

VARIETY OF ORGANIC MATTER IN STARDUST RETURN SAMPLES FROM COMET 81P/WILD 2.

B. T. De Gregorio¹, R. M. Stroud¹, L. R. Nittler², and G. D. Cody² ¹Naval Research Laboratory (Code 6366, 4555 Overlook Ave. SW, Washington, DC 20375-5320, bradley.degregorio@nrl.navy.mil), ²Carnegie Institution of Washington, Washington, DC.

Introduction: The Stardust mission captured dust particles from comet 81P/Wild 2 and returned them to Earth. Since this material has been cryogenically stored within the comet for billions of years, the Stardust samples represent early nebular condensates and some presolar material, identified by anomalous isotopic fractionation outside the range of solar values. Carbonaceous matter has been identified in the Wild 2 samples in a variety of forms [1], including solitary carbonaceous particles [2, 3], carbonaceous matter mixed with silicate and/or sulfide grains [4], and simple amine molecules implanted into the silica aerogel capture medium [5].

Cometary carbonaceous matter is derived from interstellar organic molecules and organics processed in the early solar nebula. It is generally assumed that no significant amount of carbonaceous matter is generated on the cometary body. Therefore the authentic organic matter present in the Stardust return samples represents a snapshot of the carbonaceous constituents of the early solar nebula. Presolar organics are characterized by anomalous levels of ¹⁵N or D [4, 6], while nebular organics usually contain terrestrial values for $\delta^{15}\text{N}$ and δD . This study is a continuation of the correlated analysis of cometary organic samples during the Stardust Preliminary Examination [1, 2] using synchrotron-based X-ray absorption near-edge spectroscopy (XANES), high resolution TEM, and NanoSIMS.

Methods: Samples analyzed in this study include several particles from Stardust Track 80 (C2092,6,80,39-44) and particles previously analyzed by Cody et al. [2] using XANES in a synchrotron-based scanning-transmission X-ray microscope (STXM). The new particles were embedded in sulfur and sectioned by ultramicrotomy to a thickness of 90-110 nm. Carbon bonding and organic functional groups are probed using XANES at three synchrotron beamlines: X1A1 at the National Synchrotron Light Source, 5.3.2 at the Advanced Light Source, and 10ID-1 at the Canadian Light Source. High resolution imaging, mineral identification, and qualitative chemical composition are achieved in a JEOL 2200FEG TEM at the Naval Research Lab. Anomalous $\delta^{15}\text{N}$ and δD values are measured using a Cameca 50L NanoSIMS at the Carnegie Institution of Washington.

Results: XANES analysis of several Stardust carbonaceous samples during Preliminary Examination indicated a wide variety of organic chemistry, from

nominally meteoritic organic matter to N-rich polymeric material [1, 2]. Similarly, subsequent TEM analysis indicates a wide variety of morphologies [3].

Cometary organic globules. Two presolar organic globules have been discovered [7]. Sample C2092,6,80,43,2 contains an organic globule with a significant ¹⁵N isotopic anomaly (but a terrestrial δD value) and is composed primarily of aromatic carbon (Fig. 1). Sample FC3,0,2,4,5 contains an organic globule containing little aromatic carbon but dominated by nitrile and carboxyl functional groups. This globule contains a large D isotopic anomaly but has terrestrial levels of ¹⁵N (Fig. 1). A full description of these globules is given in [7].

Nitrogen-rich cometary organics. Several Stardust sample contain N abundances significantly higher than in meteoritic organic matter (Fig. 2). The distribution of N bonding within the organic matter can be probed by N-XANES. Both organic globules described above have N/C ratios around 0.1, calculated from NanoSIMS data, and the Track 2 globule contains abundant nitrile (C \equiv N) bonding. Sample C2054,0,35,32,8, on the other hand, contains imine (C=N), amide (N-C=O), and amine (C-NH_x) but no nitrile functional groups. In sample C2115,24,22,1,5 both C-XANES and N-XANES spectra are dominated by amide photoabsorptions. Two organic sections on sample C2092,6,80,43,2 have N/C ~ 1.6 and both C- and N-XANES indicate abundant imine, nitrile, and amide bonding. Care must be taken when interpreting N-XANES spectra acquired after other techniques, since other studies show that electron microscopy and even the soft X-rays in XANES can significantly alter N bonding in organic samples [7, 8, 9].

Nanoparticles in cometary organics. Two sections contain organic matter with embedded nanoparticulate material. Sample C2115,24,22,1,5 contains six 100-180 nm TiO₂ crystallites. Sample C2092,6,80,43,2 contains many nanophase minerals under 200 nm, including Si-, Al-, Fe-, Ti-, and Zr-oxides or sulfides [3]. A few Cr-silicate crystallites, possibly chromite, are also present. These nanoparticles show up brightly in high-angle annular dark-field TEM imaging, in which contrast is based largely on atomic mass. Unfortunately, most of these nanoparticles are too small for reliable mineral identification by electron diffraction.

Cometary organics in aerogel. Several sections clearly contain aerogel from the Stardust collector tray

by TEM imaging and EDS analysis. However EDS and XANES indicate that some of the aerogel contains a significant organic component. In sample C2054,0,35,32,8 the organic matter is largely aliphatic and dominated by methyl (-CH₃) and carboxyl (-COOH) functional groups. In sample C2092,6,80,43,2 the organic matter is more similar to meteoritic organic matter, with large aromatic C, aromatic ketone, and carboxyl absorption peaks. This organic matter is also slightly enriched in ¹⁵N ($\delta^{15}\text{N} \sim +200\%$) and therefore cannot be derived from organic contaminants within the aerogel and must originate from the comet. In both samples the organic matter in the aerogel appears to be slightly more aliphatic than the remaining organics.

Epoxy-soluble cometary organics. Some samples were embedded in epoxy and contain an unusual organic phase that was extracted into the surrounding epoxy. The extracted organic is clearly distinct from epoxy by STXM and TEM imaging but is roughly compositionally and spectrally identical to epoxy. However ~10% of this organic matter is spectrally distinct from epoxy and consists of labile aliphatic molecules, likely derived from the cometary sample.

Discussion: The cometary organic samples currently analyzed present a wide variety of organic chemistry, N- and O-abundance, and isotopic fractionation. Moreover, some samples also contain heterogeneity in chemical bonding and/or isotopes on the sub-micron scale. For example, in sample C2092,6,80,43,2, which contains two sections of N-rich carbonaceous matter with embedded nanoparticles, one section is dominated by N-containing functional groups and some aromatic carbon and has terrestrial levels of D and ¹⁵N, while the other section appears to contain mainly aromatic carbon and O-containing functional groups (aromatic ketones and carboxyl) and shows a ¹⁵N anomaly (Fig. 1). Because the latter section is smaller and is surrounded by aerogel, it likely represents the outer region of a carbonaceous particle and could have been altered and oxidized during capture. This would not explain the ¹⁵N enrichment, however.

As yet there does not appear to be a group of carbonaceous samples that represents “typical” cometary organic matter, although this may be due to the limited number of samples have been analyzed. However, there seems to exist a class of N-rich organic matter present in the Stardust return samples that are not present in meteorites (Fig. 2). Molecules such as HCN and NH₃ are present in molecular clouds and would be incorporated into comets in the early solar nebula [10]. It is possible that photolysis and advanced nebular processing destroys the majority of N-rich material except for that preserved in comets.

References: [1] Sandford S. A. et al. (2006) *Science*, 314, 1720-1724. [2] Cody G. D. et al. (2008) *Meteoritics & Planet. Sci.*, 43, 353-365. [3] De Gregorio B. T. et al. (2007) *LPSC XXXIX*, Abstract #2139. [4] Matrajt G. et al. (2008) *Meteoritics & Planet. Sci.*, 43, 315-334. [5] Glavin D. P. et al. (2008) *Meteoritics & Planet. Sci.*, 43, 399-413. [6] McKeegan K. D. et al. (2006) *Science*, 314, 1724-1728. [7] De Gregorio B. T. et al. (2009) *LPSC XL*, submitted. [8] Zubavichus Y. et al. (2004) *Radiat. Res.*, 161, 346-358. [9] Leinweber P. et al. (2007) *J. Synchrotron Rad.*, 14, 500-511. [10] Irvine W. M. et al. (2000) in *Protostars and Planets IV* (University of Arizona Press, Tucson), 1159-1200. [11] Schulz R. et al. (2008) *Planet. Space Sci.*, 56, 1713-1718.

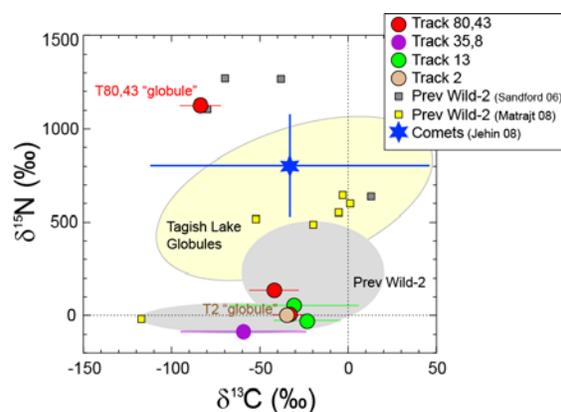


Figure 1. Comparison of ¹³C and ¹⁵N isotopic fractionation in Stardust organics. Large circles represent samples in this study, while smaller squares represent samples from other studies [1, 4, 6]. The predicted range from astronomical observations of comets is shown in blue [11], while the yellow ellipse shows the range observed in organic globules from Tagish Lake.

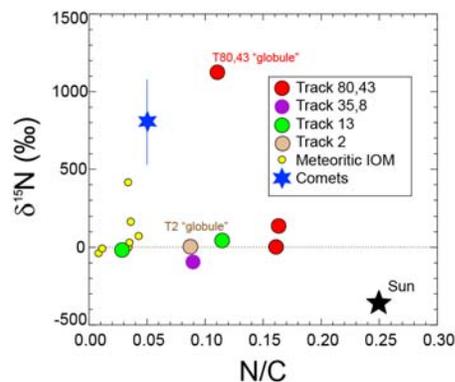


Figure 2. Comparison of nitrogen content and ¹⁵N isotopic fractionation in Stardust organics. Several samples from this study (large circles) are more N-enriched than meteoritic organic matter (yellow circles).