

DETECTION OF AMINE COMPOUNDS IN SAMPLES RETURNED BY STARDUST. D. P. Glavin, and J. P. Dworkin, Goddard Center for Astrobiology, NASA Goddard Space Flight Center, Greenbelt, MD 20771, daniel.p.glavin@nasa.gov, jason.p.dworkin@nasa.gov.

Introduction: The delivery of amino acids to the early Earth by comets and their fragments could have been a significant source of the early Earth's prebiotic organic inventory [1]. 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. Over 20 organic molecules including methane, ethane, ammonia, cyanic acid, formaldehyde, formamide, acetaldehyde, acetonitrile, and methanol have been identified by radio spectroscopic observations of the comets Hale-Bopp and Hyakutake [2,3]. 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 amines.

In situ measurements of comet 81P/Wild 2 by the Cometary and Interstellar Dust Analyzer (CIDA) time of flight mass spectrometer instrument on the Stardust spacecraft found that the dust impacting the target surface contained a nitrogen rich chemistry with large amounts of cyanide and lower abundances of oxygen [4]. Although CIDA did not detect any evidence for free amino acids in the spectra, many of the simple nitrogen rich molecules that have been identified in some Wild 2 dust grains may hydrolyze in acid to produce more complex organic compounds.

The Preliminary Examination Team (PET) analyses of organics in samples returned by Stardust were largely focused on particles that impacted the aerogel and aluminum foil [5]. 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 Liquid Chromatography with simultaneous UV Fluorescence Detection and Time of Flight-Mass Spectrometry (LC-FD/ToF-MS). Preliminary results from these analyses are reported here.

Samples and Analytical Techniques: Three pieces of the Stardust flight cometary collector tray aerogel fragment C2054,4 (piece 1, 5.2 mg; piece 2, 7.6 mg; piece 3, 8.7 mg) that were adjacent to a particle track and a single piece of aerogel sample C2086,1 (3.2 mg) that was not adjacent to any visible particle tracks were analyzed for amines. For comparison, an unflown Stardust flight-quality aerogel sample E243-13C (14 mg) that had been kept sealed under vacuum inside a glass tube since original bakeout in 1998, and

two pieces of the Stardust flight aerogel witness tile WCARMI1CPN (pieces 8 and 9, 0.2 mg) were analyzed in parallel. The witness tile was protected from dust impacts by the spacecraft's Whipple shields, therefore this sample witnessed all of the same terrestrial and space environments as the cometary collector tiles, but was not directly exposed to the comet. In addition, a Stardust flight foil sample C2092S,0 that was exposed to Wild 2, but did not contain any visible impact pits was also analyzed.

Each sample was sealed in a glass test tube with 1 ml of Millipore water for 24 h in a heating block set at 100°C. Half of the water supernatant was transferred to a separate test tube, dried under vacuum, hydrolyzed under 6 M HCl vapor at 150°C for 3 h and analyzed directly by OPA/NAC derivatization and LC-FD/ToF-MS [6]. The other half of the water supernatant was not acid hydrolyzed prior to analysis in order to determine the concentration of free amines in the samples.

Results and Discussion: With the exception of methylamine (MA) and ethylamine (EA), all of the amines detected in Stardust aerogel C2054,4 were also present in either preflight and/or witness tile aerogel samples (Fig. 1).

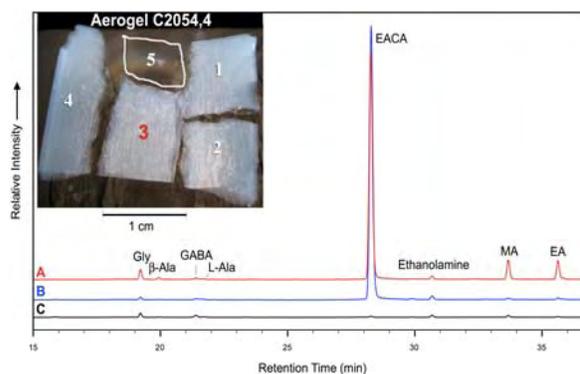


Figure 1. The fluorescence chromatograms from the LC-FD/ToF-MS analyses showing amines detected in: **A**, Stardust comet exposed aerogel C2054,4,3; **B**, Stardust aerogel witness tile WCARMI1CPN,9; and **C**, unflown aerogel E243-13C. The inset shows the Stardust aerogel C2054,4 cutting diagram oriented with the comet exposed surface at the top.

The most abundant amine present in the Stardust flight aerogels and foil was ϵ -amino-*n*-caproic acid (EACA); its most likely origin is exposure to Nylon-6 [6]. Several amines including glycine, β -alanine (BALA), L-alanine, γ -amino-*n*-butyric acid (GABA),

and ethanolamine (MEA) were also detected in the aerogels and foil at trace levels. The absence of D-amino acids and the similarity between the comet exposed aerogel C2054,4 and the witness tile, suggests that most of these amines are terrestrial in origin.

Stardust aerogel C2054,4 fragment 3 located below particle track 25 had twice the abundance of MA and EA found in aerogel fragments 1 and 2 (Fig. 1 inset). However, there was no significant difference in MA and EA abundances between fragments 1 and 2 to suggest a concentration gradient with depth. The distinct molar ratio of MA to EA in Stardust comet exposed aerogels (MA/EA \sim 1) compared to the pre-flight aerogel (MA/EA \sim 7) suggests that these two compounds are cometary in origin. MA and EA were not detected in the Stardust foil and aerogel witness tile, therefore these amines are unlikely contaminants.

Glycine, MA and EA were detected in flight aerogel samples C2054,4 and C2086,1 at relative abundances that greatly exceeded those found in controls (Fig. 2), providing additional evidence that these amines have a cometary component. Similar absolute abundances of MA and EA (\sim 35 nmol per gram aerogel) were found in both C2054,4 and aerogel sample C2086,1 that was not located adjacent to a particle track. Therefore, we believe that these amines, originate from sub-micron particles or gas that directly impacted the collector and were subsequently released from a chemically bound form by acid hydrolysis.

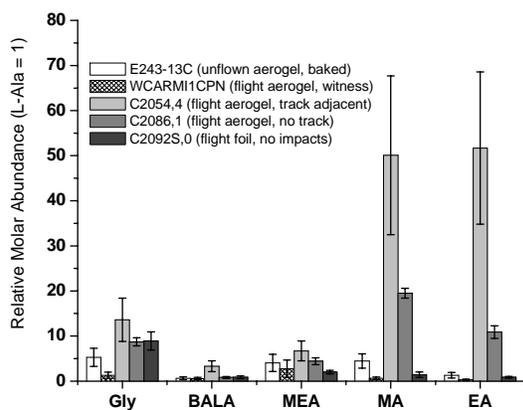


Figure 2. A comparison of the relative molar abundances of several amines in the acid-hydrolyzed water extracts of Stardust aerogel and foil. The enhanced relative abundances of glycine, MA and EA in the comet-exposed flight aerogels compared to controls suggest that these amines may have a cometary origin.

We did not detect any glycine, MA nor EA in the unhydrolyzed Stardust aerogel extracts indicating that these amines are present predominantly in an acid labile bound form, rather than as a free primary amine. These results are consistent with the XANES findings that indicate the presence of an amide rich organic polymer in some of the recovered particles [5]. Glycine, MA and EA have not been previously identified in comets via in situ measurements or spectroscopic observations. Compound specific carbon and nitrogen isotope measurements will be necessary to constrain the origin of these amines in Stardust materials.

References: [1] Chyba, C. and Sagan, C. (1992) *Nature*, 355, 125-132. [2] Crovisier, J. and Bockelée-Morvan, D. (1999) *Space Sci. Rev.*, 90, 19-32. [3] Crovisier, J. et al. (2004) *Astron. Astrophys.*, 418, 1141-1157. [4] Kissel, J. et al. (2004) *Science*, 304, 1774-1776. [5] Sandford, S. A. et al. (2006) *Science*, 314, 1720-1724. [6] Glavin D. P. et al. (2006) *MAPS*, 41, 889-902.

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