Supporting Online Material for

Interstellar Chemistry Recorded in Organic Matter from Primitive Meteorites

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Material and Methods

We used a Cameca ims-6f ion microprobe (Carnegie Institution of Washington) with a Cs^+ primary beam (~5-10 pA, 12 keV) at a spatial resolution of ~1.5 μm for the measurements of D, H and ^{12}C, and a Cameca NanoSIMS 50 (Max-Planck-Institut Mainz) at a spatial resolution of ~100 nm for the detection of ^{12}C, ^{13}C, $^{14}N^{12}C$, $^{15}N^{12}C$ and Si in multi-collection (<1 pA). Measurements were made in scanning imaging mode where the primary Cs^+ beam is rastered over the sample and secondary ions are synchronously collected, resulting in 256x256 pixel, 16-bit isotopic images. Measurements were divided into 5 to 15 planes with measurement times of about 3 and 11 minutes per image plane for the 6f and NanoSIMS measurements, respectively. Shifts between individual image planes were corrected.

We analyzed 61 fragments of high-purity insoluble organic matter (IOM), obtained by dissolution in CsF-HCl (*1*) and 33 matrix fragments. The samples, with typical diameters of 15-25 μm were pressed into clean gold foils and preheated at ~60°C in vacuum for at least 12 hours prior to analysis. Prior to data collection, all samples were exposed for 5-20 min to a high Cs^+ current (150-200 pA) in order to remove surface contamination and reach sputtering equilibrium. A few large fragments of Bells IOM were embedded in S and sectioned by ultramicrotome into slices of ~500 nm thickness. The slices were placed onto a clean Au foil and the S allowed to sublimate on a hot plate.

The instrumental mass fractionation (IMF) for D/H and C/H was determined with well-characterized terrestrial materials (a coal, an anthracite, amphibole and a lipid with the chemical formula $C_{30}H_{50}O$) and bulk meteoritic IOM. The standards cover a wide range of $-150 \leq \delta D \leq +3000‰$ and $0.6 \leq C/H \leq 6.3$ (atomic) and were calibrated with standard stable isotope mass spectrometry. For N and C, the IMF was corrected for using the measured bulk isotopic compositions of meteoritic IOM and a synthetic organic solid (1-hydroxybenzotriazole hydrate).

All elemental and isotopic distribution maps were divided into equally-sized hexagonal "regions of interest" (ROI) of 2 μm and 500 nm diameters for the 6f and NanoSIMS, respectively, to quantify isotopically anomalous regions (Table 1). These diameters are in general slightly larger than the actual beam sizes. In addition, D and ^{15}N rich hotspots were separately defined and evaluated. For the ims-6f measurements, count rates were interpolated between image planes to take into account temporal drift. Quoted uncertainties are based both on counting statistics and the uncertainty in the IMF, based on measurements of multiple standards.

Supporting Text

Some of the D hotspots found in matrix fragments of Tagish Lake (e.g., the region in the upper left of Fig. 2 of the main text) likely correspond to the "nano-globules" observed in this meteorite (*2*). Nano-globules represent a significant sub-fraction of the organic matter in Tagish Lake (up to ~1 weight %), are enriched in ^{15}N (*3*) and might be a primitive product of the irradiation of interstellar ices before or during the formation of the solar system (*1*). Our work indicates that at least some are also highly D-enriched.

We found only a few C isotope anomalies. All but one originate from presolar SiC grains (*4, 5*), e.g., in the Al Rais matrix, and in EET 92042 and Bells IOM separates, with $^{12}C/^{13}C$ ratios as low as ~30 (the solar ratio is 89). However, an assemblage in the IOM of EET 92042 (~5 μm^2) shows a large negative $\delta^{13}C$ anomaly ($-113 \pm 14‰$) and a $\delta^{15}N$ value of $1150 \pm 40‰$. This region compares well with an interstellar ^{15}N-rich region previously reported in an IDP (*6*), which exhibits a negative $\delta^{13}C$ value of $-70‰$ and a $\delta^{15}N$ anomaly of $1270‰$.

Given the potential link between the organic material incorporated into the cometary and asteroidal parent bodies of IDPs and primitive meteorites, it is instructive to contrast our isotopic data from meteoritic organics with those of cometary H_2O and HCN. Both data sets exhibit the presence of pristine signatures. The δD values of $16300‰$ and $19400‰$ in CR chondrite hotspots are slightly larger than the value of δD ~$13300‰$ found in bulk cometary HCN (*7*) and much larger than δD in cometary water (δD ~$1000‰$, *8*).

Water with δD values of up to $3700‰$ in two ordinary chondrites is presumed to be interstellar (*9*) and, although only found in one meteorite class (LL chondrites), was taken as evidence that water in comets was reprocessed during the formation of the solar system (*10, 11*), and that the detection of unaltered interstellar material (*7*) in comets would be difficult. The N isotopic composition in comets is variable (*8*). While HCN shows negative $\delta^{15}N$ values that are close to the solar composition, cometary CN yields $\delta^{15}N$ values of $600-940‰$. HCN is, thus, not a major source of CN (*12*). Consequently, the N isotope composition of cometary CN is likely that of interstellar organic compounds present in comets (*8, 12*).

Supporting References and Notes

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