

ORGANIC MATERIAL IN AEROGEL SAMPLES FROM THE STARDUST MISSION. T. Henkel and I. C. Lyon, The University of Manchester, School of Earth, Atmospheric and Environmental Sciences, Williamson Building, Oxford Road, Manchester, M13 9PL, UK, (torsten.henkel@manchester.ac.uk).

Introduction: The organic material in comets is of special interest because of its contribution to the organic budget of the Earth during its early history where it might have contributed to the beginning of life [1]. The Stardust mission collected material from comet Wild 2 for comprehensive analysis in the laboratory [2].

Organic material in the Stardust samples has been successfully analyzed with different methods like IR-spectroscopy, L^2MS and XANES [3-5]. The results from these measurements indicate high O/C and N/C ratios as well as an elevated CH_2/CH_3 ratio and low abundances of aromatic molecules. This composition is quite different from meteoritic material and IDPs [3] and most likely originates from a dense molecular cloud and/or protosolar nebula rather than the diffuse ISM or stellar source and is consistent with radiation processing of astrophysical ices [3]. A drawback of these analytical methods is that generally only functional groups can be determined [4,5].

The aim of our study is to determine the molecular structure of organic molecules from Wild 2 using time-of-flight secondary ion mass spectrometry (TOFSIMS) because it records complete mass spectra. Our TOFSIMS instrument is equipped with a primary ion gun using C_{60} ions that break up upon impact spreading the kinetic energy over the 60 carbon atoms. This leads to relatively low energy sputtering and the excavation of nano-craters. Organic molecules around the crater are lifted gently and have a low fragmentation rate making it possible to detect complete molecules in the mass spectrum [6,7]. Fractionation patterns can be used to recognize certain molecules [8] or determine functional groups of unknown molecules. Additionally, depth profiling of organic material is possible because the material underneath the sputtering craters mostly survives unaltered [7].

We have previously analyzed a longitudinally cut track (C2012,15,134,0,0) and a $100\mu m$ section of another longitudinal cut track (C2063,5,154,0,0). We reported several polycyclic aromatic hydrocarbons (PAHs) around the track in the first sample [9] as well as the possible detection of alanine in the second [10]. The PAHs were at constant levels in the aerogel and no enrichment towards the track was found making it unlikely that these were of cometary origin. This does fit with expectations as the track was a short and 'carrot-shaped', such tracks are not associated with or-

ganic-rich impactors from the comet. The alanine was found in the surrounding aerogel as well as the track area, which cast some doubt on its cometary origin. To determine whether organic material in the aerogel tracks or the surrounding area stems from the comet itself and diffused into the surroundings or if this is contamination, we analyzed samples from the backside of the aerogel tiles as well as non-flight aerogel samples which were left-over from production.

The aerogel itself was produced using tetraethylorthosilicate $[Si(C_2H_5O)_4]$ in a two-step process including acetonitrile $[CH_3CN]$ with heat-treatment and super-critical drying [11]. It's therefore expected that some of the organic material used in the production process might still be found in the aerogel. The produced aerogel initially showed a total C-abundance of 2.4% which was reduced to around 0.5% by baking the aerogel at $300^\circ C$ [11].

Samples: Blank samples were taken from the back-sides of tiles C2012, C2061 and C2063 and from the non-flight aerogel spares from production batches E232, E234 (C2063), E235, E236 (C2012, C2061), E237, E239 and E246. These samples were analyzed under the same conditions as the track samples themselves. A third track section (C2061,9,113,0,0) was analyzed in addition to the previous samples. The section is of type B which is a bulbous track associated with organic-rich impactors. The track was cut open longitudinally and into a narrow section roughly $100\mu m$ long and as wide as the track itself.

Results: The geometry of the sample makes analysis very complicated because parts of the sample are at different heights leading to different flight times and overlapping peaks. These cannot be deconvoluted for secondary ion images but mass spectra from separate regions-of-interest help to quantify results.

No significant abundances of mineral forming elements (like Mg, Al, K, Ca, Cr, Mn, Fe, Cu) were detected indicating the absence of inorganic material in the analyzed track sections.

The mass spectra are dominated by peaks from organic material and SiO-clusters as well as SiO-clusters attached to organic molecules. Amongst the detected organic molecules are pure hydrocarbons as well as some O-bearing hydrocarbons and few N-bearing hydrocarbons. Additionally, N is also found among SiO-clusters attached to organic molecules.

To compare the mass spectra from the non-flight

spare material with the back-sides of the sample tiles and the track samples themselves, the intensities for individual secondary ion species were normalized by the number of ionization events. This reduces most matrix effects but leaves differences due to changes in primary ion currents or geometric surface effects but these are considerably smaller (estimated to be less than a factor of two) compared to detected differences (up to an order of magnitude) in secondary ion species abundance between the different samples.

There are many peaks in the mass spectra that clearly result from terrestrial contamination. Samples C2063,5,154,0,0 and C2061,9,113,0,0 show high abundances at masses 73, 147 and 281 which typically stem from polydimethylsiloxane (PDMS) which is often used as mold release agent and therefore a common surface contaminant with plastic material. Additionally, peaks above mass 600 stem from a wax which was used in the production of the TEM-grids which have been used to hold down the samples. No wax was detected on any of the blank samples. Whilst these have been freshly mounted with specially cleaned grids, the track samples were stored several months in their mount before analysis giving the wax and PDMS enough time to creep along the surfaces.

There are significant differences of up to one order of magnitude between the blank samples (non-flight spares and back-sides of tiles) themselves as well as between the track samples and the blanks.

Aerogel batch E234 showed significant differences between different areas of this sample showing a strong heterogeneity.

Considering the spectra from the different sample types: C2061, C2063 (back side of tiles) show a good match with the spectrum from the track samples C2061,9,113,0,0 and C2063,5,154,0,0 but not with the non-flight spare from the same production batch, E236

and E234 respectively.

C2012 (back-side of tile) shows a considerable difference with the spectrum from the track sample C2012,15,134,0,0 but there is a good match with the spectra from the non-flight spare of this tile, E236.

Discussion: The large variation in abundances of molecular secondary ions from different areas of sample E234 already implies that the distribution of production-related organic contamination is heterogeneous. This could also explain why there are huge differences between the non-flight spare samples and the back-sides of the tiles as well as the actual track samples. A blank correction for the production-related organic material within the samples becomes therefore very difficult if not impossible. This also casts a doubt if any diffuse enrichment of organic material around a track is found as this might stem from the heterogeneous distribution of production-related organic material.

On a separate note, contamination from the sample storage/mounting could easily be separated from the aerogel-related material and therefore causes only minimal interferences allowing a proper characterization of the actual sample.

References: [1] Chyba C. and Sagan C. (1992) *Nature*, 355, 125-132. [2] Brownlee D. E. et al. (2006) *Science*, 314, 1711-1716. [3] Sandford S. A. et al. (2006) *Science* 314:1720-1724. [4] Cody G. D. et al. (2008) *Meteoritics & Planet. Sci.*, 43, 353-365. [5] De Gregorio B. T. et al. (2011) *Meteoritics & Planet. Sci.*, 46, 1376-1396. [6] Fletcher J. s. et al. (2006) *Applied Surf. Sci.*, 252, 6513-6516. [7] Henkel et al. (2009) *Rapid Comm. In Mas Spec.*, 23, 3355-3360. [8] Henkel T. et al. (2012) *Meteoritics & Planet. Sci.*, 47, #5258. [9] Rost D. et al. (2011) *Meteoritics & Planet. Sci.*, 46, A200. [10] Henkel T. et al. (2013) LPSC 44, #2554. [11] Tsou P. et al. (2003) *Jour. of Geophys. Res.*, 108(E10), 8113.