

Isotopic anomalies in organic nanoglobules from Comet 81P/Wild 2: Comparison to Murchison nanoglobules and isotopic anomalies induced in terrestrial organics by electron irradiation

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Abstract

Nanoglobules are a form of organic matter found in interplanetary dust particles and primitive meteorites and are commonly associated with ¹⁵N and D isotopic anomalies that are suggestive of interstellar processes. We report the discovery of two isotopically-anomalous organic globules from the Stardust collection of particles from Comet 81P/Wild 2 and compare them with nanoglobules from the Murchison CM2 meteorite. One globule from Stardust Cometary Track 80 contains highly aromatic organic matter and a large ¹⁵N anomaly ($\delta^{15}\text{N} = 1120\%$). Associated, non-globular, organic matter from this track is less enriched in ¹⁵N and contains a mixture of aromatic and oxidized carbon similar to bulk insoluble organic material (IOM) from primitive meteorites. The second globule, from Cometary Track 2, contains non-aromatic organic matter with abundant nitrile ($-\text{C}\equiv\text{N}$) and carboxyl ($-\text{COOH}$) functional groups. It is significantly enriched in D ($\delta\text{D} = 1000\%$) but has a terrestrial ¹⁵N/¹⁴N ratio. Experiments indicate that similar D enrichments, unaccompanied by ¹⁵N fractionation, can be reproduced in the laboratory by electron irradiation of epoxy or cyanoacrylate. Thus, a terrestrial origin for this globule cannot be ruled out, and, conversely, exposure to high-energy electron irradiation in space may be an important factor in producing D anomalies in organic materials. For comparison, we report two Murchison globules: one with a large ¹⁵N enrichment and highly aromatic chemistry analogous to the Track 80 globule and the other only moderately enriched in ¹⁵N with IOM-like chemistry. The observation of organic globules in Comet 81P/Wild 2 indicates that comets likely sampled the same reservoirs of organic matter as did the chondrite parent bodies. The observed isotopic anomalies in the globules are most likely preserved signatures of low temperature (<10 K) chemistry in the interstellar medium or perhaps the outer regions of the solar nebula. In other extraterrestrial samples, D isotopic anomalies, but not those of ¹⁵N, may be explained in part by exposure to ionizing electron radiation.

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1. INTRODUCTION

In 2006, NASA's Stardust spacecraft returned over 10^4 μm -sized particles from the dust tail of comet Wild 2 (Brownlee et al., 2006). Prior to their return, the cometary samples were anticipated to contain abundant presolar materials, including interstellar material and grains that formed around other stars or supernovae. Preliminary examination of Wild 2 returned samples indicated that the comet contains a non-equilibrium assemblage of material, including refractory crystalline materials that likely formed in the inner regions of the early solar nebula and only minor amounts of presolar grains (Brownlee et al., 2006; McKeegan et al., 2006). Although the majority of the currently analyzed cometary dust is comprised of silicate and sulfide minerals (Zolensky et al., 2006), a portion contains organic and other carbonaceous matter (Sandford et al., 2006) in the form of carbonaceous grains (Cody et al., 2008a), carbonaceous rims surrounding other minerals (Matrajt et al., 2008), and volatile organics diffused into the silica aerogel capture medium (Glavin et al., 2008). Organic matter that exhibits large excesses in D or ^{15}N isotopes relative to H and ^{14}N , respectively, compared to terrestrial isotopic ratios, is present in many extraterrestrial materials, such as carbonaceous chondrite meteorites (Busemann et al., 2006) and interplanetary dust particles (IDPs; Messenger, 2000; Floss et al., 2004; Keller et al., 2004). These anomalous isotopic enrichments are interpreted to be likely signatures of primordial chemistry that occurred in the protosolar molecular cloud or in the outer cold regions of the solar system. The most extreme isotopic enrichments are commonly concentrated within μm to sub- μm "hotspots", suggesting the presence of a granular organic carrier of the isotopic anomalies. Similar isotopic enrichments have only been observed in a few of the Stardust samples (Sandford et al., 2006; Matrajt et al., 2008; Stadermann et al., 2008).

Spherical, and typically hollow, sub- μm carbonaceous grains occur in various carbonaceous chondrite meteorites (Garvie and Buseck, 2004, 2006; Nakamura-Messenger et al., 2006) and have recently been reported in chondritic porous IDPs (Messenger et al., 2008; Busemann et al., 2009). These "nanoglobules" range in diameter from less than 50 nm up to 2 μm (Nakamura-Messenger et al., 2006). Nanoglobules in the Tagish Lake and Bells meteorites were shown to contain large ^{15}N and D enrichments and compose a portion of the isotopic hotspots observed in these meteorites (Ashley et al., 2005; Nakamura-Messenger et al., 2006; Messenger et al., 2008). Extraterrestrial organic matter may acquire ^{15}N and D isotopic enrichments in cold interstellar or outer solar nebular environments through gas-phase reactions (Aikawa and Herbst, 1999; Sandford et al., 2001; Rodgers and Charnley, 2008a,b) and ion-surface reactions on icy grains (Tielens, 1983). Several mechanisms have been hypothesized to explain the formation of a hollow globular morphology from isotopically-enriched organic matter. Organic nanoglobules may form via UV irradiation of organic-rich interstellar ice grains, followed by sublimation of the interior ice (Nakamura-Messenger et al., 2006). Alternatively, organic molecules that are

amphipathic, i.e. possessing both hydrophilic and hydrophobic properties, may spontaneously form hollow spherical structures. Upon exposure to aqueous fluids, the hydrophobic portions of such molecules aggregate in order to exclude all interaction with water, while the hydrophilic portions spread out to form a protective barrier around the hydrophobic core. Amphipathic organic matter may be synthesized by UV photolysis or other radiation processing of common interstellar organic molecules in ice grains, and they have been shown to self-organize into globules when dispersed in water (Dworkin et al., 2001). Spherical globules may also be created during aqueous alteration on meteorite parent bodies (Cody et al., 2009), but this process would be less likely to occur on cometary bodies unless, contrary to expectations, they also experienced significant episodes in which liquid water was present.

The ubiquity of nanoglobules in other primitive extraterrestrial samples suggests that they should also be present in comets. In the Wild 2 samples, however, only one spherical carbonaceous feature has been reported to date (Matrajt et al., 2008), and although it contains an isotopic anomaly, it encompasses a sulfide grain as a "rind", unlike all observed globules in meteorites and IDPs, which do not envelop mineral grains. Here we report two organic globular features found in Comet 81P/Wild 2 samples that exhibit distinct chemical and isotopic signatures, and we compare them with nanoglobules from the Murchison meteorite. The ^{15}N or D isotopic anomalies present in these objects may indicate a very primitive, and possibly presolar, heritage. However, we cannot unambiguously rule out the possibility that one of the Stardust globules is terrestrial contamination because we have also found that similar D enrichments can be induced by transmission electron microscopy (TEM) of some organic materials.

2. MATERIALS AND METHODS

2.1. Sample preparation

Several particles extracted from the bulb-like region of Cometary Track 80 were allocated from the Stardust collection at NASA Johnson Space Center (JSC). Particle C2092,6,80,43,0 (Track 80, Particle 43) was transferred via a fresh glass needle into a molten sulfur droplet, which then crystallized around the particle upon cooling. The sulfur droplet was attached to the tip of an epoxy stub with a cyanoacrylate adhesive and sectioned with a diamond knife in an ultramicrotome at the Carnegie Institution of Washington (CIW). Several 90 nm thick slices were transferred to a 200 mesh thin-bar Cu TEM grid with a SiO support film. Since this was the second TEM grid containing ultramicrotome sections of the particle, it was designated C2092,6,80,43,2. The sulfur was removed by sublimation in a 60 °C oven overnight. At no point in this process was the sample exposed to a high-energy particle beam or temperatures greater than 140 °C, which is the maximum temperature used to melt the sulfur droplet.

A second sample, FC3,0,2,4,5 (Track 2, Particle 4), was prepared in a similar manner by Keiko Nakamura-Messenger

at JSC prior to allocation as part of the preliminary examination of the Stardust samples.

For comparison with the Wild 2 samples, we also studied fresh ultramicrotomed sections of insoluble organic matter (IOM) from the Murchison (CM2) meteorite, created from a sulfur-embedded residue. This material has already been well-characterized by a variety of methods (Alexander et al., 1998, 2007; Cody and Alexander, 2005; Cody et al., 2008b) and is known to contain D and ^{15}N isotopic hotspots (Busemann et al., 2006), which may be associated with nanoglobules observed in other residues from this meteorite (Garvie and Buseck, 2004; Garvie, 2006). The ultramicrotomed sections of Murchison IOM were placed on the same type of SiO-coated TEM grids as the cometary samples, and the sulfur was removed by sublimation in a 70 °C oven for several hours.

2.2. X-ray absorption near-edge structure spectroscopy (XANES)

Samples were analyzed by synchrotron-based scanning-transmission X-ray microscopy (STXM) at beamline X1A1 at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), and beamline 5.3.2 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL). Both instruments allow XANES analysis at the C 1s absorption edge, but the STXM instrument at ALS can additionally be tuned for N 1s or O 1s analyses (Kilcoyne et al., 2003). Organic matter in microtomed samples was distinguished from the aerogel capture medium and other inorganic material by acquiring X-ray absorption images at energies above and below the C 1s absorption edge (e.g. 290 and 280 eV). Since most carbonaceous matter will begin to absorb X-rays at energies above 284 eV, organic matter could be observed in the 290 eV images but was absent in the 280 eV images.

C-XANES spectra were acquired by first recording a series of X-ray absorption images at photon energies between 270 and 320 eV with an energy step between subsequent images as small as 0.1 eV (Jacobsen et al., 2000). Prior to STXM analyses, the microscope was calibrated to well-known carbon and oxygen photoabsorptions of CO_2 , and this initial calibration was not observed to drift more than 0.1 eV over the course of the analyses. The pixel size in the X-ray images was set to 25 nm, near the maximum instrumental resolution of the microscope. Each column of pixels in an aligned image “stack” then represents a full X-ray absorption spectrum for that coordinate. Principal component analysis, followed by component cluster analysis, was used to select regions of interest with similar spectra within the image stack (Lerotic et al., 2004). From these data, an average XANES optical density (*OD*) was calculated by $OD(E) = -\log[I(E)/I_0(E)]$, where $I(E)$ and $I_0(E)$ are the average transmitted X-ray intensity of the sample and background, respectively, at a given energy E . This method also allows for subtraction of contributions from amorphous carbon coatings deposited on the sample to mitigate charging effects from high-energy electrons during transmission electron microscopy (TEM). At ALS, the procedures for acquiring N- and O-XANES spectra are

similar to those for C-XANES but at higher photon energies (N absorbs above 397 eV and O absorbs above 529 eV).

2.3. Transmission electron microscopy (TEM)

Samples were analyzed with a JEOL 2200FS field-emission TEM at the Naval Research Laboratory (NRL) at an operating voltage of 200 keV. For this particular study, bright-field TEM imaging was used to observe the morphology of the globules at much higher spatial resolution than that achievable by STXM. An energy dispersive X-ray spectrometer (EDS) attached to the TEM allowed the distinction between organic matter and spacecraft aerogel by sample morphology and composition (Stroud et al., 2004). Although a carbon-free SiO support film was beneficial for C-XANES analysis, such a non-conducting film charges under the electron beam. To mitigate sample charging in the TEM, a thin amorphous carbon coat was deposited on the back side of the TEM grid.

Murchison IOM samples were analyzed by TEM prior to XANES analysis in order to identify and locate appropriate nanoglobule targets. TEM analyses were performed primarily at low magnifications and with small condenser apertures to minimize the total electron fluence to which the sample was exposed (approximately 10^3 electrons/nm² at a fluence rate of about 2 mA/cm²). Comparison of XANES spectra for bulk Murchison IOM acquired both before and after TEM analysis indicates that this minimal TEM electron fluence does not significantly alter the bulk chemistry.

We also performed a set of experiments to address concerns that exposure to electron irradiation during TEM analysis could artificially induce D or ^{15}N isotopic enrichments in organic samples. We prepared ultramicrotome sections of cyanoacrylate adhesive and epoxy and exposed them to the electron beam under controlled conditions. These samples were chosen because cyanoacrylate shares XANES spectral features with the Track 2 sample (FC3,0,2,4,5), as described below. Cyanoacrylate and epoxy are possible laboratory contaminants during sample preparation and can exhibit contrast changes during exposure to the high-energy electron beam, most likely as removal of hydrogen.

Ultramicrotomed cyanoacrylate and epoxy sections were placed on Quantifoil Cu TEM grids containing a perforated amorphous carbon support film. Several small regions within these sections were exposed to the 200 keV electron beam to mimic typical analyses of Stardust samples, which may include high-resolution imaging, EDS or electron energy-loss spectroscopy (EELS) analysis using a converged beam, and hyperspectral EDS mapping in scanning (STEM) mode, each of which may contribute large electron fluences. In conventional TEM mode, a 1.5 μm circular region was irradiated for ~ 30 min with a semi-converged beam at 10,000 \times magnification, resulting in a total electron fluence of approximately 10^8 electrons/nm² at a fluence rate of about 500 mA/cm². In STEM mode, a converged beam with a nominal 1 nm probe size and 0.9 nA probe current was rastered over a 15 μm by 15 μm square region for ~ 60 min, resulting in an electron fluence of

approximately 10^5 electrons/nm² at a fluence rate of about 10^5 A/cm². These STEM beam conditions are typical for the acquisition of an EDS hyperspectral map for a 10 μ m Wild 2 particle. These samples were compared with adjacent ultramicrotome sections not exposed to the TEM beam in order to measure any differences in isotopic composition between the two samples.

2.4. Secondary ion mass spectrometry (SIMS)

Hydrogen, carbon, and nitrogen isotopic compositions of the samples were measured with a Cameca NanoSIMS 50L ion microprobe in the Department of Terrestrial Magnetism at the CIW. TEM grids were first attached to Al stubs with colloidal Ag paint and then coated with a thin layer of Au to eliminate charging effects. A focused 16 keV Cs⁺ primary ion beam was rastered over the samples and negative secondary ion images were acquired simultaneously in multi-collection mode. Measurements were made in two steps. In the first, a ~ 1 pA, 150 nm beam was used to acquire images of ¹²C, ¹³C, ¹²C¹⁴N, ¹²C¹⁵N, ²⁸Si, and secondary electrons. In the second step, a slightly higher beam current (~ 3 pA, 300 nm beam) was used to acquire images of H, ²H, ¹²C, and secondary electrons. The mass resolution of the instrument was sufficient to resolve all significant isobaric interferences. Well-characterized insoluble organic matter (IOM) from the carbonaceous chondrite GRO 95577 (Alexander et al., 2007) was used to calibrate the instrumental fractionation for carbon and nitrogen isotopic ratios and the relative sensitivity factor used to convert CN⁻/C⁻ ratios to N/C atomic ratios. A terrestrial organic standard was used to calibrate D/H measurements. Isotopic compositions and average atomic N/C ratios of sub-regions in the ion images were quantitatively calculated with the L'image software package (L. Nittler, CIW). Reported errors are based purely on counting statistics. The globule samples were, for all practical purposes, consumed during the NanoSIMS analyses.

3. RESULTS

3.1. Sample morphology

One of the microtomed sections of sample C2092,6,80,43,2 (Track 80) consists of organic matter surrounded by compressed aerogel on two sides (Fig. 1A, hereafter identified as Track 80 organic section) and an adjacent carbonaceous globular feature (Fig. 1B, hereafter identified as Track 80 globule). The intimate association of organic matter and aerogel in the Track 80 organic section suggests that it is cometary material captured by the Stardust spacecraft. Spot EDS analyses confirm that the center of the Track 80 organic section is composed primarily of carbonaceous matter, while the surrounding aerogel in the Track 80 organic section contains higher silica abundance. Carbonaceous matter is also present within the surrounding aerogel above background levels, indicating the presence of cometary organic matter infiltrating the aerogel.

The Track 80 globule is roughly circular with an outer diameter of 1.4 μ m and a wall thickness of approximately

450 nm. The center is not fully hollow but is consistent with a 90 nm thick ultramicrotome section sampling one end of a hollow, spherical object. The globule walls are homogeneous with no apparent layering or evidence of graphitization in higher-resolution images. The close proximity of the Track 80 globule to the nearby organic section (2.5 μ m) suggests that the two features must have been present in the same ultramicrotome slice rather than in separate slices. Most likely, the globule was initially attached to the organic section and was later separated during ultramicrotomy. Various sectioning effects may result in small relative movements of material in sulfur-embedded ultramicrotome sections, including brittle failure of the surrounding crystalline sulfur, changes in hardness or density of the embedded sample, and periodic compression of sample and/or sulfur (Malis and Steele, 1990).

Sample FC3,0,2,4,5 (Track 2) contains a few scattered microtomed slices of aerogel with no apparent cometary material. However, a globular feature is located near some of the aerogel slices (Fig. 1C, hereafter identified as Track 2 globule). The sample is wedge-shaped, decreasing in thickness to the lower left, with smooth, flat surfaces, indicating that it has been ultramicrotomed. The globule is 2.3 μ m in diameter with a wall thickness of approximately 700 nm. Unlike the Track 80 globule, the Track 2 globule is completely hollow in the center, but TEM images show increasing sample thickness from the center out to a 450 nm radius where image contrast becomes roughly constant, indicating the true void area of the globule. Again, this globule is homogenous and does not show any layering or graphitization.

Several organic nanoglobules were identified in the Murchison IOM sample and analyzed by TEM, STXM, and SIMS. Two adjacent globules of particular interest are shown in Fig. 1D. Both globules are partially hollow with approximately 100 nm thick walls. The larger (lower) globule (hereafter identified as M1) has an outer diameter of 500 nm, while the smaller globule (hereafter identified as M2) has an outer diameter of 350 nm. A detailed discussion of the entire Murchison dataset and data for other meteoritic IOM residues will be presented elsewhere.

3.2. Organic chemistry

All of the microtomed Track 80 material, including the associated aerogel, strongly absorbs X-rays at 290 eV, indicating the presence of abundant carbonaceous material. Both the cometary organic matter and that associated with aerogel in the Track 80 organic section exhibit identical XANES spectra (Fig. 2A), each containing three peaks due to $1s \rightarrow \pi^*$ (anti-bonding) electronic transitions involving doubly-bonded C atoms at 285.0, 286.7, and 288.5 eV, followed by a $1s \rightarrow \sigma^*$ (anti-bonding) absorption edge. The 285.0 eV π^* absorption is characteristic of aromatic carbon-carbon bonding (C=C) and polyaromatic domains, while carboxylic acid functional groups (—COOH) generate a well-established absorption peak at 288.5 eV (Urquhart and Ade, 2002). Photoabsorption at 286.7 eV could be due to several functional groups, including enol or phenol groups (C_{aromatic}—OH; Cody, 2000; Boyce et al., 2002), vinyl ketone groups (C_{aromatic}—C=O; Hitchcock et al.,

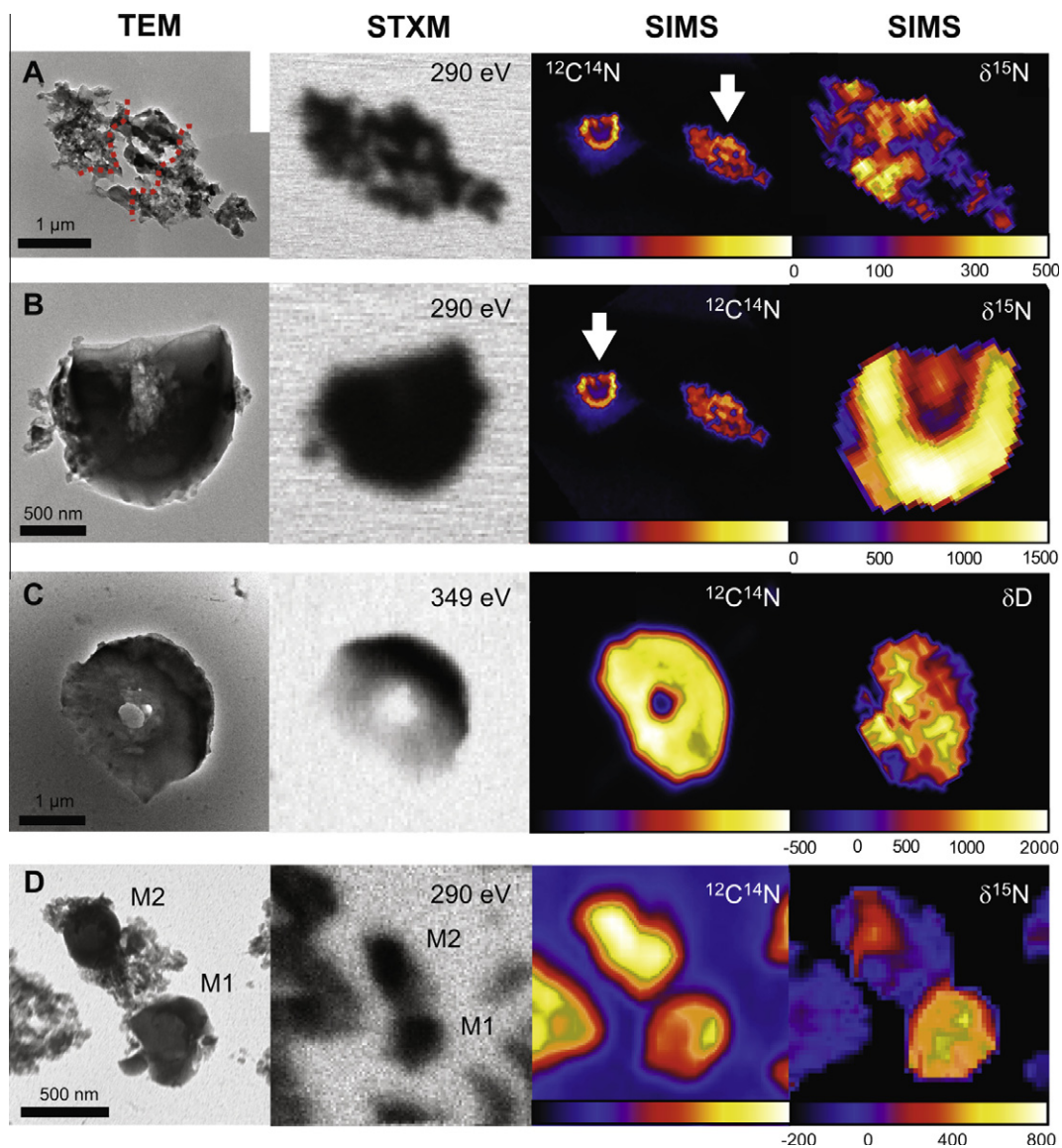


Fig. 1. TEM (left-most column) and STXM (middle left column) images and SIMS maps of CN^- (middle right column) and $\delta^{15}\text{N}$ or δD (right-most column) of extraterrestrial carbonaceous samples in this study (A) Track 80 organic section in Stardust sample C2092,6,80,43,2. Cometary organic matter is concentrated in the center of the section (bounded by dashed lines), while both aerogel and cometary organic matter are present at the two ends of the section. This division is also visible in the SIMS images. (B) Track 80 globule section in the same sample. (C) Track 2 globule in Stardust sample FC3,0,2,4,5. The SIMS δD image has been digitally smoothed to improve the statistical significance of the color scale. (D) Two organic globules (M1 and M2) found in the IOM residue from the Murchison meteorite.

1992; Cody et al., 2008a,b), aromatic amine or amide groups ($\text{C}_{\text{aromatic}}-\text{N}$; Ade and Urquhart, 2002), or nitrile groups ($-\text{C}\equiv\text{N}$; Hitchcock et al., 2001; Ade and Urquhart, 2002). Since carboxyl functionality is already present in this material, it is likely that the 286.7 eV absorption feature is due to additional carbon–oxygen bonding, although it is possible that specific carbon–nitrogen bonding may significantly contribute to this feature. Enols and phenols can also transform into ketones and other carbonyls under X-ray and electron beams (Cody, 2000). The C-XANES spectrum of the Track 80 organic section appears similar to typical meteoritic insoluble organic matter (Cody et al., 2008b), represented by the Murchison spectrum in Fig. 2.

In contrast, the Track 80 globule (Fig. 2B) exhibits a distinct C-XANES spectrum from the nearby Track 80 organic section. The C-XANES spectrum for this globule shows evidence of saturation (flattening) due to the almost complete absorption of X-rays relative to background intensity ($I/I_0 \approx 0$), most likely because the section thickness exceeds the average penetration depth of low energy X-rays. Despite this, a broad aromatic peak is still visible at 285.4 eV. The shape of this peak suggests contributions from at least two organic moieties: polyaromatic domains contributing around 285.0 eV and modified aromatic molecules with photoabsorptions shifted to slightly higher X-ray energies. A smaller peak at 291.0 eV could be related to the

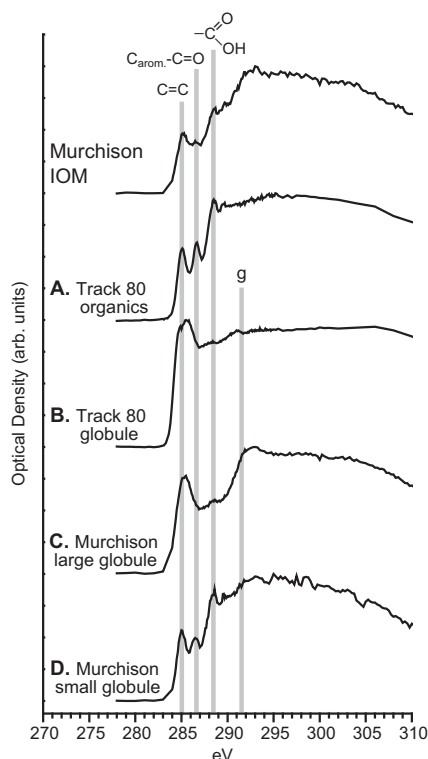


Fig. 2. Carbon XANES of cometary and meteoritic globules compared to bulk IOM from Murchison. (A) Spectrum from the Track 80 organic section in Fig. 1A. (B) Spectrum from the Track 80 globule in Fig. 1B. (C) Spectrum from the larger Murchison globule (M1) in Fig. 1D. (D) Spectrum from the smaller Murchison globule (M2) in Fig. 1D.

characteristic $1s \rightarrow \sigma^*$ (anti-bonding) electronic transition at 291.6 eV from large polyaromatic domains or graphene sheets that is sometimes referred to as a graphite exciton (Weng et al., 1989; Brühwiler et al., 1995; Ahuja et al., 1996; Wessely et al., 2005). The strength of the graphite exciton peak has been correlated to the extent of thermal metamorphism on meteorite parent bodies (Cody et al., 2008b), but it may be suppressed depending on the orientation or disorder of the graphitic domains (Rosenberg et al., 1986; Skytt et al., 1994; Gago et al., 2001; Belavin et al., 2006). The broad aromatic peak observed in the globule spectrum is not consistent with the sharp aromatic peak observed in thermally-processed graphitized material, and therefore, the 291.0 eV peak is most likely due to the partial alignment of polyaromatic domains. The spectra may contain contributions from carboxyl functional groups at 288.5 eV, but potential contributions from enols and aromatic ketones are masked by the large aromatic π^* photoabsorption. Unlike the Track 80 organic section, the Track 80 globule appears to be dominated by aromatic carbon. However, because no crystal lattice fringes, and in particular no 3.4 Å lattice fringes characteristic of the (0002) d -spacing for graphite, were observed by TEM, the aromatic carbon most likely comprises randomly oriented polyaromatic moieties similar to polycyclic aromatic hydrocarbons (PAHs).

The Track 2 globule appears to consist of a third type of N-rich organic matter. The initial C-XANES spectrum of this globule contains photoabsorptions at 286.7 eV and at 288.6 eV, but no aromatic 285.0 eV absorption (Fig. 3A). After exposure to the 200 keV electron beam during TEM analysis, the organics show evidence of damage – a 285 eV “shoulder” is present and the major peaks have decreased in intensity, most notably the 288.6 eV peak (Fig. 3B). The increased photoabsorption around 285 and 291 eV suggests that the primary damage mechanism is the cyclization of aliphatic carbon to form polyaromatic domains, with a concurrent loss of hydrogen atoms. As before, the 288.6 eV peak most likely arises from abundant carboxyl functional groups. However, the sharp 286.7 eV peak contains a large contribution from nitrile functional groups in addition to enols and ketones. This is corroborated by the dominant $1s \rightarrow \pi^*$ photoabsorption at 399.8 eV in the N-XANES spectrum (Fig. 3C; Shard et al., 2004; Leinweber et al., 2007; Cody et al., 2008a). Imine ($C=N$) bonds in aromatic imidazoles and purines may also generate a N-XANES peak at 399.8 eV (Apen et al., 1993; Leinweber et al., 2007), but since an imine photoabsorption is not observed around 286.0 eV in C-XANES, aromatic heterocycles with more than one N atom are not common in the Track 2 globule. However, the π^* peak at 398.6 eV can be reliably attributed to aliphatic imine bonds and aromatic heterocycles containing a single N atom (Jokic et al., 2004; Leinweber et al., 2007; Cody et al., 2008a). The third N-XANES peak at 401.2 eV can either be due to pyrrolic N in imidazoles and purines (Apen et al., 1993; Leinweber et al., 2007) or amide ($O=C-NH_x$) functional groups (Gordon et al., 2003; Cooper et al., 2004; Jokic et al., 2004; Leinweber et al., 2007). Because the lack of a major C-XANES photoabsorption around 286.0 eV indicates that aromatic heterocycles with more than one N atom are not present in high abundance, we attribute the N-XANES peak at 401.2 eV to amide functionality and possible peptide-like bonding. We note that the N-XANES spectrum was acquired after the organic matter was damaged during TEM imaging, and therefore the relative abundances of N-containing functional groups inferred from the N-XANES spectrum very likely do not represent the abundances present in the original undamaged globule. In particular, beam damage of amino acids has been shown to create aromatic carbon, imine, and nitrile bonding (Zubavichus et al., 2004). However, the pre-damage C-XANES spectrum (Fig. 3A) clearly shows the presence of nitrile functional groups. Using the method described by Cody et al. (2008a), an atomic N/C ratio of 0.13 is calculated for this globule based on the XANES data.

The undamaged C-XANES spectrum of the Track 2 globule is nearly identical to that of common cyanoacrylate adhesive (Fig. 3), in which the photoabsorptions at 286.7 and 288.6 eV correspond to the presence of nitrile and carboxyl functional groups, respectively. A cyanoacrylate adhesive was used during sample preparation of both Stardust samples, and ultramicrotomed sections of cyanoacrylate are often present on sulfur-embedded Stardust sample mounts in the proximity of authentic cometary material if the cyanoacrylate formed a thin layer over the sides or top of the

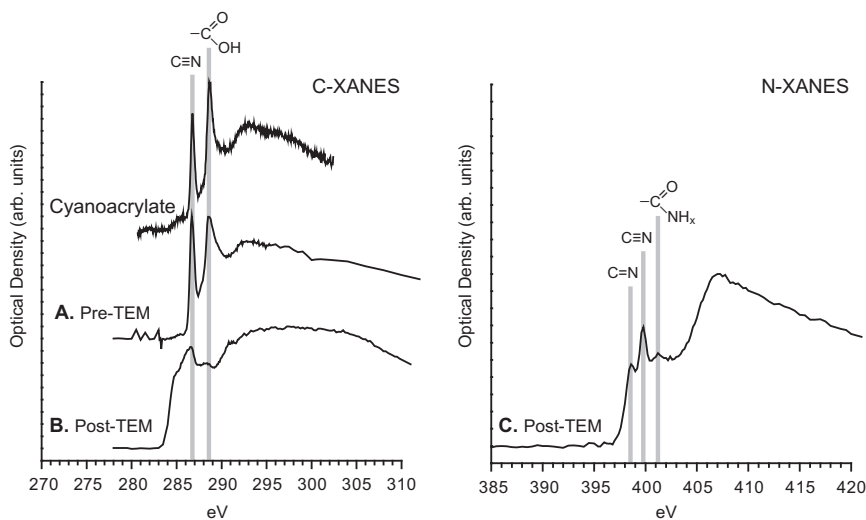


Fig. 3. Carbon and nitrogen K-edge XANES spectra of the Track 2 globule. C-XANES spectrum of the organic globule (A) before and (B) after TEM imaging, compared with a standard sample of cyanoacrylate adhesive. (C) N-XANES spectrum of the globule after TEM imaging.

crystallized sulfur droplet. Cyanoacrylate strips may also be purposely laid on TEM grids to mark the position of sulfur-embedded, microtomed Stardust particles, which may be difficult to locate otherwise once the surrounding sulfur has been removed. While we have often seen triangular, trapezoidal, or semicircular cyanoacrylate sections, we have not previously observed circular or globular sections in our ultramicrotomed samples, but they may, in principle, result from sectioning of small droplets or bubbles.

The two Murchison nanoglobules (M1 and M2) also contain distinct organic chemistries. The smaller of the two globules (M2), as well as the majority of the other Murchison globules characterized by STXM (not described in this study), show C-XANES spectra similar to that of the bulk Murchison IOM, with photoabsorptions at 285, 286.7, and 288.6 eV, corresponding to aromatic bonding, aromatic ketone and enol bonding, and carboxyl functional groups, respectively (Fig. 2D). However, the C-XANES spectrum of the larger Murchison globule (M1) is similar to that of the Stardust Track 80 globule, dominated by an aromatic peak at 285.4 eV (Fig. 2C). This aromatic Murchison globule spectrum does not appear to be saturated

like that of the aromatic Track 80 globule. Furthermore, the Murchison globule (M1) spectrum does not include a distinct exciton peak as seen in the Track 80 globule, but rather contains a well-developed σ^* peak above the C 1s absorption edge that is typical of graphite and highly aromatic material (Cody et al., 2008b). However, since graphitic lattice fringes were not observed during TEM, the M1 globule is likely composed of non-graphitic, aromatic organic matter.

3.3. Isotopic composition

Isotopic compositions of hydrogen, carbon, and/or nitrogen were measured in each of the organic globules and in the Track 80 organic section (Table 1). Not all elements were measured in each sample. The Track 80 globule is highly enriched in ^{15}N , with an average $\delta^{15}\text{N}$ value of $+1120 \pm 30\text{‰}$ (Fig. 1B) that is within the range observed spectroscopically for CN in cometary comae ($+930 \pm 400\text{‰}$; Schulz et al., 2008). It is also moderately depleted in ^{13}C ($\delta^{13}\text{C} = -77 \pm 13\text{‰}$). The Track 80 organic section is also significantly enriched in ^{15}N ($\delta^{15}\text{N} \approx +140\text{‰}$), albeit to a lesser

Table 1
Isotopic composition and atomic N/C ratios of samples in this study.

Sample	δD (‰)	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	N/C
C2092,6,80,43,2 (aerogel-rich)	n.m.	-42 ± 14	$+136 \pm 15$	0.10–0.15
C2092,6,80,43,2 (globule)	$<+1000$	-77 ± 13	$+1120 \pm 30$	0.10–0.15
FC3,0,2,4,5	$+1000 \pm 170$	-35 ± 3	-7 ± 5	0.08–0.16
Murchison (large globule)	n.m.	n.m.	$+470 \pm 35$	n.m.
Murchison (small globule)	n.m.	n.m.	$+289 \pm 39$	n.m.
Murchison (bulk IOM) ^a	$+777$	-19	-1	0.03
Cyanoacrylate (STEM)	$+500\text{--}800$	n.m.	-2 ± 5	n.m.
Epoxy (TEM)	$+1000$	n.m.	n.m.	n.m.
Epoxy (STEM)	$>+150$	n.m.	n.m.	n.m.

n.m. = not measured.

^a Data from Alexander et al. (2007).

degree than observed in the globule. The nitrogen isotopic composition in this section is heterogeneous on a sub- μm scale, and the largest ^{15}N enrichments occur in aerogel-free areas (Fig. 1A). Individual ~ 400 nm hotspots contain above-average $\delta^{15}\text{N}$ values up to $+360 \pm 70\%$. Based on CN^-/C^- ratios measured with the NanoSIMS, the Track 80 samples have atomic N/C ratios of 0.10–0.15. These values are significantly higher than typical IOM from primitive meteorites (<0.05 ; Alexander et al., 2007), but they are similar to a few N-rich nanoglobules from primitive meteorites (Garvie and Buseck, 2004) and several carbonaceous Wild 2 samples (Sandford et al., 2006; Cody et al., 2008a). Unfortunately, failure of the support film during NanoSIMS analysis precluded a robust measurement of D/H ratios within the Track 80 samples, but the partial dataset shows no evidence for a D enrichment greater than about 1000% in the Track 80 globule. However, this is not a stringent upper limit, since the highly aromatic nature of this globule suggests a relatively low intrinsic H/C ratio, potentially making the sample more susceptible to terrestrial contamination in the NanoSIMS. Nonetheless, it is highly unlikely that the Track 80 globule had a D enrichment comparable to the extreme values observed in isotopic hotspots in meteoritic and IDP organic matter.

In contrast to the Track 80 globule, the Track 2 globule contains a nitrogen isotopic composition ($\delta^{15}\text{N} = -7 \pm 5\%$) that is indistinguishable from terrestrial values and a carbon isotopic composition ($\delta^{13}\text{C} = -35 \pm 3\%$) that is within the typical range of meteoritic IOM (Alexander et al., 1998, 2007). However, this globule does contain a clearly anomalous D/H ratio, with an average $\delta\text{D} = +1000 \pm 170\%$ (Fig. 1C). Apparent variations in D/H in this sample shown in Fig. 1C are not statistically significant. The Track 2 globule is also N-rich, with an atomic N/C ratio between 0.08 and 0.16, based on NanoSIMS analysis, in good agreement with the value of 0.13 derived from XANES. This N/C ratio is comparable to that found in the Track 80 globule as well as in other carbonaceous Wild 2 samples (Sandford et al., 2006; Cody et al., 2008a). However, this value is slightly lower than the N/C ratio for cyanoacrylate (0.17–0.20). Since these measurements were performed following TEM-induced beam damage evident by XANES, it is possible that TEM analysis could have driven significant nitrogen loss within the sample. If this is the case, then the original N/C ratio of the Track 2 globule could have been higher.

Many of the Murchison nanoglobules analyzed with the NanoSIMS in this study have enhanced $^{15}\text{N}/^{14}\text{N}$ ratios (only two of which are described here), relative to the bulk IOM value of $\delta^{15}\text{N} = -1\%$ (Alexander et al., 2007). In particular, the larger of the two globules (M1) in Fig. 1D, comprised predominantly of aromatic organic matter as determined by XANES (Fig. 2C), exhibits the largest ^{15}N enrichment, with an average $\delta^{15}\text{N} = +470 \pm 35\%$. The smaller globule (M2), comprised of more oxidized and aliphatic organic matter (Fig. 2D), contains a smaller, but still anomalous, ^{15}N enrichment ($\delta^{15}\text{N} = +289 \pm 39\%$). Unfortunately, this TEM grid received a carbon coat directly onto the sample rather than onto the backside of the SiO support film prior to TEM observations. The

infiltration of the carbon coating into the porous IOM precluded the accurate measurement of carbon isotopic compositions and atomic N/C ratios for the Murchison globules. In addition, failure of the support film precluded adequate D/H measurements.

To test whether the D enrichment measured in the Track 2 globule could be an artifact of extensive TEM beam damage and hydrogen loss in cyanoacrylate, the D/H and $^{15}\text{N}/^{14}\text{N}$ isotopic compositions were analyzed in both electron-irradiated and pristine ultramicrotomed sections of cyanoacrylate adhesive and epoxy. A $15 \mu\text{m}$ by $15 \mu\text{m}$ region of cyanoacrylate exposed in scanning (STEM) mode was found to be enriched in D by $500\text{--}800\%$ relative to non-irradiated material (Fig. 4A and B). Similarly, a $3 \mu\text{m}$ damage spot in epoxy caused by a defocused TEM beam at $10,000\times$ magnification was fractionated with a $\delta\text{D} \approx 1000\%$ relative to non-irradiated epoxy (Fig. 4C and D). In contrast, no significant nitrogen isotopic fractionation ($>1\%$) of these samples was observed.

4. DISCUSSION

4.1. Cometary and meteoritic organic globules

The features described here are the first organic nanoglobules, similar to those observed in carbonaceous chondrites and IDPs, reported in the Stardust return samples from comet Wild 2. Matrajt et al. (2008) reported a donut-shaped carbonaceous feature enriched in ^{15}N in the terminal particle from Stardust Track 57 (particle “Febo”). However, this material was observed as a carbonaceous rind surrounding a sulfide grain, and no meteoritic nanoglobules have been observed to contain such embedded mineral grains. The two Stardust globules described in this study are physically, chemically, and isotopically distinct from nearby cometary organic matter. Although both globules have much larger diameters than the average meteoritic nanoglobule, they still lie within the observed size range of such nanoglobules (Garvie and Buseck, 2006; Nakamura-Messenger et al., 2006). Their morphologies are also consistent with the smallest size fraction of experimentally produced organic globules created by UV irradiation of organic molecules in ices, followed by exposure to liquid water (Dworkin et al., 2001). Because only two cometary globules have so far been discovered, it is unknown if they are representative of the entire population preserved in the comet. Because the capture of cometary dust in aerogel is a highly energetic process (Domínguez et al., 2004), it is possible that smaller organic globules with thinner walls, similar to average meteoritic nanoglobules, may be destroyed by thermal and frictional forces. Alternatively, smaller globules may be more difficult to recognize when mixed with melted or compressed aerogel and other materials. This would create a sampling bias towards the recovery of large, thick-walled organic globules in the cometary return samples.

The D/H ratio measured in the Track 2 globule ($\delta\text{D} = +1000\%$) lies well outside the range of terrestrial materials and is similar to that of other Wild 2 carbonaceous samples (McKeegan et al., 2006) and bulk IOM residues from primitive CI and CM chondrites (Alexander

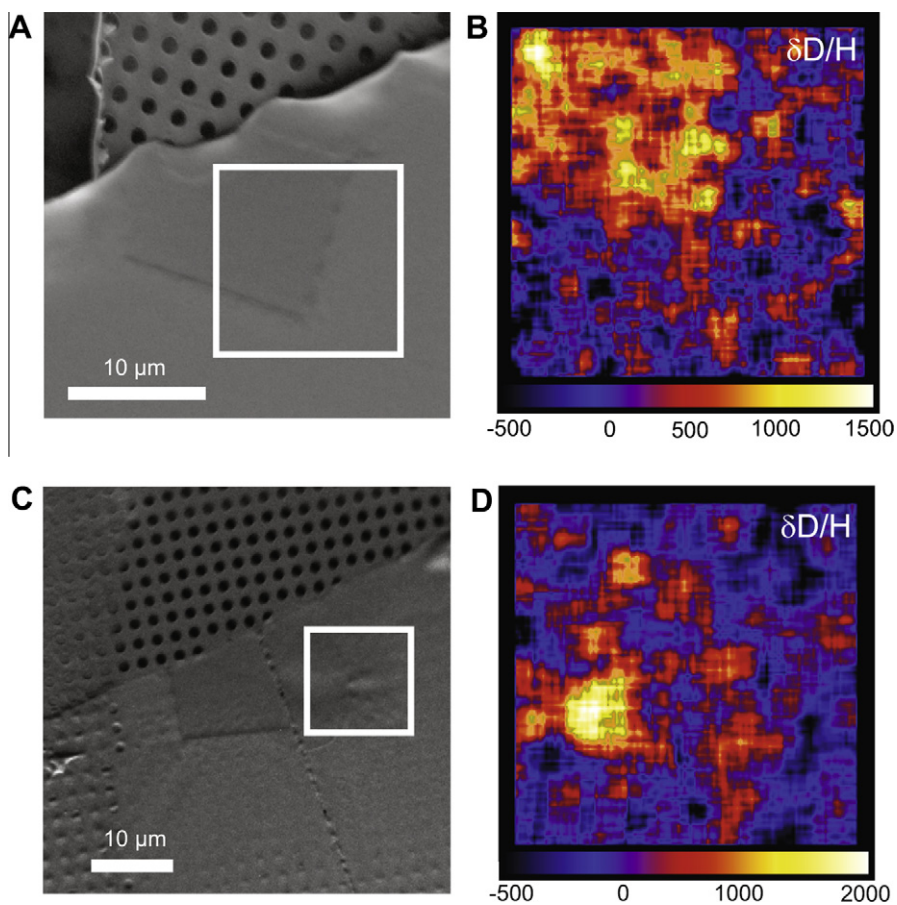


Fig. 4. NanoSIMS images of TEM-irradiated cyanoacrylate adhesive and epoxy. (A) Secondary electron image of ultramicrotomed cyanoacrylate showing a rectangular region of STEM damage. (B) $\delta D/H$ map (corresponding to the white square in (A)) showing enhanced D in the damaged region. (C) Secondary electron image of ultramicrotomed epoxy showing nearby regions of STEM and TEM damage. (D) $\delta D/H$ map (corresponding to the white square in (C)) showing enhanced D in a 1.5 μm spot from TEM damage.

et al., 2007). However, the Track 2 globule is less D-enriched than bulk IOM residues from primitive CR and ordinary chondrites (Busemann et al., 2006; Alexander et al., 2007) and organic nanoglobules from Tagish Lake (Nakamura-Messenger et al., 2006). Prior to this study, such magnitude D enrichments would have been considered unambiguous evidence for an extraterrestrial origin. However, the C-XANES spectrum of this globule that was acquired prior to TEM analysis is strikingly similar to cyanoacrylate adhesive. If this globule is indeed a cyanoacrylate contaminant from sample preparation, exposure to electron irradiation during TEM analysis could have chemically altered the organic matter and depleted it in H relative to D, resulting in an effective D enrichment. We estimate that during TEM and STEM characterization the Track 2 globule was exposed to a similar total electron fluence (about 10^7 electrons/nm²) as our irradiated cyanoacrylate and epoxy standards. Since a comparable D enrichment was observed in those irradiated adhesive samples, the D enrichment measured in the Track 2 globule could have been induced during TEM analysis. A corresponding ¹⁵N enrichment, which was not produced by our electron irradiation experiments, is not present in the Track 2 globule, despite it being N-rich. Despite these

considerations, it remains possible that the Track 2 globule is indeed cometary organic matter. Given the large variations in organic chemistry that have been observed in other organic Stardust samples (Cody et al., 2008a), the Track 2 globule may represent primitive nitrile and carboxyl-rich interstellar organic matter. In addition, the hollow spherical morphology is not consistent with other cyanoacrylate marker sections found on Stardust mounts. However, because of the similarities with cyanoacrylate, a cometary origin cannot be unambiguously determined at this time. The potential future detection of other Stardust globules with similar XANES spectra, along with isotopic measurements made on sections not previously exposed to electron irradiation, may settle this question. Therefore, in the remainder of our discussion we will focus primarily on results from the Track 80 globule.

In contrast to the Track 2 sample, the Track 80 globule contains a large enrichment in ¹⁵N and a moderate depletion in ¹³C. Unfortunately, its hydrogen isotopic composition could not be reliably determined due to substrate failure during the analysis, although our data does place an upper limit on its D/H ratio (Table 1), well below the extreme D enrichments that have been observed in some meteoritic nanoglobules (Ashley et al., 2005; Nakamura-Messenger et al.,

2006). The ^{15}N isotopic anomaly in the Track 80 globule lies significantly outside the range of terrestrial and most other solar system materials (Fig. 5). Kinetic fractionation during evaporation would tend to enrich the condensed phase in the heavy stable isotopes. Reaching the observed $^{15}\text{N}/^{14}\text{N}$ composition in the Track 80 globule through a Rayleigh-like process would require extreme loss of material and simultaneously lead to large ^{13}C enrichments. Since the Track 80 globule is depleted in ^{13}C , evaporation or condensation cannot be responsible for these isotopic anomalies. This additionally rules out laboratory isotopic enrichments generated during sample storage or preparation.

The $^{15}\text{N}/^{14}\text{N}$ and $^{13}\text{C}/^{12}\text{C}$ isotopic ratios observed in the Track 80 globule are remarkably similar to those of two anomalous “hotspots” previously reported in Wild 2 samples (McKeegan et al., 2006), one of which was located within an Al foil impact crater and one in an aerogel track sample. Although it is not known whether these other samples contained nanoglobules, the isotopic similarity strongly suggests that additional nanoglobules should be present in the Stardust sample collection. The isotopic composition of the Track 80 globule is also very similar to carbonaceous sub-grains in primitive anhydrous IDPs (Floss et al., 2004) and the CR chondrites EET 92042 (Busemann et al., 2006) and QUE 99177 (Floss and Stadermann, 2009). Unfortunately, the morphologies of most of these grains have not been observed, reported, and/or adequately determined to ascertain whether or not they are nanoglobules. Relatively few isotopic measurements have been reported

for individual meteoritic nanoglobules, with most of the extant data obtained from the Tagish Lake carbonaceous chondrite (Ashley et al., 2005; Nakamura-Messenger et al., 2006). Nanoglobules in Tagish Lake are typically enriched in ^{15}N and D, with $\delta^{15}\text{N}$ values ranging from 200‰ to 1000‰ (Nakamura-Messenger et al., 2006), significantly above the bulk IOM value of ~ 75 ‰ (Grady et al., 2002; Alexander et al., 2007). On the other hand, IOM from the Bells (anomalous CM2) meteorite has higher $\delta^{15}\text{N}$ values both in bulk material (400‰) and in hotspots (≤ 3200 ‰; Busemann et al., 2006), at least some of which contain nanoglobules (Messenger et al., 2008).

The Track 80 globule also bears a chemical resemblance to at least some meteoritic nanoglobules. Most notably, both it and the larger nanoglobule from the Murchison residue (M1; Fig. 1D) show very similar C-XANES spectra, indicating the presence of highly aromatic organic matter. Previous analyses of nanoglobule chemistry in Murchison and other primitive meteorites by electron energy-loss spectroscopy (EELS) in TEM also indicated a highly aromatic character (Garvie and Buseck, 2004; Garvie, 2006). However, the spectral resolution of this technique is significantly poorer than that of the STXM methods used in this study, and EELS may be more destructive and less sensitive than XANES for detecting particular organic functional groups, such as carboxyl or ketones (Braun et al., 2005), which are common in extraterrestrial organic matter.

Like most of the reported carbonaceous cometary samples from the Stardust collection (Sandford et al., 2006;

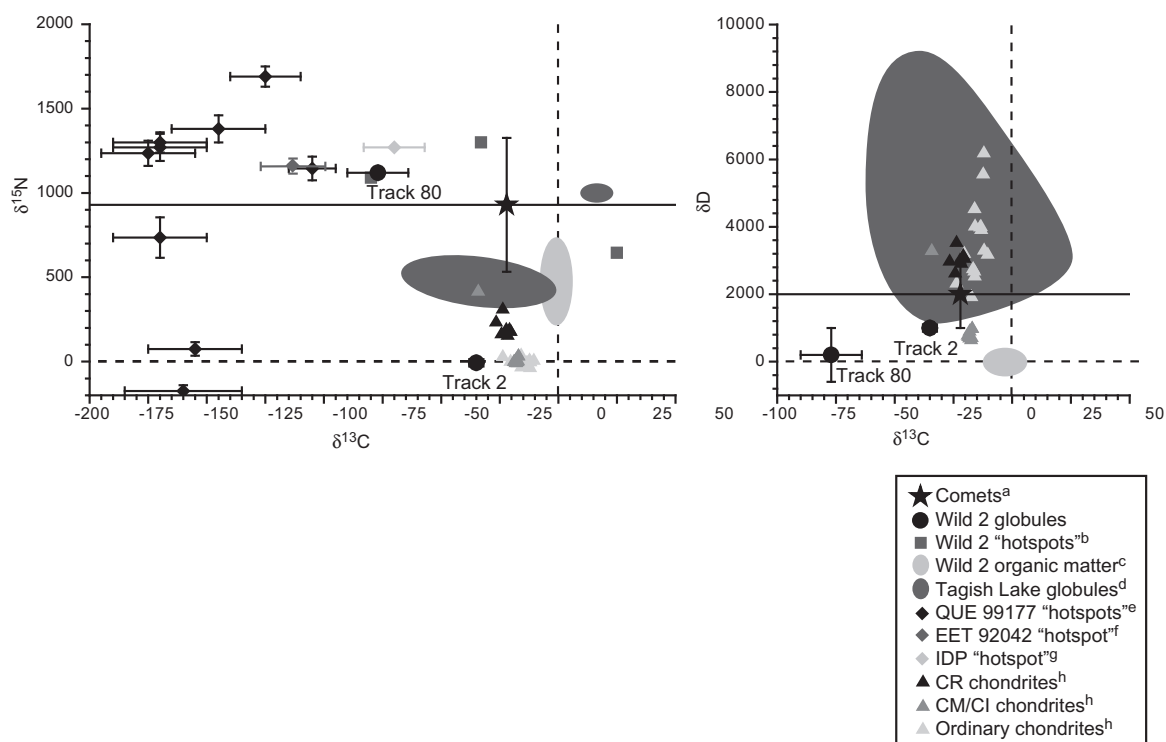


Fig. 5. Average ^{15}N and D isotopic compositions of cometary globules from this study compared with organic matter in other planetary materials. The $\delta^{15}\text{N}$ value of the Track 80 globule plots near those of a Stardust Al foil crater and an isotopically-anomalous region of organic matter in an interplanetary dust particle. References: ^aSchulz et al. (2008), ^bMcKeegan et al. (2006), ^cMatrajt et al. (2008), ^dNakamura-Messenger et al. (2006), ^eFloss and Stadermann (2009), ^fBusemann et al. (2006), ^gFloss et al. (2004), ^hAlexander et al. (2007).

Cody et al., 2008a), the Track 80 samples reported here have atomic N/C ratios (0.10–0.15) significantly higher than those measured in bulk IOM from primitive CM, CR, and CI chondrites (0.03–0.04; Alexander et al., 2007). Anhydrous IDPs, which are likely cometary in origin, also contain high nitrogen abundances (Keller et al., 2004). Atomic N/C ratios were not determined for the Murchison globules in this study. EELS measurements performed by Garvie and Buseck (2004) did provide chemical compositions for several meteoritic nanoglobules. Most of these had N/C ratios in the range of bulk IOM. However, a few did show higher nitrogen abundances, with N/C as high as 0.10–0.16 in nanoglobules from Tagish Lake (C-un-grouped) and Cold Bokkeveld (CM2), similar to that observed in the Wild 2 samples.

Taken together, the results from the Track 80 organic section and the Track 80 globule demonstrate that comets contain very similar organic solids to chondrites. Morphologically, chemically, and isotopically, the Stardust Track 80 globule resembles at least one class of the nanoglobules found in meteorites and IDPs, whereas the Track 80 organic section is morphologically, isotopically, and chemically similar to non-globular IOM in meteorites. Both IOM-like carbonaceous matter and organic nanoglobules appear to be ubiquitous in the Solar System and were sampled by comets and primitive meteorites during their accretionary phases.

4.2. Organic globule formation

Although various mechanisms have been proposed to explain the formation of organic nanoglobules, most rely on one of three general methods: (i) processes that occur in circumstellar environments, (ii) interaction with interstellar or nebular ice in extremely cold environments, or (iii) aqueous processes on parent bodies. Spherical presolar graphites and SiC grains with highly anomalous C isotopic compositions have been observed in several meteoritic acid residues and are believed to have formed in the circumstellar envelopes of asymptotic giant branch stars or within expanding supernova ejecta (Bernatowicz et al., 1996; Nittler, 2003; Croat et al., 2005). Recently, organic globules have been synthesized from simple aromatic molecules exposed to helium plasma, suggesting that such objects could form from PAHs around evolved stars or possibly within the primitive solar nebula (Saito and Kimura, 2009). Presolar graphites range in size from 250 nm to tens of μm (Croat et al., 2005), generally larger than that observed for meteoritic nanoglobules (Garvie and Buseck, 2006; Nakamura-Messenger et al., 2006), but consistent with the cometary globules described here. However, the plasma-generated globules had diameters of less than 150 nm (Saito and Kimura, 2009), much smaller than most meteoritic nanoglobules and the cometary globules. Presolar graphite and SiC grains have C and N isotopic ratios that span several orders of magnitude, including rare grains, thought to originate in supernovae, with ^{15}N enrichments and relatively close-to-solar $^{12}\text{C}/^{13}\text{C}$ ratios, as observed in the Track 80 globule. Thus, strictly speaking, an origin as a supernova condensate cannot be ruled out. However, the rarity of such compositions in the

general presolar grain population and the similarity of the Track 80 globule composition to other ^{15}N isotopic hotspots in extraterrestrial samples argue against a circumstellar origin for this globule.

Organic nanoglobules in the Tagish Lake and Bells carbonaceous chondrites have been hypothesized to form from organic molecules in ice grains in the interstellar medium or outer solar nebula (Nakamura-Messenger et al., 2006; Messenger et al., 2008). In this model, ion-molecule reactions enrich organics on the surface of ice grains in ^{15}N and/or D while simultaneously generating a coherent surface coating through the gradual accumulation of organic matter and the generation of more refractory organic matter by UV irradiation. At some point, the ice is removed through sublimation or melting, leaving a hollow spherical globule. Radiation processing may accelerate both ice removal and the formation of increasingly refractory organic matter, eventually resulting in impermeable nanoglobules. Afterwards, the hollow nanoglobules are transported throughout the protostellar disk as discrete grains, which may eventually be incorporated into comets, asteroids, and IDPs.

The highly aromatic nature of the Track 80 globule indicates that it formed from PAH-like or other refractory organic precursors, which is consistent with the formation model proposed for the Tagish Lake nanoglobules (Nakamura-Messenger et al., 2006). However, the Tagish Lake globules also appear to contain aliphatic and oxygenated functional group chemistry (Nakamura et al., 2003), which has not been observed in the Track 80 globule. In fact, a wide variety of chemical functionality may be produced by ion-molecule reactions on ice grains, which might be expected to result in chemically heterogeneous nanoglobules. Similarly, D/H and $^{15}\text{N}/^{14}\text{N}$ fractionation may proceed via several reaction pathways depending on which organic molecules/ions are present (as described below), resulting in varied levels of isotopic enrichment. In general, however, significant D enrichments should be present in organic matter that formed in cold extraterrestrial environments. Based on these assumptions, the homogeneous aromatic chemistry and the lack of a significant D enrichment in the Track 80 globule suggest either that it did not form by these mechanisms or that its chemistry and isotopic composition have been significantly altered following its formation.

If transient aqueous fluids were present on Comet Wild 2, then organic globules may have formed by interaction with water. Experimental irradiation of interstellar analog ices with UV light has been shown to synthesize amphipathic molecules, which may form organic vesicles when the ice melts (Dworkin et al., 2001). The amphipathic molecules created during these experiments require the initial presence of methanol in the ice, but other alcohols or carboxylic acid will likely perform the same function. In this model, liquid water must be present at some time so that the amphipathic molecules can arrange themselves into globules and vesicles. Evidence of aqueous parent body processing is common in meteorites, and laboratory-produced, spherical, carbonaceous grains have been generated during hydrothermal processing of meteoritic IOM analog materials (Cody et al., 2009). However, aqueous fluids are

not expected to be abundant on cometary bodies. Localized heating may occur on the comet during accretion or mass-redistribution events, which can temporarily generate small pockets of liquid water. Transient heating may also occur during shock events involving interstellar or protostellar ice, although such events would be more prevalent in dense stellar cores or during initial star formation. In these vacuum environments, however, water-ice is expected to sublime rather than melt. If liquid water does result from grain-grain collisions or shock wave events (Ciesla et al., 2003), then organic globule morphology could be formed in the protosolar nebula, even though most of the isotopic fractionation occurred in the molecular cloud.

Capture of cometary ices in Stardust aerogel is another transient heating process (Domínguez et al., 2004; Noguchi et al., 2007), which may, in principle, result in nanoglobule formation. Captured ice grains would have volatilized quickly (on the order of several microseconds), so any globule morphologies created by this process should have formed extremely quickly from small amounts of liquid water. Globules formed at the time of capture would be expected to have similar organic chemistry and functionality to nearby non-globular cometary organic matter. An exception to this rule could be made for labile organic molecules that are substantially more amphipathic than the remaining organic matter. Amphipathic organic molecules would contain polar terminal functional groups such as alcohol (C—OH), carbonyl (C=O), and nitrile (C≡N). Although polycyclic aromatic hydrocarbons are typically non-polar, carbon atoms at the edges of ring structures can be modified with polar functional groups. If present in interstellar globules, these polar functional groups should be observable by XANES, as they are in the Track 2 globule.

The organic composition of the Track 80 globule indicates that it probably did not form during transient heating of interstellar ices or particle capture. Although it and the associated Track 80 organic section are both enriched in ^{15}N , the organic functionality of the globule is very distinct from that of the other cometary organic matter and, due to its highly aromatic nature, the organic matter in the globule is significantly less amphipathic than the latter. Since a more amphipathic and more polar organic fraction would be expected to be extracted from cometary organic matter and form globule-like morphologies during transient heating events, the highly aromatic Track 80 globule could not have formed via this process and most likely did not form during particle capture. Similarly, it is not likely that the globule formed out of amphipathic organics generated by UV photolysis. Rather, the Track 80 globule morphology was present in comet Wild 2 prior to capture by the Stardust spacecraft.

It is possible that the highly aromatic chemistry observed in the Track 80 globule is a post-formation processing signature of exposure to high-energy nebular or interstellar environments. As observed in the Track 2 globule, after extensive damage during TEM analysis with 200 keV electrons, aromatic carbon may be created and other functional groups may be destroyed by radiation processing. It may be possible, then, that exposure to high-energy ionizing radiation for long periods of time may

aromatize a complex aliphatic nanoglobule, which would also likely alter its D/H composition. This process is distinct from direct “knock-on” damage from ion bombardment, which leads to significant loss of N and O, producing elemental amorphous carbon (Strazzulla and Baratta, 1992). Amorphized organic matter from irradiation has been reported in primitive chondrites (Busemann et al., 2007) and Wild 2 carbonaceous samples (Rotundi et al., 2008). Highly aromatic globules may indicate significant exposure to galactic cosmic rays, which typically include a few percent of high-energy electrons (Yoshida, 2008), or to energetic electrons in solar wind and other solar mass outflows.

Observed fluxes of high-energy electrons from such sources can be compared to the electron fluence to which the Track 2 globule was exposed during TEM analysis ($\sim 10^7$ electrons/nm²), which had completely altered its organic chemistry. It should be noted, however, that significant chemical change may be induced in organic samples exposed to far less fluence (likely as little as 10^5 electrons/nm²). Unfortunately, galactic cosmic ray electrons with energies that are most likely to affect chemical change in 1–2 μm organic particles (between 1 keV and 1 MeV) are difficult to observe directly, since such electrons with energies less than 1 GeV are modulated by the solar heliosphere (Yoshida, 2008). Within the interstellar medium, extrapolations of the observed cosmic ray electron flux spectrum to lower energies are poorly constrained (Strong et al., 2000), and the total inferred electron flux can range from 10^{-1} to 10^5 electrons/cm² per second, based on the model chosen (Padovani et al., 2009). Based on these electron fluxes, it would take anywhere from 10^7 – 10^{15} years to achieve a comparable electron fluence to which the Track 2 globule was exposed during TEM. Within the solar nebula, fast solar wind electrons with energies between 1 keV and 1 MeV can be measured by various instruments on the WIND and STEREO spacecrafts, indicating total electron fluxes on the order of 10^5 electrons/cm² per second at 1 AU (Lin et al., 1995, 2008). This value suggests that it would take about 10^7 – 10^9 years to match the electron fluence to which the Track 2 globule was exposed during TEM. Although this residence time in the solar nebula is too long to complete the irradiation before accretion onto comet or asteroid parent bodies (Nichols, 2006), there are many factors which may reduce this time. The solar wind flux has a $1/R^2$ dependence away from the Sun, which would require organic globules to be present in the inner regions of the nebula during this time. Secondly, the particle flux from the early Sun could have been as much as 1000 times larger than it is today (Wood et al., 2002), and events such as solar flares and coronal mass ejections can increase the flux of high-energy electrons by several orders of magnitude (Lin and Hudson, 1976; Simnett et al., 2002). Although our estimates are currently poorly constrained, we find it reasonable that the original organic chemistry of nanoglobules could be significantly altered by energetic electrons on achievable timescales in both the interstellar medium and within the solar nebula. This may provide a novel and relevant mechanism for both the formation of PAHs and D enrichments in molecular clouds.

4.3. Interstellar cloud chemistry

Ion–molecule and gas–grain interactions in extremely cold interstellar environments can result in large isotopic fractionation of H and N, although there are many conditions under which D may be significantly enriched without a simultaneous ^{15}N enrichment (Herbst, 2003). Although organic matter in IDPs and primitive meteorites is typically enriched in both D and ^{15}N , the enrichments are largely decoupled at the microscale, with the largest D and ^{15}N enrichments localized in distinct isotopic hotspots (Robert and Epstein, 1982; Keller et al., 2004; Busemann et al., 2006). Nonetheless, ^{15}N hotspots in these samples are generally somewhat D-rich, in contrast to the Track 80 cometary globule, in which the ^{15}N enrichment is present without a corresponding D anomaly (although, as mentioned above, we cannot rule out a modest D enrichment due failure of the support film during the D/H measurement). This observation may indicate either that there are conditions under which N isotopic fractionation occurs without H isotopic fractionation, or that the D enrichments are removed by subsequent processing.

Current models of nitrogen isotopic fractionation depend on the selective depletion or freezing out of carbon monoxide and alcohols in dense molecular cloud cores in order to reach ^{15}N enrichments observed in the Track 80 globule (Charnley and Rodgers, 2002). In the presence of gaseous CO, the ^{15}N enrichment factor cannot exceed about 1.3 above terrestrial values in the standard molecular cloud model (Terzieva and Herbst, 2000). In interstellar clouds, ^{15}N fractionation up to +10,000‰ can occur at low temperatures around 10 K in ammonia ice mantles (Rodgers and Charnley, 2008a), but is less than +4000‰ for nitrogen heterocycles in PAHs (Rodgers and Charnley, 2004) or nitrile functional groups (Rodgers and Charnley, 2008b) adsorbed onto icy grains. Astronomical observations of CN in comets (Schulz et al., 2008) suggest that nitrile functional groups may be the carriers of presolar ^{15}N , and ^{15}N enrichments in IDPs appear to be associated with amine (C–NH_x) bonds (Keller et al., 2004). However, given that the organic matter in the Track 80 globule is predominantly aromatic and lacks evidence of abundant nitrile or amine functionality, PAHs appear to be the carrier of anomalous ^{15}N . Unfortunately, N-XANES was not performed on this globule prior to NanoSIMS analysis to confirm the presence of nitrogen heterocycles, such as pyridine or pyrrole, which have nitrogen photoabsorptions at 398.8 and 402.2 eV. Due to the diversity of observed and implied organic carriers of anomalous ^{15}N , many fractionation mechanisms may regularly occur in dark molecular clouds or the outer cold regions of the solar nebula.

Models of D isotopic fractionation indicate that it is also strongly dependent on temperature, and large isotopic anomalies may be generated by ion–molecule reactions in interstellar gases with temperatures up to 70 K (Millar et al., 1989). Similar deuterating reactions may also occur in collapsing protoplanetary disks as close in as 30 astronomical units from the central star (Aikawa and Herbst, 1999) in the region of the Kuiper belt where many comets and icy

bodies accumulate. Organic molecules adsorbed to the surface of ice and dust grains may become D-enriched through gas–grain interactions (Tielens, 1983). Deuterated primary molecules within ice grains will be transformed into reactive species during UV photolysis, propagating the D enrichment to larger organic molecules (Sandford et al., 2000, 2001), which may then be released as isotopically-anomalous organic particles within the molecular cloud or solar nebula. Gas phase D enrichments can be enhanced by selective depletion of CO (Bacmann et al., 2003), which is required for large ^{15}N enrichments. In selectively depleted cold environments, both ^{15}N and D may be enriched simultaneously, producing organic molecules or globules with anomalies in both isotopes, such as those observed in globules from carbonaceous chondrites and IDPs (Nakamura-Messenger et al., 2006; Messenger et al., 2008).

As indicated by TEM-based irradiation of cyanoacrylate and epoxy by 200 keV electrons, significant D enrichments may be generated in extraterrestrial organic matter by long term exposure to high-energy electrons. Such enrichments may occur in warmer regions of the interstellar medium and do not require the specific molecular cloud compositions necessary for ion–molecule or gas–grain isotopic fractionation mechanisms. The estimated residence times (perhaps as little as 10 million years) necessary to produce significant chemical and isotopic changes in interstellar organic matter suggest that electron radiolysis is a potentially important mechanism in molecular clouds. This process would be likely to be much less effective within much of the solar nebula except for the innermost regions, where the electron flux is similar to that of cosmic rays in the interstellar medium. However likely this mechanism of D fractionation may be, the potential for D enrichment from electron irradiation should be considered in future interpretations of extreme D enrichments in meteorites and other planetary materials.

In PAHs and PAH-like organic molecules, ^{15}N atoms will be primarily located in heteroatomic, aromatic moieties, while D atoms are attached to the edges of polyaromatic domains. Due to the relative stability of nitrogen in heteroatomic sites, the ^{15}N enrichment of PAHs should not change much over time. Conversely, hydrogen and D atoms on the edges of PAHs may be exchanged relatively easily by a variety of mechanisms, including exposure to UV radiation within the solar nebula (Sandford et al., 2001). If D-rich organic matter is not protected within cometary bodies or other planetesimals, it is possible that UV-driven hydrogen exchange could drive the D/H ratio back towards solar abundances or the average isotopic composition of the local nebular environment. Closer to the protostar, D/H may be steadily increased by interactions with high-energy solar wind electrons, although the rate of D enrichment via this mechanism is likely slower than isotopic re-equilibration by UV irradiation. Similarly, exposure to aqueous fluids on a parent body may also re-equilibrate the hydrogen isotopic composition of an organic globule without affecting its nitrogen composition. The isotopic composition observed in the Track 80 globule may be a result of such processes.

5. CONCLUSIONS

Organic nanoglobules containing D and/or ^{15}N isotopic anomalies appear to have been widespread in the early solar system. At least one of the two hollow organic globules described herein was once a component of Comet 81P/Wild 2, as revealed by its isotopic composition and association with aerogel from the Stardust collector tray, and is the first authentic organic globule reported in cometary samples. The Track 80 globule, composed of highly aromatic PAH-like organic matter, contains a ^{15}N enrichment that is similar to other Wild 2 isotopic hotspots and anomalous grains in primitive IDPs and chondrites, which also likely include some nanoglobules. The similarity in chemistry and nitrogen isotopic composition to a globule from the Murchison meteorite indicates that Wild 2 and the Murchison parent body sampled similar reservoirs of primitive organic matter in the early Solar nebula. However, the N/C ratio of this cometary globule (0.10–0.15), like other carbonaceous Stardust samples, is significantly higher than typical meteoritic organic matter, suggesting that the organic matter composing the Track 80 globule is some of the most primitive in our Solar System. In contrast, the presence of a D enrichment, but isotopically normal nitrogen composition, in the Track 2 globule means that a cometary origin cannot be definitively determined. Instead, it likely represents a cyanoacrylate contaminant with a D enrichment resulting from electron irradiation during TEM analysis. We have demonstrated that relative D enrichments of 1000‰ can be induced in ultramicrotome sections of common organic adhesives during typical TEM analyses of Stardust samples, creating ambiguity for the interpretation of potentially interstellar organic matter that has been observed with TEM prior to measuring its isotopic composition. This experimental result also indicates that electrons with energies between 10^3 and 10^6 eV may play an important role in processing and deuterating organic molecules in the extraterrestrial environments.

At present, there is no model of the formation and processing history of organic nanoglobules that fully explains the range of observed morphologies, chemistries, and isotopic compositions. The widespread occurrence of globules in diverse parent bodies could reflect either their prevalence throughout the protosolar molecular cloud prior to its collapse, or formation in the solar nebula by a common process from a common set of precursors, perhaps followed by large-scale material transport (e.g. Ciesla, 2007). The anomalous abundances of ^{15}N and/or D preserved in these globules suggest isotopic fractionation in cold molecular clouds, although fractionation in the outer regions of the protosolar nebula cannot be ruled out.

The cometary Track 80 globule is highly enriched in ^{15}N and slightly depleted in ^{13}C , but appears to lack a correlated large D enrichment. This decoupling of ^{15}N and D enrichments could have occurred at the time of formation as a result of the molecular composition of the environment, or through subsequent processing events, including radiation exposure or aqueous alteration. One possible origin for the Track 80 globule is within a cold (~ 10 K), dense, molecular cloud core where PAHs were prevalent, but

carbon monoxide had been selectively depleted. The ^{15}N enrichment of organic matter in such an interstellar environment could be increased if PAHs were present on the surface of ice grains. Exposure to cosmic ray electrons may have aromatized the organic matter on the surface and volatilized the internal ice grain, leaving a hollow organic globule. Alternatively, the organic matter in a fully-formed globule may have been aromatized by residence in the inner regions of the nebula. Irradiation of the globule by UV photons while in the relatively warm nebula may also have led to isotopic re-equilibration of D/H towards typical solar values without affecting the ^{15}N protected in stable heteroatomic aromatic moieties. Due to the highly aromatic nature of the Track 80 globule, its morphology is most likely not a result of exposure to transient aqueous fluids on the cometary parent body, although such exposure may also serve to re-equilibrate its D composition.

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