## **Supporting Information**

## Cody et al. 10.1073/pnas.1015913108

## **SI Materials and Methods**

Carbon X-ray Absorption Near Edge Structure Spectroscopy (C-XANES). The analysis of organic matter in interplanetary dust particles (IDPs) and the recently returned Comet 81P/Wild2 samples/particles requires the ability to extract molecular information from organic rich domains that are in many cases no more than a micron in diameter. The most powerful tools for such analyses are scanning transmission (soft) X-ray microscopes/spectrometers (STXMs). STXMs utilize Fresnel zone plate optics providing a theoretical spot size of 30 nm, in optimum cases smaller structures (approximately 15 nm) can be resolved. In the present case, a STXM located at beamline 5.3.2 at the Advanced Light Source, Lawrence Berkeley Laboratory, was used for all analyses. The maximum scanning rates for the STXM at BL5.3.2 is 12 Hz, with a scanning range of  $4,000 \times 2,000$  pixels covering a region up to  $20 \times 4$  mm, with a minimum step size 2.5 nm. Sample position precision during spectra acquisition is better than 50 nm (controlled by laser interferometery).

C-, N-, and O-XANES spectra are typically acquired using a multispectral imaging method. The "Stacks" method relies on creating a highly aligned hyper-spectral data cube of x by y pixilated images acquired over a range of energies that span a given XANES region. In the fine structure regions of the near edge, the energy step size ( $\Delta E$ ) employed typically is 0.1 eV; in the less featured preedge and post edge regions, energy steps of 1–2 eV are typically sufficient for spectral resolution.

C-XANES reveals the presence and abundance of various organic functional groups via the detection of characteristic absorption features in the near edge (preionization) region of the X-ray absorption spectrum. In general, absorption at the lowest energies (approximately 285.0 eV) is well described by photoexcitation of carbon 1s electrons to low energy, unoccupied,  $\pi^*$ orbitals of alkenyl and aromatic species (C and H substituted). Carbon substitution with more electronegative atoms (e.g., N and O) results in shifts to higher excitation energies, e.g., 288.5 eV in the case of carboxyl 1s- $\pi^*$  transitions. Saturated carbon, i.e., methyl and methylene, also exhibit relatively intense absorption in the near edge region, where the electronic transition for saturated carbon involves photo-excitation of a 1s electron to a hybrid state involving mixing of a 3p Rydberg state with a  $\sigma^*$  C-H orbital, commonly identified as a  $1s-3p/\sigma^*$  transition. The intensity of the  $1s-3p/\sigma^*$  absorption is a strong function of the number of H's per carbon (i.e., this transition is most intense for methyl groups) and very weak for methine carbon. The energy of the  $1s-3p/\sigma^*$  transition is also effected by the electronegativity of bonded species (e.g., N and O) this leads to a shift of the  $1s-3p/\sigma^*$  transition to higher energies; e.g., from ~287.8 eV for simple hydrocarbons up to 289.3 eV for alcohols. For most organic compounds, the absorption spectrum at energies exceeding the carbon 1s ionization edge (i.e., approximately 290.8 eV for benzene) consists of very broad spectral features, corresponding to highly delocalized excited states [in some cases referred to as  $1s - \sigma^*$  virtual state transitions].

To perform STXM analysis samples must be microtomed to 100–150 nm thickness. Samples of IOM, Stardust Organics, and the formose polymer are embedded in molten sulfur (mp = 117 °C) that is then quenched to solid providing a sample that may be readily microtomed using a diamond knife with samples captured on standard SiO coated TEM grids. The sulfur-embedding matrix is removed completely through sublimation.

<sup>13</sup>C Solid-State Nuclear Magnetic Resonance Spectroscopy. All NMR experiments were performed on a Varian-Chemagnetics Infinity 300 NMR spectrometer installed in the W. M. Keck Solid State NMR facility at the Geophysical Laboratory, Carnegie Institution of Washington. One-dimensional cross-polarization (CP; <sup>1</sup>H-<sup>13</sup>C) Solid-state NMR experiments were performed using the following experimental parameters. Cross-polarization was performed by the variable amplitude method, via ramping up the power of <sup>13</sup>C channel while maintaining constant Rf power on the <sup>1</sup>H channel. The proton 90° pulse width corresponded 4 µs, the CP contact time was 4.5 ms, high power <sup>1</sup>H decoupling was performed during signal acquisition where the decoupling field  $(\omega_1/2\pi)$  was 70 KHz. Magic angle sample spinning was performed at  $(\omega_r/2\pi)$ 12 KHz. A recycle delay of 1s is sufficient to negate  $T_1$  saturation. A three-pulse (on the <sup>1</sup>H channel) background suppression scheme was implemented prior to initiation of the CP experiment to eliminate any background signal from the Vespel components in proximity to the Rf coil. The 1D experiments were performed using a Chemagnetics 5 mm double resonance probe.

The magic angle turning (MAT) experiment was performed using the Triple Echo method (1) using a Chemagnetics 7.5 mm diameter double resonance probe. Slow and steady  $(\Delta \omega_r/2\pi \text{ smaller than } \pm 1 \text{ Hz})$  sample spinning was achieved using a Chemagnetics microprocessor controlled MAS speed controller, specialized rotor drive tips and air flow restrictors provided by Varian-Chemagnetics, and employing 6 marks on the top of the rotor so that an apparent  $\omega_r/2\pi$  of  $240 \pm 1$  Hz measured at the MAS controller unit actually corresponds to 40 Hz rotation frequency. The MAT experiment was first optimized with a simple organic standard, Vanillic acid, which yielded both a high quality isotropic projection in the evolution dimension and well resolved powder patterns for different carbon atoms in the MAS dimension. During decoupling periods, the decoupler field  $(\omega_1/2\pi)$  was 62.5 KHz. Pulse widths for <sup>1</sup>H90, <sup>13</sup>C90, and <sup>13</sup>C180 were 5 µs, 5.75 µs, and 11 µs, respectively.

For analysis of Murchison IOM approximately 250 mg was isolated from the meteorite using the standard aqueous CsF method (2). The dwell period in the second dimension was set to 40 µs corresponding to a spectral width of 25 KHz in the evolution dimension vs. 50 KHz in the MAS dimension. The decay of the echo in the second dimension is relatively rapid so only 25 acquisition points were acquired. Four experiments with durations of approximately 7 days each were necessary to provide sufficient S/N for analysis. The hyper complex spectra were apodized with 200 Hz shifted Gaussian line broadening prior to the first Fourier transformation, and 200 Hz Lorenztian broadening prior to the second Fourier Transformation. Both dimensions were zero filled to 1024 points prior to Fourier transformation. The four experiments were then coadded to provide the final spectrum. Fits of the powder patterns at various isotropic frequencies are constrained by the requirement that  $\delta_{iso} = 1/3 (\delta_{33} + \delta_{22} +$  $\delta_{11}$ ); thus a slice in the MAS dimension at a given  $\delta_{iso}$  in the evolution dimension fit to a second rank tensor powder pattern must yield the same  $\delta_{iso}$  for the MAS dimension.

Synthesis of Formaldehyde Polymer. The polymerization of formaldehyde proceeds first through the condensation of formaldehyde to form glycolaldehyde. This step is typically very slow, however, the formose reaction is catalyzed by glycolaldehyde, thus the reaction is autocatalytic. Our starting composition for the formose reaction contained equimolar concentrations of formaldehyde and glycolaldehyde (following the typical formose protocol, e.g., (3). Formaldehyde was added as paraformaldehyde that hydrolyzes very rapidly at high pH to yield pure formaldehyde. The reactions were performed as suspensions over excess CaOH (solution pH approximately 12), incubated at 50 °C. The formose reaction proceeds very rapidly with the solution turning yellow within minutes then a deep red brown over hours and days. Typically within a few hours a black solid precipitate sediments at the bottom of the reaction vessel; the precipitate continues to sediment out for several days while the solution color stabilizes to a deep red-orange. Upon several days of incubation, the supernatant is removed and the black solid is washed with dilute HCL to remove the calcium ions. The solids are then dried under N<sub>2</sub> gas flow. The yield of polymer relative to the starting compounds is typically 4 to 5 wt. %; no attempt was made to increase or optimize the yield.

Heating of the formose polymer was performed in sealed glass ampules that were charged with the dry polymer and distilled, deionized water. Heating was performed in a GC oven for various durations and temperatures.

**Secondary Ion Mass Spectrometry Isotopic Measurements.** Following STXM analysis, the microtomed slice of Stardust sample FC9, 13, 1, 8 (SD2) was measured for its C and N isotopic composition with a Cameca NanoSIMS 50L ion microprobe at the Carnegie Institution of Washington. The TEM grid containing the sample was attached to an Al stub with colloidal Ag paint and the sample

 Riccardo A, Carrigan MA, Olcott AN, Benner SA (2004) Borate minerals stabilize ribose. Science 303:196. was coated in a thin layer of Au to mitigate charging under the primary ion beam. NanoSIMS data were collected in imaging mode. An approximately 1 pA, 100 nm Cs<sup>+</sup> beam was rastered over the sample with simultaneous collection of secondary ions of <sup>12</sup>C<sup>-</sup>, <sup>13</sup>C<sup>-</sup>, C<sup>14</sup>N<sup>-</sup>, C<sup>15</sup>N<sup>-</sup>, and secondary electrons. The Limage software package (L. R. Nittler, Carnegie Inst.) was used to process the resulting isotopic images to determine isotopic ratios. A synthetic Si<sub>3</sub>N<sub>4</sub> powder and insoluble organic matter from the CR chondrite GRO 95577 (4) were also measured as standards to correct for instrumental mass fractionation and differential gains of the ion detectors. SD1 was found to have  $\delta^{13}C = -57 \pm 44\%$  and  $\delta^{15}N = +70 \pm 44\%$  (2 $\sigma$  errors). The <sup>15</sup>N enrichment is clearly outside the range of terrestrial isotopic compositions and comparable to compositions observed in organic matter derived from primitive chondrites (4). This proves an extraterrestrial origin for this sample. A previous measurement on a different microtome slice of the same Stardust sample (5) also found an anomalous D enrichment:  $\delta D = 900 \pm 700\% (2\sigma)$ .

Focused Ion Beam Milling of QUE 97008. A,  $5 \times 10$  micron, ultrathin (approximately 100 nm) section of the matrix of QUE 97008 was prepared by in situ lift-out in a FEI Nova 60 focused ion beam-scanning electron microscope at the Naval Research Laboratory. SEM imaging revealed that the section transected an 800-nm hollow globule, which was confirmed by STXM to be organic carbon.

- Alexander CMO, Fogel ML, Yabuta H, Cody GD (2007) The origin and evolution of chondrites recorded in the elemental and isotopic compositions of their macromolecular organic matter. *Geochim Cosmochim Acta* 71:4380–4403.
- McKeegan KD, et al. (2006) Isotopic compositions of cometary matter returned by stardust. Science 314:1724–1728.

<sup>1.</sup> Hu JZ, et al. (1995) Magic-angle-turning experiments for measuring chemical-shift-tensor principal values in powdered solids. J Magn Reson Ser A 113:210–222.

Cody GD, Alexander CMO, Tera F (2002) Solid-state (<sup>1</sup> H and <sup>13</sup>C) nuclear magnetic resonance spectroscopy of insoluble organic residue in the Murchison meteoritre: A selfconsistent quantitative analysis. *Geochim Cosmochim Acta* 66:1851–1865.