

- 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  $2\sigma$  (standard error).
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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  $\mu\text{m}$ ) and far-IR (15 to 100  $\mu\text{m}$ ) 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  $\mu\text{m}$ ) 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

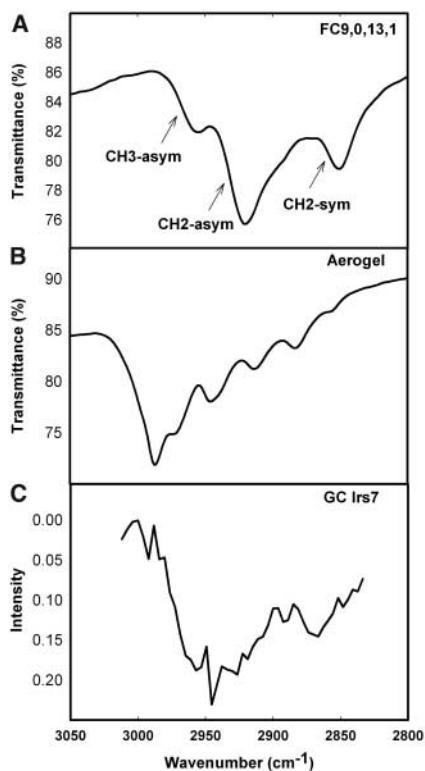
includes phases such as hydrous silicates and carbonate minerals, is already challenging long-held beliefs on the nature of comets (8). In addition, a large database (9, 10) exists on the physical properties (e.g., composition, mineralogy, isotopic systematics, IR spectra) of cometary interplanetary 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  $\text{CH}_2$  asymmetric stretch at  $\sim 2925 \text{ cm}^{-1}$  and a weaker  $\text{CH}_3$  asymmetric stretch at  $\sim 2960 \text{ cm}^{-1}$ . A third aliphatic CH stretching band is seen near  $2855 \text{ cm}^{-1}$ . In pure aliphatic hydrocarbons, this region contains two distinct features due to the symmetric stretching vibrations of  $\text{CH}_3$  and  $\text{CH}_2$  groups. However, these two modes often become strongly blended when the aliphatic groups are bound to strongly perturbing

groups (e.g., aromatic molecules) (13, 14). The Wild 2 spectra are consistent with the presence of aliphatic groups attached to other molecules. Weak

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**Fig. 1.** (A and B) The C-H stretching features from grain FC9,0,13,1 (A) showing well-resolved CH<sub>2</sub> and CH<sub>3</sub> stretching features distinct from the CH<sub>3</sub>-dominated feature from aerogel (B). (C) A C-H feature obtained through the diffuse ISM (13).

carbonyl C=O and C–C bending vibrations also occur in spectra from several grains. Hydrogen isotopic measurements show that the organic-rich grain in Fig. 1 is moderately enriched in deuterium (15). The Stardust aerogel contains organic residue from its manufacture and shows CH<sub>2</sub> symmetric and asymmetric bands at ~2872 and ~2967 cm<sup>-1</sup>, respectively, and a CH<sub>3</sub> asymmetric band at ~2928 cm<sup>-1</sup>. The aerogel C-H feature is dominated by the CH<sub>3</sub> symmetric stretch band at ~2967 cm<sup>-1</sup> and is distinct from the Wild 2 organic matter (Fig. 1). The aromatic CH feature at ~3050 cm<sup>-1</sup> has been detected in two of the grains analyzed to date by IR spectroscopy, including grain C2054,0,35,16,0 (Fig. 2). Aromatic species have also been detected in Stardust samples by two-step laser desorption–laser ionization mass spectrometry, and a highly disordered graphitic carbon has been observed with Raman spectroscopy [the G bands are characteristic of aromatic carbon (12)].

The observed C-H feature in Stardust particles bears a close resemblance to the features seen in primitive IDPs in terms of peak shapes, positions, and the CH<sub>2</sub>/CH<sub>3</sub> stretching band depth ratio (14, 16, 17). The observed CH<sub>2</sub>/CH<sub>3</sub> band depth ratio in the Wild-2 particles is ~2.5 and is the same as the average value obtained from IR spectra of anhydrous IDPs. This ratio is clearly larger than that measured for the macromolecular material extracted from primitive carbonaceous chondrite meteorites such as Orgueil and Murchison, which have CH<sub>2</sub>/CH<sub>3</sub> band depth ratios of ~1.1 (16, 18, 19). There are also large differences between the Wild 2 CH features and those observed in astronomical measurements (Fig. 1). The organic component of interstellar dust in the diffuse interstellar medium (ISM) is dominated by hydrocarbons (both aliphatic and aromatic forms) with little or no O in attached functional groups such as carbonyl and alcohols (20). The C-H stretching features of aliphatic hydrocarbons are observed along many lines of sight in the diffuse ISM (13, 18, 21–24) and show CH<sub>2</sub>/CH<sub>3</sub> band depth ratios ranging from 1.1 to 1.25 (13, 21), indicating that the aliphatic chains in Wild 2

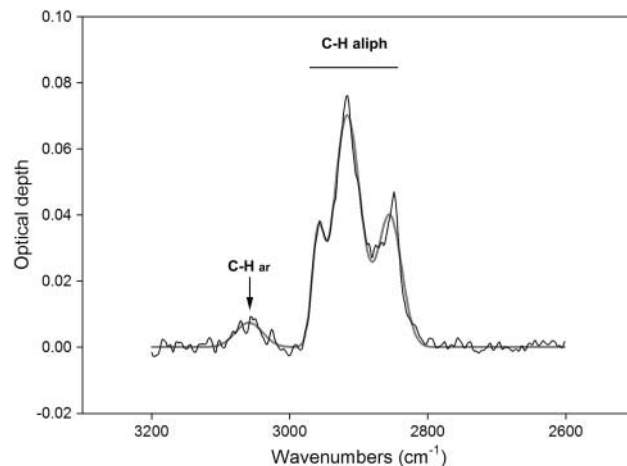
particles and IDPs are longer (or less branched) than those in the diffuse ISM. The fact that the CH<sub>2</sub>/CH<sub>3</sub> ratios of the cometary grains and the ISM grains are different suggests that the primary organic materials that formed in the ISM may have been processed before their incorporation into the parent body. Processing of Wild 2 organic matter is also supported by the higher O/C ratios of the Stardust samples relative to diffuse ISM organics (12).

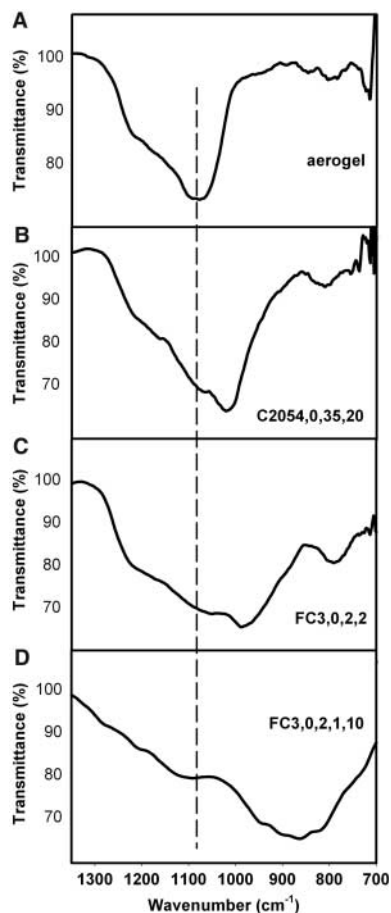
Comparison of the Wild 2 C-H feature to that in other comets is difficult. Astronomical measurement of the C-H feature in most comets (1) is complicated because it represents a mixture of gas-phase species such as CH<sub>3</sub>OH superimposed on absorption bands from solid grains (25). After subtraction of the gas-phase molecules, the remaining solid-phase carbonaceous material shows a strong contribution from the asymmetric CH<sub>2</sub> stretching vibration of aliphatic hydrocarbons (25), which is consistent with observations from the Wild-2 samples.

The extent to which the capture process modified Wild 2 organic matter is currently not fully understood. Certainly there has been redistribution of organic material along the walls and margins of the impact bulbs (12), and there is lack of petrographically recognizable carbonaceous material associated with many terminal particles (26). Labile organic material that is moderately deuterium-rich survived capture, and Raman spectroscopy data from the same grain are consistent with very primitive and poorly ordered carbonaceous material.

Amorphous silicates are the dominant silicate in the ISM and show a broad and featureless absorption band in the IR that has a maximum at 9.7 μm (27). The contribution of crystalline silicates such as olivine and pyroxene to this feature is estimated to be <2% (28, 29). Amorphous silicates are also a major component of anhydrous IDPs, many of which are believed to have a cometary origin. The majority of amorphous silicates in IDPs occur as GEMS (glass with embedded metal and sulfides) grains (30). GEMS grains are typically 0.1 to 0.5 μm in diameter, contain variable amounts of nanophase FeNi metal and Fe sulfide grains as

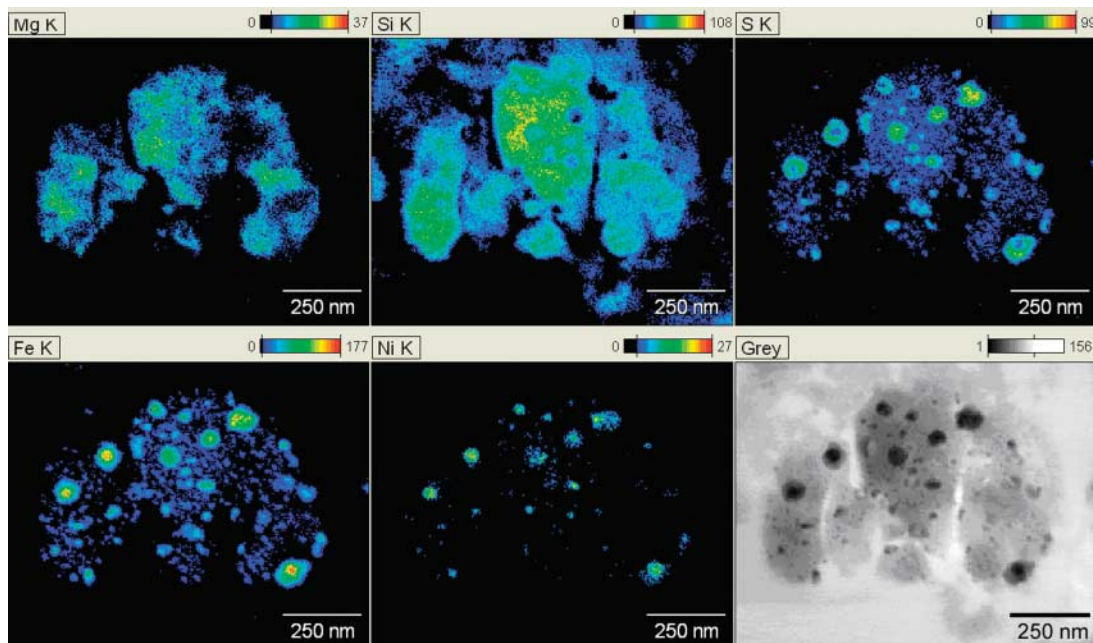
**Fig. 2.** The C-H stretch features of particle C2054,0,35,16,0 after continuum subtraction. The aromatic C-H feature is labeled C-H ar; the aliphatic C-H feature is labeled C-H aliph.





**Fig. 3.** The Si-O stretching feature in aerogel (A) compared to the range of amorphous silicate features observed in Wild-2 grains extracted from aerogel (B to D). The vertical dashed line marks the maximum absorption from aerogel.

**Fig. 4.** Elemental x-ray (k-line) maps of a GEMS-like object from a thin section of grain C044, track 7, showing preserved chemical heterogeneity at the 0.1- $\mu\text{m}$  scale typical of GEMS grains in IDPs (33). The Fe, Ni, and S maps show the locations of the nanophase FeNi metal and sulfide inclusions within the amorphous silicate matrix. The gray image is a bright-field TEM image of the GEMS-like object. The color scale in the element maps is x-ray counts.



inclusions in an amorphous silicate matrix, and have IR spectral properties in some cases similar to those of ISM amorphous silicates. One expectation based on the IDP results is that GEMS-like amorphous silicates might be similarly abundant in Wild 2. Indeed, despite complications due to overlap with the aerogel Si-O feature, the majority of Wild 2 particles analyzed to date (40 of 49) with IR spectroscopy are dominated by amorphous silicates whose maximum absorption feature occurs between 1050 and 850  $\text{cm}^{-1}$  (Fig. 3). Electron microscopy (EM) observations show that the amorphous silicates in the Wild 2 particles contain abundant nanophase FeNi metal grains and FeNi sulfides dispersed in an amorphous Mg-silicate matrix (Fig. 4) that is in general similar to GEMS grains but differs in detail (26). The IR spectrum from the GEMS-like grains mapped in Fig. 4 is similar to that observed for GEMS in IDPs (30) and the silicate feature observed in the diffuse ISM (28). The x-ray maps in Fig. 4 show compositional heterogeneity at the  $\sim 0.1\text{-}\mu\text{m}$  scale similar to that in IDP GEMS grains that were not erased by the thermal pulse experienced during capture. However, TEM observations of many of these particles also show evidence for vesiculation of the amorphous silicate matrix and partial loss of sulfur that may indicate thermal alteration during capture or interaction with aerogel (26). Without coordinated transmission electron microscopy (TEM) and perhaps ion microprobe measurements, it is not possible to distinguish primary Wild 2 amorphous silicates from secondary glasses that may have been produced during capture from their FTIR spectra.

Extracted terminal particles and some of the grains extracted from the base of the impact “bulbs” show sharp features in mid- and far-IR

spectra consistent with crystalline silicates. The silicates identified to date by IR include enstatite, olivine, and diopside with pyroxene predominating (6 of 8 grains). Similar trends are observed in anhydrous IDPs where pyroxene is more abundant than olivine (31). Far-IR measurements were obtained from terminal particles in aerogel keystones. Despite the thickness of aerogel, IR bands for enstatite, olivine, and diopside were observed. The one olivine-rich terminal particle lacked the strong 33- $\mu\text{m}$  feature commonly observed in Mg-rich olivines ( $> \text{Fo } 90$ ) such as those observed in comet Hale-Bopp (32) and young stellar objects and is consistent with a more Fe-rich olivine composition ( $\sim \text{Fo } 75$ ). The IR spectral properties of Wild 2 particles show marked similarities to astronomical IR spectra from young stellar objects and comets but are distinct from the spectra of primitive meteorites, which are dominated by crystalline silicates, mainly olivine, or phyllosilicates in the CI and CM chondrites.

No definitive FTIR evidence for hydrated silicates or carbonates at the percent level has been observed to date in any of the extracted particles. We specifically searched for 3- and 6- $\mu\text{m}$  structural OH bands and the distinctive carbonate band at 6.8  $\mu\text{m}$  in the Wild 2 spectra. The possibility exists that thermal effects from capture may have destroyed fine-grained phyllosilicates and carbonates. However, this possibility is not supported by mineralogical analysis of the particles, because the thermal breakdown products of phyllosilicates and carbonates are readily recognized by TEM and have not been observed to date (26).

The presence of crystalline silicates in the Wild 2 samples indicates that this comet is not simply an assemblage of preserved ISM silicates, but rather is a mixture of presolar and solar system materials.



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## REPORT

# Elemental Compositions of Comet 81P/Wild 2 Samples Collected by Stardust

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We measured the elemental compositions of material from 23 particles in aerogel and from residue in seven craters in aluminum foil that was collected during passage of the Stardust spacecraft through the coma of comet 81P/Wild 2. These particles are chemically heterogeneous at the largest size scale analyzed (~180 ng). The mean elemental composition of this Wild 2 material is consistent with the CI meteorite composition, which is thought to represent the bulk composition of the solar system, for the elements Mg, Si, Mn, Fe, and Ni to 35%, and for Ca and Ti to 60%. The elements Cu, Zn, and Ga appear enriched in this Wild 2 material, which suggests that the CI meteorites may not represent the solar system composition for these moderately volatile minor elements.

NASA's Stardust spacecraft collected dust particles from comet 81P/Wild 2, at an encounter speed of ~6.1 km/s, in silica aerogel capture cells and in impact craters (*I*). Analytical results from the aerogel and foils were combined to provide a more comprehensive elemental analysis of the Wild 2 particles.

The impacts in aerogel produced elongated cavities called tracks. Wedges of aerogel, called keystones (*K*), containing an entire track were extracted. The volume containing each track was analyzed by means of synchrotron-based x-ray microprobes (SXRMs), providing abundances for elements having an atomic number  $Z \geq 16$  (*S*). One

track was subsequently split open, exposing the wall for time-of-flight–secondary ion mass spectrometry (TOF-SIMS) analysis, detecting lower- $Z$  elements, particularly Mg and Al. Because Si and O are the major elements in silica aerogel, neither element could be determined in the comet material in tracks. The residues in craters were analyzed by scanning electron microscopy using energy-dispersive x-ray (SEM-EDX) analyses and TOF-SIMS, providing other element abundances, including Mg and Si.

The SXRMs produce intense, focused beams of x-rays that completely penetrate a keystone, exciting fluorescence (*F*). Elemental analysis was performed on keystones containing 23 tracks, which were selected to sample the diversity on the collector, by seven research groups with the use of six different SXRMs (*F*). These tracks range in length from ~250  $\mu\text{m}$  to almost 10,000  $\mu\text{m}$  and vary in shape from conical to bulbous. The Fe content of the tracks varies from ~180 fg to 6.4 ng (table S3), comparable to the Fe in chondritic particles ranging from ~1 to ~30  $\mu\text{m}$  in size. All 23 tracks were approximately normal to the aerogel surface, which was the arrival direction for particles collected from Wild 2 (*I*), whereas interplanetary particles, also collected, arrived over a wide range of orientations. Comets are thought to preserve dust from the early solar system, so we compared the Wild 2 dust to the elemental composition of the CI meteorites (CI) (*F*) because CI is thought to represent the nonvolatile composition of the solar system (*F*).

A map of the K-alpha fluorescence intensity for Fe from a conical track, track 19, shows that the incident particle deposited Fe along much of the entry path (Fig. 1), with only 3% of the total Fe contained in the terminal particle. The fraction of the total Fe detected in the terminal particle varies from track to track, ranging from almost 60% in one terminal particle to zero in two tracks having no detectable terminal particle. In most of the 23 tracks, most of the incident Fe mass is unevenly distributed along the track, indicating that the