

CARBON INVESTIGATION OF STARDUST PARTICLES: A TEM, NANOSIMS AND XANES STUDY. G. Matrajt, *Department of Astronomy, University of Washington, Seattle WA, 98195 (matrajt@astro.washington.edu)*, S. Wirick, *Department of Physics and Astronomy, State University of New York at Stony Brook, Stony Brook, NY 11794-3800, USA*, M. Ito, *Johnson Space Center, 2101 NASA Pkwy, Houston, TX 77058, USA*, S. Messenger, *Johnson Space Center, 2101 NASA Pkwy, Houston, TX 77058, USA*, D. Brownlee, *Department of Astronomy, University of Washington, Seattle WA, 98195*, D. Joswiak, *Department of Astronomy, University of Washington, Seattle WA, 98195*.

Introduction: The understanding and identification of cometary organic matter in the Stardust samples is a high priority because these materials preserve records of chemical processes in the early solar system and in interstellar environments. In addition, learning about the nature of the carbon held by cometary grains contributes to the understanding of the origin and delivery of prebiotic molecules to the early Earth's surface. Here we present the results of a systematic search for cometary organic matter in two Stardust terminal particles using transmission electron microscopy (TEM), XANES spectroscopy and NanoSims, to investigate the molecular nature and isotopic composition of the carbonaceous matter.

Analytical Methods: The samples, received inside aerogel keystones, were processed using the "acrylic embedding" technique developed at the University of Washington [1]. Briefly, the keystone is flattened between two glass slides and a small square area (300x300 μm) of aerogel containing the particle is cut out using a razor blade and mounted in acrylic. Ultramicrotomed sections are then prepared with various thicknesses (from 40 to 95 nm) and placed over grids coated with ultra light amorphous carbon film. Prior to TEM analysis, the grids are washed using sub-boiling chloroform vapors [1] to dissolve the acrylic and avoid interferences of the embedding medium with any possible carbon present in the sample. TEM images and energy filtered (EELS) carbon maps of the samples were obtained using a 200 kV Tecnai F20 FEG STEM electron microscope equipped with an energy dispersive X-ray (EDAX) detector and a Gatan GIF detector. High resolution images were taken using conventional TEM in bright field mode. The Gatan GIF detector was used to acquire carbon maps under the energy filtered imaging mode with slit centered at the carbon edge (285 eV) and using the three window method. The C, N, D and O isotopic compositions of the samples were determined using a NanoSims. Images of $^{12}\text{C}^-$, $^{13}\text{C}^-$, $^{12}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^{15}\text{N}^-$, $^{16}\text{O}^-$, $^{17}\text{O}^-$, and $^{18}\text{O}^-$ were acquired simultaneously in multidetection with electron multipliers. The isotopic images, covering an 8 x 8 μm field of view were acquired by rastering a 16 keV, 1 pA Cs^+ primary ion beam focused to 100 nm. Nearby grains of 1-hydroxybenzotriazole hydrate, USGS24 graphite, and San Carlos olivine were measured as N, C, and O isotopic standards respectively. Carbon and nitrogen bonding states were determined by XANES spectroscopy using the STXM located at the X1A beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. Radiation from the X1 undulator, ranging in energy from 200-800 eV, is monochromated and focused to a spot (30 nm size) using a Fresnel zone plate. The sample is raster-scanned through the focus and the transmitted intensity is recorded using a solid state detector or

a gas proportional counter. The data collected is then used to create absorption contrast images of the samples. Single pixel spectra can then be obtained from the images. We analyzed two particles using the three techniques described above, and will describe the data obtained in one terminal particle, named Febo, coming from track 57.

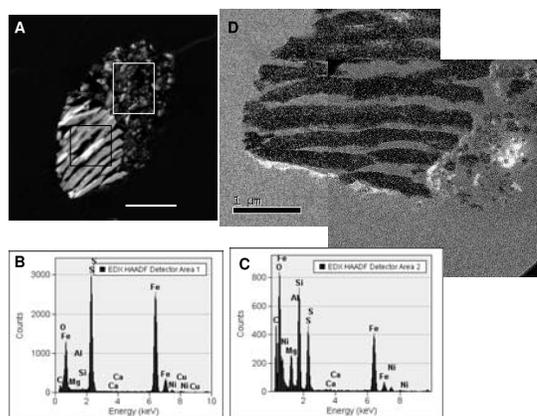


Figure 1: TEM images of the particle Febo. A) a HAADF (High angle annular dark field detector) micrograph. The scale bar is 2 μm . The black box shows the rastered area (Area 1) that corresponds to the EDX spectrum in (B). The white box shows the rastered area (Area 2) that corresponds to the EDX spectrum in (C). D) an energy filtered carbon map: the bright regions in this micrograph are the carbon-rich areas.

Results: Febo is an 8 μm terminal particle composed of three main regions (Fig. 1): one region is made of a large Fe-bearing sulfide with trace Ni and the other regions are a piece of enstatite surrounded by fine-grained material which has chondritic chemical composition (Mg,Al,Si,S,Ca,Fe,Ni ratios = solar). The EELS carbon map of Febo is shown in Fig. 1. High resolution imaging of these areas showed amorphous carbon with little order typical of a poorly ordered carbon that has been slightly heated, consistent with particle heating during the entry and deceleration in the aerogel. The carbonaceous material in Febo identified by TEM was also identified in CN isotopic images obtained by NanoSims (Fig. 2) and showed a pronounced enrichment in $^{15}\text{N}/^{14}\text{N}$ ($\delta^{15}\text{N}=420 \pm 160 \text{‰}$, 1 σ). The carbonaceous material has approximately solar C isotopic composition within broad error limits arising from the small size of the sample. The overlap between carbon and nitrogen suggests that the carbon is in an organic phase. The pronounced $\delta^{15}\text{N}$ enrichment of this organic material shows that it is cometary and not contamination. The level of the

$\delta^{15}\text{N}$ enrichment found in this particle is comparable with values previously observed in some organic compounds in IDPs [2, 3] and in some other Stardust particles [4]. The bulk oxygen isotopic composition of the sample was found to be $\delta^{17}\text{O} = -18 \pm 13\text{‰}$ and $\delta^{18}\text{O} = -37 \pm 12\text{‰}$ (1σ). The D/H ratios were determined to be within approximately 300 ‰ of the terrestrial SMOW standard.

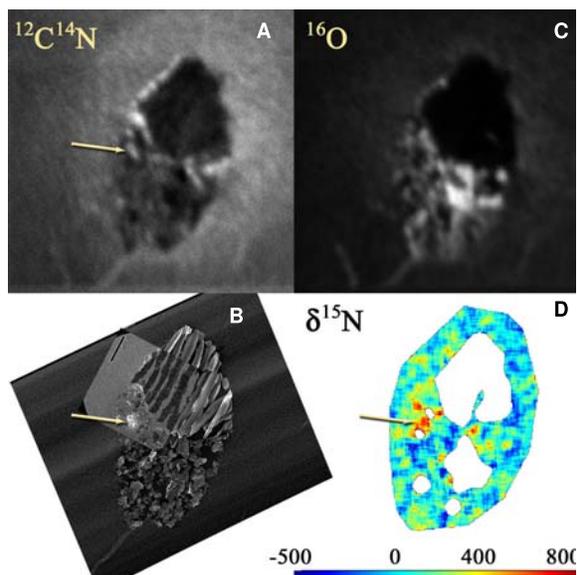


Figure 2: Isotopic maps of Febo. Upper left (A): CN^- image of Febo. The arrow indicates the position of the C-rich area detected with the TEM. Lower left (B): EELS C map overlain on a SE image of Febo. The arrow indicates the position of the C-rich material. Upper right (C): Oxygen image of Febo. The brightest area corresponds to a $1\ \mu\text{m}$ enstatite grain and the surrounding O-rich material is fine grained chondritic material. Lower right (D): N isotopic image of Febo, with low-signal surrounding background masked. The arrow indicates the position of the C-rich region and has a $\delta^{15}\text{N}$ value of $420 \pm 160\text{‰}$ (1σ).

In Fig. 3 it is shown the distribution of carbon and nitrogen obtained with XANES. It is also shown the EELS carbon map of the microtomed section and a plot with carbon XANES spectra of several carbon-rich areas. The bright areas of the XANES carbon map in Fig. 3 nicely overlap the carbon areas of the EELS carbon map showing that the carbon distribution is real at all spots and not the product of any analytical artifact. The XANES spectra vary with the areas analyzed. For example, the brown spectrum is different (it shows a narrower 285 eV peak, corresponding to C=C bonding) from

the magenta spectrum and from spectra green and yellow. In addition, this spectrum also shows a peak at 288.5 eV (which corresponds to a C=O bonding) which is absent in the spectra below. This shows a diversity in the bonding of carbon, as well as a heterogeneous distribution of the different carbonaceous phases.

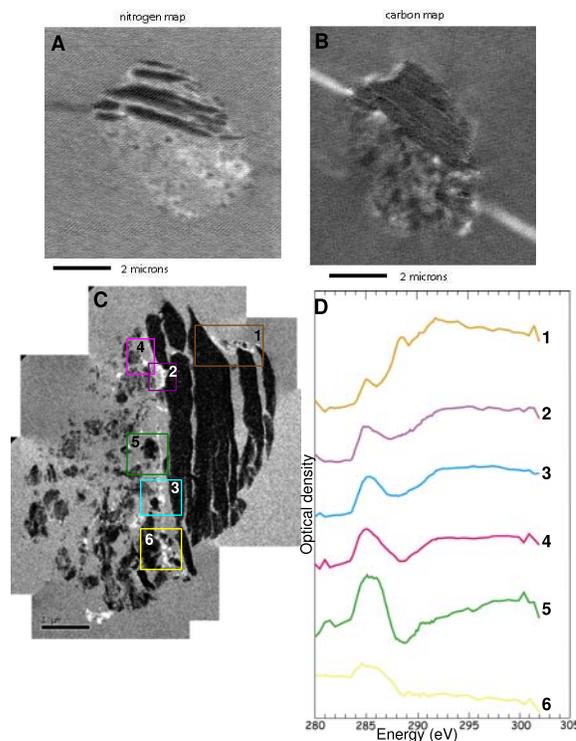


Figure 3: C and N XANES maps of Febo. A) a XANES-Nitrogen map. B) a XANES-Carbon map. For comparison, the EELS carbon map is shown in C). D) XANES carbon spectra of different carbon-rich areas, shown inside the boxes of the map in C).

Discussion and conclusions: The three techniques we used to analyze the carbon in two Stardust particles provide complementary information that is very helpful for understanding the nature of the phases that contain this carbon: a) the carbonaceous material is amorphous and slightly heated; b) The carbonaceous material contains nitrogen, as evidenced by the overlaps seen in both the XANES and NanoSIMS nitrogen and carbon maps, consistent with the presence of organic material; c) The organic material is shown to be cometary by a pronounced enrichment in $^{15}\text{N}/^{14}\text{N}$; d) The carbon is present in a variety of compounds as seen in the diversity of XANES spectra from the different carbonaceous areas both between particles and within a single particle.

References: [1] Matrajt and Brownlee (2006) *M&PS*, **41**, 1715-1720. [2] Aleon et al (2003) *GCA*, **67**, 3773-3783. [3] Floss et al (2004) *Science*, **303**, 1355-1358. [4] Mckeegan et al (2006) *Science*, **314**, 1724-1728.