FTIR ANALYSIS OF AEROGEL KEYSTONES FROM THE STARDUST INTERSTELLAR DUST COLLECTOR: ASSESSMENT OF TERRESTRIAL ORGANIC CONTAMINATION AND X-RAY MICROPROBE BEAM DAMAGE.

H. A. Bechtel, C. Allen, S. Bajt, J. Borg, F. Brenker, J. Bridges, D. E. Brownlee, M. Burchell, M. Burghammer, A. L. Butterworth, P. Cloetens, A. M. Davis, C. Floss, G. J. Flynn, D. Frank, Z. Gainsforth, E. Grün, P. R. Heck, J. K. Hillier, P. Hoppe, L. Howard, G. R. Huss, J. Huth, A. Kearsley, A. J. King, B. Lai, J. Leitner, L. Lemelle, H. Leroux, L. R. Nittler, R. C. Ogliore, F. Postberg, M. C. Price, S. A. Sandford, J. A. Sans Tresseras, S. Schmitz, T. Schoonjans, G. Silversmit, A. Simionovici, R. Srama, F. J. Stadermann, T. Stephan, J. Stodolna, R. M. Stroud, S. R. Sutton, R. Toucoulou, M. Trieloff, P. Tsou, A. Tsuchiyama, T. Tyliczszak, B. Vekemans, L. Vincze, A. J. Westphal, M. E. Zolensky, >29,000 Stardust@home dusters
Affliations are given at http://www.ssl.berkeley.edu/~westphal/ISPE/.

Introduction: The Stardust Interstellar Dust Collector (SIDC) was intended to capture and return contemporary interstellar dust. The ~0.1 m^2 collector was composed of aerogel tiles (85% of the collecting area) and aluminum foils and was exposed to the interstellar dust stream for a total exposure factor of 20 m^2·day [1]. The Stardust Interstellar Preliminary Examination (ISPE) [2,3] is a consortium-based project to characterize the collection using nondestructive techniques [4].

Sandford *et al*. [5] recently assessed numerous potential sources of organic contaminants in the Stardust cometary collector. These contaminants could greatly complicate the analysis and interperetation of any organics associated with interstellar dust, particularly because signals from these particles are expected to be exceedingly small. Here, we present a summary of FTIR analyses of over 20 aerogel keystones, many of which contained candidates for interstellar dust.

Infrared spectromicroscopy: Infrared transmission spectra were acquired with a synchrotron-based Fourier transform infrared (FTIR) microscope on Beamline 1.4.3 at the Advanced Light Source (ALS). The adventage of a synchrotron source is the diffraction-limited spot size, which is ~3 µm in the region of the C-H stretching frequencies (~3000 cm^{-1}). Because infrared radiation is non-ionizing and the peak and average powers on the sample are low, infrared microscopy is truly a noninvasive technique. The only risk of sample damage, therefore, is sample handling.

Organic contamination: To assess the chemical nature and distribution of indigenous carbon in the SIDC, infrared measurements were made from both Stardust flight and archival samples of unflown tiles from the same production batches. As shown in Figure 1, the spectra from different keystones vary considerably, and there appear to be at least 5 different classes of contamination. The first class, represented by I1017,2,1 and I1059,1,14, is consistent with “clean” aerogel, in which the only source of organic contaminant appears to be Si-CH_3 groups at ~2973 cm^{-1}. These Si-CH_3 groups are known to be the primary source of carbon in the original aerogel collector tiles and are a direct result of the aerogel manufacturing process. The other classes represent increasing levels of contamination from other sources, including features at 1720 and 1750 cm^{-1}, which can be attributed to carbonyl groups (C=O), and at ~1640 cm^{-1}, which could be attributed to adsorbed water, but may also arise from other heteroatom groups. The biggest complication from an organic analysis perspective, however, is the increased strength of the feature at ~2940 cm^{-1}, which corresponds to aliphatic –CH_2 groups. Unlike aerogel from the cometary collector, where the CH_3 peak is typically larger, infrared spectra of aerogel from the interstellar collector often have CH_2 peaks that are 2-3 times larger than the CH_3 peaks, indicating larger chain lengths and more complex organic contamination.

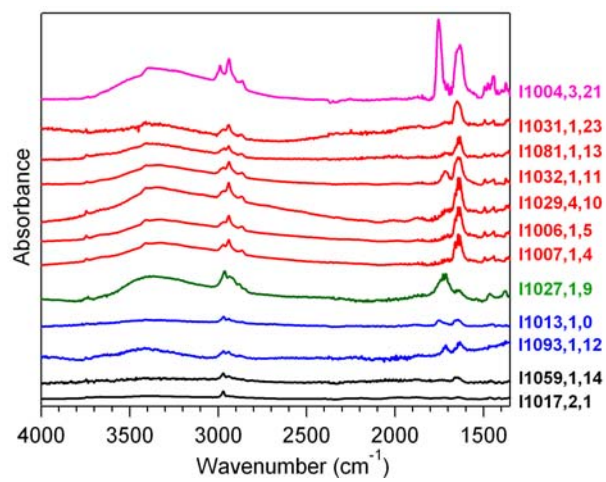

Figure 1. FTIR spectra of keystones extracted from the SIDC. The spectra are color coded to highlight different contaminant backgrounds.

The distribution of contaminants was measured by mapping the entire keystone. These maps reveal little spectroscopic changes across the keystone that cannot be attributed to changes in thickness, indicating that any contamination is relatively uniform across the keystone. Thus, high resolution maps of the tracks and/or terminal particles embedded in the picokeystone could potentially reveal any organics associated with the particle. The increased –CH_2 concentration in many of the keystones significantly complicates the search for organics, however, by reducing the sensitivity of the infrared measurement. To date, there has been no evidence for organics associated with interstellar dust candidates.

The source of the variation in contaminant levels from different keystones remains unknown, despite efforts to standardize extraction methods and reduce possible sources of contamination. There is no apparent correlation to extraction date, aerogel batch, or location on the Stardust collector. Indeed, contaminant levels vary considerably even among keystones extracted from the same tile. The homogeneous distribution of contaminants within a keystone and the lack of correlation to sample batch or location on the Stardust collector suggest that the contamination might be introduced during or after extraction. Indeed, FTIR measurements of I1007,1,4 show dramatically different spectra before and after 9 months of storage. Efforts to solve this contamination issue are ongoing.

X-ray microprobe beam damage: While FTIR measurements have the potential to measure organic content within samples, they cannot compete with X-ray microprobes in terms of elemental analysis, which is critical for eliminating samples of terrestrial origin. Consequently, keystones from the interstellar collector tray were sent to the ALS, APS, and ESRF for analysis via Scanning Transmission X-ray Microscopy (STXM) and Synchrotron X-ray Fluorescence (S-XRF). Although these techniques are considered minimally invasive, X-rays have the potential to cause beam damage under conditions of high fluence and small focal spots. To monitor the effects of these X-ray microprobes, infrared spectra were taken before and after X-ray analyses.

Examination of four keystones (I1017,2,1; I1007,1,4; I1017,6,20; I1004,3,21) before and after STXM analysis at the ALS Beamline 11.0.2 showed essentially no changes in the C-H stretching region of the spectra. Three of these keystones, however, were analyzed by S-XRF prior to the first FTIR anlysis, so it is possible that any damage that could have been done to the aerogel by X-rays already occurred during the S-XRF analysis. The evidence suggests, however, that STXM is a relatively noninvasive sample probe for these samples.

In contrast, S-XRF measurements appear to dramatically alter the organic content in the aerogel. Figure 2 shows infrared spectra in the C-H stretching region of I1017,6,20 before and after S-XRF analysis at ESRF ID13. The CH_3 / CH_2 ratio is altered, and a new feature appears at ~2990 cm^{-1}. Six of the nine keystones measured after XRF analysis show this characteristic feature. Moreover, as shown in Fig. 2, these

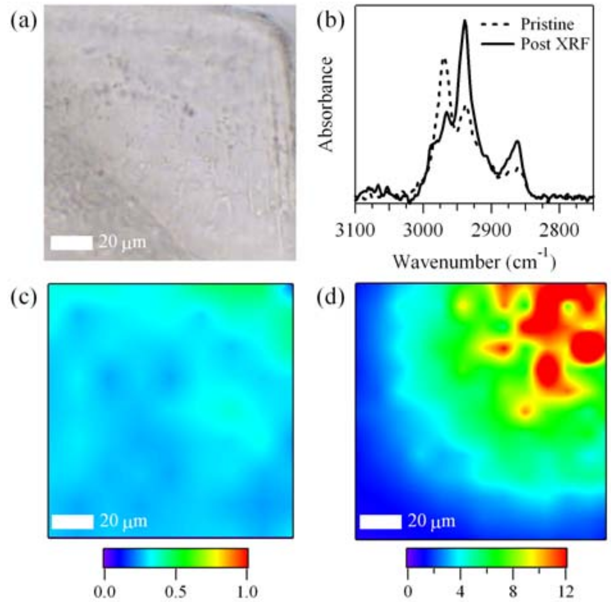

Figure 2. *(a) Optical image of I1017,6,20 keystone with the space-exposed surface at the top of the image. (b) FTIR spectra before and after S-XRF analysis at ESRF ID13. Image map corresponding to the CH_2/CH_3 area ratio (c) prior to any synchrotron X-ray analysis and (d) after S-XRF analysis on ESRF ID13. Note change in color scale.*

changes are only seen around the track and/or terminal particle, indicating that the contamination is beam induced and not from other sources during shipping or sample mounting. The ISPE science council has imposed a moratorium on S-XRF measurements on IS candidates until adequate dosing limits can be established. These findings confirm that high-fluence hard X-ray microprobe measurements have observable effects on aerogel picokeystones.

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References: [1] Tsou, P., et al. (2003) *JGR*, *108*, E10. [2] Westphal A. J. et al. (2008) 39th LPSC, 1855. [3] Westphal A. J. et al. (2009) 40th LPSC, 1786. [4] Westphal A. J. et al. (2010) *X-ray Optics and Microanalysis, Proceedings*, *1221*, 131-138. [5] Sandford et al. (2010) *Meteoritics & Planet. Sci.*, *45*, 406-433.