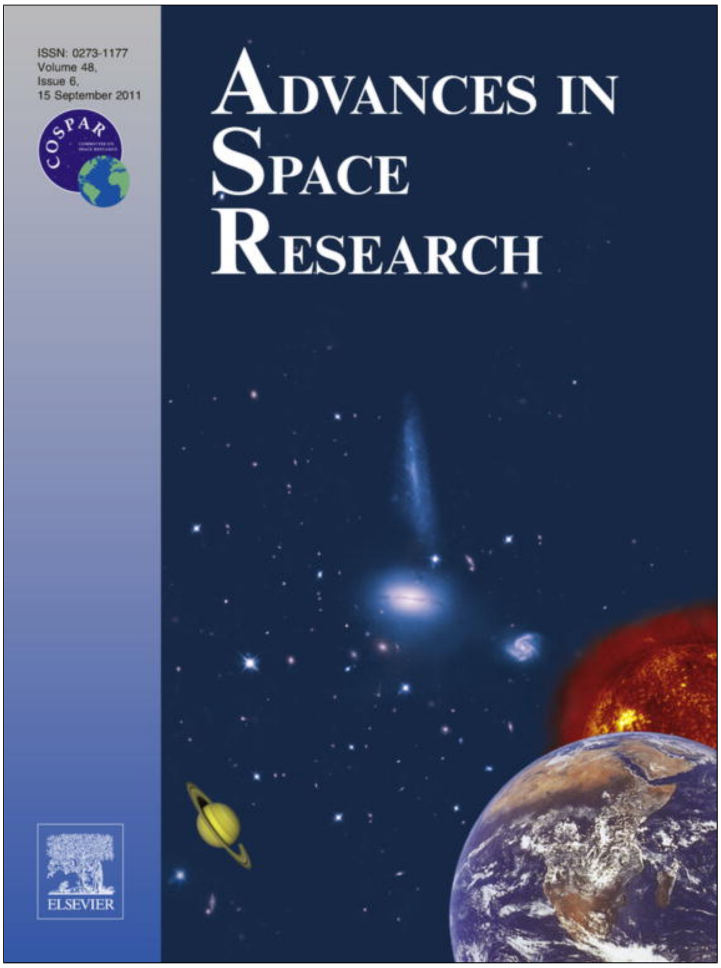
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XANES analysis of organic residues produced from the UV irradiation of astrophysical ice analogs

M. Nuevo [a,*], S.N. Milam [a,b,1], S.A. Sandford [a], B.T. De Gregorio [c,2], G.D. Cody [d], A.L.D. Kilcoyne [e]

[a] *NASA Ames Research Center, Mail Stop 245-6, Moffett Field, CA 94035, USA*
[b] *SETI Institute, 189 N. Bernardo Ave., Suite 100, Mountain View, CA 94043, USA*
[c] *Naval Research Laboratory, Code 6366, 4555 Overlook Ave. SW, Washington, DC 20375, USA*
[d] *Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. NW, Washington, DC 20015, USA*
[e] *Advanced Light Source, Lawrence Berkeley National Laboratory, 6 Cyclotron Rd., Berkeley, CA 94720, USA*

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Abstract

Organic residues formed in the laboratory from the ultraviolet (UV) photo-irradiation or ion bombardment of astrophysical ice analogs have been extensively studied for the last 15 years with a broad suite of techniques, including infrared (IR) and UV spectroscopies, as well as mass spectrometry. Analyses of these materials show that they consist of complex mixtures of organic compounds stable at room temperature, mostly soluble, that have not been fully characterized. However, the hydrolysis products of these residues have been partly identified using chromatography techniques, which indicate that they contain molecular precursors of prebiotic interest such as amino acids, nitrile-bearing compounds, and amphiphilic compounds. In this study, we present the first X-ray absorption near-edge structure (XANES) spectroscopy measurements of three organic residues made from the UV irradiation of ices having different starting compositions. XANES spectra confirm the presence of different chemical functions in these residues, and indicate that they are rich in nitrogen- and oxygen-bearing species. These data can be compared with XANES measurements of extraterrestrial materials. Finally, this study also shows how soft X rays can alter the chemical composition of samples.

Keywords: Ices; UV irradiation; XANES spectroscopy; Extraterrestrial materials

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1. Introduction

The origin of the organic molecules that constitute living organisms on Earth remains a mystery. Among the most studied scenarios are those encompassing an extraterrestrial origin of prebiotic molecules that were delivered to the early Earth by comets and meteorites (Chyba and Sagan, 1992; Oró, 1961). In such scenarios, organic species, including the building blocks of life and/or their precursors, are formed in the interstellar medium (ISM) at the surface of cold silicate and carbonaceous grains from the UV photo-irradiation and cosmic ray bombardment of condensed species such as H_2O, CO, CO_2, CH_3OH, and NH_3 (Allamandola et al., 1999; Dartois, 2005; Ehrenfreund and Charnley, 2000; Gibb et al., 2000, 2004). These organics are then incorporated into planetesimals, comets, and asteroids during the formation of the proto-planetary disk, at which time they could be further modified by nebular and parent-body processes before delivery to planets via meteoritic bombardment.

Experiments simulating such processes in which interstellar ice mixture analogs containing different combinations of

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* Corresponding author. Tel.: +1 6506040789; fax: +1 6506046779.
E-mail address: michel.nuevo-1@nasa.gov (M. Nuevo).

[1] Present address: NASA Goddard Space Flight Center, Code 691.0, 8800 Greenbelt Rd., Greenbelt, MD 20771, USA.

[2] Present address: NASA Johnson Space Center, Mail Code KT, 2101 NASA Pkwy., Houston, TX 77058, USA.

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H_2O, CO, CO_2, CH_3OH, NH_3, as well as HCN, O_2, and N_2 are irradiated either with UV photons or energetic protons have shown that organic molecules may be easily formed under astrophysical conditions, i.e., at low temperature (typically 10–20 K) and low pressure ($\leqslant 10^{-8}$ mbar) (Bernstein et al., 1995; Gerakines et al., 1996, 2001; Hudson and Moore, 1999; Muñoz Caro and Schutte, 2003). The organic residues that remain after warm up to room temperature have been extensively studied during the last 15 years using a variety of different analytical techniques including infrared (IR) and ultraviolet (UV) spectroscopies, mass spectrometry, and chromatography techniques such as high-performance liquid chromatography (HPLC) and gas chromatography coupled with mass spectrometry (GC–MS).

These laboratory residues have been shown to consist of a complex mixture of organic compounds with a mass distribution ranging from a few atomic mass units (amu) to ~350 amu (Dworkin et al., 2004). The chemical analysis of hydrolyzed residues showed that they release significant amounts of molecules of prebiotic/biological relevance, such as amino acids, the building blocks of proteins (Bernstein et al., 2002; Muñoz Caro et al., 2002; Nuevo et al., 2008), amphiphilic molecules (fatty acids), the constituents of membranes (Dworkin et al., 2001), and other molecules involved in biological processes such as urea and glycerol (Nuevo et al., 2010). When small aromatic species are mixed within the astrophysical ice analogs, molecules such as quinones (Bernstein et al., 1999) and nucleobases, the informational units of DNA and RNA (Nuevo et al., 2009), are also formed.

Many of these species have also been detected in extraterrestrial materials such as the Murchison carbonaceous chondrite (Briggs and Mamikunian, 1963; Cooper et al., 2001; Cronin and Pizzarello, 1999; Engel and Macko, 1997; Kvenvolden et al., 1970; Martins et al., 2006, 2008), and a few have been detected in cometary materials returned by the Stardust mission to Comet Wild 2 (Cody et al., 2008a; Elsila et al., 2009; Sandford et al., 2006). However, their detection in residues as well as in meteorites usually requires a chemical treatment that modifies the original composition of the material. Indeed, species such as amino acids are mainly detected after hydrolysis, and only small quantities of amino acids are detected before hydrolysis in meteorites (Shock and Schulte, 1990) and residues (Bernstein et al., 2002; Nuevo et al., 2008). Moreover, the directed search for a certain family of organic compounds gives only partial information on the full composition of the organic materials present, be they laboratory residues or extraterrestrial materials.

In order to assess the broader composition of such materials, various non-destructive spectroscopies are suitable techniques. Infrared spectroscopy of laboratory residues has confirmed their complexity by the presence of a broad variety of functional groups such as carboxylic acids, alcohols, aliphatic chains, aromatic chains, carbonyls, nitriles, esters, and amines (Bernstein et al., 1997; Muñoz Caro and Schutte, 2003; Nuevo et al., 2006). Similar IR signatures were found in extraterrestrial materials such as interplanetary dust particles (Matrajt et al., 2005; Muñoz Caro et al., 2006) and cometary grains from Stardust (Keller et al., 2006; Sandford et al., 2006), although silicate bands around 10 μm hide some of the information about their organic composition.

However, infrared spectroscopy does not give any quantitative information about the elemental abundances of the materials. X-ray absorption near-edge structure (XANES) spectroscopy is a tool that can assess both functional groups present in a sample and the relative abundances of key elements. This technique was first used in astrochemistry to analyze carbonaceous matter in very small (a few microns) particles such as interplanetary dust particles (IDPs) (Flynn et al., 2003; Keller et al., 2004; Wirick et al., 2009). More recently, XANES spectroscopy has been used to analyze cometary grains returned to Earth from Comet 81P/Wild 2 by the NASA Stardust mission (Brownlee et al., 2006; Cody et al., 2008a; De Gregorio et al., 2010; Matrajt et al., 2008; Sandford et al., 2006).

These analyses indicate the presence of oxygen-rich and nitrogen-rich organic materials, which contain a broad variety of functional groups (carbonyls, C=C bonds, aliphatic chains, amines, amides, etc.). Analyses of IDPs suggest that their organics are similar to the insoluble, highly aromatic organic material (IOM) seen in meteorites (Alexander et al., 2007; Cody et al., 2008b; Flynn et al., 2003). Wild 2 cometary samples are more varied and appear to contain material comparable to meteoritic IOM, as well as additional phases that are aromatic poor and more volatile (Sandford et al., 2006). The organic residues produced in laboratory experiments can potentially be compared with both the aromatic-poor and aromatic-rich extraterrestrial materials, but given their production from ices, one might expect laboratory residues to be more similar to the more volatile, aromatic-poor component seen only in the Wild 2 samples.

This work presents preliminary results obtained for the XANES spectroscopy analysis of three different organic residues produced in the laboratory under conditions simulating ice photochemistry in the ISM and/or the protosolar nebula. The analysis of the residues is focused on detecting the main organic chemical functions present in such materials as well as their elemental composition, in order to ultimately compare the data obtained with those of different types of extraterrestrial materials. Finally, the effects of the soft X-ray beam on our samples are also described and discussed.

2. Experimental set-up and protocol

The experimental set-up for the production of samples consisted of a vacuum chamber pumped to a few 10^{-8} mbar and cooled to 7 K with a closed-cycle helium cryocooler. Gas mixtures prepared previously in a glass line (background pressure: $\leqslant 10^{-5}$ mbar) were deposited on two transmission electronic microscopy (TEM) grids coated with SiO films (SPI Supplies) mounted onto a copper cold finger inside the vacuum chamber. Under these low pressure and temperature conditions, the gases froze on the grids and the holder to form a thin ice layer that was simultaneously photo-irradiated by a microwave-powered H_2 lamp emitting mainly UV photons at 121.6 nm (Lyman α) and a continuum centered around 160 nm with a flux of $\sim 2 \times 10^{15}$ photons s^{-1} cm^{-2} (Bernstein et al., 1999; Elsila et al., 2007). Therefore, in terms of UV photon dose, a typical experiment in which ices were irradiated for 7–8 h corresponds to about 6–7 × 10^3 years of irradiation in the diffuse ISM, and several 10^6–10^7 years of irradiation in dense interstellar environments (Mathis et al., 1983; Shen et al., 2004).

All gas mixtures chosen for our experiments contained H_2O, CH_3OH, CO, and NH_3 in relative proportions similar to their abundances in the ISM and comets, and with comparable total-ice N/C and O/C ratios (Allamandola et al., 1999; Dartois, 2005; Ehrenfreund and Charnley, 2000; Gibb et al., 2000, 2004). Three different ice mixtures were prepared and irradiated. One contained only these components: $H_2O:CH_3OH:CO:NH_3 = 100:50:1:1$ (hereafter referred to as M1), one had an added aliphatic component: $H_2O:CH_3OH:CO:NH_3:C_3H_8 = 100:50:1:1:10$ (same as M1 plus 10% of propane, hereafter referred to as M2), and the last one had an added aromatic component: $H_2O:CH_3OH:CO:NH_3:C_{10}H_8 = 100:50:1:1:1$ (same as M1 plus 1% of naphthalene, hereafter referred to as M3). H_2O was purified to an 18.2 MΩ cm resistivity by a Millipore Direct-Q UV 3 device, CH_3OH (liquid) was purchased from Aldrich (Chromasolv®, ⩾99.9% purity), CO (gas) from Matheson (CP grade, 99.5% purity), NH_3 (gas) from Matheson (anhydrous, 99.99% purity), C_3H_8 (gas) from Matheson (Instrument grade, 99.5% purity), and $C_{10}H_8$ (powder) from Aldrich (⩾99.0% purity). Mixtures M2 and M3, which contained 10% of propane (C_3H_8) and 1% of naphthalene ($C_{10}H_8$), respectively, were irradiated in order to assess the importance of the addition of aliphatic and aromatic hydrocarbon species in the starting ices, and their effect on the resulting signatures in the XANES spectra of the final residues.

After irradiation, samples were warmed to room temperature and the grids, covered with freshly-produced organic residues, were removed from their holder and kept in a closed grid holder for further analysis. For mixture M1, only one TEM grid was removed at room temperature after UV irradiation at 7 K and warm-up. The other grid was further UV irradiated with the same lamp for 3 additional days under vacuum at ~300 K. This post-photolysis was aimed at evaluating the chemical changes caused by subsequent irradiation of the residues after sublimation of the original remaining ices.

Finally, all the residues were analyzed with a scanning transmission X-ray microscope (STXM) installed on beamline 5.3.2 of the Advanced Light Source (ALS) of the Lawrence Berkeley Laboratory, California, USA (Kilcoyne et al., 2003; Warwick et al., 2002), providing photons in the 250–700 eV range with a 10^7 photons s^{-1} flux (Cody et al., 2008a). XANES spectra of several areas of each residue were recorded using the line scan mode in the 275–580 eV energy range in order to span the carbon, nitrogen, and oxygen 1s X-ray absorption edges at about 275–340, 385–440, and 520–580 eV, respectively, with an energy step size (ΔE) of 0.1 eV in the fine structure regions, and 1–2 eV in the pre- and post-edge regions. The acquisition of all three ionization edges in a single spectrum allowed us to determine the relative contributions of each element from known mass absorption coefficient curves (Henke et al., 1993) using the approach described by Cody et al. (2008a). All STXM data were reduced and analyzed with the aXis 2000 software.[3]

The structures of the residues on the SiO films, revealed by their X-ray absorption images at a given energy, appeared to look like droplets (Fig. 1) and were chosen to be analyzed according to their shape and thickness. In such absorption images, the optical density, or absorbance (A), is related to the absorption cross section (σ), the sample density in atoms per unit volume (ρ), and the material thickness (z) via (De Gregorio et al., 2011; Stöhr, 1992):

$$A = \ln \frac{I_0}{I} = \rho \sigma z, \qquad (1)$$

where I_0 and I are the incident and transmitted X-ray beam intensities, respectively. This equation indicates that within a single X-ray absorption image, relative absorbances between structures are directly related to their thicknesses.

3. Results and applications

3.1. Organic composition of the residues

The organic residues formed from the irradiation of the ice mixtures M1–M3 consist of droplet-like structures scattered all over the SiO films of the TEM grids. In some cases, parts of the SiO films were torn from the grids, due to UV photons and/or strains related to temperature changes during the warm-up from 7 to 300 K. X-ray absorption images at 390 eV of representative droplets for each of the three UV-irradiated mixture M1, M2, and M3 are shown in Fig. 1. The corresponding C-, N-, and O-XANES spectra of one representative droplet of each residue M1–M3 are given in Fig. 2 (full 275–580 eV range) and Fig. 3 (individual C-, N-, and O-XANES ranges).

Fig. 2 indicates that all three residues show significant contributions from C-, N-, and O-bearing organics, although the relative absorptions of the three edges vary with the composition of the starting mixture. These spectra also show that nitrogen is very efficiently incorporated into the residues under our experimental conditions, although

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[3] aXis 2000 is written in Interactive Data Language (IDL) and available for free for non-commercial use from http://unicorn.mcmaster.ca/aXis2000.html.

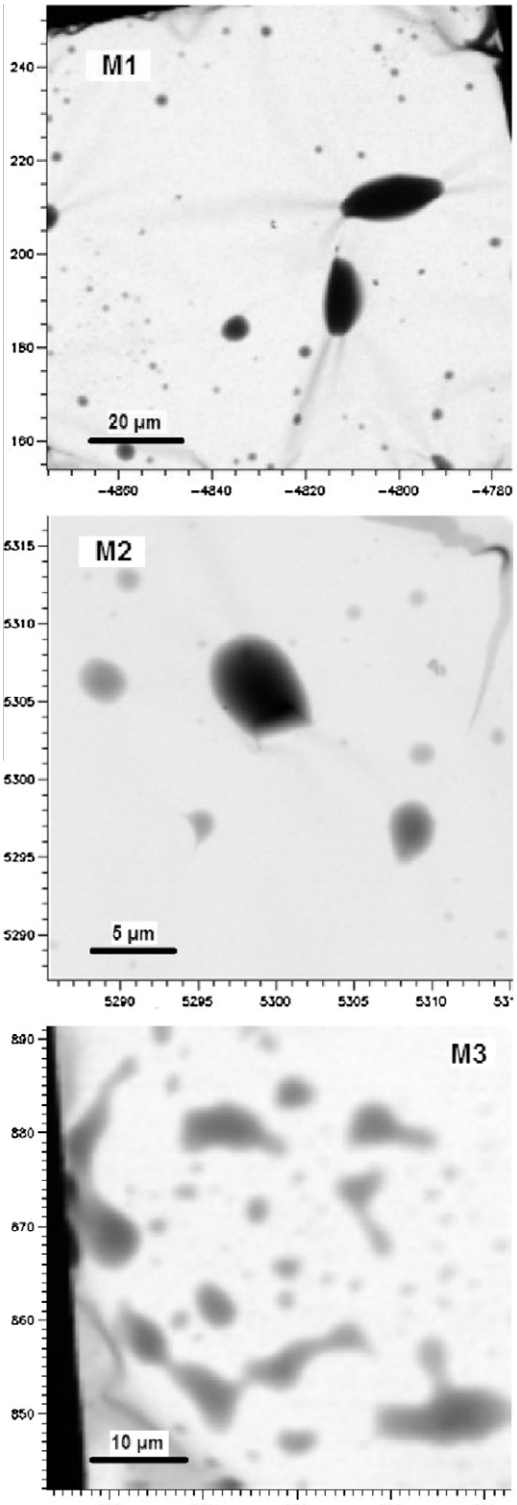

Fig. 1. X-ray absorption images at 390 eV of small sample areas chosen for the three organic residues studied in this work, produced from the UV irradiation of the M1 (H_2O:CH_3OH:CO:NH_3 = 100:50:1:1), M2 (H_2O:CH_3OH:CO:NH_3:C_3H_8 = 100:50:1:1:10), and M3 (H_2O:CH_3OH:CO:NH_3:$C_{10}H_8$ = 100:50:1:1:1) ice mixtures.

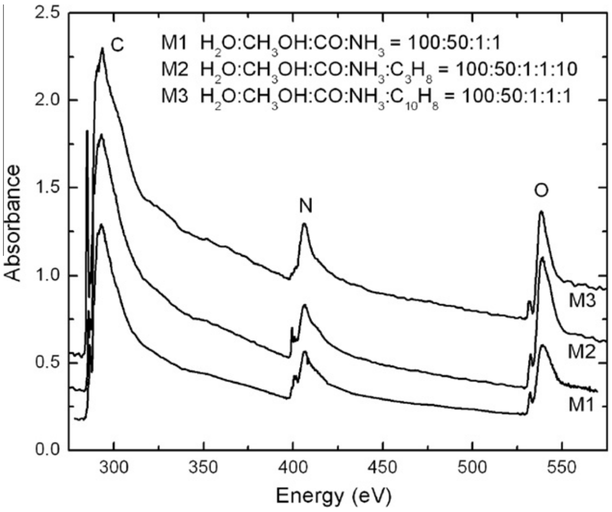

Fig. 2. Full-range XANES spectra of representative droplets of residues M1–M3 covering the C-, N-, and O- edge ranges (275–580 eV). They all show significant contributions from C-, N-, and O-bearing organics.

the relative proportion of NH_3, the only source of nitrogen in the starting mixtures, is low compared with those of H_2O and CH_3OH (see also Table 2). Indeed, the contribution from the N edge appears to be of the same order of magnitude as the C and O edges. The derivation of the N/C and O/C elemental ratios confirms the high abundances of N and O in the residues (see Section 3.3).

The C-, N-, and O-XANES spectra of the three residues (Fig. 3) show several bands assigned to organic moieties that are listed in Table 1 (Cody et al., 2008a; De Gregorio et al., 2011). The C-XANES spectra of all residues (Fig. 3a) share two common features, namely, a band at 286.6 eV (labeled C3) assigned to nitrile groups (C≡N) and/or ketones (C=O), and a band at 287.4 eV (C4) assigned to aliphatic carbon chains. Other C-XANES bands at 285.8 (C2) and 288.7 eV (C5) are due to the presence of imine (C=N) and carboxyl (O—C=O) groups, respectively. The C-XANES spectrum of residue M3 displays a unique, intense band at 285.1 eV (C1), assigned to aromatic carbon, and mainly due to naphthalene in the starting ice, as well as probably some of its aromatic photoproducts. The absence of such a band in the spectra of samples M1 and M2 indicates that the abundance of aromatic compounds formed from non-aromatic starting ices under our experimental conditions in the residues is very small.

N-XANES spectra (Fig. 3b) support the presence of nitriles in the residues through a band at 399.3 eV (N2). This band is red-shifted to 398.8 eV in M3 (N1), confirming the presence of imine (C=N) bonds. The band at 400.7 eV (N3) has tentatively been assigned to protonated imines ($C{=}NH^+$), while the band at 401.7 eV (N4) is due to the presence of amide ($O{=}C{-}NH_x$) and/or urea groups ($(NH_x)_2CO$). Finally, O-XANES spectra (Fig. 3c) confirm the presence of ketones (C=O, 531.3 eV, band O1) and carboxyl groups (O—C=O, 532.2 eV, band O2) in various proportions.

Weaker features were also tentatively identified in C-XANES spectra. They include a band at 289.5–289.7 eV present in all three residues, which may be attributed to

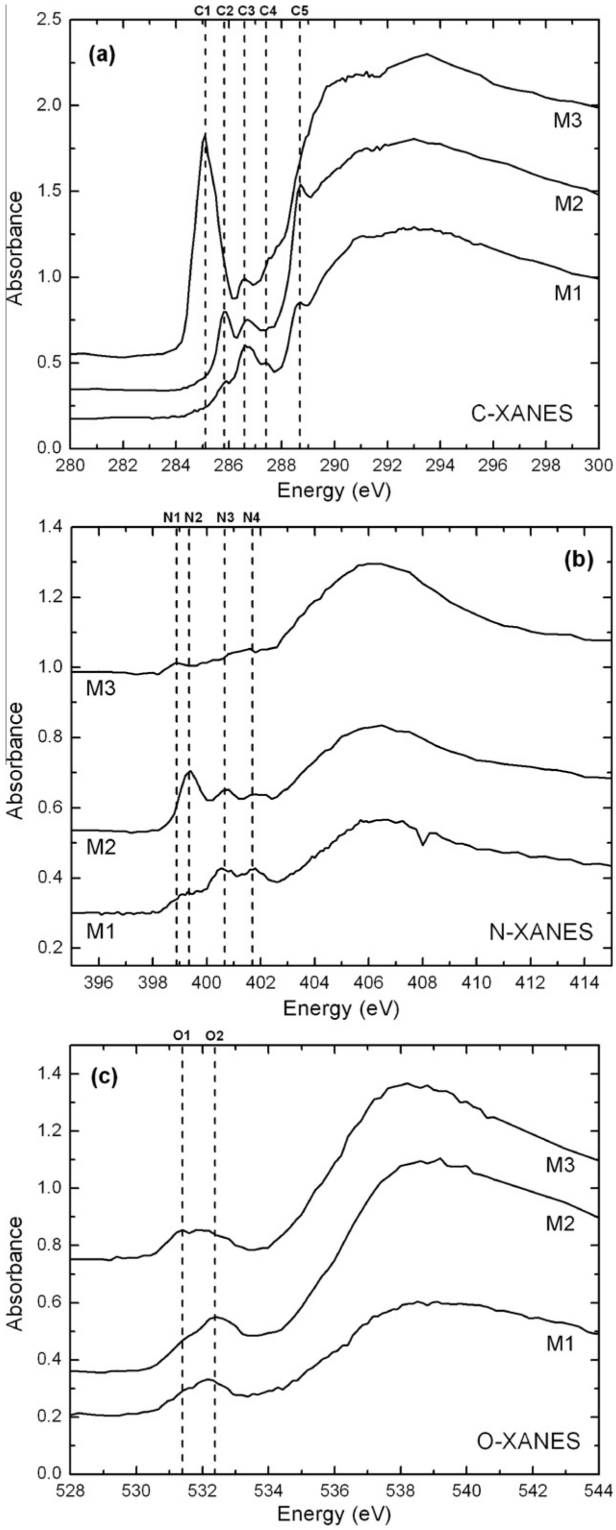

Fig. 3. XANES spectra in the **(a)** C, **(b)** N, and **(c)** O edges of representative droplets of residues M1–M3. Assignments of the bands are given in Table 1.

Table 1
Assignments of the XANES bands observed in the spectra of residues M1–M3[*].

	Band	Energy (eV)	Assignment	Transition
Carbon edge	C1	285.1	Aromatic C=C[a]	$1s \rightarrow \pi^*$
	C2	285.8	Imine C=N[b,c]	$1s \rightarrow \pi^*$
	C3	286.6	Nitrile C≡N[b,d,e]	$1s \rightarrow \pi^*$
			Ketone C=O[f,g]	$1s \rightarrow \pi^*$
	C4	287.4	Aliphatic C—C[f,h]	$1s \rightarrow 3p/s$
	C5	288.7	Carboxyl O=C-O[g]	$1s \rightarrow \pi^*$
Nitrogen edge	N1	398.8	Imine C=N[d,i]	$1s \rightarrow \pi^*$
	N2	399.3	Nitrile C≡N[c,i]	$1s \rightarrow \pi^*$
	N3	400.7	Protonated imine $C{=}NH^{+}$[j]	$1s \rightarrow \pi^*$
	N4	401.7	Amide O=C–NH_x[i,k]	$1s \rightarrow \pi^*$
			Urea group $(NH_x)_2CO$[l]	$1s \rightarrow 3p/s$
Oxygen edge	O1	531.3	Carbonyl C=O[f,g]	$1s \rightarrow \pi^*$
	O2	532.2	Carboxyl O=C—O[k]	$1s \rightarrow \pi^*$

[a] Stöhr, 1992.
[b] Dhez et al., 2003.
[c] Shard et al., 2004.
[d] Apen et al., 1993.
[e] Kikuma et al., 1998.
[f] Hitchcock and Brion, 1980.
[g] Urquhart and Ade, 2002.
[h] Ishii and Hitchcock, 1988.
[i] Leinweber et al., 2007.
[j] Hennig et al., 1998.
[k] Gordon et al., 2003.
[l] Urquhart et al., 1995.
[*] Adapted from Cody et al. (2008a) and De Gregorio et al. (2011).

urea groups ($(NH_x)_2CO$) (Urquhart and Ade, 2002; Urquhart et al., 1995), and thus support the identification of the band at 401.7 eV (N4) in the N-XANES spectra, and a band at 289.2 eV in the C-XANES spectrum of residue M3, which may be assigned to C–O bonds in alcohols or ethers (Ishii and Hitchcock, 1988).

Figure 4 shows a 390-eV X-ray absorption image of a small area of residue M2 on which several droplets of different thicknesses are clearly visible. Among those droplets, which are representative of the entire sample on this grid, we chose two of them, labeled droplets 1 and 2, and obtained full-range XANES spectra across the C, N, and O edges (Fig. 5). Since droplet 1 is relatively thick, the XANES spectrum acquired from the center of the droplet (top trace) shows an overall increase in absorption in the C, N, and O edges, relative to the edge of the droplet (middle trace). However, the flattening in the C edge between 290 and 310 eV (top trace) suggests that the XANES detector has reached, or is nearing, saturation. Therefore, this spectrum is not as reliable an indicator of the residue chemistry as the spectrum acquired from the edge of droplet 1. Droplet 2, on the other hand, is relatively thin, and its XANES spectrum (bottom trace) is very similar to that of the thin edge of droplet 1.

Absorption bands in the carbon edge for the inner part of droplet 1, its edge, and droplet 2 are fully comparable (Fig. 5). They include bands at 285.7 (C2), 286.6 (C3), and 288.7 eV (C5), assigned to imines, nitriles and/or ketones, and carbonyl groups, respectively (see Table 1). N-XANES spectra display bands at 399.2 (N2), 400.5 (N3), and 401.7 eV (N4), assigned to nitriles, protonated

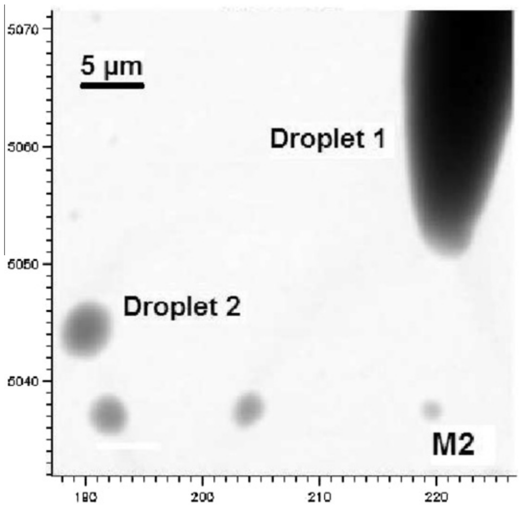

Fig. 4. X-ray absorption image at 390 eV of a portion of residue M2, for which two droplets of different thicknesses were scanned. The XANES spectra of the edge and inner part of droplet 1 (thick) and of droplet 2 (thin) are shown in Fig. 5.

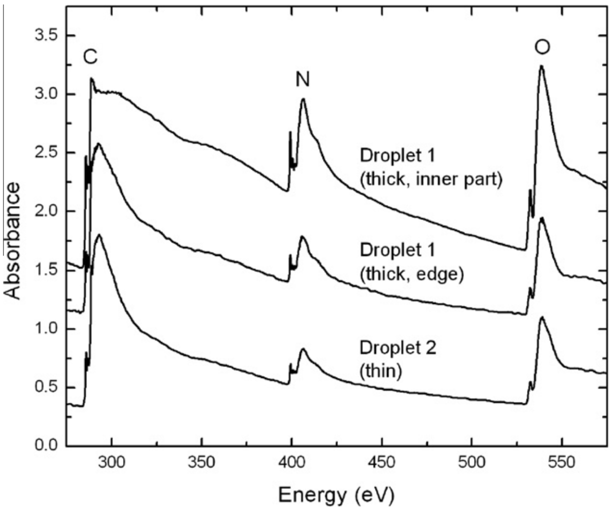

Fig. 5. Full-range XANES spectra of the inner part of droplet 1 (top trace), its edge (middle trace), and droplet 2 (bottom trace) from residue M2, shown in Fig. 4. Spectra were offset in absorbance for clarity.

imines (tentative), and amide and/or urea groups, respectively, as discussed previously. Finally, XANES spectra of both parts of droplet 1 and droplet 2 in the oxygen edge show a main band at 532.2 eV (O2), assigned to carboxyl groups. Additional spectra obtained from other droplet-like structures of residue M2 show strong similarities with those given in Fig. 5. Thus, a given sample appears to have a homogeneous organic composition, with droplets consisting of the same material and showing no evidence of phase separation formed during ice warm-up.

In summary, C-, N-, and O-XANES spectra of residues M1–M3 indicate the presence of a large variety of chemical bonds, in agreement with previous IR spectroscopy results (Bernstein et al., 1997; Muñoz Caro and Schutte, 2003; Nuevo et al., 2006). Features due to aromatic and aliphatic carbon appear to be easy to detect and distinguish from each other with XANES spectroscopy, giving important information on the nature of the macromolecular structure of the residues. In particular, the C-XANES spectra of residues M1 and M2 suggest that only very small quantities of aromatic compounds are formed when the starting ice mixtures do not originally contain any aromatic species. The analysis of additional residues produced from the UV irradiation of ices of different composition and/or different relative proportions between the components will allow us to determine how such differences in the initial composition of the ices affect the measured XANES spectra, and which features dominate others.

Finally, the XANES spectra of the material recovered on the second grid of M1 that was post-photolyzed after warm-up for 3 days at room temperature did not show significant differences compared with the residue on the first grid that was not post-photolyzed, suggesting that further UV photolysis does not rapidly alter the warmed-up residue. However, the same is not true of additional soft X-ray exposure.

3.2. Effects of post-warm-up irradiation of the samples

While STXM is a powerful tool to analyze the organic composition of small samples such as our organic residues, it also has some drawbacks. In particular, the use of a soft X-ray beam can induce unwanted chemical changes in residue samples, which may lead to sample degradation. Such an effect for carbonaceous materials has previously been reported and studied in the literature (Attwood, 2007; Cody et al., 2009; Wirick et al., 2009).

A critical parameter is the photon dose, which can be controlled by adjusting the dwell time, i.e., the time spent with the beam focused on one point or line of a sample. Increasing the dwell time for a given scan increases the number of X-ray photon interactions with the samples, and thus increases the likelihood of damage or further chemical changes altering the composition of the residues. Such damage to our samples can be clearly observed in their microscope X-ray absorption images, as shown on a droplet of residue M1 (Fig. 6), as well as in their C-XANES spectra (Fig. 7). In this particular case, the STXM image was obtained at 530 eV, so that the damage lines correspond to an overall loss in C, N, and O.

The XANES analyses presented here were obtained using the STXM line scan mode, so that the same predetermined line on one droplet of a given sample is scanned for each energy increment, from 275 eV (carbon photo-absorption pre-edge) to 580 eV (oxygen photo-absorption post-edge). In most cases, dwell times smaller than 1 ms were chosen in order to reduce the total scanning time, and thus the X-ray exposure, to avoid damage-induced changes to the samples.

The solid trace in Fig. 7 corresponds to the C-XANES spectrum of the droplet shown in Fig. 6 measured with a dwell time of 1 ms. The dashed trace

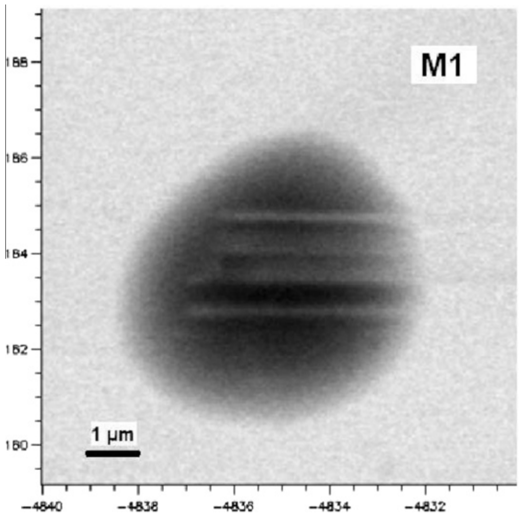

Fig. 6. X-ray absorption image at 530 eV of one droplet of residue M1 that has been analyzed by multiple horizontal line scans, and which clearly shows linear damage regions created by the interaction of the sample with the X-ray beam during STXM measurement for dwell times higher than 1–2 ms.

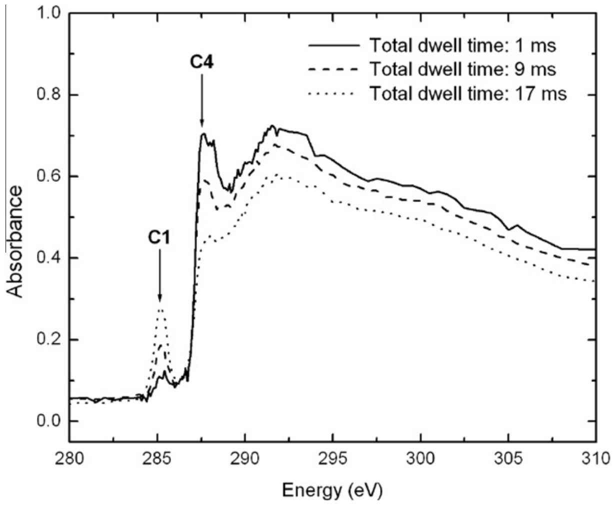

Fig. 7. C-XANES spectra of the droplet shown in Fig. 6 (residue M1) for 3 increasing dwell times: 1 ms (solid line), 9 ms (dashed line), and 17 ms (dotted line). The spectra clearly show that soft X rays alter the organic composition of the residue by converting aliphatic carbon (band C4, 287.4 eV) into aromatic carbon (band C1, 285.1 eV).

corresponds to a subsequent C-XANES spectrum acquired in the same location with an additional 8-ms dwell time, so that the total functional dwell time is 9 ms. Finally, the dotted trace corresponds to an additional 8-ms scan, representing an overall dwell time of 17 ms. These C-XANES spectra clearly show that band C4 (287.4 eV), assigned to aliphatic carbon, significantly decreases in intensity, while band C1 (285.1 eV), assigned to aromatic carbon, increases simulaneously with X-ray dose. Also, it appears on the spectra that the overall C abundance decreases with X-ray exposure, indicating a measurable loss of sample mass.

Therefore, one significant effect of excess X rays on samples is to modify their chemical composition by converting aliphatic carbon into aromatic carbon. A similar effect was not observed for UV irradiation for sample M1 that was subject to 3 days of additional UV exposure after warm up, implying that the photon energy is a critical parameter and not only the total fluence. Although damages due to X-ray beams have been previously reported for carbonaceous materials (Attwood, 2007; Cody et al., 2009; Wirick et al., 2009), our study more specificly highlights the effect of such radiation on the structure of carbonaceous compounds of astrochemical/astrobiological interest. This information is essential to understand the evolution of organics and their interaction with X-ray fields from the environment where they were formed to their incorporation into primitive objects of the Solar System such as asteroids and comets.

3.3. Determination of N/C and O/C ratios

The overall increase in absorption above the ionization edges relative to the absorption below the ionization edges allow us to determine the relative elemental abundances of C, N, and O in each sample. Such measurements are possible for low-*Z* elements, for which absorption in the soft X-ray range is dominated by photo-ionization cross sections, and for which atomic scattering is very weak (Stöhr, 1992). Quantitative estimates of N/C and O/C ratios were performed by fitting the full-range spectra with the atomic mass absorption coefficients given by Henke et al. (1993), and using an updated version of the computational model spectra described in Cody et al. (2008a) to fit our experimental data.

The N/C and O/C ratios of the scanned droplets of residues M1, M2, and M3, whose XANES spectra are shown in Fig. 2, are reported in Table 2. Uncertainties on these values vary from 3 to 17%. N/C ratios were found to be 0.28, 0.23, and 0.11 for M1, M2, and M3, respectively, which is 7–16 times higher than the ratios in the starting mixtures, and indicates that N is very efficiently incorporated into organic molecules during their formation. In contrast, O/C ratios were found to be 0.51, 0.61, and 0.43 for M1, M2, and M3, respectively, i.e., a reduction of 3–6 times compared with the initial mixtures, which suggests that significant quantities of oxygen are lost during the formation of organic compounds, maybe via sublimation of oxygen-rich gases such as O_2, CO, or CO_2 during the warm-up to room temperature. In all cases, although they vary from one sample to another, these ratios clearly indicate that laboratory organic residues are both very rich in nitrogen- and oxygen-bearing species, as supported by the presence of several bands assigned to chemical groups involving C-N and C-O bonds in the XANES spectra (see Fig. 3 and Table 1).

3.4. Comparison with extraterrestrial materials

Comparison of these data with previous XANES measurements reported in the literature for extraterrestrial

Table 2
Calculated N/C and O/C ratios for the initial ice mixtures M1–M3, and their respective residues formed after UV photo-irradiation.

Sample	N/C			O/C		
	Ice	Residue	Evolution	Ice	Residue	Evolution
M1	0.020	0.28 ± 0.05	× 14.0	2.961	0.51 ± 0.06	/5.8
M2	0.012	0.23 ± 0.02	× 16.0	1.864	0.61 ± 0.03	/3.1
M3	0.016	0.11 ± 0.01	× 7.1	2.475	0.43 ± 0.01	/5.8

materials such as the Murchison meteorite (Alexander et al., 2007; Cody et al., 2008b) and cometary particles from Stardust (Cody et al., 2008a; Sandford et al., 2006) leads to several conclusions. First, it is clear that UV photolysis of non-aromatic astrophysical ice mixtures (M1 and M2) does not result in the production of significant amounts of aromatic materials in the final residues. Thus, these materials and processes clearly cannot be the source of meteoritic insoluble organic material (IOM). However, the post-warm-up X-ray exposure of the residues (see Figs. 6 and 7) and/or the addition of aromatics to the starting ice mixture (M3) can result in the presence of aromatic carbon features in the XANES spectra of the final residues. Additional work will be required to determine if either of these processes can ultimately lead to materials that look like meteoritic IOM.

The current residues also do not match exactly the aromatic-poor fractions of the organic materials seen in some Comet Wild 2 samples, while residues M1 and M2 have similar low aromatic contents and show many of the same functional groups. The N/C ratios measured in our laboratory residues are about up to 2 times higher than measured in cometary particles, while their O/C ratios are about 1.5–2 times higher. Compared with the analysis of several types of meteorites, N/C and O/C ratios are about 5–12 and 2–3 times higher in our laboratory residues than in meteoritic residues. These differences may be explained by the fact that several compounds such as CO_2, HCN, CH_4, or other hydrocarbons including PAHs are missing in the composition of the starting ice mixtures. Such additional species could reduce the bulk N/C and O/C ratios and match better astronomical observations of the ISM and comets (Allamandola et al., 1999; Dartois, 2005; Ehrenfreund and Charnley, 2000; Gibb et al., 2004) as well as analyses of cometary particles (Cody et al., 2008a; Sandford et al., 2006) and meteorites (Alexander et al., 2007).

In future laboratory experiments we will continue to examine how the composition of the starting ice mixtures affects the final products and their similarities or dissimilarities with the organics in meteorites, cometary particles, and IDPs.

4. Conclusions

C-, N-, and O-XANES spectra of organic residues produced in the laboratory from the UV irradiation of three different ice mixtures show a diversity of photo-absorption bands due to various chemical functions such as aromatic and aliphatic carbon bonds, and several types of carbonyl and nitrogen-bearing functional groups. The organic makeup of these residues varies significantly with the composition of the starting mixture, although individual residues appear to be homogeneous.

Residues formed from the UV photolysis of ices that do not originally contain aromatic species do not contain significant amounts of new aromatic material, and thus do not look like meteoritic IOM. The addition of aromatic species to the starting ices and/or post-warm-up X-ray irradiation of the residues can however result in materials with aromatic contributions more similar to meteoritic IOM. Residues made from non-aromatic ices produce many chemical functions seen in the aromatic-poor organics observed in some Wild 2 cometary particles.

In addition, the elemental N/C and O/C ratios of laboratory residues, derived from the full-range XANES spectra, were found to be higher than in extraterrestrial materials, ranging from 0.11 to 0.28 for N/C, and from 0.43 to 0.61 for O/C. This result indicates that laboratory residues are very rich in nitrogen and oxygen compared with XANES measurements of meteorites and cometary particles. Finally, it was shown that one must be cautious when using STXM to analyze samples since it can significantly alter their chemical composition, for instance by converting aliphatic carbon into aromatic carbon when samples are exposed to an excess X-ray dose.

Further studies will focus on comparing the effect of post-warm-up exposure of the residues to UV photons and X rays, in order to simulate radiation in astrophysical environments and their interaction with organic species during the full cycle of evolution of interstellar matter. In addition, several starting mixtures will be irradiated, analyzed, and their XANES spectra compared with data obtained for extraterrestrial materials such as cometary particles collected by Stardust, interplanetary dust particles collected in the Earth's upper atmosphere, and meteorites.

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