

ORIGIN AND EVOLUTION OF ORGANIC MATTER PRESERVED IN STARDUST COMETARY AEROGEL TRACKS

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Introduction: The STARDUST spacecraft captured dust samples from Comet 81P/Wild 2 at a relative velocity of $6.1 \text{ km}\cdot\text{s}^{-1}$ in a low density silica aerogel and returned them to the Earth. One of the main of the scientific goals established for the mission was to determine whether comets contained complex organic materials and, contingently, the nature and abundance of this material. [1] Although contamination concerns due to carbonaceous impurities intrinsic to the flight aerogel remain, it is generally accepted that at least a fraction of the captured dust particles contain an indigenous organic component. [2] However, understanding the nature and abundance of this material is complicated by nature of the collection process. The rapid dissipation of particle's kinetic energy during its impact and deceleration cause both the particle and surrounding aerogel to experience an intense thermal pulse of upwards of 2000K for a period up to several hundred nanoseconds [3]. During this period thermal alteration and or destruction of organic species present in the impacting particle are likely to occur. We have used the technique of ultrafast two-step laser mass spectrometry (*ultra* L²MS) [4] to investigate how the nature and distribution of aromatic and conjugated organic species varies between and within aerogel cometary tracks and their associated terminal particles.

Samples: Two tracks from aerogel tile C2067 were analyzed and we present here the results for Track 113 shown in Fig. 1(A) from STARDUST keystone C2061,1,113,1,0. The track has a Type-B morphology [5] likely produced by a weakly bound aggregate that broke apart on impact. The track is characterized by a bulbous ellipsoidal cavity extending down from the point of impact to a base from which approximately a dozen long slender terminal particle tracks radiate.

Methods: No specific sample preparation treatments are required for *ultra* L²MS analysis other than the surface to be analyzed be physically unobstructed. For the *in situ* analysis of track walls this requires manual removal of the upper track hemisphere and overlying aerogel. The exposed track may then be secured to the sample analysis platter by friction mounting between two high transmission metal grids. Analysis of terminal particles, however, cannot be analyzed *in situ* due to the exterior rind of compacted and/or melted aerogel in which these particles are inevitably encapsulated. This necessitated particle extraction followed by mounting in epoxy and partially sectioning using an

ultramicrotome to expose the interior. Extracted thin-sections provided samples for consortium mineralogical and/or isotopic characterization, while the epoxy potted stub with the remaining sectioned particle was used for *ultra* L²MS analysis. Although the mounting epoxy substrate is organic it does not contribute to the organic species observed by the *ultra* L²MS instrument since being a macromolecular polymer it cannot be desorbed or photoionized under the experimental conditions used.

Results: Representative organic mass spectra from both the cavity wall of Track 113 and two terminal particles TP1 and TP3 are shown in Figs. 1(B-D). All spectra were acquired under identical experimental conditions. The mass peak at 106 amu present in all three spectra corresponding to a dimethyl benzene ($\text{CH}_3\text{-C}_6\text{H}_4\text{-CH}_3$), however since the *para*-isomer xylene is used as an internal mass calibrant its origin is ambiguous and should be ignored.

Terminal Particles: The organic composition of particles TP1 and TP3 differ significantly from one to another, even though mineralogically both particles are essentially enstatite grains. This argues against contamination from a common source. TP1 showed the largest organic signal of all of the terminal particles extracted and is characterized by a distribution of relatively low weight 1-3 ring fused ring aromatic hydrocarbons and associated alkylated homologs ($\text{Ar}(\text{CH}_2)_n\text{-H}$). The principal peaks at 94, 128 and 178 correspond to phenol ($\text{C}_6\text{H}_5\text{-OH}$), naphthalene (C_{10}H_8) and phenanthrene ($\text{C}_{14}\text{H}_{10}$) respectively. Although the spectral complexity is greater than that observed for carbonaceous chondrites such as Murchison, the dominant mass peaks in the main mass envelope are similar. The outlying peak at 254 amu is likely a naphthalene dimer produced via thermal induced free radical polymerization ($2\text{-Ar-H} \rightarrow 2\text{-Ar}^\bullet + \text{H}^\bullet \rightarrow \text{Ar}_2 + \text{H}_2$) during capture. In contrast TP3 was organic poor with a spectrum dominated by a few simple aromatics with mass peaks at 94, 166 and 178 amu corresponding to phenol, fluorene ($\text{C}_{13}\text{H}_{10}$) and phenanthrene.

Track Bulb: Organic species present on an ~300 long section of the interior cavity wall of Track 113 demonstrated more pronounced distribution of high mass peaks than observed from terminal particles. Consistent with previously reported analysis of STARDUST aerogel tracks, a number of prominent odd mass species are evident at 167, 219, 223 & 267 amu and have been ascribed to aromatic nitriles species. [6] Several peak series with 14 amu spacing are evident, e.g.,

peaks at 282, 296, 310, 324 amu, indicative of successive replacement of $-H$ with $-CH_2-H$. The dominant peaks at 294 and 338 amu are unusual and do not correspond to any of the simple aromatic hydrocarbons commonly observed in carbonaceous or ordinary chondrites. We are currently investigating the possibility that these species may be the by-products of the *in situ* carbothermal reduction of the silica aerogel by organic matter volatilized during impact shock heating. [7] However the absence of abundant nanophase silicon carbide (SiC), which is one of the main products of the silica carbothermal reduction, argues against this.

Conclusions: Organic matter is heterogeneously distributed both along aerogel tracks and between terminal particles. These differences in the distribution and

abundance of organics suggest that sample contamination via a common source is not responsible for the observed results. Impact shock heating has altered, although not necessarily obscured, the organic inventory of captured cometary grains.

References: [1] Brownlee et al. (2003) *J. Geophys. Res.*, **108**, 8111; [2] Sandford (2008) Proc. IAU Symp. 251, 299; [3] Roskosz et al. (2008) *EPSL*, **273**, 195; [4] Clemett & Zare (1996) Proc. IAU Symp. 178 [5] Hörz, et al. (2006) *Science* **314**, 1616; [6] Clemett et al. (2009) *MAPS* in publication; [7] Urbanová et al. (2008) *Eur. J. Inorg. Chem.* **26**, 4111.

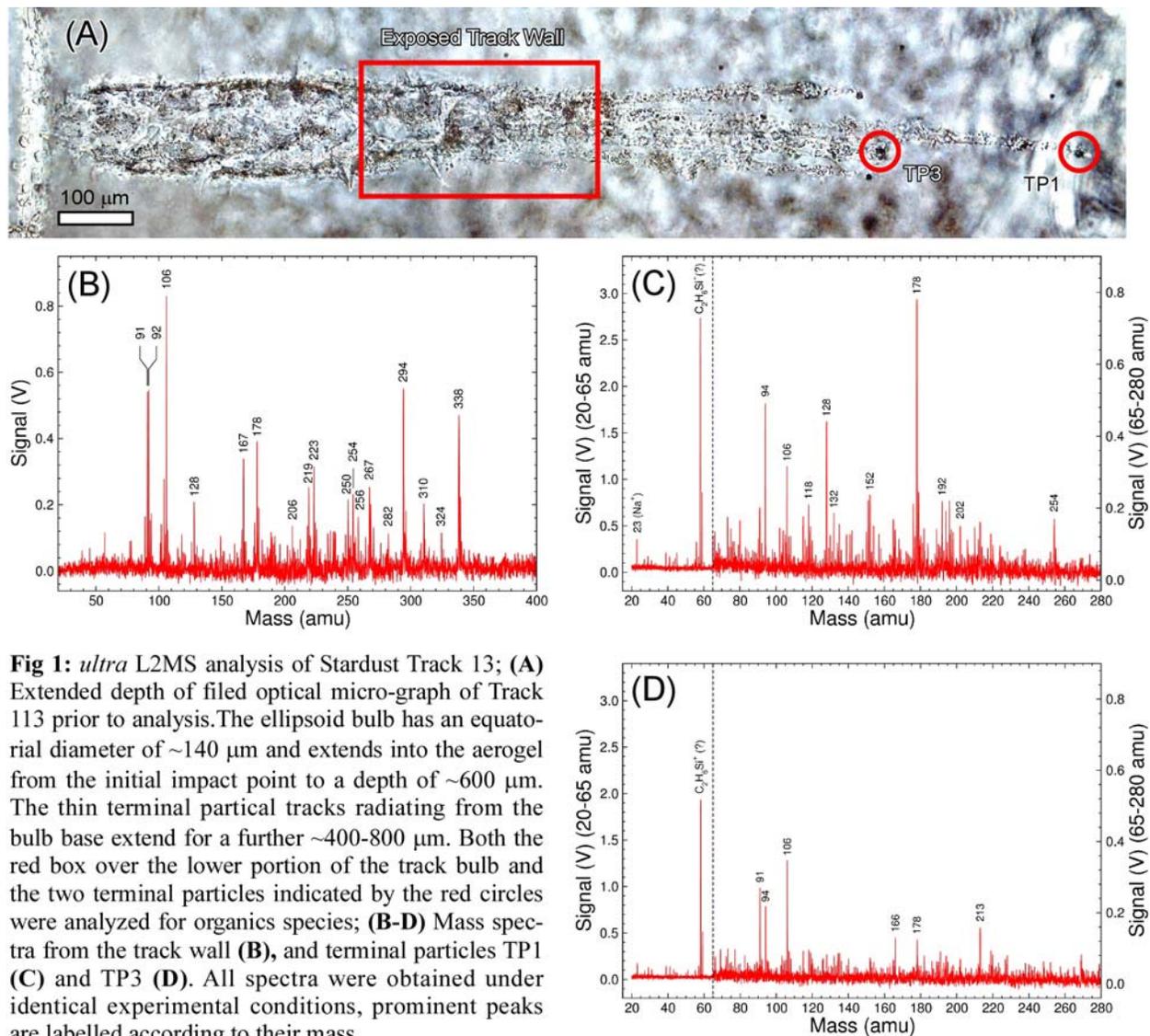


Fig 1: ultra L2MS analysis of Stardust Track 13; (A) Extended depth of filed optical micro-graph of Track 113 prior to analysis. The ellipsoid bulb has an equatorial diameter of $\sim 140 \mu\text{m}$ and extends into the aerogel from the initial impact point to a depth of $\sim 600 \mu\text{m}$. The thin terminal particle tracks radiating from the bulb base extend for a further $\sim 400\text{-}800 \mu\text{m}$. Both the red box over the lower portion of the track bulb and the two terminal particles indicated by the red circles were analyzed for organics species; (B-D) Mass spectra from the track wall (B), and terminal particles TP1 (C) and TP3 (D). All spectra were obtained under identical experimental conditions, prominent peaks are labelled according to their mass.