X-Ray Fluorescence Imaging with Synchrotron Radiation

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M. L. Rivers**Department of the Geophysical Sciences****The University of Chicago, Chicago, Illinois 60637****DISCLAIMER**

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Mark L. Rivers

**Department of the Geophysical Sciences, The University of Chicago,
5734 S. Ellis Avenue, Chicago, IL 60637**

1. INTRODUCTION

The micro-distribution of trace elements is of great interest in fields such as geochemistry, biology and material science. The synchrotron x-ray fluorescence microprobe provides a technique to quantitatively measure trace element compositions at individual points and to construct semiquantitative two dimensional maps of trace element compositions [1,2,3].

Most of the papers in this volume deal with soft x-ray microscopes for imaging biological materials in the "water window". Soft x-ray microscopes face stiff competition from optical microscopy on the one hand, which offers great simplicity and resolution of 0.25 μm or better, and from electron microscopy on the other hand, which has a resolution as good as 1 nm, but requires that the specimen be placed in vacuum. The hard x-ray microprobe has much less competition: electron microprobes have spatial resolutions of 1 μm or so, but the detection limits are typically above 50 ppm. Ion microprobes have much lower detection limits, but quantitative results are difficult to achieve. Samples must also be placed in vacuum, and are destroyed during the analysis. Even the very simple scanning x-ray microprobe described in this paper has proven to be a very useful tool for earth scientists and biologists.

2. EXPERIMENTAL

Experiments were performed on beamline X-26C at the National Synchrotron Light Source, Brookhaven National Laboratory. The microprobe used was a "first generation" device with no focussing optics or monochromators installed. Rather, white radiation from the bending magnet was collimated with two pairs of stepper motor controlled slits located 0.5 m from the sample. The electron beam source dimensions are 800 μm (horizontal) $\times$ 200 μm (vertical) for $\pm 1\sigma$. The distance from the electron beam to the slits was 20 m, and thus the minimum spot size on the sample is 20 $\mu\text{m} \times 5 \mu\text{m} \pm 1\sigma$. Actual beam sizes used were typically 30-50 μm .

The low energy photons in the incident beam were removed by the 500 μm Be windows in the beamline, and by the 20 cm air path between the end of the beamline and the sample. Additional filtering was often used, typically 100-400 μm of aluminum to reduce the flux of low energy photons which would contribute scattered background counts but not contribute to fluorescing interesting trace elements. The theoretical incident spectrum

is shown in Fig. 1. The calculated flux for all photons with energies between 5 keV and 20 keV is 2×10^7 photons/sec/ μm^2 , or about 2×10^{10} photons/sec for the 30-50 μm beam diameters normally used. These calculated fluxes compare favorably with those measured by Underwood *et al.* [4] for their focussing microprobe which uses multilayer coated Kirkpatrick-Baes mirrors.

Fig. 1: Calculated flux from the X-26C bending magnet. Upper curve is the flux before any windows or absorbers. Lower curve is the flux downstream of a 100 μm Al filter

Fluorescent photons were detected with a 30 mm² Si(Li) detector at positioned in the horizontal plane, 90° to the incident beam, to minimize the scattered background [5]. The detector has a resolution of about 160 eV at 5.9 keV and a maximum count rate of about 5000 counts/sec under normal operating conditions.

The sample is mounted on a Klinger Scientific translation/rotation stage with 100 mm of travel in the X and Y (scanning) directions and 25 mm travel in the Z (focussing) direction. The rotation stage is used to orient crystalline materials to eliminate Bragg diffraction peaks [6]. The stages have step sizes of 1 μm and backlash under 3 μm . The sample is observed with a Nikon SMZ-10 binocular zoom microscope equipped with a high resolution DAGE/MTI black and white TV camera. The field of view on the TV monitor is 2-10 mm, and the optical resolution on the monitor is about 10 μm .

The principle system electronics consist of a MicroVAX II computer, a CAMAC crate and a Nuclear Data ND9900 multichannel analyzer (MCA). The CAMAC crate houses 16 channels of intelligent stepper motor control, a frequency divider and scalars. The ND9900 is comprised of display controller and acquisition interface boards which plug directly into the MicroVAX Q-bus, and an external color monitor and keyboard. The acquisition interface can be connected to up to 4 NIM analog-to-digital converters (ADCs) and/or 8-input multi-channel scalars (MCSs).

The closely coupled nature of the MCA and the MicroVAX II minimises the overhead involved in transferring spectra to the computer for processing and storage. The ND9900 display controller contains a significant amount of local intelligence, and thus permits real-time spectral display and manipulation during scanning with minimal load on the MicroVAX host.

3. SCANNING

The x-ray microprobe can collect data in a variety of modes. The simplest is to move the specimen to a location to be analysed and to collect a fluorescent spectrum at that point. This "non-scanning" mode is in fact the way the microprobe was employed most of the time. It permits long collection times, typically 300 seconds per point, and hence low detection limits, typically 0.5-5 ppm by weight, depending upon the matrix and elements analysed [3,7].

Data can also be collected in one of 3 different "scanning" modes, sampling over a 1 or 2 dimensional array of pixels. The x-ray beam cannot be rastered electrostatically or magnetically as an electron or ion beam can, so the sample must be mechanically scanned in front of the stationary beam. In the first scanning mode a complete fluorescent spectrum is stored as a separate disk file at each pixel. The integrated ion chamber current at each pixel is stored with the spectrum for normalization purposes. This mode is often used simply to automate the collection of spectra at many points, without constructing an image of the sample. It maximises the information recorded at each point but requires a large amount of disk storage for high resolution scans, and requires substantial post-processing to construct an image. The stage motion in this mode is discontinuous, with the computer moving the stages to a new pixel, stopping, and then starting data acquisition. Each spectrum must be read from the ND9900 and saved to disk before moving to the next point. The overhead involved in these operations is about 0.5-1 second, so the minimum practical total time per pixel is about 1-2 seconds.

In the second scanning mode the user defines regions-of-interest (ROIs) at the fluorescent lines of the elements to be measured. Background windows on either side of the peaks may also be defined. At each pixel the program determines the background corrected peak areas for each ROI and stores only these values. The shaded areas in Fig. 2 show the peak areas which would be stored for a spectrum similar to those from the sample in Fig. 3. The data are normalized by dividing the net peaks areas by the integrated ion chamber current at each pixel. Up to 32 ROIs be defined in the spectrum, and the data for all of the ROIs for all of the pixels are stored in a single disk file. The overhead per pixel is again about 0.5-1 second, due to the discontinuous stage motion, the communications overhead required to read the spectrum, and the processing time to extract and normalize the peak areas.

Fig. 2: Fluorescent spectrum of the mineral pentlandite ($Fe_{4.5}Ni_{4.5}S_8$) from an ore deposit. Shaded regions are the net peak areas which are shown in the images in Fig. 3

In the third scanning mode the output of the Si(Li) detector amplifier is fed into one or more single channel analyzers (SCAs), whose output is then fed into the multichannel scaler. The window on the SCA is set to the energy of a fluorescent line of interest. In this mode scanning is continuous, with the channel advance signal to the MCS being derived from the stepper motor pulses on the scanning stage. The advantage of this scan mode is speed, the maximum scan rate being limited only by the counting statistics and not the system overhead. There are several disadvantages of this scan mode as well. It is hardware intensive, requiring an SCA and MCS channel for each element to be analysed. Background correction and ion chamber normalization also require MCS channels and post-processing if they are to be performed. Finally, it is difficult to set the SCAs accurately when there are closely spaced peaks in the spectrum.

The time required to acquire an image with the current scanning microprobe is not really limited by the overhead described for the second scan mode, and MCS scanning does not appreciably reduce the time required to collect a trace element image. The scan rate is actually limited by the nature of the detector, which can only handle a total count rate of about 5000 counts/second. On most samples most of the counts are either due to scattered x-rays or to the fluorescence of major elements. The scattered x-ray signal is minimized by the polarized nature of the synchrotron radiation and the detector geometry, but is still typically thousands of counts per second for thick targets and a 30 μm beam diameter. The major element fluorescence can sometimes be minimized by placing an absorber such as Kapton or aluminum in front of the detector to preferentially absorb lower energy photons from the major elements and pass the higher energy photons from the trace elements. In many samples, however, when the detector is counting at its

maximum rate there are only a few photons per second from the trace element of interest, and it is thus necessary to count for a few seconds to achieve reasonable statistics. The detection limits for thick samples with 300 second count times are typically about 1 ppm by weight. Since the detection limit scales with the square root of the count time, a trace element image with a collection time of 1 second will have detection limit of about 17 ppm at each pixel. This is a reasonable detection limit, but it implies a scan time of nearly 3 hours for a 100×100 pixel image. Most of the images we have made to date have been lower resolution, about 50×50 pixels.

The data from scan modes 2 and 3 are saved as image files on disk in a very general file format common to several beamlines at the NSLS, including X-1, the soft x-ray microscope. Images can contain many different data values at each pixel, e.g. the peak area of different fluorescent lines, the incident and transmitted ion chamber currents, etc. Each data value can be stored in any of 8 numerical data types; signed or unsigned 8, 16, or 32 bit integers, and 32 or 64 bit floating point. The data can be compressed with linear predictive coding, which allows 2 or 4 byte integers to be compressed to fewer bytes, or run-length limited compression, which compresses runs of identical pixel values. The compression mechanisms are completely loss-free and the different data values at each pixel can be compressed with either algorithm.

4. RESULTS

A spectrum of the mineral pentlandite ($Fe_{4.5}Ni_{4.5}S_8$) from an ore deposit is shown in Fig. 2. This spectrum was collected for 300 seconds with a $30 \mu m$ beam diameter. The Si(Li) detector was placed 40 mm from the sample with a 6 mm diameter collimator in front of it. The incident x-ray beam was filtered with $410 \mu m$ of Al and the fluorescent photons were filtered with $150 \mu m$ of Al. These filters served to reduce the intensities of the Fe and Ni lines while attenuating the trace element lines of interest (As, Se, Ru, Pd) much less. This sample contains about 200 ppm of Se and Pd, and the detection limits are about 3 ppm for each.

Six scanning images of a rock section from a Finnish ore deposit are shown in Fig. 3. Fig. 3a is a backscattered electron image made with a CAMECA electron microprobe. The major minerals in the sample (numbered in Fig. 3a) are 1) pyrrhotite ($Fe_{1-x}S$), 2) chalcopyrite ($CuFeS_2$) and 3) pentlandite ($Fe_{4.5}Ni_{4.5}S_8$). This image is 512×512 pixels with a pixel size of $2.5 \mu m$. Figures 3b-3f are scanning x-ray images, made with a $30 \mu m$ beam and a collection time of 2 seconds per pixel. The images are 40×40 pixels, for a total scanned area of 1.2×1.2 mm. The images of Fe, Ni and Cu (major elements) could have been made on an electron microprobe with much greater spatial resolution but poorer signal to noise. Note in Fig. 3c the large pentlandite grain in the lower center, the small grain in the top center and the single Ni rich pixel in the lower left. The large chalcopyrite grain on the left seems to contain a region with low copper near the center of the grain (Fig. 3d). The selenium is contained mainly in the Fe rich pyrrhotite phase (Fig. 3e) where it seems to be homogeneous, e.g. present in solid solution. There is an unidentified Se rich phase in the upper left of the image. The concentration of Pd (Fig. 3f) is much higher in the Ni rich pentlandite than in the chalcopyrite and pyrrhotite. Note

Fig. 3a: Backscattered electron image of a sulfide sample from an ore deposit.

Fig. 3b: Fe K α fluorescence image

Fig. 3c: Ni K α fluorescence image

Fig. 3d: Cu K α fluorescence image

Fig 3e: Se K α fluorescence image

Fig. 3f: Pd K α fluorescence image

the Pd rich area in the lower left of the image. This region corresponds to the single Ni rich pixel and the Cu poor region in the chalcopyrite grain. This is interpreted to be a grain of pentlandite under the surface of the chalcopyrite. The Pd K α x-rays, 21.2 keV, are sampling much deeper ($\approx 100\ \mu\text{m}$) than the Ni or Cu x-rays ($\approx 10\ \mu\text{m}$), and thus the hidden grain is more evident in the Pd image. There are two unidentified grains with high Pd contents at the top left and top center of the image. The Pd content of these grains is too low to be detected with the electron microprobe.

4. FUTURE IMPROVEMENTS

Improvements planned for the x-ray fluorescence microprobe at X-26 in the near future will significantly improve its imaging capabilities. An 8:1 ellipsoidal grazing incidence mirror [8] will increase the flux at the sample by more than a factor of 1000. This will permit the use of a curved crystal, wavelength dispersive spectrometer (WDS), rather than the Si(Li) detector for many applications. The WDS detector has much better resolution and hence will have lower background and will reduce the problem of overlapping peaks. It does not suffer from the count rate limitations due to scattered background and major element fluorescence, so scans can be made much faster. Finally, the mirror will permit the use of a monochromator in the beam, which will lower the scattered background under the peaks and allow selective excitation of particular elements.

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6. REFERENCES

1. K. W. Jones, W. M. Kwiatek, B. M. Gordon, A. L. Hanson, J. G. Pounds, M. L. Rivers, S. R. Sutton, A. C. Thompson, J. H. Underwood, R. D. Giauque, Y. Wu: In *Advances in X-ray Analysis*, 31 (1987)
2. S. R. Sutton, M. L. Rivers, J. V. Smith: *Nucl. Instr. Methods*, B24/25, 405 (1987)
3. A. L. Hanson, K. W. Jones, B. M. Gordon, J. G. Pounds, W. M. Kwiatek, M. L. Rivers, G. Schidlovsky, S. R. Sutton: *Nucl. Instr. Methods*, B24/25, 400 (1987)
4. J. H. Underwood: "X-ray Microscopy and Microprobing with Reflective Optics", this volume
5. C. J. Sparks: In *Synchrotron Radiation Research*, ed. by H. Winick and S. Doniach, (Plenum, New York, London 1980) p. 459
6. S. R. Sutton, M. L. Rivers, J. V. Smith: *Analytical Chemistry* 58, 2167 (1986)
7. B. M. Gordon, K. W. Jones: *Nucl. Instr. Methods*, B10/11, 293 (1987)
8. K. W. Jones, P. E. Takacs, J. B. Hastings, J. M. Casstevens, C. D. Pionke: *Soc. Photo-Optical Engineers*, 749, 37 (1987)