The Meteoritical Society

Meteoritics & Planetary Science 44, Nr 9, 1323–1330 (2009)
Abstract available online at http://meteoritics.org

Cometary glycine detected in samples returned by Stardust

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(Received 05 June 2009; revision accepted 24 July 2009)

Abstract–Our previous analysis of cometary samples returned to Earth by NASA's Stardust spacecraft showed several amines and amino acids, but the origin of these compounds could not be firmly established. Here, we present the stable carbon isotopic ratios of glycine and ε-amino-*n*-caproic acid (EACA), the two most abundant amino acids identified in Stardust-returned foil samples measured by gas chromatography–mass spectrometry coupled with isotope ratio mass spectrometry. The $\delta^{13}C$ value for glycine of +29 ± 6‰ strongly suggests an extraterrestrial origin for glycine, while the $\delta^{13}C$ value for EACA of −25 ± 2‰ indicates terrestrial contamination by Nylon-6 during curation. This represents the first detection of a cometary amino acid.

INTRODUCTION

In January 2006, NASA's Stardust spacecraft returned samples from comet 81P/Wild 2 to Earth (Brownlee et al. 2006). The Stardust cometary collector consisted of aerogel cells lined with aluminum foils designed to capture impacting particles and facilitate removal of the aerogel (Tsou et al. 2003). The aerogel cells were directly exposed to the cometary coma and were able to capture both particles and cometary gases. The backing foils experienced cometary exposure mediated by the adjacent aerogel and may have adsorbed cometary volatiles that diffused through the aerogel (Fig. 1). Preliminary examinations of comet-exposed materials revealed a suite of organic compounds, including several amines and amino acids (Sandford et al. 2006). The amine and amino acid content of various samples from the cometary collector were later examined in more detail (Glavin et al. 2008). Both aerogel and foil samples were analyzed and compared with control samples. Methylamine (NH_2CH_3) and ethylamine ($NH_2C_2H_5$) were detected in the exposed aerogel at concentrations greatly exceeding those found in the flight aerogel witness coupon mounted on the collector arm behind the Whipple shield; the amino acid glycine (NH_2CH_2COOH) was detected in several foil samples as well as in the comet-exposed aerogel (Glavin et al. 2008). Although the high relative abundance of glycine on the foil suggested a possible cometary component, the lack of any witness foil on the Stardust spacecraft made it difficult to establish the origin of this amino acid via the liquid chromatography method employed.

The organic inventory of comets is of particular interest because comets represent a reservoir of primitive material in the solar system and were likely a major contributor to the heavy bombardment of the early Earth (Chyba 1990). Cometary delivery of organics could have contributed to the prebiotic organic inventory from which life emerged (Chyba et al. 1990; Chyba and Sagan 1992; Oró et al. 1992). Comets are suspected to consist of interstellar material that has been moderately to heavily processed in the solar nebula (Ehrenfreund and Schutte 2000; Irvine et al. 2000). Over 140 molecular species have been identified in the interstellar medium (ISM) by their rotational spectra (Lis et al. 2006), and more than two dozen organic molecules have been detected to date from spectroscopic observations of comets (Bockelee-Morvan et al. 2004).

The list of known cometary molecules does not include methylamine, ethylamine, or glycine, all of which were observed in the Stardust samples described above. Methylamine has been observed in the ISM (Ehrenfreund and Charnley 2000). Glycine has been actively searched for in the ISM (e.g., Brown et al. 1979; Snyder 1997; Ceccarelli et al. 2000; Hollis et al. 2003) and its detection has been reported in hot, young molecular cores (Kuan et al. 2003). However, this detection remains controversial because of limitations in assignment of spectral lines (Snyder et al. 2005). Glycine has been searched for without success in comets Hale-Bopp and Hyakutake, with calculated upper limits of [glycine]/[H_2O] of 0.15 (Crovisier et al. 2004). These upper limits correspond to ~0.3% glycine by mass in cometary ice, or 0.05% glycine by mass in cometary material with a dust-to-ice ratio of 5 (Crovisier et al. 2004). By contrast, glycine concentration is ~10^{-6} to 10^{-7} by mass in CI and CM meteorites (Cronin and Chang 1993;

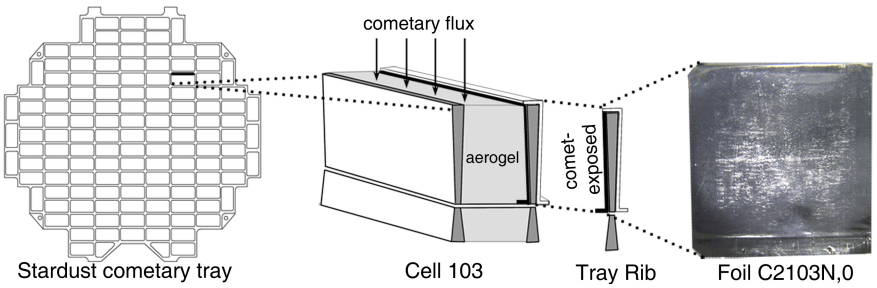

Fig. 1. The Stardust cometary collector showing the orientation of foil C2103N,0 (modified from Tsou et al. (2003).

Ehrenfreund et al. 2001a), suggesting that the lack of cometary glycine detection is due to insufficiently sensitive spectroscopic detection methods. Complex organics including amino acids can be readily formed in laboratory-simulated interstellar/cometary ices by UV or proton irradiation of ice mixtures that have been observed in comets and the ISM (Bernstein et al. 2002; Elsila et al. 2007; Hudson et al. 2008). Calculations suggest a lifetime for glycine in cometary conditions on the order of a few hours (Ehrenfreund et al. 2001b). The potential existence of glycine in comets and the ISM is of particular interest because it is the simplest amino acid and is ubiquitous in biochemistry.

The previous analyses of Stardust foil samples showed glycine and ε-amino-*n*-caproic acid (EACA, $NH_2(CH_2)_5COOH$, the hydrolysis product of Nylon-6) as the most abundant amino acids. Glycine was detected only on the aerogel (comet-exposed) side of the foils, suggesting that the glycine was not a contaminant from the foil or subsequent handling (Glavin et al. 2008). In contrast, EACA was detected on both sides of the foil at much higher abundances and is a likely contamination product from the Nylon-6 storage bags used during sample curation (Glavin et al. 2008). In this work, we re-examined the previously reported detection of glycine in foils from the Stardust cometary collector. Although glycine and EACA were also previously detected in aerogel, the low concentrations present would require at least 200 mg of aerogel for our new analyses. This is a prohibitive amount to request of bulk aerogel for destructive analysis; each of the 124 aerogel tiles in the collector contained 24 cm^3 at a density gradient of 5 mg/ml–50 mg/ml, with a total mass for each tile of 820 mg (Tsou et al. 2003). We chose instead to focus on the foils, which are more readily available. We extracted and characterized four individual Stardust foils using liquid chromatography with fluorescent detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) to determine the amino acid abundances. The remaining 99% of the extract was then analyzed by gas chromatography-mass spectrometry coupled with isotope ratio mass spectrometry (GC-MS/IRMS) to measure the stable carbon isotopic value of glycine to determine if this amino acid is extraterrestrial, and of EACA to confirm its suspected terrestrial origin.

EXPERIMENTAL TECHNIQUE

Stardust Foil Samples and Controls

Four sample foils from the Stardust cometary collector were provided from the Curatorial Facility at NASA Johnson Space Center (JSC) by the Stardust Sample Allocation Subcommittee of the Curation and Analysis Planning Team for Extraterrestrial Materials. The foils were designated as follows, indicating their position in the Stardust collector (Bastian et al. 2006): C2016N,2; C2078N,0; C2103N,0; C2017N,0. We also report data on two additional foils (C2092S,0 and C2125N,2) that were previously provided and analyzed during the Stardust Preliminary Examination period. Commercial aluminum foil that had been heated at 500 °C in air overnight was used as a control for a procedural blank. All glassware used to handle the foils and extracts was also heated at 500 °C in air overnight to remove organic contamination. Individual stock mixtures of glycine (Sigma, ≥99%) and EACA (Acros, 99+%) in Millipore Direct Q3 UV (18.2 MΩ, <5 ppb total organic carbon) ultrapure water were used as standards. A sample of Nylon-6 from a shipping bag used by NASA Johnson Space Center (JSC) was used as the terrestrial source of EACA.

Extraction and Characterization of Amino Acid Abundance

Each Stardust foil sample was weighed in order to calculate the total surface area from the foil's mass, density, and thickness (Tsou et al. 2003) and then carried through a hot water extraction and acid vapor hydrolysis protocol designed to investigate amino acids and amines in both the free and bound form (Glavin et al. 2008). Previous analyses detected glycine predominantly on the aerogel-facing side of the foil, but indicated no gradient in amino acid concentration along the foil surface (Glavin et al. 2008). It is difficult to thoroughly extract just the aerogel-facing side of the foil, so the current experiments extracted both the aerogel-facing and non-aerogel-facing sides. The extracted, acid-hydrolyzed residues were each re-suspended in 500 μL of Millipore water. From each sample, 5 μL was removed for identification and quantification of the amino acids using LC-

FD/ToF-MS with a Waters ACQUITY and LCT Premier. Sample hydrolysis, derivatization, and LC-FD/ToF-MS analyses were identical to our previously published procedures (Glavin et al. 2006).

Isotopic Measurements

The remaining acid-hydrolyzed extracts (495 μL each) from the four Stardust foils were combined in a single screw-capped conical glass tube and dried under vacuum using a Labconco CentriVap centrifugal concentrator. Samples were esterified with isopropanol and the isopropyl esters reacted with trifluoroacetic anhydride (TFAA) using published methods (e.g., Martins et al. 2007). The acidified isopropanol for esterification was made by adding 600 μL acetyl chloride dropwise to 1.4 mL isopropanol on ice. The extraction and hydrolysis procedure of Stardust foils produces insoluble salts that interfere with injection of small volumes, so the extracts were decanted to a clean vial after the esterification step before reaction with TFAA, leaving the residue behind. Derivatized samples were dissolved in 6 μL of ethyl acetate (Fisher Chemical, Optima Grade). Samples of commercial aluminum foil spiked with concentrations of glycine and EACA similar to those found in Stardust samples were carried through the entire extraction, hydrolysis, and derivatization (including decanting) process and no isotopic fractionation was observed.

The $\delta^{13}C$ values of the TFAA-isopropanol derivatized samples were analyzed by GC-MS/IRMS, which provides compound-specific structural and isotopic information from a single splitless sample injection. The GC-MS/IRMS instrument consists of a Thermo Trace GC whose output is split, with approximately 10% directed into a Thermo DSQII electron-impact quadrupole mass spectrometer that provides mass and structural information on each eluting peak. The remaining 90% passes through a Thermo GC-C III interface, where eluting amino acids are oxidized to CO_2, and then is passed into a Thermo MAT 253 isotope ratio mass spectrometer.

Derivatized extracts were injected in 2 μL aliquots into the GC, which was outfitted with a Chirasil-L-Val column (Alltech, 50 m, 0.25 mm ID, 16 μm film thickness). Helium carrier gas flow was 1.0 ml/min. The injection port was set at 220 °C. The oven program was held for 5 min at 70 °C then increased by 3 °C/min to 175 °C. Six pulses of high-purity CO_2 gas ($\delta^{13}C = -24.522$ ‰ PDB) that had been precalibrated against two commercial reference CO_2 gases (Oztech Corporation, $\delta^{13}C = -3.61$ PDB and $\delta^{13}C = -40.740$ PDB) were injected into the IRMS for computation of the $\delta^{13}C$ values of the eluting derivatized standard and sample compounds. Analysis of the MAT 253 data was performed with Thermo Isodat 2.5 software. Peaks were integrated using the BaseFit background method. To ensure the precision and accuracy of the peak integration for the very small glycine peak observed in the Stardust extract, we analyzed a dilute glycine standard that produced similarly small peaks; $\delta^{13}C$ values were consistent with those determined from the more concentrated standard, validating the integration method. The measured value and precision for the dilute standard were used in the calculations described below to determine the final $\delta^{13}C$ value of the Stardust glycine.

Stock solutions of glycine and EACA were combined to make a standard mixture that was carried through the derivatization process and run daily on the GC-MS/IRMS. The individual, underivatized stock solutions were also analyzed on a Costech ECS 4010 combustion elemental analyzer (EA) connected to the MAT 253 IRMS and compared to L-alanine with a known $\delta^{13}C$ value of –23.33‰ (Iso-Analytical). The final $\delta^{13}C$ values of the amino acids in the Stardust samples were obtained by correcting for the carbon added during derivatization using Equation 1 (rearranged from O'Brien et al. 2002):

$$\delta^{13}C_{\text{sample aa}} = \frac{n_{aa} + n_d}{n_{aa}}(\delta^{13}C_{\text{derivatized sample aa}} - \delta^{13}C_{\text{derivatized standard aa}}) + \delta^{13}C_{\text{underivatized standard aa}} \quad (1)$$

where n_{aa} is the number of carbon atoms in the underivatized amino acid, and n_d is the number of carbons added by the TFAA and isopropanol. The $\delta^{13}C$ value for the carbon added by derivatization is thus determined empirically for each individual amino acid, accounting for kinetic isotope effects during derivatization (Silfer et al. 1991). The calculated values were –35.2‰ for glycine and –33.2‰ for EACA.

The precision of the calculated value also depends on the precision of the three measurements described above (i.e., derivatized sample, derivatized standard, underivatized standard) and can be calculated using Equation 2 (Docherty et al. 2001):

$$\sigma^2_{\text{sample aa}} = \sigma^2_{\text{underivatized standard}} + \sigma^2_{\text{derivatized standard}} \left(\frac{n_{aa} + n_d}{n_{aa}}\right)^2 + \sigma^2_{\text{derivatized sample}} \left(\frac{n_{aa} + n_d}{n_{aa}}\right)^2 \quad (2)$$

The $\delta^{13}C$ value of the Nylon-6 control bag was measured on the EA, using the known L-alanine standard as a reference.

RESULTS AND DISCUSSION

Figure 2 shows the LC-FD/ToF-MS chromatogram of the hydrolyzed extract from foil C2103N,0; this chromatogram is representative of the other foils measured. The presence of glycine, β-alanine, L-alanine, and EACA was confirmed by fluorescence retention time and exact mass, and the abundances were determined by comparison of the peak areas to those in an amino acid standard run on the same day. Table 1 shows the procedural-blank-corrected amino acid concentrations measured by LC-FD/ToF-MS for the four

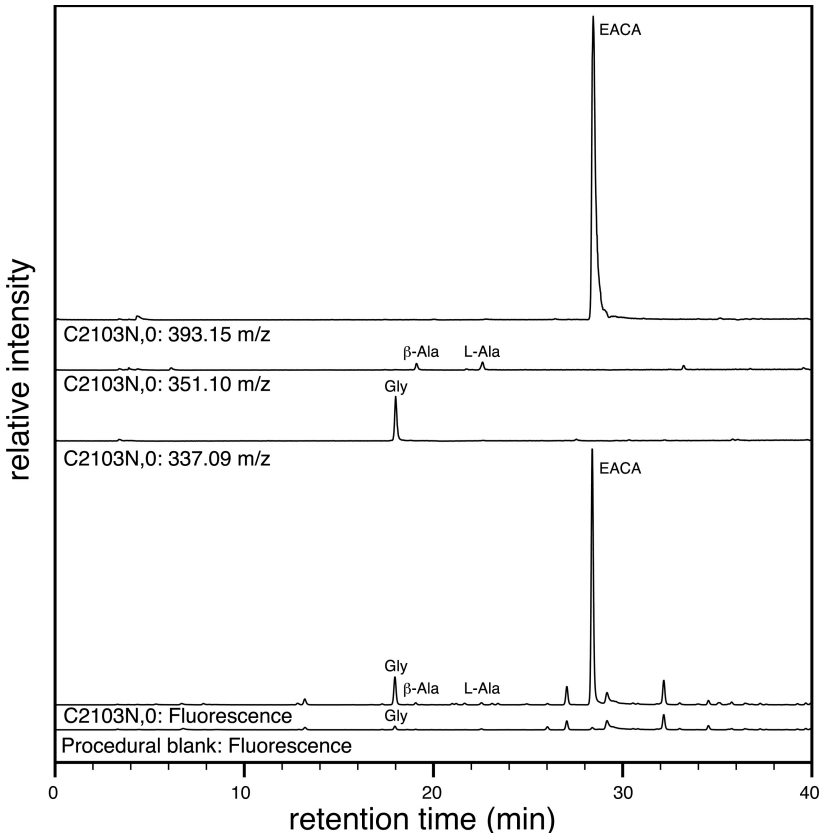

Fig. 2. The LC-FD/ToF-MS chromatogram of the derivatized acid-hydrolyzed hot water extract from Stardust foil C2103N,0. The total fluorescence chromatogram and three exact mass traces are shown. The bottom trace shows a procedural blank. Glycine, β-alanine, L-alanine, and EACA are identified. Unlabeled peaks are attributed to other primary amines (see Glavin et al. 2008 for details).

Table 1. Summary of the amino acid concentrations in water extracts of Stardust flight foils[a].

	This study						Previous study[b]	
	C2103N,0	C2016N,2	C2017N,0	C2078N,0	C2125N,2		C2092S,0	
Amino acid		Both sides (total)			Aerogel side (total)	Metal side (total)	Both sides (free)	Both sides (total)
Glycine	34	2	13	19	21	<3	27	68
β-alanine	2	1	1	3	<2	<2	1	7
D-alanine	<3	<3	<3	<3	<3	<3	<3	<4
L-alanine	2	<1	1	1	1	<3	6	12
EACA[c]	326	51	66	327	186	126	11	1,413

[a]All values are reported in 10^{-12} mol per cm^2 extracted foil surface area (pmol/cm^2). The surface area of each foil from this study was ~11 cm^2. Amino acids were extracted from both the aerogel contact side and aluminum metal contact side of Stardust flight foil C2125N,2 separately by placing a single drop (100 µl) of Millipore water on the foil (surface area ~0.5 cm^2) and allowing it to sit on the foil at room temperature for 5 min. For the four flight foils analyzed in this study, both sides were extracted in Millipore water at 100 °C for 24 h. The water extracts were then acid hydrolyzed in 6M HCl and analyzed by *o*-phthaldialdehyde/N-acetyl-L-cysteine derivatization and liquid chromatography with UV fluorescence and time of flight mass spectrometry (ToF-MS) detection to get the total amino acid abundance. For Stardust flight foil C2092S,0, a small portion of the complete foil was extracted and hydrolyzed; the water extract was also analyzed prior to acid hydrolysis to get the free amino acid abundance. Quantification of the amines included background level correction using the procedural blank foil and a comparison of the peak areas with those of an amino acid standard. The uncertainty in the values reported is ±5%.

[b]Data from C2125N,2 taken from Glavin et al. (2008); data from C2092S,0 is previously unpublished.

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

Stardust foils analyzed in this study, as well as previously measured data from a portion of Stardust foil C2092S,0 and extracts from both sides of a separate Stardust foil (C2125N,2) (Glavin et al. 2008). The data from C2125N,2 indicated that glycine is more abundant on the aerogel side of the foil compared to the metal (not comet-exposed) side, suggesting that glycine may be cometary. β-Alanine and L-alanine were also detected above background levels in the foil extracts, but the abundances of these amino acids (1 to 3 pmol/cm^2) were too low for carbon isotope measurements using current methods. The β-alanine may be cometary in origin; the lack of D-alanine suggests that

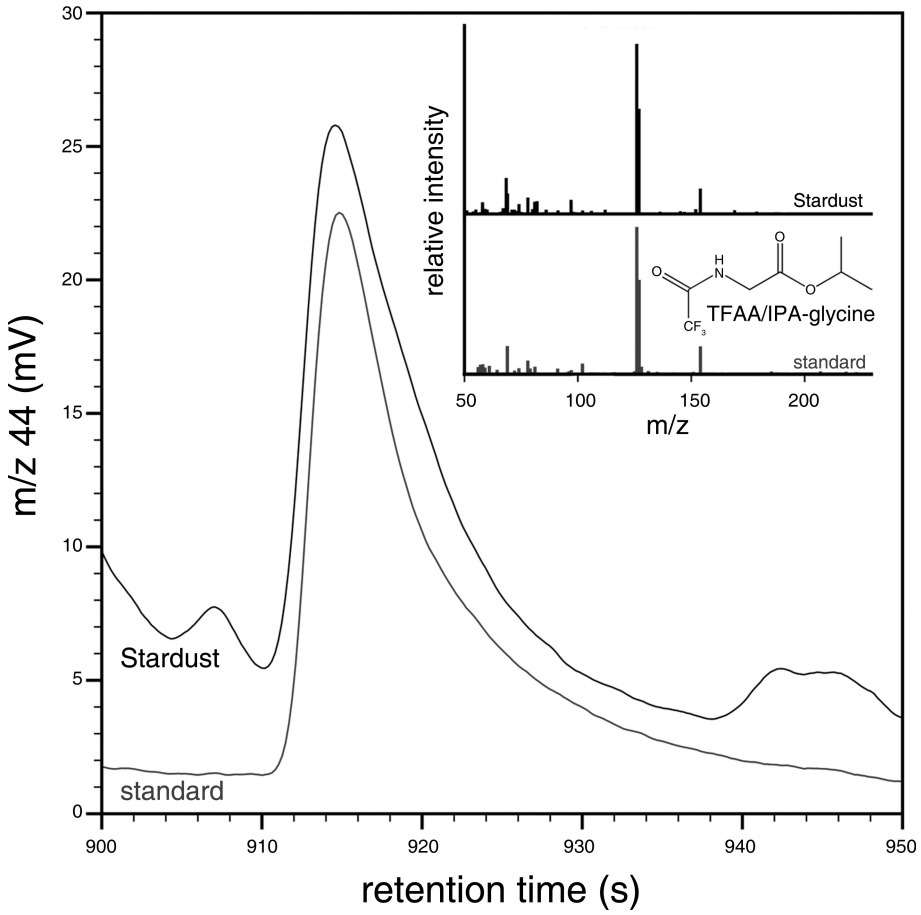

Fig. 3. GC-MS/IRMS analysis of the derivatized combined extract from four Stardust foils and of a glycine standard. The traces show the m/z 44 ($^{12}CO_2$) peak produced and measured from GC-IRMS for the peak assigned to glycine. The inset shows the simultaneously collected mass spectral fragmentation pattern for these peaks and the structure of glycine derivatized with trifluoroacetic acid/isopropanol (TFAA/IPA).

the L-alanine is likely terrestrial contamination. Comparing data from the non-hydrolyzed and hydrolyzed water extracts of foil C2092S,0 shows that approximately 40% of the glycine is in a free form, with the remaining 60% produced from acid labile precursors (e.g., HCN) during the acid hydrolysis procedure. We did not have enough glycine in the unhydrolyzed extract of the foil to make a carbon isotope measurement. The total abundances of glycine, β-alanine, and L-alanine detected in the procedural foil blank by LC-FD/ToF-MS was <0.04 nmol, which was well below the detection limit of the GC-MS/IRMS instrument. In contrast, EACA was detected at much higher abundances than the other amino acids, was predominantly in a bound form, and was detected on both sides of the foil, suggesting a probable terrestrial contamination source.

GC-MS/IRMS analysis provides compound-specific structural and isotopic information from a single injection, which permitted three replicate measurements from the 0.7 nmol of glycine and 16 nmol of EACA present in the combined foil extract. Figure 3 shows the GC-MS/IRMS data for the peak identified as glycine. The retention time and mass spectrum match that of the glycine standard, with no evidence of a coeluting compound. The $\delta^{13}C$ value for glycine was determined to be +29 ± 6‰. This value is well outside the terrestrial range for organic carbon of −6‰ to −40‰ (Bowen 1988). The Stardust glycine $\delta^{13}C$ value falls in the range previously reported for glycine from acid-hydrolyzed hot-water extracts of the CM type carbonaceous meteorite Murchison ($\delta^{13}C$ = +22‰ to +41‰) (Engel et al. 1990; Pizzarello et al. 2004) and the CI type meteorite Orgueil ($\delta^{13}C$ = +22‰) (Ehrenfreund et al. 2001a). The value reported here may include terrestrial glycine from the non-aerogel-facing side of the foil, and should thus be viewed as a lower limit on the cometary $\delta^{13}C$ enrichment.

Figure 4 shows the GC-MS/IRMS data for the EACA peak in the combined Stardust foil extracts, as well as in the EACA standard. The measured $\delta^{13}C$ value for EACA was −25 ± 2‰. Within analytical uncertainties, this value is identical to the bulk carbon isotope measurements of the Nylon-6 shipping and curation bags used by JSC measured via elemental analysis ($\delta^{13}C$ = −26.8 ± 0.2‰). These results confirm a terrestrial contamination source for EACA probably associated with the Stardust Sample Return Capsule

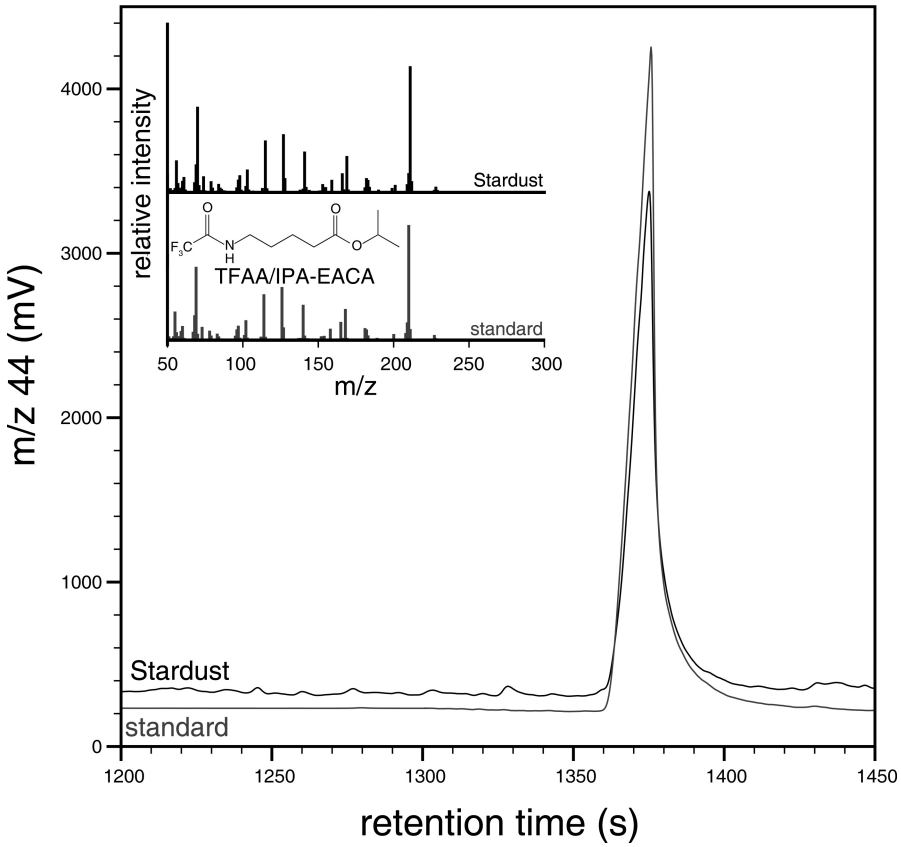

Fig. 4. GC-MS/IRMS analysis of the derivatized combined extract from four Stardust foils and an EACA standard. The traces show the m/z 44 ($^{12}CO_2$) peak produced and measured from the GC-IRMS trace for the peak assigned to EACA. The inset shows the simultaneous GC-MS mass spectrum for this peak and the structure of EACA derivatized with trifluoroacetic acid/isopropanol.

collection and sample curation. Contamination of extraterrestrial samples by EACA during curation has previously been reported (Glavin et al. 2006), although this is the first isotopic confirmation of such contamination.

The measured $\delta^{13}C$ value for glycine strongly suggests an extraterrestrial origin for this compound. Glycine has not been previously detected in comets, although it has been identified in many carbonaceous meteorites (e.g., Ehrenfreund et al. 2001a; Pizzarello et al. 2006; Martins et al. 2007). There are several possible origins for the extraterrestrial glycine detected in this work. Our data suggest that 40% of the detected glycine in one of the foils was produced in the free molecular form in the cometary environment. However, there may also be a significant contribution from "bound" precursors that liberated glycine during the acid-hydrolysis step. In the bound form, the primary amine group ($-NH_2$) of the glycine may have been covalently bonded to some other species. In the Murchison meteorite, for example, over half of the total amino acid abundance is in a bound form (Glavin et al. 2006). Polymers of HCN, a known cometary molecule (e.g., Crovisier et al. 2004), may also hydrolyze to form glycine and other amino acids (Ferris et al. 1974). LC-FD/ToF-MS analysis of both unhydrolyzed (free) and hydrolyzed (free + bound) extracts of Stardust cometary collector foil C2092S,0 during the period of the Stardust Preliminary Examination indicated that ~40% of the detected glycine is in the free form, with the remaining glycine deriving from bound precursors during acid hydrolysis. Therefore, the glycine carbon isotopic ratio measured here is likely a combination of that from free glycine as well as other cometary molecules. Further analysis of both the hydrolyzed and unhydrolyzed extracts of Stardust collector foils will be necessary to separate the carbon isotope value of free glycine from that of glycine precursors.

The glycine on these foils most likely originated from cometary gases that diffused through the adjacent aerogel. Other potential sources include release from nearby impacts of large cometary grains or delivery from very small refractory or icy grains, although this would have required an extremely high concentration of glycine in the grains. Some glycine molecules may have been destroyed or modified by impact heating during collection, forming other compounds (e.g., methylamine) (Glavin et al. 2008). Measurements by Stardust's Cometary and Interstellar Dust Analyzer (CIDA) during comet flyby did not detect any free glycine in impacting dust particles, although this instrument sampled only the uppermost few hundred monolayers of the particles and most of the ice and volatile fractions were likely lost

before analysis (Kissel et al. 2004). The CIDA instrument did show an abundance of CN^- ions, indicating a nitrogen-rich chemistry perhaps consistent with aminonitriles, which are acid-hydrolyzable precursors of amino acids. Aminoacetonitrile, an acid-hydrolyzable precursor of glycine, has been identified in the ISM (Belloche et al. 2008).

The Stardust foils likely sampled primarily the volatile component of comet Wild 2 and the detected compounds may not be representative of the more refractory organic material present in the comet nucleus. In previous laboratory experiments with Murchison, glycine was the only amino acid released from the grains heated under vacuum (Glavin and Bada 2001), although over 70 amino acids have been identified in this meteorite. By analogy, analyses of Stardust grains and future cometary nucleus sample return missions will likely reveal a much more complex amino acid inventory than reported here.

CONCLUSIONS

Carbon isotopic measurements reveal the presence of extraterrestrial glycine in the acid-hydrolyzed extracts of Stardust comet-exposed foils. This observation indicates the presence of both free glycine and bound glycine precursors in comet 81P/Wild 2, and represents the first compound-specific isotopic analysis of a cometary organic compound. Our analysis also reveals contamination of Stardust cometary collector foils from the Nylon-6 storage and shipping bags used during curation.

The detection of extraterrestrial glycine returned by Stardust enriches our understanding of comet chemistry and illustrates the potential delivery and survival of amino acids to the early Earth by comets, contributing to the prebiotic organic inventory from which life emerged.

Acknowledgments—We thank M. Fogel for helpful advice on the derivatization method and GC-IRMS analyses; J. Stern, J. Eigenbrode, S. Sandford, M. Martin, and L. Leshin for useful discussions and technical assistance; Z. Martins for providing the GC column; the Stardust Sample Allocation Team for providing the Stardust foil samples, K. Righter for providing the sample of JSC Nylon bags, NASA's Stardust Sample Analysis Program, the NASA Astrobiology Institute and the Goddard Center for Astrobiology for funding.

Editorial Handling—Dr. Scott Sandford

REFERENCES

Bastian R., Messenger K., See T. H., Warren J. L., and Zolensky M. 2006. Stardust Catalog. http://curator.jsc.nasa.gov/stardust/sample_catalog/SampleNomenclature.pdf.

Belloche A., Menten K. M., Comito C., Muller H. S. P., Schilke P., Ott J., Thorwirth S., and Hieret C. 2008. Detection of amino acetonitrile in Sgr B2(N). *Astronomy and Astrophysics* 482(1): 179-U37.

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

Bockelee-Morvan D., Crovisier J., Mumma M. J., and Weaver H. A. 2004. The composition of cometary volatiles. In *Comets II*, edited by Festou M., Keller H. U., and Weaver H. A. Tucson, Arizona: The University of Arizona Press. pp. 745.

Bowen R. 1988. Isotopes in the biosphere. In *Isotopes in the earth sciences*, edited by Bowen R. New York: Kluwer. pp. 452–469.

Brown R. D., Godfrey P. D., Storey J. W. V., Bassez M.-P., Robinson B. J., Batchelor R. A., McCulloch M. G., Rydbeck O. E. H., and Hjalmarson A. G. 1979. A search for interstellar glycine. *Monthly Notices of the Royal Astronomical Society* 186:5P–8P.

Brownlee D., Tsou P., Aleon 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. 2006. Comet 81P/Wild 2 under a microscope. *Science* 314(5806):1711–1716.

Ceccarelli C., Loinard L., Castets A., Faure A., and Lefloch B. 2000. Search for glycine in the solar type protostar IRAS 16293-2422. *Astronomy and Astrophysics* 362:1122–1126.

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

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.

Cronin J. R. and Chang S. 1993. Organic matter in meteorites: molecular and isotopic analysis of the Murchison meteorite. In *The chemistry of life's origins*, edited by Greenberg J. M., Mendoza C. X., and Pirronelle V. Dordrecht: Kluwer Academic Publishers. pp. 209–258.

Crovisier J., Bockelee-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 and Astrophysics* 418:1141–1157.

Docherty G., Jones V., and Evershed R. P. 2001. Practical and theoretical considerations in the gas chromatography/combustion/isotope ratio mass spectrometry $\delta^{13}C$ analysis of small polyfunctional compounds. *Rapid Communications in Mass Spectrometry* 15:730–738.

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(11):2177–2188.

Ehrenfreund P., Glavin D. P., Botta O., Cooper G., and Bada J. L. 2001a. 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.

Ehrenfreund P., Bernstein M. P., Dworkin J. P., Sandford S. A., and Allamandola L. J. 2001b. The photostability of amino acids in space. *The Astrophysical Journal* 550:L95–L99.

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

Engel M. H., Macko S. A., and Silfer J. A. 1990. Carbon isotope composition of individual amino acids in the Murchison meteorite. *Nature* 348:47.

Ferris J. P., Wos J. D., Ryan T. J., Lobo A. P., and Donner D. B. 1974. Biomolecules from HCN. *Origins of Life and Evolution of Biospheres* 5(1–2):153–157.

Glavin D. P. and Bada J. L. 2001. Survival of amino acids in micrometeorites during atmospheric entry. *Astrobiology* 1(3): 259–269.

Glavin D. P., Dworkin J. P., and Sandford S. A. 2008. Detection of cometary amines in samples returned by Stardust. *Meteoritics & Planetary Science* 43(1/2):399–413.

Glavin D. P., Dworkin J. P., Aubrey A., Botta O., Doty III J. H., 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(6):889–902.

Hollis J. M., Pedelty J. A., Snyder L. E., Jewell P. R., Lovas F. J., Palmer P., and Liu S.-Y. 2003. A sensitive very large array search for small-scale glycine emission toward OMC-1. *The Astrophysical Journal* 588:353–359.

Hudson R. L., Moore M. H., Dworkin J. P., Martin M. P., and Pozun Z. D. 2008. Amino acids from ion-irradiated nitrile-containing ices. *Astrobiology* 8:771–779.

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.

Kissel J., Krueger F. R., Silen 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.

Lis D. C., Blake G. A., and Herbst E. 2006. *Astrochemistry: Recent successes and current challenges*. New York: Cambridge University Press. 568 p.

Martins Z., Alexander C. M. O. D., Orzechowska G. E., Fogel M. L., and Ehrenfreund P. 2007. Indigenous amino acids in primitive CR meteorites. *Meteoritics & Planetary Science* 42: 2125–2136.

O'Brien D. M., Fogel M. L., and Boggs C. L. 2002. Renewable and nonrenewable resources: Amino acid turnover and allocation to reproduction in Lepidoptera. *Proceedings of the National Academy of Sciences* 99:4413–4418.

Oró J., Mills T., and Lazcano A. 1992. The cometary contribution to prebiotic chemistry. *Advances in Space Research* 12(4):33–41.

Pizzarello S., Huang Y., and Fuller M. 2004. The carbon isotopic distribution of Murchison amino acids. *Geochimica et Cosmochimica Acta* 68(23):4963–4969.

Pizzarello S., Cronin J. R., and Flynn G. 2006. The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles. In *Meteorites and the early solar system II*, edited by Lauretta D. S. Tucson: The University of Arizona Press. 942 p.

Sandford S. A., Aleon J., Alexander C. M. O. D., Araki T., Bajt S., Baratta G. A., Borg J., Bradley J. P., Brownlee D. E., 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 A. L. D., Leitner J., Matrajt G., Meibom A., Mennella V., Mostefaoui S., Nittler L. R., Palumbo M. E., Papanastassiou D. A., Robert F., Rotundi A., Snead C. J., Spencer M. K., Stadermann F. J., Steele A., Stephan T., Tsou P., Tyliszczak T., Westphal A. J., Wirick S., Wopenka B., Yabuta H., Zare R. N., and Zolensky M. E. 2006. Organics captured from Comet 81P/ Wild 2 by the Stardust spacecraft. *Science* 314(5806):1720–1724.

Silfer J. A., Engel M. H., Macko S. A., and Jumeau E. J. 1991. Stable carbon isotope analysis of amino acid enantiomers by conventional isotope ratio mass spectrometry and combined gas chromatography/isotope ratio mass spectrometry. *Analytical Chemistry* 63:370–374.

Snyder L. E. 1997. The search for interstellar glycine. *Origins of Life and Evolution of Biospheres* 27(1–3):115–133.

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.

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