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rites, but with even lower O/C ratios (23). This suggests that the Stardust organics are not the direct result of stellar ejecta or diffuse ISM processes but rather result from dense cloud and/or protosolar nebular processes. The high O and N contents, lower aromatic contents, and elevated $-\text{CH}_2-/-\text{CH}_3$ ratios are all qualitatively consistent with what is expected from radiation processing of astrophysical ices and the polymerization of simple species such as HCO, H_2CO , and HCN (24–26).

The Stardust samples clearly contain an organic component that is more labile than the materials seen in meteorites and IDPs. These labile materials may be absent from stratospheric IDPs because they are lost during atmospheric entry heating and/or are destroyed or modified by radiation during the IDPs' transit from parent body to Earth. Given the O- and N-rich nature of the Stardust materials, these labile organics could represent a class of materials that have been suggested as parent molecules to explain the extended coma sources of some molecular fragments like CN (27, 28). The high O/C and N/C ratios of the samples fall well outside the range of most meteorites and, interestingly enough, reach higher values than those observed at comet Halley by the Giotto spacecraft (15). In this respect, some of the returned material appears to

represent a new class of organics not previously observed in other extraterrestrial samples.

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Supporting Online Material

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Materials and Methods
Figs. S1 to S9
References

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REPORT

Isotopic Compositions of Cometary Matter Returned by Stardust

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Hydrogen, carbon, nitrogen, and oxygen isotopic compositions are heterogeneous among comet 81P/Wild 2 particle fragments; however, extreme isotopic anomalies are rare, indicating that the comet is not a pristine aggregate of presolar materials. Nonterrestrial nitrogen and neon isotope ratios suggest that indigenous organic matter and highly volatile materials were successfully collected. Except for a single ^{17}O -enriched circumstellar stardust grain, silicate and oxide minerals have oxygen isotopic compositions consistent with solar system origin. One refractory grain is ^{16}O -enriched, like refractory inclusions in meteorites, suggesting that Wild 2 contains material formed at high temperature in the inner solar system and transported to the Kuiper belt before comet accretion.

The isotopic compositions of primitive solar system materials record evidence of chemical and physical processes involved in the formation of planetary bodies ~4.6 billion years ago and, in some cases, provide a link to materials and processes in the molecular cloud that predated our solar system. The vast majority of

isotopic analyses of extraterrestrial materials have been performed on chondritic (undifferentiated) meteorites, samples of asteroids that likely accreted at 2 to 4 astronomical units (AU) within the first few million years of solar system history. Comets formed in much colder regions of the protoplanetary disk and are widely considered to

consist of more primitive matter than even the most unequilibrated meteorites.

Analyses of isotope compositions of comets are rare. Measurements of D/H, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, or $^{18}\text{O}/^{16}\text{O}$ have been made for a few abundant molecules in gases of several comet comae by ground-based spectroscopy (1–3) and of comet P/Halley by mass spectrometers on the Giotto spacecraft (4). Direct measurements of isotope compositions in the dust fraction of comets are limited to low-precision data from the Halley flyby (5). Isotopic measurements of stratosphere-collected interplanetary dust particles (IDPs) demonstrate the highly primitive nature of many anhydrous IDPs [e.g., (6, 7)]; however, a cometary origin for specific individual particles cannot be ascertained. Here, we report laboratory analyses of the light “stable” isotopes of H, C, N, O, and Ne in individual grains, particle fragments, crater debris, and/or trapped volatile materials collected from comet 81P/Wild 2 and returned to Earth by the NASA Discovery Mission, Stardust.

The goals of the Isotope Preliminary Examination Team analyses are to provide first-order answers to questions relating to the provenance of Wild 2 dust: (i) Does the comet consist of a mechanical agglomeration of essentially unprocessed, or perhaps only thermally annealed, presolar materials? (ii) Do comets provide a well-preserved reservoir of circumstellar dust grains (8) with distinct nucleosynthetic histories (i.e., stardust)? (iii) Can isotopic signatures establish whether extraterrestrial organic materials are present above contamination levels? (iv) What are the

relations to known isotope reservoirs in meteoritic samples and in IDPs? (v) What are the implications for mixing and thermal processing in the early solar system? The preliminary examination has focused on the abundant light elements H, C, N, and O and on light noble gases because they have characteristic isotopic signatures that vary widely in solar system materials [e.g., (9)] and compositions that can often be linked to distinct astrophysical environments and/or processes.

Hydrogen isotopic compositions in bulk fragments of five Wild 2 particles (see supporting online material) range from values similar to those of terrestrial and chondritic particles, up to moderate D/H enhancements of about three times the D/H in mean ocean water (Fig. 1, table S1). Variations in δD within a particle are also observed with some “hotspots” having a δD up to 2200 ± 900 per mil (‰) (10). All the observed D enrichments are associated with carbon, although only one of the samples (T17) is dominated by carbonaceous material. Although overlapping the range of values observed for IDPs (11, 12) and water in (Oort cloud) comets (4), the maximum D/H is well below that characteristic of a minor component of organic matter in anhydrous IDPs, especially of the low-

density “cluster” type thought to be derived from comets (13). The maximum D/H values of Wild 2 grains are also far less than those measured in small hotspots of insoluble organic matter separated from carbonaceous chondrites (14) and in cometary HCN ice (15), which are both thought to have close affinities to organic material produced at very low temperatures in molecular cloud environments. It is not known if this relative paucity of highly D-enriched matter signifies an intrinsic difference between Wild 2 samples and macromolecular materials in IDPs and carbonaceous chondrites. It is also possible that D/H signatures were modified during impact. Because of the association with carbon and the lack of evidence for any hydrated minerals in Wild 2 particles, it is unlikely that D/H values can be ascribed to Wild 2 water.

Some cometary volatiles appear to have been captured. Helium, neon, and argon abundances, as well as $^{20}\text{Ne}/^{22}\text{Ne}$ ratios, were analyzed in two bulbous sections of an impact track that contains fragments of fine-grained impactor material mixed with melted aerogel along its periphery. Noble gases in a control sample (unexposed aerogel taken from the rear portion of a collector cell) are consistent with system blanks, indicating that flight aerogel does not contain a detectable background of noble gases. In contrast, aerogel fragments containing the impact track show excess He and Ne above blank levels by factors of 3 to 4 (table S2), suggesting that the very rapid time scales ($< \mu\text{s}$) for melting of aerogel during deceleration of comet particles helped trap indigenous cometary volatiles. This inference is supported by measured $^{20}\text{Ne}/^{22}\text{Ne}$ ratios, which are significantly higher than that in air. In a $^{22}\text{Ne}/^{20}\text{Ne}$ versus $^4\text{He}/^{20}\text{Ne}$ diagram (fig. S1), the data do not lie on a pure mixing trajectory between air and the solar composition but instead point toward a nonatmospheric end-member with a $^4\text{He}/^{20}\text{Ne}$ ratio lower than solar, consistent with expectations for comets due to preferential trapping of heavier noble gases in ice accreted at ~ 30 K (16).

Carbon and nitrogen isotope analyses were made by isotopic mapping with NanoSIMS instruments, measuring atomic ions of C and isotopologs of the intense CN^- beam, respectively. Microtomed particles extracted from aerogel, as well as Al-foil crater debris, were mapped with a spatial resolution of ~ 100 nm to search for isotopic anomalies that could identify circumstellar dust grains like the C- and N-rich phases (SiC , Si_3N_4 , graphite) found in primitive meteorites (17). No circumstellar dust grains were definitively identified despite an intensive search comprising more than 20 slices and fragments from a dozen particles and $\sim 5700 \mu\text{m}^2$ of debris in and around six small ($< 2 \mu\text{m}$) and four large ($> 50 \mu\text{m}$) craters on Al-foil collectors. This result contrasts sharply with inferences of a population of nearly pure ^{12}C grains in comet Halley (5). One ~ 150 -nm region from the bottom of a large Al-foil crater has an isotopic composition ($\delta^{13}\text{C} = 59 \pm 61\%$; $\delta^{15}\text{N} = -518 \pm 60\%$) that falls in a range consistent with

“mainstream” presolar SiC grains (17); however, the grain was sputtered away before a mineral identification could be made. Another hotspot was enriched in ^{13}C ($\delta^{13}\text{C} = 964 \pm 219\%$) and depleted in ^{15}N ($\delta^{15}\text{N} = -415 \pm 94\%$), typical of mainstream SiC; however, the ion-emission area was not as localized as would be expected for a very small circumstellar grain and, moreover, showed a high abundance of nitrogen (inferred C/N ~ 3). This grain disappeared rapidly during analysis, as did a second spot with a low inferred C/N ratio ≈ 6 and low $\delta^{15}\text{N} \approx -350\%$. This behavior is consistent with sputtering of labile organic material. Notably, this isotopically light nitrogen component is rarely seen in IDPs (7, 18), but within $\sim 10\%$ uncertainties, is consistent with estimates of the nitrogen isotopic composition in HCN gas from comet Hale Bopp (19) and of the solar composition based on analyses of the jovian atmosphere (20) and of solar wind implanted in lunar grains (21).

On a micrometer scale, all samples are homogeneous in both C and N isotope compositions and show no correlation between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (Fig. 2). Carbon isotopes fall in a particularly restricted range with most “bulk” $\delta^{13}\text{C}$ values falling between -20 and -50% . This range is somewhat higher than recent estimates ($\delta^{13}\text{C} = -105 \pm 20\%$) of the solar carbon isotope composition (22), but is compatible with carbon isotopes in other primitive solar system matter including IDPs (6) and most organic matter in chondrites (23).

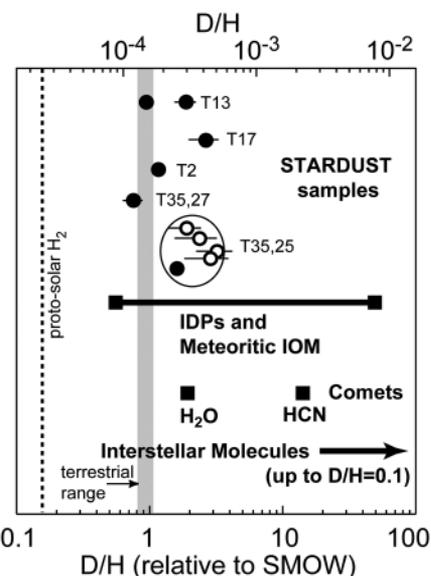


Fig. 1. Hydrogen isotopic compositions in bulk fragments (solid circles) of five Wild 2 particles and in micrometer-sized subareas of one particle (open circles) compared to SMOW and to ranges of laboratory measurements of D/H in IDPs and in insoluble organic matter (IOM) from chondritic meteorites. Also shown are an estimate for protosolar H_2 and ranges of D/H measured remotely for specific gaseous molecules from comets and for molecular clouds. Error bars are 1σ .

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A wider range is observed for “bulk” nitrogen with many samples clustering near 0‰ (atmospheric) but others showing modest $\delta^{15}\text{N}$ enrichments of +100 up to ~500‰, similar to the range observed for anhydrous IDPs (7). On a submicrometer scale, more-extreme values are found with a maximum $\delta^{15}\text{N}$ of 1300 ± 400 ‰, similar to the highest values found in refractory organic matter in IDPs (7) and meteorites (14). Unlike IDPs, however, the Wild 2 samples display both low and high $\delta^{15}\text{N}$, indicating an unequilibrated mixture of a low- $\delta^{15}\text{N}$ (perhaps icy) component and a more refractory (high C/N) organic material with high $\delta^{15}\text{N}$ and isotopically “normal” carbon. The fact that most IDPs are characterized by ^{15}N excesses may reflect the instability of the more labile, low- $\delta^{15}\text{N}$ component during atmospheric-entry heating. Thus, the Wild 2 samples could represent a different type of organic material than that available for study through the stratospheric IDPs, although it is puzzling that the Wild 2 particles analyzed thus far appear to be deficient in total organic matter compared to most IDPs. This observation contradicts expectations of comets as being very rich in organic matter and may indicate that much of the Wild 2 organic matter did not survive the capture process as discrete phases still closely associated with silicate minerals.

Oxygen is the most abundant element in rocky planets, asteroids, and comets and exhibits distinctive isotopic compositions that are essentially unique to each class of planetary materials from the inner solar system (24). Although the isotopic variations that occur on planetary scales are relatively subtle (less than a few ‰), individual components of unequilibrated meteorites have oxygen isotope compositions varying by 50‰ or more in relative abundances of ^{16}O [e.g., (9)]. These isotopic variations are fairly systematic (25) and, together with planetary-scale variations, imbue oxygen with a unique diagnostic capability to indicate sample provenance (24). Orders-of-magnitude larger isotopic variations are observed in presolar oxide and silicate dust grains that condensed in the outflows of evolved, mass-losing stars and inherited specific isotopic compositions due to local nucleosynthetic processes (26). Few definitive data exist regarding oxygen isotope compositions in cometary materials. In situ measurements of water ice from comet Halley, made by the Giotto mission, yield $\delta^{18}\text{O} = 12 \pm 75$ ‰, but no measurement of $\delta^{17}\text{O}$ is available (4).

Oxygen isotope measurements of Wild 2 samples were made by mapping techniques to search for presolar grains and by focused probe SIMS on individual particle fragments to relate the comet samples to known classes of meteoritic materials. Of some 2 dozen particle fragments prepared as microtomed (<200 nm thick) sections from aerogel keystones, no candidate presolar grains were identified on the basis of extreme oxygen isotope anomalies (supporting online material). For several samples, the measurement of oxygen isotopes was

compromised by mixing with melted aerogel, which could not be resolved even with the <100-nm spatial resolution of the NanoSIMS. Therefore, residues from impact craters in the Al-foil targets were also examined by high-resolution isotope mapping.

Thirty-seven small craters, between 320 nm and 1.5 μm in diameter, and four large craters (59, 72, 140, and >200 μm in diameter) were mapped, resulting in the identification of $\sim 10^4$ O-rich subareas. Only one presolar grain was found (Fig. 3). The ~ 250 -nm grain is highly enriched in ^{17}O and slightly depleted in ^{18}O compared to solar system samples and has a composition of $^{17}\text{O}/^{16}\text{O} = (1.01 \pm 0.20) \times 10^{-3}$ and $^{18}\text{O}/^{16}\text{O} = (1.77 \pm 0.24) \times 10^{-3}$. This isotopic composition is typical for presolar oxide (and silicate) grains belonging to “group 1,” thought to originate in red giant or asymptotic giant-branch stars (26). Unfortunately, the mineralogy of the grain could not be determined, although it is likely that it was a relatively refractory oxide or silicate.

High-precision oxygen isotope measurements were made in 5- to 10- μm spots of individual “terminal grains” separated from aerogel tracks and pressed into clean Au foil. Fragments from one enstatite-rich grain (T69) and one forsterite-rich grain (T22) have similar oxygen isotope compositions that plot slightly below the terrestrial mass-dependent fractionation (TF) line and to the low $\delta^{18}\text{O}$ side of the ^{16}O -mixing line that characterizes refractory components (calcium- and aluminum-rich inclusions, CAIs) in chondrites (Fig. 4; table S2). Although unlikely, we cannot exclude the possibility that the deviation of the T69 and T22 data from the CAI mixing line is due to minor contamination with aerogel (supporting online material). The oxygen isotopic compositions of these Mg-rich silicates from Wild 2 are compatible with those of most mafic silicate minerals from carbonaceous chondrite chondrules.

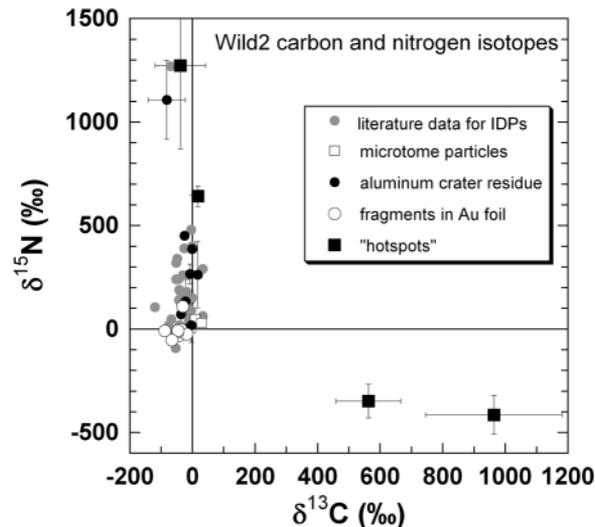
Oxygen isotopes were also measured in a polyminerallitic refractory grain (T25, “Inti”) by means of both NanoSIMS mapping and higher-precision IMS

1270 spot measurements (supporting online material). The sample consists of a fine-grained mix of spinel, Al-rich diopside, melilite, and anorthite, with a minor component of perovskite (27). Although the NanoSIMS analyses resolve individual phases, it was not possible to avoid sampling multiple mineral phases during the IMS 1270 analyses (5- μm -diameter spot). The consistency of the data (Fig. 4) demonstrates that the sample is isotopically homogeneous with an ^{16}O -rich composition compared to most planetary materials ($\delta^{18}\text{O} \approx \delta^{17}\text{O} \approx -40$ ‰). Notably, this composition is virtually identical to that of a large population of CAIs and refractory oxide grains in chondrites (9). Similarly ^{16}O -enriched compositions have been observed for rare refractory IDPs collected in the stratosphere (28), but the relation between these particles and meteoritic CAIs has not been thoroughly investigated.

As an ensemble, the isotopic compositions of the light elements—H, C, N, O, and Ne—demonstrate that the dust of comet Wild 2 is an unequilibrated aggregate of material from different sources. The H, C, and N isotope compositions indicate the presence of several minor components that are isotopically fractionated to a large extent, probably reflecting chemical reactions at very low temperatures like those characteristic of molecular cloud or, possibly, Edgeworth-Kuiper belt environments. This is consistent with a general view of Jupiter family comets as having accreted from cold materials at the edge of the solar nebula.

Two observations, however, run counter to expectations: (i) The abundance of presolar grains appears to be low compared with that of primitive meteorites and IDPs, and (ii) the comet contains high-temperature silicate and oxide minerals with oxygen isotopic compositions essentially identical to those of analogous minerals in carbonaceous chondrites. The first observation could perhaps be explained as a preservation effect, i.e., loss of presolar materials during impact, yet the one presolar grain firmly identified was found in the residue of the largest impact crater so far investigated (the grain

Fig. 2. Correlated carbon and nitrogen isotopic compositions of individual cometary grains compared with literature data (gray circles) for stratosphere-collected IDPs (7). Shown are average values for cometary grains prepared as microtome sections (open squares), for fragments extracted from aerogel and pressed into Au foil (open circles), and for residue in and surrounding craters in the Al foil collector (solid circles). Also shown are selected hotspots (solid squares) from the crushed samples. Error bars are 2 σ .



actually punctured the Al foil). If similar grains were abundant, they should have been seen in or around other craters and in the aerogel as well. However, if most of the presolar material in Wild 2 consists of interstellar amorphous silicates rather than circumstellar mineral grains, then it is possible that these would not be recognized either because of too much mixing with aerogel or, in the case of residue in Al-foil craters, because they might not possess sufficiently anomalous oxygen isotopic composi-

tions to be identified as nonsolar. On the other hand, the crystalline silicate and oxide minerals for which we have oxygen isotope data could not have formed by annealing (devitrification) of presolar amorphous silicates in the Kuiper belt. Not only is such an origin incompatible with the chemistry and mineralogy of these grains, but, because these grains differ markedly in their relative ^{16}O abundances, they also could not have formed from a single isotopic reservoir. The sim-

ilarity in O-isotope composition between Wild 2 grains and materials from carbonaceous chondrites is pronounced. Identifying precisely what regions of the inner solar system may be sampled by this comet is clearly central to understanding the scale of radial mixing outward in the solar protoplanetary disk.

Most interstellar silicate dust is thought to be amorphous (29), and with recent recognition of the relatively large fraction of crystalline silicates in comets and in protostellar disks based on infrared spectral data [e.g., (30)], astronomers have postulated mixing of dust from inner warm regions, where ambient conditions are above glass transition temperatures, outward to Kuiper belt regions [e.g., (31, 32)]. However, other observations suggest production of crystalline silicates (specifically forsterite) at large (>10 AU) stellar distances (33). That the CAI-like particle (Inti) has the same intrinsic oxygen isotopic properties as CAIs from all major classes of primitive meteorites argues strongly for an origin in the same source region as meteoritic CAIs (9). One possibility is that this region could be at the inner truncation of the accretion disk (<0.1 AU) where very high temperatures exist. Here, winds associated with bipolar outflows, driven by interactions of the young Sun with the accretion disk, can carry small refractory particles to large heliocentric distances where they can accrete together with cold, icy materials (34, 35). Other models (36) invoke turbulent transport of hot inner nebula (silicate) dust out to zones of comet accretion, which could account for the carbonaceous chondrite-like isotopic compositions of Wild 2 olivine and pyroxene grains. We conclude that the coupled oxygen isotopic and mineralogical data are best understood as indicating that a large fraction of dust in comet Wild 2 is derived from chemically and thermally processed precursors from the inner solar system, consistent with predictions of the X-wind and other models (34–36) for the protosolar disk.

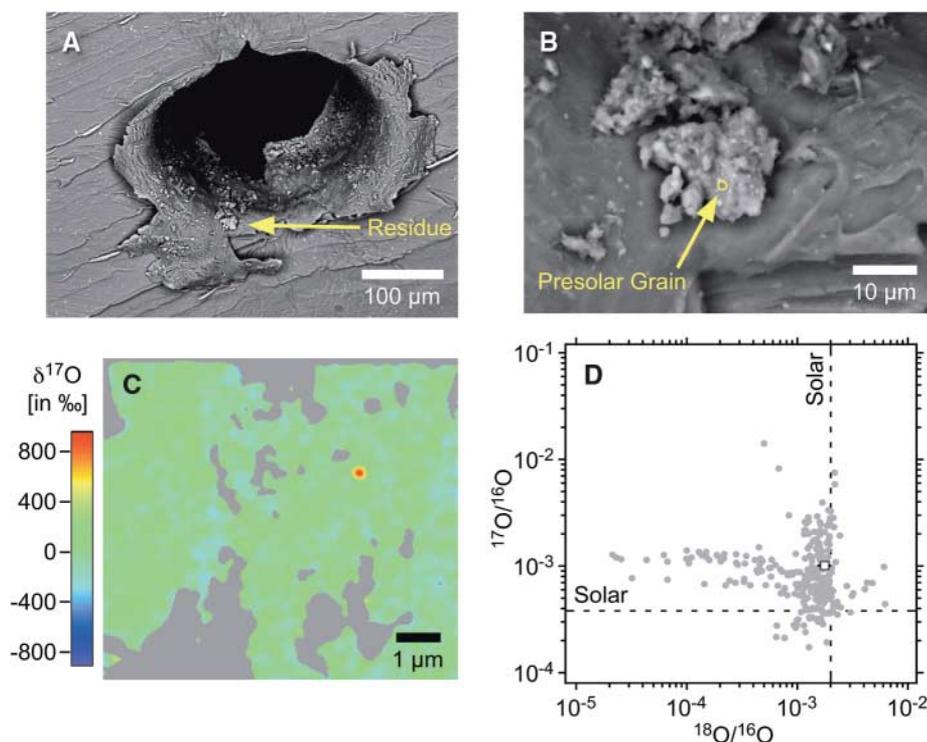
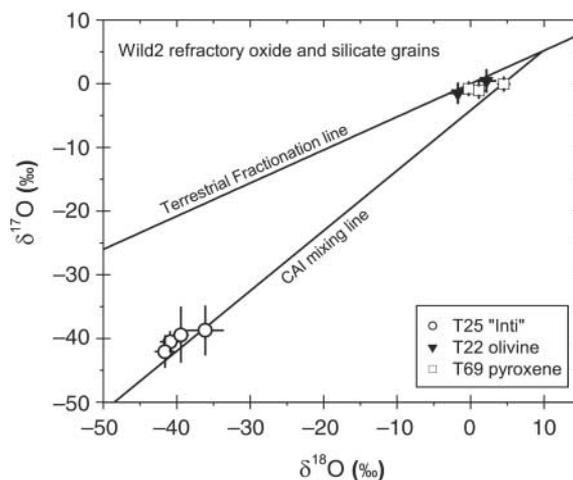


Fig. 3. Presolar grain discovered in residue of crater C2086W1. **(A)** Backscattered electron image of a crater which punctured the Al foil. **(B)** Electron image of projectile residue in crater lip. **(C)** False-color isotope map of $\delta^{17}\text{O}$ measured by high-resolution NanoSIMS. **(D)** Oxygen three-isotope plot of presolar grain (open square) compared to literature data for presolar oxide grains separated from meteorites. On this scale, all materials formed in the solar system plot at the intersection of the two dashed lines. Error bars are 1σ .

Fig. 4. Oxygen isotopic compositions of individual cometary grains. The terrestrial mass-dependent fractionation line (TF) and the CAI-mixing line are shown for reference. Error bars are 2σ .



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- H and O, Pee Dee belemnite (PDB) for C, and air for N. Absolute values for these standards are defined as $(D/H)_{SMOW} = 1.556 \times 10^{-4}$; $(^{18}O/^{16}O)_{SMOW} = 2.0052 \times 10^{-3}$; $(^{17}O/^{16}O)_{SMOW} = 3.8288 \times 10^{-4}$; $(^{13}C/^{12}C)_{PDB} = 1.12372 \times 10^{-2}$; $(^{15}N/^{14}N)_{Air} = 3.6765 \times 10^{-3}$. Unless noted, reported uncertainty estimates are 2σ (standard error).
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Supporting Online Material

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Methods

Fig. S1 to S5
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REPORT

Infrared Spectroscopy of Comet 81P/Wild 2 Samples Returned by Stardust

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Infrared spectra of material captured from comet 81P/Wild 2 by the Stardust spacecraft reveal indigenous aliphatic hydrocarbons similar to those in interplanetary dust particles thought to be derived from comets, but with longer chain lengths than those observed in the diffuse interstellar medium. Similarly, the Stardust samples contain abundant amorphous silicates in addition to crystalline silicates such as olivine and pyroxene. The presence of crystalline silicates in Wild 2 is consistent with mixing of solar system and interstellar matter. No hydrous silicates or carbonate minerals were detected, which suggests a lack of aqueous processing of Wild 2 dust.

Comets are widely believed to be repositories of the building blocks of the solar system that include both presolar and early nebular matter. The nature of the organic and inorganic materials in comets is frequently inferred through the analysis and interpretation of features in their infrared (IR) spectra, especially the mid-IR (2.5 to 15 μm) and far-IR (15 to 100 μm) parts of the spectrum where organic materials and minerals have diagnostic bands. Ground-based and spacecraft observations of comet P/Halley provided new insights into the nature of comets, including their organic inventory (1) and mineralogy with the de-

tection of crystalline olivine (2–4). In the past decade, IR spectroscopy as a method to study comets and objects outside our solar system has blossomed. The Infrared Space Observatory (ISO) obtained IR spectra over a wide spectral range (2.4 to 200 μm) tracing the widespread occurrence of crystalline silicates in many astrophysical objects including comets, young stars (e.g., Herbig Ae/Be stars), and evolved stars [(5) and references therein] following ground-based observations (6, 7). The Spitzer Space Telescope has substantially extended and broadened that view. The inferred mineralogy of dust ejecta from the Deep Impact mission, which

includes phases such as hydrous silicates and carbonate minerals, is already challenging long-held beliefs on the nature of comets (8). In addition, a large database (9, 10) exists on the physical properties (e.g., composition, mineralogy, isotopic systematics, IR spectra) of cometary interplanetary dust particles (IDPs) collected in Earth's stratosphere. With bona fide samples of a specific comet now returned by the Stardust mission (11), the detailed analysis of these samples can be used to test the chemical and mineralogical composition of comets as determined from astronomical measurements, comet encounter missions (Giotto, Puma, Deep Impact), and laboratory analyses of cometary IDPs.

We present results obtained by Fourier transform infrared (FTIR) spectroscopy on materials from comet 81P/Wild 2 returned by the Stardust mission and compare them with astronomical data and laboratory results from primitive solar system materials. Indigenous organic matter from Wild 2 was collected by the Stardust mission and survived capture [see also (12)]. It is associated with discrete grains and as finely disseminated material within impact cavities in the aerogel collection medium. FTIR measurements of extracted grains and in situ measurements from individual impact tracks show absorption features in the C-H stretching region that are consistent with long-chain aliphatic hydrocarbons (Fig. 1). The IR feature consists of a strong CH_2 asymmetric stretch at $\sim 2925 \text{ cm}^{-1}$ and a weaker CH_3 asymmetric stretch at $\sim 2960 \text{ cm}^{-1}$. A third aliphatic CH stretching band is seen near 2855 cm^{-1} . In pure aliphatic hydrocarbons, this region contains two distinct features due to the symmetric stretching vibrations of CH_3 and CH_2 groups. However, these two modes often become strongly blended when the aliphatic groups are bound to strongly perturbing