Detection of cometary amines in samples returned by Stardust

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Abstract–The abundances of amino acids and amines, as well as their enantiomeric compositions, were measured in samples of Stardust comet-exposed aerogel and foil using liquid chromatography with UV fluorescence detection and time of flight mass spectrometry (LC-FD/ToF-MS). A suite of amino acids and amines including glycine, L-alanine, β-alanine (BALA), γ-amino-*n*-butyric acid (GABA), ε-amino-*n*-caproic acid (EACA), ethanolamine (MEA), methylamine (MA), and ethylamine (EA) were identified in acid-hydrolyzed, hot-water extracts of these Stardust materials above background levels. With the exception of MA and EA, all other primary amines detected in comet-exposed aerogel fragments C2054,4 and C2086,1 were also present in the flight aerogel witness tile that was not exposed to the comet, indicating that most amines are terrestrial in origin. The enhanced relative abundances of MA and EA in comet-exposed aerogel compared to controls, coupled with MA to EA ratios (C2054,4: 1.0 ± 0.2; C2086,1: 1.8 ± 0.2) that are distinct from preflight aerogels (E243-13C and E243-13F: 7 ± 3), suggest that these volatile amines were captured from comet Wild 2. MA and EA were present predominantly in an acid-hydrolyzable bound form in the aerogel, rather than as free primary amines, which is consistent with laboratory analyses of cometary ice analog materials. It is possible that Wild 2 MA and EA were formed on energetically processed icy grains containing ammonia and approximately equal abundances of methane and ethane. The presence of cometary amines in Stardust material supports the hypothesis that comets were an important source of prebiotic organic carbon and nitrogen on the early Earth.

INTRODUCTION

After a seven-year mission, the Stardust spacecraft returned to Earth the first samples from a comet on January 15, 2006. Over the next six months, the Stardust Preliminary Examination Team (PET) analyzed the samples using a variety of laboratory techniques to understand impact features, mineralogy and petrology, elemental abundances, isotopic distribution, and organic composition of the returned samples (Brownlee et al. 2006). The organics found in the samples were discussed in more detail in Sandford et al. (2006). Results from the Organics PET analyses of amino acids and amines in material returned by Stardust will be discussed here.

Comets represent some of the most primitive material in our solar system and they were likely a major contributor of the intense heavy bombardment that occurred on the early Earth (Chyba 1990). It is also thought that the delivery of water and organic matter by comets and their fragments could have been a significant source of the early Earth's prebiotic organic inventory that led to the emergence of life (Chyba

et al. 1990; Chyba and Sagan 1992; Huebner and Boice 1992; Oró et al. 1992). The organic composition of these small solar system bodies depends on the original composition, processing, and mixing of the molecular cloud (dust, ice, and gas) and solar nebula from which our solar system formed. It is currently believed that comets represent a mixture of interstellar material that has been moderately to heavily processed in the solar nebula (Ehrenfreund and Schutte 2000; Irvine et al. 2000). To date, over 140 molecular species have now been identified in the gas phase by their rotational spectrum in the interstellar medium (Lis et al. 2006). In addition, over 20 organic species such as methane (CH_4), ethane (C_2H_6), ammonia (NH_3), cyanic acid (HCN), formic acid (HCOOH), formaldehyde (H_2CO), formamide ($HCONH_2$), acetaldehyde (CH_3CHO), acetonitrile (CH_3CN), and methanol (CH_3OH), have been identified by radio spectroscopic observations of the comets Hale-Bopp and Hyakutake (Crovisier et al. 2004; Crovisier and Bockelée-Morvan 1999). These simple molecules would have provided the organic reservoir to allow the formation of more complex

organic compounds in comets such as amino acids and amine compounds (Allamandola 1998; Bernstein et al. 2002; Muñoz-Caro et al. 2002). Glycine (NH$_2$CH$_2$COOH), the simplest amino acid, has been reported in interstellar clouds (Kuan et al. 2003), although this tentative detection remains controversial (Snyder et al. 2005). Glycine was not identified by radio spectroscopic measurements of the comets C/1995 O1 (Hale-Bopp) and C/1996 B2 (Hyakutake) above detection limits (Crovisier and Bockelée-Morvan 1999; Crovisier et al. 2004). Other simple amines such as methylamine (CH$_3$NH$_2$) and ethylamine (CH$_3$CH$_2$NH$_2$) have also not been detected in these comets (Crovisier and Bockelée-Morvan 1999; Crovisier et al. 2004). Only methylamine has been identified in the interstellar medium (Ehrenfreund and Charnley 2000).

Theoretical models of the coma of Hale-Bopp find that the observed abundances of some organic molecules including HCN and CH$_3$CN cannot be produced by gas phase chemistry, so these species were probably present in the nuclear ice (Rodgers and Charnley 2001). Indeed, complex organic compounds can be formed in laboratory-simulated interstellar/ cometary ices by UV or proton irradiation of simple ice mixtures that have been observed in the interstellar medium and in comets (Allamandola et al. 1988; Moore and Hudson 1998; Bernstein et al. 1995; Allamandola and Hudgins 2003). Analyses of the ice residues after irradiation using a variety of analytical techniques demonstrate that these materials contain a much more complex suite of volatile species than originally present in the ice as well as a refractory organic component. In addition, hexamethylenetetramine (HMT, C$_6$H$_{12}$N$_4$) was observed to be one of the major products produced by irradiation and warming of various astrophysically relevant ice mixtures (Bernstein et al. 1995; Muñoz-Caro and Schutte 2003; Muñoz-Caro et al. 2004). HMT will produce a variety of amino acids upon acid hydrolysis (Wolman et al. 1971) and analyses of irradiated ice residues after acid hydrolysis demonstrate that they do contain a rich mixture of amino acids not present in the original ice mixture (Bernstein et al. 2002; Muñoz-Caro et al. 2002; Elsila et al. 2007; R. Hudson, personal communication). Therefore, it is possible that amino acids and/ or their precursor materials (e.g., HMT) are present on interstellar dust or cometary grains that were subjected to similar sources of radiation.

In situ measurements of the coma of comet 1P/Halley by the Giotto and Vega 1 and 2 probes' mass spectrometers (which measured the composition of gas and dust grains released by the nucleus) suggested the possible presence of a variety of organic species including aliphatic hydrocarbons, amines, nitriles, imines, and heterocyclic aromatic compounds (Kissel and Krueger 1987). In addition, their spectra also contained evidence for polymeric structures of H$_2$CO and HCN (Huebner 1987; Huebner et al. 1989; Rodgers and Charnley 2001). However, due to the complexity of the molecular fragments observed in the mass spectra, only a few compounds could be clearly identified (Cottin et al. 1999). The Cometary and Interstellar Dust Analyzer (CIDA) time of flight mass spectrometer instrument on the Stardust spacecraft also detected a nitrogen-rich organic chemistry with large amounts of cyanide and lower abundances of oxygen in 29 separate spectra obtained from comet 81P/Wild 2 dust impacting the target surface (Kissel et al. 2004). It is possible that the volatile nitrogen-rich organic component detected by CIDA was captured by the Stardust comet-exposed aerogel during comet Wild 2 flyby. Although CIDA did not detect any free amino acids, many of the oxygen-poor, nitrogen-rich precursor polymers that have been identified in some Wild 2 dust particles (Kissel et al. 2004; Sandford et al. 2006) may hydrolyze in acid to form more complex organic compounds.

The PET analyses of organics in samples returned by Stardust were largely focused on particles that impacted the aerogel and aluminum foil (Sandford et al. 2006). However, it is also possible that Stardust returned a "diffuse" sample of gas-phase organic molecules that struck the aerogel directly or diffused away from the grains after impact. To test this possibility, we investigated the abundances of primary amine compounds, as well as their enantiomeric composition, in Stardust comet-exposed flight aerogel and foil using a highly sensitive liquid chromatography with simultaneous UV fluorescence detection and time of flight–mass spectrometry (LC-FD/ToF-MS) technique (Glavin et al. 2006). Here we report for the first time highly sensitive quantitative measurements of amino acids and amines in samples returned from a comet.

MATERIALS AND METHODS

Chemicals and Reagents

All glassware and sample handling tools were rinsed with Millipore water, wrapped in aluminum foil, and then heated in air at 500 °C overnight. All of the chemicals used in this study were purchased from Sigma-Aldrich and Fisher Scientific. A stock amino acid and amine solution (~10^{-5} M) was prepared by mixing individual standards (97–99% purity) in Millipore (18.2 MΩ) water. The o-phthaldialdehyde/N-acetyl-L-cysteine (OPA/NAC) reagent used as a chemical tag for enantiomeric separation and fluorescence detection of primary amine compounds was prepared by dissolving 4 mg OPA in 300 μL methanol (Fisher Optima), and then adding 685 μL 0.1 M sodium borate buffer (pH 9) and 15 μL 1 M NAC. The sodium tetraborate decahydrate (Na$_2$B$_4$O$_7$·10H$_2$O) powder (SigmaUltra, 99.5–100% purity) used to prepare the sodium borate buffer was heated in air at 500 °C for 3 h to reduce amine contamination in the reagent. A 0.1 M hydrazine (NH$_2$NH$_2$) solution used to remove excess OPA after derivatization was prepared by double vacuum distillation of anhydrous hydrazine (98% purity) and subsequent dilution in water. The 6M HCl was double-distilled, and the ammonium formate buffer used in the LC-ToF-MS analyses was prepared by NH$_4$OH titration of a 50 mM formic acid solution to pH 8. A 1 μM

phenolphthalein solution in acetonitrile with 0.1% formic acid was used for internal mass calibration of the ToF-MS instrument.

Stardust Samples and Contamination Controls

Stardust Aerogel

Three pieces of the Stardust flight cometary collector tray aerogel Cell 054, Aerogel Fragment 4 (hereafter C2054,4) and a single piece of Cell 086, Aerogel Fragment 1 (hereafter C2086,1) were shipped from the University of Washington, Seattle (UW) and the University of California, Berkeley, Space Sciences Laboratory (UCB/SSL) respectively, to NASA Goddard Space Flight Center (GSFC) for amine analyses during the Stardust preliminary examination period. The C2054,4 aerogel fragment was cut into individual pieces (piece 1, 5.2 mg; piece 2, 7.6 mg; piece 3, 8.7 mg) using a razor blade and ultrasonic drill tool and the pieces then transferred into separate Teflon-coated screw-capped glass vials prior to their shipment to GSFC (G. Matrajt, personal communication). The cometary collector flight aerogel had a density gradient ranging from 5 mg/cc at the surface to 50 mg/cc at the base (Tsou et al. 2003). Aerogel piece 3 from C2054,4 (hereafter C2054,4,3) was located directly under and adjacent to aerogel piece 5 that contained particle track 25 (Fig. 1). For a discussion of track 25 and the corresponding carbon poor CAI-like "Inti" terminal particle, see Matrajt et al. (2008). Aerogel C2086,1 (3.2 mg) was a comet-exposed surface sample taken from the corner of the cell and was not adjacent to any visible particle impact tracks (C. Snead, UCB/SSL, personal communication). This aerogel sample was shipped to GSFC inside a mounting slide that was sealed inside a Mylar bag. It should be noted that these two Stardust flight aerogel samples experienced different contamination exposure environments, since they were analyzed in two separate laboratories prior to their analyses at GSFC.

For comparison, two different preflight Stardust-quality aerogel samples including a 14 mg piece of aerogel (Flight Spare Aerogel Cell E243-13C) that had been kept sealed under vacuum inside a glass tube since original bakeout in 1998 and a 23 mg piece of unbaked aerogel (Aerogel Cell E243-10F) that had been stored in air inside a plastic container since 1998 were also investigated. All of the Stardust flight aerogel was heated at 300 °C for 72 h under filtered air inside a furnace with twice a day evacuation of the furnace to <10 torr for 30 min (Tsou et al. 2003). The total carbon content of the near flight-like aerogel after bakeout was found to be <0.5% by mass (Tsou et al. 2003). The most important control sample for the Stardust comet-exposed aerogels was the flight aerogel witness tile (WCARMI1CPN). This tile was mounted on the Stardust collector tray deployment arm, but was protected from dust impacts during the comet flyby by the spacecraft's Whipple shields. Therefore, this aerogel sample witnessed all of the same terrestrial and space environments as the cometary collector tiles, but was not directly exposed to the comet. Two
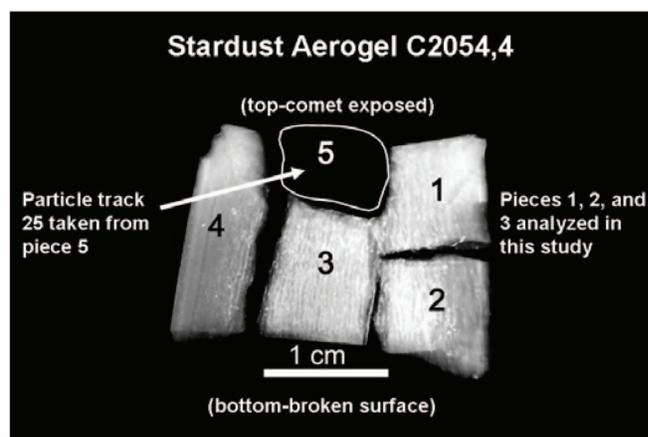

Fig. 1. The Stardust flight aerogel fragment C2054,4 sub-cutting diagram oriented with the comet exposed side at the top. Pieces 1, 2, and 3 were allocated during the preliminary examination period for LC-FD/ToF-MS analysis of amines at GSFC. Pieces 4 and 5 (which contained particle track 25) were not analyzed using this technique. Another comet-exposed aerogel sample C2086,1 that was not adjacent to a particle track was also analyzed (picture not shown). Aerogel photo courtesy D. Brownlee.

separate pieces of aerogel (Piece 8, 0.1 mg; Piece 9, 0.1 mg) were extracted from the witness tile using an ultrasonic vibration microknife (Westphal et al. 2004) on a glass slide at the NASA Johnson Space Center (JSC). The witness tile samples were shipped to GSFC inside Nylon-capped glass vials. In addition, we also analyzed a sample of the aerogel mold release (Synlube 100; 5.5 mg) used during the manufacturing process of the Stardust preflight and flight aerogel.

Stardust Foil

Each cell on the Stardust collector tray contains a set of foils (1100 aluminum) designed to capture impacting dust particles as well as facilitate the removal of the aerogel tiles (Tsou et al. 2003). For this study, two separate Stardust flight foil samples from the cometary collector tray were analyzed for amino acids and amines (Fig. 2). The foils were from the lower edge of Cell 092 (hereafter C2092S,0) and top edge of Cell 125 (hereafter C2125N,2). Each foil had a total surface area of ~24 cm^2 (both sides, see Fig. 2) and did not contain any identifiable surface impact craters (F. Hörz, personal communication). The C2092S,0 and C2125N,2 aluminum foils were shipped to GSFC inside separate plastic windowed aluminum containers that were wrapped inside a Teflon bag inside a Nylon bag. In order to minimize contact with the Stardust foils, the surface area of each was calculated from the measured mass of each foil with the specified density (2.71 g/cm^3) and thickness (102 μm) of the 1100 aluminum (Tsou et al. 2003). Three separate foil strips were cut from the top flap (double-sided surface area, 1.4 cm^2), middle section (double-sided surface area, 1.8 cm^2), and bottom flap (double-sided surface area, 1.2 cm^2) of foil C2092S,0 using a razor blade and analyzed separately to test if there was a concentrate gradient of amines with depth into the cell (Fig. 2).
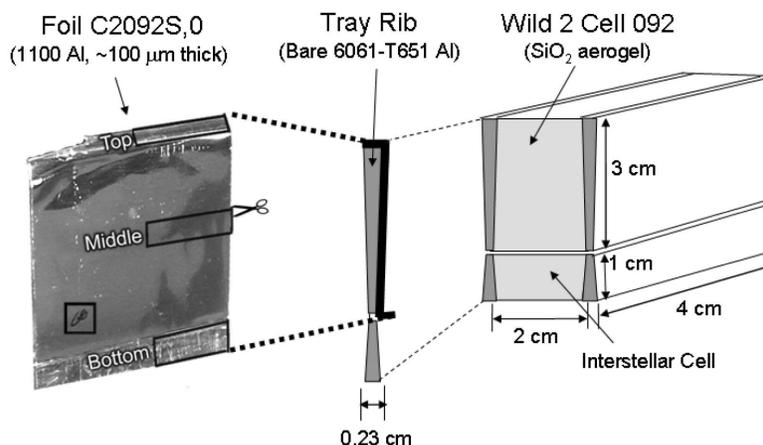
Fig. 2. The Stardust flight foil C2092S,0 showing the orientation of the foil in Wild 2 Cell 092 and the top, middle, and bottom pieces that were cut from the original foil and analyzed for amines separately. The top flap was directly exposed to Wild 2. The ink mark used to designate the aerogel contact side of the foil was removed prior to extraction of the remaining bulk foil sample. Another comet-exposed Stardust foil C2125N,2 was also analyzed in this study (picture not shown). Each foil was approximately 3 cm × 4 cm in size. Stardust collector tray rib and cell diagrams courtesy P. Tsou.

The remaining C2092S,0 foil piece (hereafter bulk foil, 18 cm^2) was also analyzed. In contrast to the Stardust flight aerogel analyses, we were not allocated a sample of "witness foil" that was not exposed directly to the comet as a control sample (e.g., foil from the interstellar collector tray). There was no foil associated with the aerogel witness tile WCARMI1CPN. Instead, background amine levels were determined by analyzing samples of commercial aluminum foil that had been heated at 500 °C overnight and carried through the same processing procedures as the Stardust flight foils.

Contamination Controls

The Stardust Spacecraft Return Capsule (SRC) was designed to pressurize with high efficiency particulate air (HEPA) filtered air during atmospheric re-entry. During pressure equilibration it is possible that atmospheric contaminants, cleanroom contaminant gasses, heatshield ablation products or landing site water and soil could have been drawn into the Sample Canister (SC) interior before disassembly. A visual inspection of the Sample Tray Assembly (STA), SC interior and HEPA filter suggested that little if any particulate contamination of the Stardust aerogel occurred. For contamination control and assessment, a mud sample (M4761,2; 109 mg wet, 93 mg dry) from the Utah Test and Training Range (UTTR) SRC landing site, samples of the heatshield paint edge (E51047; 8.9 mg) and backshell (E51049; 0.1 mg), and atmospheric samples collected from the JSC cleanroom, heatshield and backshell air entry vents were analyzed for amines. Gas chromatography mass spectrometry analyses of the collected gases showed no measurable contributions from amine compounds. Some of the amine results of the landing site mud, heatshield and backshell analyses will be discussed in this paper. For a summary of the Stardust contamination control and assessment findings see Sandford et al. (2006).

Extraction Protocol and Analytical Technique

The Stardust aerogel, foil, and contamination control samples were carried through an extraction protocol designed to investigate amino acids and amines in both the free and bound state (Glavin et al. 2006). All of the Stardust preflight and flight aerogel samples, Synlube 100, Stardust foil C2092S,0, and contamination control materials were weighed, flame-sealed inside individual glass test tubes with 1 mL of Millipore water, and then heated for 24 h in a heating block set at 100 °C. The Stardust foil sample C2125N,2 was extracted separately on both the aerogel contact side and metal frame contact side by adding a single 100 μL drop of Millipore water to each side facilitating the extraction of water soluble compounds at 25 °C for 5 min. An extracted surface area of ~0.5 cm^2 for each side of foil C2125N,2 was estimated by hovering calipers above the sample to measure the diameter of the water drop on the surface of the foil. For comparison, the empty foil container that contained foil C2125N,2 was extracted by adding 3 mL of Millipore water to the inside of the container at 25 °C for 5 min. The extracted surface area of the bottom of the foil container interior was determined by caliper measurements to be 8.2 cm^2. Background amine levels were established by analyzing procedural glass blanks and samples of aluminum foil that had been heated at 500 °C overnight and carried through the same processing procedures as the Stardust foils.

After water extraction, each sample extract was split in half, transferred into two separate test tubes, and then dried under vacuum at 45–50 °C using a Labconco centrifugal concentrator. The dried residues from one half of each of the water extracts were subjected to an acid vapor hydrolysis treatment as described elsewhere (Glavin et al. 1999, 2006). The remaining residues were not acid hydrolyzed in order to determine the concentration of free amines in the water

extracts. After acid hydrolysis the samples were dried under vacuum to remove any residual HCl from the hydrolyzed sample. A fraction of both the hydrolyzed and unhydrolyzed residues were re-suspended in 20 μL 0.1 M sodium borate buffer (pH 9) and derivatized with 5 μL OPA/NAC (Zhao and Bada 1995) in glass vials. The derivatization reaction was quenched after 1 min at room temperature with 75 μL of 0.1 M hydrazine hydrate, and the solution was loaded into the LC-FD auto sampler carousel at 4 °C within a few minutes of analysis. For the UTTR mud sample, both hydrolyzed and unhydrolyzed residues were re-dissolved in 3 mL water and desalted via a cation exchange column (AG 50W-X8, 100–200 mesh, hydrogen form, BIO-RAD) prior to analysis.

Amino acid and amine derivatives and their enantiomeric ratios in the Stardust samples and controls were analyzed after chemical derivatization by LC-FD/ToF-MS. The instrument was optimized for maximum sensitivity of OPA/NAC primary amine derivatives in the 300–450 m/z range with detection limits in the subfemtomole ($\sim 10^{-15}$ to 10^{-16} mol) range. For additional details on the LC-FD/ToF-MS instrument and operation parameters used in these analyses see Glavin et al. (2006). In addition to identifying the major fluorescent peaks present in the LC-FD/ToF-MS chromatograms by retention time and mass, we also searched for the masses of various amines corresponding to C_2–C_6 amino acids, hydroxylamine, and C_1–C_6 amines by plotting the nominal mass of each compound over the elution time.

RESULTS AND DISCUSSION

The major amino acid and amine peak identifications for all LC-FD and ToF-MS chromatograms discussed in this paper are given in Table 1. All of the procedural blank corrected amine concentrations reported for the Stardust samples and controls are the average values of between two and eight separate LC-FD/TOF-MS measurements (N) with a standard error $\delta_x = \sigma_x \times (N-1)^{-1/2}$ for each individual compound. Each peak in the chromatograms was identified by comparison of its UV fluorescence retention time and exact molecular mass with those of authentic amino acid and amine reference standards.

Amino Acid and Amine Analyses of Stardust Aerogel and Foil

Preflight Aerogel

The LC-FD chromatograms of the 6 M HCl-hydrolyzed, hot-water extracts of a procedural blank, preflight aerogel E243-13C, and the Stardust flight witness tile and comet-exposed aerogel samples are shown in Fig. 3. The chromatogram obtained for the preflight baked aerogel sample that was stored under vacuum shows only tiny peaks close in area to those found in the procedural blank. Trace levels of amines including L-aspartic and L-glutamic acids, L-serine, glycine, β-alanine (BALA), γ-

Table 1. Peak identifications and abbreviations for primary amine compounds detected in the chromatograms of the Stardust aerogel and foil extracts.

Peak	Amine compound	Peak	Amine compound
1	D-aspartic acid	8	β-alanine (BALA)
2	L-aspartic acid	9	γ-amino-*n*-butyric acid (GABA)
3	L-glutamic acid	10	L-alanine
4	D-glutamic acid	11	ε-amino-*n*-caproic acid (EACA)
5	D-serine	12	Ethanolamine (MEA)
6	L-serine	13	Methylamine (MA)
7	Glycine	14	Ethylamine (EA)

amino-*n*-butyric acid (GABA), L-alanine, ε-amino-*n*-caproic acid (EACA), ethanolamine (MEA), methylamine (MA), and ethylamine (EA) were identified in E243-13C with total concentrations ranging from 0.04 to 3.4 nmol per gram of aerogel (Table 2). There were no free amino acids or amines detected in the unhydrolyzed water extract of E243-13C (Table 2).

Another preflight aerogel sample E243-10F that was not baked out nor stored under vacuum, showed a similar abundance and distribution of amine compounds compared to E243-13C, with the exception of GABA and EACA (Table 2). The unbaked aerogel contained a much higher concentration (~8×) of the amino acid GABA compared to the baked aerogel (Table 2). These findings suggest that the abundance of GABA can be used to track the degree of bakeout cleaning of Stardust aerogel. EACA, also known as 6-aminohexanoic acid (($NH_2(CH_2)_5COOH$)), is a monomer of the Nylon-6 polymer and has previously been shown to be a good indicator of the extent of Nylon-6 contamination of Antarctic meteorite samples (Glavin et al. 2006). EACA was detected in E243-13C at much lower concentrations than in E243-10F (Table 2), which is not surprising since E243-13C was stored inside a glass tube and was not directly exposed to Nylon-6 prior to analysis. We did not detect any D-amino acids in either preflight aerogel sample above the 0.1 nmol/g level (Table 2). In addition, only trace quantities of MA and EA (0.5 to 4 nmol/g) were identified in the preflight aerogels. Ethanolamine (MEA) was detected in all of the Stardust preflight and flight aerogel extracts at similar relative abundances (Fig. 4). We believe that the source of the MEA contamination is the mold release lubricant (Synlube 100) used during the Stardust aerogel manufacturing process. MEA was by far the most abundant amine compound (~40 nmol per gram) detected in an acid-hydrolyzed, hot-water extract of Synlube 100 (data not shown).

Stardust Flight Aerogel Witness Tile

In contrast to the preflight aerogel and procedural blank, the Stardust flight aerogel witness tile WCARMI1CPN showed higher levels of L-serine, glycine, BALA, GABA, L-alanine, EACA, and MEA with concentrations ranging from 4 to 9600 nmol/g (Table 2). Comparison with the
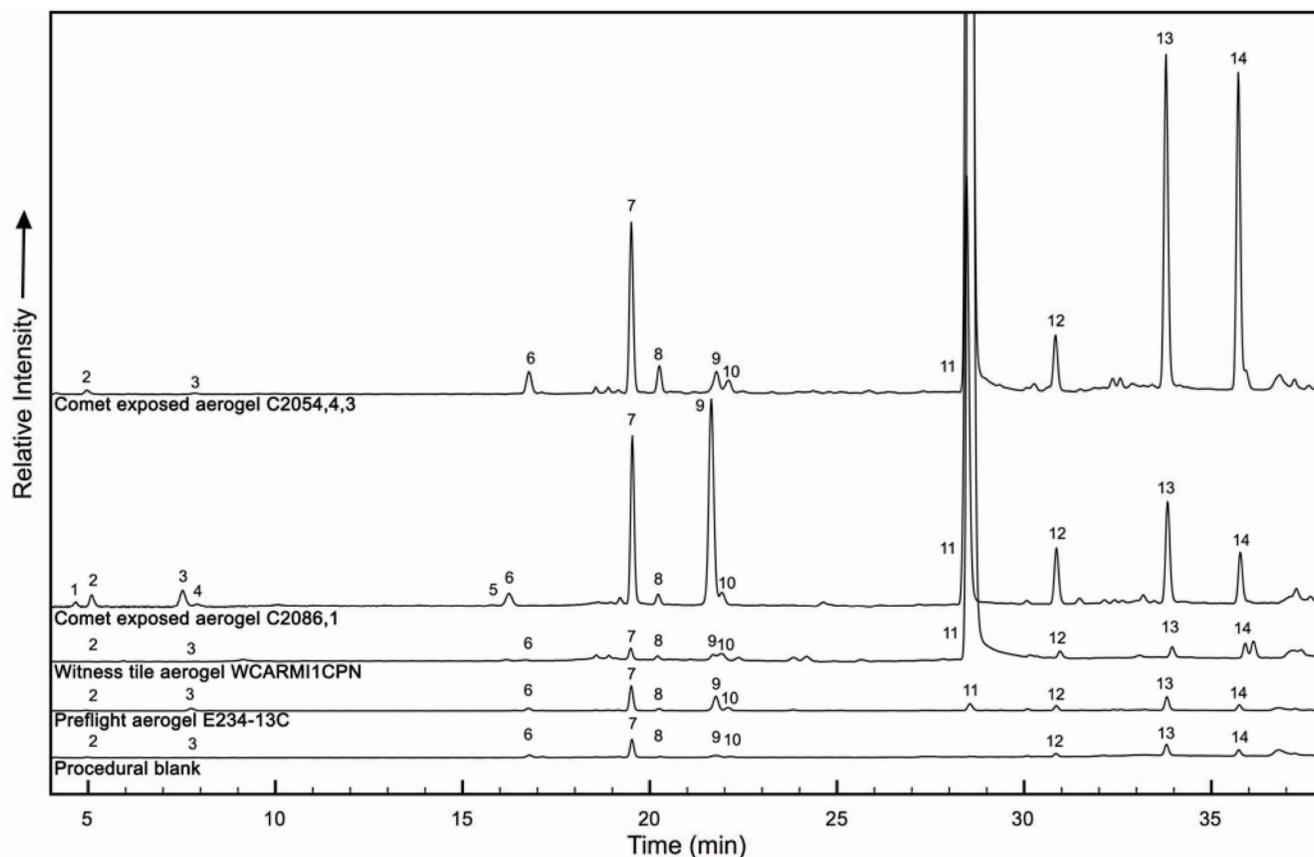
Fig. 3. LC-FD chromatograms showing OPA/NAC labeled primary amines from acid-hydrolyzed, hot-water extracts of the Stardust comet-exposed aerogel samples C2054,4,3 and C2086,1, the flight aerogel witness tile WCARMI1CPN, preflight aerogel E234-13C, and a procedural blank. All major peaks were identified by retention time and positive electrospray ToF-MS collected simultaneously. There appear to be other minor peaks in these extracts, but their identities have not been established. Identifications for the numbered peaks are shown in Table 1.

preflight aerogel, suggests that this aerogel witness coupon was contaminated with these amine compounds sometime after aerogel integration into the Stardust STA. We did not detect any D-amino acids, MA, or EA in the witness aerogel above the 0.2 to 8 nmol/g level. Only a small amount of witness coupon aerogel was available for this study (~0.2 mg total), therefore the amine detection limits for this sample are approximately two orders of magnitude higher than the preflight aerogel. MEA was also found in the witness aerogel at relative abundances similar to those found in the preflight aerogel (Fig. 4). The detection of MEA in the Stardust flight witness tile supports the claim that other volatile amine compounds, such as MA and EA, were not completely outgassed from the aerogel during flight. The high concentration of predominantly bound EACA in the witness coupon is most likely due to contamination of the aerogel with Nylon-6 polymer from the shipping vial. It should be emphasized that the EACA contaminant peak did not interfere with LC-FD/ToF-MS detection and identification of other amine compounds in any of the Stardust flight aerogel extracts.

The Stardust preflight aerogels and flight aerogel witness tile contain varying degrees of amino acid and amine contamination originating from the aerogel manufacturing process, in-flight contamination and/or storage and handling of the aerogel. The distribution and relative abundance of amine compounds found in these control samples were critical to determine the origin(s) of amines detected in Stardust comet-exposed aerogels.

Stardust Comet-Exposed Aerogel

With the exception of methylamine (MA) and ethylamine (EA), all of the amines detected in Stardust comet-exposed aerogel samples C2054,4 and C2086,1 were also present in the flight witness aerogel sample above background levels (Fig. 3). Therefore, the majority of amine compounds in the comet-exposed aerogel have a terrestrial component. It is important to note that aerogel sample C2086,1 contained a much higher relative abundance of GABA compared to aerogel C2054,4 and the witness tile WCARM1ICPN (Fig. 4), which may indicate that C2086,1 was not baked out as thoroughly compared to the other

Table 2. Summary of the average procedural blank-corrected amine concentrations in the HCl acid hydrolyzed (total) and unhydrolyzed (free) hot-water extracts of preflight and flight aerogel samples.[a]

| | Preflight aerogel | | Flight aerogel | | |
| | E243-10F (unbaked) | E243-13C (vacuum-baked) | WCARMI1CPN (witness tile) | C2054,4 (track adjacent) | C2086,1 (no visible track) |
Sample					
Amine compound			Hydrolyzed (total)		
D-aspartic acid	<0.02	<0.03	<0.5	<0.08	1.4 ± 0.1
L-aspartic acid	0.02 ± 0.01	0.04 ± 0.02	<0.5	0.2 ± 0.1	2.8 ± 0.3
D-glutamic acid	<0.02	<0.05	<0.3	<0.1	1.1 ± 0.1
L-glutamic acid	0.08 ± 0.05	0.2 ± 0.1	<0.4	0.3 ± 0.1	5.4 ± 0.5
D-serine	<0.02	<0.03	<0.2	<0.03	0.3 ± 0.1
L-serine	<0.02	0.2 ± 0.1	4.0 ± 2.2	0.3 ± 0.2	3.5 ± 0.3
Glycine	2.2 ± 0.8	2.1 ± 0.9	24.5 ± 6.0	9.5 ± 2.0	28.6 ± 2.5
BALA	0.07 ± 0.04	0.3 ± 0.1	10.4 ± 1.6	2.3 ± 0.5	2.7 ± 0.7
GABA	15.3 ± 3.5	2.0 ± 0.5	23.7 ± 2.0	3.5 ± 1.4	55.3 ± 6.5
D-alanine	<0.03	<0.06	<0.3	<0.06	<0.1
L-alanine	0.4 ± 0.2	0.4 ± 0.1	18.8 ± 8.7	0.7 ± 0.2	3.3 ± 0.2
AIB	<0.05	<0.07	<0.7	<0.04	<0.05
D,L-isovaline	<0.02	<0.04	<1.5	<0.04	<0.1
EACA[b]	5.2 ± 1.7	0.5 ± 0.3	9600 ± 850	483 ± 141	151 ± 3
MA	4.0 ± 0.9	3.4 ± 0.5	<7.9	35.1 ± 7.1	64.1 ± 0.2
EA	0.6 ± 0.2	0.5 ± 0.2	<4.0	36.2 ± 5.8	35.8 ± 4.1
MEA	2.2 ± 0.8	1.6 ± 0.6	52.0 ± 27.7	4.7 ± 0.7	14.5 ± 2.3
			Unhydrolyzed (free)		
D-aspartic acid	<0.02	<0.03	<0.5	<0.06	<0.07
L-aspartic acid	<0.08	<0.03	<0.5	<0.05	<0.05
D-glutamic acid	<0.02	<0.02	<0.3	<0.03	<0.06
L-glutamic acid	<0.02	<0.02	<0.3	<0.04	<0.06
D-serine	<0.02	<0.03	<0.2	<0.03	<0.06
L-serine	<0.02	<0.03	<0.2	<0.03	<0.06
Glycine	1.2 ± 0.2	<0.07	<0.3	<0.05	<0.2
BALA	<0.02	<0.05	<0.2	<0.04	<0.05
GABA	<0.02	<0.02	<0.1	<0.03	<0.02
D-alanine	<0.03	<0.03	<0.2	<0.05	<0.05
L-alanine	<0.2	<0.03	<0.2	<0.05	<0.05
AIB	<0.05	<0.07	<0.5	<0.05	<0.1
D,L-isovaline	<0.02	<0.04	<1.1	0.1	<0.1
EACA[b]	0.02 ± 0.01	<0.02	39.8 ± 10.2	<0.03	<0.04
MA	1.6 ± 0.6	<0.1	<2.1	0.6 ± 0.5	0.7 ± 0.6
EA	0.3 ± 0.2	<0.1	<1.5	1.1 ± 0.4	0.8 ± 0.6
MEA	1.5 ± 0.6	<0.1	9.2 ± 2.4	<0.06	0.6 ± 0.1

[a] The concentrations are the average values from LC-FD and TOF-MS measurements reported as 10^{-9} mol amine per gram (nmol/g) aerogel on a bulk sample basis. The preflight aerogel sample E243-13C was kept sealed under vacuum inside a glass tube after original bakeout in 1998 prior to extraction. Unbaked preflight aerogel E243-10F was stored in air inside a plastic container. The witness aerogel WCARMI1CPN was not directly exposed to comet Wild 2. Stardust flight aerogel C2054,4 was located adjacent to a particle track while flight aerogel C2086,1 did not contain any visible particle tracks. The concentrations for C2054,4 are average values obtained from aerogel pieces 1, 2, and 3. Upper limits are shown for amines that were not detected above procedural blank background levels.

[b] Major component of Nylon-6; also known as 6-aminohexanoic acid.

Stardust flight aerogel samples. Several D-amino acids including D-aspartic acid, D-glutamic acid, and D-serine were also detected in aerogel sample C2086,1 at low concentrations (Fig. 3, Table 2). However, these D-amino acids were not present in the other comet-exposed flight aerogel C2054,4, therefore a cometary source for these compounds is unlikely. In addition, the low D/L ratios (~0.1 to 0.5) of these protein amino acids in C2086,1 are inconsistent with an abiotic origin. Since these D-amino acids were also not found in the aerogel witness tile WCARMI1CPN, a more likely explanation for the presence of D-amino acids in C2086,1 is terrestrial contamination of the aerogel during curation. Glycine was detected in both Stardust comet-exposed aerogel sample C2054,4 and C2086,1 at relative abundances that exceeded those found in the preflight aerogels and flight witness tile (Fig. 4). At this time we cannot rule out the possibility of a cometary component of this amino acid in these aerogel samples.
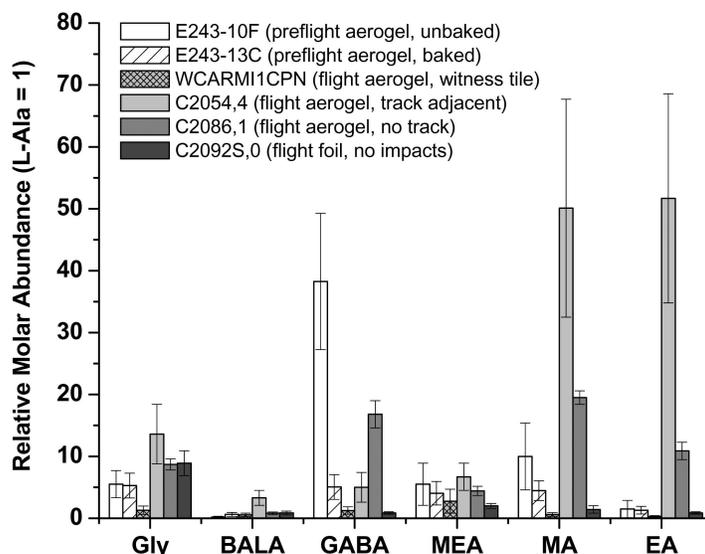
Fig. 4. A comparison of the relative molar abundances of glycine, β-alanine (BALA), γ-amino-*n*-butyric acid (GABA), ethanolamine (MEA), methylamine (MA), and ethylamine (EA) in the acid-hydrolyzed hot-water extracts of Stardust aerogel and foil. The abundances were normalized to L-alanine since this amino acid contaminant was found in all of the aerogel and foil samples. The uncertainties shown are based on the standard deviation of the average value of between two and eight separate measurements.

Two of the most abundant non-protein amino acids found in the CM type carbonaceous meteorite Murchison α-aminoisobutyric acid (AIB) and isovaline (Iva), and which are characteristic of amino acids of apparent abiotic origin (Kvenvolden et al. 1971), were not detected in any of the Stardust aerogel extracts above the analytical detection limit (Table 2). The CI type carbonaceous meteorites Orgueil and Ivuna, which may have originated from a cometary parent body (Campins and Swindle 1998; Lodders and Osborne 1999) are also depleted in AIB and Iva, but show elevated levels of BALA compared to glycine with a molar ratio of ~2 (Ehrenfreund et al. 2001). The Stardust comet-exposed aerogel samples contain much lower relative abundances of BALA to glycine (~0.1 to 0.2, Table 2), which is distinct from the CI meteorites. However, direct comparisons between the Stardust aerogel and carbonaceous meteorites must be taken with caution, since the aerogel likely only sampled the volatile amine component of Wild 2 that may not be representative of the amine distribution found inside the comet nucleus.

MA and EA were both identified in the LC-FD/ToF-MS chromatogram of comet-exposed aerogel C2054,4 by simultaneous UV fluorescence detection and exact mass measurements (Fig. 5). The exact masses in the ToF-MS chromatograms for the OPA/NAC derivatives of MA (m/z = 293.10) and EA (m/z = 307.11) show clear peaks (peaks 13 and 14) at the same retention time as the corresponding UV fluorescence peaks for these amines (Fig. 5). Individual mass peaks for other amine compounds identified in the aerogel are also shown (Fig. 5). Peaks with masses corresponding to hydroxylamine (NH_2OH) and larger amines (C_3 to C_6) were

not detected in the Stardust aerogel chromatogram (data not shown). There is one large unidentified peak labeled 'x' in the C2054,4 aerogel mass trace m/z = 365.12 equivalent to the mass of the OPA/NAC derivative of a C_4 amino acid (Fig. 5). However, the retention time of this peak did not match up with a corresponding peak in the fluorescence trace, therefore this compound is not a primary amine.

The concentration of methylamine (MA) and ethylamine (EA) present in both comet-exposed aerogel samples C2054,4 and C2086,1 ranged from 35 to 64 nmol/g, greatly exceeding the abundances of MA and EA in preflight aerogels and the aerogel witness tile (Table 2, Fig. 4), which may indicate a cometary component for these amines. Although the average EA abundances in C2054,4 and C2086,1 are identical within uncertainties, the MA concentration in C2086,1 is nearly twice that found in C2054,4 (Table 2). Given that C2086,1 contains a higher degree of terrestrial amino acid contamination compared to C2054,4, we cannot rule out the possibility that some of the MA in C2086,1 is terrestrial in origin. The presence of high L-alanine contamination levels in C2086,1 is reflected in the lower relative abundances of MA and EA in C2086,1 compared to C2054,4 (Fig. 4). MA and EA were present at much lower levels in the unhydrolyzed extracts of both C2054,4 and C2086,1 (~1 nmol/g, Table 2), which may indicate that these amines are present predominantly in an acid labile bound form, rather than as a free primary amine. This finding is supported by X-ray Absorption Near Edge Spectroscopy (XANES) results that indicate the presence of a labile amide rich organic polymer in some of the recovered particles (Sandford et al. 2006; Cody et al. 2008), and the lack of free amino acids detected in Wild 2 dust by the CIDA
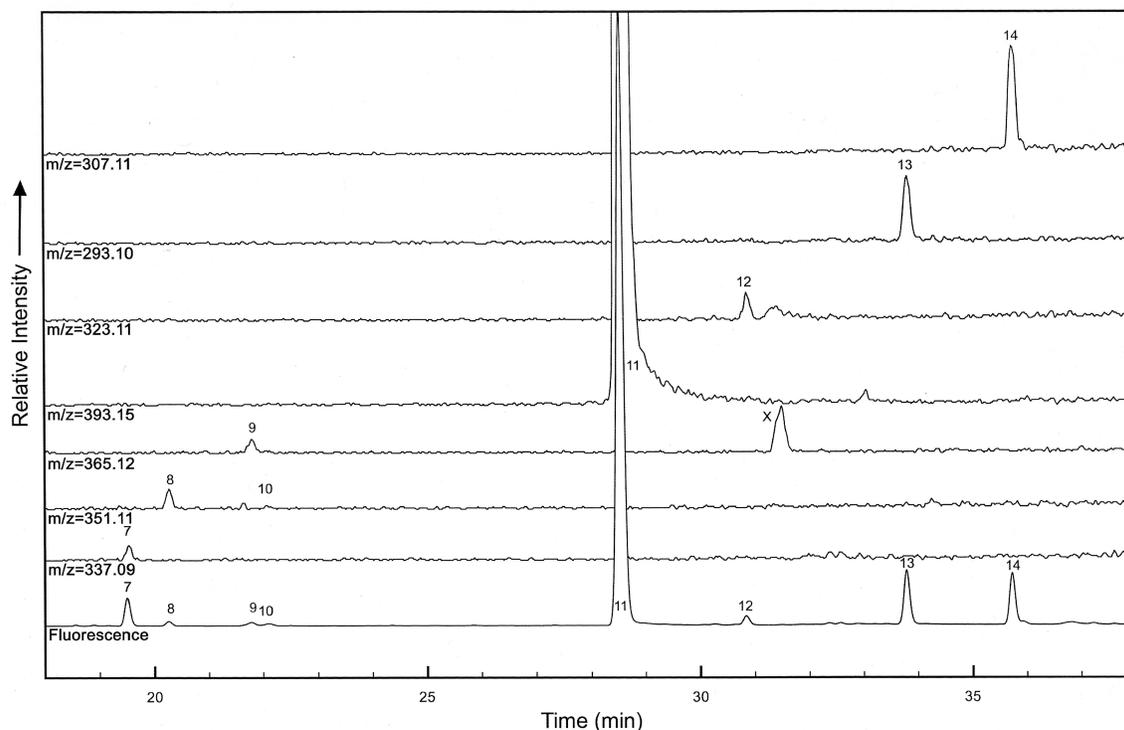
Fig. 5. LC-FD/ToF-MS chromatograms derived from the acid-hydrolyzed hot-water extract of comet-exposed aerogel sample C2054,4 show compounds detected by their fluorescence and mass. The peaks were identified by comparison of the retention time and exact molecular mass to those in the amine standard run on the same day. Only the exact mass traces corresponding to peaks detected in the fluorescence chromatogram were identified. See Table 1 for the identities of the numbered peaks.

instrument (Kissel et al. 2004). It is also possible that MA and EA were synthesized (rather than released) from cometary precursor materials during the acid hydrolysis step.

Given that MA and EA are much more volatile than amino acids present in the aerogel, it is possible that a significant fraction of these free amines were lost during the aerogel extraction process, particularly during the vacuum desiccation steps. To test this possibility, a free amine standard containing MA and EA was carried through the entire extraction protocol. We found that ~90% of free MA and EA were lost from the unhydrolyzed fraction of the water extract, while less than 5% of these amines were lost after direct acid hydrolysis of the amine standard. These results indicate that most of the bound or acid labile amines in the aerogel would have been recovered, while a much larger fraction of free MA and EA may have been lost from the aerogel during the extraction process. Therefore, the values reported for free MA and EA in the unhydrolyzed extracts listed in Table 2 must be considered to be lower limits. We also found that despite possible loss of free MA and EA, the MA to EA molar ratio did not change during the extraction process since these compounds have similar volatilities. These results do not change our conclusion that MA and EA in Stardust aerogels C2086,1 and C2054,4 are present mainly in bound form. Even assuming a 90% loss of free MA and EA, we calculate a maximum concentration of free MA and EA in

the original aerogels prior to extraction of ~6 to 11 nmol/g (based on unhydrolyzed data in Table 2), which is still substantially less than the total abundance of MA and EA (35 to 64 nmol/g) in the acid-hydrolyzed fractions (Table 2).

Amine data from the three individual pieces of Stardust track adjacent flight aerogel C2054,4 are shown in Table 3. The distributions of amines in these samples of aerogel were found to be similar. There was no significant difference in MA and EA abundances (within errors) between a comet-exposed surface aerogel sample (Piece 1) and a sample located directly underneath this piece (Piece 2) to suggest a concentration gradient with depth. This result seems to contradict what one might expect to observe if these amines were derived from Wild 2 volatile materials impacting the collector. However, it is possible that MA and EA were redistributed inside the aerogel during flight or SRC atmospheric entry when temperatures inside the capsule were predicted to have reached as high as 50 °C (Tsou et al. 2003), however the actual peak temperature may have been significantly lower (B. Clark, personal communication). Once again, it is unlikely that cometary amines captured by the aerogel during Wild 2 flyby were lost during the return trip to Earth, since MEA, another amine compound of comparable volatility present in the preflight aerogel, was detected in all three flight aerogel samples. Since the aerogels analyzed were not crushed prior to extraction, it is

Table 3. Summary of the most abundant primary amines detected in the HCl acid-hydrolyzed, hot-water extracts of Stardust flight aerogel C2054,4.[a]

	Track adjacent flight aerogel C2054,4		
Sample	Piece 1 (surface)	Piece 2 (base)	Piece 3 (below track)
Amine compound		Hydrolyzed (total)	
Glycine	13.7 ± 1.2	3.1 ± 0.6	10.6 ± 2.9
BALA	2.6 ± 1.1	1.1 ± 0.5	2.7 ± 0.8
GABA	9.0 ± 2.4	1.2 ± 0.6	1.9 ± 0.3
L-alanine	0.9 ± 0.8	0.2 ± 0.1	1.0 ± 0.1
EACA	1062 ± 193	244 ± 13	313 ± 19
MA	18.9 ± 2.0	18.9 ± 4.7	51.3 ± 5.9
EA	27.7 ± 5.3	18.2 ± 3.6	49.4 ± 3.3
MEA	7.0 ± 0.6	2.8 ± 0.9	4.5 ± 0.7

[a] All values are reported as nmol amine per gram aerogel (nmol/g).

unlikely that the MEA was physically encapsulated within the aerogel structure, thus it should have been free to degas during the Stardust cruise and reentry phases. The recent discovery of cometary neon gas inside a sample of Stardust aerogel (McKeegen et al. 2006) supports the claim that volatile amine compounds of cometary origin such as MA and EA can be adsorbed directly onto the aerogel.

We found that aerogel C2054,4 piece 3 located directly below particle track 25 had the highest abundances of MA and EA of all three pieces of aerogel tested (Table 3). Since organic compounds have been observed to diffuse from Stardust particles beyond the extent of the physical track boundary (Sandford et al. 2006; Clemett et al. 2008), it is possible that that the MA and EA in aerogel C2054,4 originated from the impacting grain. In addition, electron microscope analyses of the terminal particle "Inti" forming track 25 showed that there was no carbon present (Matrajt et al. 2008), which could indicate that organics were volatilized from the particle during capture. If we assume that all of the MA detected in track adjacent aerogel C2054,4 pieces 1, 2, and 3 (avg. conc. = 1.1 µg MA per gram aerogel; total aerogel mass = 21.5 mg) was derived from volatiles released from the Stardust particle "Inti" that formed track 25 and an estimated original mass of the ~25 µm diameter (D. Brownlee, personal communication) impacting particle of ~20 ng, then the concentration of MA in the original "Inti" dust particle was nearly pure MA ice (~10^6 µg/g). This calculation does not include additional MA contributions from C2054,4 track adjacent aerogel pieces 4 and 5 which were not analyzed in this study. Based on this calculation, the concentration of MA in the original Stardust grain would have been at least ~10^5 times higher than the total abundance of *all amines* identified in the organic rich Murchison meteorite (~10 µg/g; Pizzarello et al. 1994; Glavin et al. 2006), which seems highly unlikely. Given that similar, if not higher absolute abundances of MA and EA were found in comet-exposed aerogel C2086,1 that was not located adjacent to a particle track (Table 2), we believe that these amines, if cometary, originate from sub-micron particles or gas that directly impacted the collector.

The high relative abundances of methylamine (MA) and ethylamine (EA), and possibly glycine in comet-exposed aerogels C2054,4 and C2086,1, coupled with a MA to EA ratio of ~1 that is distinct from potential sources of contamination, suggests that these amines are cometary in origin; all other amines detected are likely terrestrial in origin. MA and EA are present predominately in an acid-labile bound form, rather than as free primary amines which is consistent with XANES results that indicate the presence of an amide rich organic polymer in some of the recovered particles. Our results suggest that MA and EA originated from cometary gas molecules or submicron grains that impacted the aerogel collector and not from "large" dust particles recovered from the aerogel.

Stardust Comet-Exposed Foil

The Stardust foil samples on the cometary collector side were exposed to Wild 2, therefore it is possible that these materials also contain cometary volatiles. We analyzed amine compounds extracted from two separate foil samples C2125N,2 and C2092S,0; neither foil contained any impact craters (F. Hörz, personal communication). An empty foil container of the same type used to store the Stardust foils was also analyzed for comparison. Preflight foil samples were not available for analysis. The results of our LC-FD/ToF-MS measurements are summarized in Table 4. Several amino acids and amines were identified above procedural blank background levels in the acid-hydrolyzed, hot-water extract of the foil sample C2092S,0 including glycine, BALA, GABA, L-alanine, EACA, and MEA. We did not see any significant differences in amine abundances between the top, middle and bottom sections of foil C2092S,0 to suggest a concentration gradient with depth (data not shown). In contrast to the Stardust comet-exposed flight aerogels, MA and EA were only present at trace levels on the surfaces of foil C2092S,0 and were not detected on either side of foil sample C2125N,2 (Table 4). This is consistent with the expectation that Stardust foils are less efficient adsorbents than aerogel. Most of the amino acid and amine compounds detected in foils C2092S,0

Table 4. Summary of the average procedural blank-corrected amine concentrations in the HCl acid hydrolyzed (total) water extracts of Stardust flight foils and an empty foil container.[a]

| | Stardust flight foil | | | |
Sample	Container[†] (inside)	C2125N,2[†] (aerogel side)	C2125N,2[†] (metal side)	C2092S,0[‡] (both sides)
Amine compound	Hydrolyzed (total)			
Glycine	4 ± 1	21 ± 11	<3	62 ± 11
BALA	1 ± 1	<2	<2	6 ± 2
GABA	4 ± 1	<3	<4	6 ± 1
L-alanine	3 ± 2	1 ± 1	<3	7 ± 1
EACA	1214 ± 150	186 ± 1	126 ± 7	504 ± 98
MA	<1	<3	<3	10 ± 4
EA	<1	<3	<3	6 ± 1
MEA	10 ± 1	31 ± 6	3 ± 2	14 ± 2

[a] Foil values are reported as 10^{-12} mol per cm^2 extracted foil surface area (pmol/cm^2).

[†] Cold water extract (25 °C 5 min).

[‡] Hot water extract (100 °C 24 h).

and C2125N,2 were also detected at similar abundances in a cold water extract of an empty foil container of the type used to store the Stardust foils (Table 4); therefore, it is highly

Table 5. List of the major amino acid and amine compounds detected in Stardust aerogel and foil and their probable source(s).

Amine detected	Source
Glycine	Aerogel, Wild 2?
BALA	Aerogel
L-alanine	Aerogel
GABA	Aerogel (partial bakeout)
EACA	Nylon-6 (sample curation)
MEA	Synlube 100, Aerogel
EA	Wild 2, Aerogel?
MA	Wild 2

likely that all of the amine compounds detected on these foils have a terrestrial component. The high concentration of EACA found in both foils and the empty container is due to exposure to Nylon-6 (Table 4). The enhancement of MEA observed on the aerogel contact side of foil C2125N,2 compared to the metal contact side provides additional evidence that this compound originates from the Synlube 100 aerogel mold release.

One of the most intriguing results from the foil analyses was the high relative abundance of the amino acid glycine extracted from some of the Stardust foil samples. For example, we found that the molar ratio of glycine to L-alanine in water extracts of C2092S,0 (8.9 ± 2.0) and the aerogel side of C2125N,2 (21 ± 11) was higher than the empty foil container (1.3 ± 0.9). Glycine was not detected on the metal frame contact side of foil C2125N,2 (Table 4), therefore this amino acid is not a contaminant associated with the foil itself or Stardust collector frame. Moreover, the similarity in relative molar abundance of glycine to L-alanine in Stardust aerogels C2054,4 (14 ± 5) and C2086,1 (8.7 ± 0.9) compared

to the Stardust foils, point to the aerogel as the source of the glycine detected on the foils. The ultimate source of the enhanced glycine abundances observed in the comet-exposed aerogel and foil extracts remains uncertain. Future analyses of Stardust flight aerogel and foil from the interstellar collector side that was not directly exposed to Wild 2 may help constrain the origin of glycine on the cometary collector aerogel and foil. Additionally, we will measure stable carbon and nitrogen isotopic ratios of glycine to establish if this amino acid has a cometary component and of EACA to confirm our assertion that it originates from Nylon-6.

Source of Amino Acids and Amines in Stardust Materials

A summary of the amino acids and amine compounds detected in Stardust aerogel and foil and their probable sources is shown in Table 5. High relative abundances of MA, EA, and glycine were detected in the Stardust comet-exposed flight aerogel samples C2054,4 and C2086,1 compared to controls (Fig. 4 and Table 2). A slight enhancement of BALA was also observed in the comet-exposed aerogel sample C2054,4 (Fig. 4). However, the corresponding BALA excess was not seen in the other comet-exposed aerogel sample C2086,1 nor the Stardust flight foils (Fig. 4), therefore a cometary origin for this amino acid is unlikely. At this time we cannot dismiss the possibility that the glycine excesses seen in both comet-exposed aerogels and foils are cometary in origin. MA and EA were present at only trace levels in the preflight aerogel and were not detected in the flight aerogel witness tile which indicates that these amines are not outgassing products from the Stardust spacecraft. In addition, MA and EA were not produced from inflight chemical reactions inside the aerogel (e.g., decomposition of EACA), since these amines were not detected in the witness aerogel that was exposed to a similar spacecraft environment.

The ratio of MA to EA found in the comet-exposed aerogel and foil compared to controls offers the strongest

evidence that these two amines are cometary in origin. The molar ratio of MA to EA in Stardust comet-exposed aerogel (C2054,4: 1.0 ± 0.2; C2086,1: 1.8 ± 0.2) and foil (C2092S,0: 1.7 ± 0.8) is distinct from the MA to EA ratio found in all contamination control samples analyzed in this study including preflight aerogel (E243-13C: 6.8 ± 2.9), SRC heatshield and backshell (E51047: 6.1 ± 3.1; E51049: 4.3 ± 0.6), and aerogel mold release (Synlube 100: 0.1 ± 0.1). MA and EA were not detected in the UTTR landing site mud sample M4761,2 above the detection limit. The ratio of MA to EA found in comet-exposed aerogels C2054,4 and C2086,1 cannot be explained by excessive Synlube mold release contamination of preflight aerogel required to bring the MA to EA ratio down to the observed values of ~1–2, since the high relative molar abundance of MEA to MA expected from Synlube 100 contamination (~70) is not observed in these Stardust aerogel samples. Therefore, the MA to EA ratio in Stardust comet-exposed materials provides strong evidence that these two amine compounds are cometary in origin.

Origin of Cometary MA and EA in Stardust Aerogel

Since the parent species of the observed MA and EA is presently unknown, it is difficult to predict the chemical mechanism(s) that generated these amines. However, to our knowledge, no interstellar or cometary laboratory ice simulation has produced approximately equal concentrations of MA and EA. Most researchers focus on amino acids and do not report MA or EA yields (e.g., Bernstein et al. 2002; Muñoz-Caro et al. 2002; Nuevo et al. 2006), while others report MA, but EA is below their detection limit (Elsila et al. 2007), and some observe MA, EA, and propylamines but with decreasing abundance with size (R. Hudson, personal communication). One could invoke the hydrolysis of trimethyl-hexamethylenetetramine, a methylated version of the HMT compound generally believed to be in cometary ices (Bernstein et al. 1995; Cottin et al. 2002), to produce a MA to EA ratio of 1, however this reaction would also produce a wide variety of amino acids (Wolman et al. 1971) including a racemic mixture of alanine (D/L ~ 1), which were not observed in any of the Stardust aerogel or foil samples analyzed in this study.

It seems more plausible to invoke the approximately equal abundance (0.8–2.6 to 1) of methane (CH_4) to ethane (C_2H_6) that has been measured in the comae of six different comets including Hale-Bopp and Hyakutake (Mumma et al. 2003 and references therein). While the methane to ethane ratio for comet Wild 2 has not been reported, it may be similar to these comets. If so, methane and ethane could be the source of the observed Wild 2 MA and EA. The radical reaction of methane and ethane with ammonia in the gas phase during transit from the comet to the aerogel collector is unlikely since the reaction rate appears to be too slow to generate measurable amines under relevant conditions (Jodkowski et al. 1995). However, reactions to form MA and EA on energetically processed icy

grains and approximately equivalent concentrations of methane and ethane before Wild 2 is plausible. Future laboratory ice experiments containing mixtures of methane, ethane and ammonia should be carried out to test this hypothesis. In addition, comets are exposed to long periods of cosmic ray bombardment, therefore chemical reactions in Wild 2 ice grains leading to the formation of MA and EA polymers on the comet surface is also possible, however it is thought that most of the materials collected by Stardust were ejected from deeper in the comet (Brownlee et al. 2006). The presence of bound MA and EA in Stardust material is consistent with the presence of an amide rich organic polymer in some of the recovered Stardust particles (Sandford et al. 2006).

Another possibility is that the detected MA and EA were produced during the impact of icy sub-micron grains onto the Stardust cometary collector aerogel. These grains could have been shock-vaporized at elevated temperatures upon hypervelocity impact with the aerogel and would not show the "carrot-shaped" tracks typically associated with larger particle impacts (Yano et al. 1999). At elevated temperatures, the amino acids glycine and BALA or alanine could undergo thermal decarboxylation producing MA and EA, respectively. The absolute abundances of MA and EA in the comet-exposed aerogels were much higher than these amino acids. Thus, the presence of MA and EA in the Stardust aerogel could imply that significant levels of these parent amino acids were originally present in the icy grains prior to impact. Although the decomposition of amino acids in icy grains during hypervelocity aerogel impact has not been investigated, previous experiments with Murchison meteorite grains have shown that glycine and BALA do not decompose into MA and EA after heating to temperatures in excess of 550 °C under reduced pressure (Glavin and Bada 2001). It should also be noted that while the abundance of GABA in the Stardust aerogel was similar to that of glycine and BALA, the lack of *n*-propylamine in the aerogel suggests that decarboxylation of GABA did not occur. A direct comparison of the carbon and nitrogen stable isotope compositions of amines in Stardust aerogel may help determine if glycine and BALA are the parent species of MA and EA.

CONCLUSIONS

Using LC-FD/ToF-MS, we have identified a simple suite of amino acids and amines in Stardust flight aerogels and foils that were exposed to comet Wild 2. With the exception of MA and EA, all of the amines detected in the Stardust flight aerogels were also present in preflight aerogels and the Stardust flight aerogel witness tile that were not exposed to Wild 2, indicating that most of the amine compounds are terrestrial in origin. Moreover, the low D/L enantiomeric ratios of aspartic and glutamic acids, serine, and alanine found in the Stardust aerogel samples provides additional evidence that these amino acids did not originate from Wild 2.

The high relative abundance of MA and EA in the comet-exposed aerogel samples compared to the unexposed witness tile, and their distinct MA to EA ratios of ~1, provides strong evidence that these two amines are cometary in origin. These amines have not been identified previously in comets. The amino acid glycine was also detected in both Stardust comet-exposed aerogel and foil samples at relative concentrations that exceeded those found in controls. At this time we cannot rule out the possibility that this amino acid has a cometary component. Future compound specific stable carbon and nitrogen isotope measurements of glycine will be required to constrain the origin of this amino acid. The presence of nitrogen-rich amines in samples returned from Wild 2 supports the hypothesis that comets were an important source of complex prebiotic organic compounds on the early Earth.

The low concentrations of MA, EA, and glycine in the unhydrolyzed water extracts compared to acid hydrolyzed extracts of the Stardust aerogel, indicates that these amines are present predominantly in an acid labile bound form, rather than as a free amine. This finding is consistent with the XANES results which indicate that some of the Stardust particles contain a labile amide-rich organic polymer. The presence of predominately bound amino acids and amines is also in agreement with previous measurements of laboratory ice residues. However, laboratory interstellar and cometary ice analog experiments have not produced the identical distribution of amines, nor the MA to EA ratio that we observe in Stardust materials. We also recognize that the Stardust aerogel sampled a highly volatile amine component of Wild 2 that may be substantially different than the rich mixture of organic compounds predicted to be present inside the cometary nucleus (Szopa et al. 2003). Future measurements by the Cometary Sampling and Composition (COSAC) instrument onboard the surface landing probe of the Rosetta mission will provide the first in situ organics analyses of the nucleus of comet 67P/Churyumov-Gerasimenko in 2014 (Goesmann et al. 2005).

Our preliminary results indicate that at least two volatile amine compounds and possibly one amino acid were captured and trapped inside the Stardust aerogel. It is possible that many other unidentified volatile organic species are also present in the aerogel. For this reason, a few representative samples of the Stardust flight aerogel should be frozen in order to reduce the loss of volatile organic compounds over time. In the future, more sensitive techniques designed to target amine compounds as well as other important classes of prebiotic organic compounds (e.g., sugars, nucleobases, and carboxylic acids) will be used to analyze the Stardust samples. We are currently optimizing and testing a new state-of-the-art Nano-LC-ToF-MS instrument with laser induced fluorescence (LIF) detection for Stardust analyses that has a sensitivity for amines that is at least 3 orders of magnitude better than the LC-FD/ToF-MS instrument used in this study. Therefore, the detection of amino acids and amines extracted from a single 10 μm sized Stardust particle may be possible with Nano-LC-ToF-MS.

Editorial Handling—Dr. A. J. Timothy Jull

REFERENCES

Allamandola L. J., Sandford S. A., and Valero G. 1988. Photochemical and thermal evolution of interstellar/pre-cometary ice analogs. *Icarus* 76:225–252.

Allamandola L. J. and Hudgins D. M. 2003. From interstellar polycyclic aromatic hydrocarbons and ice to astrobiology. In *The Proceedings of the NATO ASI entitled "Solid state chemistry,"* edited by Pirronello V. and Krelowski J. Dordrecht, The Netherlands: Kluwer. pp. 1–54.

Bernstein M. P., Sandford S. A., Allamandola L. J., Chang S., and Scharberg M. A. 1995. Organic compounds produced by photolysis of realistic interstellar and cometary ice analogs containing methanol. *The Astrophysical Journal* 454:327–344.

Bernstein M. P., Allamandola L. J., and Sandford S. A. 1997. Complex organics in laboratory simulations of interstellar/cometary ices. *Advances in Space Research* 19:991–998.

Bernstein M. P., Dworkin J. P., Cooper G. W., Sandford S. A., and Allamandola L. J. 2002. Racemic amino acids from the ultraviolet photolysis of interstellar ice analogues. *Nature* 416:401–403.

Bockelée-Morvan D., Lis D. C., Wink J. E., Despois D., Crovisier J., Bachiller R., Benford D. J., Biver N., Colom P., Davies J. K., Gerard E., Germain B., Houde M., Moreno R., Paubert G., Phillips T. G., and Rauer H. 2000. New molecules found in comet C/1995 O1 (Hale-Bopp). Investigating the link between cometary and interstellar material. *Astronomy & Astrophysics* 353:1101–1114.

Briggs R., Ertem G., Ferris J. P., Greenberg J. M., McCain P. J., Mendoza-Gomez C. X., and Schutte W. 1992. Comet Halley as an aggregate of interstellar dust and further evidence for the photochemical formation of organics in the interstellar medium. *Origins of Life and Evolution of the Biosphere* 22:287–307.

Brownlee D. E., Tsou P., Aléon J., Alexander C. M. O' D., Araki T., Bajt S., Baratta G. A., Bastien R., Bland P., Bleuet P., Borg J., Bradley J. P., Brearley A., Brenker F., Brennan S., Bridges J. C., Browning N. D., Brucato J. R., Bullock E., Burchell M. J., Busemann H., Butterworth A., Chaussidon M., Cheuvront A., Chi M., Cintala M. J., Clark B. C., Clemett S. J., Cody G., Colangeli L., Cooper G., Cordier P., Daghlian C., Dai Z., D'Hendecourt L., Djouadi Z., Dominguez G., Duxbury T., Dworkin J. P., Ebel D. S., Economou T. E., Fakra S., Fairey S. A. J., Fallon S., Ferrini G., Ferroir T., Fleckenstein H., Floss C., Flynn G., Franchi I. A., Fries M., Gainsforth Z., Gallien J.-P., Genge M., Gilles M. K., Gillet P., Gilmour J., Glavin D. P., Gounelle M., Grady M. M., Graham G. A., Grant P. G., Green S. F., Grossemy F., Grossman L., Grossman J. N., Guan Y.,

Hagiya K., Harvey R., Heck P., Herzog G. F., Hoppe P., Hörz F.,
Huth J., Hutcheon I. D., Ignatyev K., Ishii H., Ito M., Jacob D.,
Jacobsen C., Jacobsen S., Jones S., Joswiak D., Jurewicz A.,
Kearsley A. T., Keller L. P., Khodja H., Kilcoyne A. L. D.,
Kissel J., Krot A., Langenhorst F., Lanzirotti A., Le L., Leshin
L. A., Leitner J., Lemelle L., Leroux H., Liu M.-C., Luening K.,
Lyon I., MacPherson G., Marcus M. A., Marhas K., Marty B.,
Matrajt G., McKeegan K., Meibom A., Mennella V.,
Messenger K., Messenger S., Mikouchi T., Mostefaoui S.,
Nakamura T., Nakano T., Newville M., Nittler L. R., Ohnishi I.,
Ohsumi K., Okudaira K., Papanastassiou D. A., Palma R.,
Palumbo M. E., Pepin R. O., Perkins D., Perronnet M.,
Pianetta P., Rao W., Rietmeijer F. J. M., Robert F., Rost D.,
Rotundi A., Ryan R., Sandford S. A., Schwandt C. S., See T. H.,
Schlutter D., Sheffield-Parker J., Simionovici A., Simon S.,
Sitnitsky I., Snead C. J., Spencer M. K., Stadermann F. J.,
Steele A., Stephan T., Stroud R., Susini J., Sutton S. R.,
Suzuki Y., Taheri M., Taylor S., Teslich N., Tomeoka K.,
Tomioka N., Toppani A., Trigo-Rodríguez J. M., Troadec D.,
Tsuchiyama A., Tuzzolino A. J., Tyliszczak T., Uesugi K.,
Velbel M., Vellenga J., Vicenzi E., Vincze L., Warren J.,
Weber I., Weisberg M., Westphal A. J., Wirick S., Wooden D.,
Wopenka B., Wozniakiewicz P., Wright I., Yabuta H., Yano H.,
Young E. D., Zare R. N., Zega T., Ziegler K., Zimmerman L.,
Zinner E., and Zolensky M. 2006. Comet 81P/Wild 2 under a
microscope. *Science* 314:1711–1716.

Campins H. and Swindle T. D. 1998. Expected characteristics of
cometary meteorites. *Meteoritics & Planetary Science* 33:1201–
1211.

Charnley S. B. and Rodgers S. D. 2002. The end of interstellar
chemistry as the origin of nitrogen in comets and meteorites. *The
Astrophysical Journal* 569:133–137.

Chyba C. F. 1990. Impact delivery and erosion of planetary oceans
in the early inner solar system. *Nature* 343:129–133.

Chyba C. and Sagan C. 1992. Endogenous production, exogenous
delivery and impact-shock synthesis of organic molecules: an
inventory for the origins of life. *Nature* 355:125–132.

Chyba C. F., Thomas P. J., Brookshaw L., and Sagan C. 1990.
Cometary delivery of organic molecules to the early Earth.
Science 249:366–373.

Clemett S. J., Spencer M. K., Sandford S. A., Hörz F., McKay D. S.,
and Zare R. N. 2008. Hydrocarbons in Stardust samples collected
from comet 81P/Wild 2. *Meteoritics & Planetary Science* 43.
This issue.

Cody G., Ade H., Alexander C. M. O'D., Araki T., Butterworth A.,
Fleckenstein H., Flynn G., Gilles M. K., Jacobsen C., Kilcoyne
A. L. D., Messenger K., Sandford S. A., Tyliszczak T., Westphal
A. J., Wirick S., and Yabuta H. 2008. Quantitative organic and
light-element analysis of comet 81P/Wild 2 particles using C-, N-
, and O-μ-XANES. *Meteoritics & Planetary Science* 43. This
issue.

Cottin H., Bachir S., Raulin F., and Gazeau M.-C. 2002.
Photodegradation of hexamethylenetetramine by VUV and its
relevance for CN and HCN extended sources in comets.
Advances in Space Research 30:1481–1488.

Cottin H., Gazeau M.-C., and Raulin F. 1999. Cometary organic
chemistry: A review from observations, numerical and
experimental simulations. *Planetary and Space Science* 47:
1141–1162.

Crovisier J. and Bockelée-Morvan D. 1999. Remote observations of
the composition of cometary volatiles. *Space Science Reviews* 90:
19–32.

Crovisier J., Bockelée-Morvan D., Colom P., Biver N., Despois D.,
Lis D. C., and the Team for Target-of-Opportunity Radio
observatIons of Comets. 2004. The composition of ices in comet
C/1995 O1 (Hale-Bopp) from radio spectroscopy. Further results
and upper limits on undetected species. *Astronomy &
Astrophysics* 418:1141–1157.

Elsila J. E., Dworkin J. P., Bernstein M. A., Martin M. P., and
Sandford S. A. 2007. Mechanisms of amino acid formation in
interstellar ice analogs. *The Astrophysical Journal* 660:911–918.

Ehrenfreund P. and Charnley S. B. 2000. Organic molecules in the
interstellar medium, comets, and meteorites: A voyage from dark
clouds to the early Earth. *Annual Review of Astronomy and
Astrophysics* 38:427–483.

Ehrenfreund P. and Schutte W. A. 2000. ISO observations of
interstellar ices: Implications for the pristinity of comets.
Advances in Space Research 25:2177–2188.

Ehrenfreund P., Glavin D. P., Botta O., Cooper G., and Bada J. L.
2001. Extraterrestrial amino acids in Orgueil and Ivuna: Tracing
the parent body of CI type carbonaceous chondrites. *Proceedings
of the National Academy of Sciences* 98:2138–2141.

Glavin D. P. and Bada J. L. 2001. Survival of amino acids in
micrometeorites during atmospheric entry. *Astrobiology* 1:
259–269.

Glavin D. P., Bada J. L., Brinton K. L. F., and McDonald G. D. 1999.
Amino acids in the Martian meteorite Nakhla. *Proceedings of
the National Academy of Sciences* 96:8835–8838.

Glavin D. P., Dworkin J. P., Aubrey A., Botta O., Doty J. H. III,
Martins Z., and Bada J. L. 2006. Amino acid analyses of
Antarctic CM2 meteorites using liquid chromatography-time of
flight-mass spectrometry. *Meteoritics & Planetary Science* 41:
889–902.

Goesmann F., Rosenbauer H., Roll R., and Böhnhardt H. 2005.
COSAC onboard Rosetta: A bioastronomy experiment for the
short-period comet 67P/Churyumov-Gerasimenko. *Astrobiology* 5:
622–631.

Huebner W. F. 1987. First polymer in space identified in comet
Halley. *Science* 237:628–630.

Huebner W. F. and Boice D. C. 1992. Comets as a possible source of
prebiotic molecules. *Origins of Life and Evolution of the Biosphere*
21:299–315.

Huebner W. F., Boice D. C., and Korth A. 1989. Halley's polymeric
organic molecules. *Advances in Space Research* 9:29–34.

Irvine W. M., Crovisier J., Fegley B., and Mumma M. J. 2000.
Comets: A link between interstellar and nebular chemistry. In
Protostars and planets IV, edited by Mannings V., Boss A. P.,
and Russell S. S. Tucson, Arizona: The University of Arizona
Press. pp. 1159–1200.

Jodkowski J. T., Ratajczak E., Fagerström K., Lund A., Stothard N.
D., Humpfer R., and Grotheer H.-H. 1995. Kinetics of cross
reaction between amidogen and methyl radicals. *Chemical
Physics Letters* 240:63–71.

Kissel J. and Kreuger F. R. 1987. The organic component in dust
from comet Halley as measured by the PUMA mass spectrometer
on board Vega 1. *Nature* 326:755–760.

Kissel J., Krueger F. R., Silén J., and Clark B. C. 2004. The cometary
and interstellar dust analyzer at comet 81P/Wild 2. *Science* 304:
1774–1776.

Kuan Y. J., Charnley S. B., Huang H. C., Tseng W. L., and Kisiel Z.
2003. Interstellar glycine. *The Astrophysical Journal* 593:848–
867.

Kvenvolden K. A., Lawless J., Pering K., Peterson E., Flores J.,
Ponnamperuma C., Kaplan I., and Moore C. 1970. Evidence for
extraterrestrial amino-acids and hydrocarbons in the Murchison
meteorite. *Nature* 228:923–926.

Kvenvolden K. A., Lawless J. G., and Ponnamperuma C. 1971. Non-
protein amino acids in the Murchison meteorite. *Proceedings of
the National Academy of Sciences* 68:486–490.

Lis D. C., Blake G. A., and Herbst E., eds. 2006. In *Astrochemistry:*

Recent successes and current challenges. New York: Cambridge University Press. 568 p.

Lodders K. and Osborne R. 1999. Perspectives on the comet-asteroid-meteorite link. *Space Science Reviews* 90:289–297.

Matrajt G., Ito M., Wirick S., Messenger S., Brownlee D., Joswiak D., Flynn G., Sandford S. A., Snead C., and Westphal A. 2008. Carbon investigation of Stardust particles: A TEM, NanoSIMS, and XANES study. *Meteoritics & Planetary Science* 43. This issue.

McKeegan K. D., Aléon J., Bradley J., Brownlee D., Busemann H., Butterworth A., Chaussidon M., Fallon S., Floss C., Gilmour J., Gounelle M., Graham G., Guan Y., Heck P. R., Hoppe P., Hutcheon I. D., Huth J., Ishii H., Ito M., Jacobsen S. B., Kearsley A., Leshin L. A., Liu M.-C., Lyon I., Marhas K., Marty B., Matrajt G., Meibom A., Messenger S., Mostefaoui S., Mukhopadhyay S., Nakamura-Messenger K., Nittler L., Palma R., Pepin R. O., Papanastassiou D. A., Robert F., Schlutter D., Snead C. J., Stadermann F. J., Stroud R., Tsou P., Westphal A., Young E. D., Ziegler K., Zimmermann L., and Zinner E. 2006. Isotopic compositions of cometary matter returned by Stardust. *Science* 314:1724–1727.

Moore M. R. and Hudson R. L. 1998. Infrared study of ion-irradiated water-ice mixtures with hydrocarbons relevant to comets. *Icarus* 135:518–527.

Mumma M. J., DiSanti M. A., Dello Russo N., Magee-Sauer K., Gibb E., and Novak R. 2003. Remote infrared observations of parent volatiles in comets: A window on the early solar system. *Advances in Space Research* 31:2563–2575.

Muñoz-Caro G. M., Meierhenrich U. J., Schutte W. A., Barbier B., Arcones-Segovia A., Rosenbauer H., Thiemann W. H. P., Brack A., and Greenberg J. M. 2002. Amino acids from ultraviolet irradiation of interstellar ice analogues. *Nature* 416:403–406.

Muñoz-Caro G. M. and Schutte W. A. 2003. UV-photoprocessing of interstellar ice analogs: New infrared spectroscopic results. *Astronomy & Astrophysics* 412:121–132.

Muñoz-Caro G. M., Meierhenrich U. J., Schutte W. A., Thiemann W. H. P., and Greenberg J. M. 2004. UV-photoprocessing of interstellar ice analogs: Detection of hexamethylenetetramine-based species. *Astronomy & Astrophysics* 413:209–216.

Nuevo M., Meierhenrich U. J., Muñoz Caro G. M., Dartois E., d'Hendecourt L., Deboffle D., Auger G., Blanot D., Bredehöft J. H., and Nahon L. 2006. The effects of circularly polarized light on amino acid enantiomers produced by the UV irradiation of interstellar ice analogs. *Astronomy & Astrophysics* 457:741–751.

Oró J., Mills T., and Lazcano A. 1992. The cometary contribution to prebiotic chemistry. *Advances in Space Research* 12:33–41.

Pizzarello S., Feng X., Epstein S., and Cronin J. R. 1994. Isotopic analyses of nitrogenous compounds from the Murchison meteorite: Ammonia, amines, amino acids, and polar hydrocarbons. *Geochimica et Cosmochimica Acta* 58:5579–5587.

Rodgers S. D. and Charnley S. B. 2001. Organic synthesis in the coma of comet Hale-Bopp? *Monthly Notices of the Royal Astronomical Society* 320:L61–L64.

Sandford S. A., Aléon J., Alexander C. M. O'D., Araki T., Bajt S., Baratta G. A., Borg J., Brucato J. R., Burchell M. J., Busemann H., Butterworth A., Clemett S. J., Cody G., Colangeli L., Cooper G., D'Hendecourt L., Djouadi Z., Dworkin J. P., Ferrini G., Fleckenstein H., Flynn G. J., Franchi I. A., Fries M., Gilles M. K., Glavin D. P., Gounelle M., Grossemy F., Jacobsen C., Keller L. P., Kilcoyne D., Leitner J., Matrajt G., Meibom A., Mennella V., Mostefaoui S., Nittler L. R., Palumbo M. E., Robert F., Rotundi A., Snead C. J., Spender M. K., Steele A., Stephan T., Tyliszczak T., Westphal A. J., Wirick S., Wopenka B., Yabuta H., Zare R. N., and Zolensky M. 2006. Organics captured from comet Wild 2 by the Stardust spacecraft. *Science* 314:1720–1724.

Snyder L. E., Lovas F. J., Hollis J. M., Friedel D. N., Jewell P. R., Remijan A., Ilyushin V. V., Alekseev E. A., and Dyubko S. F. 2005. A rigorous attempt to verify interstellar glycine. *The Astrophysical Journal* 619:914–930.

Szopa C., Sternberg R., Raulin F., and Rosenbauer H. 2003. What can we expect from the in situ chemical investigation of a cometary nucleus by gas chromatography: First results from laboratory studies. *Planetary and Space Science* 51:863–877.

Tsou P., Brownlee D. E., Sandford S. A., Hörz F., and Zolensky M. E. 2003. Wild 2 and interstellar sample collection and Earth return. *Journal of Geophysical Research* 108 (E10), 8113.

Westphal A. J., Snead C., Butterworth A., Graham G. A., Bradley J. P., Bajt S., Grant P. G., Bench G., Brennan S., and Pianetta P. 2004. Aerogel keystones: Extraction of complete hypervelocity impact events from aerogel collectors. *Meteoritics & Planetary Science* 39:1375–1386.

Wolman Y., Miller S. L., Ibanez J., and Oró J. 1971. Formaldehyde and ammonia as precursors to prebiotic amino acids. *Science* 174:1039–1040.

Yano H., Arakawa M., Michikami T., and Fujiwara A. 1999. Sub-millimeter-sized ice grain impacts on aerogels: Implications to a cometary dust sample return mission (abstract #1961). 30th Lunar and Planetary Science Conference. CD-ROM.

Zhao M. and Bada J. L. 1995. Determination of alpha-dialkylamino acids and their enantiomers in geological samples by high-performance liquid chromatography after derivatization with a chiral adduct of *o*-phthaldialdehyde. *Journal of Chromatography A* 690:55–63.