ADVANCED CHEMICAL ANALYSIS OF COMETARY MATERIAL AND INTERSTELLAR DUST USING A MICROCALORIMETER AND A LOW VACUUM SCANNING ELECTRON MICROSCOPE*,

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Introduction: The STARDUST cometary material and interstellar dust collections were collected in a low-density silica aerogel. They are arguably the most technically challenging of all of NASA's extraterrestrial collections. Cometary impactors are fine-grained and fragile, so they disintegrate on impact with the aerogel. The largest and most robust particles penetrate deep into the aerogel, but the smallest fragments are distributed non-uniformly along the lengths of carrot-shaped impact tracks. The fragments of the original impactor are mixed with melted and compressed aerogel in the ratio of ~1:100 in mass. Tracks are now routinely extracted from aerogel tiles in wedge-shaped *keystones*. The technique employs pulled glass needles and precision (200nm) motorized micromanipulators to automatically machine the aerogel on a microscopic scale. A typical keystoning extraction requires >50,000 discrete motions and many hours. The precision of the machining operation is of order 5µm. Following extraction, the keystone is flattened and embedded in epoxy, then sectioned, mounted on the end of an epoxy bullet, and ultramicrotomed to produce TEM ultramicrotomed thin sections.

To advance the chemical analysis of cometary particles and interstellar dust returned by STARDUST, we have combined two, state-of-the art technologies. The first is a cryogenic microcalorimeter spectrometer originally developed for measuring x-ray spectra from astrophysical sources [1,2,3]. The second is a high resolution, environmental scanning electron microscope (ESEM) modified to permit material-selective, gas-mediated, electron beam-induced etching (EBIE). This commercially unavailable, research-grade system was designed and built by the FEI Company for the development of future generation ESEM technologies [4]. As an integrated system, the microcalorimeter-ESEM capabilities are unique -- it can remove in-situ the aerogel encapsulating the cometary particles without damaging or modifiying the sample material. Once the particles are exposed, broad band, high resolution x-ray analysis using the microcalorimeter is performed.

EBIE holds the promise of enabling much finer machining of aerogel, before or after flattening, to expose individual small particles. This may be particularly useful in the bulbs of Stardust tracks where it is currently difficult to identify cometary particles optically. EBIE might be used to remove aerogel in track bulbs in keystones flattened on Si, resulting in a *strewn field* of particles. The ability to collect and monitor broad band, high resolution x-ray spectra during EBIE etching should minimize or entirely prevent etching of cometary particles during exposure.

With the aerogel overburden removed by EBIE, major elemental abundances in particles can be characterized by the microcalorimeter. The increased spectral resolution (2.5 - 6 eV) and consequent signal-to-background ratio of the microcalorimeter over the energy range of 0.2 keV to 10 keV compared with present generation EDS (Si(Li), germanium or silicon drift) detectors provides better element-to-element discrimination and the added ability to observe shifts in characteristic emission lines due to chemical bonds.

The Microcalorimeter: In a microcalorimeter (operating at ~60 mK), x-ray photons are absorbed by a metal foil and converted into heat. The temperature of the foil will increase because the heat capacity of the super-cold foil is ~10^{-14} J/K. This temperature rise (~10 mK for a 6 keV x-ray) is proportional to the x-ray energy and is transformed by a thermistor into an electronic signal. The thermistor is fabricated by neutron transmutation doping (NTD) of germanium (Ge). The dopant concentration establishes a well-known relationship between resistivity and temperature [4]. Our instrument can incorporate a microcalorimeter array of 16 pixels, configured as a 4 x 4 or 2 x 8. Each pixel consists of an NTD Ge thermistor attached to a superconducting tin (Sn) absorbing foil. The Sn is 0.3 mm x 0.3 mm x 7 µm thick.

An example of the spectral performance of the microcalorimeter is presented in Figure 1 where a high resolution spectral analysis of Monazite is displayed. Monazite is composed of rare Earth elements which are all well resolved, a feat that is impossible with a traditional EDS detector; the smooth black curve is the spectrum that an EDS detector would measure. Given this performance, microcalorimetry can be used to resolve interferences for measurement of minor elements in STARDUST particles (e.g., V in low V/Ti phases, Mn in low Mn/Cr phases, etc). Although etching of the aerogel near the target particles may pose some risk to the particles, the results presented here demonstrate that this risk is minimal.

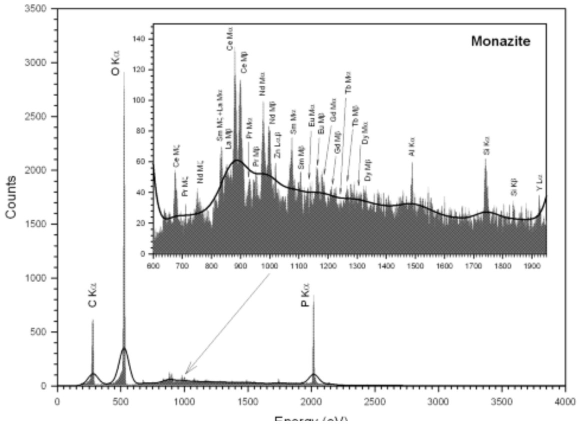

Figure 1. The microcalorimeter x-ray spectrum obtained from monazite, a rare earth phosphate mineral, using a conventional SEM. Extremely fine spectral detail in the high resolution microcalorimeter data is apparent (particularly regarding closely spaced rare earth element M x-ray lines) and is shown in dark gray. The smooth black curve is the spectrum that would be obtained with a traditional energy dispersive (EDS) x-ray detector.

Electron Beam-induced Etching (EBIE): EBIE is a room temperature, direct-write, maskless technique capable of etching a wide range of materials with high spatial resolution [5]. In the EBIE process an electron beam is used to induce etching by stimulating chemical reactions between surface absorbed gas molecules and the sample. The *key* difference between EBIE and conventional dry and wet etch processes is that etching *only* takes place in areas of the sample that are irradiated by electrons. In preparation for analyzing STARDUST samples, NKT-1G basaltic glass was experimentally shot into aerogel at 6 km/sec, thus encapsulating them. EBIE was performed on the sample and Figure 2 shows the crater produced by the etching and the exposed basaltic particles. Figure 3 shows examples of what to expect when the etching is monitored in real time. During the etch, the predominant signal will come from the SiO_2 as shown in the spectrum in the top of Figure 3. As the electron interaction volume reaches the STARDUST particle, the x-ray signature changes (e.g., increases in Mg, Ca, Fe) indicating that most of the aerogel has been removed. This is evident in the bottom of Figure 3.

High resolution spectral maps from meteorites and aerogel-encapsulated basaltic glass will be presented that demonstrate how the microcalorimeter and ESEM will be used with EBIE to expose and chemically analyze cometary and insterstellar dust returned by STARDUST.

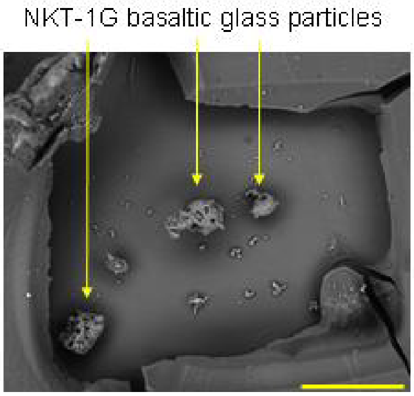

Figure 2. The crater in the aerogel etched away by the EBIE process. The arrows point to the basaltic glass particles exposed by the etching.

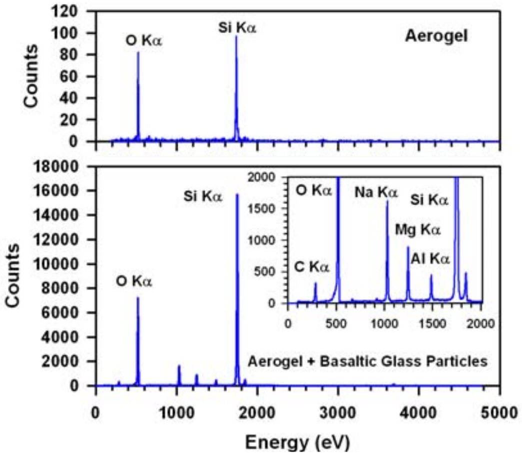

Figure 3 Spectra are examples of what to expect when the etching is monitored in real time. (Top) X-ray spectra at the beginning of the etching process; only SiO_2 x-ray emission will be observed. (Bottom) As the aerogel is removed, other elements contribute to the x-ray signal.

References

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