ISOTOPICALLY ANOMALOUS ORGANIC GLOBULES FROM COMET 81P/WILD 2. B. T. De Gregorio[1], R. M. Stroud[1], L. R. Nittler[2], G. D. Cody[2], and A. L. D. Kilcoyne[3] [1]Naval Research Laboratory (Code 6366, 4555 Overlook Ave. SW, Washington, DC 20375-5320, bradley.degregorio@nrl.navy.mil), [2]Carnegie Institution of Washington, Washington, DC, [3]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA.

Introduction: Comets preserve some of the most "primitive" material in the solar system. Proto-nebular and/or interstellar organic matter can be identified by anomalous δD and δ^{15}N values well outside the range of solar values (eg. [1]). Since carbonaceous nanoglobules are often the carriers of anomalous δD and δ^{15}N in carbonaceous chondrites [2] and interplanetary dust [3], organic globules should be present in cometary samples.

Organic matter is present in several particles from comet 81P/Wild 2 captured in silica aerogel by the Stardust spacecraft [4, 5]. One terminal particle contains a sulfide grain surrounded by a carbonaceous rim [6], but due to the limited number of carbonaceous samples analyzed by TEM, hollow organic globules were not observed during preliminary examination. Here we describe two organic globules from comet 81P/Wild 2 which also contain anomalous δD or δ^{15}N, likely signifying a presolar origin.

Materials and Methods: Stardust samples C2092,6,80,43,2 (Track 80, Particle 43) and FC3,0,2,4,5 (Track 2, Particle 4) were S-embedded, ultramicrotomed, and placed on SiO-coated Cu TEM grids (Track 2 sections prepared by K. Nakamura-Messenger). Sections were first analyzed by X-ray absorption near-edge structure spectroscopy (XANES) at beamline X1A1 at the National Synchrotron Light Source (NSLS) or at beamline 5.3.2 at the Advanced Light Source (ALS) to determine the local C, N, and O bonding environments. Sample morphology was observed using a JEOL 2200FEG TEM at the Naval Research Laboratory (NRL). After XANES and TEM analyses, δD and δ^{15}N were measured using a Cameca NanoSIMS 50L at the Carnegie Institution of Washington (CIW).

Results: Each organic globule is near aerogel from the Stardust sample collector, and both globules show evidence of a hollow interior. The Track 80 globule has a 1.4 µm diameter with a wall thickness of 450 nm, while the Track 2 globule has a 2.3 µm diameter with a wall thickness of 700 nm (Fig. 1).

Isotopic Anomalies. The Track 80 globule is highly enriched in ^{15}N and has an average δ^{15}N value of +1120 ± 30‰ (Fig. 1A), above the upper limit observed in cometary comae [7] and at the upper end of previously observed values for "hotspots" in Wild 2 samples [4, 8]. A nearby section containing cometary organic matter and aerogel also shows a small ^{15}N enrichment (δ^{15}N ~ +200‰). The support film sputtered away before a reliable D/H measurement could be made, but the partial data limit the magnitude of any D enrichment in the globule to < 500‰. The globule also shows a small ^{13}C depletion, with δ^{13}C = -77 ± 13‰. In contrast, the Track 2 globule has an average terrestrial δ^{15}N = -7 ± 5‰ but a modest D enrichment of +1000 ±170‰ (Fig. 1B). Carbon isotopes in this globule are less depleted, with δ^{13}C = -35 ± 3‰, well within the range of meteoritic organic matter [9].

Organic Chemistry. The two globules have fundamentally different organic bonding. C-XANES spectra of cometary organic matter from Track 80 show peaks at 285.0 eV due to carbon-carbon double bonds and polyaromatic domains, at 286.7 eV most likely due to enol, phenol, and vinyl ketone functional groups, and at 288.5 eV due to carboxyl functional groups (Fig. 2A). However, the Track 80 globule is dominated by aromatic carbon with only small contributions from carbon-oxygen bonding (Fig. 2B). In contrast, C-XANES spectra of the Track 2 globule do not show any aromatic carbon but rather intense 286.7 eV and 288.5 eV (carboxyl) photoabsorptions (Fig. 2C). This organic matter is beam sensitive and changed dramatically after TEM imaging, although the

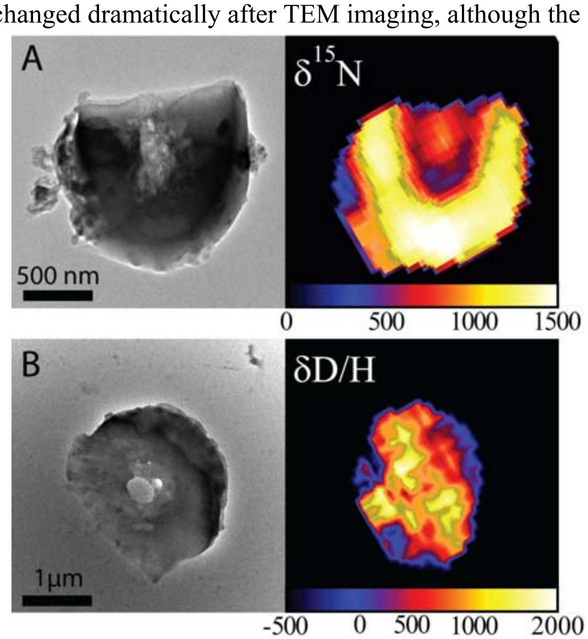

Figure 1. TEM images and corresponding NanoSIMS isotopic measurements of cometary organic globules in (A) Stardust Track 80 and (B) Track 2.

major peaks still exist (Fig. 2D). A distinction between dominantly aromatic and aliphatic organic globules has been implied by previous analyses of meteoritic globules [10, 11].

Both globules are N-rich (N/C ~ 0.1) as seen by NanoSIMS and N-XANES. The major photoabsorption in N-XANES spectra of the Track 2 globule is due to nitrile (C≡N) functional groups, which strongly absorb 286.7 eV X-rays. Enols or aromatic ketones cannot account for this peak due to the lack of an aromatic 285.0 eV absorption in C-XANES spectra. N-XANES was not performed on the Track 80 globule, so concentration of nitrile groups is unknown.

Discussion: These organic globules contain D and ^{15}N anomalies inconsistent with isotope fractionation

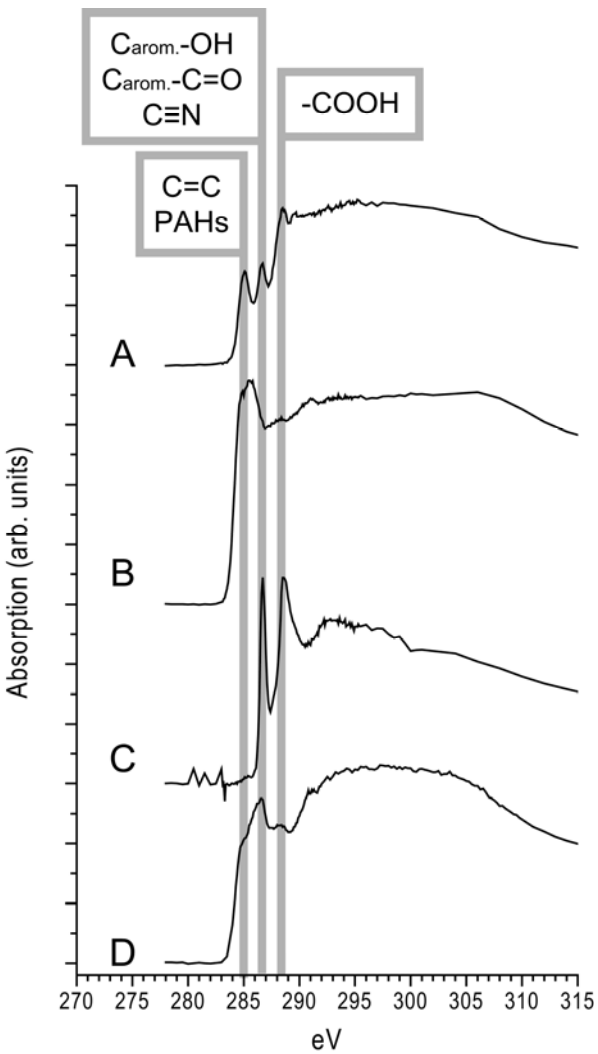

Figure 2. XANES spectra of cometary organic matter. (A) Organic matter from Track 80, Particle 43. (B) Organic globule from Track 80. (C) Organic globule from Track 2, Particle 4. (D) Track 2 globule after TEM analysis.

within our solar system and therefore likely predate the formation of the sun. The two cometary globules appear similar to their meteoritic counterparts, although the cometary globules are larger than average with thicker walls.

Molecular Cloud Chemistry. It has been suggested that H and N are fractionated simultaneously on ice grains in the interstellar medium [2]. However, the distinct fractionation patterns in the two globules indicates that H and N are not necessarily fractionated simultaneously. A decoupling of H and N isotopic anomalies has been observed in meteoritic organic matter [1]. Moreover, the distinct organic bonding in the two globules also suggests diversity of organic precursors and molecular cloud chemistry. These variations may be driven by local changes in organic reaction kinetics affected by temperature and density. The Track 80 globule, which is predominantly aromatic carbon, may have formed in a region where polyaromatic hydrocarbon (PAH) molecules are favored. The Track 2 globule, with its almost complete lack of aromatic carbon, must have formed in a region of the molecular cloud depleted in PAHs but enriched in molecules such as HCN and formaldehyde (H_2CO).

Organic Globule Formation. A leading model of presolar globule formation involves the capture of organic matter around ice grains that are later sublimated, leaving a hollow globule [2]. It is also possible to create globules by photolysis of organic-containing ices followed by exposure to liquid water [12]. The size range of globules formed by this method match the two cometary globules. Ices capturing different types of interstellar organic molecules could generate globules with distinct and limited organic chemistries upon melting. However, this method requires the presence of transient liquid water within the comet, possibly during shock heating.

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