Supplementary Information for

Multiple generations of grain aggregation in different environments preceded solar system body formation

Hope A. Ishii, John P. Bradley, Hans A. Bechtel, Donald E. Brownlee, Karen C. Bustillo, James Ciston, Jeffrey N. Cuzzi, Christine Floss and David J. Joswiak

Email: hope.ishii@hawaii.edu
Materials and Methods

Specimen preparation and analysis. U217B19, a non-porous, compact IDP, was embedded in a ~200 µm diameter elemental sulfur (S) bead that was then embedded in epoxy to provide support during thin-sectioning using an ultramicrotome equipped with a diamond knife (Fig. S1) (1). The sections, ~75 nm in thickness, were transferred to thin-film carbon substrates on copper and gold mesh TEM support grids, and the S was permitted to sublime to enable analysis of the bare particle. LT39 is a non-porous organic carbon-rich fragment, or ‘clast’, of a large so-called “giant cluster” IDP, U220GCA, that was embedded directly in epoxy and prepared using the same procedures as above. Since the epoxy contains no detectable N, and the organic carbon in U217B19 and LT39 does, the epoxy can be distinguished from the organic carbon indigenous to the IDP. Following electron microscopy, energy dispersive x-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS), several of the thin sections of U217B19 on TEM grids were analyzed by Fourier transform infrared spectroscopy (FTIR), and a few were prepared for isotope measurements by using an FEI Helios 660 dual beam Focused Ion Beam (FIB) instrument at University of Hawaii (Honolulu, Hawaii) to deposit platinum (Pt) in site-specific and defined shapes to the underside of the 10-20 nm thick carbon substrate immediately below the IDP thin section (Fig. S2) (2). Without the Pt back-coating, the carbon support film would rapidly erode in the ion beam with consequent catastrophic loss of the sample.

Secondary ion mass spectroscopy. C, N and O isotopic compositions were measured using the Cameca 50 at Washington University in St Louis (St. Louis, Missouri). The measurements were made by rastering a ~1 pA Cs+ beam over the sections and collecting secondary ions as well as secondary electrons. The rastered beam was ~75-100 nm in diameter. Two separate measurement setups were used. In one case, we measured C and O (12C–16O–18O), and in the other, we measured C and N, with N measured as the CN molecule (12C–12C–15N–12C). Isotopic compositions are normalized to the surrounding material, which is assumed to have a normal (‘solar’) composition. Regions are considered anomalous if they deviate from normal at the 5σ level (or more) and are present 2 or more succeeding measurement layers. No C or O isotope anomalies were observed. Due to the small sizes of the components in these samples, it was not possible to distinguish terrestrial and solar O isotope compositions. (The gains in improved spatial resolution, necessary to analyze such small objects, are offset by degraded signal-to-noise.) We were unable to measure D/H due to insufficient sample mass for statistical significance. Three 15N/14N hotspots were identified with δ15N = 412 ± 37, 342 ± 34, and 326 ± 33 ‰. These hotspots, which were associated with nanoglobules in two sections, had C isotopic compositions that, within errors, were indistinguishable from terrestrial (or solar). Insufficient N signal from the lower density organic carbon matrix, only ~75 nm thick, and thin higher density mantles precluded statistically significant assessment of their N isotopic compositions.

Fourier transform infrared spectroscopy. Fourier transform infrared spectra were acquired at Advanced Light Source (Berkeley, California) Beamline 1.4, which provides diffraction-limited spatial resolution using a Nicolet Nieplan IR microscope and Magna 760 spectrometer coupled to the synchrotron source. Spectra were measured in transmission from sections of U217B19 mounted on carbon-film substrate TEM grids (Fig. 2, main manuscript). Due to the diffraction-limited spatial resolution, spectra were averaged over entire IDP sections. Other analysis methods indicate heterogeneity in the particle suggesting that IR signatures are an average of all components.
Electron microscopy. Sections were analyzed using three scanning transmission electron microscopes. Two are monochromated and dual aberration-corrected Titan scanning transmission electron microscopes (FEI Co.), the UH Titan at University of Hawaii at Manoa (UH, Honolulu, Hawaii) and the LBL TEAM 0.5 at Lawrence Berkeley Laboratory (LBL, Berkeley, California). The UH Titan is equipped with a Genesis 4000 Si(Li) solid-state x-ray energy-dispersive spectrometer (EDAX Inc.), and both instruments are equipped with Tridiem Imaging Filters/electron energy loss spectrometers (Gatan) (3). High-angle annular dark-field (HAADF) and conventional bright-field images were acquired at magnifications between 5000× and 100,000×.

Quantitative compositional mapping by energy dispersive x-ray spectroscopy (EDX) was performed using a third scanning transmission electron microscope, an uncorrected FEI Titan 80-300kV at LBL, the LBL TitanX, equipped with four windowless energy dispersive x-ray detectors with a total solid angle of 0.7 steradians. Multi-spectral images (maps) were acquired by rastering a sub-nanometer electron probe with 1.6 or 3.3 nm pixel spacings. Using Esprit 1.9 software (Bruker Corporation), rastering over iterative map frames results in a full x-ray fluorescence spectrum accumulated in each pixel. Maps were collected at 200 kV, ~700 pA beam current and a dispersion of 10 eV/pixel. Maps range from 500 to 800 pixels on a side with acquisition times from 15 to 190 minutes. Dark field images were compared before and after mapping and confirm that there was no significant alteration in shape, relative grain positions or element abundances of the specimens during mapping. The Esprit software presents element distributions in color-coded maps with intensity level at each pixel based on the integrated counts in an energy window set around characteristic K-edge x-ray energies for each element. User-specified colors indicate the spatial distribution of each element. Element maps include 3-pixel averaging to improve visualization (Fig. 1 of main manuscript and Figs. S3 and S4). Element maps are for visualization only and are not accurate representations of quantitative composition.

Spectra from selected regions of the maps of U217B19 and LT39 were summed, fit and quantified using a thin-film x-ray correction procedure (4) to obtain normalized element abundances of C, N, O Mg, Al, Si, S, Ca, Cr, Fe and Ni, given in Table S1. Experimental K-factors used in quantification were calibrated against mineral standards of known compositions to within ±2%. Only a few GEMS grains met the criteria of being sufficiently large that they extend through the entire ultramicrotomed section thickness and present in mapped regions containing an area of exposed substrate for background subtraction. The composition of the GEMS mantle on the nanoglobule (Fig. 1g) was measured by integrating a spectrum from a beam rastered over a rectangular area within the GEMS mantle on the lower left side of the nanoglobule. Because a spectrum of the underlying carbon substrate was not acquired from that sample prior to NanoSIMS analyses, C is not quantified for the GEMS mantle in Table S1, and N is below the detection limit in that region. Excluding C and N abundances, the GEMS mantle is compositionally very similar to the individual GEMS regions. Carbon, N and O abundances in organic carbon regions are given in Table S2 and were determined by fitting of the EDX spectra over the low energy range up to ~700 eV and subtracting the C background x-ray signal arising from the thin film carbon substrate from the same number of pixels (Fig. S5). At locations near the perimeter of the IDPs where contamination by silicone oil from stratospheric collection was evident (around some nanoglobule locations and in some matrix organic carbon), O content was corrected by removal of excess O according to stoichiometric assignment of one O to each Si. (Silicone oil is N-free.) Silicone oil contamination, which can be evident in Si “halos” around IDP components, was not observed in the interior regions where GEMS were mapped (Fig. S4 and Supporting Text below). At locations near GEMS amorphous silicate grains, O content was corrected in two ways to provide a lower and upper limit to the O content. Since amorphous silica, SiOx, is expected to have 1<x<2, the upper limit correction was applied by removing one O
for each Si, and the lower limit correction by removal of two O to each Si and one O to each Mg, where sufficient Mg was present to impact quantification. We chose this conservative approach to explore whether O/C ratios in organic carbon mantles on GEMS and bright organic carbon blebs (rounded regions that appear denser in C) are significantly different from those in low density organic carbon matrix (Table S1). These corrections typically result in a reduction in the O/C ratio of as much as 0.08. Resulting O/C ratios are consistently higher in mantle and bleb carbon (average O/C between 0.18 and 0.24) than in matrix organic carbon (average O/C of 0.07). (We also identified a high O/C mantle around one exotic spinel-like grain.) Stoichiometric excesses of O in GEMS can be calculated by assigning O to cations present in oxide stoichiometries. Consideration of potential O/C ratios in organic carbon within GEMS and comparison with those stoichiometric excesses of O indicates that as little as 20% to as much as 100% of excess O in the GEMS in Table S1 may be attributed to O-bearing organic carbon, depending on the abundance and type of organic carbon present. Carbon and N quantifications were refined to within ±5%, using C and N k-factors calibrated against carbon nitride (C\textsubscript{3}N\textsubscript{4}) nanowires mounted on a SiO\textsubscript{x} thin-film substrate. In this manner, the average composition of the matrix organic carbon is found to be \textasciitilde C\textsubscript{88}N\textsubscript{6}O\textsubscript{6} in U217B19 and \textasciitilde C\textsubscript{92}N\textsubscript{2}O\textsubscript{6} in LT39 (Table S2). Since the quantification procedure does not consider x-ray absorption within the specimen, the EDX measurements may underestimate abundances of low atomic number elements like C, N and O. We used the Center for X-Ray Optics (LBL) x-ray transmission calculator to evaluate x-ray absorption effects (http://henke.lbl.gov/optical_constants/). Assuming a specimen thickness of 75 nm, the N/C ratio in U217B19 may be up to 6% higher and the O/C ratio up to 3% higher than the ratios we determine using EDX. Within an ultramicrotomed section, absorption will affect relative abundance similarly in all organic carbon regions so that the differences in average O/C ratios reported in Table S2 are significant.

We used electron energy-loss spectroscopy (EELS) to quantify relative C and N abundances and investigate C, N and O bonding in the matrix organic carbon (Fig. 3 of main manuscript and Fig. S6). EEL spectra were collected on the UH Titan and LBL TEAM 0.5 microscopes. Spectra were acquired at 80 and 300 keV using an incident electron probe \~ 2Å in diameter (at focus) and 60-80 pA probe current. Energy resolution determined by zero-loss peak FWHM was 0.18 eV at 80 keV (monochromated mode) and 0.6 eV (non-monochromated mode) at 300 keV. Spectrum acquisition times varied between 1 and 30 seconds using a dispersion of 0.03 eV/channel at 80 keV and 0.5 eV/channel at 300 keV. At 80 keV, the spectrometer collection angle was 40 milliradians (mrad), and the convergence angle of the electron probe was 30 mrad. We used diffraction-coupled mode where spectra are acquired by continuously scanning the beam over a pre-defined rectangular region in order to distribute electron dose over the specimen with continuous observation of core edge fine structures, and we saw no time-dependent loss of fine structure that would result from significant radiation damage, as is observed in beam-sensitive organics at high beam currents and doses. Following background subtraction and deconvolution, C and N relative abundances were quantified to within 14% using a Fourier log procedure (5) (Fig. S6). Carbon-to-nitrogen (C/N) ratios quantified using EELS are consistent with those measured using EDX (Fig. S5).

Carbon x-ray intensity in elemental maps in Fig. 1 (main manuscript) and Fig. S3 were collected from GEMS sufficiently large that they extend through the entire ultramicrotomed section thickness and were thresholded so the thin carbon support film appears black. More intense HAADF contrast, corresponding to electron density of the components in the sample, correlates with more intense C x-ray signal from the organic nanoglobules, rims on grains and other “blebs” in the low density organic matrix and with more intense energy-loss plasmon scattered intensity (Fig. S7). These effects could be assigned to greater thickness or greater electron density, the latter caused either by compositional variations or by porosity. We attribute it primarily to higher
density for the following reasons: Nanoglobules (Figs. 1e-g) contain higher fractions of polyaromatic hydrocarbons (PAHs) in their organic carbon relative to the surrounding matrix. They exhibit a stronger ~5.7 eV feature than the matrix carbon (Fig. 3a), and nanoglobules significantly enriched in $^{15}$N, like those in U217B19, have been found to contain highly aromatic organics (6). The concentric morphologies and, in some cases, hollow cores in nanoglobules are consistent with layering of planar PAHs into dense, onion-like forms similar to those observed in ordered graphene “onions” (7). The denser packing of organic carbon in nanoglobules results in higher electron density and higher C atomic density. Although there is insufficient signal to observe whether mantles on GEMS and blebs contain higher abundances of PAHs than the organic matrix itself, it is likely that the more intense C x-ray signal from rims on GEMS and blebs are due to more compact PAH packing. EELS thickness measurements comparing the zero loss-to-plasmon scattered intensities (Fig. S7) indicate that, in order to explain the higher C x-ray signal by thickness variations, ~2× variations in thickness would be required, highly implausible in ultramicrotomed sections on the scale of the dimensions of higher intensity, C-rich organic regions. Finally, composition measurements (Table S2) indicate that bright mantle and bright bleb organic carbon regions have higher O/C ratios than those in the matrix regions.

Supporting Text

**Chondritic interplanetary dust particles in this study.** U217B19 is a small, ~10 µm diameter chondritic IDP, and LT39 is a ~10 µm diameter fragment of a large “giant cluster” IDP (U220GCA) (8). Both belong to the CF subset of chondritic IDPs, one end of a continuum of morphologies ranging from low-porosity CF (chondritic filled) to high-porosity CP (chondritic porous) IDPs (9,10). CF IDPs are likely the most carbon-rich end member of the continuum and, although common, have been rarely studied in favor of CP IDPs and much larger (typically > 50 µm) “cluster” CP IDPs. IDPs belonging to a third subset, the chondritic smooth (CS) IDPs, are morphologically similar to CF IDPs, but in contrast to CF-CP IDPs, they are hydrated and contain layer lattice silicates. IDPs are collected in the stratosphere at an altitude of ~20 km by impact onto silicone oil-coated substrates or “flags” mounted on wing pylons on National Aeronautics and Space Administration high altitude aircraft, first on U2 and, more recently, ER2 and WB57 aircraft (11).

Chondritic porous IDPs are believed to be among the most cosmically primitive meteoritic objects available for laboratory investigations. They are distinct from other classes of IDPs and chondritic meteorites by their anhydrous mineralogy, higher organic carbon content and abundance of amorphous silicates (GEMS). The anhydrous porous subclass of chondritic IDPs can contain >10× more isotopically anomalous presolar constituents than other meteoritic materials, and they have not been exposed to parent body secondary alteration processes like compaction, aqueous alteration and heating that have altered even the most primitive meteorites (12).

Approximately half of the particles collected belong to the CF-CP continuum (9,10). Kuiper Belt and, possibly, Oort cloud comets and small frozen bodies in the outer asteroid belt are their likely sources (11-14). The silicate mineralogy and mid-infrared (IR) spectral properties of CF-CP IDPs are like those of the comets Halley and Hale-Bopp and dissimilar to other classes of meteoritic materials (14). Some have been collected in the stratosphere during meteor showers associated with specific comets (e.g. Grigg–Skjellerup) (15). Some rare and much larger (up to 400 µm diameter) ultracarbonaceous Antarctic micrometeorites (UCAMMs) are collected from
snow and ice and are closely related to CP IDPs because they contain GEMS and abundant organic carbon (16,17).

A size-density relationship has previously been observed in CP IDPs between single crystal silicate and sulfide grains that indicates that the crystalline fraction experienced aerodynamic sorting prior to accretion onto their parent icy body: Individual IDPs show different, but well-defined, size \times density products (18). It has been proposed that this may provide an indication of the heliocentric distance at which the parent body formed; however, local sorting during accretion in the parent body formation region is also possible (19).

Although IDPs are frictionally heated for several seconds during atmospheric entry, small low-density IDPs like U217B19 are less likely to be strongly heated, and the interiors of some much larger IDPs like U220GCA are protected by a thermal gradient (20,21). A densified carbonaceous “skin” and partial magnetite (Fe$_3$O$_4$) rims on Fe-sulfides that were exposed along some outer surfaces of U217B19 are indicative of heating and oxidation during atmospheric entry, but the organic matrix (and concomitant lack of porosity) shielded the interior from significant alteration and may also have served as an ablation shield, protecting the interior from heating. We estimate that the interior of U217B19 was not heated above \sim 473K for two reasons: First, C=O and C≡N bearing meteoritic organics are labile and decompose at temperatures as low as \sim 425K (22-24). Second, the surfaces of most GEMS are not decorated with Fe sulfides: In situ experiments using a TEM heating stage show that, at \sim 573K, Fe sulfide sub-grains in GEMS’ interiors begin to melt and migrate, and at \sim 673K, they decorate GEMS’ surfaces (25). IDPs are also exposed to terrestrial contamination. Minor Si in the organic carbon matrix and around nanoglobules near the outer surface of some sections of U217B19 is consistent with residual silicone oil used in its collection (25). We note that the low porosity of the organic matrix in the CF IDPs serves to shield the interior from silicone oil contamination, and interior regions in which GEMS grains were mapped show no Si “halos”. Minor S unassociated with Fe sulfide grains may be residue from S embedding used for ultramicrotomy. Epoxy was used as a support in sectioning of the particle by ultramicrotomy, and a lack of detectable N and infrared spectroscopy rule it out as a significant contaminant (Fig. S8). Locally elevated levels of minor elements, including Na, P, Cl and K detected in some locations in some sections, may indicate a terrestrial contamination component.

**Organic carbon in GEMS in chondritic IDPs.** The bulk abundance of organic carbon, as much as \sim 90\% by volume, in some CP IDPs and UCAMMs, is up to an order of magnitude higher than in chondritic meteorites (26). It has been investigated using a variety of methods including optical spectroscopy (Raman and Fourier transform infrared), x-ray absorption near edge spectroscopy (XANES), phase contrast tomography, secondary ion mass spectroscopy and analytical electron microscopy (26-29). The organic carbon in IDPs includes both aromatic and aliphatic compounds, and associated CO and CN moieties. H and N isotopic anomalies in the organic matter are common in IDPs and consistent with formation of the organic carbon by chemical fractionation in extremely cold astrophysical environments (30).

Establishing that the GEMS in carbon-rich chondritic IDPs contain carbon, in addition to the organic matrix, has historically been challenging, in part because its abundance varies among GEMS. We hypothesize that organic carbon density may reflect post-accretion irradiation exposure ages of GEMS, with higher density organic carbon resulting from increased exposure. It has long been recognized, based first on textural properties and later on spectroscopy, that at least some GEMS contain carbon, and they were initially described as “tar balls” and “reduced aggregates” (29,31). Subsequently, HF acid dissolutions, where the amorphous silicate in GEMS was removed, enabled direct imaging of the residue of carbonaceous matter associated with
GEMS (32), albeit with spatial resolutions of ~500 nm. While suggestive, these experiments were unable to distinguish whether the organic carbon was originally on the surfaces or in the interiors of the GEMS. Later, bulk compositional analyses of (unetched) GEMS using combined x-ray and energy loss spectroscopy revealed an inverse relationship between C and Si abundances, greater than that attributable to self-absorption effects: The higher the Si, the lower the C, and vice versa (33). For our study, the thin sections of U217B19 were mounted on a uniform thin-film carbon substrate 10-15 nm thick, and its contribution to total C x-ray signal was subtracted in the compositional maps. Mapping the distribution of C with unprecedented 1-3 nm spatial resolution reveals how GEMS subgrains acquire C, specifically as mantles of organic carbon or its icy, volatile-rich precursor(s) on grains, during dust agglomeration, the earliest stage in planetary body accretion (Fig. 1 of main manuscript and Fig. S3).

Additional details from FTIR and EELS data. The infrared spectrum from U217B19 (Fig. 2, main manuscript) reflects a complex organic chemistry. We assign the broad features at ~3400 and 2900 cm\(^{-1}\) to hydroxyl and aliphatic CH\(_2\) and CH\(_3\) stretching modes respectively. The lack of distinct peaks for CH\(_2\) and CH\(_3\) in the 2900-3000 cm\(^{-1}\) feature indicates a mixture of hydrocarbons. The weak ~2200 cm\(^{-1}\) feature is consistent with cyano (C≡N) moieties, but it is broader and at lower frequency than the typically very sharp feature at 2250 cm\(^{-1}\) for cyano, indicating that a distribution of molecules including cyano, isocyanate, isothiocyanate, or even alkyne (C≡C) functional groups are present. The broad structured feature peaked at ~1710 cm\(^{-1}\) can be assigned to carbonyl (C=O), but it is also broader than typical, suggesting the presence of several types of carbonyl species including aldehydes, ketones and carboxylic acids. The hydroxyl (-OH) feature at ~3400 cm\(^{-1}\) is also consistent with a carboxylic acid. A weak shoulder feature at ~1640 cm\(^{-1}\) could be a type of amide bond or vinylic C=C or aromatic C=C. We can also not rule out the possibility of –OH bending mode in this region, from adsorbed water, particularly given the strong –OH stretching features. A nitro (R-NO\(_2\)) species is a likely carrier of the 1350 cm\(^{-1}\) feature and would also contribute to the ~1600 cm\(^{-1}\) feature. The feature at 1020 cm\(^{-1}\) is due to the amorphous silicates (GEMS) in U217B19 (14). The feature at 1900 cm\(^{-1}\) is consistent with the aromatic C-H bending mode. Additional evidence for these modes is provided by possible =C-H features around 3100 cm\(^{-1}\) and the features around 1660 and 1450 cm\(^{-1}\). The ~1600 cm\(^{-1}\) feature likely reflects aromatic C=C modes, but could also be associated with the C=O stretch of an amide. The fundamental C-H out-of-plane bending modes are out of the detection range with the experimental setup used and could not be identified, and the region where aromatic C-H stretching would manifest is obscured by the broad -OH feature at >3000 cm\(^{-1}\). As a result of the congestion around the 1600 cm\(^{-1}\) region, which could indicate a number of functional groups, we have not labeled the 1900 cm\(^{-1}\) feature as aromatic. Aromatic features are typically much less intense than aliphatic features in infrared measurements. For a listing of IR absorption bands, see (26).

Electron energy loss spectroscopy from U217B19 (Fig. 3, main manuscript) also supports complex organic chemistry and molecular functionalities similar to those observed in other carbon-rich IDPs and MMs using XANES and EELS (26,34,35). Functional group assignments were made with consideration of published core-loss N, C and O EELS features and taking into account our FTIR results (26,36). C-K and N-K core-loss EELS edges from both forms of carbon exhibit fine structures consistent with a mixture of aromatic and aliphatic functionalities (Fig. 3). Fine structures on the C-K edges are consistent with the following functional groups: 285 eV, aliphatic and/or aromatic ring C=C; 287.2-288.3 eV, aliphatic C-C; 285.7 eV, imine C=N; 286.1-286.8 eV, aldehydes C=OH, ketones C=O, cyano C≡N; 287.2 eV, aliphatic C=C; 288.1-288.5 eV, amide O=C–NH\(_2\), carboxyl O=C-O. Fine structure on the N-K edges are consistent with the following functional groups: 401.5 eV, cyano C≡N, imine C≡N, and/or amide O=CNH\(_2\).
The debate regarding the origins of GEMS. Two very different mechanisms and environments of GEMS formation have been proposed. We present here a summary of the two theories that is, by no means, complete, and we refer the interested reader to the cited literature for more details. The first theory proposes that all GEMS grains formed by irradiation processing of mineral grains (37). It is based on the similarity of chemical and physical properties of GEMS to solar wind irradiated surfaces on lunar and asteroidal regolith grains and laboratory-irradiated minerals. Since the physical properties of GEMS grains uniquely resemble those of amorphous silicate grains that are ubiquitous in interstellar medium, the irradiation processing was proposed to have occurred in the cold interstellar medium. This theory has the advantage that isotope analyses have proven some GEMS grains to be presolar amorphous silicates inherited from the interstellar medium (38). It has the additional advantage that GEMS grain would have experienced gradual homogenization leading to ~solar elemental and isotopic compositions observed for most GEMS grains (39). Counterarguments to this theory (40) are that remnant mineral cores are difficult to find and that more GEMS grains should show significant O isotope anomalies, although this has been contested on the basis of instrumental sensitivity limits (39). An additional counterargument is that nano-scale elemental inhomogeneities observed are inconsistent with heavy irradiation processing which, it is argued, should homogenize elemental abundances as thoroughly as isotopic abundances, also contested on the basis of natural chemical affinities (41).

The second theory proposes that most GEMS grains formed by non-equilibrium condensation from a hot gas of solar composition (40). The basis for this theory is that the bulk compositions of the cometary IDPs that host GEMS grains are ~solar, while the compositions of GEMS are sub-solar in certain element/Si ratios. This suggests that the non-GEMS components, predominantly Mg-rich silicates and FeNi sulfides, must be super-solar in those same elements to create the average solar composition of the host IDPs and that both formed from the same gas of solar composition in the solar nebula, with GEMS forming after the crystalline silicates. The temperatures required suggest an inner solar nebula region. This theory has the advantage that it naturally explains the ~solar isotope compositions of most GEMS grains. Counterarguments to this theory are that it requires two populations of GEMS grains, one inherited from the interstellar medium, that otherwise show no differences in their compositions or morphologies (39) and that complementarity between IDP components has not been demonstrated, with bulk analyses made by different techniques than GEMS grain analyses and a large margin for classification as ~solar (2-3x CI). In addition, atmospheric entry pulse heating, weathering and/or silicone oil contamination during collection cause sub-solar GEMS compositions in element/Si ratios that are not evident using a different ratio element and also cause sulfide mobilization to GEMS grain surfaces (10,25,42,43), although this has been contested with data on a very limited number of IDPs collected without silicone oil (44).
**Fig. S1.** Chondritic filled interplanetary dust particle U217B19. (a) Secondary electron image, and (b) high angle annular darkfield (HAADF) image of a ~75 nm thick ultramicrotomed section through the particle center. Bright inclusions are mostly GEMS, glass embedded with metal and sulfides, and uniform grey matrix is organic carbon. The bright rim along the lower left edge is a thin Pd coating deposited to permit scanning electron microscopy in (a).
**Fig. S2.** Secondary electron (SE) and isotope imaging of a thin section of IDP U217B19. (a) SE image of the underside side of a carbon support film TEM grid after deposition of a Pt support substrate. Dashed outline shows the position of the thin section on the opposite side of the grid. (b) SE image of the thin section on the top side of the grid. (c-f) Maps of isotope ratios in delta notation (parts per 1000 relative to terrestrial standards): (c) $\delta^{12}C^{15}N/^{12}C^{14}N$ isotope map, (d) $\delta^{13}C/^{12}C$ isotope map, (e) $\delta^{17}O/^{16}O$ isotope map, and (f) $\delta^{18}O/^{16}O$ isotope map.
Fig. S3. Scanning transmission electron microscopy imaging and mapping of IDP U217B19. (a) High-angle annular darkfield image, (b) corresponding carbon x-ray map and (c) corresponding map of C, Mg, Si, S and Fe in a region of a section of U217B19. The composition of the entire field of view, as well as the compositions of regions 1-13, are included in Table S1 and S2. Regions 12 and 13 encompass higher density C rims around GEMS grains.
Fig. S4. Maps of Si (light blue) and C (red) in regions of IDP U217B19. a) Residual silicone oil contamination is evident in Si “halos” around nanoglobules located near the particle periphery. b) No residual silicone oil is observable around GEMS located in the interior of the particle.
Fig. S5. Energy-dispersive x-ray spectrum from organic carbon matrix from a region in U217B19 after removal of background, acquired at 200 kV using the LBL TitanX.
Fig. S6. Electron energy loss spectrum from organic carbon matrix from the same location in U217B19 as in Figure S5 collected using the LBL TEAM 0.5. The spectrum includes the C-K and N-K core scattering edges and shows the background (red) subtraction and fit (blue). The quantified N/C atomic ratio is $0.07 \pm 0.010$. 
Fig. S7. Comparison of zero loss-to-plasmon scattering intensity ratios in the -2.5 to +2.5 eV and 10-40 eV energy windows respectively from the organic carbon mantle (rim) on a GEMS grain and surrounding organic carbon matrix (see Figs. 1c & 1d). Zero loss peak integrated areas are scaled to show the relative heights of other features. The ratio in the rim is 0.513 and matrix 0341. The more intense plasmon signal from the mantle is consistent with a higher density organic carbon.
**Fig. S8.** FTIR spectra from CP IDP U217B19 (top), as shown in Figure 2 of main manuscript, and epoxy (bottom). Both spectra were obtained from the same thin section on a TEM grid. Baselines in both spectra were corrected manually. The absence of epoxy features, particularly the sharp feature at 1510 cm\(^{-1}\), in the upper spectrum rules out significant epoxy contamination of thin sections of U217B19.
Table S1. Elemental compositions of a region in U217B19 containing amorphous silicate and organic carbon, regions containing individual amorphous silicate GEMS, and a region containing GEMS material partially-mantling a carbon nanoglobule. Element abundances are given as atomic % and normalized to 100% for C, N, O, Mg, Al, Si, S, Ca, Cr, Fe and Ni. The abundances in the GEMS mantle are normalized to 100% for those elements excluding C and N. Percent relative errors are given as 1σ values in italics below the abundance. The bulk analysis includes the full field of view and numbered regions correspond to those indicated in Figure S4. The GEMS mantle corresponds to that in Figure 1g.

|                  | C     | N    | O    | Mg   | Al   | Si   | S    | Ca   | Cr   | Fe   | Ni   |
|------------------|-------|------|------|------|------|------|------|------|------|------|------|
| **U217B19**      |       |      |      |      |      |      |      |      |      |      |      |
| **Full field**   | 27.81 | 1.58 | 40.74| 9.52 | 0.97 | 10.56| 3.31 | 0.37 | 0.07 | 4.66 | 0.40 |
| **U217B19**      |       |      |      |      |      |      |      |      |      |      |      |
| **Region 1**     |       |      |      |      |      |      |      |      |      |      |      |
| GEMS             | 12.95 | 0.69 | 43.74| 11.15| 1.14 | 12.65| 8.03 | 0.46 | 0.15 | 8.38 | 0.66 |
| **Region 2**     |       |      |      |      |      |      |      |      |      |      |      |
| GEMS             | 3.09  | 1.08 | 52.93| 14.27| 1.83 | 15.37| 0.15 | 1.61 | 0.22 | 8.52 | 0.93 |
| **Region 3**     |       |      |      |      |      |      |      |      |      |      |      |
| GEMS             | 11.05 | 0.15 | 49.07| 8.54 | 0.85 | 10.24| 4.13 | 0.63 | 0.10 | 14.51| 0.73 |
| **Region 4**     |       |      |      |      |      |      |      |      |      |      |      |
| GEMS             | 11.09 | 1.76 | 50.98| 12.07| 0.78 | 11.67| 0.77 | 0.56 | 0.11 | 9.73 | 0.48 |
| **GEMS mantle on** |     |      |      |      |      |      |      |      |      |      |      |
| ng               | nr    | nr   | 55.55| 8.21 | 3.68 | 20.72| 3.38 | 0.80 | 0.11 | 6.84 | 0.67 |

ng = nanoglobule
nr = not reported. Carbon contribution from the substrate was not measured, so C could not be corrected and is not reported. Nitrogen signal is not sufficiently above background to permit quantification.
Table S2. Elemental compositions of organic carbon in U217B19 and LT39. Element abundances are given as atomic % and normalized to 100% for C, N and O. Percent relative errors are given as 1σ values in italics below the abundance. For averages, the standard error of the mean is given in italics below the mean. LD=low-density organic carbon, HD=high-density organic carbon, and ng=nanoglobule.

|        | C  | N  | O  | N/C | O/C |
|--------|----|----|----|-----|-----|
| U217B19 HD ng 1 | 87.48 | 2.41 | 10.11 | 0.03 | 0.12 |
|         | 3  | 5  | 3  | 6  | 5  |
| U217B19 HD ng 2 | 88.14 | 3.49 | 8.37 | 0.04 | 0.09 |
|         | 3  | 4  | 3  | 5  | 5  |
| HD ng average | 87.81 | 2.95 | 9.24 | 0.03 | 0.11 |
|         | 0.33 | 0.54 | 0.87 | 0.01 | 0.01 |
| U217B19 LD matrix | 87.33 | 6.28 | 5.69 | 0.07 | 0.00 |
|         | 3  | 5  | 3  | 5  | 5  |
| Region 5 LD matrix | 88.97 | 6.35 | 4.68 | 0.07 | 0.05 |
|         | 3  | 4  | 3  | 5  | 5  |
| U217B19 HD Rim | 90.72 | 2.22 | 7.06 | 0.02 | 0.08 |
|         | 3  | 5  | 3  | 6  | 5  |
| LT39 LD matrix | 92.25 | 2.15 | 5.60 | 0.02 | 0.06 |
|         | 3  | 4  | 3  | 5  | 5  |
| Region 2 LD matrix | 89.72 | 6.32 | 5.54 | 0.07 | 0.06 |
|         | 3  | 5  | 3  | 6  | 5  |
| LT39 HD Rim | 82.16 | 4.27 | 13.57 | 0.05 | 0.17 |
|         | 3  | 5  | 3  | 6  | 5  |
| Region 5 LT39 | 91.49 | 2.19 | 6.33 | 0.02 | 0.07 |
|         | 0.77 | 0.04 | 0.73 | 0.00 | 0.01 |
| Region 6 LT39 | 88.15 | 6.32 | 5.54 | 0.07 | 0.06 |
|         | 0.82 | 0.03 | 0.85 | 0.00 | 0.01 |
| Region 6 LT39 matrix avg | 91.49 | 2.19 | 6.33 | 0.02 | 0.07 |
|         | 0.77 | 0.04 | 0.73 | 0.00 | 0.01 |

### O/C upper bound

|        | C  | N  | O  | N/C | O/C |
|--------|----|----|----|-----|-----|
| U217B19 HD bleb | 84.32 | 3.84 | 11.84 | 0.05 | 0.14 |
| Region 7 | 3  | 3  | 3  | 6  | 6  |
| U217B19 HD bleb | 72.74 | 5.48 | 21.78 | 0.08 | 0.30 |
| Region 8 | 3  | 4  | 3  | 5  | 4  |
| U217B19 HD bleb | 82.87 | 5.09 | 12.05 | 0.06 | 0.15 |
| Region 9 | 3  | 4  | 3  | 5  | 4  |
| LT39 HD Rim | 70.91 | 5.42 | 23.67 | 0.08 | 0.33 |
| Region 12 | 3  | 4  | 3  | 5  | 4  |
| LT39 HD Rim | 82.16 | 4.27 | 13.57 | 0.05 | 0.17 |
| Region 13 | 3  | 5  | 3  | 6  | 5  |
| LT39 HD Rim | 76.38 | 5.61 | 18.01 | 0.08 | 0.24 |
| Region 5 | 3  | 5  | 3  | 6  | 5  |

### O/C lower bound

|        | C  | N  | O  | N/C | O/C |
|--------|----|----|----|-----|-----|
| U217B19 LD matrix | 85.58 | 3.90 | 10.52 | 0.05 | 0.12 |
|         | 3  | 5  | 3  | 6  | 5  |
| Region 9 LD matrix | 72.79 | 8.79 | 22.41 | 0.13 | 0.33 |
|         | 3  | 4  | 3  | 5  | 4  |
| LT39 HD Rim | 77.12 | 5.89 | 16.99 | 0.08 | 0.22 |
| Region 12 | 3  | 4  | 3  | 5  | 4  |
| LT39 HD Rim | 76.30 | 6.66 | 17.04 | 0.09 | 0.22 |
| Region 13 | 3  | 4  | 3  | 5  | 4  |
| LT39 HD Rim | 84.24 | 4.38 | 11.37 | 0.05 | 0.13 |
| Region 5 | 3  | 5  | 3  | 6  | 5  |

C, O and N compositions corrected for any silicone oil contamination by removing one O for each Si present. Silicone oil is the most likely source of Si in the organic carbon matrix and nanoglobules.

C, O and N compositions corrected for any contamination by neighboring amorphous silicate by removing two O for each Si present and 1 O for each Mg present. Amorphous silicate is the most likely source of Si and Mg in the high density organic carbon rims around GEMS and high density blebs near GEMS. (This may be an overcorrection since amorphous silica typically has less than two O per Si atom.)
References

1. Bradley JP, Keller L, Thomas KL, van der Wood TB and Brownlee DE (1993) Carbon analyses of IDPs sectioned in sulfur and supported on beryllium films. *Proc Lunar Planet Sci* 24: 205.
2. Matzel JEP et al. (2010) Constraints on the formation age of cometary material from the NASA Stardust mission. *Science* 328:483-486.
3. Bradley JP and Dai ZR (2009) Analytical SuperSTEM for extraterrestrial materials research. *Meteorit Planet Sci* 44:1627-1642.
4. Longo DM, Howe JM and Johnson WC (1999) Experimental method for determining Cliff–Lorimer factors in transmission electron microscopy (TEM) utilizing stepped wedge-shaped specimens prepared by focused ion beam (FIB) thinning. *Ultramicroscopy* 80:85-97.
5. Hofer F and Kothleitner G (1996) Quantitative microanalysis using electron energy-loss spectrometry: II. Compounds with heavier elements. *Microsc Microanal Microstruct* 7:265-277.
6. de Gregorio B et al. (2013) Isotopic and chemical variation of organic nanoglobules in primitive meteorites. *Meteorit Planet Sci* 28:904-928.
7. Zheng Y et al. (2013) Hexagonal Graphene Onion Rings. *J Am Chem Soc* 135:10755-10762.
8. Joswiak DJ, Brownlee DE, Nguyen AN and Messenger S (2017) Refractory materials in comet samples. *Meteorit Planet Sci* 52:1612-1648.
9. Brownlee DE, Olszewsky E and Wheelock M (1982) A working taxonomy for micrometeorites. *Proc Lunar Planet Sci* 13:71-71.
10. Schramm LS, Wheelock MM and Brownlee DE (1989) Major element composition of stratospheric micrometeorites. *Meteoritics* 24:99-112.
11. Brownlee DE (1985) Cosmic dust. *Ann Rev Earth Planet Sci* 13:147–173.
12. Bradley JP (2014) Early solar nebula grains – interplanetary dust particles. *Treatise of Geochemistry, 2nd ed*, eds Holland H, Turekian K (Elsevier-Pergamon, Oxford) pp. 297-308.
13. Dartois E et al. (2013) UltraCarbonaceous Antarctic micrometeorites, probing the Solar System beyond the nitrogen snow-line. *Icarus* 224:243-252.
14. Bradley JP et al. (1999) An infrared spectral match between GEMS and interstellar grains. *Science* 285:1716-1718.
15. Busemann H et al. (2009) Ultra-primitive interplanetary dust particles from the comet 26P/Grigg-Skjellerup dust stream collection. *Earth Planet Sci Lett* 288:44-57.
16. Dobrica E, Engrand C, Leroux H, Rouzaud J-N and Duprat J. (2012) Transmission electron microscopy of CONCORDIA ultraCarbonaceous Antarctic micrometeorites (UCAMMs): Mineralogical properties. *Geochim Cosmochim Acta* 76:68-82.
17. Noguchi T et al. (2015) Cometary dust in Antarctic ice and snow: Past and present chondritic porous micrometeorites preserved on the Earth’s surface. *Earth Planet Sci Lett* 410:1-11.
18. Wozniakiewicz P, Bradley JP, Ishii HA, Price MC and Brownlee DE (2013) Pre-accretional sorting of grains in the outer solar nebula. *Astron Astrophys* 779:164-170.
19. Cuzzi JN, Hartlep T, Simon JI and Cato MJ (2017) Aggregates: The fundamental building blocks of planetesimals? *Proc Lunar Planet Sci* 48:2364.
20. Love SG and Brownlee DE (1993) Peak atmospheric entry temperatures of micrometeorites. *Science* 262:550-553.
21. Bradley JP et al. (2014) Detection of solar wind-produced water in irradiated rims on silicate minerals. *Proc Natl Acad Sci U.S.A.* 111:1732-1735.
22. Duvernay F et al. (2015) Formaldehyde chemistry in cometary ices: On the prospective detection of NH2CH2OH, HOCH2OH, and POM by the on-board ROSINA instrument of the ROSETTA mission. *Astrophys J* 791:75.

23. Fray N et al. (2004) Experimental study of the degradation of polymers: Application to the origin of extended sources in cometary atmospheres. *Meteorit Planet Sci* 39:581–587.

24. He A and Smith MA (2014) Solubility and stability investigation of Titan aerosol analogs: New insight from NMR analysis. *Icarus* 232:54-59.

25. Bradley JP and Ishii HA (2017) An inconvenient reality: Terrestrial alteration of interplanetary dust particles (IDPs) and micrometeorites (MMs). *Meteorit Planet Sci* 52:A33.

26. Matrajt G, Flynn G, Brownlee D, Joswiak D and Bajt S (2013) The origin of the 3.4 μm feature in Wild 2 cometary particles and in ultracarbonaceous interplanetary dust particles. *Astrophys J* 765:145-163.

27. Sandford SA, Engrand C and Rotundi A (2016) Organic matter in cosmic dust. *Elements* 12:185-190.

28. Cleett SJ, Maechling CR, Zare RN, Swan PD and Walker RM (1993) Identification of complex aromatic molecules in individual interplanetary dust particles. *Science* 262:721-725.

29. Bradley JP (1988) Analysis of chondritic interplanetary dust thin-sections. *Geochim Cosmochim Acta* 52:889-900.

30. Messenger S (2000) Identification of molecular cloud material in interplanetary dust particles. *Nature* 404:968-971.

31. Bradley JP (1993) Unequilibrated, equilibrated, and reduced aggregates in anhydrous interplanetary dust particles. *Proc Lunar Planet Sci* 23:171-172.

32. Dai ZR et al. (2002) Possible in situ formation of meteoritic nanodiamonds in the early Solar System. *Nature* 418:157-159.

33. Ishii HA, Ciston J and Bradley JP (2016) Advanced electron energy-loss methods for applications to Stardust and other fine-grained meteoritic materials. *Proc Lunar Planet Sci* 37:1805.

34. Flynn GJ, Keller LP, Feser M, Wirick S and Jacobsen C (2003) The origin of organic matter in the solar system: Evidence from interplanetary dust particles. *Geochim Cosmochim Acta* 67:4791-4806.

35. de Gregorio B et al. (2011) Correlated microanalysis of cometary organic grains returned by Stardust. *Meteorit Planet Sci* 46:1376-1396.

36. Kim K, Zhu P, Li N, Ma X and Chen Y (2011) Characterization of oxygen functional groups on carbon materials with oxygen K-edge X-ray absorption near edge structure spectroscopy. *Carbon* 49:1745-1751.

37. Bradley JP (1994) Chemically anomalous, preaccretionally irradiated grains in interplanetary dust from comets. *Science* 265:925-929.

38. Messenger S, Keller LP, Stadermann F J, Walker RM and Zinner E (2003) Samples of Stars Beyond the Solar System: Silicate Grains in Interplanetary Dust. *Science* 300:105-108.

39. Bradley JP and Ishii HA (2008) Comment on “The shape and composition of interstellar silicate grains”. *Astron & Astrophys* 486:781–784.

40. Keller LP and Messenger S (2011) On the origin of GEMS grains. *Geochim Cosmochim Acta* 75:5336-5365.

41. Wooden DH, Ishii HA and Zolensky ME (2017) Cometary dust: the diversity of primitive refractory grains. *Phil Trans A* 375:20160260.
42. Bradley JP, Ishii HA, Wozniakiewicz P, Noguchi T, Engrand C and Brownlee DE (2014) Impact of the terrestrial environment on the composition of GEMS. *Proc Lunar Planet Sci* 45:1178.

43. Yabuta H, et al. (2017) Formation of an ultracarbonaceous Antarctic micrometeorite through minimal aqueous alteration in a small porous icy body. *Geochim Cosmochim Acta* 214:172-190.

44. Messenger S, Nakamura-Messenger K, Keller LP and Clemett SJ (2015) Pristine stratospheric collection of interplanetary dust on an oil-free polyurethane foam substrate. *Meteorit Planet Sci* 50:1468-1485.