

Organic matter from comet 81P/Wild 2, IDPs, and carbonaceous meteorites; similarities and differences

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Abstract—During preliminary examination of 81P/Wild 2 particles collected by the NASA Stardust spacecraft, we analyzed seven, sulfur embedded and ultramicrotomed particles extracted from five different tracks. Sections were analyzed using a scanning transmission X-ray microscope (SXTM) and carbon X-ray absorption near edge structure (XANES) spectra were collected. We compared the carbon XANES spectra of these Wild 2 samples with a database of spectra on thirty-four interplanetary dust particles (IDPs) and with several meteorites. Two of the particles analyzed are iron sulfides and there is evidence that an aliphatic compound associated with these particles can survive high temperatures. An iron sulfide from an IDP demonstrates the same phenomenon. Another, mostly carbon free containing particle radiation damaged, something we have not observed in any IDPs we have analyzed or any indigenous organic matter from the carbonaceous meteorites, Tagish Lake, Orgueil, Bells and Murchison. The carbonaceous material associated with this particle showed no mass loss during the initial analysis but chemically changed over a period of two months. The carbon XANES spectra of the other four particles varied more than spectra from IDPs and indigenous organic matter from meteorites. Comparison of the carbon XANES spectra from these particles with 1. the carbon XANES spectra from thirty-four IDPs (<15 micron in size) and 2. the carbon XANES spectra from carbonaceous material from the Tagish Lake, Orgueil, Bells, and Murchison meteorites show that 81P/Wild 2 carbon XANES spectra are more similar to IDP carbon XANES spectra than to the carbon XANES spectra of meteorites.

INTRODUCTION

Our understanding of the processes that form organic matter in space is limited by our ability to remotely measure organic matter in extraterrestrial bodies such as comets and asteroids as well as outside of our solar system using infrared, sub-millimeter and radio spectroscopies and of these only IR spectroscopy can measure solid material. Though laboratory analogs are produced to calibrate instruments used for remote sensing, without samples from these extraterrestrial bodies, there is no way to confirm whether the interpretation of the remotely collected data is correct (Sandford 2001). In addition, with the exception of the January 18, 2000, collection of the Tagish Lake meteorite, most of the meteoritic collection has been exposed to terrestrial organic matter so there is always concern that some of the organic

material found in these samples has a terrestrial origin. Interplanetary dust particles are collected in the Earth's stratosphere, the particles are collected into silicon oil which inhibits the particles from interacting with terrestrial atmospheric gases, making IDPs pristine samples to look for preserved extraterrestrial organic matter. But the identification of IDPs as extraterrestrial is not straight forward, and unless solar flare tracks (Bradley and Brownlee 1984, 1986; Sandford 1986; Thiel et al. 1991), solar wind noble gasses (Kehm et al. 2002), and/or anomalous isotopic ratios (McKeegan et al. 1985; Messenger et al. 1995; Keller et al. 2000) are found, it is difficult to know if the particle is extraterrestrial. Other identification methods such as olivine composition (Klock et al. 1986; Zolensky and Lindstrom 1992), atmospheric entry heating (Sandford and Bradley 1989; Keller et al. 1992; Rietmeijer 1996; Flynn et al. 1998),

and chondritic-like compositions (Flynn et al. 1997) can also be used to gather clues to determine IDPs origins. However, sample return missions are the only way to (1) know the sample has an extraterrestrial origin and (2) have control and knowledge as to any possible exposure to terrestrial organic matter. For these reasons, samples collected by the Stardust mission are among the most important samples we now have to help us understand what types of organic matter form in space.

NASA's Stardust sample return mission collected dust from comet 81P/Wild 2's coma. Tsou et al. (2004) have described the mission in detail. A comprehensive characterization of the successful capture of dust from comet 81P/Wild 2 was published by Brownlee et al. (2006). Organic matter identified in the collected dust and along tracks in the aerogel include polyaromatic hydrocarbons (PAHs), long chain aliphatic hydrocarbons, methylamine, ethylamine, and glycine. Organic functional groups include keto/aldehydic, carboxyl, amide, nitrile, alcohol, and ether (Sandford et al. 2006; Keller et al. 2006). IDPs are collected in the Earth's stratosphere at an altitude ~19 km using high altitude aircraft. The IDPs are collected onto a surface coated with a highly viscous silicon oil. Because of the gradual increase in density of the Earth's atmosphere, IDPs decelerate slowly thereby reducing heating effects (Brownlee 1985). Aliphatic hydrocarbons attached to macromolecular molecules, PAHs and carbonyl and amine functional groups have been identified in IDPS (Clemett et al. 1993; Flynn et al. 2004; Keller et al. 2004). The number of different organic material identified in carbonaceous chondrites is extensive. Pizzarello et al. (2006), have written a comprehensive report listing these different organic compounds, which range from simple sugars and amino acids to large, acid insoluble macromolecules.

SAMPLES

Samples from 81P/Wild 2 were collected via hypervelocity impact into silica aerogel (Brownlee et al. 2006). During the preliminary examination period particles were extracted from tracks in the aerogel at the Space Science Laboratory at the University of California, Berkeley, embedded in sulfur and shipped to Johnson Space Center (JSC) where the samples were ultra-microtomed. Some particles were also extracted, sulfur embedded and ultra-microtomed at JSC (Zolensky et al. 2008). All sections were placed onto silicon monoxide backed, copper TEM grids. All of the IDPs discussed in this paper were sulfur embedded, ultra-microtomed and sections were placed onto silicon monoxide backed copper TEM grids. Organic matter from the Tagish Lake, Orgueil and Murchison meteorites was extracted by crushing 1mm size pieces of the meteorites between two, clean glass slides, tapping off the larger pieces that remained on the slide, suspending what remained on the

slide in a 300 μ l droplet of Sigma water (part number 270733), stirred with a stainless steel wire rod and the water insoluble particles were allowed to settle. A silicon monoxide backed copper TEM grid was touched to the surface of the water droplet and micron to submicron particles are collected onto the TEM grid (Wirick et al. 2006). The size of the particles are known by imaging them using the STXM. Samples of the Bells meteorite were sulfur embedded and ultra-microtomed. All samples were stored in dark boxes at ambient temperature and pressure when not being measured. No samples were stored under inert gases.

STXM

The scanning transmission X-ray microscope (STXM) located at the X1A1 beamline at the National Synchrotron Light Source (NSLS) was used to collect both X-ray imaging and carbon XANES spectra at energies between 280–310 eV. Both spectral and imaging resolutions of the beamline are described in depth elsewhere (Winn et al. 2000). A zone plate with a focused spatial resolution of 50 nm was used to probe the samples. Data was collected using a technique called STACK, where one collects a series of images taken at different energies by stepping the spherical grating monochromator in small increments. The energy steps in this study were 0.3 eV for the energy range 280–283.5 eV, 0.1 eV for the energy range 283.5–292.0, 0.3 eV for the energy range 292–302 eV, and 0.5 eV for energy range 302–310 eV. The monochromator was calibrated using known peak positions of CO₂ (Ma et al. 1991) The images are aligned using Fourier cross correlation. Principal component analysis and CLUSTER grouping analysis were applied to spatially aligned STACK data sets (Jacobsen et al. 2000; Lerotic et al. 2004). For principal component analysis, a covariance matrix is formed from a STACK data set where each element of the covariance matrix is an inner product of 2 optical density vectors. The eigen values of this matrix result in a set of principal components (Osanna 2000). From this set of principal components, one can choose a sub-set to use in the CLUSTER analysis. CLUSTER analysis uses this subset of principal components to group similar spectra in the STACK data set (Lerotic et al. 2004). Another technique referred to as point spectra was also used to analyze IDPs and meteorites. The focused beam is kept stationary on the sample and only the monochromator is moved over an energy range from 280–310 eV with 0.1 eV step sizes and dwell times of 120 msec. Dwell times used in the STACK technique range between 1–5 msec.

One advantage to low energy spectromicroscopy is carbon data can be collected on small areas, on the order of 50 nm sized pixels with an energy resolution at the carbon K edge of 0.05 eV (Winn et al. 2000). Though with unknown material it is difficult to interpret the carbon spectra one can easily tell the difference between inorganic and organic forms

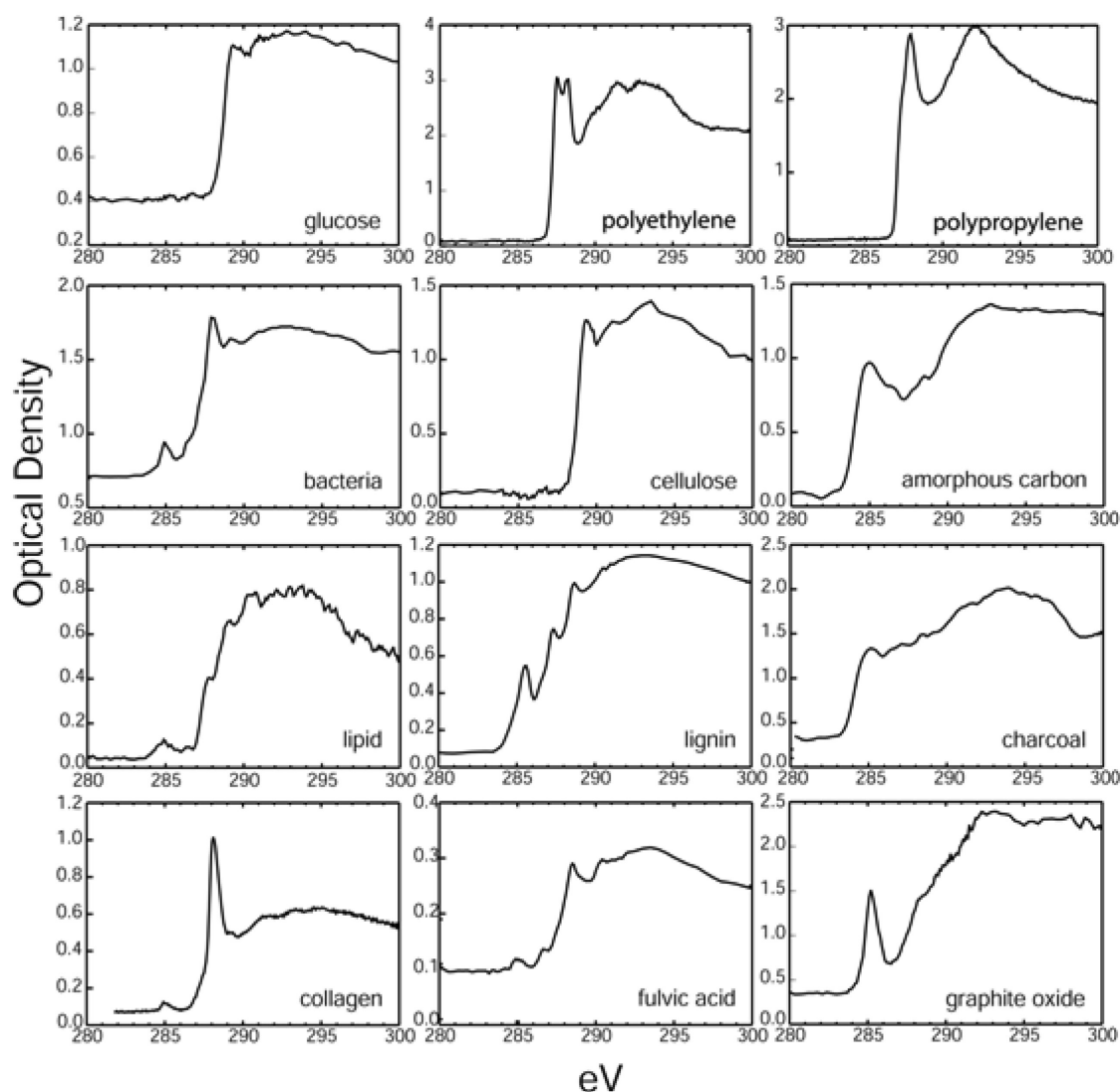


Fig. 1. Carbon XANES spectra from standard compounds showing the spectral variations produced by the presence of C in different bonding states. Polypropylene and polyethylene spectra were obtained from H. Ade's website <http://www.physics.ncsu.edu/stxm/polymerspectro/>. The charcoal spectrum was provided by J. Lehmann, Cornell University. The graphite oxide sample was obtained from L. Piper, Boston University. Peak positions are as follows: [glucose 289.2], [bacteria 285.0, 286.4, 288.2], [lipid, 284.9, 287.8, 289.1], [collagen, 288.1], [polyethylene, 287.6, 288.2], [cellulose, 289.5], [lignin, 285.5, 287.3, 288.6], [fulvic acid, 285.0, 286.7, 288.5], [polypropylene, 287.2, 287.9], [amorphous carbon, 285.0], [charcoal, 285.1], [graphite oxide, 285.2]. Peak positions were measured using a Gaussian fit.

of carbon (Flynn et al. 2003) (Fig. 1). When the sample size is small there are only a few techniques available to collect carbon bonding and abundance data and even fewer techniques that are relatively non-destructive. One can also compare differences in the carbon XANES spectra between sample locations. In addition to the spectral data, carbon maps can be produced by taking the ratio of an image at an energy where carbon absorbs to an image taken at an energy where carbon does not absorb.

Interpretation of XANES spectra has its limitations. Carbon π bond energies occur in a relatively narrow energy band between 283.5 eV and 289.0 eV. Because this energy range is small, there is often overlap in bond absorption

energies and it is difficult to assign specific energies to specific carbon bonds with samples even where the chemistry is known. One can only report absorption energies in a general sense. For instance, often a C=O occurs at an energy of 288.2 eV. This is however not always the case and so care must be taken to not over interpret XANES spectra. The C=C bond in a ring or carbon chain almost always occurs at an energy near 285 eV. While this energy will shift a small amount depending on substitution in a carbon ring and aliphatic chains hanging off of a carbon ring, the C=C bond has the least shift in peak energies due to inter and intra molecular effects (Stohr 1992). Table 1 lists different carbon bonds assigned to energies ranging between 285.5–286.9 eV.

Table 1. Energies for different carbon functional groups reported in the literature.

Energy (eV)	Transition	Compound or group	Reference
285.5–286.5	1 s 2π*	Aromatic C=O	Haberstrohetal. 2006
285.5–286.5	1 s 2π*	Pyridinic C	Haberstrohetal. 2006
285.8–286.4	1 s π*	Aromatic phenol	Cody et al. 1998
285.8–286.4	1 s π*	Ketone C=O	Cody et al. 1998
286.0–286.5		Unsaturated C	Kaznacheyev et al. 2002
286.0–286.5		Unsaturated aromatic C	Brandes et al. 2004
286.0–286.5		C-N	Cooper et al. 2004
286.1	1 s 2π*	Pyridinic C	Cody et al. 1998
286.3	1 s π*	C=O Acetaldehyde	Urquhart and Ade 2002
286.4	1 s 5π*	Amorphous carbon	Jimenez et al. 2003
286.4		HC≡N	Bose 1996
286.4	1 s 2π*	Beta Carotene C=C	Legall et al. 2006
286.6		C=N of N substituted in a phenyl ring	Lehmann et al. 2005
286.7	1 s 2π*	Aromatic C	Cody et al. 1996
286.8	1 s π*	C=O Acetone	Urquhart and Ade 2002
286.8	1 s π*	C=O PVMK	Urquhart and Ade 2002
286.8		Hexane, C-CH2	Hitchcock et al. 1987
286.9		Ethane, C-CH2	Hitchcock et al. 1987

Several different bonding environments are reported in the literature for this small energy range and Table 1 includes only a small percentage of the bonds reported that occur in this energy range.

RESULTS

Change in the Carbon Chemistry over Time

Cometary particle FC3,0,2,4,4 was extracted from carrot shaped track 2. There were two sections from this particle on the TEM grid, the second section will be discussed later. It is known that X-rays at and near the carbon K edge can sometimes damage organic matter (Zhang et al. 1995; Braun et al. 2009; Cody et al. 2009; Schaefer et al. 2009; Wang et al. 2009). This damage can alter the bonding environment of the molecules being analyzed and can result in mass loss or chemical change (photodissociation/photoionization). By producing ions and free radicals secondary reactions can occur after samples are no longer exposed to the X-ray beam (Beetz et al. 2003). By the end of a 7-hour STACK (a dose of

$\sim 3.2 \times 10^8$ gray), most of this particle had been altered by the X-ray beam and extensive mass loss had occurred (Fig. 2). The image on the left in Fig. 2 was the first STACK image taken at an energy of 280 eV where non-carbon containing elements absorb. Elements, other than carbon, have a nearly uniform absorption between the energy range 280–300 eV. The image on the right in Fig. 2 was a STACK image collected at 299 eV. The mass loss is clearly visible by comparing these two images. It is interesting to note here that the damaged material contained elements besides carbon as evidenced by the absorption below the carbon K edge at 280 eV (Fig. 2).

It is difficult to determine if there was any carbon associated with the area of this particle where the mass loss occurred. The spectrum in Fig. 2 suggests there was no carbon associated with this region of the sample due to the complete lack of any absorption features. It is possible this material was sulfur left from the embedding process. However, no other samples analyzed showed any evidence of sulfur left from the embedding/sectioning process. Two small carbon-rich pieces in this particle survived the X-ray beam. The areas that did survive the X-ray beam and the carbon XANES spectrum are shown in Fig. 3A. This spectrum is most similar to the collagen spectrum in Fig. 1 which suggests we are seeing a carboxyl bond, though carbonyl bonds absorb at this energy (288.2 eV) as well. Two months after we first analyzed FC3,0,2,4,4, we re-analyzed the remaining fragments left on the grid and the carbon XANES spectrum was different from the initial spectrum (Fig. 3A). It is possible the change in this material could have been induced by the X-ray beam. The major change between these spectra is the decrease in the absorption at 288.2 eV. There is also a slight increase in an absorption at 287.6 eV. These samples were also stored in air and the change observed may be due to reactions with O₂ and H₂O.

We have previously seen similar changes in the carbon XANES spectra from some of the IDPs we have analyzed. We first analyzed IDP L2008F16, a typical hydrated IDP in 1999 and the image and spectrum from this particle are shown in Fig. 3B. L2008F16 showed no evidence of any mass loss or other forms of radiation damage during the initial analysis. We analyzed the same area of this particle in June of 2004 and saw a change in the spectrum. The 285 eV absorption was greatly reduced compared to the 1999 spectrum and the absorption at 286 eV had increased. We re-analyzed this particle again in March of 2009 and the carbon XANES spectrum had again changed with absorption peaks at 285.4 eV, 286.7 eV and 288.2 eV (Fig. 3B). The spectrum from the March 2009 analysis is commonly found in the IDPs we have analyzed (Flynn et al. 2003). Two hydrated and one anhydrous IDP were exposed to the X-ray beam to check for radiation damage. For one of the hydrated IDPs, we collected a series of STACKS over a 17 day period. For the 2 other IDPs a series of twenty point spectra were

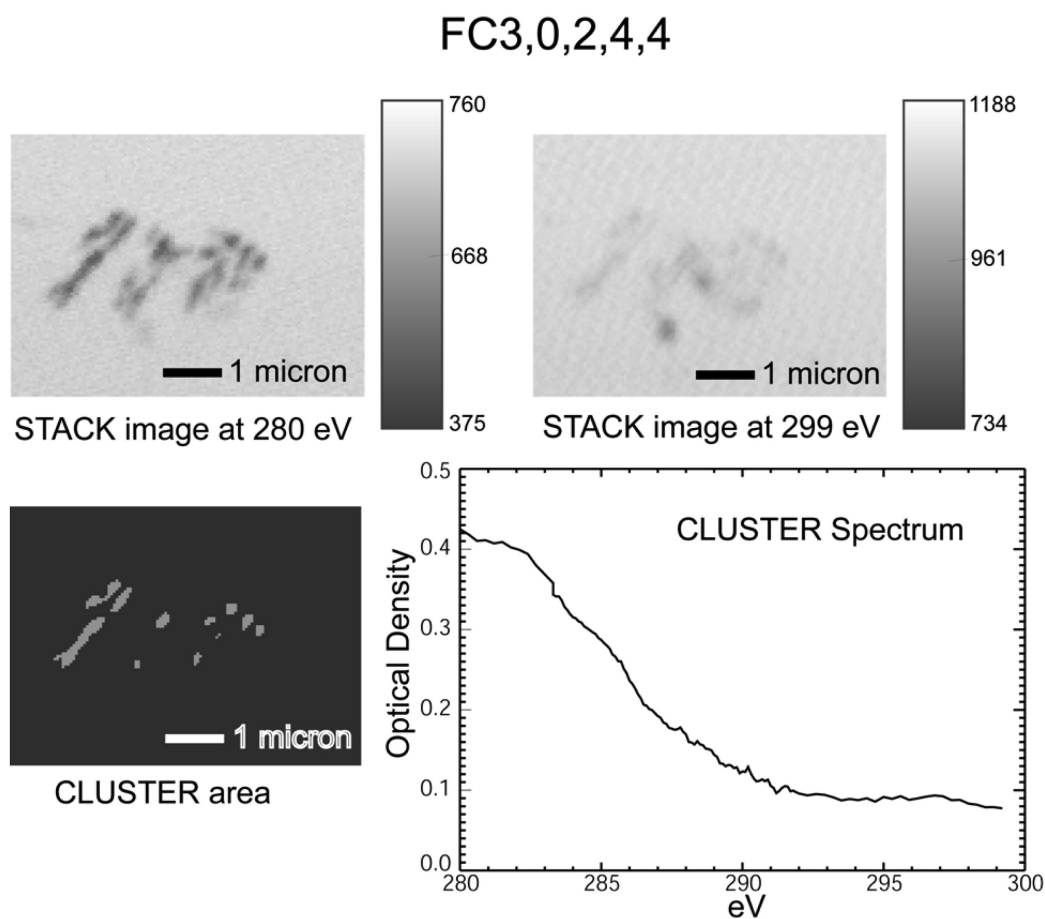


Fig. 2. Image on the left was the first STACK image taken at an energy of 280 eV of sample FC3,0,2,4,4. The image on the right is a STACK image collected at an energy of 299 eV.

collected. There was little change in the carbon XANES spectra from these three IDPs. The initial carbon XANES spectra from FC3,0,2,4,4 and L2008F16 are different. The 81P/Wild 2 particle's spectrum contains only a small absorption in the 285 eV region (C=C) with a large absorption at 288.4 eV while the IDP's spectrum is absorbing in the 285–290 eV region and does not show any well-defined absorption peaks (refer to Fig. 1, charcoal spectrum). After 2 months the Stardust particle has a carbon spectrum similar to a typical IDP spectrum (Flynn et al. 2003). This is for the region in the particle that was not initially ablated away by the X-ray beam (circled area in Fig. 3A). The same is true for L2008F16, but what appears to have happened after 9 years is most of the carbon is gone from the IDP, presumably the carbon reacted with atmospheric gases to form volatile carbon phases and only a small amount of the initial carbon remains on the grid.

Preservation of Organic Matter in Iron Sulfides

Stardust samples C2044,0,36,1,6 and C2044,0,36,1,3 were terminal particles extracted from carrot shaped Track 36.

The particles were identified as pyrrhotite (Zolensky 2009). There are two, significantly different types of carbon spectra associated with these particles, one group of spectra that represent amorphous and/or graphitic-like carbon (Fig. 4B) and another group of spectra that represent an aliphatic compound (Fig. 4A). The amorphous carbon standard we use was made by evaporating pure carbon and condensing it as a thin film, the spectrum obtained from this standard is shown in Fig. 1. Any material having spectra similar to this standard is assumed here to be amorphous carbon. Graphite is identified by a spectrum which has an absorption at 285 eV and a small, sharp absorption at 291.65 eV (Ma et al. 1995) (Fig. 4B). The spectrum from particle C2044,0,36,1,6 in Fig. 4B contains a small sharp absorption peak at 291.7 eV, the same absorption peak as graphite. The other spectra found associated with both of these particles are similar to spectra of saturated hydrocarbons. An example of a carbon XANES spectrum from a saturated aliphatic hydrocarbon is the polypropylene spectrum shown in Fig. 1. Most hydrocarbons would not survive temperatures in excess of 300 °C. Lehmann et al. (2008), Wan et al. (2007) and Benzerara et al. (2007) have reported similar carbon XANES spectra found

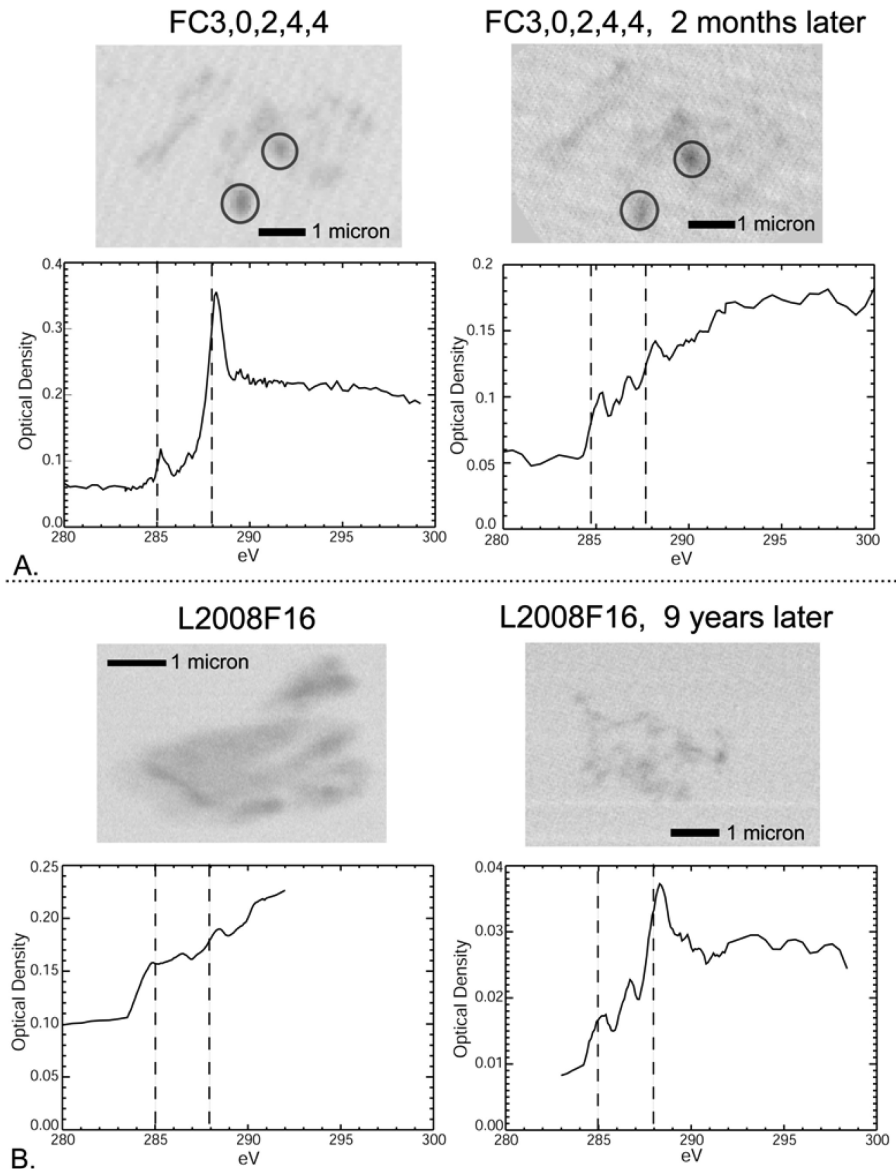


Fig. 3. A. Images of FC3,0,2,4,4 were collected at 290 eV. Image on the left was collected on 3 March 2006. The image on the right was collected on 12 May 2006. The spectra located directly below each image were collected from the circled areas in the images. B. The images for L2008F16 were taken at 288.0 eV. Image on the left was collected on 17 April 2009, and the image on the right was collected on 09 March 2008. The spectra located below these images were collected from the entire particle.

associated with both soil micro-assemblages and carbonates where the aliphatic compounds form a network along pore structures, though none of these samples reached temperatures comparable to temperatures in comet 81P/Wild 2 samples (Zolensky et al. 2006; Leroux et al. 2008). The images and CLUSTER areas (regions displayed in pink and blue) in Fig. 4 labeled SD from particle C2044,0,36,1,3 show that both the graphitic-like and aliphatic-like carbon spectra are found within the interior of the particle.

We found similar spectra associated with an iron sulfide from IDP L2009*E6. A magnetite rim was found on the exterior of this particle indicating that it had been heated to ~ 1000 °C (Rietmeijer 1993; Nozaki et al. 2006). Figure 4

shows two CLUSTER spectra from L2009*E6, one spectrum which is similar to amorphous carbon (Fig. 1). This spectrum is shown in Fig. 4B and the CLUSTER area is indicated in pink on the image of particle L2009E6. The other carbon spectrum is similar to spectra from saturated hydrocarbons (Fig. 4, brown area). Some of the amorphous carbon is located just off of the particle. This is due to a microtoming effect, occasionally seen in IDP samples, where the carbonaceous matter is pushed off of the particle by the microtome blade. The rest of the amorphous carbon is found around the edge of the particle. From the CLUSTER area we see, however, that the aliphatic compound is closely associated with the sulfide and is not removed by microtoming.

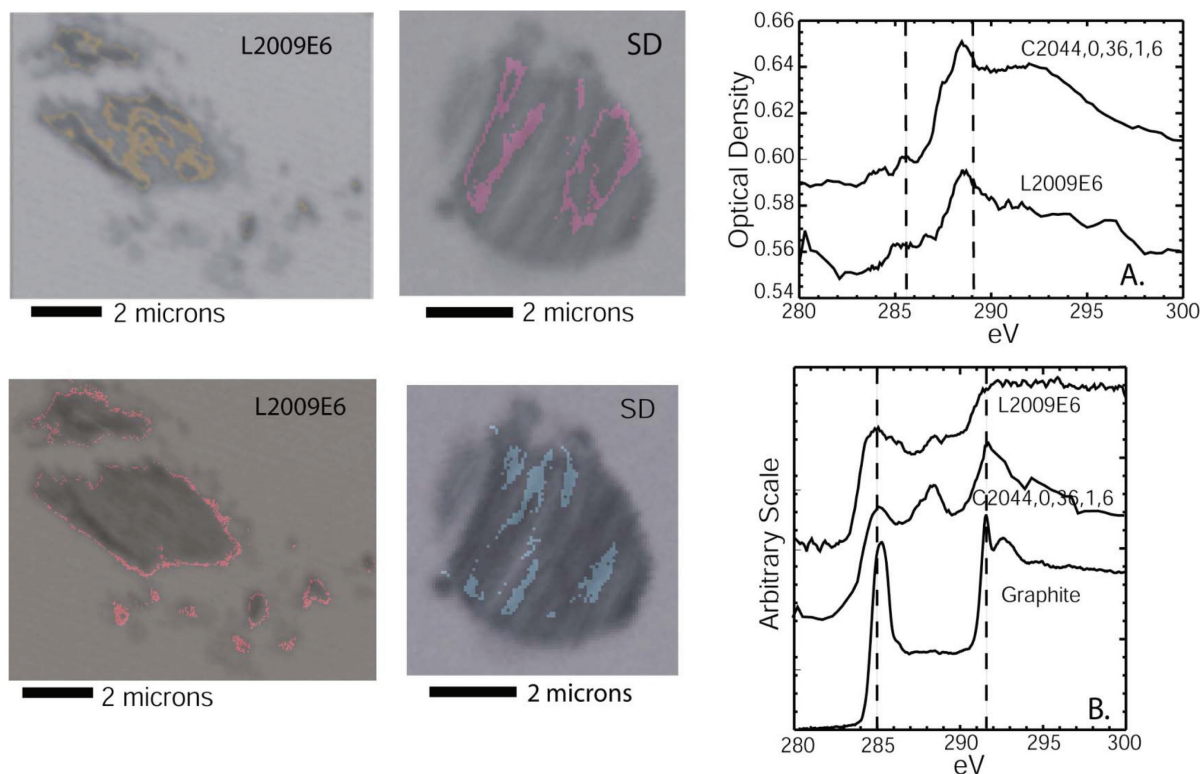


Fig. 4. Comparison of a heated IDP iron sulfide to an 81P/Wild 2 iron sulfide (SD=Stardust). The colored regions are CLUSTER areas with the CLUSTER spectra from these areas plotted in the graphs to the right of the images. The CLUSTER areas were overlaid onto STXM images of both of the particles.

Carbon-Rich Particles

Four particles contained pieces of organic matter not associated with any inorganic material. Because there is no absorption of carbon below 282 eV images taken at energies at and near 280 eV show only carbon free species. We assume this absorption is from either aerogel or minerals found in the extracted particles. The pieces of carbon-rich organic matter ranged in size from 2–6 microns. Figure 5 shows the images, carbon maps and spectra from these sections. If one refers to Fig. 1, one sees similarities in the spectra to common organic compounds from this planet such as collagen, bacteria, and fulvic acid that would give one cause to suspect these particles. However, DeGregorio et al. (2009) found similar carbon-rich organic matter in their Stardust samples that have high deuterium isotopic anomalies, it is possible these carbon-rich particles are cometary, though there is unpublished evidence to show that high deuterium isotopic anomalies may be caused by sample damage in a transmission electron microscope (DeGregorio, personal communication). IDP organic matter generally occurs as coatings on grains or sub-micron sized pieces of organic matter associated with minerals. The method we use to collect indigenous organic material from meteorites selects for micron to sub-micron size particles, so this is not entirely a fair comparison but these 2–6 micron sized pieces of organic material, if from

comet 81P/Wild 2 have no counterpart in the IDPs or the meteorites we have analyzed.

Organic Matter Associated with Minerals or Aerogel

Besides the iron sulfides previously mentioned, three other comet 81P/Wild 2 particles we analyzed had organic matter closely associated with minerals or aerogel. Figure 6 shows spectra with strong absorption in the 285 eV region, an energy where C=C in a ring or unsaturated aliphatic carbon would absorb, and spectra where there is little or no absorption in this energy region and a large absorption in the 288 eV region, where saturated aliphatic hydrocarbons absorb. Spectra containing large absorption peaks around 288 eV were more common in these samples than spectra containing absorption peaks at 285 eV.

To understand the carbon bonding environment in these samples we compare the spectra from comet 81P/Wild 2 particles to spectra we have collected from the Bells, Tagish Lake, Orgueil, and Murchison meteorites; and from hydrated and anhydrous IDPs. Figure 7 contains meteoritic carbon spectra commonly found in the Murchison, Tagish Lake, Orgueil, and Bells meteorite. The spectra were collected from indigenous carbon, not acid extracted insoluble organic carbon matter (IOM). The carbon XANES spectra of the acid extracted IOM from carbonaceous meteorites is very similar to the carbon

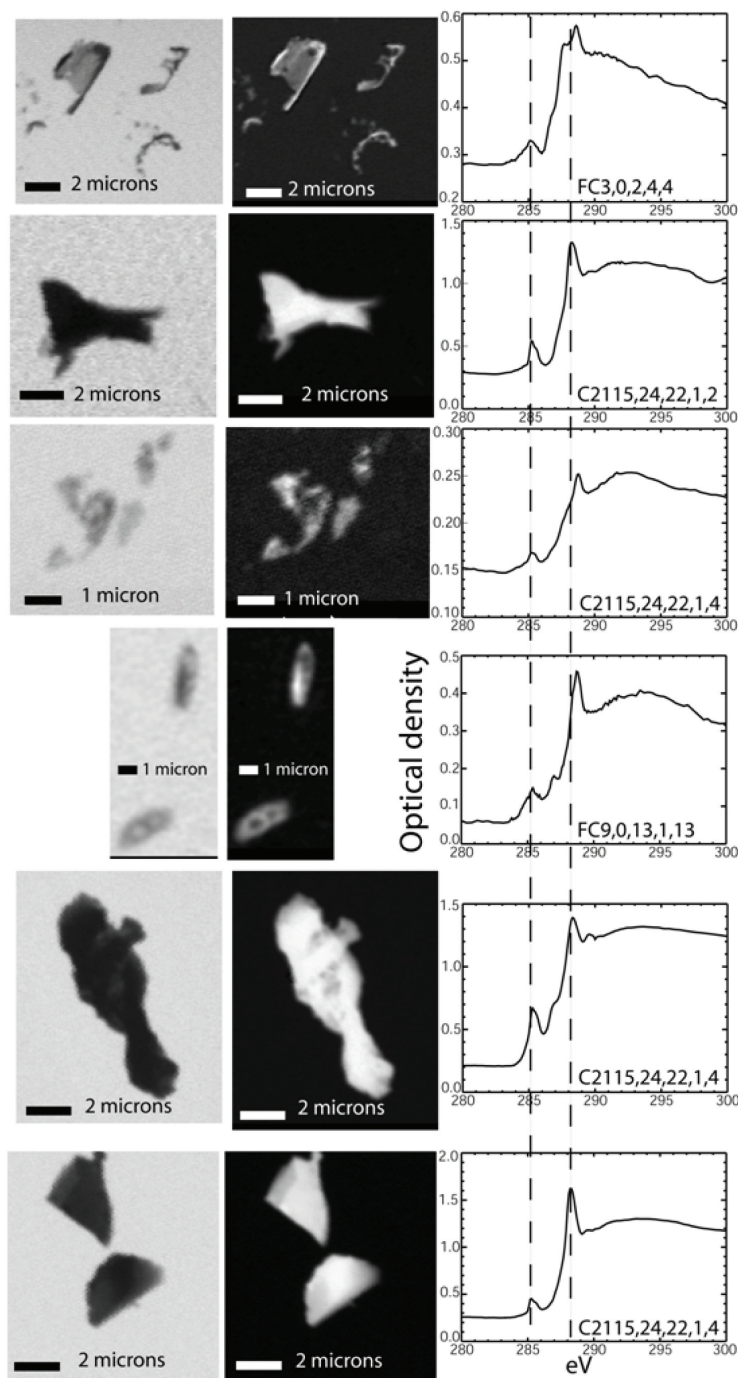


Fig. 5. Carbon-rich particles from 81P/Wild 2. Each row contains a STXM image, carbon map and spectrum from the particle identified on the spectral plot.

XANES spectra reported here (Cody et al. 2006). The carbon XANES spectra in the left hand column of Fig. 7 is water insoluble organic matter and the right hand column is water soluble organic matter. Most of the organic matter associated with these meteorites is represented by the spectra in the left column. These show the presence of aromatic or alkene carbon compounds with some of the spectra containing an absorption

peak in the 286.7 eV region. Some of the water soluble material yield spectra similar to the glucose spectrum in Fig. 1.

There is one type of carbon XANES spectrum commonly found in IDPs (see, for example, L2008U13 in Fig. 8), but there are other carbon XANES spectra also found in IDPs (Fig. 8). If one compares the carbon XANES spectra from comet 81P/Wild 2 particles in Fig. 6 with the carbon XANES

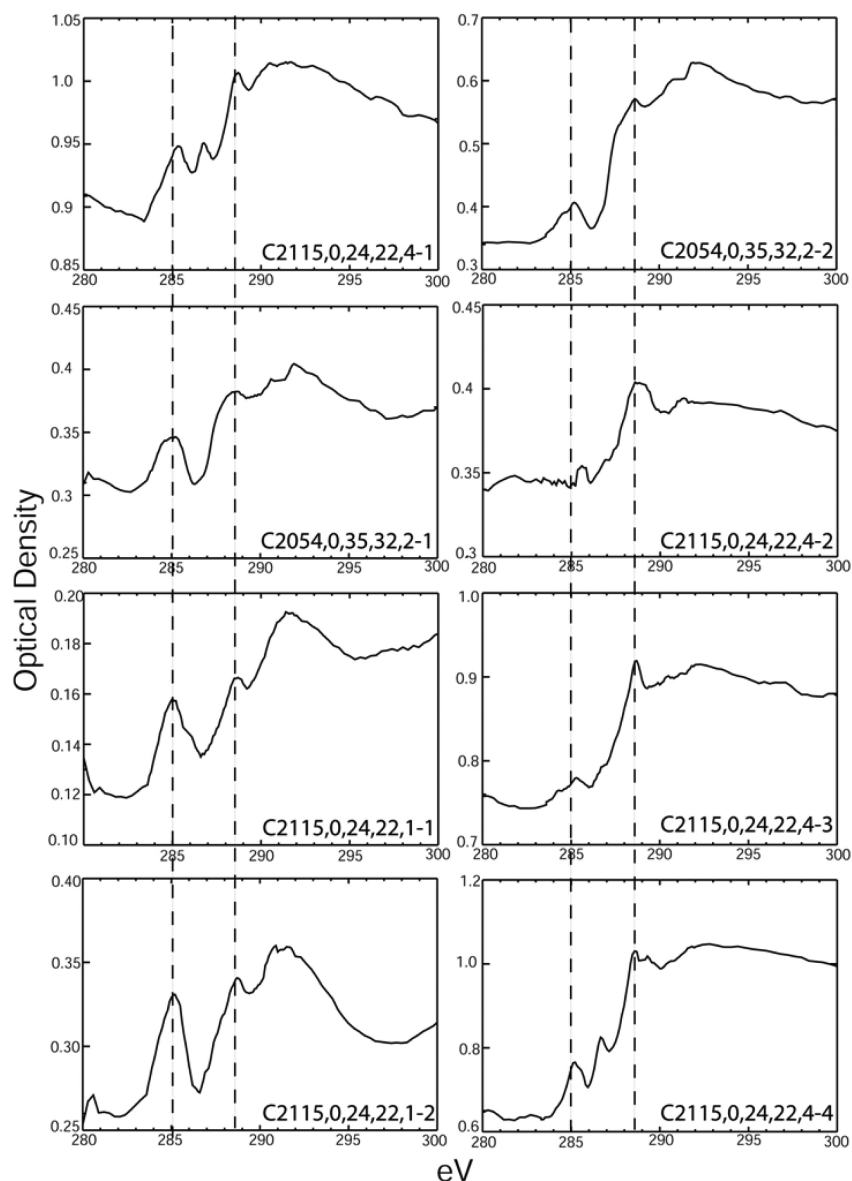


Fig. 6. Carbon XANES spectra from 81P/Wild 2 particles associated with minerals or aerogel.

spectra of carbonaceous meteorites (Fig. 7) and IDPs (Fig. 8) one sees that the carbon environment from comet 81P/Wild 2 is more similar to the carbon bonding environment of the IDPs (both anhydrous and hydrated) than the carbon bonding environment in the carbonaceous meteorites. Amorphous carbon (Fig. 1) is found in IDPs, the Bells, Tagish Lake, Murchison, and Orgueil meteorites as well as in comet 81P/Wild 2 particles (Fig. 6, C2115,0,24,22,1, Fig. 7 Bells, and Fig. 8 L2008G12) but this is the only common carbon form found in IDPs, these meteorites, and comet 81P/Wild 2 particles. The spectra labeled C2115,0,24,22,4-1 and C2115,0,24,22,4-4 are spectra most similar to the typical IDP spectrum (L2008U13) with the exception that the 285 eV absorption is shifted to higher energies in comet 81P/Wild 2 samples. Careful comparison of the spectra from the IDPs

with the spectra from comet 81P/Wild 2 shows there is no single spectrum that matches completely, though some spectra are similar.

DISCUSSION

Cometary sample FC3,0,2,4,4 damaged in our low energy X-ray beam. Because this particle lose mass it is difficult to determine how much carbon was initially present but the absorption at 280 eV indicates that other elements besides carbon were present. However, because some of the particle had ablated away before reaching energies where carbon absorbs it is impossible to say if this portion of the sample contained carbon or not. Cases in which radiation damage of samples containing high concentrations of carbon

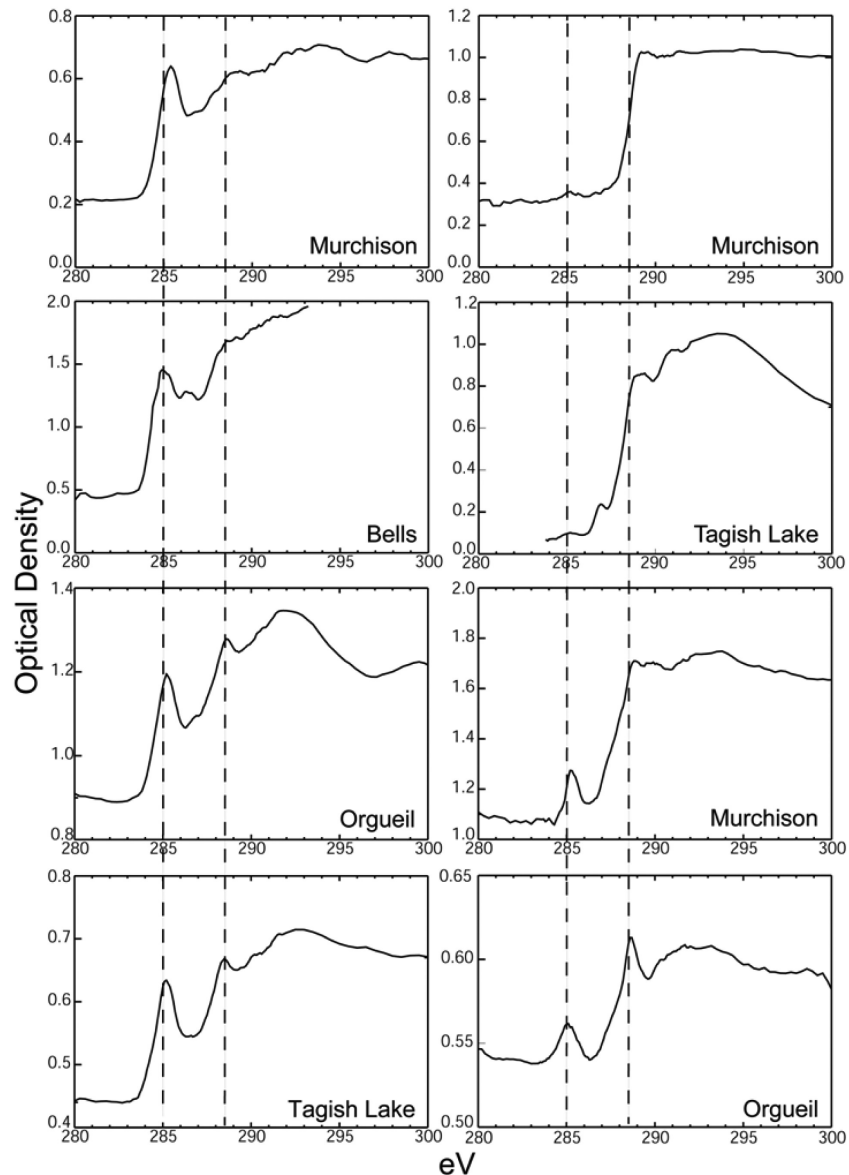


Fig. 7. Carbon XANES spectra from indigenous carbon from 4 carbonaceous meteorites.

using both electrons and X-rays have been well documented (Rightor et al. 1997; Braun et al. 2009). There were three different compounds that damaged at different doses in FC3,0,2,4,4. This was determined by comparing images at different energies, not all of the material ablated away at the same time. The first material ablated away by a dose of $\sim 1.3 \times 10^7$ gray, the second compound lasted until a dose of 1.2×10^8 gray and the third until a dose of 2.8×10^8 gray. The dose on the sample was calculated according to the equation used by Zhang et al. (1995). All the dose numbers here were calculated using carbon as the element, so the dose is only an approximation. For comparison, PolyMethylMethAcrylate (PMMA), an ultraviolet (UV) sensitive photoresist ablates away a thickness of PMMA equal to ~ 120 nm from a dose of 7.0×10^6 gray (Zhang et al. 1995). For the most sensitive

material in this sample, a dose of 1.3×10^7 gray ablated away ~ 70 nm of material so some of this particle was nearly as sensitive to the X-ray beam as a UV photoresist. From the spectra of the areas that radiation damaged it appears there was no carbon associated with these sections of the particle due to a complete lack of any carbon spectral features (Fig. 2). For comparison, we have exposed typical IDP organic matter to a dose of 1.1×10^9 gray and did not see any alteration of the carbon XANES spectra of the original carbonaceous matter or any mass loss.

Two small areas in FC3,0,2,4,4 were not initially ablated away by the X-ray beam. A comparison of the spectrum from this area to the spectrum initially collected from L2008F16 show very different carbon moieties. Both forms of carbon changed over time but the cometary carbon changed more

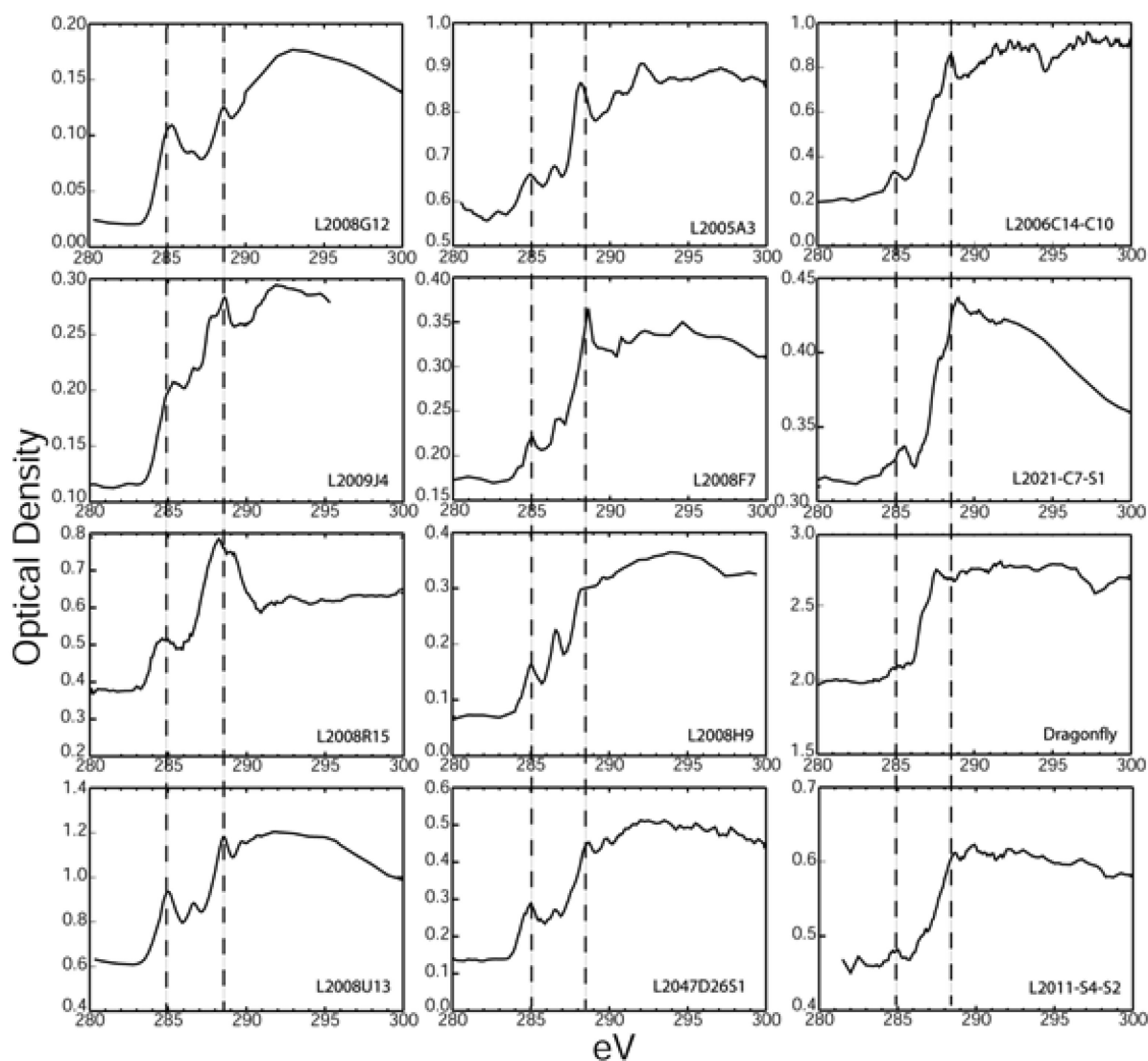


Fig. 8. Carbon XANES spectra from anhydrous and hydrated IDPs. L2008G12, L2005A3, L2006C14-C10, and Dragonfly are anhydrous IDPs. L2009J4, L2008R15, L2008U13, L2008F7, L2047D26S1, L2021-C7-S1, and L2011-S4-S2 are hydrated IDPs.

rapidly. A carbonaceous labile material in comet 81P/Wild 2 have been reported by others (Sandford et al. 2006, Cody et al. 2008, Rotundi et al. 2008). IDP L2008F6 was analyzed over a time period of years and there is no data on the same time frame as cometary particle FC3,0,2,4,4 to confirm whether this IDP had changed over a few months though other IDPs were exposed to comparable doses over several days and showed no change. We think the change in organic matter in this IDP and other IDPs is not a result of exposure to the X-ray beam but to an interaction with atmospheric gases. Weber et al. (2001) reported changes in IDPs over a time frame of a year where their IDPs were stored under similar conditions. The comet 81P/Wild 2 particle's carbon chemistry may have changed only as a result of exposure to the X-ray beam and not because of any interaction with atmospheric gases. Further study is needed to determine if any of the organic matter in comet 81P/Wild 2 is reactive with

atmospheric gases. The results from IDP L2008F6 suggest that IDPs may originally have contained some of these labile components observed in comet 81P/Wild 2 samples but this material may have been largely lost from most IDPs during interplanetary transit and/or atmospheric entry.

In contrast to this extremely fragile sample, the iron sulfide particles we analyzed have an aliphatic compound that appears to survive not only low energy X-ray exposure but also high temperatures. The aliphatic compound associated with comet 81P/Wild 2 iron sulfides is similar to an aliphatic compound found in an IDP iron sulfide which also contains a magnetite rim that likely formed at a temperature of ~ 1000 °C (Rietmeijer 1993). A second form of carbon associated with the iron sulfide in IDP L2009E6 is amorphous and is found only on the exterior of the iron sulfide while the second form of carbon we see associated with the comet 81P/Wild 2 iron sulfides contain both amorphous and graphitic carbon and

these forms of carbon are found in the interior of the iron sulfides, closely associated with the aliphatic compound. Graphite can form by many processes. The commercial production of graphite requires temperatures near 3000 °C, though there are also low temperature processes that form graphite. Many investigators have reported finding melted aerogel in their comet 81P/Wild 2 samples (Leroux et al. 2008; Roskosa et al. 2008; Rietmeijer 2008; Tomeoka et al. 2008; Noguchi et al. 2008). Due to the presence of melted aerogel, which melts at temperatures greater than 1000 °C, (Zolensky et al. 2006) it is possible the graphitic-like carbon we see in the Stardust particles may have formed at a high temperature as a result of the capture process. Cody et al. 2008, demonstrate one can use carbon XANES spectra and graphite's 1 s- σ^* exciton to determine the degree of parent body heating in carbonaceous meteorites where the increase in the size of the graphite exciton is correlated to temperatures determined by other methods. The spectra in Fig. 4 is closely matched to the spectrum from the Allende meteorite where the reported temperatures for parent body thermal processing range between 300–600 °C and reported by Cody et al. (2008) at 550 °C. Another possibility is the graphite is indigenous to the cometary samples which is consistent with the observation that some of components of comet 81P/Wild 2 were exposed to high temperature processing prior to assembly of the comet as evidenced, for example, by the presence of olivines (Zolensky et al. 2006) and refractory mineral assemblages (McKeegan et al. 2006).

Because of the presence of a graphitic-like carbon closely associated with an aliphatic carbon in the interior of two iron sulfides from comet 81P/Wild 2, this suggests the interior of the particles may have experienced temperatures as high as 550 °C. If this happened during the capture process or when the iron sulfides initially formed we cannot tell. How could an aliphatic compound survive temperatures as high as 550 °C? Several long chain alkanes such as n-tricosane and octacosane have boiling points above 400 °C and 760 torr. Boiling point temperature's increase with increasing pressure, the iron sulfide particle may simply act as a pressure vessel for the aliphatic compound observed here. Another process that may also occur is as this aliphatic is heated, S may also be incorporated into this aliphatic molecule, helping to stabilize the molecule at high temperatures. Boussafir et al. (1995) studied kerogens from the Kimmeridge Clay formation in the UK and found that both lipids and their fatty acid moieties, by incorporating sulfur into their structure, formed insoluble macromolecules and thus were less susceptible to diagenesis. They referred to this process as lipid vulcanization. Fernandez et al. (2001), while studying the effect of forest fires on the surrounding soil, found the lipid fraction of the organic matter in the soil survived temperatures around 350 °C. Matrajt et al. (2006) found that a small percentage of a PAH, a ketone and an amino acid on a microporous substrate survived pulse heating to 900 °C. It may be possible

for an aliphatic compound to survive temperatures as high as 550 °C, especially when this organic matter is associated with S-bearing or porous minerals. It is likely this organic matter would be high carbon number alkanes, lipids, and/or the fatty acid fraction of lipids. It is also possible this aliphatic material formed as a condensate at lower temperatures than the temperature at which the graphitic carbon formed.

We have found several, >2 micron in size, carbon-rich particles in our 81P/Wild 2 samples. In some cases, the spectra from these particles are similar to spectra from certain types of terrestrial matter but DeGregorio et al. (2009) have measured high D/H ratios in similar 81P/Wild 2 particles, suggesting that these carbon-rich particles could be cometary. Recent findings suggest however, these D rich anomalies are artifacts caused by an electron beam. These carbon rich particles were located in areas on the TEM grids where maps indicated sections were placed and are assumed to be cometary. Compared to both IDP and meteoritic organic matter these carbon-rich particles from 81P/Wild 2 are large. Most of the carbon-rich matter in IDPs and meteorites are 1 micron to submicron in size. Our mounting process for the meteoritic material selects for particles sizes 1 micron or less but C. O'D Alexander (personal communication) has found that the particle size of IOM from meteorites roughly follows a typical power law distribution with the largest particles ~5 microns in size, but most of the particles fall in the sub-micron size range. If these six, carbon-rich particles we have found are representative of 81P/Wild2 then the carbon-rich organic matter from Wild 2 resides in larger size domains than either IDP and meteoritic organic matter.

Typical IDP organic matter is closely associated with minerals embedded in a carbon-rich matrix (Keller et al. 2004). The meteorites we have analyzed also have organic coatings on small grains. We have only analyzed a small fraction of cometary material associated with minerals and aerogel in the 81P/Wild 2 samples. Comparing our analyses of cometary, IDP and meteoritic organics associated with minerals, we find that, in general, 81P/Wild 2's carbon spectra are more similar to IDP carbon spectra than to meteoritic carbon spectra, particularly in terms of the presence of higher absorption in the 288 eV region. However, there are few spectra in the 81P/Wild 2 samples that closely match any of our IDP or meteoritic carbon spectra, and only amorphous carbon is found in all three categories [Fig. 6, C2115,0,24,22,1-1; Fig. 7, Bells, Fig. 8, L2008G12].

CONCLUSIONS

The carbon XANES spectra and the size distribution of carbonaceous matter in the 81P/Wild 2 particles we have examined do not match those of IDPs or meteorites but the spectra more closely resemble those of IDPs than they do the meteorites. IDPs, meteorites, and 81P/Wild 2 all contain

amorphous carbon but the 81P/Wild 2 spectra contain components which are prominently more aliphatic than IDP or meteoritic organics.

The carbon XANES spectra of an 81P/Wild 2 particle and an IDP show a change with time. In these cases, the change is in the direction of approaching the spectrum of “typical IDP” carbon suggesting that some cometary and IDP samples contain reactive organics and IDPs may have originally contained reactive organics that were lost during interplanetary transit and/or atmospheric entry. There is also evidence to show, however, that there is an aliphatic compound in both IDPs and comet 81P/Wild 2 that survives temperatures >500 °C and represents a very refractory component of comet 81P/Wild 2 particles and IDPs. It is also possible this aliphatic compound may have condensed out of a vapor phase at lower temperatures.

Particle FC3,0,2,4,4 from comet 81P/Wild 2 photodissociated/photoionized when exposed to photons in the energy range 280–310 eV. These photons are in the energy range of extreme UV (EUV) and X-ray UV (XUV) photons emitted by the Sun. It is highly unlikely this particle, not protected by a parent body, could have formed or survived for any length of time in the inner solar system where the flux of photons in this energy range is comparable to the photon flux of the STXM (Guinan and Ribas 2000; Winn 2000; Tobiska 2005).

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