HARD X-RAY SPECTRO-MICROSCOPY TECHNIQUES AT SSRL FOR ASTROMATERIALS ANALYSIS. H.A. Ishii1, S. Brennan2, K. Luening3, P. Pianetta2, J.P. Bradley4, C.J. Sneyd3 and A.J. Westphal5, Bay Area Particle Analysis Consortium, 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), 3Space Science Laboratory, University of California at Berkeley, Berkeley, CA 94720, USA.

Introduction: Sample return missions allow the laboratory study of material from other parts of our solar system which until recently were accessible only by astronomical observation. In January of 2006, NASA’s Stardust Mission will return to Earth with particles captured in silica aerogel collected from the coma of Comet Wild-2 as well as fresh interstellar dust. The primary objective of the mission is the collection of 1000 analyzable particles of diameter >15 micron [1]. Estimates from on-board instrumentation indicate 3 times that number were collected [2]. Each of these femto- to nanogram particles is potentially a heavyweight in terms of scientific return.

Scientific and technical preparations for Stardust’s return have long been underway via analysis of analogues like interplanetary dust particles (IDPs) collected in the stratosphere and micrometeoroids captured in low earth orbit in aerogel collectors (e.g. the Orbital Debris Collector Experiment). To study such small volumes of material non-destructively, synchrotron radiation techniques have been used with increasing frequency [3 and references therein, 4, 5]. These techniques include microdiffraction to determine mineralogy, X-Ray Fluorescence spectroscopy (XRF) to determine elemental compositions and distributions, Fourier Transform Infrared (FTIR) spectrometry and Scanning Transmission X-ray Microscopy (STXM) combined with soft X-ray Absorption Near Edge Structure (XANES) spectroscopy at the C and O absorption thresholds to study the chemical environment of organic compounds and hard x-ray XANES to study chemical states of transition metal elements.

Of key importance in analysis of Stardust particles is a non-destructive means of extracting chemical information on both major and trace elemental constituents. We describe a collaborative effort at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 6-2 to use micro-focus x-ray beams for the study of meteoritic and cometary materials.

Capabilities: The SSRL beamline 6-2 scanning fluorescence microprobe uses a Kirkpatrick-Baez mirror pair to focus a monochromatic x-ray beam to less than 1 micron in both horizontal and vertical dimensions. The useful energy range spans the K absorption edges of the transition metals so that both XRF and micro-XANES are possible on scientifically interesting elements such as Ti, Fe, and Ni. Several examples of recent work with the facility are presented below.

High-resolution XRF mapping. X-ray fluorescence mapping with spatial resolution at the micron level has been achieved on particles embedded in aerogel (Fig. 1). Both major and trace elements down to Si can be mapped and quantified in this manner. The x-ray probe beam size can be adjusted to scan the sample at different “magnifications” enabling fast coarse maps as well as fine detail on regions of interest. Because the microprobe can non-destructively study particles still embedded in the aerogel capture medium, it is attractive for initial examinations on Stardust and future missions.

Fig. 1: Clockwise from lower left: Optical micrograph of aerogel keystone, low resolution XRF maps in Si and Fe showing locations of the silicon sample mount and the Fe-bearing particles including a grain of Murchison meteorite embedded in the aerogel, high resolution XRF maps of the Ca and Fe distributions in the Murchison grain and a log-scale XRF spectrum from the most Fe-rich location in the grain.

As another example of the mapping capability, Figure 2 shows the distribution of Fe and Ca fluo-
from a deceleration track of a fragment of Allende which has been implanted in aerogel using a light gas gun.

Fig. 2: Maps of a particle track from a gas gun shot of Allende particles. Top: optical image; Middle: Fe fluorescence map; Bottom: Ca fluorescence map. Distances are in microns, so the full x-range is ~6 mm. Red denotes high signal, blue, low signal.

The similarities between the optical image and the two fluorescence maps are striking. The enhanced Fe fluorescence near the surface of the aerogel is likely due to additional gun debris. This is a two-dimensional map, integrating over the volume of the block of aerogel, so low levels of surface contamination are over-emphasized.

**Micro-XANES.** Prior to the installation of the beamline 6-2 fluorescence microprobe, tests on particles were performed on a total external reflection x-ray fluorescence (TXRF) facility at SSRL [6]. Full particle XANES spectra of a grain of Orgueil meteorite mounted on a Si wafer were collected in grazing incidence geometry at the Fe (Fig. 3) and Ni K edges. Beamline 6-2 has since been rebuilt with improved optics that make spatially-resolved micro-XANES possible at micron resolution with excellent signal-to-noise ratios. This allows mapping of the oxidation state distributions of the majority species within IDPs, micrometeoroids and Stardust comet dust. The low-Z limit for this capability depends on the size of the particle being analyzed since the 1/e escape depth of the characteristic x-rays is energy dependent; however, Ti and higher Z elements will be readily accessible for most particles. Using Principle Component Analysis methods, mixed valence states can be quantified for each element of interest in a sample using standards containing the relevant valence states. For Fe oxidation states, Sutton et al. [7] have shown that pre-edge peak energy (caused by 1s – 3d electronic transitions) varies linearly with the proportion of Fe$^{3+}$. Wherever possible, such simplifications may be used to speed up analysis.

Fig. 3: Example of Fe K-edge XANES previously collected from a grain of Orgueil meteorite (labeled ‘Chondrite’) in a grazing incidence geometry [from Fig 3 ref 6]. The data are consistent with pure FeO$_3$.


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