Cometary Glycine Detected in Stardust-Returned Samples. J. E. Elsila[1], D. P. Glavin[1] and J. P. Dworkin[1]. [1]Goddard Center for Astrobiology, NASA Goddard Space Flight Center, Greenbelt, MD 20771, Jamie.Elsila@nasa.gov.

Introduction: In January 2006, NASA's Stardust spacecraft returned samples from comet 81P/Wild 2 to Earth [1]. The Stardust cometary collector consisted of aerogel cells lined with aluminum foils designed to capture impacting particles and facilitate removal of the aerogel [2] (Fig 1). Preliminary examinations of these comet-exposed materials revealed a suite of organic compounds, including several amines and amino acids [3], which were later examined in more detail [4]. Methylamine (NH_2CH_3) and ethylamine ($NH_2C_2H_5$) were detected in the exposed aerogel at concentrations greatly exceeding those found in control samples, while the amino acid glycine (NH_2CH_2COOH) was detected in several foil samples as well as in the comet-exposed aerogel [4]. None of these three compounds had been previously detected in comets, although methylamine had been observed in the interstellar medium [5]. Although comparison with control samples suggested that the detected glycine was cometary, the previous work was not able to conclusively identify its origin. Here, we present the results of compound-specific carbon isotopic analysis of glycine in Stardust cometary collector foils [6]. Several foils from the interstellar side of the Stardust collector were also analyzed for amino acid abundance, but concentrations were too low to perform isotopic analysis.

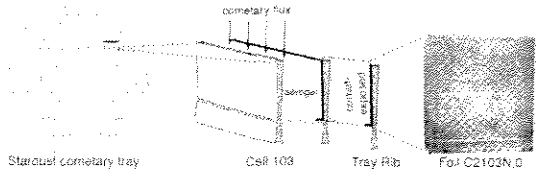

Fig. 1. The Stardust cometary collector, showing the orientation of the comet-exposed aluminum foils that lined the aerogel cells (modified from [2]).

Materials and Methods: Four sample foils from the Stardust cometary collector were provided from the Curatorial Facility at NASA Johnson Space Center (JSC). We also report data on two additional foils that were analyzed during the Stardust Preliminary Examination period. Commercial aluminum foil that had been heated at 500°C in air overnight was used as a procedural blank. A sample of Nylon-6 from a sample shipping bag used by NASA Johnson Space Center (JSC) was used as a control for curatorial contamination.

Each sample was 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 [4]. The extracted, acid-hydrolyzed residues were then analyzed with two methods: (1) liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) coupled with o-phthaldialdehyde/N-acetyl-L-cysteine (OPA/NAC) derivatization to determine amino acid abundance and distribution [4,7]; and (2) gas chromatography with mass spectrometry and isotope-ratio mass spectrometry (GC-MS/IRMS), coupled with trifluoroacetic anhydride/isopropanol (TFAA/IPA) derivatization, which permits compound-specific isotopic analysis and structural identification [6]. The four samples were combined prior to GC-MS/IRMS analysis to ensure sufficient analyte concentration.

Results and Discussion: The LC-FD/ToF-MS chromatogram of the hydrolyzed extract from a representative foil sample is shown in Figure 2. Peaks corresponding to the amino acids glycine, β-alanine, L-alanine, and ε-amino-*n*-caproic acid (EACA, the hydrolysis product of Nylon-6) were observed. EACA was also previously observed in samples curated by JSC [7].

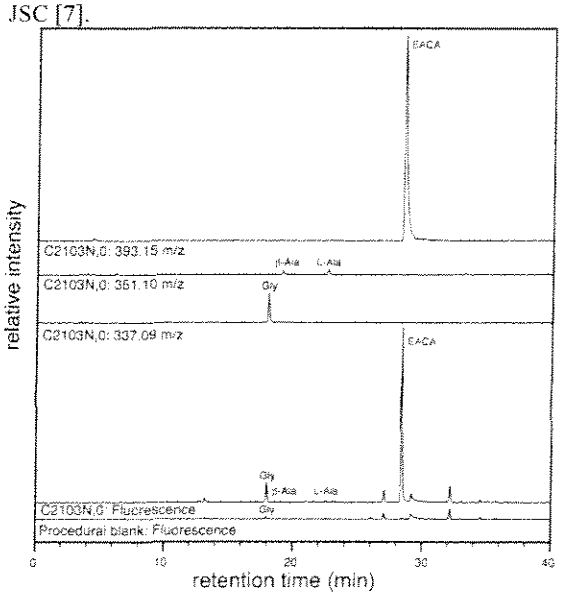

Fig. 2. The LC-FD/ToF-MS chromatogram of the derivatized acid-hydrolyzed hot water extract from Stardust foil C2103N,0. The total fluorescence chromatogram and three exact mass traces are shown. The bottom trace shows a procedural blank. Glycine, β-alanine, L-alanine, and EACA are identified. Unlabeled peaks are attributed to other primary amines [see 4 for details].

GC-MS/IRMS analysis of the combined foil samples provided compound-specific structural and isotopic measurements for the glycine and EACA peaks only; the abundances of the other amino acids were below detection limits. Figure 3 shows the GC-MS/IRMS data for the peak identified as glycine. The retention time and mass spectrum match that of a 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 ‰ [8], and falls in the range previously reported for glycine from acid-hydrolyzed hot-water extracts of the CM2 carbonaceous meteorite Murchison ($\delta^{13}C$ = +22‰ to +41‰) [9,10] and the CI1 meteorite Orgueil ($\delta^{13}C$ = +22‰) [11]. **The measured value strongly suggests an extraterrestrial (cometary) source of the detected glycine.** 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.

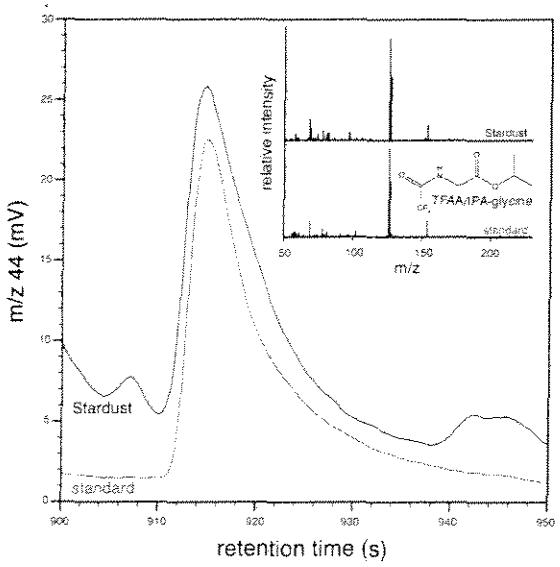

Fig. 3. GC-MS/IRMS analysis of the derivatized combined extract from four Stardust foils and of a glycine standard. The traces show the m/z 44 ($^{12}CO_2$) peak produced and measured from GC-IRMS for the peak assigned to glycine. The inset shows the simultaneously collected mass spectral fragmentation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

In contrast, 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 combustion elemental analysis-IRMS ($\delta^{13}C$ = -26.8 ± 0.2‰). These results confirm a terrestrial contamination source for EACA probably associated with the Stardust Sample Return Capsule collection and sample curation. Contamination of extraterrestrial samples by EACA during curation has previously been reported [7], although this is the first isotopic confirmation of such contamination.

LC-FD/ToF-MS analyses of foils from the interstellar side of the collector revealed very low levels of glycine, as well as EACA abundances similar to those seen from the cometary foils. Glycine abundances were too low to determine the isotopic composition and the terrestrial vs. extraterrestrial nature of this compound.

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 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.

References: [1] Brownlee D. et al. (2006) *Science, 314*, 1711-1716. [2] Tsou P. et al. (2003) *J. Geophys. Res.-Planets, 108*, 8113. [3] Sandford S. A. et al. (2006) *Science, 314*, 1720-1724. [4] Glavin D. P. et al. (2008) *Meteorit. Planet. Sci., 43*, 399-413. [5] Ehrenfreund P. & Charnley S. B. (2000) *Ann. Rev. Astron. Astrophys., 38*. [6] Elsila J. E. et al. (2009) *Meteoritics and Planetary Science, 44*, 1323-1330. [7] Glavin D. P. et al. (2006) *Meteorit. Planet. Sci., 41*, 889-902. [8] Bowen R. in *Isotopes in the Earth Sciences* (ed R. Bowen) 452-469 (Kluwer, 1988). [9] Pizzarello S. et al. (2004) *Geochim. Cosmochim. Acta, 68*, 4963-4969. [10] Engel M. H. et al. (1990) *Nature, 348*, 47. [11] Ehrenfreund P. et al. (2001) *Proc. Natl. Acad. Sci., 98*, 2138-2141.

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