction. The performance of the system will be described as will some of the initial experiments that cover the various disciplines of Earth, Material and Life Sciences.

Keywords: x-ray, micro-focusing, x-ray diffraction, x-ray absorption, adaptive optics, bent mirrors, four crystal monochromator.

1. INTRODUCTION

Progress continues with the development of x-ray focusing optics in order to utilize the available new source brightness of third generation synchrotron storage rings. The brightness of these new x-ray sources lend themselves to the development of new types of microscopy and micro analysis. All of these 'micro' techniques require the focusing of x-rays by means of the various x-ray focusing optics such as capillary optics,[1] zone plate optics, [2] Kumakov whispering galleries,[3] Bragg Fresnel optics[4] and grazing incidence reflection mirrors.[5,6,7] All have their advantages and disadvantages dependant on the particular application. In the hard x-ray energy range the techniques of x-ray diffraction and x-ray absorption spectroscopy have become ubiquitous in the physical sciences when applied on the macro scale. Application of these techniques on the micro scale is one of the motivations for third generation synchrotron sources. At the Advanced Light Source (ALS), we have developed grazing incidence single metal film mirrors in the Kirkpatrick-Baez (KB) focusing geometry [5] to provide the achromatic micro focusing capability required for the wide photon energy range required for micro x-ray diffraction (μXRD) and x-ray absorption spectroscopy (μXAS).

2. X-RAY OPTICAL REQUIREMENTS

Our requirement is to perform μXRD and μXAS in the photon energy range of 4-12 keV. Sample sizes are intended to be on the micron scale. The customary way of performing x-ray diffraction is to fix the photon energy and map the Bragg reflection peaks by rotating the sample while detecting the diffracted x-rays on a 2-dimensional detector. Such a scheme is appropriate for macro sized samples (>100 μm), but for micron sized samples, the mechanical difficulty in rotating such a small sample while ensuring the focused beam does not move from it, suggests that alternative ways of carrying out x-ray diffraction on micron sized samples should be considered. Our scheme is to scan the photon energy whilst keeping the sample and detector fixed. One problem that arises with all microscopy techniques is the ability to

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find the sample by means of some detectable signal - preferably the signal should be that of the technique employed - in our case, x-ray diffraction. Simply irradiating the micron sized sample with monochromatic x-rays will not generate any signal unless the photon energy, sample crystal planes and detector all happen to satisfy Bragg's Law. A much simpler procedure is to irradiate the sample with a focused beam of white radiation. This will result in a Laue x-ray pattern which can be indexed from a known or trial structure to give orientation. From the energy and direction of the Laue beams, d-spacing measurements can be made. Thus the x-ray optics are required to be able to switch between white and monochromatic x-rays without changing the point on the sample being irradiated. Measurement of the energy of the Laue beam can be carried out by monitoring the Laue beam while scanning the energy of the illuminating x-rays. It should be noted that for μXRD the optics are required to scan in photon energy whilst maintaining a fixed spot position on the sample. This is also the requirement needed for μXAS and thus the same equipment is capable of carrying out these two powerful synchrotron based techniques.

3. EQUIPMENT DESCRIPTION

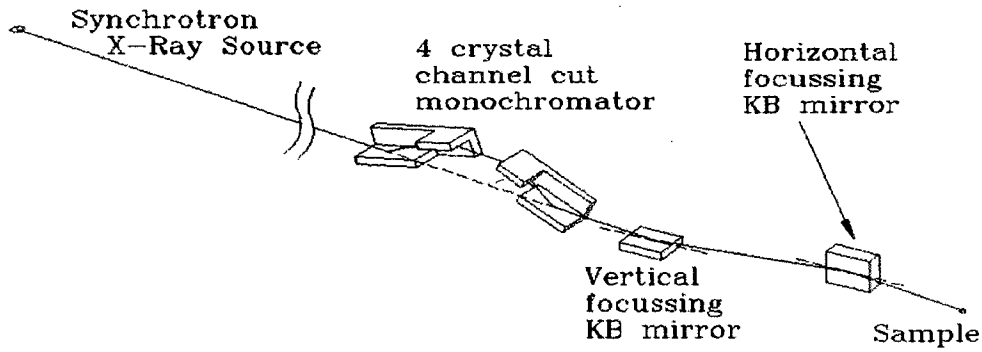

Figure 1. Schematic layout of the K-B mirrors and the four crystal channel cut monochromator

Figure 1 shows the schematic layout of such an x-ray μXRD /μXAS beamline. It consists of a 4 crystal monochromator located 31m from the bending magnet source of the ALS. The monochromator crystals are in the +--+ configuration[8], which has the property of directing the monochromatic x-rays along the same axis as the incoming white light. Following the monochromator are the KB mirrors that image the synchrotron source onto the sample. The monochromator is made from 2 pairs of identical Si(III) channel cut monochromators[9]. The crystals are mounted off axis such that when they are positioned for a Bragg angle equal to zero, the crystals are rotated out of the beam and white light passes through to the KB focusing optics. Rotating the crystals into the beam results in monochromatic light passing through to the KB focusing optics. The Bragg angular range of the monochromator is 7-70 degrees, which for Si(III) results in an energy range of 16222 - 2104 eV - this being quite an adequate energy range for the techniques in question. The monochromator crystals themselves are 59mm long as determined by their off axis rotation point and the 30 μrad vertical aperture of the vertical focusing KB mirror. The mechanical mechanism for the 4 crystal monochromator is of a design similar to that of Tolentino et al [10] consisting of two rotational stages onto which the two channel cut crystals mount. For scanning the monochromator the two stages rotate in opposite directions by means of a tape drive, which is driven by a linear slide. The mechanical tracking deviation of the two rotation axes of the crystals has been measured to be <0.001 degrees over several tens of degrees of crystal rotation. We find we are able to operate the monochromator with no feedback with regard to the alignment of the 2 crystal pairs. Minor long term drift is apparent with the monochromator requiring tune up every day or so, which is viewed as adequate for the present status of the facility.

The K-B mirrors have been described in detail before[7]. Briefly they are platinum coated flat pieces of fused silica, bent to the required ellipsoidal shape by means of a leaf spring bender that exerts different couples on either end of the mirror. Additional fine tuning to the required ellipsoidal shape is achieved by adjusting the moment of inertia of the mirror along its length by means of tapering the mirror width along its length. Grazing angles of 5.8 mrad (0.33 degrees) are used which allows for a cut off of ~12keV. The source size in the ALS bending magnet is typically around 260 x

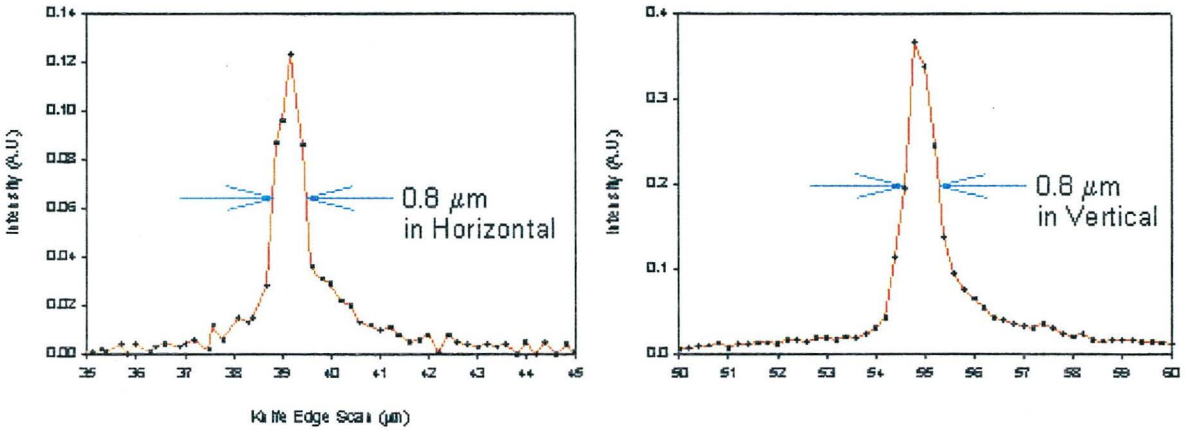

Figure 2. Differentiated knife edge profiles of the focused spot. The knife edge used was a 50μm wide gold coated tungsten wire.

20 μm FWHM (horizontal x vertical (h x v)). Demagnification is 300 x 60 (h x v) which should result in a spot size of 0.86 x 0.33 μm FWHM. The best achieved focus has been 0.8 x 0.8 μm as indicated in Fig.2. The horizontal spot size achieved is consistent with expectations given the small mirror length, the consequent low rms slope error of 0.6μrads and the short mirror to focus distance (10cm)[7]. In the vertical the larger spot size can be attributed to slope errors of the longer vertical focusing mirror (1.4μrads rms) and the large mirror to focus distance (50cm)[7]. The spot profiles of Fig. 2 have wings indicative of possible coma and/or scattering from the mirror surface. The flux on the sample is typically in the 10^7 to 10^8 photons/sec range. The beam stability of the spot on the sample was measured to be less than ±0.5μm when switching between white and monochromatic light. This measurement was limited by noise on the detector used with the knife edge equipment and it may be expected that beam stability is better than this due to constant beam output nature of the 4 crystal monochromator and additional demagnification of beam displacement errors by the KB mirrors.

3. APPLICATIONS - X-RAY MICRO-DIFFRACTION

A current primary problem in the semiconductor industry is the electromigration problem in the metallic interconnects between the semiconductor devices on high density silicon wafer circuits. Electromigration is the physical movements of atoms in metallic interconnect lines passing current at high electron density (typically in the range of 10^5 amp/cm^2). Significant material movement results in voids that consequently lead to breakage and circuit failure in the metal lines. This problem gets more severe as the line dimensions continue to shrink on integrated circuits. In spite of much effort in this field [11,12,13], electromigration is not understood in any depth or detail, but is strongly associated with the physical material properties (stress and strain) within the interconnect material. X-rays are quite well suited to such measurements as they are able to penetrate several microns into matter. This is relevant as these interconnect lines are buried within an insulator (silicon dioxide or silicon nitride) and the x-rays are able to penetrate and study the buried wires in the environment that they are to be used. Removal of the dielectric layers has the effect of completely altering the stress state of the wires, so examination of them in their native environment is vital.

Aluminum interconnect wires are most commonly used in the industry at the moment. With wire widths of 1 μm and less, the microcrystalline structure along the wire length can be described as a bamboo structure, being made up from a series of single crystals of aluminum each of size ~1μm. It is considered that the electromigration properties of such a wire will be dependent on the grain orientation of adjacent grains in the line and the strain characteristics of the separate grains. Therefore the requirement for a micro-diffraction experiment will be to map out the grain orientation of each of the crystals along the wire length. Ortho-normal strain measurements within each crystal can be determined by accurately measuring (1 part in 10^{-5}) the d spacing of several crystal planes and using the observed d -spacing change as an internal strain gauge. Current flowing through the wire during the measurements is also a requirement. Such in-situ measurements, are expected to yield insight into this problem. The following describes progress to date:-

A sample consisting of a 2-μm wide aluminum wire deposited to 0.5-μm thickness on an oxidized silicon (100)

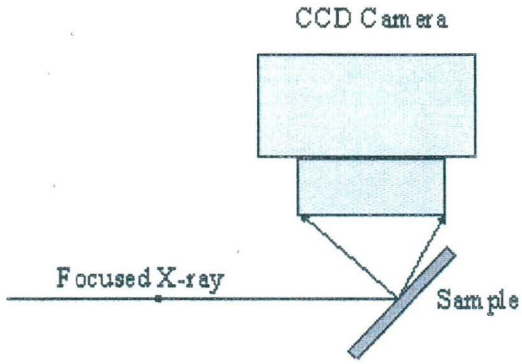

Figure 3. Schematic arrangement of x-ray direction, sample and CCD.

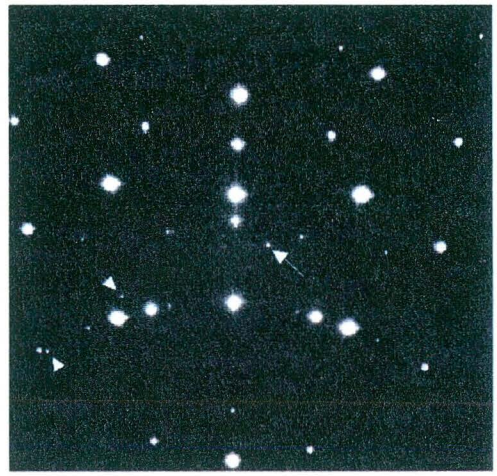

Figure 4. Two overlapped Laue patterns - the 3 fold symmetric dominant pattern is from the silicon substrate, the much weaker pattern indicated by arrows is from a single aluminum grain.

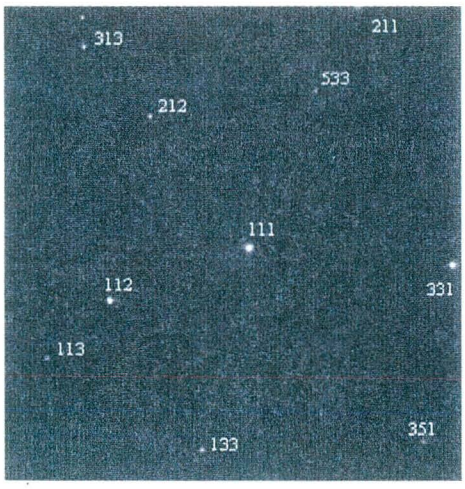

Figure 5. Laue pattern from the single aluminum grain shown in figure 4 with the silicon Laue pattern digitally subtracted.

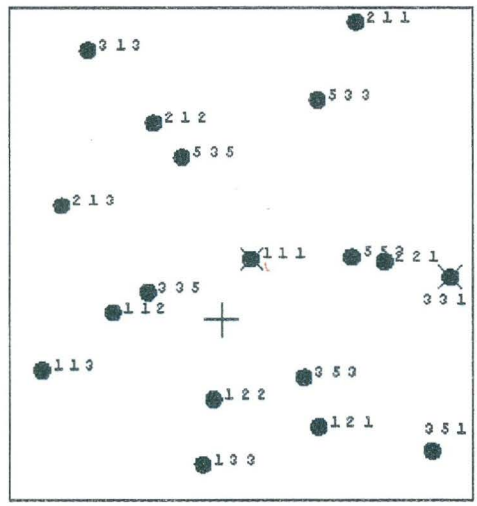

Figure 6. Simulated Laue pattern with the aluminum spots indexed.

substrate. The line was insulated with a plasma-enhanced chemical vapor deposition of silicon nitride at 300°C to 0.3μm thickness. Laue patterns were collected using white radiation and a x-ray CCD camera in the 90 degree scattering geometry indicated in figure 3. White light was focused onto the aluminum wire and Laue patterns were recorded by the x-ray CCD camera. The exposure time was 0.5 sec, the sample-to-CCD distance was 16.4 mm and the CCD active area was 25.9 x 27.5mm. Figure 4 shows the Laue pattern from the silicon substrate with the fainter diffraction spots from a single grain in the aluminum line - some of these spots are indicated in the figure. The silicon substrate Laue pattern dominates as the x-rays interact with much more silicon than the 0.5μm thick aluminum crystal. To extract the aluminum Laue pattern, the sample was moved to position the x-ray spot off the aluminum line, the silicon substrate Laue pattern was recorded and digitally subtracted from figure 4. This yields the Laue pattern from the single aluminum grain as shown in figure 5. The pattern was indexed using the Laue simulation software package - LaueX[14]. The Laue pattern simulation from the aluminum grain is shown in figure 6 which shows that all the low index spots with indices less than 5 are recorded. The aluminum grain orientation can be referenced to the silicon substrate orientation via a suitable matrix conversion. The next stage is to measure the d-spacing of various diffraction spots and thus build up the ortho-normal strain within the crystal. The 4 crystal monochromator was inserted into the beam thus illuminating

the aluminum grain with monochromatic light. The photon energy was scanned and the rocking curve (of the central Al(111) spot in figure 5) mapped out. The photon energy of the diffracted light was measured to an adequate accuracy (7323eV), however the angular accuracy for the Bragg angle determination was limited by the present equipment. Equipment upgrade is underway to allow this measurement to be performed. In priciple the process of measuring orientation and strain can be repeated incrementally along the aluminum wire until the orientation and strain map of the entire wire length has been characterized.

4. APPLICATIONS - MICRO X-RAY ABSORPTION SPECTROSCOPY

Environmental Science, including Geochemistry, Soil Science and Biogeochemistry involve systems which are highly heterogeneous with spatial variations typically on the micron to mm scale. To date the application of macro-XAS to this field has been limited to the understanding of homogeneous and model systems[15, 16]. "Real world" heterogeneous samples have not been addressed by the macro-XAS technique. However, μXAS, has the ability to carry out spectroscopy on the micron scale and can thus address the heterogeneity problem with its ability to locate and chemically speciate entities within a given system. We have developed fluorescence μXAS which being a photon in - photon out experiment is able to carry out the measurement whilst maintaining the sample in its natural state. This technique will be of enormous benefit to the Environmental Science field. Here we show two initial examples showing the power of the technique:-

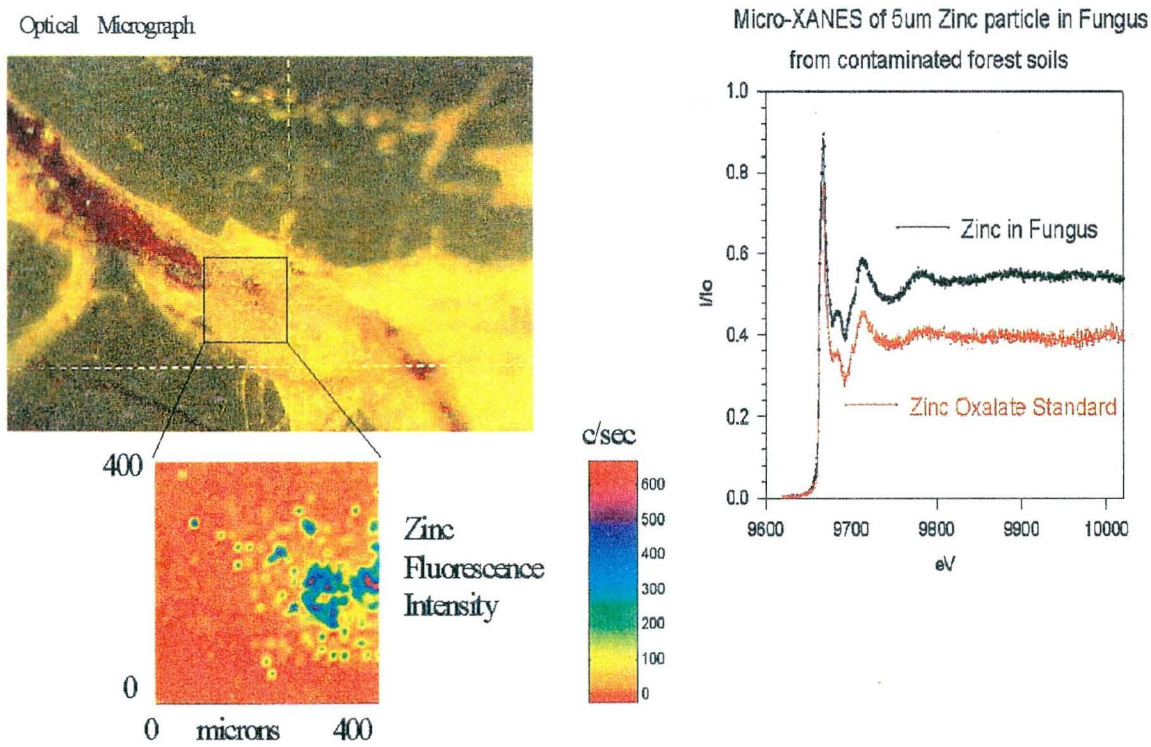

Figure 7. Optical micrograph of fungi in its natural state (top left) with Zinc elemental fluorescence map (lower left). Also included are the near edge zinc μXAS spectra of the high concentration zinc particles and a zinc oxalate standard.

Large areas of the forest land in Southern Norway are contaminated with various metals, including Zn, Cu, Pb, Cd. The main source of contamination are metal refining industries, with consequent accumulation of the metal discharge over the past twenty years. Large quantities of the contaminant metals are taken up by soil fungi in the top organic layer of the forest surface soils. These species are called ectomycorrhizal fungi and they are known to form symbiotic relationships with the trees via the root network. The fungi obtain carbohydrate from the tree roots in return for mineral

supplies from the fungi. Whilst it is known that the fungi take up great quantities of the heavy metals, little is known of the precise forms in which they are retained nor of the mechanisms of uptake and conversion. Figure 7 shows an optical micro-graph of an area on a sample of the live fungus. A 400 x 400 micron area of interest is marked on the image. The elemental distribution of zinc within that area is indicated by the X-ray fluorescence intensity map shown below the micro-graph. This map shows that the zinc is localized in very small regions of dimensions of only a few microns. Maximum count rates on the high concentration regions of zinc were 600c/sec excited by means of monochromatic light and detected by a single channel solid state detector having a collection angle of ~0.5 steradian. On the right hand side we see the μXAFS scans taken by placing the monochromatic micro-beam on the area of greatest concentration and scanning over the zinc K edge at 9659 eV. The signal/noise is sufficiently good to scan some way into the Extended XAFS region, which indicates the potential for extracting structural parameters for this system. In this case a preliminary analysis of the short extended region is consistent with the observation by simple comparison with the very distinctive XAFS from the zinc oxalate standard, that there is a high likelihood that this species is zinc oxalate. In addition, our conclusion supports that of recent work by Sarret et al[17]., which showed using conventional XAFS, that for zinc sequestered by lichen (a symbiotic microorganism consisting of an algae and a fungi) under similar conditions of contaminant exposure, the dominant product is zinc oxalate. The results suggest that zinc oxalate is important in the mechanism of contaminant uptake, retention or conversion in its symbiosis with higher plants.

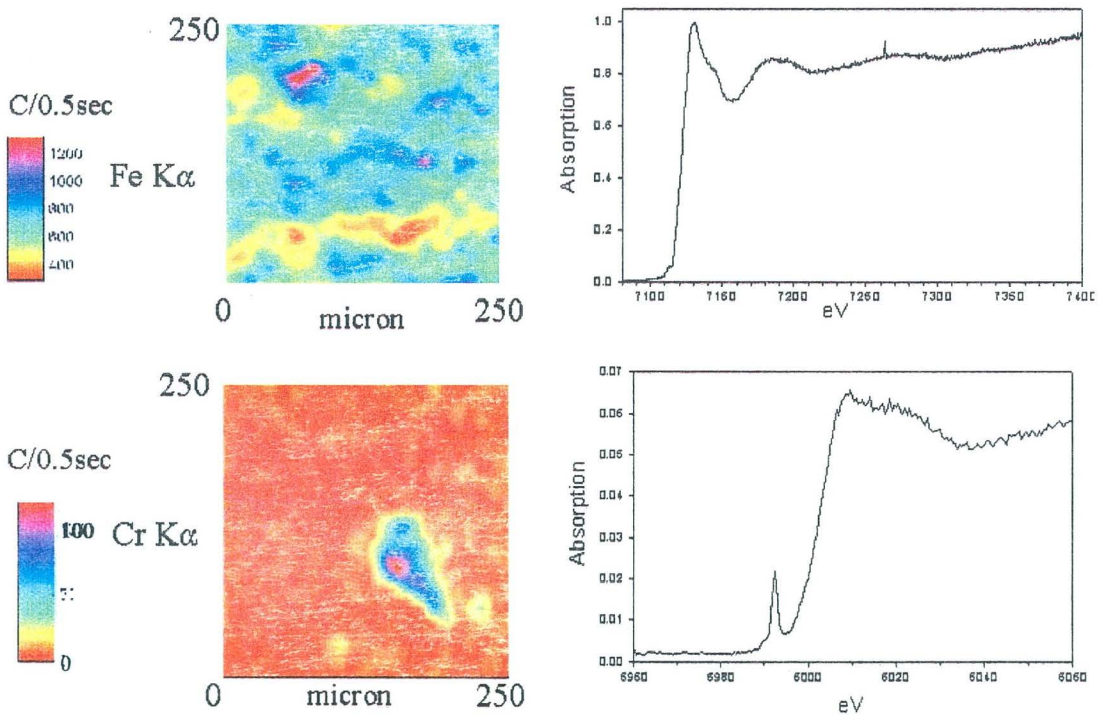

Figure 8. Contaminated Alameda soil. Elemental maps of iron (top left) and chromium (lower left) are shown with their associated x-ray absorption spectra to the right.

The second example is that is that of sediment containing 350ppm of chromium contamination from the Alameda Naval Base, California. Traditional macro-XAS was unable to help in speciating the chromium due to the poor signal/noise ratio due to the heavy absorbing matrix that the chromium exist in. Figure 8 shows on the left, the elemental maps of iron and chromium. Clearly chromium is present in a significant localized concentration that allows easy detection with the μ-XAS technique. Often chromium exists with iron oxide/hydroxide but in this case it is apparent that this is not the case. The sharp pre-edge feature in the chromium absorption spectra is indicative of the mobile and highly toxic chromium VI state.

5. FUTURE DEVELOPMENTS

As was noted in the discussion on μXRD a new goniometer assembly is under construction to allow for accurate measurement of Bragg angles of diffracted x-rays from micron sized samples. This will establish a dedicated μXRD facility at the ALS. The new facility will be developed on a new bending magnet beamline (beamline 7.3.3), which has the ability to trade flux on the sample for spot size. This is achieved by the use of an intermediate toroidal optic that images the synchrotron source with 1:1 magnification onto an adjustable slit in the end station hutch. This slit then acts as an adjustable sized source for the 4 crystal monochromator and KB mirror assembly.

The μXAS development facility is still undergoing the optimization of its specifications for the final custom built facility. It is apparent that many of the Earth Science type experiments being suggested do not gain by having sub-micron x-ray spots. These experiments would prefer spots sizes in the 3μm range, this being adequate to see the heterogeneity and comparable to the penetration and escape depth of the in-going and out-going photons. Such a purpose built μXAS line would be expected to have fluxes x30 higher than the present development facility from spot size considerations alone. Other factors of x2-4 can be gained by increasing the KB mirror acceptance, x2 if Ge(111) crystals are used, ~x4 with the use of a multi-element detector capable of accepting a larger solid angle. The use of a multilayer monochromator for elemental mapping rather than the output from the Si(111) monochromator would be expected to increase sample fluorescence signal by ~x100. To gain full advantage of this will require the development of a fast scanning stage with photon time tagging as is used in the established scanning electron microscopy technique of electron dispersive spectroscopy (EDS).

It is clear that smaller spot sizes will be required for future experiments at synchrotrons. We note that the Raleigh criteria diffraction limit of the KB mirrors used here is 60nm at 10keV. Mirror figure error will have to be improved to achieve this, but this appears to be an ongoing process and is likely achievable in the next few years.

6. CONCLUSIONS

Grazing incidence KB mirror systems are capable of high spatial resolution, and large collection aperture. Their achromatic nature offers a number of attractive features in comparison to diffractive focusing elements. The use of μXRD and μXAS is likely to have a profound effect in a wide range of the physical sciences.

7. ACKNOWLEDGMENTS

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