EXTREME ALIPHATIC AND AROMATIC ORGANIC MATTER PRESERVED IN COMET 81P/WILD 2.

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Introduction: Comets are relatively pristine reservoirs of early solar system materials, including presolar grains, interstellar grains, and nebular condensates. In addition to mineral samples from Comet 81P/Wild 2, NASA's Stardust mission also captured cometary volatile and refractory organic matter [1-4]. Refractory organic matter appears to span a wide range of chemical functionality and composition, but some of this variety may be due to intrinsic organic contamination in the aerogel [5] or high-velocity capture effects [3,6]. Here we describe two new refractory carbonaceous cometary particles, representing disparate endmembers of the variety of organic matter preserved in Wild 2.

Samples and Methods: A Stardust particle from Track 80 (C2092,6,80,45,0) and an aerogel wafer containing a particle from Track 183 (C2103,24,183,1,0) were allocated to RMS at the Naval Research Laboratory (NRL). The Track 183 particle was extracted from the aerogel with a micromanipulator, and both particles were embedded in S and sectioned with an ultramicrotome. Samples designated for transmission electron microscopy (TEM) were placed on C-supported TEM grids, while alternating sections were placed on SiO-supported grids for scanning-transmission X-ray microscopy (STXM) and X-ray absorption near-edge structure spectroscopy (XANES). Thicker sections were also prepared for secondary ion mass spectrometry (SIMS) and placed on Si_3N_4 window grids.

Sample morphology and composition were characterized using a JEOL 2200FS field-emission TEM at NRL, and the organic functional chemistry of adjacent sections sharing the same carbonaceous matter were characterized by synchrotron-based STXM at beam line 5.3.2.2 at the Advanced Light Source. The H, C, N, and O isotopic compositions of the carbonaceous matter were measured with a Cameca NanoSIMS 50L at the Carnegie Institution of Washington.

Track 80, Particle 45: This particle consists of smooth-textured organic matter and associated silica aerogel (Fig. 1). Two types of organic matter are present, distinguished by a small change in mass-density (Fig. 1A) and variations in functional chemistry, visible in STXM photoabsorption maps (Fig. 1B). The largest fragment of organic matter is highly enriched in nitrile functional groups (Fig. 2), which contribute to the 286.6 eV ketone absorption peak. Relatively low absorption from aromatic C at 285 eV indicates that this refractory organic matter is highly aliphatic (Fig. 1C), and the sample damaged rapidly under intense exposure to linear scans of the X-ray beam (reddish lines in Fig. 1B). The smaller associated fragments and the upper portion of the large fragment (blue portion in Fig. 1B) also contain low levels of Ca, indicated by TEM-based energy dispersive X-ray spectroscopy (EDS) and STXM-based Ca absorption maps. The H, C, N, and O isotopic compositions of two adjacent sections of the particle were consistent with terrestrial compositions.

Track 183, Terminal Particle 3: This unusual particle consists primarily of nanoscale Cr-rich magnetite, with inclusions of carbonaceous matter (Fig. 3A). The carbonaceous matter forms a layered shell around 10 nm Fe-rich core grains. Electron diffraction of the carbonaceous inclusions show ring patterns with lattice spacings typical of graphite or highly graphitic carbon (Fig. 3B), and the C-XANES spectrum of the inclusions is very similar to that of disordered graphite, dominated by a large 285 eV absorption due to

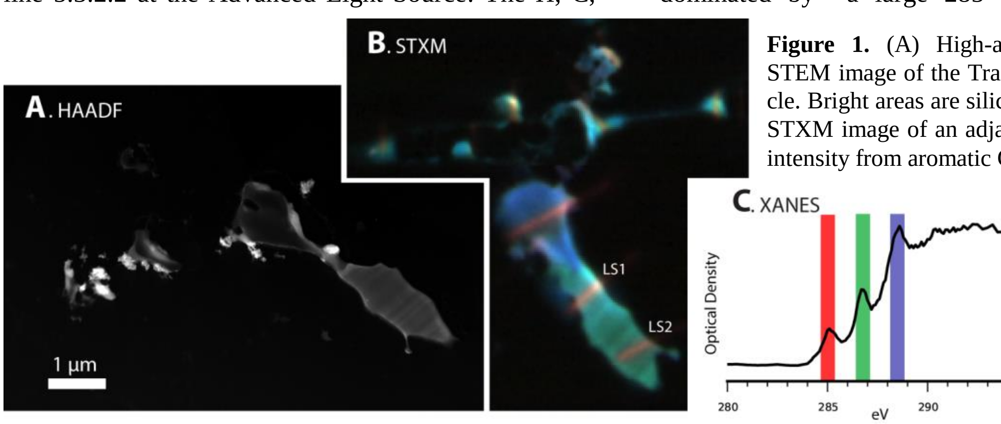

Figure 1. (A) High-angle annular dark field STEM image of the Track 80 carbonaceous particle. Bright areas are silica aerogel. (B) False-color STXM image of an adjacent slice. **Red** = 285 eV intensity from aromatic C=C; **Green** = 286.7 eV intensity from nitrile and ketone functional groups; **Blue** = 288.6 eV intensity from carboxyl functional groups. (C) Average XANES spectrum of the large organic fragment.

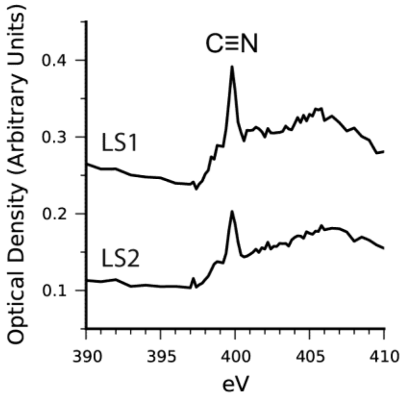

Figure 2. N-XANES spectra from the large organic fragment from Track 80 Particle 45. Positions of the linescans are shown in Fig. 1B.

C=C bonds and a graphitic exciton peak at 291.1 eV, but lacks the extended fine structure above 291 eV characteristic of crystalline graphite. N-XANES and NanoSIMS measurements indicate only minor abundance of N, consistent with graphitic carbon. The isotopic compositions of two adjacent sections of the particle were consistent with terrestrial compositions.

Discussion: Previous studies have reported highly aliphatic refractory organic matter in the Stardust collection, e.g. [1], however higher resolution observation (often TEM) of these samples raised the possibility of contamination and/or alteration during collection of high-speed particles in the aerogel [3]. The aliphatic C-XANES spectrum of the Track 80 organic matter is similar to that observed in the terminal particle of Track 13 [1], one of the most aliphatic samples considered representative of pristine cometary organic matter [3]. However, the Track 13 organic matter lacks the extreme nitrile enrichment present in the Track 80 particle, which represents a unique aliphatic endmember of carbonaceous matter in Wild 2.

Similarly, the Track 183 sample represents a unique graphitic endmember of carbonaceous matter in Wild 2. Graphite *sensu stricto* has not been reported in the Stardust collection, but disordered graphitic carbon has been observed in Track 141 ("Coki") [4] and Track 81 [7]. Graphitic rims on Fe-metal and Fe-carbide grains, similar to the core-shell structure observed in the Track 183 graphitic inclusions, have been observed in interplanetary dust particles, but have been attributed to heating during atmospheric entry [8,9], and in meteorites [10-12], where the actual graphitization has been attributed to parent body heating. In contrast, the graphitic carbon in the Track 183 particle most likely formed within the solar nebula by gas-grain reactions under high temperature and extremely reducing conditions. However, low temperature formation of amorphous carbonaceous rims on the comet, followed by rapid heating during hypervelocity capture, cannot be ruled out. Such capture heating must also have left the surrounding Cr-rich magnetite undisturbed.

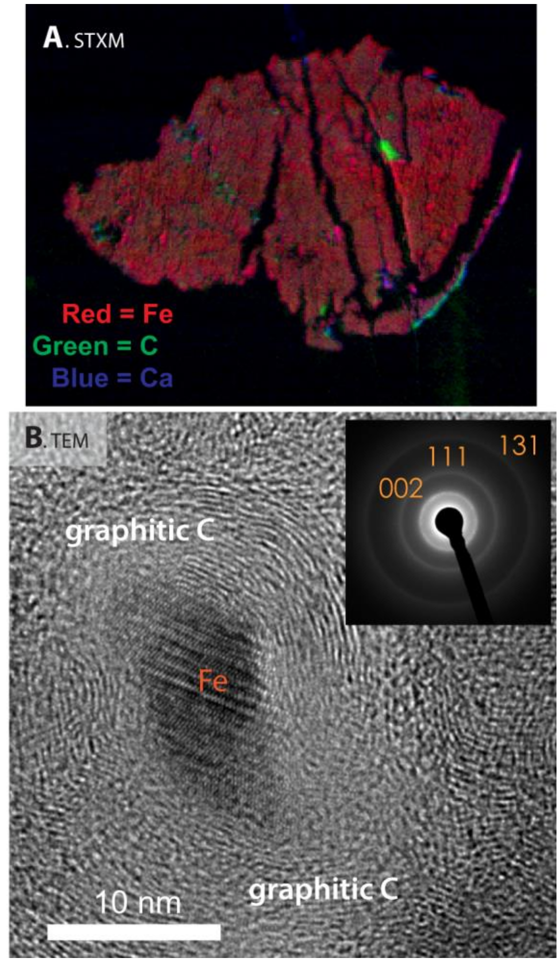

Figure 3. (A) STXM elemental map of Terminal Particle 3 from Track 183 showing carbonaceous inclusions. (B) The carbonaceous matter consists of highly aromatic carbon surrounding Fe-rich core grains. Electron diffraction of the carbon (inset) show lattice spacings for graphitic carbon.

The carbonaceous samples described in this study illuminate the wide variety of carbonaceous matter that formed in the early solar nebula, indicating that complex carbon chemistry was occurring in local reducing environments. Some of the products of this diverse nebular organic chemistry later accreted onto comets like Wild 2 and other parent bodies.

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