SYNCHROTRON X-RAY FLUORESCENCE ANALYSIS OF DUST PARTICLES. H. A. Ishii, K. Luening, S. Brennan, P. Pianetta, G. Matrajt and J. P. Bradley, 1Institute for Geophysics and Planetary Physics, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA (hope.ishii@llnl.gov), 2Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Stanford, CA 94025, USA (brennan@stanford.edu), 3Department of Astronomy, University of Washington, Seattle, WA 98195.

Introduction: Synchrotron x-ray fluorescence (SXRF) studies carried out on a microprobe endstation allow non-destructive analysis of both major and trace element abundances in particles only microns in size. The technique has been applied to IDPs captured in the stratosphere to study atmospheric entry effects such as stratospheric contamination and frictional heating [1, 2]. SXRF will also be applied to the analysis of samples from NASA’s Stardust mission [3] returning to Earth in January of 2006 with cometary dust particles captured in silica aerogel collectors during its flyby of the comet Wild-2. For Stardust particles, as for IDPs, trace element analysis of volatiles may provide an indication of the degree of thermal processing during capture in the aerogel collectors. Assuming negligible processing, trace elements can be used to study petrogenetic relationships between Stardust particles and other known extraterrestrial materials. In general, analysis of trace element abundances in extraterrestrial materials is highly relevant because variations in concentration patterns of these elements may act as signatures for origin and conditions of formation of the carrier mineral phases [4].

A number of challenges must be overcome for trace element studies by SXRF: sample preparation, contamination, choice of sample mount, potential for sample damage in the x-ray beam and positional stability of the beam on the sample. IDP SXRF studies to date offer only limited discussion of experimental setup and analytical limitations. We discuss here the experimental requirements for obtaining high quality SXRF data on small particles for trace element analysis and our progress in achieving this goal.

Experimental Methods: We collected SXRF data from several chondritic porous IDPs on a scanning fluorescence microprobe endstation currently being commissioned on Beamline 6-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). The final focus is provided by a Kirkpatrick-Baez mirror pair capable of focusing monochromatic x-rays into a micron-sized spot. The current non-optimized photon flux for a ~3 μm spot is ~5x10^8 photons/s, and the x-ray energy range extends past the Br K absorption edge. We have previously demonstrated SXRF mapping of major elements at low and high spatial resolutions [5]. For this early trace element work during endstation commissioning, there was unusual beam motion at the source, and we used a ~10 μm spot size to encompass entire IDP particles and sections. In future work, we will combine trace element mapping with TEM imaging and EDS analysis as discussed below.

Experimental Requirements and Results: To obtain the best quality SXRF data on small particles, we want no sample damage and high sample stability with no extraneous fluorescence to obscure peaks of interest and reduce signal-to-noise ratios.

Fig. 1: Evidence of ozone damage without a He environment: Bright field TEM images of a 200 nm section of IDP W715411 before (left) and after (right) 7 hours of x-ray irradiation.

Damage to the sample by x-rays. In an initial estimation of particle heating in the beam, a microthermocouple (35 micron welded bead) showed a rise of only 0.5°C before stabilizing in temperature in the x-ray beam. In addition, a 200 nm thick TEM section of a chondritic porous IDP was scanned in the x-ray beam for 7 hours with a 3 μm spot. TEM analysis before and after x-ray irradiation showed no evidence of structural or chemical changes due to heating in the x-ray beam. (Sample heating will be reevaluated with the final optimized photon flux.) There is clear evidence of attack by ozone formed by x-rays interacting with air. Ozone etches the sample, especially organics like the embedding epoxy, particularly near voids (Figure 1). We subsequently employed a He “shower”, a gentle flow of He over the sample and most of the beam path to the detector to eliminate ozone damage by excluding air. This has the important advantage of greatly reducing the Ar fluorescence and improving detection of low Z elements such as Na, Al and Mg.
Sample mounting. Mounting is a critical challenge for particle sizes on the order of 10 \( \mu \)m. We require excellent positional stability since sample motion, due to mechanical or thermal instability, results in the x-ray beam wandering on the sample or off the sample completely. We collected spectra from two forms of samples: thin sections and whole IDPs.

For bulk analysis of whole, intact IDPs, a 10 \( \mu \)m diameter C fiber was glued to the end of a 1 mm diameter silica needle leaving 100-200 \( \mu \)m of fiber extending from the end of the needle. Each IDP was mounted by micromanipulator on the end of the C fiber with a tiny amount of partially-cured embedding epoxy (Figure 2). These mounts proved highly stable and presented the particle to the x-rays free of any substrate. For whole IDPs, 13.5 keV incident x-rays accessed trace elements up to Br. Figure 3 shows the SXRF spectrum (unprocessed) of a mounted IDP.

Microtomed particle thin sections allow correlation of SXRF and TEM data. In this way, local trace element abundances in particles can be correlated with local mineralogy to gain insight into particle origins and processing. IDP sections were precision-centered in 400 \( \mu \)m aperture Cu TEM grids on C/Formvar substrates using a method developed in the cosmic dust lab at U. of Washington (Brownlee). To avoid exciting fluorescence from the grid, spectra from thin sections were collected ~200 eV below the Cu K edge at 8780 eV. Due to overlap of the Cu K\( \alpha \) resonant Raman scattering peak (~940 eV below the incident energy) with Fe or Ni, Cu is a poor grid material even at energies below the Cu K edge. To access higher-Z trace elements in thin sections, future studies will be carried out using low-Z (C, Be) grids. Figure 4 shows a microtomed thin section in a Cu TEM aperture grid and its SXRF spectrum (collected in He). Knowledge of trace element contaminants in mounting media is critical. The Na and Cl peaks in Figure 4, for example, are likely due to salt in the epoxy, and the Cu shoulder on the Ni peak in Figure 3 is not associated with the particle.

We have made much progress in attaining high quality SXRF spectra from small particles. Sample damage in the beam is being assessed and addressed. C fiber mounts are well-suited to whole IDP studies, and appropriate TEM grids have been identified for thin section studies. Spectra obtained show excellent signal-to-noise, and we are in the process of analyzing them for quantitative results.


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