

Supporting Information

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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 20×4 mm, with a minimum step size 2.5 nm. Sample position precision during spectra acquisition is better than 50 nm (controlled by laser interferometry).

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 pixelated 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 (ΔE) 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 photo-excitation of carbon 1s electrons to low energy, unoccupied, π^* 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- π^* 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 σ^* C-H orbital, commonly identified as a 1s-3p/ σ^* transition. The intensity of the 1s-3p/ σ^* 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/ σ^* transition is also effected by the electronegativity of bonded species (e.g., N and O) this leads to a shift of the 1s-3p/ σ^* 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- σ^* 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 ($mp = 117^\circ\text{C}$) 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.

^{13}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; ^1H - ^{13}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 ^{13}C channel while maintaining constant Rf power on the ^1H channel. The proton 90° pulse width corresponded 4 μs , the CP contact time was 4.5 ms, high power ^1H 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 ^1H 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 ($\Delta\omega_r/2\pi$ smaller than ± 1 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 ± 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 $^1\text{H}90$, $^{13}\text{C}90$, and $^{13}\text{C}180$ 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 Lorentzian 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 $\delta_{\text{iso}} = 1/3 (\delta_{33} + \delta_{22} + \delta_{11})$; thus a slice in the MAS dimension at a given δ_{iso} in the evolution dimension fit to a second rank tensor powder pattern must yield the same δ_{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,

