

The Nature and Distribution of the Organic Material in Carbonaceous Chondrites and Interplanetary Dust Particles

S. Pizzarello

Arizona State University

G. W. Cooper

NASA Ames Research Center

G. J. Flynn

State University of New York at Plattsburgh

Most of the carbon in carbonaceous chondrites is organic material that displays structures as diverse as kerogen-like macromolecules and simpler soluble compounds ranging from polar amino acids and polyols to nonpolar hydrocarbons. Overall, the large molecular and isotopic diversity of meteorite organics verifies their extraterrestrial origin and points to synthetic pathways in a variety of chemical regimes. These include exothermic reactions in the cold, H-fractionating interstellar gas phase and aqueous reactions in asteroidal parent bodies. Reactions on interstellar grains and during nebular processes were most likely involved but are inferred with less certainty. The unique L-asymmetry of some meteoritic amino acids suggests their possible contribution to terrestrial molecular evolution. Many interplanetary dust particles show a primitive composition that distinguishes them from known meteorites and could offer unique insights into unaltered nebular material. So far, micrometer sizes have prevented their wide-ranging molecular characterization.

1. INTRODUCTION

Organic material has been detected within the solar system in planetary satellites (*Courting et al.*, 1991), the coma of comets (*Kissel and Kruger*, 1987; *Bockelée-Morvan*, 2001; *Mumma et al.*, 2001), interplanetary dust particles (IDPs) (*Clemett et al.*, 1993; *Flynn et al.*, 2000), micrometeorites recovered from polar ice (*Brinton et al.*, 1998; *Matrajt et al.*, 2001), and meteorites. While the first two observations are limited to remote sensing or spacecraft findings, the organics in meteorites and, to a lesser degree, the related smaller IDPs and micrometeorites have received direct scrutiny in laboratory analyses. Studies have been extensive for the carbonaceous chondrites (CC) and several earlier reviews have followed their progress; the most recent ones, *Botta and Bada* (2002), *Sephton* (2002), and *Cronin and Chang* (1993), provide references to earlier reviews as well as to most of this introduction.

The organic content of CC is high in relation to total carbon and is complex in composition; it consists almost exclusively of an insoluble kerogen-like material in the CO, CV, and CK classes of these meteorites, while in the CI, CM, and CR classes it also includes numerous soluble organic compounds (see chapters in Part I of this volume for meteorite classification). The relative abundance of insoluble to soluble organic carbon varies between meteorites; in the more soluble-rich chondrites, e.g., the CM2s Murchison

and Murray, the insoluble organic material constitutes ~70% of the total while in others, such as the ungrouped Tagish Lake meteorite, it surpasses 99%.

Variability of composition is one of the common characteristics of the organic material of CC and is shown not only by the relative abundance variations described above but also by compositional differences in both insoluble (*Cody et al.*, 2005) and extracted organic materials between meteorites of the same class. In particular, the complex soluble organic suite of CMs varies significantly in abundance and composition between and even within individual meteorites (*Cronin and Pizzarello*, 1983; *Pizzarello et al.*, 2001, 2003). Several of the organic compounds found in meteorites are also common terrestrial biomolecules; however, in CC they are components of a diverse and random mixture, a fact that is consistent with abiotic processes and that contrasts with the structural specificity seen in their terrestrial counterparts. For example, over 80 isomeric and homologous amino acid species up to C₈ have been identified in the Murchison meteorite in contrast to just 20 that make up terrestrial proteins.

A portion of the soluble and insoluble meteoritic organic material, as well as IDPs, share an enrichment in the heavier stable isotopes of H, C, and N. The findings, in particular the magnitude of the positive δD of some soluble meteoritic compounds, have been related to the large D-enrichments observed in cold interstellar clouds and suggest that meteoritic compounds had interstellar precursors. However,

this enrichment is either absent or less pronounced in other meteorite organics, such as much of the insoluble carbon and the aliphatic hydrocarbons.

Given these large compositional and isotopic differences, an inclusive theory for the origin of all the varied organic constituents in CC appears hard to formulate. Moreover, the variability in molecular, chiral, and isotopic distribution shown by discreet soluble organic compounds indicates that their formation was likely a diverse and multistep process. On the basis of the constraints posed by the overall molecular and isotopic data, it is possible to estimate that several processes contributed to meteorite organic syntheses, either singularly or in concurrence, at different points in their histories: presolar syntheses, solar nebular reactions of organic material, and parent-body water chemistry.

Many organic molecules have been observed in interstellar and circumstellar environments where they are, for the most part, detected in the gas phase by infrared and microwave spectroscopy (see The National Radio Astronomy Observatory Web site, www.nrao.edu, for updated lists of interstellar and circumstellar molecules). It is expected that refractory interstellar grains could host the syntheses of an even larger variety of molecules. Many interstellar molecules have shown molecular and isotopic features that are characteristic of the low temperatures and energetic conditions at which they were formed (e.g., *Roueff and Gerin, 2003*). Some of the CC organics appear to have kept, at least in part, some of those features such as D-enrichment and highly branched carbon structures. We have to assume, therefore, that presolar syntheses provided an inventory of simple organics and precursor species to the collapsing solar nebula. A significantly larger D-enrichment found for some of the amino and monocarboxylic acids in the Murchison meteorite further indicates that some of these syntheses must have been more advanced for distinct subgroups of meteoritic compounds and may have produced several of the compounds observed in meteorites or their direct precursors.

Very little is known about the conditions and processes that could have altered, destroyed, or formed organic compounds during the periods of interstellar cloud collapse, stellar origin, and solar nebular formation. Even if poorly understood, however, interactions of gas and solids in the nebula have to be assumed and could include both reactions of infalling interstellar material and the syntheses of new molecular species. Guidelines within the many uncertainties that exist in regard to nebular conditions are provided by spectroscopic observation of young stellar objects (e.g., *Qi et al., 2003*) and theoretical models of collapsing interstellar cores (e.g., *Aikawa et al., 2003*), protoplanetary disks (e.g., *Aikawa et al., 2002*), and planetesimal mass distribution (e.g., *Kortenkamp et al., 2001*) that could affect the primordial asteroid belt. Also, *Aikawa and Herbst (2001)* estimated large D/H ratios for some molecules in cold protoplanetary disk regions. This D-enrichment could derive from H-fractionating chemistry in the disk similar to that in the interstellar cloud and not just from the incorporation of interstellar material.

Certain scenarios of solar system formation (*Boss et al., 2002*) allow for a flux of UV radiation in the inner nebula that could lead to photolysis of planetesimal ices and an extensive organic chemistry of the kind observed on Titan (*Boss, 2002*). Classic Fisher Tropch-type (FTT) reactions, i.e., involving CO, H₂, and the minerals of a condensing nebula, have been invoked for the formation of many meteoritic compounds but failed to be confirmed by the isotopic data. However, catalytic gas-solid reactions could be possible in the nebula (*Kress and Tielens, 2001*) on the surface of condensing grains, small bodies, and planetesimals; catalytic liquid-solid reactions could have occurred during a liquid phase as well. Heating by shock waves, impacts, and gravitational collapse could have contributed to the chemistry of organics at different stages of nebular condensation.

Parent-body water alteration processes are recorded in CC not only by the matrix mineralogy but also by their soluble organic composition. For example, a Strecker-like reaction of aldehyde and ketone precursors with ammonia and HCN in water (Scheme 2) is consistent with the finding in meteorites of comparable suites of α -amino, α -hydroxy, and imino acids. Although similar indirect proofs are not found for other subgroups of the same compounds, in general, the breadth of water-soluble organics found in CC, their coexistence with clay minerals in these meteorites, as well as some of the plausible hypotheses formulated for their synthesis would reasonably suggest that at least the final formation stages of most of these organic compounds were affected by reactions with water, such as hydrolysis of nitriles and saturation of double bonds.

2. THE INSOLUBLE CARBONACEOUS MATERIAL

The larger fraction of the organic carbon in CC, amounting to 70–99% of the total, is present as a complex and insoluble macromolecular material that is obtained from meteorite powders only after repeated extractions with solvents and demineralization by concentrated hydrofluoric and hydrochloric acids (e.g., *Cronin et al., 1987*) or CsF (*Cody et al., 2002*). In addition to C, this insoluble organic material (IOM) also contains H, O, N, and S, with elemental composition that varies between classes and subclasses of CC, e.g., similar combustion methods gave the general formulas C₁₀₀H₇₀N₃O₁₂S₂ and C₁₀₀H₄₆N₁₀O₁₅S_{4.5} for the Murchison (*Hayatsu et al., 1980*) and Tagish Lake (*Pizzarello et al., 2001*) meteorites, respectively. The Murchison IOM isotopic composition, as averaged from several studies (*Kerridge et al., 1987*), is given by the values $\delta D = +727.6\text{‰}$, $\delta^{13}C = -14.3\text{‰}$, and $\delta^{14}N = +6.6\text{‰}$, while two analyses of Tagish Lake IOM gave $\delta D = 930\text{‰}$ (*Pizzarello et al., 2001*) and a summed $\delta^{13}C \approx +24.3\text{‰}$ (*Brown et al., 2000*).

Macromolecular carbonaceous material free of minerals can also be found in untreated CC powders as distinct nanometer-sized entities such as aromatic flakes, solid or hollow spheres, and tubes (*Nagy et al., 1962*; *Rossignol-Strick and Barghoorn, 1971*; *Pflug, 1984*; *Nakamura et al., 2002*;

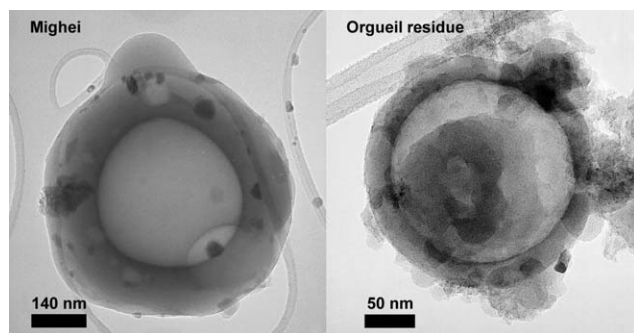


Fig. 1. TEM images of hollow carbonaceous particles from the Mighei (unprocessed powders) and Orgueil (HF/HCl acid residue) carbonaceous chondrites. The Orgueil sphere is surrounded by adhering IOM. From Garvie and Buseck (2004b).

Garvie and Buseck, 2004b), which are observed in several CI and CM powders as well as in the acid insoluble residues (Garvie and Buseck, 2004a) (Fig. 1). They are analyzed by transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS). By visual estimate, they appear to have an abundance of up to 10% of total IOM in Orgueil (L. Garvie, personal communication, 2004) and are heterogeneous in composition, size, and distribution in all meteorites analyzed. In Tagish Lake alone, hollow nanospheres range in outside diameter from 166 to 830 nm and in internal volumes from 6.9×10^3 to $3.3 \times 10^5 \text{ nm}^3$ (Garvie and Buseck, 2004b). Their carbon is aromatic in nature, varying in composition from close to pure graphitic C (>99%) to containing several percent of O, N, and S; e.g., the elemental composition of a Tagish Lake carbonaceous flake was observed to be $\text{C}_{100}\text{S}_{10.1}$ while that of a globule in the same meteorite was $\text{C}_{100}\text{S}_{2.7}\text{N}_{5.0}\text{O}_{10}$ (bonded H is not detected by EELS and is excluded from the above calculations). Functional groups such as C=O and C=N are also observed in some nanostructures. Other well-characterized carbon structures identified in the IOM are sometimes described as exotic C species by their association with isotopically exotic He, Xe, and Ne. These are the nanodiamonds (Lewis et al., 1987; Blake et al., 1988), silicon carbide (Tang et al., 1989), graphite (Smith and Buseck, 1981; Amari et al., 1990), and fullerenes (Becker et al., 2000). All have been considered of presolar origin and possibly formed in the outflows of carbon stars.

The remaining larger portion of the insoluble carbon can be seen by TEM to be an unstructured and heterogeneous material that does not show any clear resolution in its continuity (Derenne et al., 2002; Garvie and Buseck, 2004a). Given its complex nature and inaccessibility to solvents, so far, the IOM of CC has been mainly analyzed as a whole by either decomposition techniques, such as chemical degradation and pyrolysis, or solid-state nuclear magnetic resonance (NMR) spectroscopy. These approaches, although limited in their capability to provide a complete chemical definition of all IOM macromolecular phases, have been useful to characterize many of their compositional features.

Oxidative degradation carried out by Hayatsu et al. (1977, 1980) on Murchison IOM, together with detailed analyses of the composition and abundance of the fragmentation products, gave a general structure for the material that is still plausible today. It would consist of condensed aromatic, hydroaromatic, and heteroaromatic macromolecules that contain alkyl branching, functional groups such as OH and COOH, and are bridged by alkyl chains and ether linkages. Vacuum pyrolysis analyses of Orgueil and Cold Bokkeveld IOM (Bandurski and Nagy, 1976) are in general agreement with this model and in addition provided identification of several IOM nitrile species. Hydrous pyrolysis studies conducted by Sephton et al. (1998, 2000) on the IOM of several CC have further constrained this macromolecular model. The authors found that these pyrolytic conditions release a set of aromatic compounds such as toluene, naphthalene, methyl naphthalenes, and others that are also found in the solvent extracts of the meteorite, while leaving behind a residue of virtually unaffected material. On the basis of C-isotopic differences between soluble, pyrolysable, and residual material, the hypothesis was put forward (Sephton et al., 1998) that the macromolecular C comprises at least two components: a more labile portion, which during parent-body alteration processes might already have generated some of the aromatic compounds detected in whole meteorite extracts, and a refractory material. This hypothesis of diverse IOM phases agrees with isotopic data (Kerridge et al., 1987) that showed a two-temperature release of carbonaceous components from the IOM (at $\sim 250^\circ\text{--}350^\circ\text{C}$ and over 400°C , respectively) where the more labile phase was enriched in D ($\delta\text{D} \geq +1165\text{‰}$). The $\delta^{15}\text{N}$ values measured by step combustion of several CC IOMs (Alexander et al., 1998) showed a two-component distribution for this element also. However, a third component of heavier N ($\delta^{15}\text{N} \geq +260\text{‰}$) was released above 500°C , a finding that was later expanded by Sephton et al. (2003) and would indicate that the makeup of the IOM residue left after hydrous pyrolysis is itself heterogeneous.

The possibility of parent-body thermal alteration of the IOM subsequent to the aqueous processes has also been considered and studied by pyrolysis-GC (Murae et al., 1991; Kitajima et al., 2002). Analyses assessed the relative abundances of lower- and higher-temperature pyrolysates released from several meteorite IOMs, on the assumption that more thermally altered material would be more graphitic and yield less of the lower molecular weight products such as naphthalenes. Pyrolysate results confirmed this assumption and indicated that the possible metamorphic variations observed in the IOMs correlate well with the estimated heating of the corresponding meteorites. Shimoyama et al. (1991) reached similar conclusions from their analysis of thermal decomposition products from whole meteorite powders.

Infrared (IR), solid-state ^{13}C and ^1H NMR, and electron paramagnetic resonance (EPR) spectroscopic analyses of the IOM in CC have been complementary to the decomposition analyses described above and offer an overview of the chemical nature of the IOM as a whole, with emphasis on its

bonding, functional group composition, and radical abundance properties (e.g., see Fig. 2). The ^{13}C NMR spectra of the Orgueil (Cronin *et al.*, 1987; Gardinier *et al.*, 2000) and Murchison (Cronin *et al.*, 1987; Gardinier *et al.*, 2000; Cody *et al.*, 2002) IOM were collected by magic-angle spinning, employing both cross polarization (CP) and single pulse (SP) techniques [see Cody *et al.* (2002) for a summary of these techniques]. The spectra confirm the complex nature of the IOM revealed upon its degradation and show two main broad features characteristic of sp^2 and sp^3 hybridized C atoms, i.e., olefinic/aromatic and aliphatic features, respectively. The relative abundance of aromatic carbon varies between these meteorites and is largest in Murchison, where it represents 0.61–0.66 of the IOM carbon (Cody *et al.*, 2002). The Tagish Lake meteorite presents an NMR spectrum that is substantially different from those of Orgueil and Murchison, with a predominant aromatic feature that represents over 80% of the IOM carbon (Pizzarello *et al.*, 2001; Cody *et al.*, 2005).

In the meteorites analyzed so far, the aromatic carbon appears to comprise mainly rather small (smaller than C_{24} coronene) and highly substituted (Gardinier *et al.*, 2000; Cody *et al.*, 2005) ring aggregates, where larger unprotonated structures make up, at most, only 10% of total aromatics (Cody *et al.*, 2002). Insoluble organic material aliphatic carbon in Murchison and other meteorites includes methyl, methylene, and methine groups (Gardinier *et al.*, 2000; Cody *et al.*, 2005) and appears to be composed of highly branched short chains that could be related to the aromatic fraction via extensive cross linking. In Murchison,

the IOM aliphatic carbon contains the majority (~70%) of total hydrogen (Cody *et al.*, 2002).

Nuclear magnetic resonance spectra have also identified several IOM functional groups; most of them are O-containing (e.g., carboxylate and carbonyl) and vary between meteorites in their relative proportion to other functionalities. When their abundance is plotted in relation to aliphatic carbon, which is more susceptible to oxidation than the aromatic material, it shows different levels of IOM oxidation between various CC with the comparative distribution: $\text{CR2} < \text{CI1} < \text{CM2} < \text{Tagish Lake}$ (Cody *et al.*, 2005). Insoluble organic matter organic S functionalities, which are not measured by NMR but should be abundant given the material overall elemental composition, were observed by X-ray absorption near-edge structure (XANES) analyses to be of numerous kinds (Derenne *et al.*, 2002). Interestingly, comparative analyses of Orgueil (Binet *et al.*, 2002), Murchison (Binet *et al.*, 2004a), and Tagish Lake (Binet *et al.*, 2004b) IOM by EPR and electron nuclear double resonance studies (ENDOR) have shown that these materials, in spite of dissimilarities in their makeup, all show the same feature of abundant and heterogeneously distributed mono- and di-radicals. The equal presence and similarity of distribution of these aromatic features in meteorites that differ in degrees of mineral alteration and organic content could indicate that at least a portion of the IOM predated and survived parent-body environments.

What conclusions do the analytical studies allow in regard to the formation of the IOM in CC, its origin, and genetic relationship, if any, with the soluble organic material? Carbonaceous material organized in well-defined macromolecular structures, most or all of which do not appear to alter through the harsh demineralization procedures, seems to indicate that the origin of at least a sizable portion of the IOM predated parent-body processes. Garvie and Buseck (2004b) point out that some of the nanostructure compositional differences, such as the example of sharp dissimilarities between contiguous formations in the Bells meteorite (a CM2 fall), are not compatible with their asteroidal aggregation during an aqueous phase since such water processes would have likely acted as compositional equalizers, at least at short distances. Moreover, the enrichment in D and ^{15}N found for discrete IOM phases points to a distinct origin related to interstellar syntheses for some of the IOM constituents, in spite of the lack of identification of their carrier moieties.

On the other end, IOM isotopic, pyrolytic, and comparative NMR analyses give convincing evidence that at least a portion of this material can be and probably was modified during parent-body processes, resulting in the graphitization and chemical oxidation we observe and the possible release of soluble organic compounds. However, the latter processes must have been more complex than one directly comparable with laboratory IOM hydrous pyrolysis, which is conducted in the absence of minerals and any control of oxygen fugacity (Shock and Schulte, 1998). For example, it has been observed that simpler aromatic species are py-

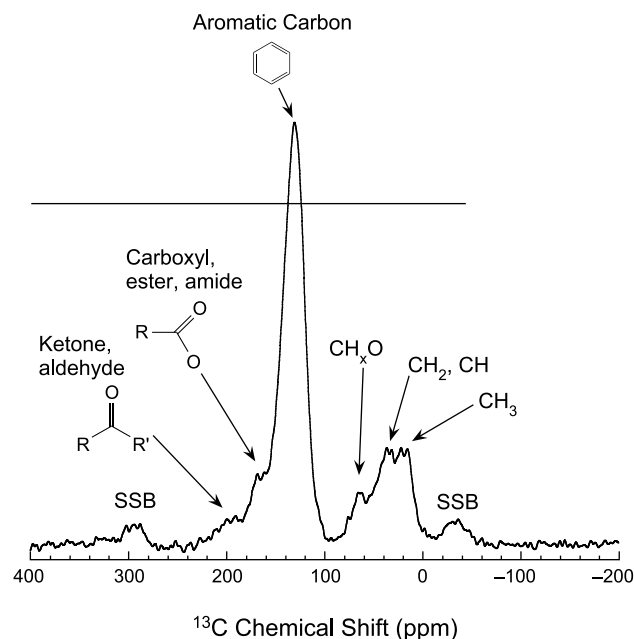


Fig. 2. ^{13}C -NMR spectrum of Murchison IOM showing the range of organic functionalities in the insoluble carbon (by variable amplitude cross polarization magic angle spinning). From Cody *et al.*, 2002.

TABLE 1. Soluble organic compounds in the Tagish Lake and Murchison meteorites.

Class	Tagish Lake ^[1]		Murchison ^[2]	
	Concentration (ppm)	Compounds Identified ^[3]	Concentration (ppm)	Compounds Identified
Aliphatic hydrocarbons	5	12*	>35	140
Aromatic hydrocarbons	≥1	13	15–28	87
Polar hydrocarbons	n.d.	2*	<120	10*
Carboxylic acids	40.0	7	>300	48 ^[4] *
Amino acids	<0.1	4	60	74*
Hydroxy acids	b.d.	0	15	7
Dicarboxylic acids	17.5	18*	>30	17 ^[5] *
Dicarboximides	5.5	9	>50	2 ^[6]
Pyridine carboxylic acids	7.5	7	>7	7 ^[1]
Sulfonic acids	≥20	1	67	4 ^[7]
Phosphonic acids	n.d.	n.d.	2	4 ^[7]
N-heterocycles	n.d.	n.d.	7	31
Amines	<0.1	3	13	20 ^[8]
Amides	<0.1	1	n.d.	27 ^[6] *
Polyols	n.d.	n.d.	30	19 ^[9]
Imino acids	n.d.	n.d.	n.d.	10 ^[10]

*The compound group comprises significantly more molecular species than those unequivocally identified.

References: [1] Pizzarello et al. (2001); [2] Cronin et al. (1988) and references therein, unless otherwise indicated; [3] By reference standards or unequivocal matching of compound and library mass spectra; [4] Huang et al. (2005); [5] Pizzarello and Huang (2002); [6] Cooper and Cronin (1995); [7] Cooper et al. (1992); [8] Pizzarello et al. (1994); [9] Cooper et al. (2001); [10] Lerner and Cooper (2005).

rolytically released from the IOMs of more altered meteorites such as Orgueil (Sephton et al., 1999); however, if the more open macromolecular structure implied by this release had been the effect of aqueous alteration, the liquid extracts of this meteorite should also show a larger abundance of soluble aromatics than less-altered meteorites, which does not seem to be the case. The Tagish Lake molecular distribution also speaks to a complex relation between IOM and soluble organics. This meteorite displays the largest amount of carbonates among CC, a lack of several soluble compound classes, e.g., most of the amino acids (see section 3.1.1 below), and higher levels of IOM oxidation relative to other meteorites, data that would point to long parent-body aqueous processes and possible oxidative degradation. Yet Tagish Lake solvent extracts display an unusual (compared to Murchison) abundance of nitriles and other cyanospecies (Gilmour et al., 2001; Pizzarello et al., 2001), which would have been hydrolyzed by such water exposure. In the case of this meteorite, therefore, the overall data appear to indicate that at least some of the IOM and soluble aromatic hydrocarbons resulted from synthetic and/or accretion histories that were independent from each other.

The less labile of the insoluble carbon remains the most poorly characterized phase in the IOM. It contains “exotic” carbon of dissimilar ¹³C content, such as nanodiamonds and silicon carbide ($\delta^{13}\text{C} \approx -38$ and $>+60\%$, respectively). Overall, this refractory material appears depleted in the heavy isotopes of carbon but retains δD values of 400‰ (Kerridge et al., 1987), an isotopic content that would be compatible with cold nebular as well as presolar processes. The seem-

ingly constant quantitative distribution of nanodiamonds to IOM, indirectly measured by Alexander et al. (1998) in several CC, would seem to be consistent with the latter possibility.

Although the relation between nanostructures and IOM is difficult to ascertain due to the lack of comparable isotopic data, the studies of the structured carbonaceous material may possibly reveal features lost in the overall analysis of the IOM. Their large compositional heterogeneity, when taken together with the isotopic inhomogeneity observed for the IOM, strongly suggest that the various phases of the insoluble carbon in meteorites are the complex end products of formative conditions, chemical regimes, and cosmic environments that varied extensively.

3. THE SOLUBLE METEORITIC ORGANIC COMPOUNDS

Soluble organics in CC comprise a varied and complex suite of compounds that span the range from large species, such as polycyclic aromatic hydrocarbons (PAHs) or long alkyl acids and diacids at the limit of solubility, to small molecules like methane and formic acid. Table 1 lists the organic composition of the Murchison and Tagish Lake meteorites, a CM2 and ungrouped chondrite, respectively, which are two of the most comprehensively studied CC and representative of the compositional variability among these meteorites. The isotopic composition of CC soluble organics varies as well and is given in Tables 3–6 and in Fig. 3. It should be noted that the carbonaceous chondrites studied

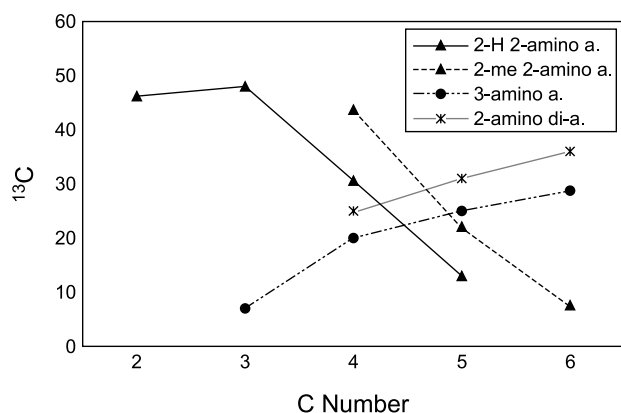


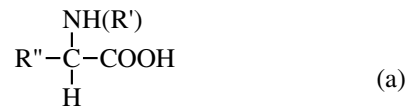
Fig. 3. Plot of $\delta^{13}\text{C}$ values vs. C number for 2-H-2-amino acids (solid line), 2-methyl-2-amino acids (dashed line), 3-amino acids (dash-dot line), and 2-amino dicarboxylic acids (gray line). Data points represent averages when more than one is available for given C# (see Table 3).

so far for their content of soluble organic compounds have been relatively few and that future falls, studies of the abundant Antarctica meteorite reservoir, and additional analyses of the known meteorites will likely expand these available data.

3.1. Amino Acids

Amino acids are amphoteric compounds (i.e., contain both the basic amino and acidic carboxyl functions) that are extensively distributed in the biosphere where they are represented primarily by 20 compounds as the monomeric components of proteins. Many other less-common amino acids are found in bacteria and molds or as metabolites in higher organisms. Terrestrial amino acids include both aliphatic and aromatic molecules, are almost exclusively of the L-configuration, and their chiral homogeneity (homochirality) appears to be indispensable to the organization and function of biopolymers. In meteorites, amino acids have been found in the water extracts of CI (*Lawless et al.*, 1972), CM falls (*Kvenvolden et al.*, 1970; *Raia*, 1966; *Cronin and Pizzarello*, 1983; *Komiya et al.*, 2003), Antarctica finds (*Shimoyama et al.*, 1979; *Cronin et al.*, 1979), CR (S. Pizzarello and J. R. Cronin, unpublished data, 1987), and the ungrouped Tagish Lake (*Pizzarello et al.*, 2001) meteorites, although with large compositional variability. When abundant, as in some CM chondrites, they comprise a diverse suite of over 80 aliphatic species of up to eight-carbon (C_8) alkyl chain length that include all possible molecular subgroups [generalized structures are shown in Scheme 1, where R is an alkyl group and (R) indicates alkyl or H]. This diverse and random distribution is one of the traits that differentiate meteoritic from terrestrial amino acids, the others being the lack of single chiral configuration (but see section 3.1.1 for discussion of certain anomalous D/L ratios); enrichment in the heavier isotopes of H, C, and N; and de-

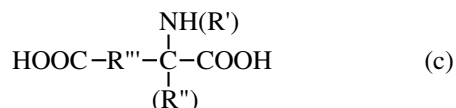
clining abundance with increasing chain length. The complex molecular and isotopic composition of meteoritic amino acid has posed many analytical challenges and, in spite of extensive studies of over 30 years, new information is being revealed by novel techniques even for the most analyzed meteorites.



α -H α -amino acids



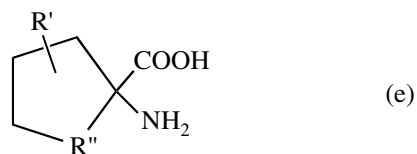
α -alkyl α -amino acids



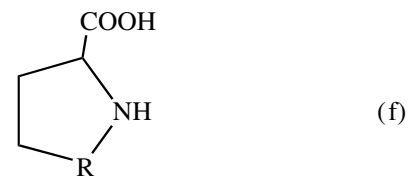
α -amino alkanedioic acids



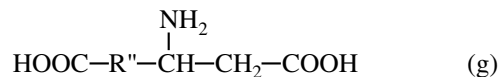
β -, γ -, etc., amino acids



α -amino cycloalkane acids



Proline + homologs and isomers



β -amino alkanedioic acids



diamino acids

Scheme 1

3.1.1. Molecular analyses. Molecular analyses of Murchison meteorite water extracts show that nearly all-possible isomeric and homologous species having the basic formulas (a)–(f) listed in Scheme 1 may be present up to the limit of solubility, approximately C₈, although identifications may vary between subgroups, depending upon the availability of reference standards. Diamino acids have been identified up to C₅ (Meierhenrich et al., 2004) and only one β-aminodicarboxylic acid has been found so far (Pizzarello et al., 2004). For α-amino acids (2-aminoalkanoic acids) that have been extensively characterized with the help of synthetic standards, all compounds up to C₇ have been identified (Cronin and Pizzarello, 1983, 1986). For the β-, γ-, and δ-amino acids [3-, 4-, 5-aminoalkanoic acids (Cronin et al., 1985)] or α-amino dicarboxylic acids (Cronin et al., 1993; Pizzarello et al., 2004), complete identification is limited to C₅ and C₆ compounds, respectively. For the remaining subgroups, fewer compounds have been identified: N-methylglycine (sarcosine), N-methylalanine, and N-methyl-α-aminoisobutyric acid; cycloleucine and 1-amino-1-cyclohexane carboxylic acid; proline and pipercolic acid. Besides these positively identified compounds, longer chain amino acid homologs are clearly recognized within all subgroups on the basis of their mass-fragmentation spectra by gas chromatography-mass spectrometry (GC-MS) (e.g., Cronin et al., 1982; Pizzarello et al., 2004). Eight of the proteins amino acids — glycine, alanine, proline, valine, leucine, isoleucine, and aspartic and glutamic acids — are also found in meteorites.

The amino acids of these various isomeric subgroups show differences in their abundance as well as their chemical and/or physical binding in the meteorite. For example, the non-α-amino acids and diamino acids (Meierhenrich et al., 2004) are released in some Murchison extracts only after acid hydrolysis of acid-labile derivatives. Similarly, α-amino α-H species require a higher extraction temperature and hydrolysis of the extract for full release, while the α-alkyl α-amino acids are easily extracted in water at room temperature (Pizzarello and Cronin, 2000). Allowing for variability between meteorites, the rough estimate is that the three subgroups of branched α-amino acids, non-α-amino acids, and α-amino dicarboxylic acids are represented approximately in equal amount in Murchison acid hydrolyzed extracts; the linear α-amino acids trail in abundance by about one-third. Cyclic α-amino acids are present in many isomeric forms up to at least C₈ and have consistently higher abundances than branched species of comparable chain length (S. Pizzarello, unpublished data, 2004). The N-substituted amino acids are also present in several isomeric forms and, within approximation, compare in amounts to the linear α-amino acids. Many compounds that release amino acids upon acid hydrolysis have been identified and are discussed in section 3.3.2. Peptides and amino acid dimers have been searched for in two CMs (the Yamato-791198 and Murchison meteorites) and were not found, with the only exception of the glycine dipeptide and diketopiperazine, which were observed in low amounts (Shimoyama and Ogasawara, 2002).

The distinction between linear and α-substituted α-amino acids (Scheme 1) is of particular interest and is based on the different molecular, isotopic, and chiral distribution found for the branched compounds in CM chondrites. Although it has been studied in depth for CM α-amino acids, isotopic data seem to indicate that a distinction between compounds based on alkyl chain branching may be justified for other amino acid subgroups as well (see section 3.1.3 below) (Pizzarello and Huang, 2005). The α-methyl α-amino acids are rare or unknown in the biosphere but abundant in CM chondrites such as Murchison and Murray where the first homolog of the series, α-amino isobutyric acid, is present at ~10 ppm and is often the most-abundant compound in the amino acid suite. Their abundance declines with chain length, as with other meteoritic compounds; however, their total abundance varies independently from that of α-H amino acids (Cronin et al., 1993; Pizzarello et al., 2003).

Uniquely, the chiral homologs of this amino acid series display L-enantiomeric excesses (ee) (Cronin and Pizzarello, 1997; Pizzarello and Cronin, 2000), whose magnitude varies within the meteorite and is largest, up to 15%, for isovaline (2-methyl-2-aminobutyric acid). The indigeneity of amino acid ee in CC is supported by compound-specific C- (Pizzarello et al., 2003) (Table 2) and H- (Pizzarello and Huang, 2005) isotopic data obtained for Murchison and Murray isovaline enantiomers (Table 3). The origin of these ee is still unknown; the first hypothesis to be proposed was that of an asymmetric photolysis of meteorite organics by UV circularly polarized light (CPL) irradiation during their synthesis (Rubenstein et al., 1983; Cronin and Pizzarello, 1997; Engel and Macko, 1997). This proposal appeared to set a preplanetary locale for the formation of meteoritic amino acids, or at least the α-methyl α-amino acids, since it is likely that an asymmetry-causing UV radiation would have been shielded in the meteorite parent bodies (Pizzarello and Cronin, 2000). Compound specific analyses (Pizzarello et al., 2003), however, have revealed data that were unexpected in the context of this irradiation hypothesis and found that isovaline ee are sometimes larger than would be theoretically allowed (Balavoine et al., 1974) if photolysis by UV CPL had been the only source of this amino-acid asymmetry (Table 2). This work also suggested a possible correla-

TABLE 2. δ¹³C (‰ PDB) values of meteoritic L- and D-isovaline.

Sample	L-ival ee%	L-ival δ ¹³ C	D-ival δ ¹³ C
1. Murchison I*	13.2	+18.0	+16.0
2. Murchison I	6.0	+17.8	+11.5
3. Murchison E†	12.6	+21.9	+19.9
4. Murchison E	0	+17.5	+17.3
5. Murray I	6.0	+20.0	+18.8
6. Standard‡		-28.0	-31.9

*I = interior.

†E = exterior.

‡Combined DL-peak: -30.5‰.

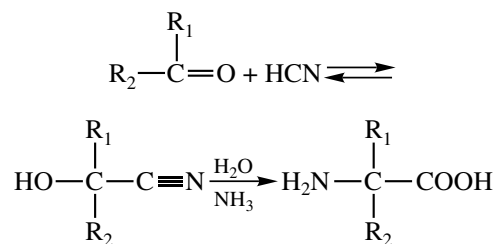
From Pizzarello et al. (2003).

tion between the distribution of nonracemic amino acids and the abundance of hydrous silicates; however, the formation of primary asymmetric mineral phases and the possible influence they may have yielded on the molecular asymmetry of meteorite organics is still undefined and will require extensive new studies. It is possible that the α -H-amino acids were also affected by asymmetric processes but their ee were lost due to racemization, to which substituted species such as α -methyl α -amino acids are resistant. Thus far, no unequivocal sign of this possibility has been found (Engel and Macko, 1997, 2001; Pizzarello and Cronin, 1998) and isotopic analyses of a Murchison sample have shown that the L-enantiomers of alanine, aspartic, and glutamic acids, each having terrestrial counterparts, all show significantly lower ^{13}C content (Pizzarello *et al.*, 2004), as would be expected by contributions from terrestrial L-amino acid contaminants.

An amino-acid composition with general similarity to that of Murchison has been described for the Murray meteorite (Cronin and Moore, 1971; Pizzarello and Cronin, 2000) and, by single analyses, for the Yamato-791198 (Shimoyama *et al.*, 1985), Santa Cruz, Mighei, Nogoya, and Cold Bokkeld (Cronin and Pizzarello, 1983) CM meteorites. However, an exponential decay was also observed in the abundance of α -amino isobutyric acid with the terrestrial age of all these meteorites except Nogoya, suggesting that comparisons between data from meteorites with different fall ages may not be accurate (Cronin and Pizzarello, 1983). In the newly analyzed Sayama meteorite, whose fall dates to 1986, amino acid abundance was found to be orders of magnitude lower than in Murchison (Komiya *et al.*, 2003). Murray is the only meteorite other than Murchison for which chiral analyses of branched amino acids have been conducted, with results comparable to those of Murchison (Pizzarello and Cronin, 2000). The CI chondrites Orgueil and Ivuna show a distinctly different amino-acid composition (Ehrenfreund *et al.*, 2001) that is characterized by less overall abundance and diversity of compounds, where β -alanine is the largest component, and the α -methyl amino-acid series is represented by only the first homolog, α -aminoisobutyric, found in low abundance. In Tagish Lake amino acids are present in far lower amounts than in Murchison (by ~ 3 orders of magnitude) and are limited to three linear homologs: glycine, alanine, and α -amino-n-butyric acid (Pizzarello *et al.*, 2001).

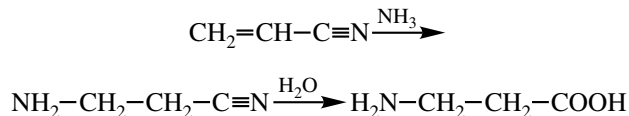
3.1.2. Synthetic processes. The synthetic processes capable of producing amino acids as chemically diverse as those found in CC were, most likely, diverse as well. For α -amino acids, the current view is that they possibly formed during the parent-body aqueous alteration period by a Strecker-like reaction of precursor aldehydes and ketones, ammonia, and HCN (Scheme 2), as proposed by Peltzer and Bada (1978). The supporting evidence for this hypothesis has been the finding in the Murchison meteorite of comparable suites of α -amino and α -hydroxy linear acids (Peltzer and Bada, 1978) [although this correspondence is not valid for the α -methyl compounds (Cronin *et al.*, 1993)] and of imino acids

(Pizzarello and Cooper, 2001; Lerner and Cooper, 2005). These are compounds where two carboxyl-containing alkyl chains are bonded at the same amino group and would likely result from a Strecker synthesis, e.g., when an amino-acid product becomes the reactant in place of ammonia.



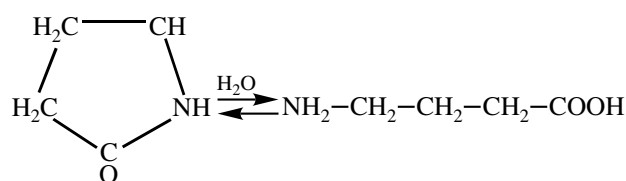
Scheme 2

This synthesis does not lend itself to the direct formation of asymmetric products, although it could be part of processes that involved asymmetric catalysts (see Cronin and Reiss, 2005, for a review). Also, the Strecker route is not allowed for non- α -amino acids (this reaction involves the addition of HCN to the carbonyl carbon, i.e., the α -carbon in the amino and/or hydroxy acid product) and other pathways need to be postulated for their syntheses. For β -amino acids, it has been proposed that they could derive from unsaturated nitriles by the addition of ammonia to the double bond(s), as from acrylonitrile in the case of β -alanine (Cronin and Chang, 1993, and references therein).



Scheme 3

Although the addition of ammonia to a 3–4 double bond of unsaturated nitriles would be less favored (unsaturated aldehydes and ketones with conjugated double bonds are energetically favored), this process could still be invoked for the formation of γ - and δ -amino acids under favorable conditions, e.g., had their precursors evaded the energetic requirements through ion molecule reactions and subsequently avoided the expected isomerization to 2=3 species during an aqueous phase by rapid ammonia addition. A known source of at least some meteoritic γ -amino acids is the hydrolysis of four carbon lactams, such as butanelactam (Scheme 4), which are abundant in Murchison (Cooper and Cronin, 1995).



Scheme 4

TABLE 3. Stable-isotope composition of individual amino acids in CM2 chondrites.

Amino Acid	Murray $\delta D\text{‰}^{[1]}$	Murchison	
		$\delta^{13}C\text{‰}^{[2]}$	$\delta^{15}N\text{‰}^{[3]}$
Glycine	399	41, 22 ^[4]	37
D-alanine	614	52, 30 ^[4]	60
L-alanine	510	38, 27 ^[4]	57
D-2-aminobutyric acid	1633	29	
L-2-aminobutyric acid	—	28	
2-aminoisobutyric acid	3097	43, 5 ^[4]	184
DL ^[1] isovaline	3181	22, 17 ^[4]	66
L-isovaline	3282		
D-norvaline	1505	15	
D-valine	2432		
L-valine	2266		
L-isoleucine	1819		
D-allo isoleucine	2251		
L-allo isoleucine	2465		
DL 2-methylnorvaline	2986	7	
DL 2-amino-2,3-methylbutyric a.	3604	22	
β -alanine	1063	5	61
4-aminobutyric a.	763	18	
DL 4-aminovaleric a.	965	29	
5-aminovaleric a.	552	24	
3-amino 2,2-methylpropanoic a.	2590	25	
3-amino-3-methylbutyric a.	1141		
DL 4-amino-2-methylbutyric a.			
+DL 4-amino-3-methylbutyric a.	1697		
D-glutamic a.	221	29, 33 ^[5]	60
DL 2-aminoadipic a.	619	35	
DL 2-methylglutamic a.	1563	32	
DL threo 3-methylglutamic a.	1343	34	
DL proline	478	4	50
Cyclo leucine	850	24	
Sarcosine	1337	53	129
N-methylalanine	1267		
N-methyl-2-aminoisobutyric a.	3446		

[1] Pizzarello and Huang (2005), by GCHT-IRMS and listed by chemical subgroup; [2] Pizzarello et al. (2004), unless otherwise stated, by GC-C-IRMS; [3] Engel and Macko (1997), by GC-C-IRMS; [4] Engel et al. (1990), by GC-C-IRMS; [5] Pizzarello and Cooper (2001), by GC-C-IRMS.

Besides these synthetic pathways, the Tagish Lake distribution of low abundance and few linear amino acids may indicate that, in protracted aqueous processes of the parent body, some catalytic syntheses of amino acids could take place, e.g., by magnetite catalysis as observed with model experiments (Pizzarello, 2002a).

3.1.3. Isotopic analyses. Isotopic analyses of meteoritic amino acids have significantly sorted out the possible formative processes suggested by their molecular analyses. The first isotopic analyses to target these compounds were conducted by dual-inlet, dual-collector mass spectrometry of combined or partially separated groups of Murchison amino acids (Epstein et al., 1987; Pizzarello et al., 1991). They revealed an enrichment in D, ^{13}C , and ^{15}N with ‰ ranges of $\delta D = 1014\text{--}2448$, $\delta^{13}C = 23\text{--}44$, and $\delta^{15}N = 90$. The $\delta^{13}C$ values of six amino acids subsequently obtained by gas chromatography-combustion-isotope ratio mass spectrom-

etry (GS-C-IRMS) (Engel et al., 1990; Pizzarello and Cooper, 2001) were in general agreement with the previous data ranges while ^{15}N measurements of 12 amino acids expanded the $\delta^{15}N$ values to a range of 37–184‰ (Engel and Macko, 1997) (Table 3). In view of the large isotopic enrichment observed for interstellar molecules, these findings were interpreted by Epstein et al. (1987) to indicate a relationship between meteoritic amino acids and interstellar chemistry. More specifically, according to an interstellar/parent-body hypothesis (Cronin and Chang, 1993), they would result from syntheses of amino acids from highly D-enriched interstellar precursor [e.g., the aldehydes and ketones involved in Strecker reactions (Lerner et al., 1993)] during the asteroidal parent-body water-alteration period.

Comprehensive C- and D-isotopic analyses of several individual amino acids by GC-C-IRMS have provided more details on the isotopic distribution of these compounds and

offered additional understanding of their possible synthetic history. Murchison amino acids $\delta^{13}\text{C}$ values were found to range from 4.9 (norvaline) to 52.8‰ (sarcosine) (Table 3), with statistically significant differences observed both within and between amino acid subgroups (Pizzarello *et al.*, 2004). Within α -amino acids, the α -methyl compounds have larger $\delta^{13}\text{C}$ values than those having an α -H, and the ^{13}C content of homologs in both subgroups declines with increasing chain length (Fig. 3). This isotopic trend is remarkably similar to that observed by Yuen *et al.* (1984) for Murchison carboxylic acids and lower hydrocarbons. Both hypotheses postulated by those authors as to the possible cause of these trends, i.e., the growth of the compound alkyl chains by addition of single moieties and/or ^{13}C intramolecular differences between the acids' alkyl and carboxyl moieties (see section 3.4 below), could apply to meteoritic α -amino acid syntheses as well. For example, a Strecker reaction of interstellar precursors with HCN, water, and ammonia could account for the observed isotopic decline with increasing C-number, had the reactant HCN been heavier in ^{13}C than the precursor alkyl chains. Another possibility is ^{13}C fractionation in cold interstellar clouds; the reaction of ^{12}CO with C ions, such as $^{12}\text{CO} + ^{13}\text{C}^+$ to give $^{13}\text{CO} + ^{12}\text{C}^+$ (Sandford *et al.*, 2001), would result in C species other than CO and its protonated form HCO^+ (Charnley *et al.*, 2004) to be depleted in ^{13}C . According to this scheme, the interstellar precursors (e.g., aldehydes and ketones) of higher amino acids would be expected to have a ^{13}C enrichment that decreases with increasing chain length.

Non- α -amino acid values do not show a decreasing trend in $\delta^{13}\text{C}$ from lower to higher homologs; in fact, those obtained for β -amino acids could show an increasing trend, if not for the possibility that the lower $\delta^{13}\text{C}$ value of β -alanine could be due to terrestrial contamination (Fig. 3). The data do not contradict the possibility of nitriles as precursors of non- α -amino acid; nitriles are observed as interstellar species of up to C_{11} (Bell *et al.*, 1992) and their long chains, were they formed through a synthetic pathway that did not involve CO (Ehrenfreund and Charnley, 2000) and enriched in ^{13}C , could have sustained little parent-body/nebular C-isotopic alteration and, thereby, account for the high $\delta^{13}\text{C}$ values of higher homologs in this subgroup of meteoritic amino acids. The $\delta^{13}\text{C}$ values obtained for the α -amino dicarboxylic acids are surprising when viewed in relation to meteoritic α -amino acid. These compounds have been considered likely products of a Strecker synthesis (Cronin and Chang, 1993) and are consistently found in meteorite water extracts containing α -amino acids, yet they do not appear to share the same isotopic trend of declining $\delta^{13}\text{C}$ with increasing C number. Instead, they resemble isotopically the dicarboxylic acids both in the magnitude of the $\delta^{13}\text{C}$ values and their invariance with chain length (see section 3.5).

Overall, the C-isotopic data for Murchison amino acids and the differences observed between the individual isomeric and/or homologous species reflect the molecular complexity of these compounds and support the hypothesis of their diverse syntheses. By contrast, the H-isotopic analyses

of individual Murchison and Murray amino acids offer a surprisingly simple distribution (Pizzarello and Huang, 2005) (Table 3). In fact, while all the compounds analyzed show δD values that are higher than terrestrial and confirm the general D-enrichment observed by bulk samples, in some of these amino acids the enrichment is much higher and for 2-amino-2,3-methylbutyric acid reaches a δD value of 3604‰, the highest ever recorded for a discrete meteoritic compound. In contrast to their differences in ^{13}C composition, α -amino as well as non- α -amino acids and dicarboxylic amino acids display high D content as long as they have a branching methyl group. That is, the magnitude of amino-acid δD values in this meteorite appears to vary more with the structure of their C-chains than with their number and distribution of functionalities, differences in synthetic histories, or ^{13}C content.

Thus, the ^{13}C data indicate that C-chain elongation for meteoritic amino acid followed at least two synthetic paths, one that produced declining ^{13}C content with increasing carbon number and another where ^{13}C content remained unchanged, if not increased, with increasing chain length. At the same time, H-isotopic analyses show that the formation of amino acids in meteorites involved only two different H-fractionating chemical processes, with each being capable of producing compounds of all homologous series in spite of their ^{13}C differences.

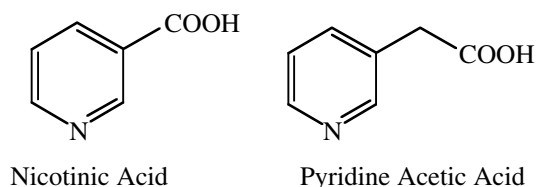
We have to conclude, therefore, that each of these two H-fractionating processes comprised diverse synthetic pathways to amino acids and/or their precursors that encompassed both C-fractionating processes. If we assume that D enrichment indicates a synthetic relation to cold chemical regimes, then we have also to conclude that branched amino acids, or their precursors, were synthesized more abundantly and farther along in C-chain saturation with H and/or D in such regimes. Cold, preaccretionary environments may also have been the source of the chiral and molecular traits of these meteoritic amino acids by providing asymmetric influences toward enantiomeric excesses and an abundance of reactions involving radicals and ions for the syntheses of highly branched species.

For α -methyl α -amino acids, it is plausible that both H-fractionating processes may have occurred to a different extent, thus explaining the large variability of both their amount ratios to α -H amino acids and their ee within and between meteorites. In a less-D-enriching process, a Strecker-type synthesis was likely involved in the production of the α -H- α -amino acids and could have resulted in parent-body D-H exchanges during the aqueous phase as well as racemization, had the precursors of these amino acids been endowed with ee.

3.2. Pyridine Carboxylic Acids

Nicotinic acid and its isomers and homologs are amphoteric compounds that are separated with the amino acids during procedural preparations of meteorite water extracts. As with the amino acids, they have prebiotic significance;

nicotinic acid (niacin) occurs in the biosphere as part of the co-factor (NAD, NADP) of several enzymes that catalyze oxidation-reduction reactions in cell metabolism.



Scheme 5

Carboxylated pyridines have been described in the Tagish Lake and Murchison meteorites (Pizzarello et al., 2001) where they occur as very similar suites that contain nicotinic acid, the most abundant species, its two isomers, and at least 12 methyl and dimethyl homologs. Hydrogen- and C-isotopic analyses of nicotinic acid gave the values of $\delta D = 129\text{‰}$ and $\delta^{13}C = 20\text{‰}$, respectively (Pizzarello and Huang, 2005; Pizzarello et al., 2004). Both these isotopic enrichments are lower than those of amino acids with comparable carbon number and, with respect to δD , those of heteroatom-containing aromatic compounds as a group (Krishnamurthy et al., 1992).

The origin of these water-soluble compounds in meteorites is not clear; their approximately equal abundance and distribution in two meteorites that have a largely different content of amino acids would indicate that the synthetic environments of the two suites of compounds were not similar. This finding also hinders the attempt to find a comprehensive relation between the organic distribution and other compositional features of the Tagish Lake meteorite, for example, between this meteorite's protracted water phase, large abundance of carbonates, oxidative alteration of the IOM, and possible decomposition of soluble organics such as amino acids. In fact, it would be difficult to explain how a pyridine carboxylic acid suite exactly matching that of Murchison's could have survived unchanged the oxidative conditions capable of producing those features. The solution of this apparent contradiction, if found, could help in the overall understanding of meteorite organics formation.

3.3. Amines and Aliphatic Amides

3.3.1. Amines. Amines are an abundant group of water-soluble organics found in all meteorites where amino acids are present. In Murchison, they consist of a varied series of alkyl compounds of one- to at least five-carbon chain length (Jungclauss et al., 1976; Pizzarello et al., 1994) whose abundances are comparable to those of the amino acids and decrease with increasing molecular weight. Meteoritic amine preparations show isotopic enrichments in D, ^{13}C , and ^{15}N with bulk values of $\delta D = 1221\text{‰}$, $\delta^{13}C = 22.4\text{‰}$, and $\delta^{15}N = 93.4\text{‰}$. These values validate the compounds' indigeneity

and, as an average, are comparable to those displayed by amino acids in the same meteorite; in particular, the N composition is very similar in both classes of compounds [90 vs. 94‰ (Pizzarello et al., 1994)]. In view of these similarities it has been proposed that at least a fraction of meteoritic amines could have derived from amino acids via decarboxylation, which is a common pathway of thermal decomposition for α -amino acids. The molecular distribution of Murchison amines would be compatible with this suggestion, since 16 of the 20 amines identified in the meteorite could have derived from known Murchison α -amino acids.

Because *sec*-butyl amine could have formed via decarboxylation of isovaline, an amino acid found in Murchison with ee that may exceed 15%, its chiral distribution was analyzed in the Murchison meteorite (Pizzarello, 2002b). While one sample showed a fairly large L-ee (~20%), analysis of another stone did not show any significant ee. It is not yet clear if this reflects the same heterogeneity observed for isovaline in Murchison (Pizzarello et al., 2003) or indicates that the first sample had carried terrestrial contamination, possibly by transfer of vapors during curatorial storage (this amine has only minor terrestrial distribution).

3.3.2. Alkyl amides. Alkyl amides are represented in the Murchison meteorite water extracts by an extensive series of linear and cyclic aliphatic compounds (Cooper and Cronin, 1995). These include amides that, upon acid hydrolysis, yield mono- and dicarboxylic acids, α - and non- α -amino acids and hydroxy acids, i.e., monocarboxylic acid amides, dicarboxylic acid monoamides, cyclic imides, carboxy lactams, N-acetyl amino acids, amino acid hydantoin, lactams, and hydroxy acid amides. With the possible exception of the hydantoin and N-acetyl amino acids, numerous isomers and homologs through at least C₈ were observed. Carboxy lactams, lactams, hydantoin, and N-acetyl amino acids are converted to amino acids by hydrolysis, thus these compounds qualitatively account for the earlier observation of acid-labile amino acid precursors in the meteorite extracts (Cronin, 1976).

One apparent possibility for the formation of at least some of the amides is the partial hydrolysis of known interstellar nitriles, e.g., CH₃CN, CH₃CH₂CN, etc. However, based on laboratory studies, Cooper and Cronin (1995) also proposed an unusual formation reaction involving the addition of cyanate (a known interstellar molecule) to amino acids or amino acid derivatives. The reactions of amino acids with cyanate and thiocyanate ions are well known (Ware, 1950) and there is at least a suggestive similarity in the distribution of dicarboxylic acids and their corresponding amides in Murchison, where the straight-chained C₄, C₅, and C₆ dicarboxylic monoamides are each more abundant than their branched isomers (Cooper and Cronin, 1995). A series of alkyl dicarboximides were also found in both the Tagish Lake and Murchison meteorites and have distributions that reflect those of the corresponding dicarboxylic acids (Pizzarello and Huang, 2002; Cooper and Cronin, 1995).

Ketene addition to amino acids (or amino acid derivatives) was invoked by Cooper and Cronin (1995) as a possi-

ble means of producing N-acetyl amino acids in meteorites. Ketene is a molecule detected in the interstellar medium and has been shown to be an effective acetylating agent for amino acids in aqueous solution. Given the well-known reactivity of molecules such as ketene and cyanate in aqueous solution, the authors suggested that amide formation occurred relatively late in the period of aqueous phase chemistry.

3.4. Carboxylic Acids

Carboxylic acids have been analyzed in the Murchison (*Yuen and Kvenvolden, 1974; Lawless and Yuen, 1979; Huang et al., 2005*), Murray (*Yuen and Kvenvolden, 1974*), Yamato (*Shimoyama et al., 1989*), and Asuka (*Naraoka et al., 1996*) CM2 chondrites, and in the Tagish Lake meteorite (*Pizzarello et al., 2001*). In CM2, they are more abundant than the amino acids by factors of 1–2 and most of the possible isomeric species C_1 (*Kimball, 1988; Huang et al., 2005*) to C_{10} (*Yuen and Lawless, 1979; Naraoka et al., 1996; Huang et al., 2005*) and linear species up to C_{11} (*Naraoka et al., 1996*) have been identified. As with many groups of water-soluble compounds, several more branched acids can be clearly recognized by their mass spectra (*Naraoka et al., 1996; S. Pizzarello, unpublished data, 1998*). Branched acids appear to be as abundant as linear compounds and all acids show declining abundance with increasing carbon number. By contrast, only the first two homologs of the linear acid series, formic and acetic, were observed in the Tagish Lake meteorite (*Pizzarello et al., 2001*).

The H- and C-isotopic compositions of combined Murchison carboxylic acids have ranges of $\delta D = 377\text{‰}$ to 697‰ and $\delta^{13}C = -3\text{‰}$ to $+7\text{‰}$, respectively (*Epstein et al., 1987; Krishnamurthy et al., 1992*). Carbon-isotopic analyses of individual C_2 to C_5 acids (*Yuen et al., 1984*) showed that $\delta^{13}C$ values are lower for all acids than for meteorite CO_2 , higher for branched than linear C_4 and C_5 acids, and decline with increased C number (Table 4). This isotopic trend would be consistent with syntheses of higher molecular weight compounds from lower homologs either under kinetically controlled conditions (*Yuen et al., 1984*), such as possible in warmer interstellar or nebular regions, or by ion-molecule processes as described above in regard to meteoritic α -amino acids (*Pizzarello et al., 2004*). Either proc-

ess should have been independent of those yielding CO in the meteorite, given that CO displays a far lower $\delta^{13}C$ value (-32‰) than the carboxylic acids and thus was an unlikely source of these compounds (*Yuen et al., 1984*).

Yuen et al. (1984) also proposed that an intramolecular difference in ^{13}C content between the carboxyl and alkyl moieties could be responsible for the declining ^{13}C content of Murchison carboxylic acids. This, in turn, could result from primary synthetic processes or from secondary exchanges, e.g., during the parent-body aqueous phase. The second scenario is suggested by the theoretical work of *Shock (1988)*. He proposed that under geologic conditions where high concentrations of aqueous carboxylic acids are in equilibrium with dissolved CO_2 , the acids might become unstable toward decarboxylation. On the basis of this possibility, and by extending its implications to include a carboxyl carbon exchange with dissolved CO_2 from inorganic sources, *Diaz et al. (2002)* explained their finding of decreasing $\delta^{13}C$ with increasing chain-length in low molecular weight acids from six oil-producing rocks. Whether a similar exchange between carbonyl carbon and other heavier C, such as found in carbonates, might be invoked for aqueous processes in a meteorite parent body remains to be seen. Also, it cannot be excluded that primary and secondary effects could have both contributed, at unknown extent, to the meteoritic carboxylic acid isotopic composition.

Comprehensive deuterium analyses of several individual Murchison carboxylic acids (*Huang et al., 2005*) have shown that the δD values of all branched acids in the meteorite are significantly and consistently higher than those of linear species (approximately $1770\text{--}2000\text{‰}$ vs. $600\text{--}700\text{‰}$). These findings are in agreement with those established for amino acids and, similarly, point to a distinct relation of the branched compounds to cold and H-fractionating processes that could have comprised diverse syntheses and C-fractionation pathways.

3.5. Aliphatic Dicarboxylic Acids

Aliphatic dicarboxylic acids are notable among meteoritic compounds in that they have been found in remarkably similar amounts and homolog-distribution patterns in meteorites that differ in their overall soluble organic content, such as Murchison, Tagish Lake, and Orgueil (*Pizzarello and Huang, 2002*), as well as in a Yamato CM2 find (*Shimoyama and Shigematsu, 1994*). In these meteorites, they comprise a homologous series of over 40 saturated and at least 6 unsaturated species of C_3 through C_{10} . Linear saturated acids are predominant; however, variability of the glutaric/methyl succinic ratio has been observed between fragments of a Tagish Lake stone that could indicate a different zonal distribution of linear and branched diacids in the meteorite similar to that observed for amino acids. As for other soluble meteoritic compounds, the diacids show decreasing abundance with increasing chain length and the most abundance, succinic acid, is present at approximately 40 nmol/g of meteorite (~ 4 ppm). Four chiral diacids, the 2-methyl and 2-ethyl

TABLE 4. $\delta^{13}C$ (‰ PDB) of Murchison CO , CO_2 , and alkyl monocarboxylic acids.

Compound	$\delta^{13}C\text{‰}$
Carbon dioxide	+29.1
Carbon monoxide	-32.0
Acetic acid	+22.7
Propionic acid	+17.4
Isobutyric acid	+16.9
Butyric acid	+11.0
Isovaleric acid	+8.0
Valeric acid	+4.5

From *Yuen et al. (1984)*.

TABLE 5. Hydrogen- and C-isotopic composition of individual meteoritic alkyl dicarboxylic acids.

Acid	Tagish Lake		Murchison		Orgueil	
	$\delta D\text{‰}^*$	$\delta^{13}\text{C}^\dagger$	$\delta D\text{‰}$	$\delta^{13}\text{C}\text{‰}$	$\delta D\text{‰}$	$\delta^{13}\text{C}\text{‰}$
Succinic	+1121	+23	+390	+28		-24
Methylsuccinic	+1109	+15	+1225	+26		-20
Glutaric	+1355	+23	+795	+27		-20
2-methylglutaric	+1364	+19	+1551	+28		-10
3-methylglutaric		+13		+19		
Adipic		+6		+21		

*Relative to VSMOW.

†Relative to PVBD.

From Pizzarello and Huang (2002).

isomers of succinic and glutaric acids, were found to be racemic in the Yamato meteorite (*Shimoyama and Shigematsu, 1994*), as was 2-methyl glutaric in the Tagish Lake meteorite (*Pizzarello and Huang, 2002*). These findings, however, may not be relevant toward assessing the distribution of ee in diacids in meteorites, since all the compounds analyzed contain an H-containing carbon adjacent to the carboxyl group and would have the same opportunity to racemize in water, as would, for example, nonracemic α -H amino acids in the Murchison and Murray meteorites.

The C- and H-isotopic composition obtained for the individual dicarboxylic acids of three meteorites (*Pizzarello and Huang, 2002*) (Table 5) shows that all the compounds analyzed in the Murchison and Tagish Lake suites are enriched in the heavier isotopes of both elements while those of Orgueil are depleted in ^{13}C . Given that the dicarboxylic acids display a similar molecular composition in the three meteorites and that these compounds, with the exception of succinic and glutaric acids, are not widely distributed in the biosphere, the data reported for Orgueil should not be attributed solely to terrestrial contamination, even if it is not evident how the observed differences in isotopic composition were produced.

The isotopic data do not show any C- or D-enrichment trends with increasing chain length or the branching of their alkyl chains that would resemble those observed for some amino acids or low molecular weight carboxylic acids. The isotopic values are, however, in the range of those compounds and indicate at least a general relationship to interstellar precursors. Dinitriles and dicyanopolyynes have been proposed for this role (*Pizzarello et al., 2001*); however, fully unsaturated precursors to alkyl dicarboxylic acids seem unlikely based on the molecular and isotopic data. These precursors would hydrolyze into only linear, odd C compounds and their hydrogenation in a parent body most probably would not have resulted in their high δD values. On the other hand, partially unsaturated nitriles, which like cyanopolyynes have been detected in the interstellar medium, may be considered as presolar precursor candidates to diacids (*Pizzarello and Huang, 2002*). The more direct dinitrile precursors could have derived from nitriles in interstellar and/or

nebular and parent-body environments as, for example, by HCN addition (*Peltzer et al., 1984*).

The singularity of diacid distributions in meteorites of otherwise different composition has been explained with the possibility that precursors to diacids and the majority of other organic compounds in meteorites had different volatilities and only the less volatile survived under parent-body conditions that allowed the more volatile to escape (*Pizzarello et al., 2001*). Dinitriles, as precursors to dicarboxylic acids, would satisfy the requisite of not being easily sublimed, as could have been the more volatile aldehydes and ketones, precursors to the amino acids (e.g., succino nitrile's boiling point at 20 torr is $158^\circ\text{--}160^\circ\text{C}$ while that of butyraldehyde is -12°C).

The synthetic locale of meteoritic dicarboxylic acid is difficult to assess. Their isotopic values point to possible formation in cold interstellar media; however, the preponderance of linear species in the diacid suite, which contrasts with the highly branched distribution of most meteorite soluble organics, suggests the possibility of other preaccretionary processes (*Pizzarello and Huang, 2002*).

3.6. Sulfonic and Phosphonic Acids

These compounds have the general formula $\text{R-CH}_2\text{SO}_3\text{H}$ and $\text{R-PO}_3\text{H}$ (where R equals methyl-, ethyl-, propyl-, and butyl-groups) and were identified as homologous series in aqueous extracts of the Murchison meteorite (*Cooper et al., 1992*). The sulfonic acids are roughly 40 \times more abundant than the phosphonic acids, 380 nmol/g for methanesulfonic acid (MSA) vs. 9 nmol/g for methylphosphonic acid. As with other homologous series of meteoritic organic compounds, these acids show a distribution of declining abundance with increasing carbon number and structural diversity, with the majority of possible structural isomers through C_4 being identified in the meteorite.

Cooper et al. (1997) performed C, H, and S stable-isotopic measurements on the C_1 to C_3 sulfonic acids. The $\delta^{13}\text{C}$ values ranged from +29.8 ‰ (MSA) to -0.9 ‰ (isopropanesulfonic) and δD values were from 483 ‰ (MSA) to 852 ‰ (isopropanesulfonic). Sulfur-isotopic measurements showed

MSA to be somewhat apart from the other sulfonic acids, with enrichments in ^{33}S (7.63‰), ^{34}S (11.27‰), and ^{36}S (22.5‰) being clearly above its higher homologs, which have average values 0.28‰ (^{33}S), 1.0‰ (^{34}S), and 1.9‰ (^{36}S). Bulk-isotope measurements of the phosphonic acids gave values of -20‰ for $\delta^{13}\text{C}$ and $+219\text{‰}$ for δD ; these values were uncorrected for procedural blanks and thus are considered minimums.

Because S has four stable isotopes, one can also construct a three-isotope plot with Murchison sulfonic acid data to detect possible non-mass-dependent isotope effects. Again MSA proved to be unusual relative to the other acids: it displayed an anomalous non-mass-dependent enrichment in ^{33}S of $\Delta^{33}\text{S} = 2.0\text{‰}$ ($\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.5 \delta^{34}\text{S}$ where $0.5 \delta^{34}\text{S}$ is the normal mass-dependent value of $\delta^{33}\text{S}$). However, two of the other sulfonic acids did display anomalous depletions in ^{33}S : $\Delta^{33}\text{S} = -0.24$ (ethanesulfonic acid) and $\Delta^{33}\text{S} = -0.40$ (n-propanesulfonic acid). The authors indicated that extra-terrestrial gas-phase irradiation of symmetrical precursors to the meteoritic sulfonic acids, e.g., CS_2 in the case of MSA, SCCS for ESA, etc., may have produced the anomalous $\Delta^{33}\text{S}$ values. *Cooper et al.* (1992) had speculated that the precursors to meteoritic sulfonic and phosphonic acids could have been the interstellar molecules CxS and CxP, respectively; the sulfonic acid isotopic analyses give additional indication for an interstellar and/or presolar formation of these compounds.

Cooper et al. (1997) further suggested that CS, ubiquitous in interstellar space, might have played a role in the production of meteoritic macromolecular material due to its known ability to form an insoluble solid phase on surfaces when condensed at very low temperatures (*Moltzen et al.*, 1988; *Klabunde et al.*, 1989). The unusual finding of just one sulfonic acid (MSA) in the Tagish Lake meteorite (*Pizzarello et al.*, 2001) may be consistent with these distinct isotopic properties of MSA relative to the other sulfonic acids. Phosphonic acids were not seen in Tagish Lake possibly due to abundances below the detection limit of GC-MS.

3.7. Alcohols and Carbonyls

Alcohols and carbonyls were identified in Murchison shortly after the meteorite's fall (*Jungclaus et al.*, 1976) but their study has not been revisited. C_4 (R-OH, R-CHO) to C_5 (R-CO-R) molecular species were identified that include all homologs to C_4 and show declining abundance with increasing C number.

3.8. Hydroxy and Keto Acids

Peltzer and Bada (1978) first reported a suite of α -hydroxy acids in the Murchison meteorite and identified seven acids up to C_5 , with structures comparable to those of meteoritic amino acids. Enantiomeric analysis on four of these compounds (lactic acid, α -hydroxy-n-butyric acid, α -hydroxy-n-valeric acid, and α -hydroxyisovaleric acid) showed them to be racemic, or nearly so. Based on their abundances

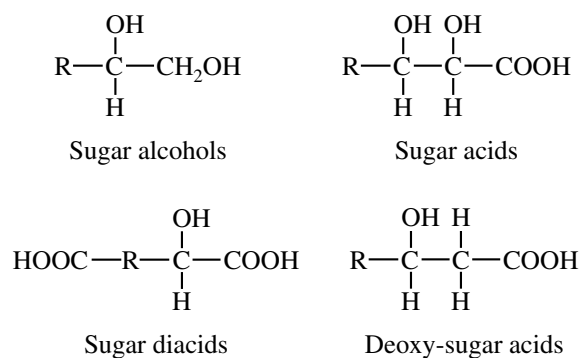
and distribution patterns, which are similar to those of Murchison α -H amino acids, the authors suggested that both groups of compounds could have been synthesized in the meteorite by the Strecker-cyanohydrin reaction (Scheme 1). *Cronin et al.* (1993) extended these analyses by the GC-MS characterization of a total of 60 hydroxy monocarboxylic acids up to C_8 (14 of these compounds were identified with reference standards) and of a suite of hydroxy dicarboxylic acids that included several species up to C_9 . This study confirmed the correspondence previously observed between α -H- α -amino, and α -H- α -hydroxy acid distributions; however, it also showed that α -methyl- and non- α -hydroxy acids are far less abundant within the meteoritic hydroxy acid suite. Other molecular subgroups have not been searched for.

Murchison bulk-isotopic analyses (*Cronin et al.*, 1993) gave values of $\delta^{13}\text{C} = 4\text{‰}$ and $\delta\text{D} = 573\text{‰}$ for hydroxy acids and $\delta^{13}\text{C} = -6\text{‰}$ and $\delta\text{D} = +357\text{‰}$ for a combined sample of hydroxydicarboxylic and dicarboxylic acids. The average isotopic composition of hydroxy acids differs from those of amino acids in the same meteorite. The finding in Murchison of large D-enrichment in the individual amino acids in the subset of branched compounds (Table 3) and the low abundance of this subset of hydroxy acids may explain the observed difference in isotopic values. The molecular and isotopic findings for hydroxy acids also support the proposal of different venues of formation for linear and branched amino acids (section 3.1.3) and that the branched amino- and hydroxy acids may have been synthesized less abundantly via the Strecker reaction.

A series of keto acids have been identified in the Murchison and Murray meteorites by *Cooper et al.* (2005); it includes acetoacetic acid and its higher homologs having the keto group adjacent to the terminal C in the alkyl chain. This series shows the common meteoritic features of decreased abundance with increasing C number and extensive isomerism. Hydrolysis of interstellar nitriles, e.g., HCCN, HC_2CN , etc., and their reaction with ketene could be suggested as a possible formation route to these meteoritic compounds.

3.9. Polyols

Several polyhydroxylated organic compounds (polyols) have been discovered in water extracts of the Murchison and Murray meteorites by *Cooper et al.* (2001). These include one sugar and several compounds that are called sugar derivatives on the basis of their molecular structures, i.e., sugar alcohols, sugar mono-acids, sugar di-acids, and deoxy-sugar acids [Scheme 6, R=H or $(-\text{CH}_2\text{OH})_x$; for deoxy-sugar acids, the structure shows just one possible placement of the "deoxy" carbon]. In general, these meteoritic sugar derivatives display the abiotic pattern of decreasing abundance with increasing carbon number within a class of compounds, many (if not all) possible isomers at each carbon number, and distributions that are similar in the Murchison and Murray meteorites.



Scheme 6

The sugar dihydroxyacetone was found in both Murchison and Murray. A search in Murchison water extracts for the C₂ analog of dihydroxyacetone, glycolaldehyde, was inconclusive and C₄ and C₅ sugars (e.g., erythrose, ribose, etc.) were not found. The sugar alcohol series begins with the C₂ ethylene glycol, and extends through at least the C₆ homologs. In multiple analyses ethylene glycol and glycerol are the most abundant of all identified polyols; glycerol is present in Murchison at ~160 nmol/g, i.e., roughly the same as the highest concentration found for an individual amino acid in the same meteorite. After acid hydrolysis and fractionation by ion exchange chromatography, bulk isotope values (‰) of Murchison sugar alcohols were $\delta^{13}\text{C} = -5.89$ and $\delta\text{D} = +119$ (Cooper et al., 2001). These values were uncorrected for procedural blanks and are thus considered lower limits. Even so, they lie outside the range of typical terrestrial organic compounds and are consistent with values obtained for other indigenous classes of meteoritic organic compounds.

The sugar mono-acids (“aldonic” acids) comprise compounds from C₃ glyceric acid through at least the C₆ homologs. The abundance of glyceric acid, ~80 nmol/g, is comparable to those of the more-abundant amino acids in CM chondrites. Deoxy-sugar acids (“saccharinic” acids), less common in nature than sugars, were also present: four C₄, one C₅, and two C₆ compounds were identified; other unidentified compounds were possibly branched deoxy acids. Enantiomeric analyses of some of the acids (G. Cooper, unpublished data, 2005) have shown glyceric, 2-methylglyceric, and 2,4-dihydroxybutyric acids to have approximately equal abundances of their respective D- and L-isomers, also suggestive of extraterrestrial origins.

For some of the meteoritic polyols, Cooper et al. (2001) suggested low-temperature UV photolysis of interstellar grains. Under simulated interstellar conditions, photolysis has been shown to produce at least the smaller of the meteoritic polyols, e.g., ethylene glycol, glycerol, and glyceric acid, from simple starting compounds found in interstellar environments such as CO, methanol, etc. (Agarwal et al., 1985; McDonald et al., 1996; Bernstein et al., 2002). In the case of the wider range of meteoritic polyols, Cooper et al. (2001) suggested the possibility that interstellar formaldehyde chemistry was a contributor to their synthesis. Formal-

dehyde (CH₂O) condenses to produce a variety of hydroxylated compounds, predominately sugars and sugar alcohols, in neutral to slightly basic aqueous solution, i.e., in a pH range consistently found for meteorite water extracts and also estimated for the meteorite parent body (DuFresne and Anders, 1962; Bunch and Chang, 1980; Zolensky et al., 1989; Schulte and Shock, 2004). From sugars, the formation of sugar-acids is a relatively facile process in alkaline solution; the sugars would undergo various reactions including oxidation to acids of corresponding (or lower) carbon numbers, e.g., ribose to ribonic acid and fragmentation/rearrangement to deoxy sugar acids.

Extraterrestrial origins for these meteoritic polyols, as well as a direct chemical connection between interstellar environments and primitive solar system bodies, are further suggested by the finding of a relatively high abundance of ethylene glycol in Comet Hale-Bopp (Crovisier et al., 2004) and the identification of interstellar ethylene glycol, glycolaldehyde (Hollis et al., 2000, 2002), and dihydroxyacetone (Widicus-Weaver and Blake, 2005) in Sagittarius B2(N-LMH). All the preceding authors pointed out that the production of these compounds would be consistent with models of interstellar grain chemistry, a possibility supported by the identification on these grains of phases of water, formaldehyde, and methanol (Schutte et al., 1996).

3.10. Hydrocarbons

Hydrocarbons, as a class of compounds, were first identified in meteorites shortly after the first recorded falls in the 1800s (see Mullie and Reisse, 1987, for a historical review). At the time, their indigeneity was never in doubt. Later, however, their wide distribution in fossil fuel, soil humic acids, and many other terrestrial environments made the study of meteoritic hydrocarbons, and straight chain aliphatic compounds in particular, difficult and often controversial.

3.10.1. Aliphatic hydrocarbons. Aliphatic hydrocarbons are found in meteorites with a wide range of molecular sizes, from methane and its volatile homologs up to C₃₀ nonvolatile molecules that must be extracted with solvents. Obtaining hydrocarbons of the first group is challenging, since most have been lost to evaporation and only a portion that is adsorbed, trapped, or otherwise bound in the matrix can be obtained. For example, Yuen et al. (1984) used freeze-thaw disaggregation of meteorite stones and subsequent treatment of the powders with sulfuric acid for the release of volatile hydrocarbons; Table 6 shows the C₁ to C₅ compounds found in this study and their C-isotopic composition.

The analyses of meteoritic nonvolatile hydrocarbons led at first to contradictory results. A Murchison study conducted shortly after the meteorite’s fall (Kvenvolden et al., 1970) described an aliphatic suite made up of a large number of isomeric alkanes, alkenes, and bi- and tricyclic saturated species that were poorly separated under the analytical conditions used. Oró et al. (1971) confirmed these

TABLE 6. $\delta^{13}\text{C}$ (‰ PDB) of Murchison lower molecular weight hydrocarbons.

Compound	$\delta^{13}\text{C}$ ‰
Methane	+9.2
Ethane	+3.7
Propane	+1.2
Isobutane	+4.4
Butane	+2.4
Ethene	-0.1
Benzene	-28.7

From Yuen *et al.* (1984).

results while Studier *et al.* (1972) identified predominantly linear aliphatic hydrocarbons in a Murchison sample, attributing their results to better analytical resolution.

The ensuing debate on the origin of these compounds has been extensively reviewed by others (e.g., Cronin *et al.*, 1988). Briefly, it centered on two models proposed for the formation of the Murchison organics. One hypothesis was that of a FTT catalytic synthesis of organics from simple gases (CO , H_2 , NH_3) in a cooling nebula. The second envisioned organic syntheses in a reduced planetary atmosphere by the energetic production, recombination, and ultimate reaction of radicals in water. Both these early theories fell short of matching the molecular and/or isotopic distribution of organics later found in meteorites; particularly decisive was the finding by Yuen *et al.* (1984) that in the Murchison meteorite the CO $\delta^{13}\text{C}$ value was lighter than those of the lower alkanes. In fact, the kinetic model of C-fractionation for FTT syntheses of hydrocarbons from CO predicts the opposite, i.e., that residual CO would be isotopically heavier than the hydrocarbon products.

Molecular distribution studies that followed were able to show that the presence of some hydrocarbons was related to increasing contamination in meteorite samples (see section 3.10.4 below) (Cronin and Pizzarello, 1990), while recently Kissin (2003) argued that some of the alkanes in meteorites could derive from the slow thermal decomposition of meteoritic complex cross-linked polymers.

The long debate on the indigenous nature of the aliphatic hydrocarbon distribution in meteorites has been aided by the prompt analyses of the Tagish Lake meteorite after its fall. This meteorite suite comprises saturated and cyclic and/or unsaturated aliphatic hydrocarbons, where n-alkanes are predominant and C_{23} the most abundant (Pizzarello *et al.*, 2001). Twelve were individually identified, i.e., substantially fewer than were reported in the Murchison meteorite; however, their presence indicates that linear alkanes can be found in meteorites independently of terrestrial contamination. Whether the hydrocarbon suite of this ungrouped meteorite can be validly compared to those of CM2 chondrites, such as Murchison and Murray, or represents oxidative alteration products remains to be seen.

Deuterium- and C-isotopic analyses of combined aliphatic preparations from the Murchison meteorite gave average values of $\delta\text{D} = 211\text{‰}$ and $\delta^{13}\text{C} = 9\text{‰}$ (Krishnamurthy *et al.*,

1992). The bulk $\delta^{13}\text{C}$ is higher than the weighted average value obtained by compound specific analyses of individual volatile hydrocarbons. Sephton *et al.* (2001) measured the ^{13}C content of individual n-alkanes (C_{12} to C_{26}) from six chondrites, Murchison, Orgueil, Cold Bokkeveld, Vigarano, Ornans, and Bishunpur. They found $\delta^{13}\text{C}$ values that fall within the relatively narrow range of approximately -25‰ to -39‰ and concluded that these compounds were likely terrestrial contaminants. However, Pizzarello *et al.* (2001) determined that the $\delta^{13}\text{C}$ values for the Tagish Lake n-alkane suite range from -18.8‰ (C_{16}) to -29.0‰ (C_{20}), with those for branched, unsaturated, and cyclic alkanes varying similarly from -18.4‰ to -27.1‰ . Although the Tagish Lake data are also in the terrestrial range, several points appear to support their indigeneity. These are the pristine nature of the meteorite sample; the relatively low $\delta^{13}\text{C}$ values of other species in Tagish Lake, e.g., phenanthrene at -25‰ , that possibly indicate a general depletion of ^{13}C for hydrocarbons; and the data of Yuen *et al.* (1984), showing that $\delta^{13}\text{C}$ values were already declining below 2.5‰ at C_4 .

Overall, the C-isotopic data of Yuen *et al.* suggest that the formative processes for aliphatic hydrocarbons in CMs involved chain growth by addition of single moieties and were possibly kinetically controlled. Compound-specific deuterium data are sorely missing and would help to constrain their synthetic locales. If the D-range found by Krishnamurthy *et al.* (1992) for a combined sample were confirmed for individual compounds, their syntheses would have to be framed within cold environments like for other meteoritic compounds, at least at some point in their history. In this regard, it should be noted that the first two members of the n-alkane family, methane and ethane, have been identified in comets (e.g., Mumma *et al.*, 1996; Kawakita *et al.*, 2003), raising the possibility that comets could also contain higher homologs.

3.10.2. Aromatic hydrocarbons. Aromatic hydrocarbons have been analyzed in CC by solvent or supercritical fluid extraction (SFE) combined with GC-MS and by laser-desorption/laser-ionization mass spectrometry (L^2MS). The latter technique, by exploiting the volatility and susceptibility of PAHs to UV ionization without molecular fragmentation, targets aromatic compounds on the surface of meteorite stones, offers the advantage of determining their spatial distribution, and is the most sensitive method for these compounds. As a disadvantage, it lacks the possibility of isomeric differentiation and the more reliable quantification provided by GC-MS.

The most-abundant aromatic hydrocarbons obtained by solvent extraction of the Murchison, as well as other CM2 Antarctic meteorites, are pyrene and fluoranthene, followed by phenanthrene and acenaphthene. Other unsubstituted, alkyl substituted, and partially hydrogenated compounds make up a complex suite that comprises several ring forms and extends to polycyclic $\text{C}_{22}\text{H}_{12}$ isomers [e.g., benzo(ghi)perylene] (Sephton, 2002, and references therein). Extraction with supercritical fluid CO_2 (SFE), which reduces losses of more volatile compounds, demonstrates that lower molecular weight aromatic compounds such as toluene, alkyl ben-

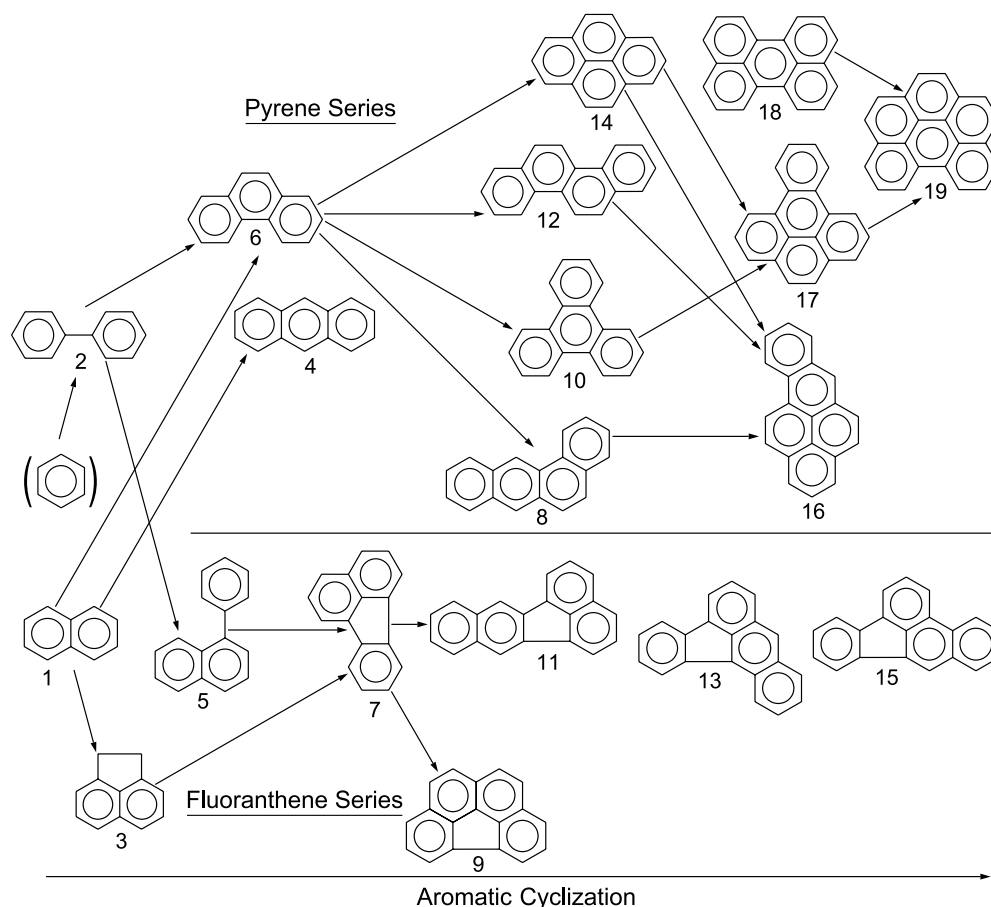


Fig. 4. Possible reaction pathways in the formation of meteoritic PAHs. (1) naphthalene, (2) biphenyl, (3) acenaphthene, (4) anthracene, (5) 1-phenyl naphthalene, (6) phenanthrene, (7) fluoranthene, (8) benz(a)anthracene, (9) benzo(ghi)fluoranthene, (10) triphenylene, (11,13,15) benzofluoranthenes, (12) crysene, (14) pyrene, (16,17) benzopyrenes, (18) perylene, (19) benzo(ghi)perylene. Re-drawn from *Naraoka et al., 2000*.

zenes, and naphthalene can also be abundant in the Murchison meteorite (*Sephton et al., 1998*). $\mu\text{L}^2\text{MS}$ analyses of CM (Murchison, Murray, Mighei, and Harripura) (*Hahn et al., 1988*) and CV (Allende) (*Hahn et al., 1988; Zenobi et al., 1989*) meteorites gave results that, although showing differences in the relative distribution of individual polycyclic compounds at m/z higher than 178, were qualitatively similar to the meteorites' solvent extract. By contrast, $\mu\text{L}^2\text{MS}$ analysis of the Ivuna (CI) meteorite showed only three major masses for naphthalene, phenanthrene/anthracene, and pyrene/fluoranthene. Extraction with supercritical fluid CO_2 extracts of the CI Orgueil meteorite also showed a different distribution of only lower molecular weight species with a predominance of hydrated naphthalenes (*Sephton et al., 2001*). In the Tagish Lake meteorite many lower molecular weight aromatic compounds, such as alkyl and di-alkyl benzenes, were observed directly in the solvent extracts (*Gilmour et al., 2001*), a finding likely due to the prompt recovery of this meteorite. Naphthalene, alkyl- and phenylnaphthalenes, phenanthrene, anthracene, pyrene, and fluoranthene were also observed in the extracts (*Pizzarello et al., 2001*, and unpublished data).

The average isotopic values obtained for preparations of Murchison aromatic hydrocarbons are $\delta\text{D} = 353\text{‰}$ and $\delta^{13}\text{C} = 5.5\text{‰}$ (*Krishnamurthy et al., 1992*). All C-isotopic values established for individual aromatic compounds in the meteorite have been lower than the above average; with the less-volatile larger aromatic clusters giving values from -5.9‰ for fluoranthene to -22.3‰ for benzopyrene (*Gilmour and Pillinger, 1992, 1994*). The only trend apparent in these data was that the addition of a ring to a given cluster structure appeared to decrease the ^{13}C content of the product compound, a finding that would be suggestive of condensation of larger ring clusters from lower homologs. *Naraoka et al. (2000)* confirmed and expanded this dataset by analysis of a CM2 Asuka Antarctic meteorite. The authors evaluated the molecular and isotopic distributions of the meteoritic PAHs to assess any indication of possible thermodynamic equilibration during their formation. They found none and observed instead a significant difference in C-isotopic composition between PAHs having very similar thermodynamic characteristics, such as pyrene and fluoranthene. In view of this, they proposed that the compounds could have formed through two reaction pathways. As shown in Fig. 4,

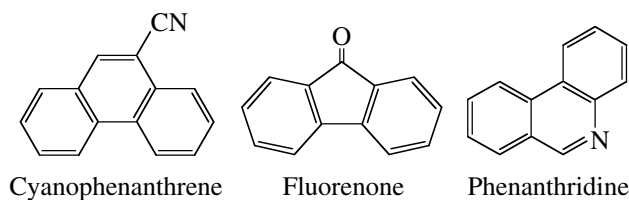
higher ring structures for each PAH series would be produced from the lower homologs under kinetic control and with large isotopic fractionation for each cyclization step.

This C kinetic isotope effect proposed for meteoritic PAHs is not seen in their terrestrial counterparts, which are mostly produced at high temperature, and is suggestive of low-temperature synthetic processes in meteorites. However, the isotopic data available to date do not allow the unambiguous proposal of a single synthetic locale and it is plausible that the aromatic compounds we find in meteorites, both free and condensed in the IOM, have a diverse origin.

The $\delta^{13}\text{C}$ values of lower aromatic species have been found to vary from -28.8‰ to -12.6‰ for toluene and naphthalene, respectively (Sephton *et al.*, 1998), a range that is in agreement with the value of -28.7‰ reported for benzene by Yuen *et al.* (1984). The data appear to indicate opposite trends for the lower and higher ring number species; however, Naraoka *et al.* (2000) point to the similarities between these and terrestrial C-isotopic values and warn of a possible mixture of indigenous and contaminant volatile species in meteorites.

3.11. Polar Hydrocarbons

The heteroatom-containing hydrocarbons (i.e., having N, S, and O either in the aromatic ring or attached to it) represent the most abundant hydrocarbon component in the meteorites where it has been analyzed. In the Murchison meteorite polar hydrocarbons are 69–74% of total solvent extract (Krishnamurthy *et al.*, 1992) and include alkyl aryl ketones, e.g., anthracyl/phenanthryl ketones, aromatic ketones, and diketones, e.g., anthracenone and anthracenedione, nitrogen-heterocyclic (section 3.10.2), and sulfur-heterocyclic compounds, such as dibenzothiophene. In the Tagish Lake meteorite many polar species have been identified, although some, e.g., the nitrogen heterocycles, could not be specifically searched for. The many identified include both smaller species, such as benzaldehyde, benzonitrile, phenol, di-cyano benzene, phenyl pyridine, isocyano naphthalene (Gilmour *et al.*, 2001), dicyano toluene, and larger compounds such as the ones shown in Scheme 6 (Pizzarello *et al.*, 2001, and unpublished data).



Scheme 7

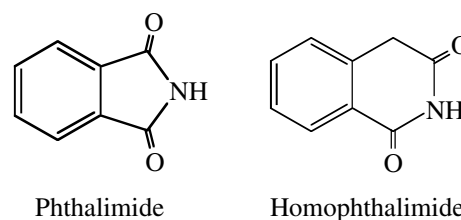
Murchison polar hydrocarbon bulk samples showed larger D- and ^{13}C -isotopic enrichments than the aromatic and ali-

phatic compounds, with average values of $\delta\text{D} = 881\text{‰}$ and $\delta^{13}\text{C} = 5.7\text{‰}$ (Krishnamurthy *et al.*, 1992).

3.11.1. Nitrogen-containing heterocycles. Nitrogen-containing heterocycles are aromatic compounds having one or more N atoms replacing C in their rings. As a group of compounds, they have been systematically searched for and identified only in the Murchison meteorite. They comprise a series of pyridines, quinolines, isoquinolines, including several of their methyl isomers (Stoks and Schwartz, 1982), and benzoquinolines (Scheme 7) (Krishnamurthy *et al.*, 1992). Although isotopic analyses have not been performed, this diverse distribution is evidence of their abiotic origin. However, only one pyrimidine (uracil) and four purines (xanthine, hypoxanthine, guanine, and adenine) have been found in low amounts. Because they all have biological distribution, isotopic analyses are needed to prove their indigeneity.

Pyridine carboxylic acids have been described in both Murchison and the Tagish Lake meteorites (section 3.2). Aromatic amides were first described in the early work of Hayatsu (1964) and Hayatsu *et al.* (1968), who identified guanine, guanylurea, and melamine, among other compounds, in the Orgueil meteorite. In the Murchison meteorite, Hayatsu *et al.* (1975) found guanine, cyanuric acid, and guanylurea.

3.11.2. Aromatic dicarboximides. Aromatic dicarboximides (Scheme 8) have been identified in the Tagish Lake meteorite, where their indigeneity was corroborated by isotopic analyses (Pizzarello *et al.*, 2001).



Scheme 8

They comprise the imide derivatives of phthalic and homophthalic acids, and some of their methyl and dimethyl homologs; a total of nine have been detected. Phthalic acid, its isomers, and some of their ester derivatives and anhydrides are commonly used as industrial plasticizers and have been viewed before as possible contaminants. Phthalates were, in fact, observed in Murchison samples and attributed to contamination (Cronin and Pizzarello, 1990). However, the imide derivatives of these acids were found in a pristine Tagish Lake sample with $\delta^{13}\text{C}$ values that indicate a non-terrestrial origin (Table 7). It is plausible that the exclusive presence of these compounds in the Tagish Lake meteorite is related to some synthetic environments that were not shared by Murchison. The abundance of the carbonates in this meteorite (Zolensky *et al.*, 2002), as well as that of magnetite, are good indicators of a particularly long aqueous alteration

TABLE 7. $\delta^{13}\text{C}$ (‰ PDB) of aromatic dicarboximides in the Tagish Lake meteorite.

Compound	$\delta^{13}\text{C}$ ‰
Homophthalimide	1.5
Methylphthalimide	7.7
Dimethylphthalimide	5.9
Dimethylphthalimide	10.5
Dimethylphthalimide	17.5

From Pizzarello et al. (2001).

process that could be associated with the formation of aromatic dicarboxylic acids, for example, by oxidation of alkyl benzenes or substituted naphthalenes. Alkyl and aromatic diacid anhydrides and imides would have formed from the acids upon loss of water and in the presence of ammonia.

3.11.3. Amphiphilic material. Amphiphilic material, i.e., having both polar and hydrophobic moieties, has been extracted from Murchison powders by dissolution in chloroform. This material contains large, complex molecules and includes a fluorescent yellow pigment of unknown composition that can be observed directly in the matrix of cut meteorite stones (Deamer, 1985); infrared spectroscopy suggests it may contain aromatic hydrocarbon polymers as well as phenolic and carboxyl groups. The material assumes different structures in water depending on the pH, apparently from the titration of polar functions, and in alkaline solutions forms hydrated gels that assemble into membranous vesicles (see section 5).

4. INTERPLANETARY DUST PARTICLES

Interplanetary dust particles (IDPs), which are fragments of comets and asteroids ranging in size from $\sim 5\ \mu\text{m}$ to $\sim 50\ \mu\text{m}$, have been collected from Earth's stratosphere by NASA aircraft since the mid-1970s (Brownlee, 1985). Due to their small size, the IDPs may radiate energy efficiently upon atmospheric entry, avoid severe heating during deceleration, and preserve any organic matter either incorporated into the dust at formation or produced on the parent body during later processes, e.g., aqueous activity. Each particle contains a number of "internal thermometers" such as moderately volatile elements (e.g., Zn and S), minerals with low thermal stability (e.g., hydrated minerals and sulfides), solar-wind-implanted noble gases (e.g., He, which is lost at 600° to 1200°C), and solar flare damage tracks. When available, all can be used to select IDPs that have experienced minimal entry heating and subject them to organic analysis (Flynn, 1989).

Anhydrous and hydrated IDPs are collected from the stratosphere in roughly equal abundances (Fraundorf et al., 1982) and, for most, their major rock-forming element content is within a factor of 2 of that found for CI meteorites (Schramm et al., 1989). Interplanetary dust particles are enriched in the moderately volatile elements and C by a fac-

tor of 2 to 3 over the CI meteorites (Flynn et al., 1996), indicating that temperatures throughout and following their formation were low enough to condense and retain these elements. This chemical composition distinguishes the anhydrous group of IDPs from all known anhydrous meteorites, which are depleted relative to CI in the moderately volatile elements. Thus, the anhydrous IDPs appear to be less altered by thermal and aqueous processing, i.e., they are more primitive than any known meteorite. As a result, these particles have the highest likelihood of preserving the interstellar organic matter that was present in the solar nebula and of providing samples of the first organic matter that formed in our solar system as well.

Few organic analysis techniques have both the required sensitivity and the high spatial resolution necessary to study the organic matter in IDPs. Those that do include L²MS, laser Raman, IR, and X-ray absorption near-edge structure (XANES) spectroscopy. However, each of these techniques is functional group specific, rather than providing characterization of the entire organic molecule. Thus, the information obtained from the organic matter in IDPs is different from that available for organic matter in carbonaceous meteorites.

The C of the IDPs varies in content between particles and is heterogeneously distributed within most IDPs. Schramm et al. (1989) analyzed 30 IDPs, using thin-window energy dispersive X-ray (EDX) fluorescence, and found a mean carbon abundance $\sim 2.5\times$ that of the CI carbonaceous meteorites. The porous IDPs, a group dominated by anhydrous particles, have almost twice the carbon content of the smooth IDPs, which are dominated by hydrated particles. Thomas et al. (1994) used the same technique on ~ 100 IDPs and found that the carbon content was highly variable, with a mean weight value of $\sim 12\%$ (i.e., $\sim 3\times$ CI). Flynn et al. (2000) confirmed the high carbon abundance in IDPs by mapping the C spatial distribution in ultramicrotomed thin-sections using a scanning transmission X-ray microscope (STXM).

Wopenka et al. (1988) performed Raman spectroscopy, a technique that is particularly sensitive to the structure of carbon, on 20 IDPs. The spectra were dominated by poorly crystallized carbon exhibiting a wide range of disorder but no specific signature of organic matter; only amorphous elemental carbon was detected. Raynal et al. (2001) obtained Raman spectra of six IDPs; two, dominated by Fe-sulfides, showed no Raman features, indicating they contained little or no carbon. The remaining four silicate IDPs contained carbonaceous material having a significantly different structure than that in the acid insoluble residues from carbonaceous meteorites, with the carbonaceous material in the IDPs being slightly more disordered than the meteorite residue but being "marginally similar to . . . immature type II kerogens," i.e., a H-rich (H/C between 1 and 1.3) type of organic matter that is insoluble in nonpolar solvents and nonoxidizing acids.

Clemett et al. (1993) provided the first significant evidence for the presence of indigenous organic matter in some

IDPs using $\mu\text{L}^2\text{MS}$. Two of the eight IDPs they analyzed, Aurelian and Florianus, both of which also exhibit large D-enrichments detected by secondary-ion mass spectrometry, gave a series of mass peaks consistent with PAHs, while none of the remaining six IDPs gave detectable signatures of PAHs. The mass spectra of both Aurelian and Florianus show three major mass envelopes near 60, 250, and 370 amu. The lowest mass envelope contains inorganic species including Na, K, and Al as well as hydrocarbon fragments. The two higher envelopes contain signatures of PAHs and their alkylated derivatives separated by 14 amu (i.e., indicative of the successive addition of methylene groups to the PAH skeleton), plus a unique distribution of odd mass peaks in the range of 180–340 amu. This technique was also applied to the analysis of multiple fragments from a single “cluster IDP,” L2008#5, which was so weak that it broke apart in hundreds of fragments upon hitting the collector surface (Thomas *et al.*, 1995). Analysis of the multiple fragments indicates this cluster particle contained ~ 7 wt% carbon, but comparison of $\mu\text{L}^2\text{MS}$ results from several fragments shows that carbon and organic matter are distributed inhomogeneously and that some of these fragments contain PAHs with masses in the 400–500 amu range. Thomas *et al.* (1995) suggest that these high-mass PAHs may either be organic compounds unique to the IDPs or they may be the product of polymerization of lower molecular weight species, possibly by thermal processing during atmospheric entry.

Swan *et al.* (1987) detected CH_2 and CH_3 stretching absorption consistent in energy with those of aliphatic hydrocarbons in four anhydrous and four hydrated IDPs using conventional globar-based FTIR. However, the authors could not eliminate the possibility that the weak features observed

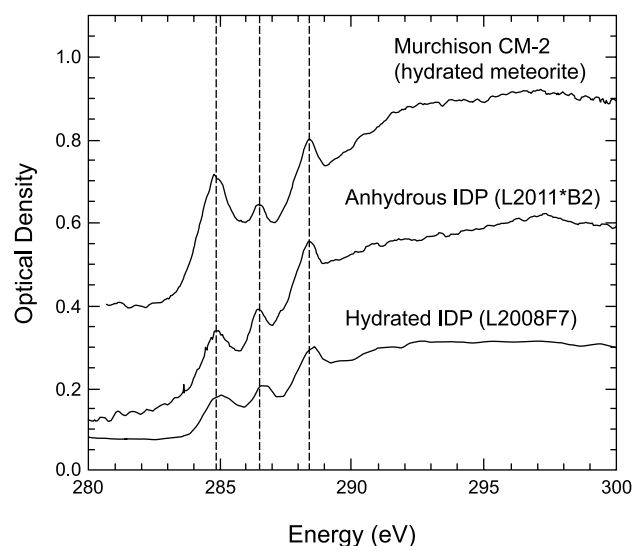


Fig. 5. Comparison of the C XANES spectra of a hydrated IDP, an anhydrous IDP, and the Murchison meteorite. Adapted from Flynn *et al.*, 2003.

were due to contamination. Flynn *et al.* (2000, 2003), employing a synchrotron-based FTIR with about 100 \times the signal/noise of globar-based FTIR, were able to unambiguously characterize the organic matter in 11 anhydrous and 5 hydrated IDPs. They detected the CH_2 and CH_3 stretching absorptions near 2960, 2926, 2880, and 2854 cm^{-1} (Fig. 5) that are characteristic of aliphatic hydrocarbon and distinctly different from the signature of the silicone oil in which the IDPs are collected (Flynn *et al.*, 2000). Raynal *et al.* (2000) obtained similar results on a smaller group of IDPs; they also analyzed a Fe-sulfide IDP, but detected no organic matter (Raynal *et al.*, 2000).

The C-H stretching region in the infrared spectra of the anhydrous and the hydrated IDPs differ from the spectrum of Murchison acid insoluble organic residue in two significant ways. First, the aliphatic CH_3 to CH_2 absorption depth ratio is much larger in Murchison than in the IDPs, suggesting that the mean aliphatic chain length in the IDPs is longer than in Murchison (Flynn *et al.*, 2003). Second, the aromatic C-H stretches are easily detected in Murchison, as a broad feature centered near 3050 cm^{-1} , but this absorption is seen in only 1 of the 19 IDPs analyzed by Flynn *et al.* (2003), indicating that most IDPs have a considerably lower aromatic to aliphatic CH content than does the Murchison residue. Thus, we should conclude that in the IDPs the aromatic content is lower and/or the aromatic rings are less hydrogenated than in Murchison acid residues.

In most IDPs the higher-energy features from C- to O- and C- to N-bonding are obscured by the stronger absorption features from the major mineral phases, silicates, oxides, and carbonates. To eliminate the mineral features and reveal underlying organic features Flynn *et al.* (2002) performed FTIR analyses on IDPs that had been acid etched by a technique developed by Brownlee *et al.* (2000) to remove the major minerals. The acid etched IDPs showed several carbonyl (C=O) absorption features; the strongest at ~ 1705 cm^{-1} is characteristic of the carbonyl of an aliphatic ketone, but the anhydrous IDP also showed a significant absorption near ~ 1760 cm^{-1} , indicative of an ester carbonyl (Flynn *et al.*, 2002).

Flynn *et al.* (2003) and Feser *et al.* (2003) also analyzed the IDPs using C-, N-, and O-XANES spectroscopy, a sensitive indicator of functional groups. They found that the dominant type of carbonaceous material in most anhydrous and hydrated IDPs have similar C-XANES spectra (see Fig. 5). The IDP spectra exhibit two strong absorptions, one at ~ 285 eV attributed to C=C, which is found in both elemental carbon (graphite and amorphous carbon) and organic carbon (aromatic or olefinic); one at ~ 288.5 eV, which can result from either the C=O or C-H functional group; and a weaker absorption near 286.5 eV. Flynn *et al.* (2001, 2003) performed O-XANES spectroscopy on the same region of one of the IDPs, and detected a 532 eV absorption feature, consistent with C=O, confirming that a significant fraction of the 288.5 eV absorption in the IDPs is from the C=O functional group. The assignment of a specific functional group to the weaker 286.5 eV absorption in the IDPs has

not yet been possible because both oxygen bonded to an aromatic ring and the C-N bond of an amide group give rise to a feature near that energy.

The ratio of the area of the C=C absorption feature to the C=O absorption feature is nearly identical in the anhydrous and the hydrated IDPs. This ratio is found to be higher in the Murchison acid insoluble organic residue, indicating that a higher proportion of the C in the IDPs is carbonyl compared to Murchison (Flynn et al., 2003). A comparison of the height of the C-edge to the height of the O-edge provides a measure of the C/O ratio in the organic phase of the IDPs and Murchison. The one anhydrous IDP measured has a C:O ratio of ~2 (Flynn et al., 2001), compared to ~8.3 reported by Zinner (1988) for a Murchison acid insoluble organic residue.

Nitrogen is present in IDPs at a much lower concentration than carbon and oxygen and is more difficult to detect and characterize. Keller et al. (1995) reported a mean C/N ratio of ~10 in several IDPs measured by electron energy loss spectroscopy (EELS). Matrajt et al. (2003) measured three IDPs using a nuclear microprobe that irradiates the sample with an intense beam of D ions and detects the products from $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$ and $^{14}\text{N}(\text{d},\text{p}_0)^{15}\text{N}$ reactions, and found an average C/N ratio of ~22. Both N-XANES and N-EELS spectra show two broad pre-edge absorption features consistent with literature data for amides or amines (Feser et al., 2003; Keller et al., 1995). As mentioned previously, the two IDPs Aurelian and Florianus display several $\mu\text{L}^2\text{MS}$ odd-mass peaks that could be explained by the presence of N-bearing heterocycles (Clemett et al., 1993); by contrast, the spectra of the fragments from L2008#5 were dominated by even mass peaks (Thomas et al., 1995).

Many of the IDPs, particularly the anhydrous cluster IDPs, have regions where the D/H ratio far exceeds that found in terrestrial materials, suggesting that these D-rich IDPs contain relatively well-preserved interstellar material (Messenger, 2000). Aleon et al. (2001) mapped the spatial distribution of H, D, $^{12,13}\text{C}$, $^{16,18}\text{O}$, ^{27}Al , and $^{28,29,30}\text{Si}$ in five IDPs. They concluded that water in these IDPs had an approximately chondritic D/H ratio, while some of the organic matter was D-rich. Stephan et al. (2003), using time of flight-secondary ion mass spectrometry (TOF-SIMS), also concluded that the host of the anomalous deuterium in IDPs is an organic phase. Messenger (2000) has mapped the spatial distribution of the deuterium using SIMS, and Keller et al. (2004) have prepared ultramicrotomed sections, preserving the spatial relationships, to examine the D-rich spots by C-XANES and FTIR spectroscopy. They found that the organic C, with a C-XANES spectrum showing the same three absorption peaks found in most other IDPs, was spatially associated with the D-rich spot, indicating that the D host is organic matter rather than water. Further, the infrared analysis showed a high aliphatic C-H content in two D-rich IDPs but a low aliphatic C-H content in a D-poor IDP, resulting in Keller et al. (2004) suggesting that the D host is aliphatic. However, Mukhopadhyay and Nittler (2003) have identified water as the D-host in one IDP.

Based on the similarity of the types and abundance of organic matter in the anhydrous IDPs and the hydrated IDPs, Flynn et al. (2003) suggest that the bulk of the prebiotic organic matter in the solar system formed prior to or concurrent with dust condensation in the solar nebula, and was not produced by aqueous processing on an asteroidal parent body.

5. METEORITE ORGANICS AND THE ORIGIN OF LIFE

Organic compounds, as their name originally was meant to indicate, have their largest molecular representation in the terrestrial biosphere. Here, their C is arranged in a multiplicity of chains and rings to which other atoms are attached, mainly H, but also O, N, S, and P. In living systems these compounds attain structures, functions, and selection possibilities that allow and sustain life. Not surprisingly, the study of organic compounds discovered in the solar system and beyond has often been framed in regard to origins of life, i.e., how abiotic organic compounds could possibly be linked to the development of planetary life, either here on Earth or elsewhere. Even before these discoveries, Haldane (1928) and Oparin (1938) independently proposed that the onset of terrestrial life was preceded by the abiotic formation of simple organic precursors and their subsequent development into increasingly complex molecules that ultimately yielded life. Carbonaceous chondrite meteorites provide an unparalleled record of such organic prebiotic chemistry in the early solar system, as found in a planetary setting and closest to the onset of life. Because the majority of known organic compounds in meteorites are also found in Earth's biosphere and an exogenous delivery of asteroidal material has undoubtedly showered Earth throughout its history (Anders, 1989; Delsemme, 1992; Chyba and Sagan, 1992), it is reasonable to consider the possibility that meteorites and comets could have provided the early Earth with life's precursor molecules.

As noted throughout this chapter, however, the overall abundances and composition of meteorite organics are distinguished by randomness and diversity that contrast with the structural specificity that characterizes terrestrial biomolecules. Also, as Cronin and Chang (1993) have pointedly remarked, an inventory of suitable organics "... is clearly not the recipe for constructing the progenote" and a basic challenge resides in finding "... where diversity that characterizes chemical evolution ... gives way to the selectivity of life". An intriguing exception to the organic diversity in CC is the presence in some meteorites of amino acids that share, to some degree, the trait of chiral asymmetry with biomolecules. These are the α -methyl- α -amino acids that display enantiomeric excesses that, if not very extensive, have the same sign (L-) as terrestrial amino acids. This finding has raised anew speculations that extra-terrestrial prebiotic processes might have provided the early Earth with a "primed" inventory of essential organic molecules holding an advantage in molecular evolution.

The α -methylamino acids, which are generally unimportant in terrestrial biochemistry and that may not be viewed as relevant to the origin of life, are abundant in meteorites and could be well suited for such a role. First, their ee can be as high as 15%. Although the chemical pathways of early bioprecursors may have been largely different from those of contemporary metabolism, homochirality is essential to the structural organization of the biopolymers necessary for life. Therefore, we may assume chiral selection to have been an early evolutionary achievement. Second, α -substituted amino acids do not racemize, as α -H isomers do. This is a definite advantage in water on which, we have also to assume, early life was based. Third, α -methyl amino acids are known to have strong helix inducing and stabilizing effects (Altman *et al.*, 1988; Formaggio *et al.*, 1995) and we know that polymerization accompanied by formation of regular secondary structures can be an effective way to amplify modest initial ee (see Cronin and Reisse, 2005, for a review). It is conceivable, therefore, that meteoritic amino acids may have played a significant early role in the chemical evolution of homochirality and perhaps the biochemistry of a pre-RNA world.

The exogenous delivery of prebiotic material may also have contributed to molecular evolution in combination with early Earth endogenous processes. Amino acids are catalysts in reactions that could be pathways to biogenesis; for example, the condensation of simple aldehydes such as formaldehyde and glycolaldehyde to give sugar and amino acids (Weber, 2001). It has been shown that ee are catalytically transferred from both isovaline and alanine when tetroses are synthesized from glycolaldehyde in water, that such an effect is larger for isovaline than for alanine, and that it occurs at levels of amino acid ee comparable to those seen in meteorites (Pizzarello and Weber, 2004). Therefore, meteoritic amino acids could have provided the symmetry breaking necessary for the evolution of RNA by acting as catalysts or promoters of asymmetric syntheses leading to D-ribose.

Among the possible effects of exogenous delivery of carbonaceous material, the extraction from the Murchison meteorite of vesicle-forming molecules (Deamer, 1985) may hold a particular significance. For example, Mauntner *et al.* (1995) demonstrated that hydrothermal conditions release from the meteorite a mixture of amphiphilic components, longer chain carboxylic acids among others, that collaborate efficiently in giving water solutions a sustained increase of surface tension toward the formation of membranes and vesicles. The findings therefore raise the interesting prospect that meteoritic components could also have contributed self-assembly capabilities to the early Earth milieu (Deamer *et al.*, 2003).

In the larger context of the possible distribution of life around other stars, the finding in meteorites of a variety of amino acids with large D-enrichment would show that potential precursors to prebiotic molecules are already abundant and varied in cold interstellar environments. On the

assumption that chemical evolution was relevant to the origin of terrestrial life, this abundance of biomolecule precursors in cosmic environments therefore implies that similar life would be facilitated elsewhere as well.

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