The origin of organic matter in the solar system: Evidence from the interplanetary dust particles

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Abstract—The detailed examination of meteorites and interplanetary dust particles provides an opportunity to infer the origin of the organic matter found in primitive Solar System materials. If this organic matter were produced by aqueous alteration of elemental (graphitic or amorphous) carbon on an asteroid, then we would expect to see the organic matter occurring preferentially in interplanetary materials that exhibit evidence of aqueous activity, such as the presence of hydrated silicates. On the other hand, if the organic matter were produced either during the nebula phase of Solar System evolution or in the interstellar medium, we might expect this organic matter to be incorporated into the dust as it formed. In that case pre-biotic organic matter would be present in both the anhydrous and the hydrated interplanetary materials. We have performed carbon X-ray absorption near-edge structure spectroscopy and infrared spectroscopy on primitive anhydrous and hydrated interplanetary dust particles (IDPs) collected by NASA from the Earth's stratosphere. We find that organic matter is present in similar types and abundances in both the anhydrous and the hydrated IDPs, and, in the anhydrous IDPs some of this organic matter is the "glue" that holds grains together. These measurements provide the first direct, experimental evidence from the comparison of extraterrestrial samples that the bulk of the pre-biotic organic matter occurs in similar types and abundances in both hydrated and anhydrous samples. This indicates that the bulk of the pre-biotic organic matter in the Solar System did not form by aqueous processing, but, instead, had already formed at the time that primitive, anhydrous dust was being assembled. Thus, the bulk of the pre-biotic organic matter in the Solar System was formed by non-aqueous processing, occurring in either the Solar nebula or in an interstellar environment. Aqueous processing on asteroids may have altered this pre-existing organic matter, but such processing did not affect in any substantial way the C=O content of the organic matter, the aliphatic C-H abundance, or the mean aliphatic chain length. *Copyright © 2003 Elsevier Ltd*

1. INTRODUCTION

Organic molecules have been detected in extraterrestrial materials by the laboratory analysis of primitive meteorites (Cronin et al., 1988), interplanetary dust particles (Clemett et al., 1993; Flynn, et al., 2000), and a meteorite from Mars (McKay et al., 1996), by spacecraft measurements of dust in the coma of Comet Halley (Kissel and Kruger, 1987), and by astronomical measurements of comets (Knacke et al., 1986), the atmosphere of Titan (Courtin et al., 1991), and grains in interstellar space (Sandford et al., 1991). These organic molecules are generally believed to be abiogenic (Cronin et al., 1988: Kerridge, 1999), having been produced by chemical rather than biologic processing. However, the mechanism(s) for the production of the organic molecules observed in interplanetary and interstellar materials have not been established.

The primitive carbonaceous chondrite meteorites deliver to the Earth samples of the pre-biotic organic matter present in our Solar System. About 10% of the organic matter in these primitive, hydrated carbonaceous chondrites is present in the form of soluble molecules, which can be easily extracted and studied, while the remaining ~90% of the organic matter consists of insoluble macromolecular material that superficially resem-

bles terrestrial kerogen (Kerridge, 1999). Some of this macromolecular organic matter is presumed to be interstellar based on the detection of significant excesses of D, ^{13}C and ^{15}N (Kerridge, 1999).

A variety of mechanisms for the origin of the pre-biotic Solar System organic matter have been proposed. Kerridge (1993) describes 12 possible mechanisms that may have been involved in the production of this pre-biotic organic matter, and he further notes that the organic synthesis could have taken place in a variety of locations ranging from stellar outflows to aquifers on asteroids. No single mechanism or formation location appears capable of fully explaining the diversity of organic compounds and their isotopic composition (see the review by Kerridge, 1999). Current models suggest that many of the organic molecules found in the hydrated carbonaceous chondrite meteorites were synthesized by aqueous processing of a suite of precursor molecules, some of which were interstellar (Cronin and Chang, 1993; Kerridge, 1999). However, the specific precursor molecules and the degree of modification by aqueous processing are unknown.

The comparison of the organic matter in the anhydrous to the hydrated meteorites and interplanetary dust particles provides an opportunity to determine the abundance and the type(s) of precursor molecules and thus the degree of organic complexity in the Solar System before aqueous alteration and to assess the effects of aqueous alteration on these precursor molecules.

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1.1. Results from Meteorites

The abundance and types of organic matter in meteorites have been used as an indicator of the origin of organic matter in the Solar System. If aqueous alteration, which is presumed to occur on some asteroids after the formation of large bodies in the Solar System, was responsible for the production of the bulk of the pre-biotic organic matter in the Solar System, then we would expect to see organic matter concentrated in meteorites that exhibit a high abundance of aqueous minerals, as is seen in the hydrated CI and CM carbonaceous chondrite meteorites. On the other hand, if the bulk of the pre-biotic organic matter in the Solar System was produced either in an interstellar environment or in the early Solar Nebula, then we would expect to see roughly equal concentrations of organic matter in anhydrous extraterrestrial material (e.g., the CV and CO carbonaceous chondrites) and hydrated extraterrestrial material (like the CI and CM meteorites), unless the organic matter originally incorporated into these materials was destroyed by either thermal or aqueous processing later in the history of the material. The detailed characterization of the organic matter in anhydrous and hydrated meteorites would provide indications of the initial organic matter, present in the anhydrous meteorites, and determine the importance of aqueous processing in producing biologically important compounds, by comparison of the hydrated to the anhydrous extraterrestrial materials.

Indigenous complex organic matter, including amino acids, has been found in hydrated carbonaceous chondrite meteorites, such as the Murchison carbonaceous chondrite (Cronin et al., 1988). Much lower amounts of complex organic matter have been found in anhydrous carbonaceous chondrite meteorites, such as Allende, that contain most of their carbon in elemental form (Cronin et al., 1988). These results from the comparison of hydrated and anhydrous carbonaceous meteorites seem to favor production of the bulk of the organic matter in the Solar System by aqueous processing on parent bodies such as asteroids. However, the hydrated carbonaceous chondrite meteorites have approximately solar abundances of the moderately volatile elements, while all anhydrous carbonaceous chondrite meteorites have significantly lower contents of these moderately volatile elements (Palme, 2002). Two mechanisms, incomplete condensation or evaporation, both of which involve processes occurring at temperatures as high as ~1200 °C or more, have been suggested to explain the lower content of the moderately volatile elements in all anhydrous meteorites (Palme, 2002). Brearley (1999) concluded that the poorly graphitized carbon in the anhydrous carbonaceous meteorite Allende was formed by thermal metamorphism, possibly of a kerogen-like precursor. Brearley's (1999) results suggest that the reason Allende contains almost no organic carbon is that the pre-biotic organic carbon it once contained has been transformed into graphitic or amorphous carbon by thermal processing. The high temperature associated with either the incomplete condensation or the subsequent vaporization that produced the under-abundance of moderately volatile elements in the anhydrous meteorites is likely to be sufficient to remove or destroy most organic matter in the anhydrous meteorites, indicating that meteorite studies comparing the abundance of organic matter in hydrated and anhydrous carbonaceous chondrites do not constrain the origin of organic matter. However, this type of comparison would provide useful constraints on the origin of the pre-biotic organic matter in the Solar System if anhydrous extraterrestrial samples that had not experienced significant heating were available for laboratory analysis.

1.2. Interplanetary Dust Particles

Interplanetary dust particles (IDPs), ranging from ~5 μm to ~50 μm in size, have been collected from the Earth's stratosphere by NASA aircraft, flying at an altitude of about 20 km, since the mid-1970s (Brownlee, 1985). The IDPs are so small that they can radiate energy rapidly enough to avoid severe heating during atmospheric deceleration. As a result, many IDPs:

1. retain solar flare "tracks," which are lost in pulse heating to ~600 to 700 °C depending on the mineral that records these tracks (Fraundorf et al., 1982b; Sandford and Bradley, 1989),
2. retain solar wind He, which is lost over the 400 to 1200 °C temperature range (Nier and Schlutter, 1993),
3. retain moderately volatile elements such as S and Se, which are lost in pulse heating to 900 °C (Greshake et al., 1998), and
4. contain minerals with low thermal stability (e.g., clays, carbonates, etc.).

Most of the IDPs are believed to be particles from asteroids or comets, both of which are known to produce significant quantities of dust based on the detection by the Infrared Astronomy Satellite (IRAS) of dust bands associated with families of main-belt asteroids (Low et al., 1984) and dust trails associated with comets (Sykes et al., 1986).

Anhydrous IDPs, which are dominated by silicate minerals (olivine and pyroxene) or by silicate glass, and hydrated IDPs, which are dominated by clay minerals, are collected from the stratosphere in roughly equal abundances (Fraundorf et al., 1982a). Most of the IDPs have a major element composition that is generally similar to that of the CI meteorites (Schramm et al., 1989), which have a composition similar to the solar photosphere (Anders and Grevesse, 1989). These "chondritic" IDPs have been confirmed to be extraterrestrial by the detection of solar wind noble gases (Hudson et al., 1981), solar flare heavy-ion "tracks" (Bradley et al., 1984), and/or non-solar isotopic compositions of H, N and O (Zinner et al., 1983; Messenger, 2000; Messenger et al., 2002).

On average the IDPs are enriched in the moderately volatile elements and carbon by a factor of 2 to 3 over the CI meteorites (Flynn et al., 1996). This indicates that the IDPs formed at a low enough temperature to condense the moderately volatile elements and that, subsequent to their formation, the IDPs were never heated sufficiently to result in loss of these moderately volatile elements. In this context the hydrated IDPs are similar to the hydrated CI meteorites. However, this chemical composition distinguishes the anhydrous group of IDPs, which are rich in the moderately volatile elements, from all known anhydrous meteorites, which are depleted relative to the CI composition in the moderately volatile elements. Thus, these anhydrous IDPs are more primitive, that is they have been less altered by thermal processing, than any known anhydrous meteorite.
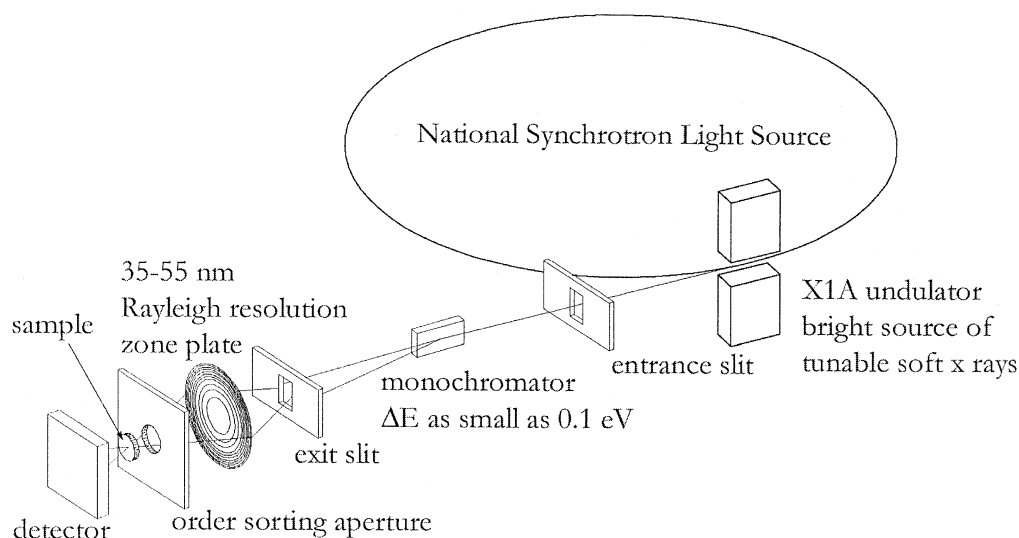
Fig. 1. Diagram of a Scanning Transmission X-Ray Microscope (STXM) on Beamline X1A of the National Synchrotron Light Source at Brookhaven National Laboratory.

Many IDPs have unequilibrated mineralogies, which indicates they never experienced significant heating (Fraundorf, 1981). Some IDPs have regions with high deuterium to hydrogen ratios (D/H) within a few μm of other phases with lower D/H, indicating these IDPs were not heated to the point of D equilibration since their formation (Zinner et al., 1983; Messenger, 2000). Some also exhibit ^{15}N isotopic excesses (Messenger, 2000). More recently, ^{16}O excesses, which have not been reported in meteorites, have been observed in IDP silicates (Messenger et al., 2002). We have characterized the material associated with the H isotopic anomalies, and report those results in a separate paper (Keller et al., 2003).

Terrestrial particles, injected into the stratosphere by large volcanic eruptions, above-ground nuclear weapons tests, and the exhaust from solid fuel rocket motors, are also collected. However, the terrestrial particles can be distinguished from the chondritic IDPs by their chemical compositions. Volcanic dust, for example, is highly depleted in Ni and other elements that are concentrated in the Earth's Fe-core compared to the primitive (undifferentiated) composition of the chondritic meteorites.

To infer the origin of organic matter in the Solar System we measured the abundance and types of carbon in *all three kinds* of primitive (i.e., not thermally processed) extraterrestrial materials available for laboratory analysis: anhydrous IDPs, hydrated IDPs, and hydrated carbonaceous chondrite meteorites.

2. MATERIAL AND METHODS

The typical 10 μm IDP has a mass of only ~1 ng, and carbon is only a minor component of the particle, with a mean carbon content of ~12 wt.% (Thomas et al., 1994). Thus, the mass of any particular organic species present in an IDP is below the detection limit for most traditional laboratory analysis techniques.

Clemett et al. (1993) detected several polycyclic aromatic hydrocarbons (PAHs) in IDPs using two-step laser desorption – laser ionization mass spectroscopy. However, they did not determine the abundance of organic carbon in these IDPs.

Because of the low amount of carbonaceous material being examined, we employ two synchrotron-based instruments at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (Upton, NY):

1. a Scanning Transmission X-ray Microscope (STXM), to map the carbon distribution and determine the carbon abundance, and to perform Carbon X-ray Absorption Near Edge Structure (XANES) spectroscopy, to identify the carbon functional groups in IDPs, and
2. a Fourier Transform Infrared (FTIR) spectrometer, to detect and identify the functional groups of organic compounds in the particles.

2.1. The Scanning Transmission X-Ray Microscope

The STXM, shown diagrammatically in Figure 1, operates on an undulator beamline of the NSLS, which produces a bright, tunable beam of soft x-rays. A spherical grating monochromator allows one to tune the X-ray energy over the range from 250 to 800 eV with a resolving power of ~5000 (i.e., ~0.05 eV at 250 eV). This energy range covers the K-absorption edges of the light elements C, N, and O, which are important constituents of organic compounds, as well as the L-absorption edges of heavier elements from K through Fe, which include important rock-forming elements. Beam defining slits select one spatially coherent mode of the undulator and illuminate a zone plate, which focuses the x-rays to a diffraction limited spot <50 nm in diameter on the sample. The monochromator position is calibrated by measuring the absorption spectrum of CO_2 gas, which has a series of sharp absorption features near 290 eV, injected into the sample chamber before each run. An X-ray counter located behind the sample measures the intensity of the x-rays transmitted through the sample.

The STXM can be operated in three modes: Mapping Mode, Spectrum Mode, and Stack Imaging Mode. In the Mapping Mode the monochromator energy is fixed and the sample is raster scanned in the X-ray beam at the focus of the zone plate. This produces an X-ray transmission image, with sub50 nm spatial resolution, at a specific X-ray energy. In Spectrum Mode the sample position is fixed, and the monochromator energy is varied. This produces a transmission spectrum of the spot being analyzed. Since the focus position of the zone plate changes with X-ray energy, the zone plate to sample distance must be adjusted during acquisition of the spectrum. Sample drift and wobble due to refocusing during acquisition of a spectrum can result in drift of the analysis spot on the sample. To avoid this problem, Jacobsen et al. (2000) developed the Stack Imaging Mode, in which a sequence of images at closely spaced energies is acquired, forming a 3 dimensional dataset in x- and y-position and energy. These several hundred images are subsequently aligned, using a cross-correlation
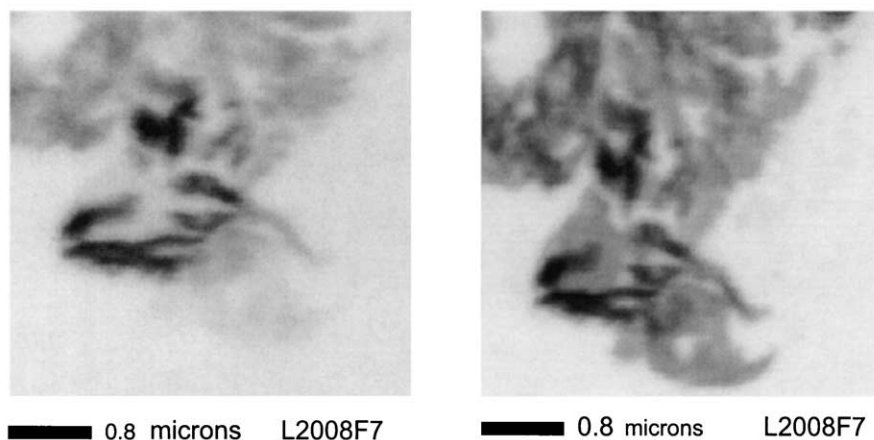
Fig. 2. X-ray absorption images of a small area of an IDP taken below the carbon K-edge (left) and above the carbon K-edge (right). Areas that absorb more strongly above the carbon K-edge (darker areas) are carbon-rich. The image is ~3 μm wide, and there is a small offset in the positions of the two images on the particle due to the need to refocus between images at different energies.

algorithm to properly register features common in all the images, e.g., silicate and sulfide grains, with respect to each other, thus compensating for any sample drift during the data acquisition. The XANES spectra from single spots or regions of interest can then be extracted from the data (Jacobsen et al., 2000). The STXM can detect and perform C-XANES spectroscopy on spots <100 nm on a sample containing several percent carbon, allowing identification of carbon functional groups in <10^{-15} grams of carbonaceous material. Thus, the analytical capability of this STXM is well-matched to the size and abundance of carbon in IDPs.

2.2. Infrared Microspectroscopy

Infrared spectroscopy is a well-established technique for the identification of organic functional groups. The midinfrared spectral region, from 650 to 4000 cm^{-1}, is frequently referred to as the molecular fingerprint region because of the unique absorption features exhibited by many functional groups in that wavenumber range.

Swan et al. (1987) reported the detection of a "poorly resolved band around 2960 cm^{-1}" accompanied by weak bands near 2926 and 2860 cm^{-1}, a region characteristic of C-H stretching absorptions in aliphatic hydrocarbon, in several IDPs. However, the C-H stretching features observed were very weak, and they were unable to exclude the possibility of contamination.

We have examined IDPs using much more sensitive FTIR instruments, consisting of conventional Spectra-Tech IRμs and Nicollet Continuum FTIR microscopes coupled to a synchrotron-generated infrared beam that achieves ~1000 times the intensity of a conventional globar infrared source. As a result these infrared microscopes at the NSLS have ~400 times better signal/noise than conventional globar FTIR instruments (Carr et al., 1995).

2.3. Sample Preparation

After collection from the Earth's stratosphere, the IDPs are curated at the NASA Johnson Space Center. The Cosmic Dust Curatorial Facility washes the silicone oil off the particles using hexane and catalogs the particles, providing a Scanning Electron Microscope (SEM) image and an energy dispersive X-ray fluorescence spectrum of each particle. The particles used for this study were provided by the Curatorial Facility.

Because the STXM measurements are made in transmission, the STXM samples must be thin enough to transmit a significant fraction of the incident x-rays. Carbon analysis, which is performed with x-rays having an energy near the C K-edge, ~290 eV, need to be ~70 to 200 nm thick, roughly comparable to the thickness of samples prepared for the Transmission Electron Microscope (TEM). TEM samples are usu-

ally prepared by ultramicrotomy, with the sample embedded in epoxy, sliced on an ultramicrotome, and deposited on a carbonaceous substrate on a TEM grid. Both the carbonaceous substrate and the epoxy can interfere with the analysis of carbon in the samples.

We prepare STXM samples by embedding the IDP in liquid, elemental sulfur, slicing the particle on an ultramicrotome, and depositing the slice on a TEM grid having an SiO substrate, thus avoiding interferences from the embedding epoxy and the carbonaceous substrate used in conventional preparation of samples for TEM examination. The S is then evaporated by heating the sample to about 60 °C, leaving a "clean" IDP section on the grid. Generally we slice only one half of each IDP, preparing sufficient sections for the STXM and TEM, and retain the remainder of the sample for infrared analysis or examination by other techniques that require a more massive sample. However, some IDPs were sliced completely before we began the FTIR analysis program. In those cases we have obtained FTIR spectra on the ultramicrotome sections.

3. RESULTS

3.1. STXM Carbon Mapping

Carbon absorbs x-rays very strongly just above the C K-edge (at ~290 eV), but very weakly just below the C K-edge, because x-rays with an energy just above the K-edge can induce electron transitions from the core electronic state to the continuum. We map the carbon in interplanetary dust by taking two transmission images of the sample: one with x-rays having an energy just below the C K-edge (~282 eV) and the second with x-rays having an energy just above the C K-edge (~292 eV), as shown in Figure 2. The absorption of elements other than carbon does not change significantly over this narrow (~10 eV) energy range. Thus, pixels that show a significant increase in absorption from the low to the higher energy image are carbon-rich. Carbon that is distributed uniformly at low concentration (<a few percent) is not included in our carbon assessment, thus we obtain a lower limit on the C-abundance.

We can achieve a spatial resolution of ~100 nm, or 2 × 2 pixels, in these carbon maps. The maps show that carbon occurs in the IDPs in three different morphologies:

1. as thin (~100 nm) coatings on individual mineral grains,

2. as thicker (~1/2 micron) coatings on aggregates of grains, apparently the "glue" holding these subunits together, and
3. as discrete submicron- to micron-size carbonaceous units.

The observation that carbon occurs as coatings on grains, apparently being the material that holds the subunits of the IDPs together, indicates that this carbon existed at the time when the grains were being assembled into dust-size particles. The formation of dust presumably predates the formation of the asteroids, moons, and planets in the Solar System, and thus predates any aqueous alteration event on an asteroid.

We determine the carbon content of a section by comparing the number of pixels showing a significant increase in absorption at the C K-edge to the total number of pixels on the particle. STXM carbon maps of 12 IDPs indicate they have highly variable carbon contents, ranging from a few vol.-% up to 90 vol. %. This is consistent with the high carbon abundance variation seen in energy dispersive X-ray fluorescence analysis on IDPs by Thomas et al. (1994), who report a mean of 12 wt-% carbon in about 100 IDPs they studied. Schramm et al. (1989) reported a similar carbon content for the set of IDPs they examined. The average carbon contents reported by Thomas et al. (1994) and Schramm et al. (1989) are not substantially different between the hydrated and anhydrous subgroups of IDPs.

3.2. STXM Functional Group Identification

X-ray Absorption Near Edge Structure (XANES) spectroscopy excites transitions from the core electronic state to various bound states at energies below the ionization threshold. The energy of each of these transitions is determined by the type of neighboring atoms and the bond, so, for example, $C=C$ and $C=O$ have different energies, and the energy of a $C=C$ or $C=O$ transition is itself "chemically shifted" by a few tenths of an eV due to the neighboring atoms. Thus, XANES is a sensitive probe of the functional group in which an element is bonded. The association of an absorption feature with a specific functional group is accomplished by measuring the absorption spectra of a variety of well-characterized compounds. Since C-XANES has been used to characterize polymers, many of the compounds used as standards are synthetic or natural polymers. We have used literature reference spectra and we have also measured the C-XANES spectrum of the acid-insoluble organic matter extracted from the CM2 carbonaceous chondrite meteorite Murchison for comparison to the absorption spectra of carbonaceous material in the IDPs. The XANES measurement technique and the absorption energies associated with a wide variety of C-, N-, and O-bearing functional groups have been reviewed by Ade and Urquhart (2002).

Carbon-XANES analysis can easily distinguish elemental carbon, as graphite, amorphous carbon, or C_{60}, from organic carbon by the identification of carbon bonded to H, N or O in organic matter. Figure 3 compares the C-XANES spectra of graphite, amorphous carbon, and carbonate to the spectrum of the acid insoluble organic extract from the Murchison carbonaceous chondrite meteorite. The Murchison spectrum is easily distinguished from either type of elemental carbon and from carbonate by the strong absorption near 288.5 eV in Murchison, a feature not seen in the spectra of graphite, amorphous carbon, or carbonate.
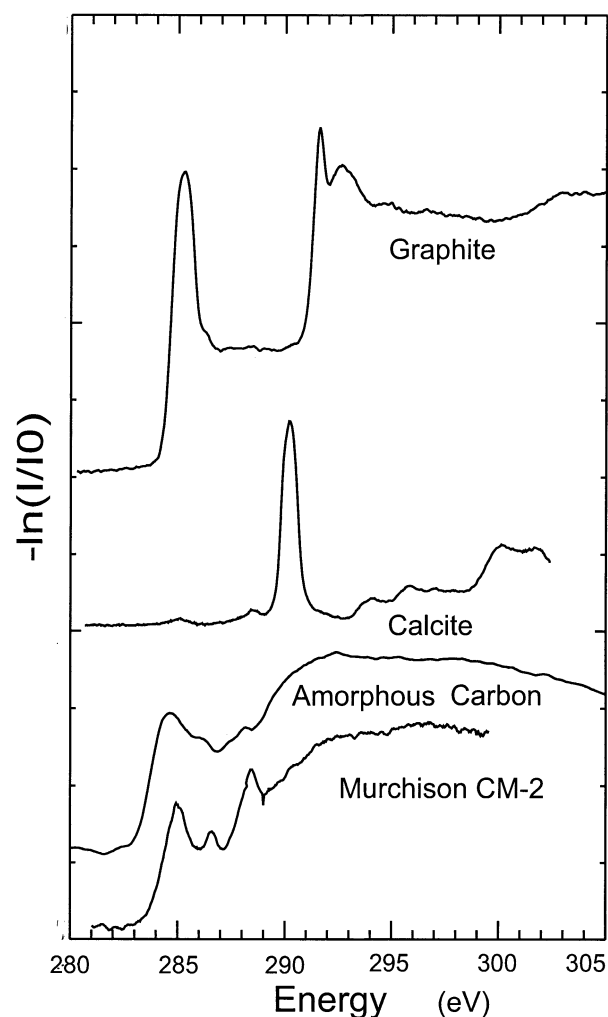

Fig. 3. Carbon-XANES spectra of Murchison acid residue, amorphous carbon, carbonate, and graphite. The strong $C=O$ absorption near 288.5 eV distinguishes the kerogen-like Murchison residue from either of the three forms of inorganic carbon. Graphite has a strong preedge absorption centered near 285 eV and a sharp exciton absorption near 291.6 eV. Carbonate has only very weak preedge absorptions in the 284 to 289 eV energy range, probably due to organic contamination, but has a very strong absorption near 290.7 eV. Amorphous carbon has a preedge absorption near 285 eV, with a pronounced shoulder on the high energy side of this feature. Murchison residue has two strong, preedge absorptions, one near 285 eV, from $C=C$ in a ring structure, and the second near 288.5 eV, from $C=O$. (Graphite spectrum provided by J. Brandes.)

Initially we mapped the carbon in ultramicrotome thin sections of IDPs, then performed C-XANES analyses of the C-rich spots in each particle. The first 3 hydrated IDPs and 7 of the first 9 anhydrous IDPs we examined had very similar C-XANES spectra (Flynn et al., 2000). The IDP spectra are also generally similar to the C-XANES spectrum of organic matter in the Murchison (CM2) meteorite, and quite different from the C-XANES spectrum of silicone oil, in which the particles were collected. Figure 4 shows the C-XANES spectra of an anhydrous IDP, a hydrated IDP, and acid-insoluble extract from the CM2 carbonaceous chondrite meteorite Murchison. Each of
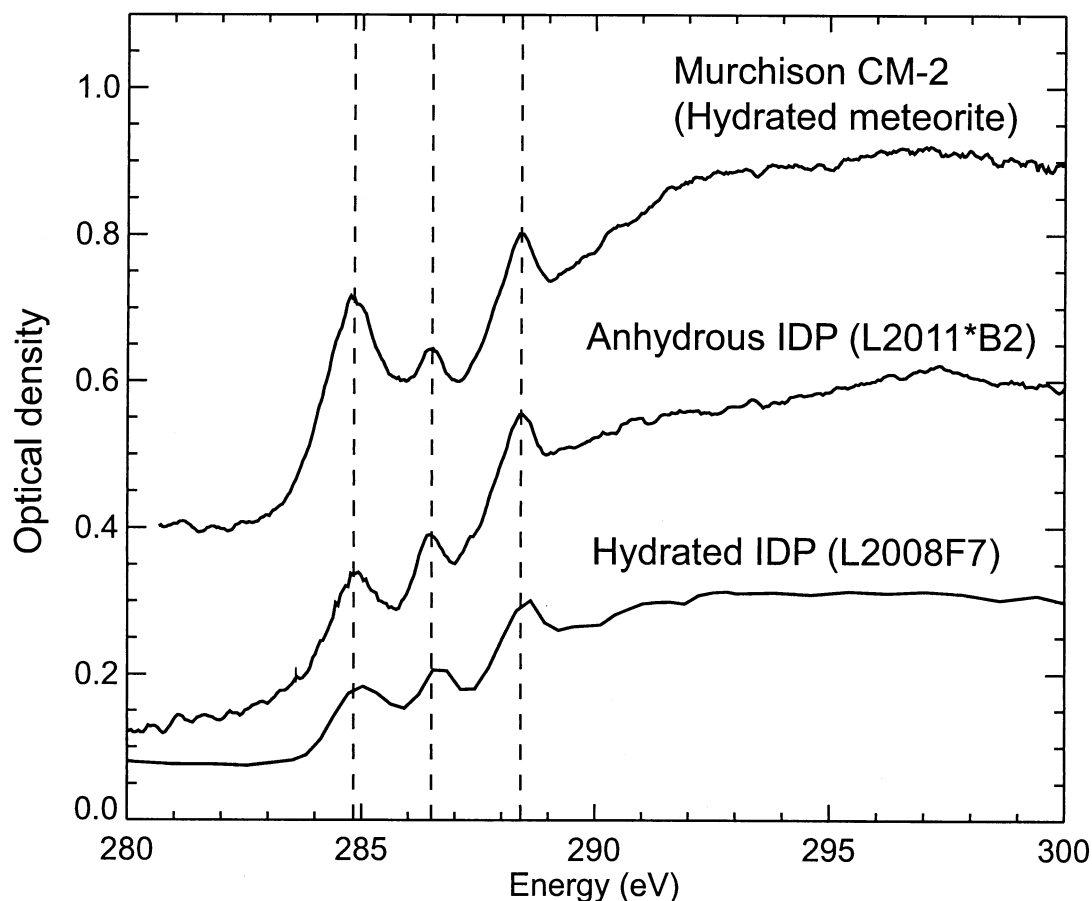
Fig. 4. Carbon K-edge XANES spectra of an organic-rich spot on a microtome section of Murchison, an anhydrous IDP, L2011*B2, and a hydrated IDP, L2008F7.

these C-XANES spectra shows two sharp absorptions, at ~285 eV and at ~288.5 eV, and a much weaker absorption at ~286.5 eV.

The strong absorption feature, at ~285 eV, is consistent with literature data for the 1s to $\pi^*_{C=C}$ transition in aromatic or olefinic carbon (Ade and Urquhart, 2002). However, C=C occurs in both elemental (graphitic or amorphous) carbon and some types of organic carbon (e.g., PAHs), as shown in Figure 3. Ordered graphite exhibits a strong, narrow exciton absorption at ~290 eV (Ma et al., 1993). The absence of the graphite exciton in the C-XANES spectra of these IDPs and Murchison indicates that ordered graphite is not contributing significantly to the C=C absorption. The amorphous carbon standards that we have measured exhibit a shoulder on the high-energy side of the ~285 eV absorption. This shoulder is not seen in most of the IDP spectra or in the Murchison spectrum (shown in Fig. 4), suggesting that amorphous carbon of the type we have examined is not the major contributor to the C=C absorption. Since PAHs have been detected in IDPs by laser-desorption/laser-ionization Mass Spectroscopy (Clemett et al., 1993), the C=C absorption we detect in most of the IDPs is most likely from PAHs, but we cannot rule out amorphous carbon different in structure from the standards we have examined.

The second strong absorption feature, at ~288.5 eV, occurs

in an energy range where the absorptions from several functional groups overlap, complicating the identification of the species responsible for this feature. A 1s to 3p transition for C-H_2 and C-H_3 in aliphatic hydrocarbon occurs at ~288 eV (Cody et al., 1995). However, the C-H features detected in polymers are generally significantly broader than the feature we detect in the IDPs (see Fig. 3 of Dhez et al., 2003), suggesting that the sharp 288.5 eV transition in the IDPs is from C=O rather than C-H. In addition, theoretical calculations used to deconvolve spectra of humic acids used a gaussian C-H absorption whose full-width half-maximum is twice that of the C=O absorption, and they found that the energy assigned to the C1s → C-H transitions of both π and σ character of the carbon backbone occur at ~289 eV (Naachegal, 2003), rather than 288.5 eV.

The 1s to π^* transitions in both aromatic and aliphatic carboxylic acids have large oscillator strengths and the carboxyl functional group transitions occur over the range from 288.2 to 288.6 eV in COOH (Cody et al., 1998). The 1s to π^* transition in carbonyl has been measured to occur over the range from 286.6 eV, in polyvinyl methyl ketone, to 290.4 eV, in polycarbonate (Urquhart and Ade, 2002). As these measurements indicate, the absorption energy of a specific functional group can be chemically shifted by more than 1.0 eV, depend-
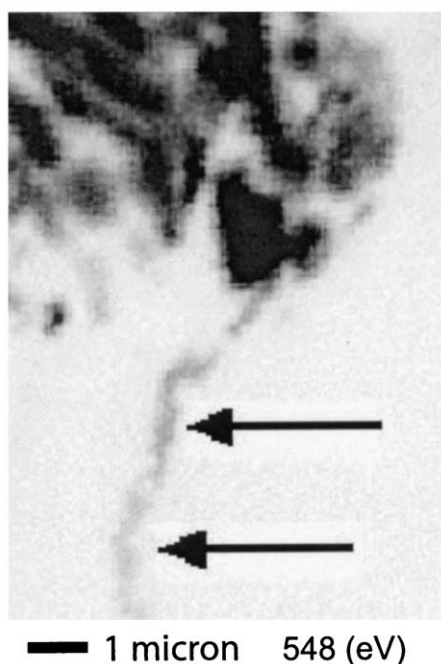
Fig. 5. Oxygen absorption image of the ultramicrotome section of L2011*B2, showing the carbon-rich material (indicated by the arrows) pushed from the edge of the particle by the microtome preparation.
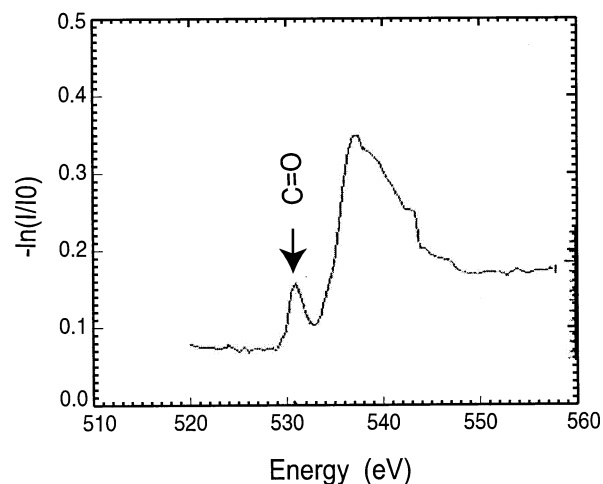

Fig. 6. O-XANES spectrum of the carbon-rich material in L2011*B2, showing a strong increase in absorption at the O-edge and a preedge absorption at ~532 eV.

ing on the neighbor to which that functional group is bonded. Thus the 288.5 eV absorption we detect in the IDP and Murchison spectra could result from the C-H, carboxyl, or carbonyl functional group, or even from a combination of all three. The presence of any one or more of these functional groups demonstrates that the sample contains organic matter, thus we can use the 288.5 eV absorption feature as an indicator of organic carbon in these IDPs.

To determine if the 288.5 eV absorption feature indicates C to O bonding, rather than C to H bonding, we performed O-XANES analysis on an IDP, L2011*B2, that we had already analyzed by C-XANES. Unlike C, which occurs in discrete regions in each IDP, the O is widespread throughout an IDPs. Most IDPs are dominated by O-bearing silicates, and many IDPs contain carbonates and/or metal oxides as well. Thus, O-XANES spectroscopy is complicated by the possibility that absorption features from adjacent O-rich silicate, carbonate, or metal oxide could contribute to the O-XANES spectrum of the carbonaceous material if the analysis cannot be restricted to the generally small areas of carbonaceous material.

L2011*B2 is a fragment from a "cluster IDP," a particle that broke into many fragments on the collector surface. This fragment consists of roughly spherical ~5 μm pyroxene aggregate surrounded by an ~1/2 μm thick rim of carbonaceous material. The carbonaceous material, which has a C-XANES spectrum like those of the other IDPs, was pushed away from one side of the pyroxene during the microtoming procedure, providing an isolated region of carbonaceous material for analysis (see Fig. 5).

The O-XANES spectrum of the carbonaceous material in L2011*B2 shows a strong increase in absorption at the O-edge and has a single, strong preedge absorption at ~532 eV (see

Fig. 6), while the O-XANES spectrum of the pyroxene has no preedge absorption. The increase in absorption at the O-edge, ~540 eV, in the carbon-rich region of this IDP demonstrates that O is spatially correlated with the carbonaceous material in this IDP. Reference spectra of the amino acids alanine, cysteine and cystine have a carboxyl absorption at 532.4 eV. Urquhart and Ade (2002) report that the O 1s to π^* transition in carbonyl (C=O) occurs at 532.1 eV in polymethyl methacylate (PMMA) and at 532.2 eV in polyethylene succinate (PES). These compounds have C 1s to $\pi^*_{C=O}$ transitions at 288.6 and 288.5 eV respectively (Urquhart and Ade, 2002). Thus both the C-XANES absorption at ~288.5 eV and the O-XANES absorption at ~532 eV are consistent with carbonyl. Urquhart and Ade (2002) report that polymers with two chemically inequivalent oxygen sites there is a second, weaker preedge absorption, which occurs at ~534.5 eV in PMMA and PES. We do not see this feature in the IDP spectrum. Although the 532 eV absorption in the IDP is closer in energy to the carbonyl value reported by Urquart and Ade (2002), the magnitude of the chemical shifts does not allow us to unambiguously decide between the carboxyl and the carbonyl functional group on the basis of C-, and O-XANES alone. Nonetheless, the O-XANES results demonstrate the presence of a significant amount of C=O in the carbonaceous material in this IDP.

The weaker absorption at ~286.5 eV is also difficult to assign to a specific functional group. Ade and Urquhart (2002) have associated an absorption feature near 286.5 eV with a transition in phenyl carbon attached to an amide group, while Cody et al. (1998) identify an ~286.3 eV absorption with a carbonyl substituted aromatic. Keller et al. (1995) have reported C:N ratios of ~0.1 in IDPs, so there may be sufficient N in the IDPs for this feature to be associated with an amide group. In addition, Clemett et al. (1993) reported odd mass peaks in the laser desorption/laser ionization mass spectra of the IDPs which they indicated were suggestive of N-bearing functional groups attached to aromatic structures. If so, the amide group would give rise to preedge absorption features at the N-edge. Nitrogen preedge features have been observed in

IDPs by N-XANES using the STXM (Feser et al., 2003) and by Electron Energy Loss Spectroscopy (EELS) (Keller et al., 1995) providing evidence of an amide or amine group. Therefore, the 286.5 eV peak observed in the C-XANES spectra could be a C-N bond of an amide. An ~286.5 eV absorption peak has also been observed in the spectra from cell walls of vascular plants (Cody, 2000), but has not been observed in terrestrial kerogen (G. C. Cody, Pers. Comm. 2003). At present we cannot make an unambiguous assignment of a functional group to the 286.5 eV absorption feature. Either C-N bonding in an amide or O bonded to a C-ring remains viable candidates to explain this feature. Whatever organic functional group gives rise to the 286.5 eV absorption, the similarity in energy and strength relative to the C-edge of this feature in the anhydrous and the hydrated IDPs suggests they both contain the same functional group in roughly the same proportion relative to the total C content.

Combined C-XANES and O-XANES spectroscopy on IDPs demonstrates that carbon and oxygen are spatially associated in IDPs, and the absorption feature at 532 eV in the O-XANES spectrum indicates the presence of O bonded to C in the IDPs. The 288.5 eV absorption feature detected by C-XANES and the 532 eV absorption feature detected by O-XANES are both consistent with carbonyl (Urquhart and Ade, 2002), but could be due to carboxyl as well. We have detected carbonyl in acid-etched IDPs by FTIR (Flynn et al., 2002), indicating that some of the absorption at ~288.5 eV is from the carbonyl.

More recently, we have employed the Stack Imaging Mode for STXM analysis of the IDPs. In the Stack Imaging Mode we take X-ray absorption images of the ultramicrotome section at a sequence of energies from 280 eV to 300 or 310 eV. The spacing of the images is 0.1 eV over the energy range of the preedge absorptions, from about 284 to 292 eV, with larger energy spacing (0.25 or 0.50 eV) over the rest of the energy range. The resulting set of 200 or more images is computer-aligned, correcting for sample drift, and spectra are derived at each pixel.

Computer-based Principle Component Analysis (PCA) is used to examine each spectrum and to identify and group pixels with similar spectra. Thus, the PCA technique is used to identify regions of each particle having specific types of carbon bonding. Typically each particle has regions with several different C-XANES spectra, as shown in Figure 7 for L2008U13. L2008U13 has areas of organic carbon, characterized by the 285 eV and 288.5 eV absorption features and a large increase in absorption at the C-edge, regions with much smaller 285 and 288.5 eV absorption, a much smaller carbon edge, and a large absorption below 285 eV, consistent with a region of silicate or sulfide containing a small amount of carbonaceous material, and sometimes regions with a large absorption near 290 eV and a large increase in absorption at the C-edge, consistent with carbonate.

Our goal in this project is to compare the organic matter in different IDPs. To do this we select from the various spectra identified by PCA in each IDP the spectrum with the largest increase in absorption at the C-edge (i.e., the area that has the highest carbon content). The C-XANES spectra of these C-rich regions of 7 anhydrous and 4 hydrated IDPs are shown in Figure 8.

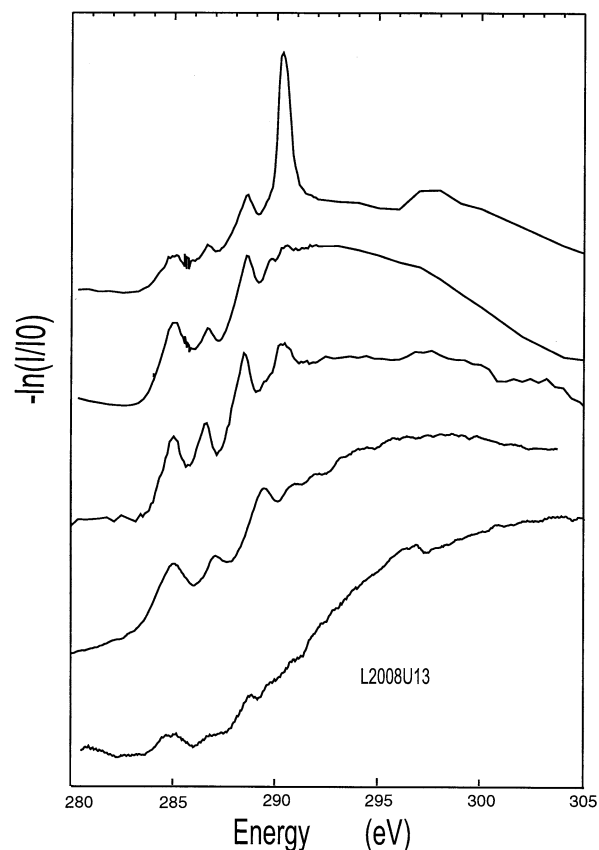Only one IDP, L2008G12, has an area showing a pro-

Fig. 7. PCA analysis of L2008U13 identified areas with different C-XANES spectra. These include: 1) regions of organic carbon, characterized by the 285 eV and 288.5 eV absorption features and a large increase in absorption at the C-edge, 2) regions with much smaller 285 and 288.5 eV absorption, a much smaller carbon edge and a large absorption below 285 eV, consistent with silicate or sulfide containing a small amount of carbonaceous material, and, sometimes, 3) regions with a large absorption near 290 eV and a large increase in absorption at the C-edge, consistent with carbonate.

nounced shoulder on the 285 eV absorption, suggesting the presence of a significant amount of amorphous carbon (see Fig. 9). L2008G12 is an unusual IDP in that this particle is mostly carbon, although it contains a few silicate grains. L2008G12 also shows some areas of organic carbon very similar in XANES spectrum to that in the other IDPs (see Fig. 9). Transmission electron microscope examination shows that much of the carbon in L2008G12 is vesicular, and that the silicates have no solar flare tracks. Solar flare tracks in silicates anneal at ~600 to 700 °C (Fraundorf et al., 1982b), thus the absence of solar flare tracks indicates that either L2008G12 was heated above the track annealing temperature during atmospheric entry or that it had an unusually short space exposure as a small particle so it never recorded tracks in its silicates. Vesicular carbon, which is seen in some IDPs and polar micrometeorites, is generally taken to be an indicator of significant entry heating, causing outgasing of solar wind H and/or other gases incorporated into the particle. Both of these features taken together suggest that L2008G12 was heated significantly on atmospheric entry. This severe heating may have transformed some of the initially organic carbon in L2008G12 to amorphous
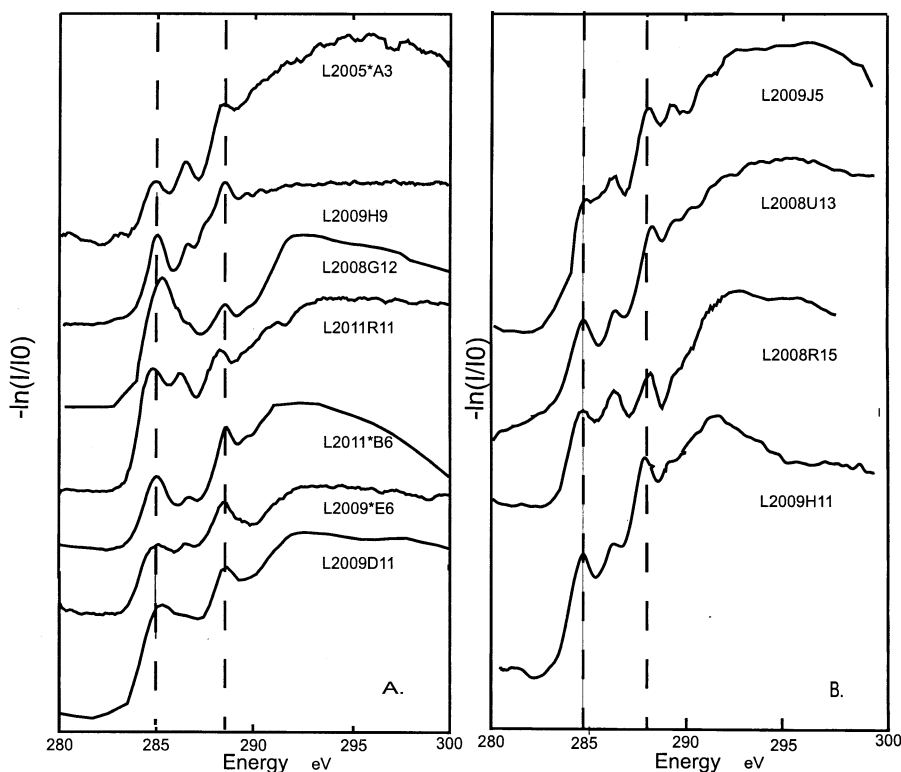
Fig. 8. Carbon K-edge XANES spectra of 7 anhydrous IDPs (left) and 4 hydrated IDPs (right).

carbon, as Brearley (1999) suggests for the alteration of a possible kerogen-like component into poorly graphitized carbon in Allende.

The other 12 IDPs, 7 anhydrous and 5 hydrated, have C=C and C=O absorption features similar to those we detect in the acid insoluble extract from Murchison (see Fig. 8). The detection of the C=O absorption feature demonstrates that these
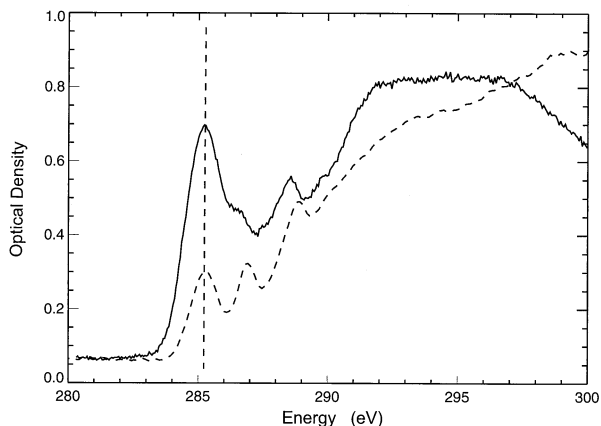

Fig. 9. Carbon-XANES spectra of the two spectrally distinct, carbon-rich areas on the IDP L2008G12. One area (bottom spectrum) exhibits an XANES spectrum similar to that seen for organic carbon in most other IDPs, while the second area (top spectrum) shows a pronounced shoulder on the high-energy side of the ~285 eV absorption, consistent with the presence of some amorphous carbon.

IDPs contain organic carbon, and the similarity of the spectra indicates that anhydrous and hydrated IDPs both contain organic carbon that is very similar in the types and abundances of its major functional groups.

The strength of the C=O absorption indicates that a substantial fraction of the carbon in the IDPs is organic rather than elemental. The height of the C-edge, at ~290 eV, is a measure of the total mass of carbon in the analysis beam while the area of the C=O absorption is proportional to the abundance of that functional group. This ratio is approximately the same in the hydrated IDPs, the anhydrous IDPs, and the Murchison acid-insoluble residue, indicating that all three materials have similar C=O to total C. Nuclear magnetic resonance analysis of the acid insoluble organic extract from Murchison indicates it contains about 9 wt-% carbonyl and about 15 wt-% carboxyl (Cody et al., 2002). Since, on average, the IDPs contain ~12 wt-% carbon (Thomas et al., 1994), about 4 times the C content of Murchison, we estimate that, on average, the IDPs that we studied contain several percent C=O.

3.4. FTIR Results

Infrared spectroscopy has the advantage that it is a relatively "mature" organic characterization technique, with functional group assignment being relatively straightforward. However, diffraction imposes a minimum size on the infrared analysis spot comparable to the wavelength being employed (commonly ~2.5 to ~25 μm). Thus, the infrared analysis spot is larger than most of the organic-rich regions we detected in the IDPs using the STXM.
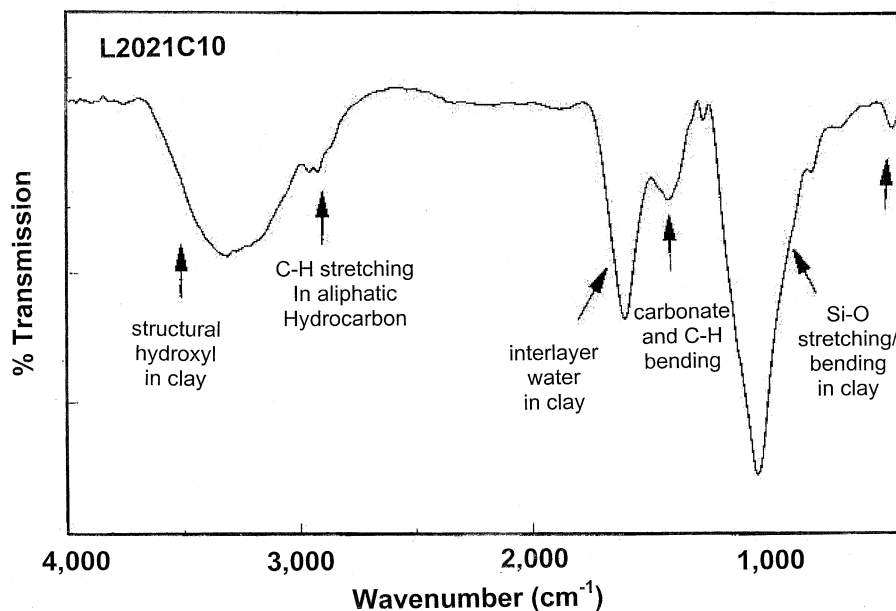
Fig. 10. Infrared spectrum, over the range from 4000 to 650 cm^{-1}, of L2021C10 showing the strong absorptions from the silicates, carbonates, and water that interfere with the detection of organic absorption features. The C-H stretching vibrations occur in a region where no sharp features from the dominant minerals occur, and these C-H stretching features are easily detected.

Most IDPs are dominated by anhydrous and/or hydrated silicates, carbonates, sulfides, and oxides (see Fraundorf et al., 1982a), which have strong absorptions over most of the 4000 to 650 cm^{-1} range we analyze by FTIR (see Fig. 10). The IDPs in this study all show silicate absorption features near 1000 cm^{-1}, and many show carbonate and sulfide absorption features as well. These absorption features interfere with the detection of organic features over much of the infrared spectrum. However, these phases do not interfere in the region from 2700 to 3100 cm^{-1}, where C-H stretching vibrations occur. So, we have focused our efforts on examining this region of the infrared spectrum. We have measured the infrared spectra of 19 IDPs, 14 anhydrous and 5 hydrated. The C-H stretching regions of their spectra are shown in Figures 11a,b. The asymmetric and symmetric stretching absorptions of C-H$_3$ occur at ~2960 and 2880 cm^{-1} respectively, and the asymmetric and symmetric stretching absorptions of C-H$_2$ occur at ~2926 and 2854 cm^{-1} respectively.

Because most IDPs are dominated by silicate minerals, we have scaled the C-H stretching region of each spectrum so the depth of the Si-O stretching absorption, which occurs near 1000 cm^{-1}, is the same in each case. Thus, if all the IDPs have similar silicate absorption, the depth of the C-H stretching absorption is roughly proportional to the aliphatic hydrocarbon abundance in each particle.

Sixteen of the 19 IDPs examined by FTIR showed strong C-H$_2$ and C-H$_3$ stretching vibrations of aliphatic hydrocarbon, as shown in Figures 11a,b. Only two anhydrous IDPs, L2009*E2 and L2008V42, and one hydrated IDP, L2009H11, show no obvious C-H stretching absorption. The 2700 to 3100 cm^{-1} region of the spectra of the remaining 16 hydrated and anhydrous IDPs are very similar to one another.

3.4. Possible Contamination of IDPs

The IDPs are collected from the Earth's stratosphere by impact onto a silicone oil covered surface. This silicone oil is subsequently removed from each IDP by washing in hexane, but the presence of residual silicone oil must be considered.

We measured the C-XANES spectrum of silicone oil (see Fig. 12), provided by the NASA Johnson Space Center (JSC) Curatorial Facility. This spectrum is quite distinct from the spectra of the carbon-rich material in the IDPs. Silicone oil has a weak absorption near 285.5 eV, about 0.5 eV higher in energy than the feature we detect in the IDPs, and strong, broad, twin-peaked absorptions centered near 287.8 and 289.0 eV. The silicone oil spectrum is easily distinguishable from the C-XANES spectra of the carbonaceous material in IDPs and Murchison, particularly by the strong absorption feature near 287.8 eV, which we have never detected in IDPs or Murchison.

We measured the infrared absorption spectrum of silicone oil. The silicone oil shows a large absorption feature at 2960 cm^{-1} (Fig. 13), displaced by about 6 cm^{-1} from the C-H$_3$ absorption feature we detected in the IDPs. The silicone oil shows only weak absorption features near 2926 or 2854 cm^{-1}, where we detected the strong C-H$_2$ absorption feature in the IDPs. We measured the absorption spectra of KBr onto which we had deposited an amount of hexane similar to that used by the JSC Curatorial Facility for cleaning an IDP. The hexane evaporates quickly, and we detected no C-H absorption features on the KBr. We also analyzed the sulfur used for sectioning the IDPs, and detected no C-H absorption features.

When we perform FTIR spectroscopy on whole IDPs (~10 μm in size), which are too thick for good transmission of infrared light through the thickest portion of the particle, we detect the 10 μm silicate absorption features but generally do
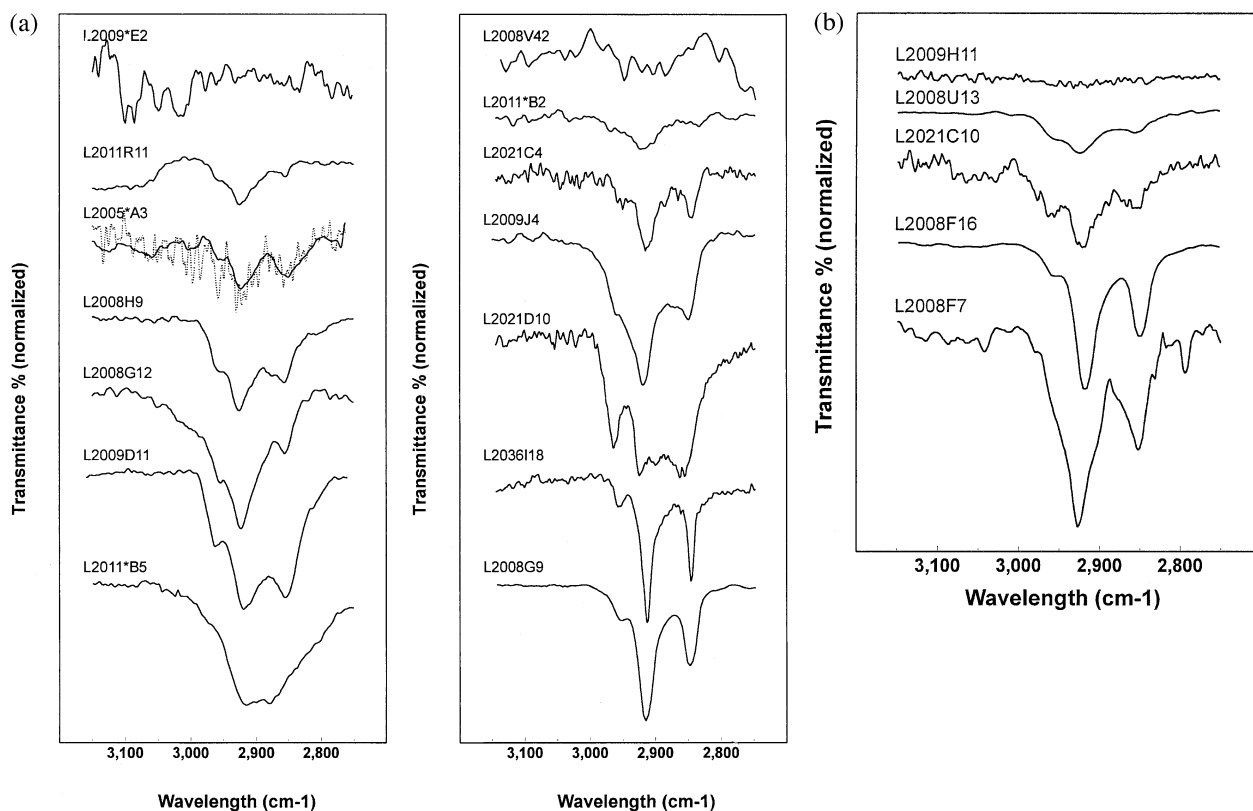
Fig. 11. a. FTIR spectra, in the C-H stretching region, of 14 anhydrous IDPs. These data are scaled to have the same Si-O absorption depth. b. FTIR spectra, in the C-H stretching region, of 5 hydrated IDPs. These data are scaled to have the same Si-O absorption depth.

not see the ~ 3.4 μm C-H stretching features. When we crush the IDP, exposing the interior, we detect the 10 μm and the 3.4 μm features, suggesting that organic matter is not present near the surface of the IDP but is present in the interior. The loss of near-surface organic matter would be expected for IDPs exposed to damaging ultraviolet light and particle radiation in space, and this provides some evidence that the aliphatic hy-

Fig. 12. Carbon-XANES spectrum of silicone oil. The strong absorption at ~ 297.8 eV, which has never been detected in the IDPs, can be used to constrain the silicone oil contamination of the IDPs.

drocarbon is indigenous to the IDPs. However, the absence of aliphatic hydrocarbons near the surface of the IDPs might also result from the hexane washing, used to remove the surface coating of silicone oil from the IDPs, or from surface heating during atmospheric entry.

As a final test for possible contamination, we analyzed three particles classified as "TCN," or "terrestrial contaminant natural" particles, collected from the stratosphere, curated, and prepared for analysis in the same manner as the IDPs. Each of these three terrestrial particles showed a C-H_3 absorption feature at ~ 2960 cm^{-1}, and much weaker, broad absorptions at positions near, but not identical to, those seen in the IDPs. The TCN particle spectra are easily distinguishable from those of the IDPs. Only one IDP, L2009J5, has a C-H stretching region spectrum dominated by the C-H_3 absorption, suggesting that the silicone oil was not well removed from that IDP. Thus, the aliphatic C-H_2 absorption features detected in the other IDPs appear to be indigenous, and most of the C-H_3 absorption is likely to be indigenous as well.

4. DISCUSSION

Our comparison of the organic content of anhydrous to hydrated IDPs gives a significantly different result from the earlier comparisons between anhydrous and hydrated meteorites. While the hydrated meteorites contain a few percent organic carbon, the anhydrous meteorites have a much lower
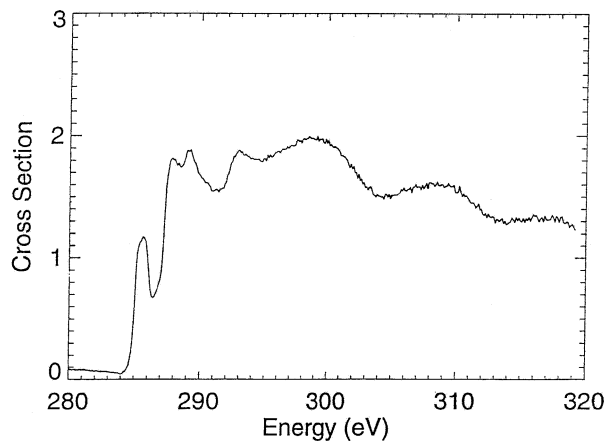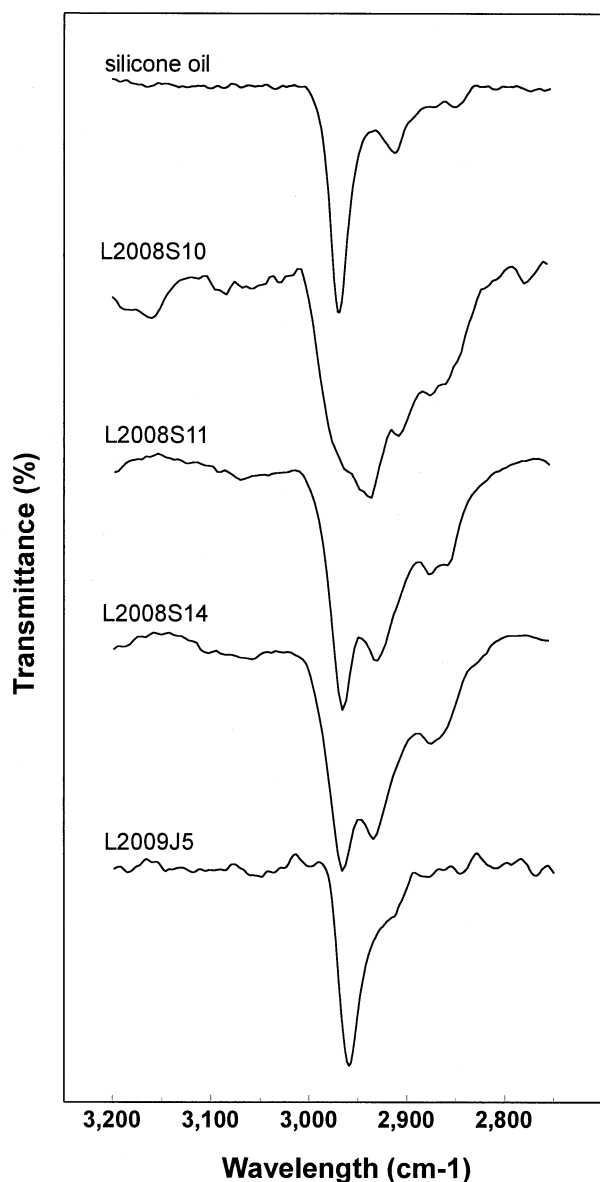
Fig. 13. FTIR spectra, in the 3.4 μm C-H stretching region, of silicone oil, three TCN particles (L2009S10, L2008S11, and L2008S14) collected from the Earth's stratosphere and curated in the same manner as the IDPs, and the one IDP that shows a C-H$_3$ dominated infrared spectrum, L2009J5.

Table 1. Peak heights in C-XANES spectra.

Sample	C=C Area C-edge Height	C=O Area C-edge Height	C=C Area C=O Area
Anhydrous IDPs			
L2011R11	2.03	2.03	1.00
L2005*A3	1.00	1.46	0.68
L2009D11	7.14	5.71	1.25
L2009H9	3.14	3.84	0.82
L2008G12	2.43	1.48	1.64
L2009E6	5.00	5.94	0.84
L2011B6	6.35	5.65	1.12
L2011*B2	1.14	2.23	0.51
Average Anhydrous IDPs	3.52	3.54	0.92
Hydrated IDPs			
L2009H11	1.68	2.46	0.68
L2008U13	1.76	2.05	0.86
L2008R15	5.80	4.20	1.38
L2009J5	1.54	1.79	0.87
L2008F7	5.63	5.47	1.03
Average Hydrated IDPs	3.82	3.19	0.96
Murchison (CM2)			
Microtome Section	5.64	4.36	1.29
Acid Residue	1.42	1.43	0.99

tra (see Figs. 6, 8a,b), and these C-XANES spectra are generally similar to the C-XANES spectrum of acid-insoluble organic matter extracted from the Murchison (CM2) meteorite. Each of these C-XANES spectra shows a large absorption at ~285 eV, characteristic of the C=C bond, and a second strong absorption at ~288.5 eV, characteristic of the C=O bond (and distinct from the ~290 eV absorption of the C=O in carbonate). The high C=O abundance indicates that a substantial fraction of the carbon is organic rather than elemental (Flynn et al., 2000)

In crystalline material the strength of a particular absorption feature can depend significantly on the orientation of the crystal axes relative to the polarization axis of the synchrotron radiation. However, TEM examination of the carbonaceous material in these IDPs indicates that it is amorphous. For amorphous material the ratio of the area in the C=C absorption peak to the height of the C-edge is a measure of the fraction of the carbon that is bonded in the C=C functional group, and the ratio of the area of the C=O absorption to the height of the C-edge is a measure of the fraction of the carbon that is bonded in the C=O functional group. In addition, the ratio of the area in the C=C absorption to the area of the C=O absorption is proportional to the ratio of the C=C to the C=O functional groups. The peak areas were fit with a single gaussian and the C-edge was also fit using the WINXAS program (developed by Ressler, Fritz-Haber-Institut, Germany).

The C=O area to C-edge ratio varies significantly among the IDPs (as shown in Table 1), however the average ratio for the anhydrous IDPs (~3.5) is not significantly different from the average ratio for the hydrated IDPs (~3.2), indicating that the organic content, as measured by the fraction of the carbon that is present in C=O, is, on average, very similar in the anhydrous and the hydrated IDPs.

Table 1 shows that the C=C to C=O peak area ratio varies from one IDP to another by about a factor of three. This suggests that the organic matter in the IDPs consists of a

carbon content, and much of that carbon is elemental (Cronin et al., 1988). As previously observed by Thomas et al. (1994), the hydrated and the anhydrous IDPs both show wide variability in their carbon contents, but both types of IDPs have a similar mean carbon content. Further, we find that both the anhydrous and hydrated IDPs contain organic carbon, with variable but generally similar amounts of C=O and aliphatic hydrocarbon, as well as C=C groups that are likely to be organic.

4.1. Carbon Functional Groups in IDPs

The 5 hydrated IDPs and 7 of the 8 anhydrous IDPs we examined using the STXM have very similar C-XANES spec-

Table 2. Infrared characterization of IDPs.

IDP	Type	Sample prep	CH_2	CH_3	CH_2/CH_3	Si-O
L2021C4	anhy	KBr	0.10	0.04	2.5	1
L2036I18	anhyd	KBr	0.28	0.05	5.6	1
L2021D10	anhyd	KBr	0.25	0.19	1.3	1
L2008V42A	anhyd	KBr	0.03	0.02	1.5	1
L2008G9	anhyd	KBr	0.32	0.08	4.0	1
L2009J4	anhyd	TS	0.31	0.16	1.9	1
L2011*B2	anhyd	TS	0.04	0.02	2.0	1
L2008G12	anhyd	TS	0.17	0.14	1.2	1
L2008H9	anhyd	TS	0.13	0.08	1.6	1
L2011R11	anhyd	TS	0.05	0.02	2.5	1
L2011*B5	anhyd	TS	0.32	0.11	2.9	1
Average Anhydrous			0.18	0.08	2.46	
St. Dev.			0.12	0.06	1.32	
L2008F16	hyd	KBr	0.16	0.03	5.3	1
L2021C10	hyd	KBr	0.09	0.06	1.5	1
L2008U13	hyd	TS	0.04	0.025	1.6	1
L2009H11	hyd	TS	0.01	0.01	1.0	1
L2008F7	hyd	TS	0.21	0.1	2.1	1
Average Hydrated			0.10	0.05	2.31	
St. Dev.			0.08	0.04	1.74	
Murchison						
Acid Residue					1.09	

non-uniform mixture of compounds containing the C=C and C=O functional groups. However, the average ratio of C=C to C=O area for the anhydrous IDPs (~0.92) is essentially identical to the average for the hydrated IDPs (~0.96). Thus, these results indicate that in the anhydrous IDPs and the hydrated IDPs a substantial fraction of the carbon is oxygen substituted, hence it is organic rather than elemental. This result on IDPs is consistent with NMR spectroscopic measurements on Murchison by Cody et al. (2002).

In the simplest case, aliphatic hydrocarbons consist of chains of C-H_2 terminated on each end by a C-H_3 group. Thus, the ratio of the depth of the C-H_2 absorption to the C-H_3 absorption is a measure of the mean length of the aliphatic hydrocarbon chain. The similarity of the spectra, shown in Figures 11a,b, indicates that the anhydrous IDPs and the hydrated IDPs both contain a mixture of aliphatic hydrocarbons having approximately the same mean aliphatic chain length, but the relative C-H_2 to C-H_3 absorption depths vary from particle to particle. The C-H_2 absorption depth, the C-H_3 absorption depth, and the C-H_2/C-H_3 depth ratio are given for each IDP in Table 2. The variation in the depth of the C-H_3 to C-H_2 ratio from sample to sample suggests that the aliphatic organic matter in the IDPs is an inhomogeneous mixture of organic material including two or more aliphatic hydrocarbon components having significantly different chain lengths.

Overall, however, the mean C-H_2 to C-H_3 ratio is quite similar in the anhydrous IDPs (average C-H_2/C-H_3 = ~2.46) and the hydrated IDPs (average C-H_2/C-H_3 = ~2.31), suggesting that both types of IDPs contain similar aliphatic hydrocarbons. Further, the average C-H_2 absorption depth, normalized to the Si-O absorption depth, is comparable in the two types of IDPs, suggesting that the anhydrous and the hydrated IDPs contain roughly similar concentrations of aliphatic hydrocarbons.

Only a few of the IDPs, for example L2021C10 (see Fig. 11b), show very weak aromatic C-H absorption features, which

occur between 3000 and 3050 cm^{-1}. The aromatic C-H absorption is easily detected in the Murchison acid insoluble residue (Fig. 14). Thus, it appears that the IDPs have a lower fraction of their total carbon present as aromatic hydrocarbon than Murchison.

4.2. Comparison of the Organic Matter in IDPs with That in the Murchison Meteorite

We have examined the carbon in two different samples of the Murchison CM2 carbonaceous chondrite. One sample is an ultramicrotome section of the meteorite, containing a few small, organic-rich spots that were examined by C-XANES and by FTIR. The second sample is a Murchison acid insoluble residue. The acid treatment, which is designed to concentrate the carbonaceous material by dissolving the silicates, is known to remove the water soluble organic matter, which constitutes about 10% of the total organic matter, as well (Kerridge, 1999).

The C=C/C=O area ratio is somewhat higher in the Murchison ultramicrotome section than in either the anhydrous or the hydrated IDPs (see Table 1). This suggests that Murchison contains a mixture of carbon molecules that is richer in the C=C functional group, most likely aromatic carbon, than either type of IDP. Much of the C=C carbon appears to be acid soluble, since the acid residue has a lower C=C to C=O area ratio, roughly comparable the ratio we detect in the anhydrous and the hydrated IDPs.

We measured the infrared spectrum of the Murchison acid insoluble residue (see Fig. 14). The C-H stretching regions of the infrared spectra of the hydrated and the anhydrous IDPs differ from that of Murchison acid residue in two significant ways. First, the Murchison residue has a much higher ratio of aliphatic C-H_3 to C-H_2, seen as a much deeper C-H_3 absorption for the Murchison residue in Figure 14. This indicates that the mean aliphatic chain length in the Murchison residue is much shorter than in either of the two types of IDPs. Second, the
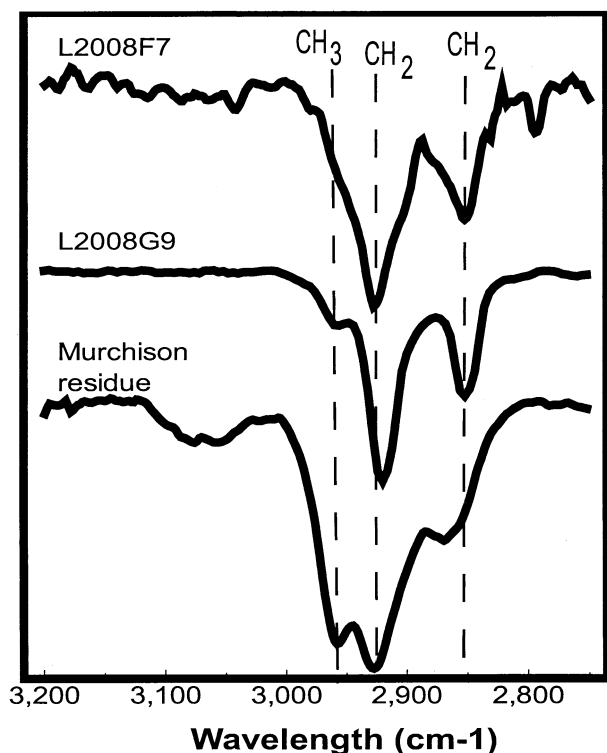
Fig. 14. Infrared absorption spectra of a hydrated IDP, L2008F7, an anhydrous IDP, L2008G9, and acid residue from the Murchison CM2 meteorite. The pair of absorptions near 2960 and 2880 cm-1 result from the C-H3 stretching vibrations, and the pair of absorptions near 2926 and 2854 cm-1 result from the C-H2 stretching vibrations of aliphatic hydrocarbon. The broad absorption near 3050 cm^{-1}, detected in the Murchison residue but not in the IDPs, results from C-H stretching vibrations in aromatic hydrocarbons.

Murchison residue shows an aromatic or olefinic C-H absorption feature at 3050 cm^{-1}, which is absent from the IDP spectra. This indicates that a significantly larger fraction of the hydrogen in Murchison is bound to aromatic structures than is the case in the IDPs.

4.3. Comparison of the Organic Matter in IDPs to That in Interstellar Grains

Organic matter has been identified in interstellar grains by infrared spectroscopy (see e.g., Sandford et al., 1991). The relative depths of the aliphatic C-H3 to C-H2 in the published spectra of interstellar organic matter is comparable to what we detect in the Murchison acid residue. The IDPs we measured have a significantly smaller ratio of C-H3 to C-H2 than has been reported in the interstellar grains, indicating that the mean aliphatic chain length is greater in the IDPs than in the interstellar organic matter.

5. CONCLUSIONS

The detailed comparison of carbonaceous material in the hydrated and the anhydrous meteorites does not significantly constrain the origin of the pre-biotic organic matter in the Solar System because all known anhydrous meteorites exhibit deple-

tions of the moderately volatile elements indicating that these anhydrous meteorites were formed or processed at relatively high temperatures. We have performed the first direct comparison of the organic components of primitive (i.e., not significantly altered by thermal processing) anhydrous and hydrated extraterrestrial samples, the IDPs.

The C-XANES detection of significant concentrations of C=O and the infrared detection of significant concentrations of aliphatic hydrocarbons in anhydrous IDPs provide direct, experimental evidence that primitive, anhydrous Solar System material contains a significant concentration of organic matter. These aliphatic hydrocarbons and C=O frequently occur between mineral grains, apparently being the "glue" that holds the mineral grains in some IDPs together. This indicates the organic matter was incorporated into the anhydrous dust as the individual, submicron grains accreted into dust particles, before the incorporation of the dust into the asteroids and comets. Thus, pre-biotic organic matter was abundant in the early Solar System at the time of dust formation, and aqueous processing on the asteroids was not necessary to transform initially elemental carbon into the organic carbon seen in hydrated meteorites.

These measurements provide direct experimental evidence that pre-biotic organic matter occurs in similar types and abundances in both the anhydrous and the hydrated IDPs. The similarity of the C abundance, C-XANES and infrared spectra of the anhydrous IDPs and the hydrated IDPs indicates that aqueous processing did not significantly alter the bulk of the organic matter already present in the Solar System. The production of these organic species occurred much earlier, possibly by irradiation of C-bearing ices or even by processing in the interstellar medium given large D excess in the organic matter of some IDPs (see Keller et al., 2003). Aqueous processing may, however, have altered some of these initial organic compounds, producing small amounts of more complex organic compounds that are present in concentrations below our current detection limits. Future comparison of the organic matter in anhydrous IDPs with that in hydrated IDPs may permit the effects of aqueous processing to be identified.

The differences between Murchison and the hydrated IDPs – a higher C=C/C=O ratio in Murchison, a higher C-H3 to C-H2 ratio in Murchison acid residue, and a higher concentration of aromatic hydrocarbons in Murchison acid residue – may result from the higher degree of thermal processing experienced by the Murchison (CM2) meteorite, but these differences need to be investigated in more detail.

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