

Carbon XANES Data from Six Aerogel Picokeystones Cut From the Top and Bottom Sides of the Stardust Comet Sample Tray . S. Wirick¹, G. J. Flynn², D. Frank³, S. A. Sandford⁴, M. E. Zolensky³, P. Tsou,⁵ C. Peltzer¹, C. Jacobsen¹, ¹Dept. of Physics and Astronomy, SUNY StonyBrook, NY 11794, USA,(swirick@bnl.gov), ²Dept. of Physics, SUNY Plattsburgh, NY 12901 USA, ³NASA Johnson Space Center, Houston, TX, 77058, USA, ⁴ NASA Ames Research Center, Moffett Field, CA 94035, USA, ⁵ JPL, Caltech, CA, 91125, USA

Introduction: Great care and a large effort was made to minimize the amount of organic matter contained within the flight aerogel used to collect Comet 81P/Wild 2 samples [1]. Even so, by the very nature of the production process and silica aerogel's affinity for volatile organics keeping silica aerogel free from organics is a monumental task.

Silica aerogel from three production batches was flown on the Stardust sample return mission. All 3 types had layered densities varying from 5mg/ml to 50 mg/ml where the densest aerogel was farthest away from the collection area. A 2 step gelation process was used to make the flight aerogel and organics used in this process were tetraethylorthosilicate, ethanol and acetonitrile. Both ammonium hydroxide and nitric acid were also used in the aerogel production process. The flight aerogel was baked at JPL at 300 ° C for 72 hours, most of the baking was done at atmosphere but twice a day the oven was pumped to 10 torr for ½ hour [1]. After the aerogel was baked it was stored in a nitrogen purged cabinet until flight time. One aerogel cell was located in the SRC away from any sample collection area as a witness to possible contamination from out gassing of the space craft, re-entry gasses and any other organic encounter. This aerogel was aerogel used in the interstellar collection sample tray and is the least dense of the 3 batches of aerogel flown. Organics found in the witness tile include organics containing Si-CH₃ bonds, amines and PAHS [2,3].

Besides organic contamination, hot spots of calcium were reported in the flight aerogel [4]. Carbonates have been detected in comet 81P/Wild2 samples [5]. During preflight analyses, no technique was used to analyze for carbonates in aerogel. To determine if the carbonates found in 81P/Wild2 samples were from the comet, it is necessary to analyze the flight aerogel for carbonate as well as for organics.

Samples: Because the witness aerogel tile was not of the same batch as the comet tiles, we requested and were allocated 9 aerogel picokeystones cut from the comet tray tiles C2103 and C2061 (Fig. 1). C2061 contains 1 carrot shaped track, as does cell C2103. Location of the tiles can be found at http://www-curator.jsc.nasa.gov/stardust/sample_catalog/Cometary/Level3/Level3MosaiccsCometaryTray.pdf. Seven picokeystones were cut from tile C2103, one of these

was cut from the top (comet collection side) of the tile and the other 6 were cut from the bottom (most dense region) of this cell. Two other picokeystones were cut from tile C2061, both from the top of the tile. The picokeystones are triangular shaped, ~ 0.5mm on a side, ~70 microns thick and are sandwiched in between 2 silicon nitride windows and these windows were anchored to our sample mounts using scotch tape. The samples were fedexed overnight to the National Synchrotron Light Source (NSLS) where upon arrival were immediately placed into a nitrogen purged cabinet. Samples are only removed from this cabinet during analysis where they are then kept in a helium purged environment.

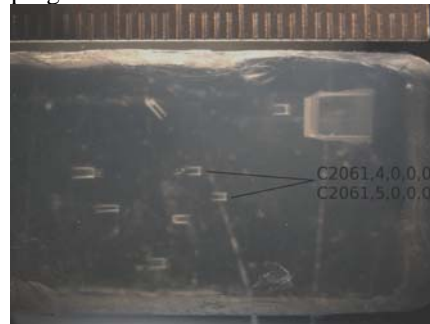


Figure 1. Area in cell C2061 where 2 picokeystones were cut.

Results: Carbon X-ray Absorption Near Edge Structure (XANES) spectra were collected using a scanning transmission X-ray microscopy (STXM) located at the X1A beamline at the NSLS, BNL, Upton, NY. Spectra were collected using a technique known as STACKS where an image is collected, the energy is changed by a small increment, then another image is collected; this is done over an energy range of interest [6]. For this study, the energy range was 280-295 eV with energy increments varying from 0.1-0.3 eV. Because the carbonates found in the 81P/Wild2 samples are smaller than 0.5 micron, all image step sizes were 0.2 microns. To date we have analyzed a total area of ~0.03 mm² from 6 of the 9 picokeystones and no carbonates have been detected.

The picokeystones are too thick for the STXM to analyze the interior regions so the analysis area was limited to a width of ~70microns from the edge where the keystones are thin enough to get X-rays thru (~<300nm). After one collects a STACK data set one then can perform principal component analysis of this data set and based on the major principal components

one can then use a clustering algorithm to group the principal spectra in a sample [7]. Figure 2 shows an image from cutting the picokeystone because the spectra vary significantly and are not related to any edge effect either. For instance, image of the CLUSTER indices and the CLUSTER spectra from one STACK data set collected from picokeystone C2061,5,0,0. This is a picokeystone cut from the comet collection side of the aerogel cell. The cluster indice image is typical of all of the cluster indice images for all of the 6 picokeystones analyzed so far, where one sees a banded variation in the carbon spectra on the scale of a few microns wide. We do not believe this banding is a compression effect the black spectrum in fig.1 is found both near the edge and in the interior region of the image. It is likely that this banding effect is a result of the production of the aerogel.

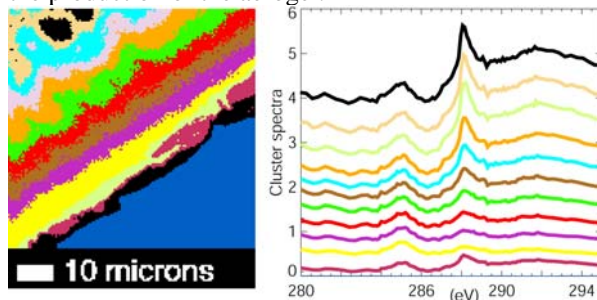


Fig 2. Cluster indices image and cluster spectra from C2061,5,0,0.

We have found 4 different carbon XANES spectra in the aerogel; one spectrum contains a 285 eV absorption and this absorption is likely due to a multiple C=C in varying carbon ring bonds (fig. 3A), one spectrum that contains minimal absorption in the 285 eV region compared to the absorption at the 288.2 eV, this absorption is usually assigned to a C=O bond (fig. 3C); the 3rd spectrum contains both a 285eV and 288.2 eV absorptions (fig. 3B); and the 4th spectrum has the greatest absorption at 288.2 eV (fig. 3D).

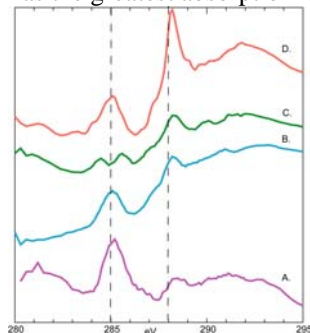


Figure 3. Different carbon XANES spectra from comet aerogel

As seen in fig. 2, the carbon XANES spectra are variable even in a small region of the aerogel. However, in general, cell C061, where the picokeystones were cut only from the top (comet) side of the sample tray contains more carbon than cell C103

and the carbon in cell C2061 contains more 288.2 eV absorption. We have not observed any difference in the carbon XANES spectra from the denser (bottom) aerogel.

Discussion: To date, we have only analyzed a small area of the picokeystones cut from the comet tiles. The motivation to analyze non-track containing aerogel from the comet tray is to understand the carbon XANES spectra collected from 81P/Wild2 samples. On the spatial scale of the STXM (50nm) it appears that some (though not all) of what we observed during the preliminary examination period of the Stardust samples was carbon XANES spectra of the carbon contained in the aerogel. The collection of particles generated enough heat to melt some aerogel and some of the carbon XANES spectra we obtained from samples containing minerals must be due to melted aerogel closely associated with these minerals. How the organics in the aerogel changes with heat we do not know. Wright, et al found when they heated pre-flight aerogel to both 300 and 500° C, organics were released at both of these temperatures but the aerogel became more dense at 500° C so the flight aerogel was only baked to 300° C [8]. The process by which the flight aerogel was made must result in the organics being incorporated into the silica structure on an angstrom size scale or even bond to the Si for organics to survive being baked to 300 °C for several days.

Conclusions: We have found 4 different forms of organic carbon in the comet sample tiles aerogel and these forms vary on a spatial scale of a few microns. We have handled the aerogel so as to minimize exposure of the aerogel to any airborne organics. Some of the carbon XANES spectra in the aerogel are similar to carbon XANES spectra obtained from 81P/Wild2 samples. There appears to be more carbon in the top side of cell C2061 but there does not appear to be any difference in the spectra from the least to the most dense areas. We have not detected any carbonates in the 0.03mm² area analyzed.

Acknowledgements: Many thanks for support from Stardust Discovery Data Analysis Program grants NNX07AM856, NNX07AM78G, SRLIDAP grant NAG512884 and the Dept. of Energy.

References: [1] Tsou, P., et al. (2003), J. Geophy. Res. 108, E10, [2] Sandford, S. et al. (2006), Science, 314, 1720-1724, [3] Spencer, M.K. and Zare, R. N. (2007), Science, 317, 1680C, [4], Flynn G.J., et al. (2006), Science, 314, 1731-1735, [5] Wirick, S. et al. , (2007) LPSC XXXVIII # 1534, [6] Jacobsen, et al. (2000) J. Microscopy, 197, 173-184, [7] Lerotic, M., et al. (2005), J. El. Spec. Relat. Phen., 144-147, 1137-1143 [8] Wright, I.P., et al. (1994), LPSC XXV, #1515