

Comment on "Organics Captured from Comet 81P/Wild 2 by the Stardust Spacecraft"

Maegan K. Spencer and Richard N. Zare*

Sandford *et al.* (Reports, 15 December 2006, p. 1720) reported on organic compounds captured from Comet 81P/Wild 2 by the Stardust spacecraft. We emphasize the difficulty in assigning the origin of compounds detected diffusely along particle impact tracks and show that rapid heating of aerogel that has never been exposed to cometary particle capture can generate complex aromatic molecules from low-mass carbon impurities present in the aerogel.

The NASA Stardust Mission, which robotically returned samples of cometary dust from comet 81P/Wild2 from deep space to Earth, was an extraordinary triumph (1–5). One limitation of the mission design is the known carbon impurity content of the dust collection material, aerogel. This residual carbon can give rise to an artifactual signature that makes the interpretation of some classes of organic compounds problematic (1, 6). The potential for misinterpretation of organic compounds lying diffusely along particle impact tracks in aerogel was mentioned briefly in (1), which stated that "not all the collected organics in the samples will be fully representative of the original cometary material because some may have been modified during impact with the aerogel collectors." We emphasize here that the generation of low-mass polycyclic aromatic hydrocarbons (PAHs) during hypervelocity impact of particles into Stardust silica aerogel can complicate the interpretation of related observations.

Thermal energy dissipated during hypervelocity particle capture is calculated to induce temperatures greater than the silica melting temperature (>1200 K) along portions of the impact track (7). Such temperatures may induce synthesis of complex organic molecules from innate aerogel carbon, present at the level of $\leq 2\%$ (8). To assess this problem, we used high-power infrared (IR) laser pulses on a sample of Stardust witness coupon aerogel, as part of our Stardust Organics Preliminary Examination Team (PET) studies (9). The witness coupon is an aerogel tile employed for contamination assessment during the mission flight period. It was located near the cometary collection aerogel tiles but shielded from particle impacts. Witness coupon aerogel acts as an ideal organic contamination control for the entire Stardust Mission period.

It has been shown that laser pulses can approximate the type of rapid heating introduced

during hypervelocity particle impact (10–12). We performed a laser heating experiment at various depths in witness coupon aerogel to allow for the distinction between external and internal contamination sources. External contamination sources would be most concentrated on exposed areas of the witness coupon, decreasing in concentration with increasing depth. In contrast, internal contamination sources (i.e., introduced during Stardust aerogel preparation) would be distributed uniformly throughout the aerogel tile.

Analysis of PAHs on this aerogel was performed using microprobe laser desorption laser ionization mass spectrometry ($\mu\text{L}^2\text{MS}$) (13, 14) (Fig. 1). The $\mu\text{L}^2\text{MS}$ technique is particularly well suited for the spatially resolved surface analysis of PAHs, having sensitivity in the attomole regime for some PAHs (15). Initial $\mu\text{L}^2\text{MS}$ analysis of the witness coupon (WCARMI1CPN 0,6 and 7) revealed the presence of no PAHs at normal operating parameters: 22 μJ per CO_2 laser pulse and $\sim 10^6$ W/cm^2 power density (Fig. 1E). As the laser desorption power was increased, however, a low-mass envelope of aromatic compounds was detected that was uncorrelated with depth in the witness coupon (Fig. 1, B to E). Similar masses were found in previous aerogel studies that used a laser microprobe mass spectrometer, and these were attributed to volatiles trapped in the aerogel macrostructure (16, 17). Laser desorption parameters used in (17) [e.g., 1.06 μm ; 4×10^9 W peak power (18)] differ from those used here, but in both cases the laser energy is high enough to release trapped organic volatiles and/or to disrupt carbon-carbon bonds in the aerogel macrostructure.

To examine the source of detected PAHs, high-power laser pulse positions were reanalyzed 14 days after the initial analysis (Fig. 2). Using normal, low-power operating parameters, PAHs were detected at earlier high-power laser pulse sites (Fig. 2B). These compounds are identical in mass-to-charge ratio (m/z) and close in relative abundance to those detected previously during high-power IR laser pulses (Fig. 2A). Synthesis of new organic compounds from carbon pre-

cursors in Stardust aerogel by rapid pulsed heating would likely leave localized residual products on the surface of the aerogel, as we found. The data imply that PAHs detected after high-power laser shots were synthesized, not just released, during rapid heating of the aerogel. Comparison of PAHs found during high-power laser pulse studies of witness coupon aerogel to those found diffusely along a Wild 2 cometary particle impact track [C2115,26,22 track 6; (9)] reveals that they are very close in identity and relative abundance (compare Fig. 1, A and B). Although it is difficult to assess quantitatively the relevance of using IR laser pulses as a hypervelocity particle impact analog for aerogel, the masses found in these two samples are strikingly similar, which suggests a close correlation in thermal processing for these two processes. This study demonstrates the difficulty in distinguishing between cometary and noncometary organic compounds lying along particle impact tracks in aerogel.

Our study highlights the need for extreme caution in interpreting analyses of this type. As pointed out in (1), our work shows that simple correlation of low-mass PAHs with an impact track in aerogel is not conclusive evidence that they belong to the original impactor, although it does not rule out this conclusion. It has been shown that higher-mass PAHs can be detected along Wild 2 particle impact tracks in aerogel (1). These PAHs do not correlate with those detected in our experiment, which suggests a cometary origin, albeit potentially thermally altered from their pristine condition. For the analysis of organic compounds along impact tracks in aerogel, our study emphasizes the essential need for comparison with control experiments.

We stress that these results do not call into doubt that cometary organic compounds have been detected in the Stardust return as evidenced by nonterrestrial D/H and $^{15}\text{N}/^{14}\text{N}$ isotopic ratios, which are found in organic particles intimately associated with terminal grains (1, 4). Large particles, which survive aerogel capture and are found at impact track termini, likely experience much lower temperatures in comparison with ablated material lying along the track in aerogel. Several experiments have produced results that show organic compounds located within large terminal particles retain their original composition, owing to their decreased exposure to high temperatures (7, 19). It is continued work on these materials that will likely best further our growing understanding of cometary organic compounds.

References and Notes

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Department of Chemistry, Stanford University, Stanford, CA 94305–5080, USA.

*To whom correspondence should be addressed. E-mail: zare@stanford.edu

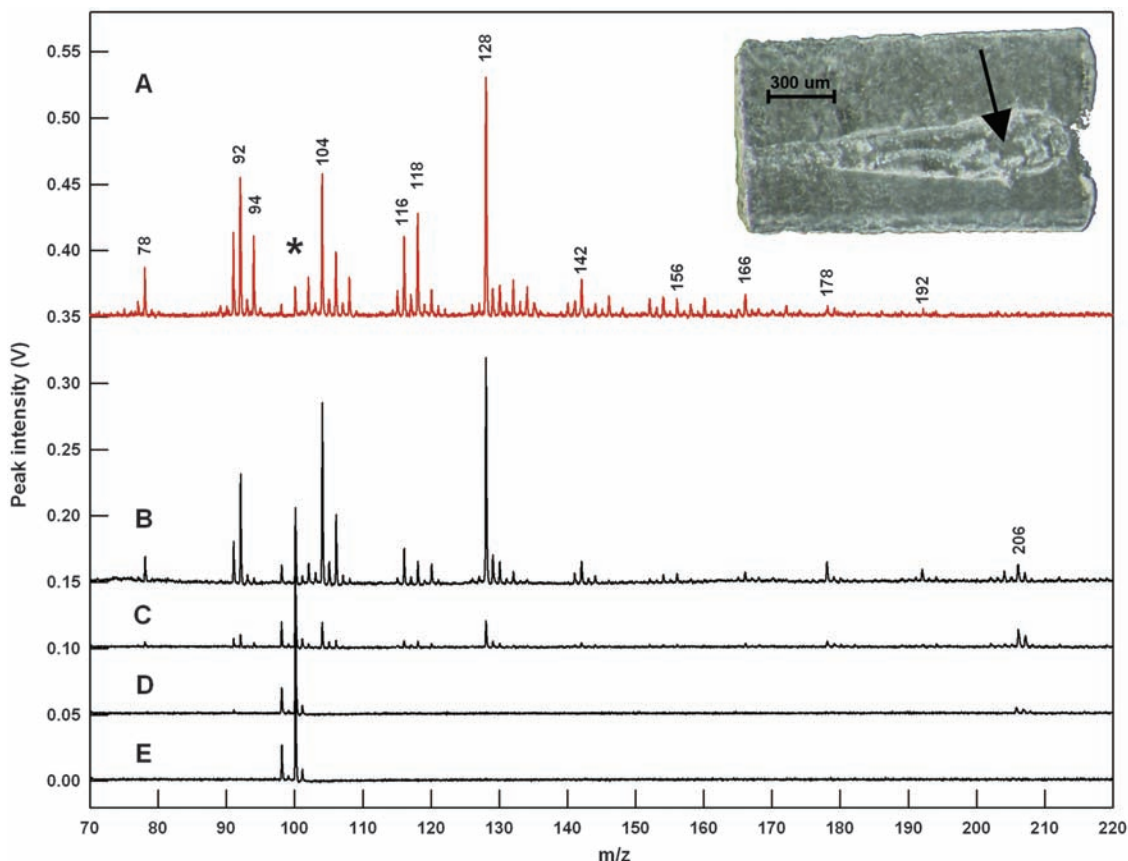


Fig. 1. $\mu\text{L}^2\text{MS}$ mass spectra comparing PAHs detected during laser pulse heating of Stardust witness coupon aerogel to those detected on a cometary impact track. **(A)** Mass spectrum taken at the entry portion of Wild2 cometary particle impact track (C2115,26,22 track 6); scaled down by a factor of 4. Main m/z peaks are indicated. This distribution consists of aromatic compounds with masses between 78 (benzene) and 178 (phenanthrene) atomic mass units (amu). A series of alkylated components was found for masses 78 amu (benzene), 128 amu (naphthalene), and 178 amu (phenanthrene), as evidenced by mass peaks separated by 14 amu (CH_2) corresponding to the loss of H and the addition of CH_3 (Fig. 2A). No PAHs in the area of interest were detected on

aerogel away from the track. The asterisk indicates mass calibration peaks for D_2 -toluene. The inset shows an optical microscope image of dissected impact track C2115,26,22. The arrow points to the location of the mass spectrum shown in (A). **(B to E)** Mass spectra, which are each composed of 50 averaged mass spectra taken over the surface of a witness coupon sample (WCARM11CPN,0,6) at various laser desorption powers. **(B)** High power [two attenuation grids (15)]. Detected compounds range in mass from 78 (benzene) to 206 amu (phenanthrene + 2CH_2) and include mainly volatile aromatic compounds. **(C)** Intermediate power (three attenuation grids). **(D)** Normal operating power (four attenuation grids). **(E)** Low power (five attenuation grids).

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Supporting Online Material

www.sciencemag.org/cgi/content/full/317/5845/1680c/DC1
Materials and Methods

Fig. S1
Table S1
References

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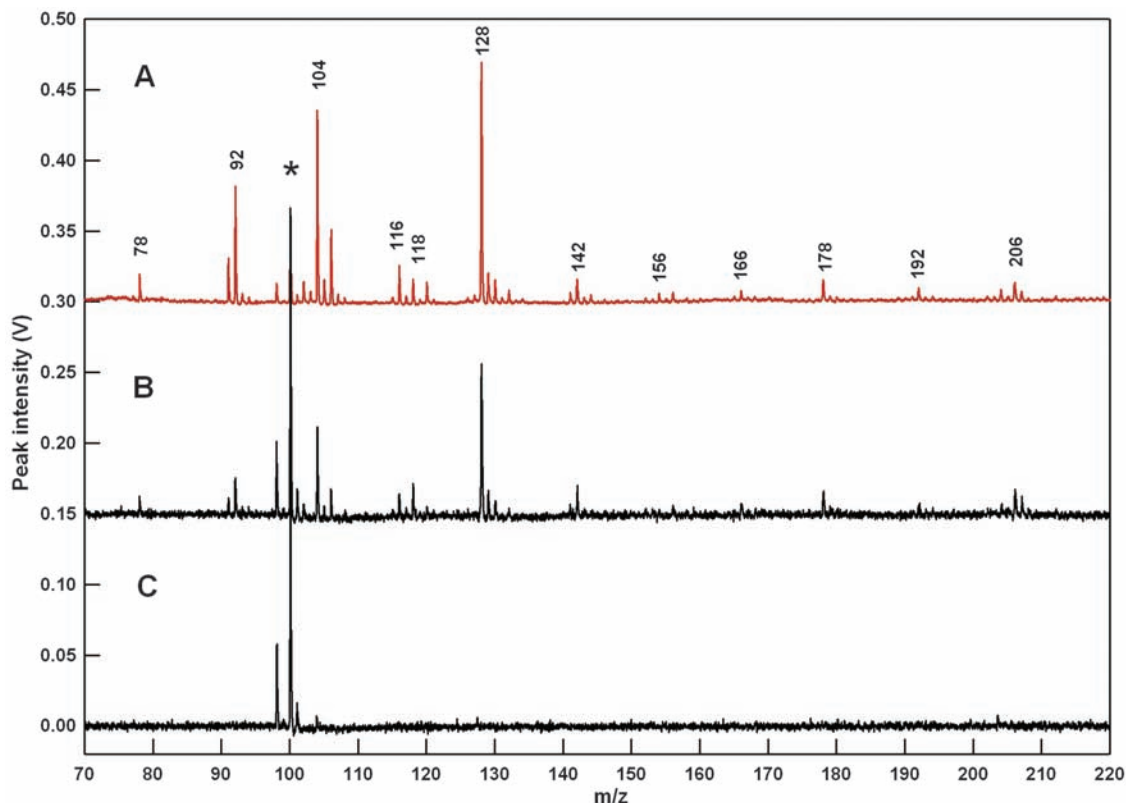


Fig. 2. $\mu\text{L}^2\text{MS}$ mass spectra comparing PAHs detected during laser pulse heating of Stardust witness coupon aerogel to those detected at the same position 14 days later using normal operating parameters, both on and off of the original high-power laser shot position. Main m/z peaks are indicated. The asterisk indicates mass calibration peaks for D_8 -toluene. **(A)** Mass spectrum composed of 50 averaged mass spectra taken over the surface of a witness coupon sample (WCARMI1CPN,0,6) at high laser desorption power (two attenuation grids). Prominent peaks include 78 amu (benzene), 92 amu (toluene), and 104 amu (styrene). Masses at 104 amu (styrene) and 128 amu

(naphthalene) are the most intense peaks observed in the mass spectrum. Several higher order PAHs are detected with relatively low abundance, including 178 amu (phenanthrene), 202 amu (pyrene), and 228 amu (chrysene). **(B)** Single mass spectrum, taken 14 days after (A), on the previous high-power laser pulse position. Normal operating parameters used; mass spectrum scaled up by a factor of 3. **(C)** Single mass spectrum, taken 14 days after (A), on aerogel away from the previous high-power laser pulse position. Normal operating parameters used; mass spectrum scaled up by a factor of 3.