

## Quantitative Organic and Light Element analysis of Comet

### 81P/Wild 2 particles using C-, N-, and O- $\mu$ -XANES

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**Abstract** Synchrotron based soft X-ray micro-analysis was performed on particles extracted from the Stardust aerogel collector in order to obtain detailed organic functional group information on any organic solids captured as part of the Principal Examination suite of analyses for samples from Comet 81P/Wild 2. It is observed that cometary organic carbon captured in aerogel is present in a number of different manifestations and often intimately associated with silicates. Carbon X-ray Absorption Near Edge Structure (XANES) spectra reveal considerable chemical complexity in all of the organic particles

studied so far. Universally, the Comet 81P/Wild 2 organic particles contain low concentrations aromatic and/or olefinic carbon and proportionately greater concentrations of heteroatom-containing functional groups, e.g. amide, carboxyl, and alcohol/ethers. N-XANES confirms the presence and assignments of these functional groups. In general, the XANES data record considerable chemical complexity across the range of organic samples currently analyzed. The atomic ratios, N/C and O/C, derived from XANES data reveal a wide range in heteroatom content; in all cases these elemental ratios are higher than that of primitive meteoritic organic matter. The wide range in chemistry, both in elemental abundances and specific organic functional groups, suggests that the Comet 81P/Wild 2 organic solids may have multiple origins.

### **Introduction:**

The Stardust comet sample return mission from Comet 81P/Wild 2 provides an unprecedented opportunity to assess the organic chemistry of what may be the most primitive Solar System material providing a link to the molecular cloud material that was the source of matter from which our Solar System originated. Prior to the Stardust mission, our understanding of the early history of the Solar System, in terms of extraterrestrial organic carbon, has been restricted to the analysis of carbonaceous chondrites and interplanetary dust particles (IDP's). In the case of the former, it is clearly evident that the parent body accretion and subsequent alteration has altered the organic matter to an unknown extent from its most primitive origins (Cody and Alexander 2005). In the case of IDPs, thermal processing due to atmospheric heating during re-entry may

also transform labile organic matter (Flynn et al. 2003). In the case of the STARDUST mission to Comet 81P/Wild 2, sample capture was designed to be as benign as possible (Brownlee et al. 2006) by using silica aerogel with a density of 5 to 50 mg/cm<sup>3</sup> to provides a means of slowing down very high velocity particles (~ 6 km/sec relative velocity). It appears inevitable, however, that some heating must have occurred during the short period of particle deceleration. A high degree of heating will lead to some chemical processing. The outstanding question is how hot did the organics get and for how long were they heated?

From the perspective of the organic analysis/examination, the crux of the problem is to obtain the relative abundance of organic functional groups within organic particles extracted from the aerogel collectors and place these data into context with information already available on the state of extraterrestrial organic matter in pristine and thermally processed chondritic meteorites. The chemical analysis of organic matter contained within IDPs constitutes a challenge similar to that facing analysis of organic matter in Stardust particles. First, only IDPs with diameters on the order of 10's  $\mu\text{m}$  are considered small enough to have escaped extensive re-entry heating (Flynn et al. 2003); in the case of Stardust most of the particles captured are in the  $< 10 \mu\text{m}$  size range (Horz et al. 2006). Second, organic matter in IDPs is dispersed amidst mineral grains, e.g. olivine, pyroxene, and the so-called GEMs (glass with embedded metals and sulfides) in particles that are heterogeneous at scales less than a micron (see for example Rietmeijer 1998 and references therein). Preliminary analyses reveal that the Stardust particles share similar fine scale heterogeneity (Brownlee et al. 2006; Flynn et al. 2006; and Zolensky et al. 2006). Obtaining a quantitative analysis of the organics contained within these particles

provides a significant challenge requiring a detailed assessment of organic functional group concentrations at a spatial resolving power of less than a micron.

Over the past couple decades, the development of high brilliance X-ray sources via synchrotrons, coupled with advances in soft X-ray optics (soft X-rays being defined as spanning the energy range  $\sim 200$  to  $800$  eV), have led to the development of Synchrotron based Scanning Transmission X-ray Microscopes (STXMs)(Jacobson et al. 1991; Kilcoyne et al. 2003). Under optimum conditions, these microscopes provide a focused monochromatic X-ray beam with a spot size on the order of  $30$  to  $40$  nm, depending on the specific zone plate used. This combination of high spatial and energy resolution yields soft X-ray spectra spanning the carbon, nitrogen, and oxygen  $1s$  X-ray Absorption edges (X-ray Absorption Near Edge Structure, XANES, spectra) of sub-micron domains and provides an accurate assessment of the types of the organic functionality present. These microscopes have been shown to be very useful for solving long-standing problems involving fine scale heterogeneity in research areas such as environmental chemistry (Myneni 2002), paleontology (Boyce et al. 2002), and organic geochemistry (Cody et al. 1996). STXM micro XANES has also been shown to be extremely useful in unraveling the complex organic chemistry of hydrous and anhydrous IDP's (Flynn et al. 2003; Keller et al. 2004) and has already been proven useful for the study of Comet 81P/Wild 2 samples (Sandford et al. 2006).

We describe below the results of STXM micro-XANES analyses performed on organic containing particles extracted from cometary particle tracks identified in the aerogel tiles of the Stardust particle collector tray. A very cursory discussion of these analyses has been included in a recent report from the Organics sub-team of the Principal

Examination Team (PET) (Sandford et al. 2006); the emphasis of the present paper is to provide more detail on the experimental methods and greater in depth discussion regarding the implications of the data.

## **METHODS AND MATERIAL**

### **Particle Extraction**

Microscopic imaging is used to identify particles along obvious impact tracks. For the analysis of the track itself, the methodology involved first isolating an entire track into a small wedge-shaped volume of aerogel; referred to as a "keystone", that completely contains the track of the terminal dust particle. The particles were then extracted from the aerogel using sharp glass needles and computer-controlled micromanipulators (Westphal et al. 2004).

### **Particle Sectioning**

Comet 81P/Wild 2 grains are extracted from the aerogel cells with disposable pre-cleaned glass needles and transferred to either molen high-purity S or uncured Electron Microscopy grade sectioning epoxy for embedding prior to sectioning. As will be shown below, it is worthwhile in studying both Epoxy and sulfur embedded particles. Samples were sliced into 120~ 140 nm-thick sections with an ultramicrotome equipped with a diamond knife. The sections were floated onto ultra-pure water and transferred to amorphous C or SiO<sub>2</sub>-supported Cu Transmission Electron Microscopy (TEM) grids. In the case of the S embedded samples, sulfur was sublimed prior to analysis under vacuum. Sulfur is an ideal embedding medium to avoid the complexity of co-mingling of organic matter in the samples with insoluble epoxy (typically composed of poly[dimethyl

bisphenol]) normally used for ultramicrotomy. Sulfur beads containing the samples were attached to a sample-holding bullet using cyanoacrylate. To evaluate the potential for cyanoacrylate contributing spectral contamination, hence hindering sample analysis, sulfur beads devoid of sample were prepared in the same manner. No evidence has been observed that cyanoacrylate penetrated the S bead during subsequent TEM investigation of the sample-free S slices. Significantly, Electron Energy-Loss Spectroscopy (EELS) spectra acquired from the S test slices do not show any evidence of the pronounced CN peak characteristic of cyanoacrylate. The samples and their designations, sectioning media, and associated mineralogy are summarized in Table 1.

### **Scanning Transmission X-ray Microscopy (STXM) and $\mu$ -XANES on Carbon, Nitrogen, and Oxygen 1s absorption edges**

The STXMs employed in this principal examination phase of the Stardust organics analysis are located at beam lines 5.3.2 and 11.3.2 at the Advanced Light Source (ALS), Lawrence Berkeley Laboratory and beam line X1A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The STXM's at beamlines 5.3.2 and 11.0.2 at the ALS are built from very similar designs. They differ, however, in the means by which soft X-rays are generated. BL5.3.2 employs a bending magnet providing a useful photon range spanning  $\sim 250$  to  $700$  eV with a photon flux of  $10^7$  photons/sec. Energy selection on BL5.3.2 is performed with a low dispersion spherical grating monochromator affording an energy resolution of  $5000$ . BL11.0.2 utilizes an elliptical polarization undulator, with gap correlated with monochromator position, that provides a wider Energy range:  $80$  eV -  $2100$  eV with a photon flux of  $10^{12}$  to  $10^{13}$  photons/sec,  $10^9$

photons/sec with full spatial resolution and employs a monochromator that can provide energy resolution up to 7500.

The STXM at beamline X1A also uses an undulator for X-ray generation, however, unlike beamline 11.0, there is no STXM control of the undulator gap, rather the X1A undulator is intrinsically detuned providing sufficient band width to span a given ionization edge region, e.g. the C-XANES region from  $\sim 280$  to 320 eV. Energy selection is performed with a spherical grating monochromator, higher order energy contamination is removed with order sorting mirrors, and X-ray microfocusing is performed with Fresnel Zone plate optics (Jacobson et al. 1991).

All of the STXMs utilize Fresnel zone plate optics providing a theoretical spot size of 30 nm, in optimum cases smaller structures ( $\sim 15$  nm) can be resolved. Maximum scanning rate for both BL5.3.2 and 11.0.2 is 12 Hz, with a scanning range of 4000x2000 pixels covering a region up to 20 x 4 mm, with a minimum step size 2.5 nm. Sample position precision during spectra acquisition is better than 50 nm (controlled by laser interferometry) (Kilcoyne et al. 2003).

C-, N-, and O-XANES spectra were typically acquired using a multispectral imaging method (“Stacks”, Jacobsen et al. 2000). The “Stacks” method relies on creating a highly aligned hyper-spectral data cube of x and y pixilated images acquired over a range of energies that span a given XANES region. In the fine structure regions of the near edge, the energy step size ( $\Delta E$ ) employed typically was 0.1 eV; in the less feature pre-edge and post edge regions energy steps of 1 eV are typically sufficient for spectral resolution.

## RESULTS

### Carbon XANES

C-XANES reveals the presence and abundance of various organic functional groups via the detection of characteristic absorption features in the near edge (pre-ionization) region of the X-ray absorption spectrum. In general, absorption at the lowest energies ( $\sim 285.0$  eV) is well described by photo-excitation of carbon 1s electrons to low energy, unoccupied,  $\pi^*$  orbitals of alkenyl and aromatic species (C and H substituted). Carbon substitution with more electronegative atoms, e.g. N and O, results in shifts to higher excitation energies, e.g. 288.5 eV in the case of carboxyl 1s-  $\pi^*$  transitions (Urquhart and Ade 2002). Saturated carbon, i.e. methyl and methylene, also exhibit relatively intense absorption in the near edge region (e.g. Hitchcock and Mancini 1994), where the electronic transition for saturated carbon involves photo-excitation of a 1s electron to a hybrid state involving mixing of a 3p Rydberg state with a  $\sigma^*$  C-H orbital, commonly identified as a 1s-3p/ $\sigma^*$  transition (Stöhr 1991). The intensity of the 1s-3p/ $\sigma^*$  absorption is a strong function of the number of H's per carbon, i.e., this transition is most intense for methyl groups, and very weak for methine carbon. The energy of the 1s-3p/ $\sigma^*$  transition is also effected by the electronegativity of bonded species, e.g. N and O, this leads to a shift of the 1s-3p/ $\sigma^*$  transition to higher energies, e.g., from  $\sim 287.8$  eV for simple hydrocarbons up to 289.5 eV for alcohols (Hitchcock and Mancini 1994). For most organic compounds, the absorption spectrum at energies exceeding the carbon 1s ionization edge (i.e.,  $\sim 290.8$  eV for benzene, Hitchcock and Mancini 1994) consists of very broad spectral features, corresponding to highly delocalized excited states [in some cases referred to as 1s- $\sigma^*$  virtual state transitions (Stöhr 1991)]. Representative



assignments of functional groups with characteristic absorption energies are presented in Table 2.

Commonly, the samples analyzed in this particular study were intimately associated with silica, likely derived from aerogel, and in many cases embedded in epoxy for sectioning (see Table 2 for sample designations and descriptions). In order to acquire C-XANES spectra from samples that were embedded in epoxy, it is necessary to subtract the epoxy C-XANES spectrum from the particle spectrum. This is easily done, due to the fact that the epoxy spectrum exhibits extremely sharp, characteristic, absorption bands at 285.15 and 287.2 eV, respectively. Analysis of the derivative of the combined particle plus epoxy spectrum clearly reveals the contribution due to the epoxy allowing for an objective determination of the fractional contribution of pure epoxy to the total spectral intensity. In the case of silicate intermingled with organics, there exists no overlapping fine structure to worry about as the tail of the Si (2p, L edge) absorption passes smoothly under the carbon, nitrogen, and oxygen k-edges. For presentation purposes, a simple base line correction is all that is necessary. In order to obtain elemental ratios, N/C and O/C, however, a precise estimate of the contribution of Si absorption must be determined as is described below.

C-XANES spectra of eight organic samples extracted from the Stardust aerogel collector are presented in Figure 1. In addition, representative C-XANES spectra of an anhydrous Interplanetary Dust Particle (IDP) (L2011R11, (Flynn et al. 2003), insoluble organic matter (IOM) from a very primitive chondritic meteorite, EET92042 (Cody and Alexander 2005, Busemann et al. 2006), and a moderately thermally altered chondrite, Allende (Brearley and Jones 1998) are also included for comparison. It is immediately

clear that the majority of organic samples extracted from the STARDUST aerogel collector are complex, with C-XANES spectra showing the presence of carbon in a range of electronic environments. One exception is particle 1 (Table 2), that exhibits a relatively simple C-XANES spectrum dominated by a broad peak centered at  $\sim 289.3$  eV (F, Fig. 1). Intensity in this energy range could correspond to either a  $1s-\pi^*$  transition of the carbonyl in urea-like moieties or a  $1s-3p/\sigma^*$  transition corresponding to either alcohol or ether moieties. It is notable that the oscillator strength of pure urea is relatively strong (Hitchcock and Mancini 1994); thus if urea is present it must exist along with an abundance of alcohol and/or ether.

Samples 2 and 3 share a similar chemical characteristic not observed in the other samples analyzed. This is a very intense peak at 288.2 eV (D, Fig. 1) that most likely corresponds to a carbonyl group in an amide moiety (Table 2). This assignment is supported by N-XANES as is described below. Particle 2 also exhibits a well-developed shoulder at  $\sim 286.5$  eV and a weak peak at 285.2 eV (B and A, respectively). Peak A corresponds to  $sp^2$  bonded carbon substituted with either C or H, i.e. olefinic and/or aromatic carbon hydrocarbon. Note that all of the samples, with the exception of #1 exhibit some intensity at  $\sim 285$  eV (A, Fig. 1) signifying the presence of minor amounts of either olefinic or aromatic carbon; the relative concentration of such carbon in any of the samples, however, is considerably less than that observed in either the IDP or the chondritic organic samples (Fig. 1).

The peak at 286.5 eV likely indicates the presence of vinyl-keto groups (Hitchcock and Mancini 1994). Absorption at this energy is observed to varying extents in all of the samples (excluding 1), and is particularly intense in samples 7 and 8. Note

that both the IDP, L2011R11, and the chondritic IOM from EET92042 also exhibit significant intensity in this region. Very commonly, vinyl-keto groups observed in C-XANES spectra from both terrestrial and extraterrestrial organics actually form during acquisition as a consequence of X-ray induced damage. Specifically, labile polyol moieties (e.g., polysaccharides) suffer OH elimination reactions through collision with energetic secondary electrons generated by the photoabsorption process (Cody 2000). The observation of this band in the Comet 81P/Wild 2 organics, therefore, provides indirect evidence for the presence of poly-hydroxylated moieties (for example, sugar derivatives). Finally, it is also noted that both imine and nitrile carbon exhibit  $1s-\pi^*$  transitions in the range 286.7 to 286.9 eV (Table 2) and their presence cannot be ruled out based on C-XANES alone. N-XANES, however, (see below) does not support the presence of imine or nitrile in sufficient quantities to be detected in the C-XANES spectra amidst the other functional groups.

Several of the samples (e.g., 4, 5, and 6) exhibit considerable intensity at 287.5 eV (C, Fig. 1). Particle 5, for example exhibits a distinct peak at this energy. Absorption in this energy range generally points to aliphatic moieties (Table 2), although the energy of peak C is on the low side for typical aliphatic hydrocarbons. The methyl groups of ethane, for example, exhibit a relatively sharp peak at 287.9 eV corresponding to the  $1s-3p/\sigma^*$  transition (Stöhr 1991), methyl groups decorating aromatic rings exhibit a characteristic peak at 288.3 eV (Hitchcock and Mancini 1994). Interestingly, methyl groups in tetramethyl-silane exhibit their  $1s-3p/\sigma^*$  transition at 287.3 eV (Hitchcock and Mancini 1994), suggesting that the peak at 287.5 eV may be due to methyl-groups decorating silicon. Solid-state  $^{29}\text{Si}$  Nuclear Magnetic Resonance (NMR) spectroscopy of

bulk aerogel reveal the presence of silicone moieties and solid state  $^{13}\text{C}$  NMR spectroscopy show that the predominant form of carbon is methyl-silica moieties (Sandford et al. in prep.). In Fig 2 a C-XANES spectrum of silicone oil is presented revealing a sharp peak at 287.5 eV corresponding to  $\text{CH}_3\text{-Si}$  groups. Thus, at least some of the carbon in samples 4, 5, and 6 may be organic carbon intrinsic to bulk aerogel. It is noted C-XANES analysis of silica rich regions of some of the samples yield spectra that are very similar to that of silicon oil (Fig 2) and is consistent with what is expected in terms of the intrinsic background carbon signal associated with the aerogel.

Samples 7 and 8 are different ultra-thin sections acquired from the same particle, hence it is expected that they share similar chemistry. Among the samples analyzed so far, these two samples exhibit the greatest amount of olefinic and/or aromatic hydrocarbon, i.e., intensity at 285 eV, as well as the most intensity at 286.6 eV (A & B, Fig. 1, respectively). In this regard samples 7 and 8 bear the greatest chemical similarity to the anhydrous IDP, L20211R11, and the primitive chondrite IOM, EET92042, in terms of the types and relative abundance of functional groups present.

In the course of analyzing the samples that were embedded in liquid epoxy (prior to sectioning) it became immediately apparent that there exists a carbonaceous phase in these samples that is soluble and extracted by the liquid epoxy. During curing this soluble phase migrates from the particle into the surrounding liquid epoxy. The presence of such a soluble phase has been observed in every particle analyzed so far that was embedded in epoxy; an example is presented in Fig. 3. The soluble phase extracted from the silicate rich particle in Fig 3a is contrast-resolved from epoxy particularly well at energies just below the C-XANES region, e.g., 280 eV, and on the peak of O-XANES

absorption, e.g. 540 eV. In Fig 3b a C-XANES spectrum of pure epoxy is presented along with a C-XANES spectrum of the soluble phase obtained by subtracting the pure epoxy C-XANES spectrum from the combined Epoxy + soluble phase spectrum. We find that the  $\sim 10\%$  of the intensity of the dark region in Fig 3a corresponds to the presence of carbon, that is not epoxy, associated with an apparently soluble phase extracted from the embedded particle.

The C-XANES spectrum of the soluble organic phase is expanded vertically in Fig. 2 and presented with a C-XANES spectra of pure silicone oil (Fig 2, bottom) and that of silicone moieties intrinsic to the aerogel. It is clear from this C-XANES spectrum that the soluble phase is neither silicone oil nor aerogel, rather the dominant organic species includes carboxyl and alcohol/ether moieties along with minor olefinic/aromatic and other species. At this point we cannot attribute this phase to any obvious contaminant and include this extractible phase in subsequent discussions as if it were a genuine Comet 81P/Wild 2 organic phase.

**Nitrogen XANES:** Nitrogen XANES provides complementary information to the C-XANES data, revealing the distribution of nitrogen containing functional groups. Characteristic energies corresponding to nitrogen in various unsaturated and saturated moieties are presented in Table 2. Unsaturated nitrogen species are readily distinguished as there are significant shifts in energy corresponding to imine and nitrile  $1s-\pi^*$  transitions (Table 2). Similarly, the  $1s-3p/\sigma^*$  transitions of amino NH may be distinguished from aliphatic and aromatic amine and from pyrrolic NH. Similar to C-XANES behavior of  $CH_x$  moieties, the intensities of the  $NH_x$   $1s-3p/\sigma^*$  transitions are

proportional to the number of hydrogen atoms, i.e. primary amines are expected to exhibit considerably more intense  $1s-3p/\sigma^*$  transitions than secondary amines.

Given that the nitrogen abundance is a fraction of that of carbon, the signal-to-noise (S/N) of the N-XANES spectra is generally much worse than that of C-XANES. Only the samples that provided sufficient S/N N-XANES spectra are presented in Fig. 4, along with N-XANES spectra for the IDP L20211R11 and chondritic organic matter from EET92042 and Allende.

Similar to what was observed in the C-XANES data presented in Fig. 1, considerable variation in nitrogen chemistry is observed across the various samples analyzed (Fig 4). The generally broad N-XANES spectra also reveal that nitrogen speciation within most of samples is relatively complex. For example, samples 1, 5, and 8 exhibit nearly featureless N-XANES spectra with absorption growing continuously from  $\sim 398$  eV up to the ionization threshold (IP) at  $\sim 405$  eV (Henke et al. 1993). Given that the absorption intensity peaks near the ionization threshold strongly suggests that the dominant nitrogen functional groups are amino, urea, and carbamate moieties, with lesser amounts of imine, nitrile, and amido nitrogen (Fig. 4).

Samples 2 and 3 exhibit better resolved fine structure in the their respective N-XANES spectra (Fig. 4) as compared with the other samples, meteorite IOM, and IDP. In particular, a relatively sharp peak at 401.4 eV (I, Fig. 4) dominates the spectrum of particle 3. The C-XANES spectra of these two samples are similarly dominated with a single sharp peak at 288.2 eV (D, Fig. 1) that likely corresponds to a  $1s-\pi^*$  transition of a carbonyl (Urquhart and Ade 2002). Assignment of the 401.4 eV feature to amido nitrogen, therefore, appears reasonable, even though a pure compound study places the

amido-N absorption at  $\sim 401.9$  eV (Hitchcock and Mancini 1994, Table 2). It is also noteworthy that relative to the other samples, samples 2 and 3 exhibit weaker intensity in the region around 402.3 eV (J, Fig. 4) indicating proportionally less amine and amino functionality. Particle 2 exhibits clearly defined intensity in the 399 to 400 eV (G and H, Fig. 4) energy region supporting the presence of some imine and nitrile N. Nitrile N exhibits a very intense  $1s-\pi^*$  absorption band relative to the ionization cross-section. This means that the intensity at  $\sim 400$  eV, although most likely indicative of the presence of nitrile, actually reflects only a low concentration (likely less than  $\sim 5\%$ ) relative to the other N-bearing species.

Comparing the N-XANES spectra of these organic samples obtained from particles extracted from the Stardust aerogel collector with that derived from the anhydrous IDP L2011R11 and chondritic organic matter from EET92042 and Allende reveals some similarities. The N-XANES from L20211R11 and EET92042 are similar, clearly exhibiting intensity that could be ascribed to the presence of imine/nitrile (G and H,  $\sim 399$ -400 eV) as well as amido-N (J,  $\sim 401.4$ -401.9 eV). Similar to samples 2 and 3; L2011R11 exhibits a valley in the spectral region where amine and amino nitrogen are expected; EET92042 exhibits somewhat greater intensity in this region. At least superficially, the N-XANES spectrum of particle 2 appears similar to that of L2011R11; whereas the N-XANES spectrum of particle 5 shares greater similarity with EET92042. Samples 1 and 8 exhibit similar N-XANES spectra that differ from the other samples as well as the IDP and meteoritic IOM by virtue of minimal nitrile intensity (A, Fig. 4). In general, it can be said that the N-XANES spectra for all of these organic samples indicate a wide range of nitrogen containing functional groups, across these samples, however,

there also exists considerable variation in the relative abundance of many nitrogen containing functional groups.

### **Oxygen XANES**

While O-XANES of Comet 81P/Wild 2 organics were acquired these are not discussed in any detail here. This is because there tends to be considerably less chemical information obtained from the O K edge beyond the ratio of single to double bonded oxygen. This ratio, while a useful piece of information, is unreliable in many of the samples due to the contribution of a relatively high oxygen back-ground signal derived from associated silica. As is discussed below, however, O-XANES data are still useful for the purpose of deriving quantitative O/C ratios.

### **Elemental Abundances**

While the near edge fine structure of the carbon, nitrogen, and oxygen 1s absorption edges provides valuable information regarding the presence of specific organic functional groups, the overall intensity of absorption spanning both below and well above a given ionization edge provides a quantitative measure of the atomic abundances of carbon, nitrogen, oxygen, and silica. This is because for the lower Z elements absorption in the soft X-ray range is dominated by the photo ionization cross sections, whereas atomic scattering is very weak (Stöhr 1991). In order to obtain quantitative estimates of N/C and O/C we employ the mass absorption coefficients of Henke et al. (1993) and fit our C-, N-, and O-XANES data directly. The majority of samples analyzed in the present study are intimately associated with silicate derived



primarily from the aerogel. Silicon exhibits relatively intense absorption across the spectra range 200 to 600 eV due primarily to photo-absorption by the 2p and 2s electronic levels (Thompson et al. 2001). The presence of silicate obviously presents a particular problem with determining the oxygen content of the organic samples. The estimated oxygen content will be the sum of both silicate and the organic matter. If the fraction of non-bridging oxygen (NBO) intrinsic to the aerogel is known then one can correct the oxygen content based on the silica content. For example, if NBO = 0 as in the case of quartz then one silicon is balanced with twice as much oxygen. As a product of solid-state  $^{29}\text{Si}$  NMR analysis of bulk aerogel (Sandford et al. in prep.), the fraction of NBO has been established for Stardust aerogel yielding an average formula for the aerogel of  $\text{SiO}_{2.13}$ .

An example of a typical fit of the combined C-, N-, and O-XANES data for sample 5 is presented in Fig. 5. The individual contributions from C, N, O, and Si are summed to provide the best fit of the photo-absorption cross section. Note that at both the carbon and oxygen edges there exists considerable absorption intensity above the ionization edge that exceeds that predicted based on the Henke et al. (26) data. This intensity results from the so called  $\sigma^*$  shape or Feshbach resonances (Stöhr, 1991). The data presented in Fig. 5 are derived from a total particle analysis and indicate an elemental formula of  $\text{C}_{100}\text{N}_{13}\text{O}_{154}\text{Si}_{57.5}$ .

The edge structure of the apparently epoxy extractible phase of carbon (Figs 2 & 3) requires a contribution from an element other than C, N, and O in order to account for all of the absorption. In Table 3, we calculate the total absorption including the contribution of either silicon or sulfur and find that in either case, a relatively high Si/C

or S/C is required to fully account for the absorption characteristics. The elemental ratios O/C, N/C, and Si/C are presented in Table 3 and in Fig. 6. Also included in Fig. 6 are elemental ratios representative of type 1, 2, and 3 chondritic IOM (Alexander et al. in press) and elemental data derived for the anhydrous IDP L2011R11 (Feser et al. 2003). In order to obtain an estimate of O/C from the published data obtained for the whole particle of anhydrous IDP L2011R11, it was necessary to estimate the degree of polymerization of the silicates in the GEMS (glass embedded with metals and sulfides, see review by Rietmeijer 1998 and references therein) as well as the modal abundance of enstatite. As it is not well known what the relative modal abundances of enstatite and GEMS are in this particular IDP, we considered a wide range spanning from 30 % to 70 % enstatite, this model uncertainty provides the greatest uncertainty in the elemental ratios presented in Table 3 and Fig. 6.

It is interesting that the elemental chemistry of the anhydrous IDP L2011R11 is richer in oxygen than the majority of samples analyzed in this study; if anhydrous IDP's do constitute remnants of cometary matter (Brownlee et al. 1995; Rietmeijer 1998); then it may be possible that the relative reduction in oxygen evident in the organic samples retrieved from the aerogel is evidence of alteration during the energetic phase of particle capture. It is worth noting, however, that while this IDP clearly has not suffered any aqueous alteration since its formation, it has undergone mild thermal processing during atmospheric re-entry (Flynn et al. 2003, Keller et al. 2004). Furthermore, the C-XANES spectrum of L2011R11 reveals considerable intensity at 286.5 eV, possibly indicative of significant secondary electron damage (Cody 2000).

In general, the Comet 81P/Wild 2 samples analyzed (so far) are distinct in terms of their respective O/C and N/C from primitive chondritic organic matter. Perhaps more significantly, however, it is clear that the cometary organics exhibit a spectacularly large degree of variation in their elemental chemistry. Is this variation a primary feature of the cometary organics or a secondary feature overprinted during the energetic phases of sample capture? Deriving an unequivocal answer to this question will likely require considerably more analyses. It should be noted, however, that the scatter in the range of N/C and O/C is not what would be expected if a single cometary organic precursor was chemically evolved to various degrees by thermal transformation.

The trajectory of the change in elemental ratios with progressive thermal transformation of terrestrial kerogens is well established (van Krevelan 1992). What is observed is large losses in oxygen parallel less significant losses in nitrogen. Acknowledging that the macromolecular of terrestrial kerogen must differ enormously from that of extraterrestrial organic solids; neither the oxygen and nitrogen containing functionalities in the cometary organic matter are particularly exotic and considering a single primitive, cometary, end-member one would expect the signature of thermal modification to be much more covariance between O/C and N/C (e.g. that which is observed for meteoritic organics, Fig. 6), not the scatter observed in Fig. 6.

The spectacular inter-particle heterogeneity detected in this preliminary analysis of Comet 81P/Wild 2 organics is striking as it suggests that there may not be a unique cometary organic precursor. Rather, intrinsic heterogeneity of the organic particles may be the rule and is consistent with the wide range of heterogeneity observed

mineralogically (Brownlee et al. 2006, Zolensky et al. 2006), chemically (Flynn et al. 2006; Sandford et al. 2006), and isotopically (McKeegan et al. 2006).

The variation in the types of O- and N-bearing functional groups is similarly intriguing as there exists no simple means of transforming (at least via a fast thermal process as might have occurred during aerogel capture) the organic solids detected in some of the particles into that observed in other particles. Rather, the spread in chemistry may suggest that the particles captured by the Stardust spacecraft cannot be linked to a common precursor. This raises the interesting question as to whether the organic solids extracted from the aerogel collector universally represent solids that formed via cometary processes or whether some of the solids could have formed from reactive low molecular weight precursors either during or after capture. It is notable in this regard, that particle # 1 (Fig. 1, Table 1) stands out from the others with functional group characteristics that are similar to that expected in simple condensation polymers such as poly[oxymethylene] derived from formaldehyde and urea-formaldehyde-derived polymeric resins.

### **Intra-particle Heterogeneity**

One of the intriguing aspects of interplanetary dust samples is the sub-micron scale spatial heterogeneity evident both in terms of organic chemistry (e.g. Flynn et al. 2003) and in terms of isotopic abundances, e.g. H/D and/or  $^{15}\text{N}/^{14}\text{N}$  (e.g. Keller et al. 2004). In this regard it is interesting that while samples 7 and 8 (Table 1) were obtained from sequential sections of a single large particle, it is clear from the C-, N-XANES, and elemental data (Figs 1, 3, and 6) that the chemical characteristics of samples 7 and 8 are not identical, suggesting that the organic solids captured by the Stardust mission may also

be heterogeneous at a fine scale. Such sub-micron scale heterogeneity in Comet 81P/Wild 2 organic samples is dramatically confirmed in the case of sample 5.

Recalling that all spectroscopic data was acquired via multi-spectral (“Stacks” imaging (Jacobsen et al. 2000)), the C-, N-, and O-XANES data and the elemental data presented in Figs 1, 4, and 6 constitute the sum (the average) of all pixels. This was done to optimize the signal to noise; and was originally justified because none of the samples exhibited evidence of heterogeneity. The exception to this is sample 5. An optical density image (on the Carbon K edge) of sample 5 (Figure 7a) reveals considerable variation in absorption intensity across the particle, with considerable intensity in the particle center. Variations in absorption intensity may be due to characteristics other than organic chemical heterogeneity. For example, variations in absorption may be due entirely to variation in carbon density or variation in relative concentration of silica intermixed with organics. In the case of sample 5, the average the Si/C ratio is on the order of 0.52 (Table 3), thus the bright region in Fig 7a may very well reflect increased silica. Analyzing only those pixels that correspond to the bright (“center”) region in Fig 7a and comparing these with the homogenous “lobe” region (Fig 7a) reveals that the molar abundance of carbon in both regions is essentially the same, but the contribution to total absorption due to silica is very different (with a Si/C ratio of 0.51 for the “lobe” region and 0.88 for the “center” region); hence the apparent increased brightness in the optical density image (Fig 7a). Given that the capture medium of the Stardust mission was low-density aerogel, it is not surprising that the organic samples would be intimately associated with silica. One would, however, reasonably expect a higher concentration of silica at the edge of the particle, rather than the center.

Based on image contrast alone, therefore, the apparent chemical heterogeneity of sample 5 might only reflect variations in silica content. We find, however, that XANES spectroscopy (particularly on the N L edge) reveals considerable differences in the nitrogen and oxygen content within these two domains; i.e. Fig. 7b shows that the O/C and N/C of the “lobe” region is considerably less than that of the center region. The C- and N-XANES spectra of the “lobe” and “center” regions are presented in Fig. 8a and b. Whereas there are subtle differences in the C-XANES spectra of the two regions, the N-XANES differs considerably. In particular, it is clear that the nitrogen chemistry associated with the “center” region differs from that of that of the “lobe” region more than just in relative abundance. Whereas both the center and lobe regions exhibit intensity consistent with amido and amino nitrogen (I and J, Fig 8b), unsaturated nitrogen, e.g. imine and nitrile nitrogen (G, Fig 8b), are nearly absent in the N-XANES spectrum of the “lobe” region.

The enormous difference in nitrogen content and variation in nitrogen chemistry across sample 5 is extremely interesting and the origin and/or significance of this heterogeneity is not well understood at this point in time. It is worth noting that while in the case of sample 5 the high nitrogen content does correlate spatially with elevated silica, among all of the samples analyzed so far, there is not an obvious correlation between high nitrogen and high silica. Samples 2 and 3, for example, have high N/C but relatively low silica contents. Sample 4 has a moderately high silica content, but low N/C. Clearly many more Comet 81P/Wild 2 samples will have to be analyzed before the statistical significance of such heterogeneity, as well as an explanation regarding its origin, is determined. At this point it can be stated, however, that the organic particles

obtained from Comet 81P/Wild 2 exhibit fine scale organic heterogeneity that matches if not exceeds that of anhydrous IDP's.

## CONCLUSIONS

The unique capability of  $\mu$ -XANES to interrogate small organic particles has provided our first view into the nature of cometary organics. All of the samples described in this paper exhibit highly complex organic structures composed a many different functional groups, in particular, a rich inventory of heteroatom bearing functional groups. Perhaps the most important aspect of these data is, however, the remarkable range in both elemental and corresponding organic functional group chemistry seen across the Comet 81P/Wild 2 samples. Given such a wide range in chemistry, extended over a relatively small set of particles analyzed thus far, means that it is not yet possible to describe in any statistically significant way the average organic structure of comet 81P/Wild 2. Similarly, it cannot be unequivocally stated whether the compositional scatter lies around a single organic composition or whether there will emerge a pattern revealing chemical distinct populations organics.

It is clear from these preliminary studies that the organic chemistry manifested in the organic particles extracted from the Stardust aerogel collector is rich and highly variable. Considerably more analyses will be required before we can sort out 1) the possible chemical effects associated with high velocity capture, 2) an explanation for the tremendous range in chemical composition, and 3) a statistically reliable picture of the state of organic matter in the Comet Wild2.

## **ACKNOWLEDGMENTS**

Financial support for these analyses was provided by NASA's Stardust Analysis Program. During the Preliminary Examination period data were acquired at the Advanced Light Source, Lawrence Berkeley National Laboratory, beam lines 5.3.2 and 11, as well as the National Synchrotron Light Source, Brookhaven National Laboratory, beam line X1A. Each of these facilities are supported by the Department of Energy, Basic Energy Sciences Program. Financial Support for the individual beam lines is generously provided by the DOE, the NSF, and NASA.

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**Table 1**

Sample Designations for Comet 81P/Wild 2 Particles analyzed in this study

<b><u>Sample ID</u></b>	<b><u>Generic</u></b>	<b><u>Track</u></b>	<b><u>Grain</u></b>	<b><u>Mount</u></b>	<b><u>Medium</u></b>	<b><u>Fe-present</u></b>	<b><u>Silicate</u></b>
1	FC12	16	1	10	epoxy	ND	trace
2	C2054	35	16	4	epoxy	Yes	Yes
3	C2115	22	1	5	sulfur	ND	Yes
4	C2054	35	10	10	sulfur	ND	Yes
5	C2054	35	8	8	sulfur	ND	Yes
6	C2044				sulfur	Yes	Yes
7 <sup>a</sup>	FC9	13	1	8	sulfur	ND	Yes
8 <sup>a</sup>	FC9	13	1	8	sulfur	ND	Yes
9	C2115	22	1	5	sulfur	ND	Yes

**a:** These are different slices of the same particle, with significantly different cross-sections and positions on the grids. ND=not detected.

**Table 2**  
Various C-, N-, and O-XANES transitions and associated functional groups

<b>C-XANES</b>		<b>Assignments<sup>a</sup></b>	
<b><u>Photon Energy</u></b>	<b><u>Transition</u></b>	<b><u>Functional Group</u></b>	
283.7	1s- $\pi^*$	C=C*-C=O,	quinone
285.2	1s- $\pi^*$	C=C*-H,C,	aromatic & olefinic carbon
286.1-286.3	1s- $\pi^*$	C=C*-C=O	Aryl, vinyl-keto
286.5	1s- $\pi^*$	C=C-C*=O	Vinyl-keto
286.7-286.9	1s- $\pi^*$	C* $\equiv$ N	nitrile
287.2	1s- $\pi^*$	C=C*-OR	enol
287.3-288.1	1s-3p/s*	CH <sub>x</sub> -C,H	aliphatics
287.9-288.2	1s- $\pi^*$	NH <sub>x</sub> (C*=O)C	amidyl
288.4-288.7	1s- $\pi^*$	OR(C*=O)C	carboxyl
288.9-289.8	1s- $\pi^*$	NH <sub>x</sub> (C*=O)NH <sub>x</sub>	urea
289.3-289.5	1s-3p/s*	CH <sub>x</sub> -OR	Alcohol, ether
290	1s- $\pi^*$	NH <sub>x</sub> (C*=O)OR	carbamoyle
292-296	1s- $\pi^*$	RO(C*=O)OR	carbonate
<b>N-XANES</b>		<b>Assignments</b>	
<b><u>Photon Energy</u></b>	<b><u>Transition</u></b>	<b><u>Functional Group</u></b>	
398.8	1s- $\pi^*$	C=N*	imine
399.8	1s- $\pi^*$	C $\equiv$ N*	nitrile
401.9	1s- $\pi^*$	N*H <sub>x</sub> (C=O)C	amidyl
402.1-402.3	1s-3p/s*	C-N*H <sub>x</sub>	Amine, pyrrole
402.5-402.6	1s-3p/s*	C-N*H <sub>x</sub>	amino
403	1s-3p/s*	CO- N*H <sub>x</sub>	urea
<b>O-XANES</b>		<b>Assignments</b>	
<b><u>Photon Energy</u></b>	<b><u>Transition</u></b>	<b><u>Functional Group</u></b>	
531.2	1s- $\pi^*$	C=O*	Ketone
532.0	1s- $\pi^*$	O-C=O*	carboxyl
534.4	1s-3p/s*	CH <sub>x</sub> O	Alcohol, ether
534.9	1s-3p/s*	C=C-O*	enol

<sup>a</sup>These assignments are derived from both the gas phase Electron Energy Loss spectral data base of simple compounds Hitchcock and Macinini (1994), updated to the present at the Hitchcock group of McMaster University (<http://unicorn.mcmaster.ca/>), as well as polymer STXM data base supported by the Harald Ade and the Polymer STXM group at NSCU (<http://www.physics.ncsu.edu/stxm/polymerspectro/>).

**Table 3**

Elemental Chemistry Derived for Comet 81P/Wild 2 Samples via C, N, and O-XANES

<u>Sample ID</u>	<u>O/C</u>	$\pm$	<u>N/C</u>	$\pm$	<u>Si/C</u>	<u>S/C</u> <sup>a</sup>	<u>Fe/C</u> <sup>b</sup>
1	0.67	0.02	0.07	0.01	0.02		
2	0.11	0.01	0.23	0.03	0.13		
3	0.18	0.02	0.24	0.03	0.13		
4	0.25	0.03	0.07	0.02	0.52		
5	0.28	0.03	0.12	0.01	0.51		
6	0.27	0.03	NA	-	-	-	1.15
7	0.19	0.01	0.07	0.01	0.19		
8	0.22	0.01	0.12	0.01	0.17		
L20211R11	0.49	0.06	0.12	0.01	0.69	-	-
Sol. Phase	0.59	0.05	0.12		1.06	0.92	
Bulk aerogel	-	-	-	-	20-100 <sup>c</sup>	-	-

**a:** It is possible that in the case of the soluble phase baseline shift could also be due to presence of sulfur instead of silica. **b:** Sample 6 is closely associated with an iron rich particle not silica, **c:** these values were determined by solid state <sup>13</sup>C and <sup>29</sup>Si NMR (Sandford et al. in press). NA = not analyzed.

### Figure Captions:

**Figure 1:** A stack plot of C-XANES spectra obtained of organics associated with particles extracted from the Stardust aerogel collector (sample numbers 1- 8, Table 1). Included for comparison are a spectrum of an anhydrous IDP (L2011R11), and insoluble organic matter isolated from a CR2 meteorite (EET92042) and a CV3 meteorite (Allende). Peaks corresponding to specific functional groups are highlighted with the letters **A-F**; where **A** ( $\sim 285$  eV) corresponds to a  $1s-\pi^*$  transition associated with aromatic or olefinic carbon, **B** ( $\sim 286.5$  eV) corresponds to a  $1s-\pi^*$  transition associated with oxygen substituted double bonded carbon, e.g. enolic carbon, **C** ( $\sim 287.5$  eV), corresponds to a  $1s-s^*/3p$  transition associated with methyl groups: **D** ( $\sim 288.2$  eV) corresponds to a  $1s-\pi^*$  transition associated with carbonyl carbon in amide moieties: **E** ( $\sim 288.5$  eV) corresponds to a  $1s-\pi^*$  transition associated with carbonyl carbon in carboxyl moieties: and **F** ( $\sim 289.5$ ) corresponds to a  $1s-s^*/3p$  transition associated with alcohol/ether moieties. The approximate position of the carbon  $1s$  ionization threshold is designated with a dashed line (labelled **IP**).

**Figure 2:** C-XANES spectra of pure silicone oil (bottom), a highly silica rich region (middle), and the soluble phase that was extracted by the epoxy from embedded particles (top). Note that the low signal to noise exhibited in silica rich region spectrum (middle) is due to the very low carbon content. The dominant functionality in both the silicone oil and the silica rich regions are silica bonded methyl groups. The epoxy soluble material is clearly not silicone oil or aerogel.



**Figure 3: A:** X-ray image of a particle from track 35, grain 16, (sample 2) acquired at 280 eV, just below the carbon 1s XANES region. Note the particle, largely granular and silica rich (outlined with a solid line) is embedded in epoxy, **E**. Highlighted with dashed lines is a region of some other organic phase that was extracted by the liquid epoxy from the particle (**E + ?**). **B:** C-XANES spectra of the epoxy and the soluble phase, obtained by subtraction of epoxy from the spectrum acquired in the **E+?** field. The extracted phase constitutes ~ 10 % of the carbon contributed by the epoxy.

**Figure 4:** N-XANES spectra obtained of organics associated with particles extracted from the aerogel collector (samples 1- 8, Table 1). Included for comparison are a spectrum of an anhydrous IDP (L2011R11, 2), and insoluble organic matter isolated from meteorites, CR2 (EET92042) and CV3 (Allende). Peaks corresponding to specific functional groups are highlighted with the letters **G-K**; where **G** (~ 399 eV) corresponds to a  $1s-\pi^*$  transition associated with imine nitrogen ( $C=N^*$ ): **H** (~ 400 eV) corresponds to a  $1s-\pi^*$  transition associated nitrile nitrogen ( $C\equiv N^*$ ): **I** (~ 401.4 eV), corresponds to a  $1s-\pi^*$  transition associated amidyl nitrogen ( $O=C-N^*$ ): **J** (~ 402.5 eV) corresponds to a  $1s-s^*/3p$  transition associated with amino nitrogen: **K** (~403.5 eV) corresponds to a  $1s-s^*/3p$  transition associated with urea nitrogen. The approximate position of nitrogen's 1s ionization threshold is designated by a dashed line (labeled **IP**).

Figure 5: An example of a computational fit of C-, N-, and O-XANES spectra of a cometary organic solid (sample 5; bold solid line). Atomic absorption cross sections are used directly, where the contribution from carbon is included with close spaced fine

dashed line, nitrogen (solid line), oxygen (broad dashed line), and silica (fine open spaced dashed line). The sum of these provides the quantitative fit resulting in a precise determination of atomic C, N, O, and Si, e.g.,  $N/C = 0.12 \pm 0.01$ ,  $O/C = 0.28 \pm 0.03$  (corrected for oxygen associated with silica), and  $Si/C = 0.51$ .

**Figure 6:** Atomic N/C vs O/C derived from C-, N-, and O-XANES of organics associated with particles extracted from the Stardust aerogel collectors (□). Included are elemental data for meteoritic organic matter isolated from type 1, 2, and 3 chondrites (■) and the anhydrous IDP L20211R11 (●).

**Figure 7: A:** An optical density image on the Carbon (1s) absorption edge of sample 5 (track 35, grain 8, mount 8). Note, the significant variations in optical density could be due to variations in particle density or chemical heterogeneity. **B:** Elemental data (N/C and O/C) from the “lobe region” and the “center band” reveal that the variation in optical density observed (left) reflects significant chemical heterogeneity within the sample.

**Figure 8: A:** C-XANES spectra of sample 5 “lobe” (bottom) and “center band” (top) revealing significant differences in the relative distribution of specific functional groups. **B:** N-XANES spectra of the same regions revealing significantly less abundant N in the “lobe” region (bottom) and considerable differences in the relative abundance of N functional groups. The obvious peaks corresponding to specific functional groups are identified as: **A)** C=C,  $1s-\pi^*$ , **C)**  $CH_3$   $1s-\sigma^*/3p$ , **D)** O-C=O,  $1s-\pi^*$ , **G-H)** C=N and/or  $C\equiv N$   $1s-\pi^*$ , **I)** amidyl  $1s-\pi^*$ , and **J)** amino N  $1s-\sigma^*/3p$ .



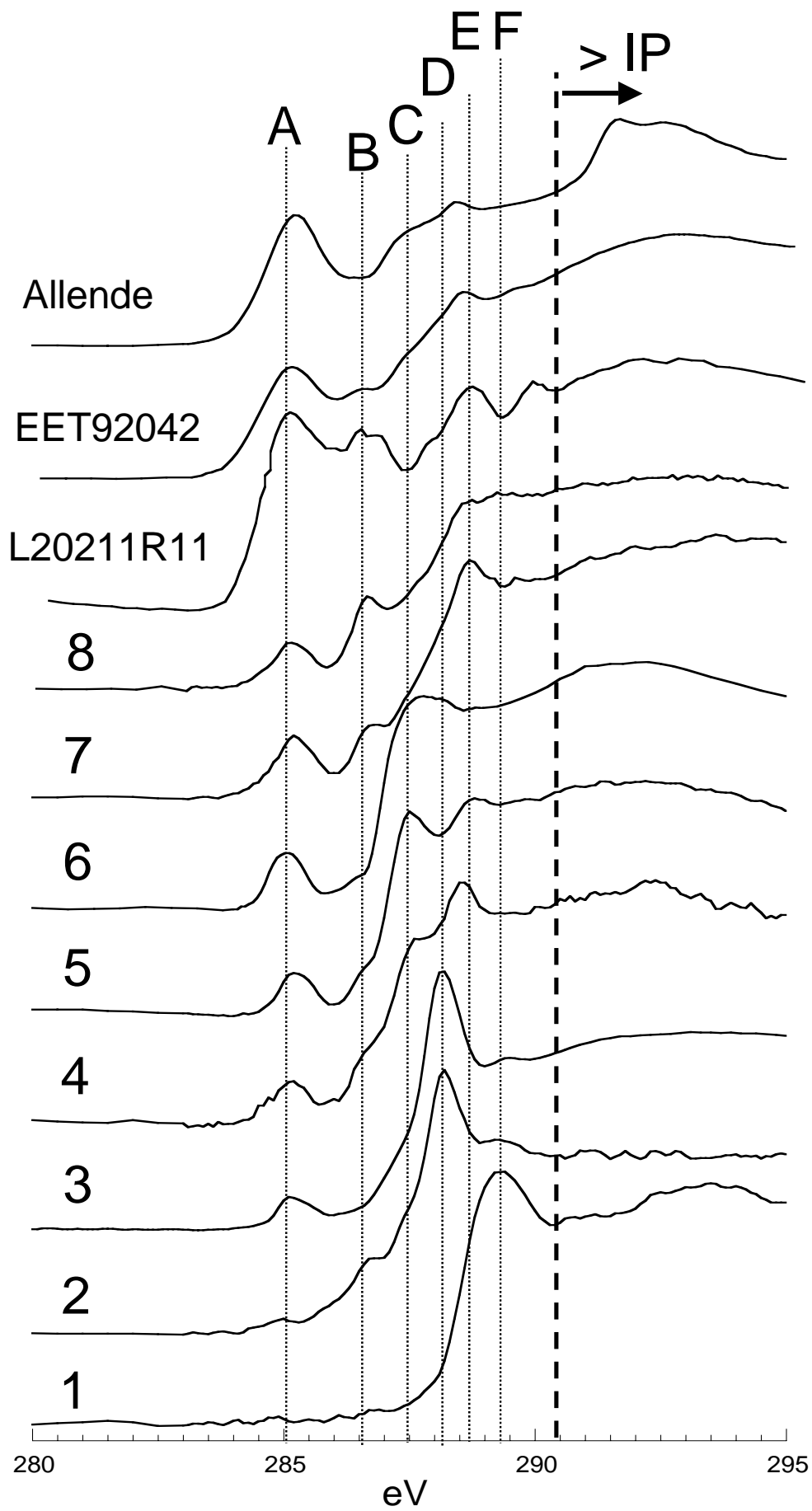


Figure 1

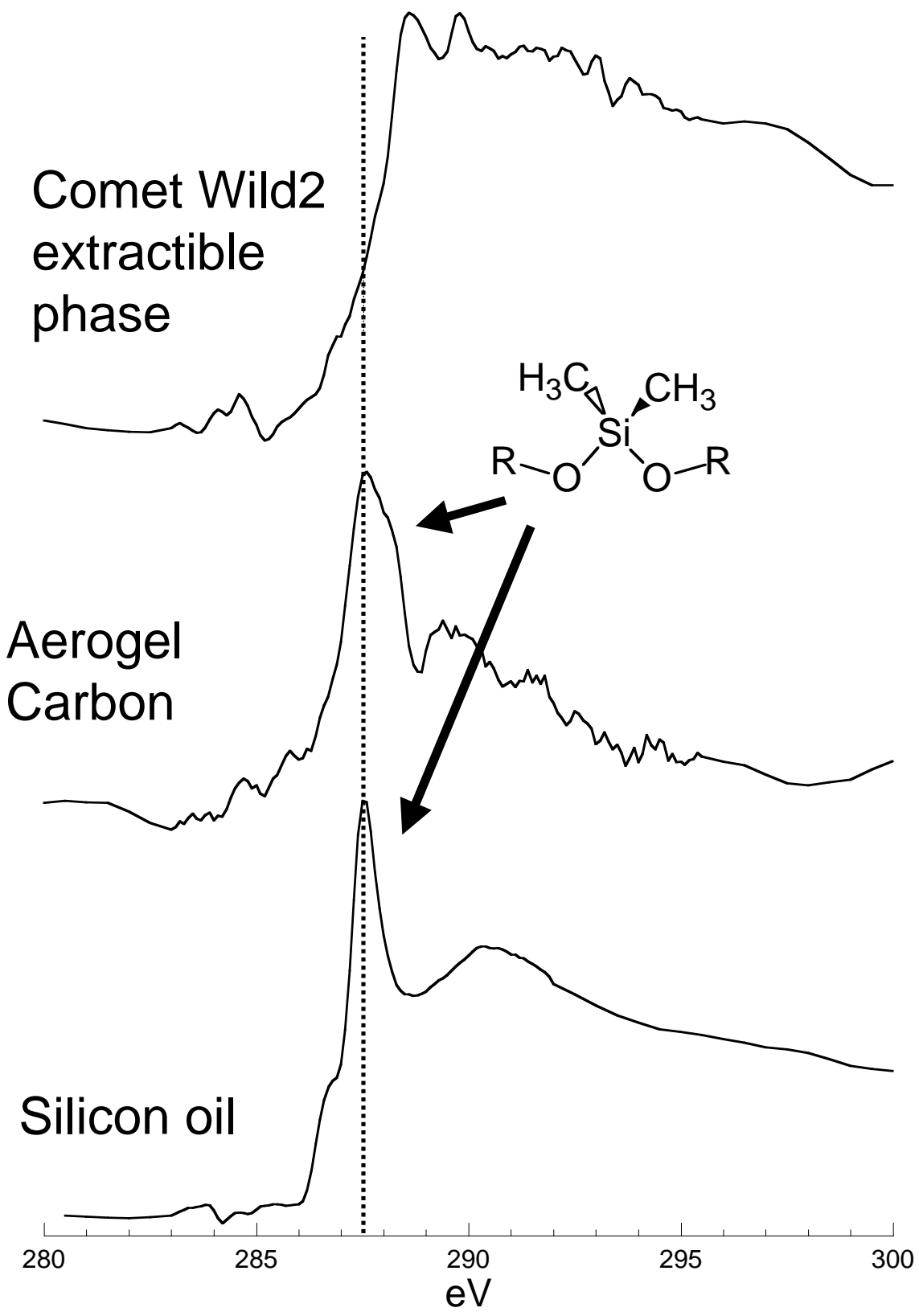
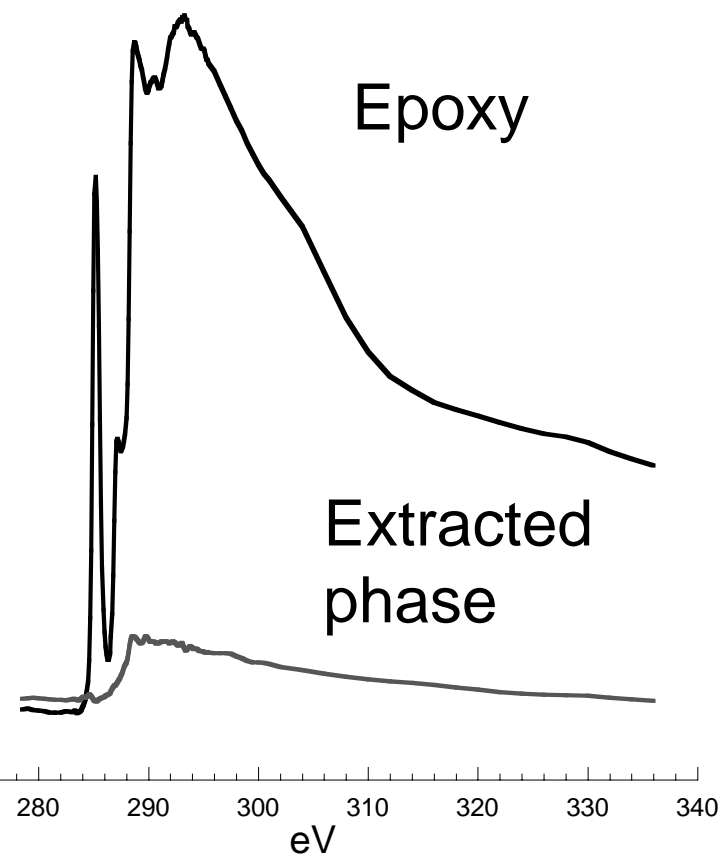
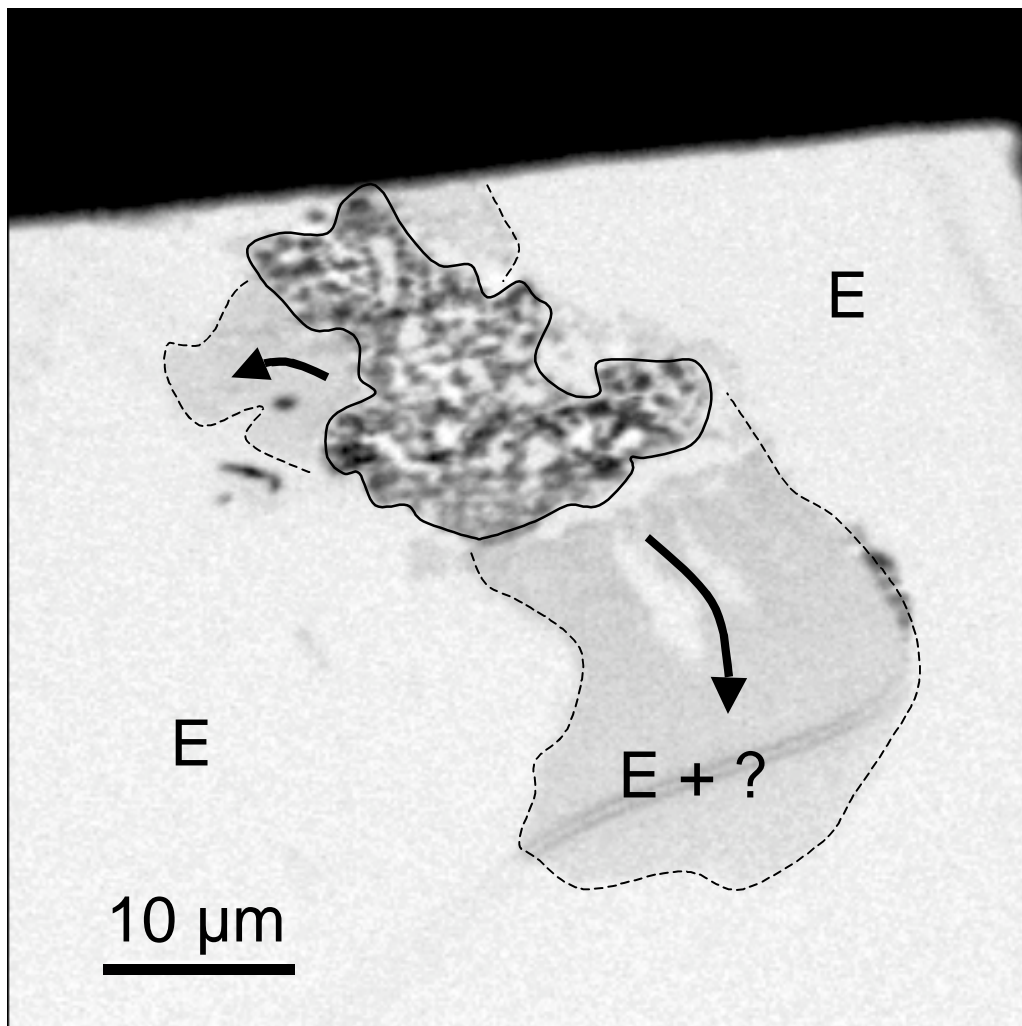


Figure 2



A

B

Figure 3

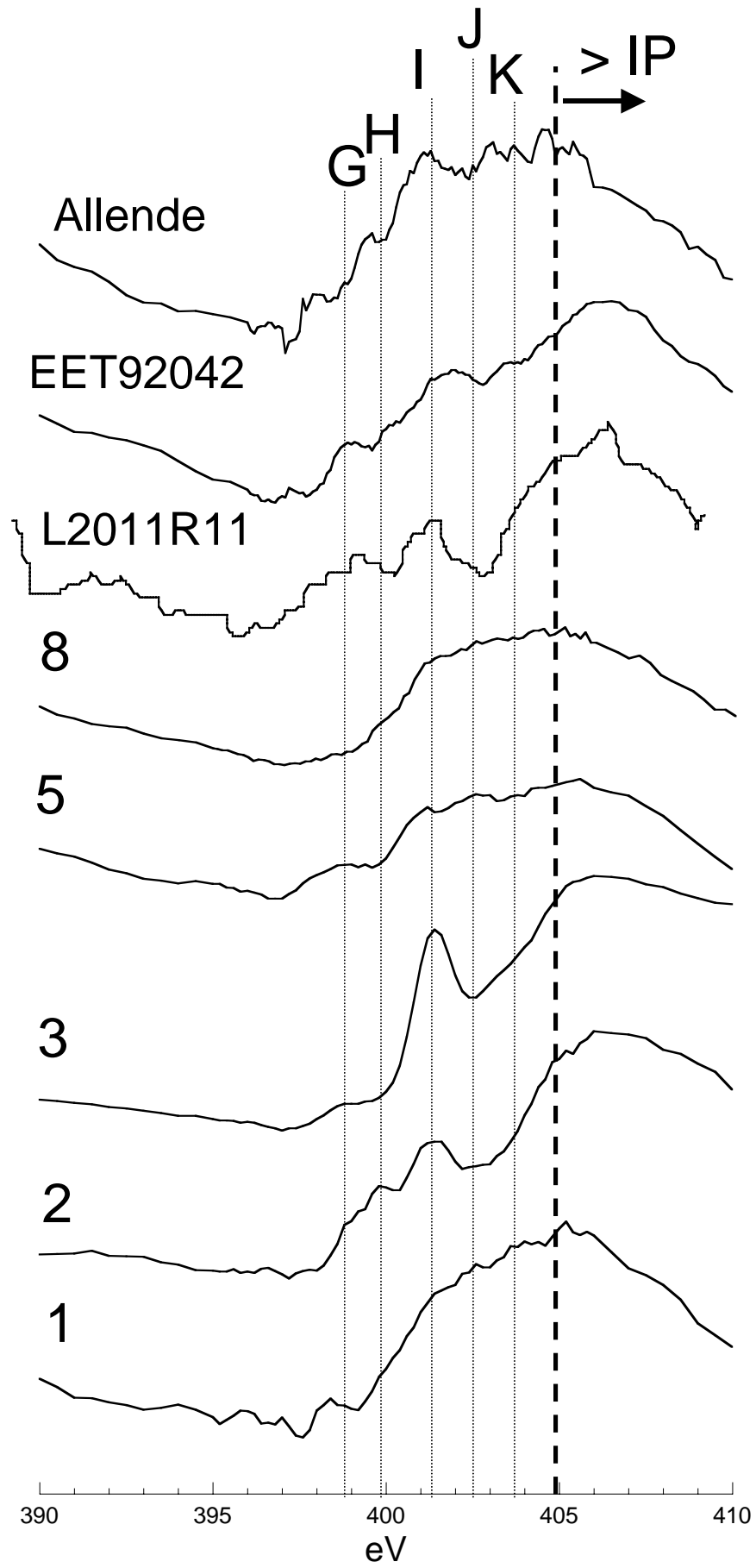


Figure 4

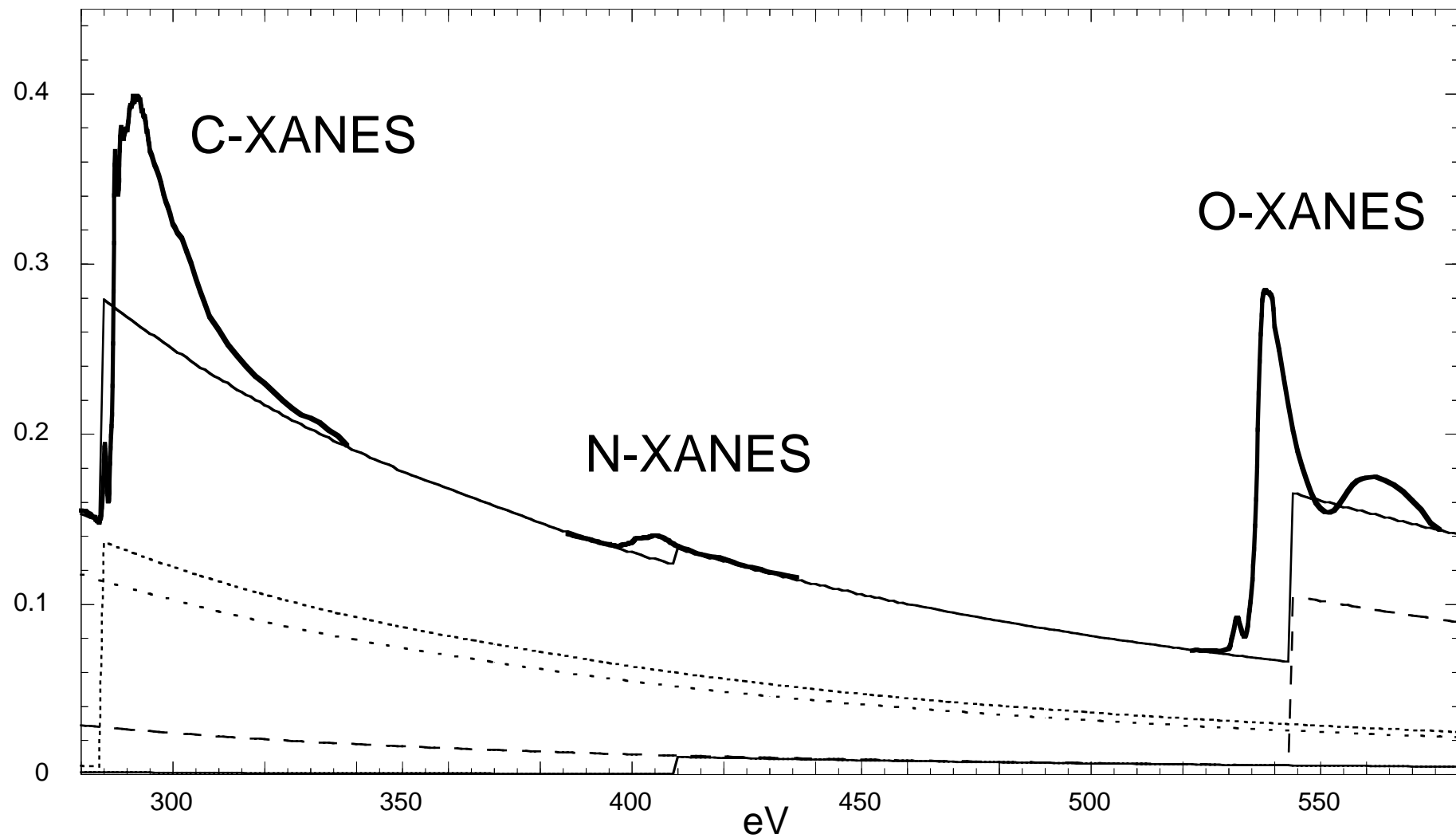


Figure 5



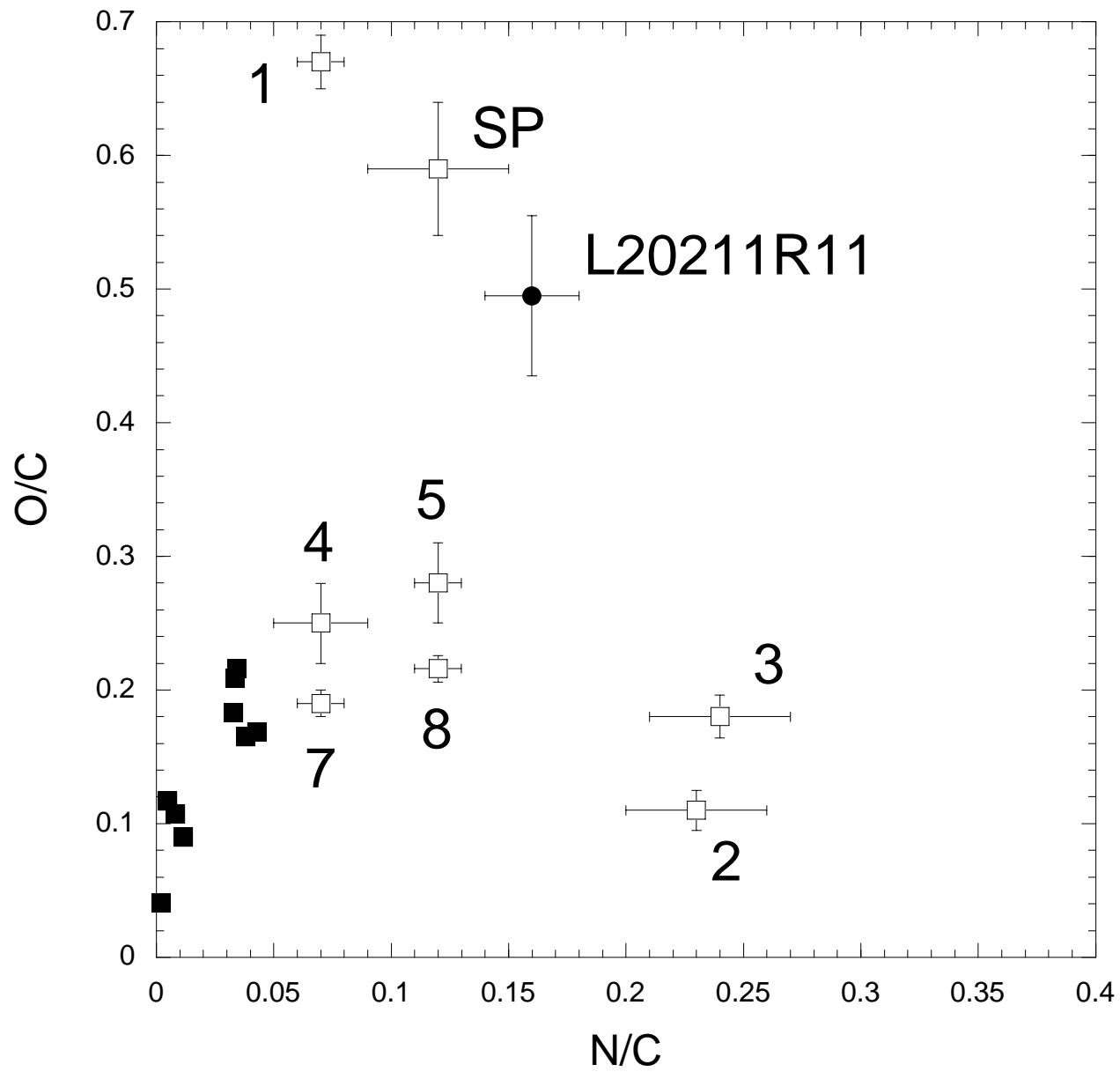
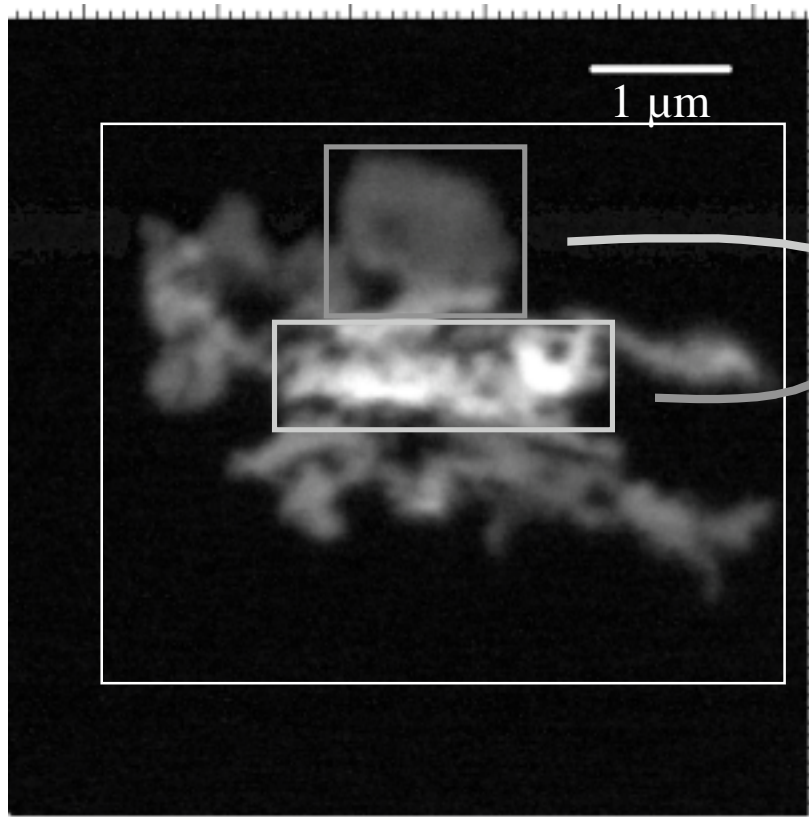
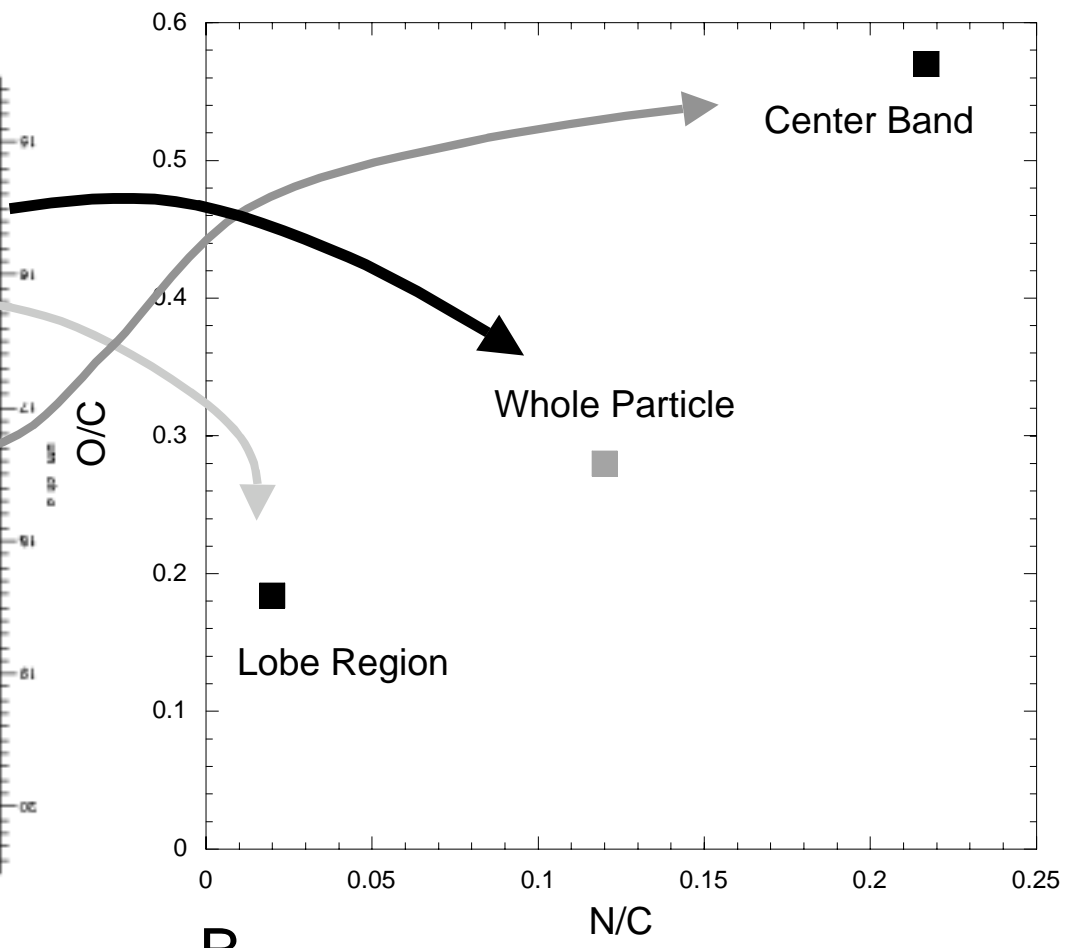


Figure 6



A

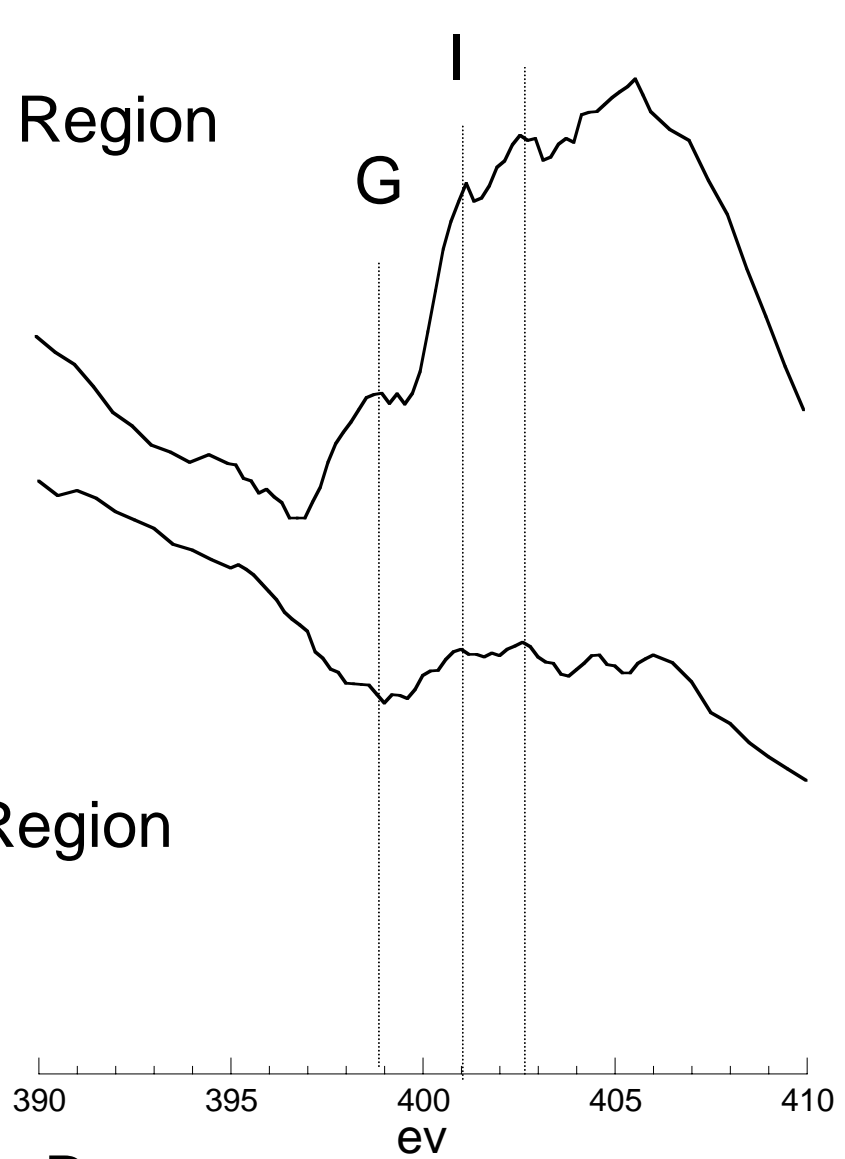
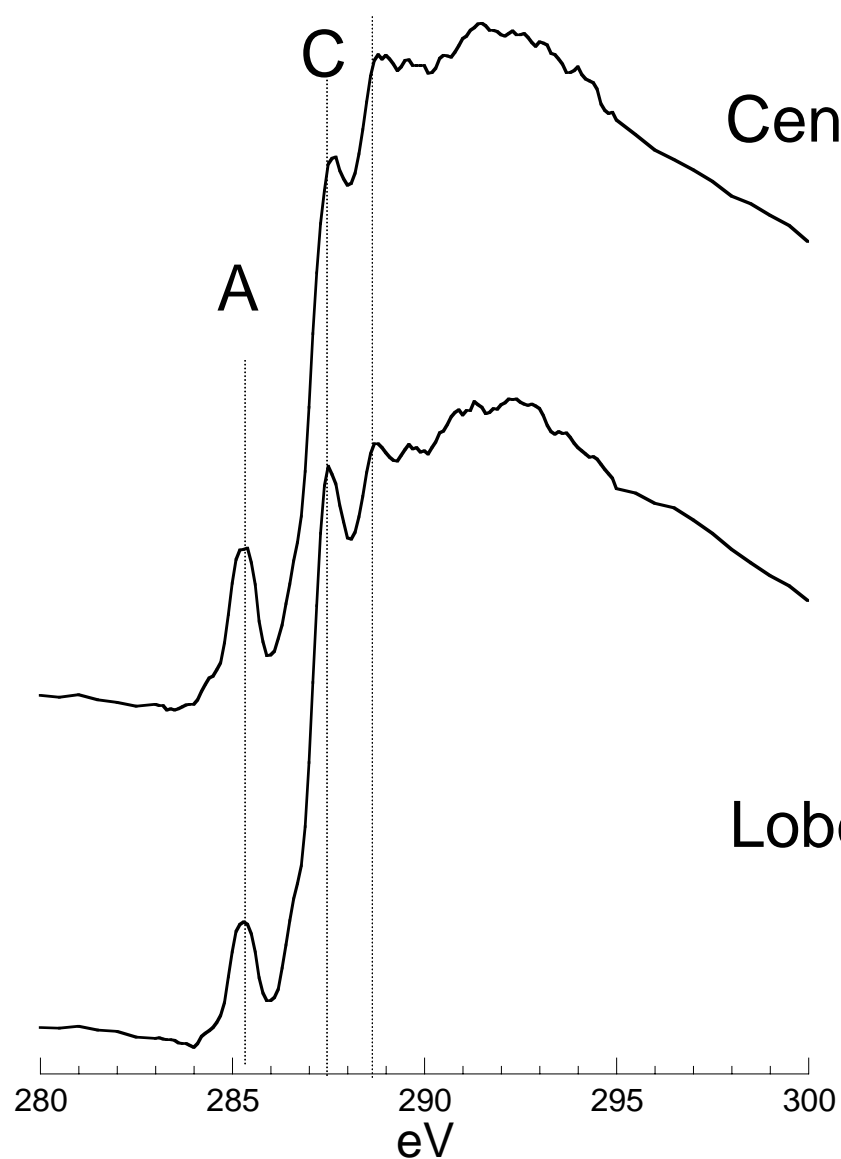


B

Figure 7

C-XANES

N-XANES



A

B

Figure 8