

Carbonates Found in Stardust Aerogel Tracks. S. Wirick¹, H. Leroux², K. Tomeoka³, M. Zolensky⁴, G. J. Flynn⁵, T. Tylliszczak⁶, A. Butterworth⁷, N. Tomioka³, I. Ohnishi³, K. Nakamura Messenger⁴, S. Sandford⁸, L. Keller⁴, C. Jacobsen¹. ¹Dept. of Physics and Astronomy, SUNY Stony Brook, NY 11794, USA, (swirick@bnl.gov) ²Laboratoire de Structure et Proprietes de l'Etat Solide, Univ. de Lille, d'Ascq, France, ³Depart. Earth&Planetary Sci, Kobe Univ., Nada, Kobe 657-8501 Japan, ⁴NASA Johnson Space Center, Houston, TX, 77058, USA, ⁵Depart. Of Physics, SUNY Plattsburgh, NY 12901 USA, ⁶Advance Light Source, LBL, Berkeley, CA 94720, USA, ⁷Space Science Lab., Univ. Calif. Berkeley, CA 94720, USA, ⁸NASA AMES Research Center, Moffett Field, CA 94035

Introduction: Preliminary examination of particles collected from Comet Wild 2 suggest that this comet is chondritic and formed under multiple processes. The lack of any hydrated minerals strongly suggests that most, if not all of these processes were anhydrous [1,2,3]. However, carbonates were found in particles extracted from 4 different tracks in the aerogel. It is our belief that these carbonates have a terrestrial origin and are a contaminant in these samples.

Samples: Comet Wild 2's particles were collected into silica aerogel. The Sample Tray Assembly (STA) consisted of two trays. One of these trays was used to collect interstellar dust particles, the other tray to collect Comet Wild 2 particles. The trays were arranged inside the Sample Return Canister (SRC) such that the interstellar tray was on top of the cometary tray and located 4 cm away from the re-entry air intake filter. The air filter was designed to stop particles greater than 2 microns from entering the SRC [4]. When the SRC was initially opened, a few corners of the aerogel cells from the comet's sample tray were broken off and lying on the surface of the aluminum base plate. These broken off pieces contained tracks in the aerogel. It is in 3 tracks from these broken pieces where carbonates were identified. Carbonate was also identified in Cell number 027. This was an aerogel cell, in tact, on the sample tray, located on the bottom edge of the track.

Results: Carbonates were detected in samples FC3,0,2,2,1; FC4,0,3,1,1 and 2; FC12,0,16,1, and 2 and 3; and C2027,2,69,1,4. For FC4 and FC12 carbonates were found in multiple microtomed sections (last number in the sample number) The carbonates were initially detected by the TEM group at Laboratoire de Structure et Proprietes de l'Etat Solide using Transmission Electron Microscopy (TEM) with energy dispersive spectroscopy (EDS) and electron diffraction. The presence of these carbonates were confirmed using Scanning Transmission X-ray Microscopes (STXM) and carbon X-ray Absorption Near Edge Structure (XANES) spectroscopy. The carbonate spectrum from carbon XANES is nearly unique with only CO₂ also having a sharp, well defined peak in this energy region.

From Figure 1 it is clear the TEM has better spatial resolution than a STXM by about 2 orders of

magnitude. In almost all of the samples analyzed there were multiple areas where carbonates were found. For

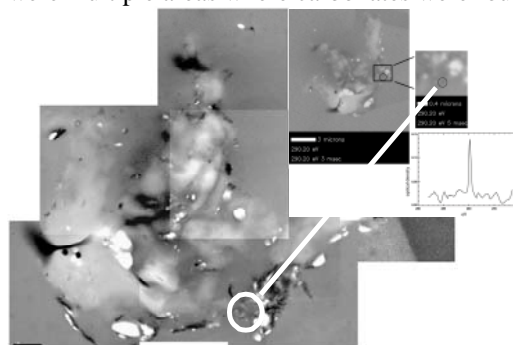


Figure 1 Montage of both TEM and STXM images of Stardust particle FC12,0,16,1,3 Black circled area is where carbon XANES spectra were obtained and white circled area is where EDS and electron diffraction identified a possible carbonate.

the STXM, areas smaller than 50 nm are difficult to identify when embedded in a carbonaceous media such as epoxy. This is not an issue for the TEM. The size of the carbonates as determined by the TEM ranged between 50 nm and 500 nm and are calcium carbonates as identified by EDS and electron diffraction. The difficulty in definitively identifying the carbonates using the TEM however, was the small carbonate particles literally fell apart in the electron beam. With the STXM this was not the case and spectra could be easily obtained from areas 50nm or larger.

Figure 2 is a graph of carbon XANES spectra from two soils collected at the Stardust capsule landing sight, M4672_6 and M4762_5, a scraping from the heat shield of the capsule, M 5213_3, and Stardust samples FC4,0,3,1,2 and FC12,0,16,1,1. The carbonate pi* peak occurs at 290.2 eV for the carbonates from the landing sight, at 290.38 eV from the heat shield and at 290.4 eV from the carbonates found in the aerogel tracks. The carbonate spectra from the Comet samples also contain a significant amount of some organic material. These particles were embedded in epoxy and

the epoxy spectrum was removed from the total spectrum so the organic spectra we are seeing associated with the carbonate is not from the epoxy. The landing sight carbonates had potassium associated with them as well as a small amount of organic matter

(carbon spectra pre-edge region from 285-289 eV).

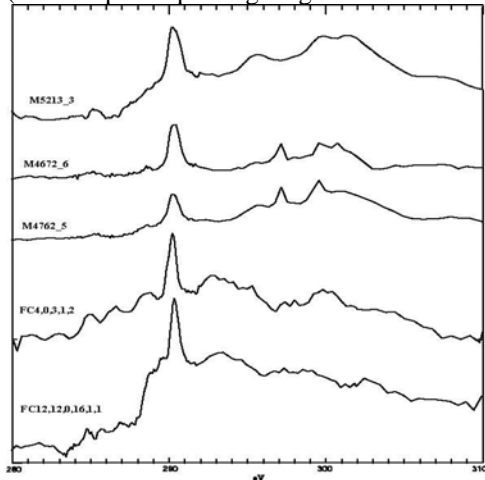


Figure 2 Carbon XANES spectra from the Stardust landing sight, heat shield, and carbonates found in Stardust particles

The carbonate associated with the heat shield scrapings is similar to spectrum from FC12,0,16,1,1, containing organic material. The landing sight samples and the heatshield samples were not microtomed.

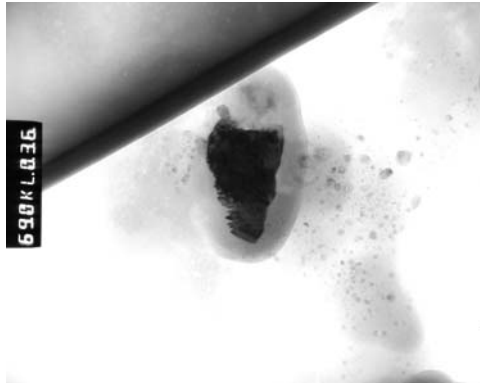


Figure 3 TEM image of a carbonate (dark area) surrounded by a SiO₂ layer. The field of view is 1.5 microns.

Figure 3 is a TEM image from sample FC3,0,2,2,1. The carbonate is covered by a thick layer of dense SiO₂ suggesting that this carbonate is surrounded by melted aerogel. The carbonate was identified as calcite using electron diffraction and is 250 nm in size. In sample C2027-2-69-1-4 calcite aggregates ranging in size from 1-3 microns were found on a terminal particle. The aggregates were associated with Zn bearing grains and all of these were embedded in an SiO₂ glass. These carbonates were identified as calcite using EDS and electron diffraction.

Discussion: There are several possible sources of carbonate contamination in the Comet Wild 2 samples. The silica aerogel is known to contain organics, identified by NMR, and hot spots of many elements, including calcium, identified by X-ray fluorescence. These calcium hot spots could be calcium carbonates though this identification has not been confirmed and

to date there is no definitive identification of carbonate in the aerogel. If the dense layer of SiO₂ around two of the carbonates is melted aerogel this points to either carbonate present in the aerogel that encountered a cometary particle during collection or this carbonate is from Wild 2. Carbonate could also be present in the embedding material used to microtome the sections (i.e. epoxy). Preliminary examination of the epoxy however, using STXM, did not find any carbonate present in the epoxy. It is unlikely the embedding medium was the source of the carbonate. The soil in the Stardust mission landing sight is rich in carbonates and clays. Scrapings from the outside of the SRC also contained carbonates. Though extreme care was taken to minimize contamination of the interior of the SRC, it is possible that sub micron sized pieces of carbonate from the landing site found their way inside the sample canister, possibly through the air intake filter. The sample aerogel trays were arranged so that the interstellar dust collection tray was nearest to the air intake filter. The interstellar dust collection tray covered the cometary dust collection tray and so would have protected the cometary dust collection tray to some extent from any dust particles in the SRC. The fact that 3 of the aerogel pieces that were broken off from the tray are where we find carbonates suggest this is a possibility. The air filter was designed to only keep out particles of 2 microns in size or larger. Particles this size are not visible to the human eye. It is very possible that the inside of the SRC was contaminated with particles smaller than 2 microns during the landing process.

Carbonates were also identified in an intact sample cell and these carbonates are surrounded by melted aerogel. Also in one of the FC samples we have a carbonate coated by amorphous silica. These carbonates could not be contamination from particles inside the SRC. The carbonate found in the C2027 sample was also associated with a high Zn bearing grain, also considered a contaminant. What the source of these contaminants are is not clear.

Conclusions: All of these results are preliminary. Less than 1% of the total mass of all of the returned cometary particles have been analyzed. More analysis needs to be performed on the flight silica aerogel as well as samples from the heat shield and the interior of the SRC. It will also be interesting to see if the interstellar dust samples contain carbonate particles.

References: [1] Zolensky et al (2006) Science, 314, 17**-17** [2] Flynn, G. J. et al (2006), Science, 314, 17**-17**, [3] Brownlee, D. et al (2006), Science 314, 17**-17**, [4] Tsou, P. (2003) J. Geophysical Res., 108, 8113