Organic compounds in carbonaceous meteorites

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Covering: 1950s to the present day

The carbonaceous chondrite meteorites are fragments of asteroids that have remained relatively unprocessed since the formation of the solar system 4.6 billion years ago. These carbon-rich objects contain a variety of extraterrestrial organic molecules that constitute a record of chemical evolution prior to the origin of life. Compound classes include aliphatic hydrocarbons, aromatic hydrocarbons, amino acids, carboxylic acids, sulfonic acids, phosphonic acids, alcohols, aldehydes, ketones, sugars, amines, amides, nitrogen heterocycles, sulfur heterocycles and a relatively abundant high molecular weight macromolecular material. Structural and stable isotopic characteristics suggest that a number of environments may have contributed to the organic inventory, including interstellar space, the solar nebula and the asteroidal meteorite parent body. This review covers work published between 1950 and the present day and cites 193 references.

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Mark Sephton was born in Merseyside in 1966. He obtained his BSc in Geology from the University of Durham in 1991 and his MSc in Organic Geochemistry, Organic Petrology and Petroleum Geochemistry from the University of Newcastle upon Tyne in 1992. Between 1993 and 1996 he studied for a PhD in Organic Compounds in Meteorites at the Open University and then spent two years investigating the molecular and isotopic record of the Permian–Triassic mass extinction at the Netherlands Institute for Sea Research and University of Utrecht. Subsequently, he returned to the Open University to develop stable isotope methods for the forensic detection of steroid abuse in association with the Horeseracing Forensic Laboratory in Newmarket. In 2000, he became a Lecturer in the Planetary and Space Sciences Research Institute and Department of Earth Sciences at the Open University. His current research interests include molecular and isotopic investigations of the extra-terrestrial organic matter in meteorites and the causes and consequences of mass extinctions in the geological record.

1 Introduction

This review covers the organic analyses of carbonaceous chondrite meteorites performed during and since the second half of the 20th century. The field lay inactive during the first half of the 20th century but a rising interest in space science and the development of new analytical methods led to its revival in the 1950s and 1960s. Current theories rely heavily on analyses

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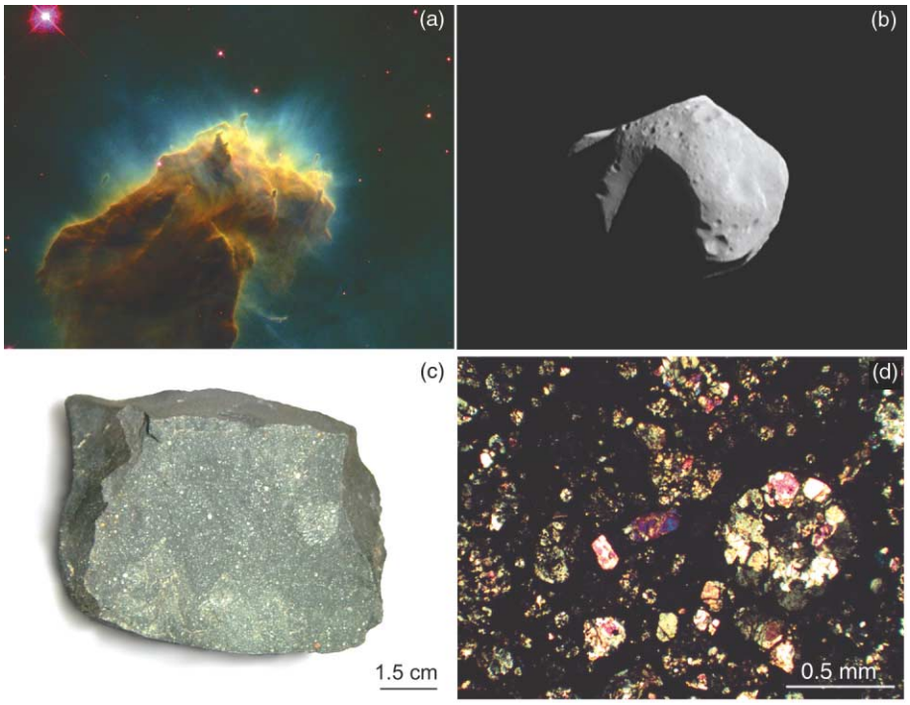

Fig. 1 The journey from interstellar space to the laboratory illustrated in pictures: a) the Eagle Nebula (Photo courtesy of NASA) is a molecular cloud where stars are being born and a rich interstellar chemistry is taking place, b) Mathilde (Photo courtesy of NASA), a member of the C-type asteroids that have remained relatively unchanged since the birth of the solar system and which may be the parent bodies for the carbonaceous chondrite meteorites, c) the Murchison (CM2) carbonaceous chondrite which fell in Australia in 1969 and contains a variety of organic molecules, d) a thin section of the Dar al Gani 186 carbonaceous chondrite showing spherical silicate chondrules surrounded by a matrix composed primarily of clay minerals, oxides and organic matter.

performed since 1969 when new contaminant free samples became available and modern techniques were developed in anticipation of sample returns from spaceflight missions. Some older results, however, are valuable when considered with modern knowledge and this review examines and often re-interprets material presented in papers published both before and after 1969. A number of key reviews have been published on the organic analyses of carbonaceous chondrites over the last forty years.[1–5]

1.1 Carbonaceous chondrites and their origin

Meteorites are fragments of extraterrestrial material that fall to the Earth's surface. The Earth acquires 100 000 to 1 000 000 kg of such material each day, but only 1% or less arrives in pieces large enough for identification and recovery.[6] The surface of the meteorite usually melts and emits a glowing tail and a trail of smoke, but the interior of the meteorite is unaffected by passage through the Earth's atmosphere. It is generally agreed that most meteorites are fragments of asteroids propelled into Earth-crossing orbits by relatively recent collisions in the asteroid belt, initiated by the gravitational effects of Jupiter's orbit.[7] The asteroids have escaped many of the geological processes experienced on the planets and they, and the meteorites derived from them, preserve some of the most primitive materials in the solar system. The carbonaceous chondrites are the most ancient meteorites and contain a record of the birth of the solar system and, to some extent, the presolar molecular cloud from which it was constructed (Fig. 1). The name "carbonaceous chondrite" is highly descriptive as these meteorites contain a carbon-rich matrix composed primarily of clay minerals, oxides and organic matter and most contain spherules of silicate glass termed chondrules.

1.2 Collection of meteorites

"Falls" are meteorites that have been observed to fall and were subsequently collected; "finds" are meteorites that were not seen to fall. Before the 1970s the total number of known meteorites amounted to less than 1000 falls and 1706 authenticated finds. Since then, it has been recognised that certain parts of the Earth's surface preserve and concentrate meteorites. More than 20 000 meteorite fragments have been collected from the Antarctic ice. Meteorites landing on huge areas of ice are transported by glacier movement and concentrated in distinct zones where the ice is lifted and ablated near coastal mountain chains. The cryogenic storage conditions for Antarctic meteorites ensures their relatively pristine nature. Several 10 000 meteorite fragments have also been collected from hot deserts, particularly the Sahara. The large featureless desert areas underlain by light coloured sediments facilitate the collection of dark meteorite samples.

1.3 Classification of carbonaceous chondrites

The carbonaceous chondrites are classified according to their primary and secondary characteristics (Fig. 2). The primary classification (CI, CM, CR, CO, CV, CK) reflects the original properties of the meteorites such as bulk chemistry and mineralogy. The label is derived from the carbonaceous chondrite accepted as the type specimen, *e.g.* CI = Ivuna. The secondary classification reflects petrographic type which indicates the extent and type of alteration that the meteorite has undergone on its parent body.

2 Carbon in carbonaceous chondrites

The carbon in the carbonaceous chondrites is present in a number of forms. One way in which these components can be detected is by stepped heating experiments. Stepped heating distinguishes between carbon phases by their susceptibility to combustion. Table 1 lists the most important components, their typical abundances, and combustion temperatures.

Organic matter is, quantitatively, the most important carbon bearing phase (Table 1) but can be subdivided into two phases. Solvent-soluble or "free" organic material can be isolated from the meteorite by dissolving it in common organic solvents and accounts for around 30% of meteoritic organic matter in CI1

Table 1 The carbon-bearing components in carbonaceous chondrites, their combustion temperatures and the stable isotopic compositions of released gases. The table was compiled from refs. 8–19

	Abundance (wt%)	δ^{13}C (‰)	δD (‰)	δ^{15}N (‰)	Combustion temp./°C
Whole rock	—	0 to −25	−188 to +644	−50 to +335	—
Organic matter	2.0	−13 to −21	+480 to +680	+25 to +150	250 to 450
Carbonate	0.2	+20 to +80	—	—	400 to 700
Diamond	0.04	−38	+180 to +284	−350	400 to 500
Graphite	0.005	−50 to +340	—	—	500 to 700
Silicon carbide	0.009	+1200	—	−500	1200 to 1400

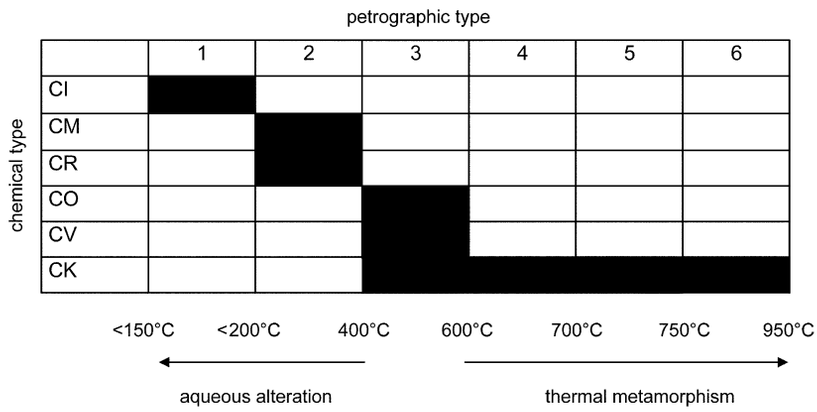

Fig. 2 The carbonaceous chondrites are classified based on a combination of their primary (chemical) composition and levels of secondary (aqueous and thermal) processing. Currently known samples (excluding the recently fallen Tagish Lake meteorite) are indicated by black shading.

and CM2 meteorites. The remaining 70% or so is present as an organic macromolecular material which is insoluble in common organic solvents.[1] Insoluble organic material can be progressively isolated from the rest of the meteorite by using solvents to remove soluble organic material, hydrofluoric acid (HF) to remove silicates, and hydrochloric acid (HCl) to remove carbonates.

The remaining carbon-bearing phases in carbonaceous meteorites are inorganic. Carbonates form a significant proportion of the carbon inventory in carbonaceous meteorites (Table 1). "Exotic" carbon (diamond, silicon carbide and graphite) is contained within the insoluble carbon but can be isolated by progressive oxidative techniques (*e.g.* dichromate and perchloric acids).

3 Stable isotopes and carbonaceous chondrites

The stable isotopic composition of extraterrestrial materials may be determined by nucleosynthesis, nuclear processing, and chemical fractionation processes.[20] By establishing the isotopic composition of carbon-bearing phases, the origin of the extraterrestrial component may be constrained. The abundances of stable isotopes are generally expressed as δ values. These indicate the difference, in per mil (‰), between the relevant ratio in the sample and the same ratio in an international standard [standard mean ocean water (SMOW) for hydrogen, Pee Dee Belemnite (PDB) for carbon; air for nitrogen] as follows:

$$\delta‰ = (R_{\text{sample}} - R_{\text{standard}} / R_{\text{standard}}) \times 1000$$

where $R = {}^{2}\text{H}/{}^{1}\text{H}$, ${}^{13}\text{C}/{}^{12}\text{C}$ or ${}^{15}\text{N}/{}^{14}\text{N}$. The carbon-bearing components in carbonaceous meteorites have a wide range of stable isotopic compositions. Some common stable isotopic values are listed in Table 1. Stable isotopic measurements have been especially useful for determining the origin and history of meteoritic organic matter. Early studies of this kind obtained isotopic measurements on broad assemblages of meteoritic compounds in the form of either the bulk macromolecular material, acid residue, or evaporated unfractionated solvent extracts. Later work achieved higher resolution, and measured isolated fractions that contained compounds with broadly similar chemical structures. Such crude fractions were isolated by standard preparative chromatography, and subjected to combustion-isotope ratio mass spectrometry (combustion-IRMS).

These studies represent significant advances in confirming the indigenous nature of organic matter by detecting noticeable enrichments in the heavy isotopes of carbon (^{13}C), nitrogen (^{15}N), and hydrogen (deuterium or D) when compared to terrestrial values. Typical terrestrial values are δD = < −30‰, δ^{13}C = −5 to < −30‰, δ^{15}N = −5 to +20‰.[21] These measurements also provide valuable clues as to the extraterrestrial environments that contributed to the various classes of meteoritic organic matter, with perhaps the most notable of these being D-enrichments characteristic of interstellar space. However, these isotopic measurements can only be averages of a wide variety of organic compounds.

Isotopic analysis at the molecular level, known as compound-specific isotope analysis (CSIA), represents a further stage in the deconvolution of the structural and isotopic constitution of meteoritic organic matter. The combination of separation, combustion, and isotopic measurement into a single procedure known as gas chromatography-isotope ratio mass spectrometry (GC-IRMS) allows the relatively rapid determination of the isotopic compositions of individual molecules within complex organic mixtures.[22] In recent years, this type of analysis has produced a significant data set for meteoritic organic components. Such measurements are particularly useful because they can expose the reaction mechanisms and source environments from which the organic constituents have been formed. The CSIA data set for meteoritic compounds has been reviewed recently by Sephton and Gilmour.[23]

4 The organic compounds in carbonaceous chondrites

Much of our current understanding of meteoritic organic matter has come from investigations of the Murchison (CM2) meteorite, approximately 100 kg of which fell in western Australia in 1969. Analyses prior to 1969 were always subject to doubt because of the possibility of terrestrial contamination. The fall of Murchison (CM2) provided a large amount of sample in a relatively good state of preservation.[24] The collection of carbonaceous chondrites from Antarctica has provided

Table 2 Types of organic matter in the Murchison (CM2) carbonaceous chondrite and their abundances (updated from ref. 3)

Compounds	Abundances (%)	Abundances μg g^{-1} (ppm)	Ref.
Macromolecular material	1.45		26
Carbon dioxide		106	27
Carbon monoxide		0.06	27
Methane		0.14	27
Hydrocarbons: aliphatic		12–35	28
aromatic		15–28	29
Acids: monocarboxylic		332	27, 30
dicarboxylic		25.7	31
α-hydroxycarboxylic		14.6	32
Amino acids		60	4
Alcohols		11	33
Aldehydes		11	33
Ketones		16	33
Sugar-related compounds		~60	34
Ammonia		19	35
Amines		8	36
Urea		25	37
Basic N-heterocycles (pyridines, quinolines)		0.05–0.5	38
Pyridinecarboxylic acids		>7	39
Dicarboximides		>50	39
Pyrimidines (uracil and thymine)		0.06	40
Purines		1.2	41
Benzothiophenes		0.3	42
Sulfonic acids		67	43
Phosphonic acids		1.5	44

an additional relatively terrestrial contaminant-free source of samples. Over the last three decades Murchison (CM2) has been the focus of intensive research using the most modern techniques. The Murchison (CM2) organic inventory has become a valuable reference to which all other extraterrestrial organic matter may be compared. The abundances of the various types of organic matter in Murchison (CM2) are listed in Table 2. The recent fall of the Tagish Lake meteorite (January 2000) has provided an additional amount (over 5 kg) of relatively pristine carbonaceous chondrite for the scientific community.[25] The classification of this meteorite is as yet uncertain but has been tentatively assigned as the first example of a CI2 meteorite.[25]

4.1 Aromatic hydrocarbons

4.1.1 Solvent and thermal extracts

Early analyses of the aromatic hydrocarbons in meteorites focused on solvent extracts or fractions of solvent extracts from meteorites such as Orgueil (CI1), Murray (CM2), Cold Bokkeveld (CM2) and Allende (CV3). Several analytical techniques were used to characterise the extracts including mass spectroscopy,[45–47] low temperature fluorescence spectroscopy,[48, 49] infrared (IR) and ultraviolet (UV) spectroscopy[45–47, 50] and gas chromatography (GC).[45, 51–53] These studies detected a large number of aromatic and alkyl aromatic compounds ranging from naphthalene to coronene and, in many cases, high molecular weight compounds dominated.

Distillation or vaporization, either by directly heating the sample (at temperatures at or below 300 °C) in the ion source of a mass spectrometer or *via* some sort of pyrolysis unit coupled to a GC column, was another common technique for the extraction of aromatic compounds from meteorites. Thermally-extracted compounds ranging from benzene to pyrene were detected by mass spectrometry;[54–57] GC[58, 59] and gas chromatography-mass spectrometry (GC-MS).[55]

Since the fall of the Murchison (CM2) meteorite and the collection of meteorites from Antarctica, a number of aromatic compounds have been detected in these relatively pristine samples. Soon after Murchison (CM2) fell, analyses of two benzene eluates from benzene–methanol solvent extracts yielded similar results. Oró *et al.*[24] used GC-MS to find a series of alkyl substituted dicyclic and tricyclic aromatic compounds. Pering and Ponnamperuma[29] used GC and GC-MS to detect 23 compounds, most of which were polynuclear and included naphthalene, acenaphthene, anthracene, fluoranthene, pyrene and some alkyl naphthalenes and phenanthrenes.

Thermal extraction methods were also employed shortly after the fall of Murchison (CM2). Studier *et al.*[60] directly volatilised 34 compounds including benzene, toluene, alkyl benzenes, indanes and naphthalene. Levy *et al.*[61] used a similar volatilisation technique in conjunction with GC-MS to detect small amounts of toluene and naphthalene.

A series of studies of carbonaceous chondrites, particularly Murchison (CM2), were performed in the 1980s and 1990s using solvent extraction and GC-MS. Basile *et al.*[62] found 30 polycyclic and heterocyclic aromatic compounds in a benzene eluate of a Murchison (CM2) solvent extract with fluoranthene and pyrene as the most abundant components. Deamer,[63] Krishnamurthy *et al.*[64] and Gilmour and Pillinger[65] analysed solvent extracts of the Murchison (CM2) meteorite; Naraoka *et al.*[66] and Shimoyama *et al.*[67] analysed solvent extracts of the Antarctic CM2 meteorites, Yamato-791198 and Yamato-74662, respectively. In all cases the most abundant compounds in the extracts were phenanthrene, fluoranthene and pyrene.

Several conclusions can be drawn from these studies:

i) The molecular weight range of the aromatic compounds detected correlates with the extraction technique employed, with high molecular weight compounds dominating in solvent extracts and low molecular weight compounds dominating in thermal extracts. Perhaps the most likely explanation of the discrepancies between the solvent and thermal extraction results in the literature is that the process of drying solvent extracts under a stream of nitrogen results in a loss of the aromatic compounds more volatile than the three-ring polyaromatic hydrocarbons (PAH).[1]

ii) There is evidence of significant heterogeneity in the compound distribution and concentration of the free aromatic hydrocarbons in carbonaceous chondrites. For example, Commins and Harington[50] analysed two separate samples of Cold Bokkeveld (CM2) and discovered that one sample had abundant fluorene and fluoranthene while the other sample had phenanthrene and pyrene as its most abundant compounds. Further evidence of sample heterogeneity was detected by

Table 3 Stable isotopic values for organic fractions from Murchison (CM2)

Sample	δ^{13}C (‰)	δ^{15}N (‰)	δD (‰)	Ref.
Benzene–methanol extract	+5			28
Methanol extract	+7	+88	+406	75
	+4		+957	64
Vol. hydrocarbons: freeze–thaw	0		−92	64
hot water	+6		+217	64
H_2SO_4	+17		+410	64
Aliphatic fraction: Chicago	−11.5		+264	64
ASU	−5		+103	64
Aromatic fraction: Chicago	−5.5		+407	64
ASU	−5		+244	64
Polar fraction: Chicago	+6		+946	64
ASU	+5		+751	64
Amino acids		+102		35
	+23	+90	+1370	76
		+94		77
Monocarboxylic acids	+7	−1	+377	76
	−1		+652	64
Hydroxy acids	+4		+573	78
Dicarboxylic and hydroxydicarboxylic acids	+6		+357	78
Volatile bases (ammonia, amines)	+22	+93	+1221	35
Neutral polyhydroxylated compounds	−6		+119	34
Macromolecular material	−13	+18	+830	14
		+10		79

Olson *et al.*[51] in the form of the wild variations in aromatic compound concentration between different samples of Orgueil (CI1) (a few μg g^{-1} to 180 μg g^{-1}).

iii) If the biases of the extraction procedures is ignored, there appears to be a positive correlation with free aromatic concentration and volatility.[51] This observation is particularly important because abiotic reaction mechanisms tend to generate products which decline in amount with increasing carbon number. Sephton *et al.*[68] confirmed that this was the case by avoiding volatile loss by using supercritical fluid extraction (SFE) for the extraction of Murchison (CM2). Supercritical CO_2 was used as a solvent and a positive correlation between aromatic concentration and volatility was detected. Thus, the higher molecular weight free aromatics are relatively minor components which become concentrated following volatile loss.

iv) There is the suggestion that low petrographic type meteorites contain more volatile aromatic molecules, while the converse is true in meteorites of higher petrographic type.[51] Recently, the extraction of the free aromatic content of Orgueil (CI1) and Cold Bokkeveld (CM2) with SFE has confirmed this relationship which is presumably generated by varying levels of aqueous and thermal processing on the meteorite parent body.[69]

v) At least some of the aromatic compounds are contaminants. Han *et al.*[53] analysed Allende (CV3) shortly after its fall and revealed small amounts of aromatic contamination which consisted mainly of a phenyl alkane structure. Similar fractions obtained from the interior of the meteorite contained no aromatic material indicating a terrestrial source for the compound.

4.1.2 Laser desorption-mass spectrometry

Laser desorption/laser ionisation-mass spectrometry (L^2MS) has become a popular technique and has detected a number of medium to high molecular weight PAH in the Murchison (CM2) meteorite. Using this approach, Hahn *et al.*[70] used IR laser desorption followed by UV laser ionisation to detect naphthalene, phenanthrene (or anthracene), pyrene (or fluoranthene) and various alkyl derivatives in four CM2 meteorites (Murchison, Mighei, Murray and Haripura) and one CV3 (Allende). Interestingly, Hahn *et al.*[70] also detected a predominance of three-ring PAH in Ivuna (CI1), which Wing and Bada[71,72] attributed to "geochromatography" (the separation of mixtures during fluid flow on the meteorite parent body). Tingle *et al.*[73] used thermal desorption followed by UV laser ionisation to establish that unsubstituted aromatics are dominant in Murchison (CM2). De Vries *et al.*[74] used UV laser desorption and UV ionisation to extend the high molecular weight range of the aromatic content of Murchison (CM2) to coronene and its methyl substituents (up to 340 Da) by analysing HF/HCl vacuum sublimates.

4.1.3 Stable isotopes and aromatic hydrocarbons

Krishnamurthy *et al.*[64] analysed the isolated aromatic fractions (benzene eluates) from Murchison (CM2) solvent extracts by combustion-IRMS and found them to be D- and ^{13}C-rich. δD values ranged from +244 to +468‰; the δ^{13}C values ranged from −5 to −6‰ (average values given in Table 3). These non-terrestrial values confirmed the indigeneity of most of the aromatic hydrocarbons and the D-enrichment was suggestive of a contribution from interstellar organic compounds.

The first compound-specific isotope measurement by GC-IRMS for the free aromatic hydrocarbons was performed by Yuen *et al.*[27] who obtained a δ^{13}C value for benzene from Murchison (CM2) (Table 4). Gilmour and Pillinger[65] made the first isotopic measurements of individual C_{14} to C_{22} PAH from a Murchison (CM2) solvent extract and Sephton *et al.*[68] used SFE to determine δ^{13}C values for C_6 to C_{11} aromatic hydrocarbons. δ^{13}C values for individual aromatic compounds from other carbonaceous meteorites were provided when Sephton and Gilmour[80] analysed solvent and SFE extracts of Orgueil (CI1) and Cold Bokkeveld (CM2), Naraoka *et al.*[81] analysed a solvent extract of the Antarctic CM2 Asuka-881458 and Pizzarello *et al.*[39] studied a solvent extract of the Tagish Lake (CI2) meteorite.

A number of salient points can be extracted from the free aromatic CSIA data set:

i) Many free aromatic entities have non-terrestrial δ^{13}C values confirming their indigeneity (*e.g.* Murchison free 2-methylnaphthalene: −5‰).

ii) The C_6 to C_{22} free aromatic compounds from Murchison and other CM2 meteorites appear to follow a definite trend when their δ^{13}C values are plotted against carbon number (Fig. 3). For the higher molecular weight aromatic hydrocarbons δ^{13}C values generally decrease as the amount of carbon in the molecules increase. This type of trend has been interpreted as the result of a kinetic isotope effect during the stepwise formation of higher molecular weight compounds from simpler precursors.[27] The more reactive ^{12}C is preferentially added during

Table 4 Stable carbon isotopic values for individual free aromatic molecules from carbonaceous chondrites

Compound	Orgueil (CI1)		Tagish Lake (CI2)		Cold Bokkeveld (CM2)		Murchison (CM2)		A-881458 (CM2)	
	δ^{13}C (‰)	Ref.	δ^{13}C (‰)	Ref.	δ^{13}C (‰)	Ref.	δ^{13}C (‰)	Ref.	δ^{13}C (‰)	Ref.
Benzene							−28.7±0.2	27		
Toluene					−24	80	−28.8±1.1	68		
Naphthalene							−12.6±2.3	68	−26.2±1.2	81
2-Methylnaphthalene							−5.8	68		
1-Methylnaphthalene							−11.1	68		
Biphenyl									−25.9±0.9	81
Phenanthrene	−23	80	−25	39	−27±1.3	80	−7.5±1.2	65	−12.9±0.3	81
Methylphenanthrenes									−13.4±0.8	81
Fluoranthene	−19	80					−5.9±1.1	65	−8.3±0.5	81
Pyrene	−17	80					−13.1±1.3	65	−15.8±0.8	81
Chrysene	−23	80					−14.5±2.2	65		
Benzo[*ghi*]fluoranthene	−15	80					−14.2±2.2	65	−15.8±0.8	81
Benzanthracene	−15	80								
Benz[*a*]anthracene, chrysene and triphenylene									−11.7±2.4	81
Benzo[*e*]pyrene							−22.3±4.1	65		
Benzopyrenes and perylene									−19.1±1.5	81
Benzo[*j*]fluoranthene							−15.4±3.3	65		
Benzofluoranthenes									−14.0±0.5	81
Dibenzanthracene	−17	80								
Benzo[*ghi*]perylene									−25.2±0.5	81

the synthesis of the carbon skeleton of these compounds. For the lower molecular weight aromatic hydrocarbons δ^{13}C values generally increase as the amount of carbon in the molecules increase. If this lower molecular weight trend is also the result of a kinetic isotope effect, then it suggests that bond destruction or "cracking" has produced these aromatic entities.[68] During cracking, the more reactive ^{12}C bonds are preferentially broken, leading to a concentration of this isotope in the products. Therefore, the free aromatic units in the CM2 meteorites seem to have been produced by a process in which bond formation and destruction were both significant.

iii) In the CM2 data set there is significant isotopic heterogeneity with free aromatic compound classes displaying variations reaching over 20‰. Furthermore, there are relatively large and systematic differences in δ^{13}C values for sizeable compounds which differ by only one or two carbon atoms. Such an effect is not seen in terrestrial organic systems and suggests that during bond formation and destruction, fractionation was at its most extreme. This acute fractionation may imply an origin by low temperature, possibly interstellar, reaction mechanisms.[80]

iv) In detail, δ^{13}C values for the two C_{16} structural isomers, pyrene and fluoranthene, differ by approximately 7.5‰. This variation in δ^{13}C is believed to reflect the two different pathways of formation for pyrene and fluoranthene and the relative difficulty encountered when their precursors underwent cyclization.[65,81]

v) δ^{13}C values for 1-methylnaphthalene in free molecules and meteorite pyrolysates are consistently lighter than 2-methylnaphthalene reflecting the greater reactivity of the ^{12}C-enriched reactants and their preference for the 1-position on the naphthalene molecule during bond formation.[82]

4.2 Aliphatic hydrocarbons

4.2.1 Volatile aliphatics

Early analyses using thermal extraction in conjunction with GC and/or mass spectrometry of Orgueil (CI1), Cold Bokkeveld (CM2), Murray (CM2) and Murchison (CM2) detected methane but commented on a scarcity of higher molecular weight hydrocarbons up to C_{10}.[54–56] Results from other studies appeared to conflict with these findings. Belsky and Kaplan[58] analysed eight carbonaceous chondrites for light hydrocarbon gases by thermal extraction and GC. Aliphatic compounds ranging from C_1 to C_7 were identified. The distribution of compounds was dissimilar in the different meteorites studied and both saturated and unsaturated hydrocarbons were detected. It was concluded that the trace constituents identified were present as gases trapped between crystal boundaries. Other workers used thermal extraction in conjunction with GC and GC-MS to detect low molecular weight aliphatic compounds in Allende (CV3)[57,59] and Murchison (CM2).[60,61]

Yuen *et al.*[27] used freeze–thaw disaggregation to release C_1 to C_5 straight chain hydrocarbons in addition to one branched hydrocarbon (isobutane) in Murchison (CM2). Saturated alkanes are more abundant than unsaturated alkanes. Carbon isotopic compositions for individual volatile hydrocarbons from Murchison (δ^{13}C +9.2 to −0.1‰) are substantially isotopically heavier than their terrestrial counterparts, signifying their extraterrestrial origin (Table 5). δ ^{13}C values decrease with increasing carbon number consistent with the kinetically controlled synthesis of higher homologues from lower ones (Fig. 3).

In a continuation of the Yuen *et al.* experiment, volatile hydrocarbon fractions were collected during the progressive decomposition of the Murchison (CM2) meteorite matrix by Krishnamurthy *et al.*[64] Freeze–thaw disaggregation was followed by treatment with boiling water and then H_2SO_4. The isotopic compositions of the volatile hydrocarbon fractions released displayed increasingly heavier δD and δ^{13}C values (Table 3). This data revealed that progressively more rigorous treatment of the meteorite liberated volatile hydrocarbons from an indigenous and D- and ^{13}C-enriched reservoir.

4.2.2 *n*-Alkanes

The first evidence of *n*-alkanes in the carbonaceous chondrites was provided when Nagy *et al.*[84] obtained mass spectra for distillates of the Orgueil (CI1) meteorite. These authors discovered that saturated hydrocarbons were "abundantly present" in "parts per thousand of solid meteorite". Controversially, Nagy *et al.*[84] noted the similarity of these hydrocarbons to those found in biological materials, including butter, and suggested that the Orgueil (CI1) *n*-alkanes provided "evidence for biogenic activity".

In a short time following the research of Nagy *et al.*,[84] several other carbonaceous chondrites were investigated for evidence of hydrocarbons using solvent extraction, silica gel chromatography and mass spectrometry. As a result, alkanes were also detected in Alais (CI1), Tonk (CI1), Ivuna (CI1) and Murray (CM2).[45–47] The interpretations of these findings followed a

Table 5 Results from carbon isotopic measurements performed on individual volatile alkanes[27] and normal alkanes[83] from carbonaceous chondrites. Tagish Lake (CI2) data are from ref. 39

Compound	Orgueil (CI1) δ^{13}C (‰)	Tagish Lake (CI2) δ^{13}C (‰)	Cold Bokkeveld (CM2) δ^{13}C (‰)	Murchison (CM2) δ^{13}C (‰)	Vigarano (CV3) δ^{13}C (‰)	Ornans (CO3) δ^{13}C (‰)
Methane				+9.2±1.0		
Ethane				+3.7±0.1		
Propane				+1.2±0.1		
Isobutane				+4.4±0.1		
Butane				+2.4±0.1		
Ethene				+0.1±0.4		
n-C_{12}				−35.5		
n-C_{13}				−28.5	−29.0±1.0	
n-C_{14}				−33.2	−28.0±1.5	−28.2±0.3
n-C_{15}				−28.2	−28.8±0.5	−28.8±0.2
n-C_{16}		−18.8		−25.3		−29.5±0.5
n-C_{17}	−28.9±0.7			−31.0		−27.2±2.6
n-C_{18}	−38.7			−30.6		
n-C_{19}	−32.0		−28.3			
n-C_{20}	−29.4±0.8	−29	−28.4±1.5			
n-C_{21}	−32.5±0.7		−27.8±0.4			
n-C_{22}			−28.8±1.1			
n-C_{23}			−28.5±1.1			
n-C_{24}			−28.3±1.6			
n-C_{25}			−27.2±0.8			
n-C_{26}			−27.0±0.6			

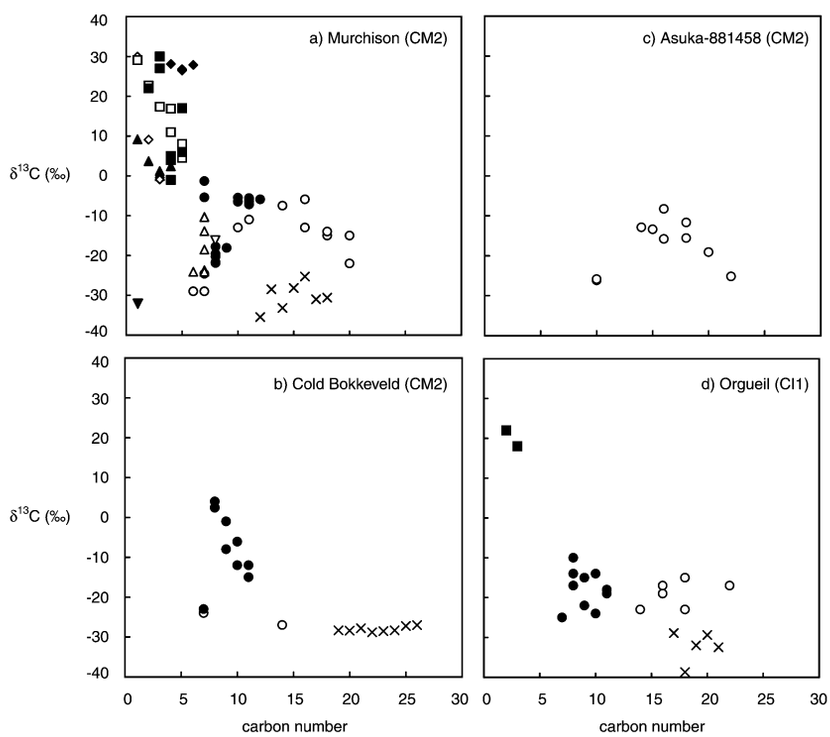

Fig. 3 Carbon isotopic compositions plotted against carbon number for individual compounds from the following meteorites: a) Murchison (CM2), b) Cold Bokkeveld (CM2), c) Asuka-881458 (CM2), and d) Orgueil (CI1). Assignments are as follows: (▲) free aliphatic hydrocarbon, (■) free amino acid, (◇) free sulfonic acid, (6) free carboxylic acid, (◆) free dicarboxylic acid, (○) free aromatic compound, (●) macromolecular aromatic compound, (△) macromolecular oxygen-containing compound, (▼) free CO, (▽) macromolecular benzothiophene, and (×) free normal alkane. The small Tagish Lake (CI2) CSIA data set is not displayed.

similar format to those for Orgueil (CI1), as the n-alkanes in these carbonaceous chondrites were proposed as "evidence of organisms that may have lived on a parent body of meteorites".[46]

The distribution of n-alkanes in Orgueil (CI1) was investigated by Oró *et al.*,[85] who used a similar experimental scheme to Meinschein *et al.*,[45–47] to isolate and identify these compounds. By analysing both interior and exterior portions of Orgueil (CI1), it was established that these hydrocarbons decreased in abundance away from the surface of the meteorite. In addition, the isoprenoidal hydrocarbons, pristane and phytane, were also detected. Such hydrocarbons based on isoprene units are generally accepted to indicate an ultimately biological origin. The work of Oró *et al.*[85] also established the ubiquity of n-alkanes in meteorites when 19 chondrites, including types of CI1, CM2, CO3 and CV3, contained these compounds in varying amounts and practically all contained pristane and phytane.

When more analyses began comparing the exterior and interior parts of meteorites, the repeated concentration of n-alkanes in the surface portions, and the frequent association of these compounds with pristane and phytane, persuaded authors to give serious consideration to terrestrial

contamination as a source for these hydrocarbons.[52,86] Furthermore, hydrocarbons in graphite–troilite nodules of iron meteorites were found to be similar to those found in the chondritic meteorites. As the high temperature history of the iron meteorites would preclude the survival of indigenous hydrocarbons, an origin by terrestrial contamination was implied.[52] This provided support for suggestions that the *n*-alkanes in chondrites were also terrestrial contaminants.

By 1968, contamination by terrestrial fossil hydrocarbons was considered, by some, to be the most likely source for the *n*-alkanes.[87] If these compounds were contaminants, then the rapidity of the contamination process was demonstrated in 1969, following the fall of the Allende (CV3) meteorite. This meteorite was collected just seven days after it fell and was found to have *n*-alkanes, pristane and phytane concentrated at its surface.[53] The seriousness of the contamination problem led Gelpi and Oró[88] to state pessimistically that "the contributions of our terrestrial environment to the aliphatic hydrocarbon patterns of carbonaceous chondrites may be significant enough as to mask the presence of any indigenous component".

In 1968, the work of Studier *et al.*[55] led to a revival in the belief that the *n*-alkanes in meteorites were indigenous extraterrestrial compounds. These authors suggested that the *n*-alkanes may have been produced abiotically in the condensing solar nebula by a Fischer–Tropsch reaction. Such a reaction involves the production of primarily *n*-alkanes from CO and H_2 on the surfaces of mineral catalysts. This model gained early support from good matches between the laboratory reaction products and the compound distributions observed in the meteorite extracts of Orgueil (CI1) and Murray (CM2). Both extracts were dominated by *n*-alkanes above C_{10}. Further supporting evidence was provided by laboratory Fischer–Tropsch synthesis experiments which appeared to reproduce the correct sign and magnitude of isotopic fractionation seen between CO_2, carbonate and organic matter in carbonaceous chondrites.[89]

Several years later, analysis of the more recently fallen Murchison (CM2) meteorite, by Studier *et al.*,[60] revealed a hydrocarbon distribution similar to that seen in Orgueil (CI1) and Murray (CM2), *i.e.* a dominance of *n*-alkanes. These authors used solvent extraction, silica gel chromatography and GC-MS and believed that the Fischer–Tropsch reaction could account for these compounds. However, it should be noted that two separate studies on the same meteorite failed to detect these presumed Fischer–Tropsch products as the predominant type of aliphatic hydrocarbon present.[24,28]

The Fischer–Tropsch theory began to develop problems when petrographic evidence indicated that the catalysts necessary to trigger the reaction in the primitive solar nebula were formed much later on the meteorite parent body,[90,91] an observation made earlier but overlooked in this context.[92,93] Further problems developed when isotopic measurements made on the carbon containing phases of the Murchison (CM2) meteorite revealed that CO was substantially lighter than the aliphatic hydrocarbons.[27] If this CO represented residual source gas for the Fischer–Tropsch produced organic matter, then this measurement was inconsistent with the laboratory-produced results of Lancet and Anders.[89] The Yuen *et al.*[27] results suggested that the Fischer–Tropsch synthesis was unlikely to have created the meteoritic alkanes. In addition, analyses on the Murchison (CM2) meteorite in the two decades following its fall established that the majority of meteoritic organic compounds were characterised by isomeric diversity and the structural specificity of the *n*-alkanes appeared inconsistent with this common feature.[4] Despite these emerging problems, the Fischer–Tropsch reaction was still advanced by some to represent "the best candidate" for producing the meteoritic hydrocarbons.[3]

Cronin and Pizzarello[94] used solvent extraction, silica gel chromatography, GC-MS, IR spectroscopy and nuclear magnetic resonance (NMR) spectroscopy to analyse interior and exterior portions of the Murchison (CM2), Murray (CM2) and Allende (CV3) meteorites in addition to the highly metamorphosed New Concord chondrite. These authors found alkanes to be concentrated towards the surfaces of these meteorites and believed the straight chain hydrocarbons to be terrestrial contaminants.

4.2.3 Stable isotopes and aliphatic hydrocarbons

Krishnamurthy *et al.*[64] analysed the isolated aliphatic fractions (hexane eluates) from Murchison (CM2) solvent extracts and found them to be D-rich with δD values ranging from +103 to +280‰ indicating the presence of some indigenous aliphatic organic matter (Table 3). When δ^{13}C values were obtained for aliphatic fractions from two Murchison (CM2) samples, one (the Chicago stone) was *n*-alkane rich, whereas the other (the ASU stone) was not (Table 3). Krishnamurthy *et al.*[64] discovered that the aliphatic fraction from the *n*-alkane rich Chicago stone (−11.5‰) was ^{13}C-depleted when compared to its *n*-alkane poor counterpart from the ASU stone (−5‰). The data were consistent with the addition of different amounts of isotopically light terrestrial *n*-alkanes to heavier indigenous material for the two samples.

The terrestrial origin of the meteoritic *n*-alkanes was substantiated by Sephton *et al.*[83] who performed CSIA on the *n*-alkanes. The δ^{13}C values for the *n*-alkanes from Orgueil (CI1), Murchison (CM2) and Cold Bokkeveld (CM2) exhibited none of the ^{13}C-enrichment characteristic of other classes of organic molecules found in these meteorites (Table 5; Fig. 3). The δ^{13}C values for the *n*-alkanes from these and other carbonaceous chondrites were identical to those of petroleum products or other terrestrial fossil hydrocarbons. Furthermore, the *n*-alkanes in the CM2 meteorites lack the distinctive increase or decrease in δ^{13}C values with carbon number common to the other CM2 compound classes (Fig. 3). These features confirmed the long-held suspicion that these molecules are contaminants from the terrestrial environment added to the meteorites following their fall to Earth. Most recently *n*-alkanes in a solvent extract of Tagish Lake (CI2) have revealed terrestrial values.[39]

4.3 Amino acids

4.3.1 Amino acids in meteorites

The search for amino acids in meteorites began in the 1960s using paper and thin layer chromatography. Prompted by reports of fossil remnants of extraterrestrial life in meteorites,[95] several authors searched for, and found, amino acids in a number of chondrites.[96–98] However, these initially positive results were somewhat discredited when more advanced techniques based on ion exchange chromatography discovered amino acid concentrations and distributions which suggested an origin by terrestrial contamination during storage and sample handling.[99–101] Paul B. Hamilton captured the mood of the moment with the statement "What appears to be the pitter-patter of heavenly feet is probably instead the print of an earthly thumb".[1]

The fall of the Murchison (CM2) meteorite in 1969 provided fresh sample on which to test for the presence of indigenous amino acids, utilising ion exchange chromatography, GC and GC-MS. Kvenvolden *et al.*[28] detected the presence of five protein and two non-protein amino acids and four of the protein amino acids were racemic (Table 6). These observations suggested an abiotic and extraterrestrial origin for the compounds. Kvenvolden *et al.*[28] detected a further protein amino acid, aspartic acid, and 10 more non-protein amino acids, four of which were present as racemic mixtures. Analyses by Oró *et al.*[24] confirmed the presence and racemic nature of the protein amino acids and identified some leucines.

Hence, two years after the fall of Murchison (CM2) it was clear that this meteorite contained extraterrestrial amino acids based on the presence of:

Table 6 A summary of the amino acid data reported from Murchison (CM2) in 1970 and 1971

Protein amino acid	Racemic	Ref.	Non-protein amino acids	Racemic	Ref.
Glycine	Not chiral	24, 28	α-Amino-*n*-butyric acid	Yes	102
Alanine	Yes	24, 28	β-Aminoisobutyric acid	Yes	102
Glutamic acid	Yes	24, 28	Norvaline	Yes	102
Valine	Yes	24, 28	Pipecolic acid	Yes	102
Proline	Yes	24, 28	Isovaline	n.d.	102
Aspartic acid	n.d.[a]	102	*N*-Methylalanine	n.d.	102
Leucine	n.d.	24	β-Amino-*n*-butyric acid	n.d.	102
			N-Methylglycine (sarcosine)	Not chiral	28, 102
			β-Alanine	Not chiral	102
			N-Ethylglycine	Not chiral	102
			α-Aminoisobutyric acid (2-methylalanine)	Not chiral	24, 28, 102
			γ-Amino-*n*-butyric acid	Not chiral	102

[a] n.d.: not determined

i) non-protein amino acids,

ii) racemic mixtures, and

iii) complete structural diversity (all C_2 and C_3 structural isomers had been detected).

Armed with the new criteria for establishing indigeneity, the amino acid content of other carbonaceous chondrites was re-examined. One report[24] determined that Orgueil (CI1), Murray (CM2) and Mokoia (CV3) contained mainly L-forms of amino acids, indicating an origin by terrestrial contamination, but that Murray (CM2) did contain almost racemic alanine. The recently fallen Allende (CV3) was practically barren.[103] Further investigations revealed that Murray (CM2) contained 17 amino acids, seven of which were racemic and 11 of which were not found in proteins.[103,104] Orgueil (CI1) contained 11 amino acids, one of which was racemic and six of which were non-protein.[105] These investigations were indicating that despite being attributed previously to contamination, some of the amino acids in these carbonaceous chondrites were indigenous and merely overprinted by terrestrially-derived molecules.[106] A comparison of the amino acid abundances and distributions in five carbonaceous chondrites (Murchison (CM2), Murray (CM2), Nogoya (CM2), Mokoia (CV3) and Allende (CV3)) detected wide variations that may reflect differences in primary synthesis or secondary processing for the different meteorites.[107]

Back in 1970, Kvenvolden *et al.*[108] raised the possibility that detecting racemic mixtures of amino acids in meteorites may not be a concrete indicator of a nonbiological origin for these compounds; the quantities of D-enantiomers of amino acids in sediments in Puget Sound, British Columbia, appeared to increase with age, *i.e.* they approached racemization. To address this uncertainty, Pollock *et al.*[109] determined that isovaline, which cannot undergo racemization because it has no hydrogen atom on its asymmetric α-carbon atom,[110] is present in the Murchison (CM2) meteorite as a racemic mixture. This implied that isovaline and other chiral amino acids were probably originally synthesized as racemic mixtures and were not transformed to their current state by racemization of non-racemic starting materials.

In 1979 those carbonaceous chondrites which had been recovered from Antarctica began to have their amino acid content investigated. Analyses of Alan Hills 77306 (CM2)[111,112] and Yamato 74662 (CM2)[113] revealed an amino acid content similar to that seen in Murchison (CM2) and minimal terrestrial contamination. Subsequent analyses of the Yamato 793321 (CM2) and Belgica-7904 (CM2) revealed a depletion in amino acids for this type of meteorite suggesting loss by parent body processing or leaching in the Antarctic ice[114] while Yamato-791198 (CM2) became the most amino acid rich meteorite ever discovered.[115]

Investigations of the amino acids in Murchison (CM2) continued[110,116–119] and today it is known that they exhibit the following structural features:

i) carbon numbers of C_2 through C_8,

ii) two simple structural types are present: monoamino alkanoic acids and monoamino dialkanoic acids,

iii) within the two simple structural types there is complete structural diversity,

iv) branched chain isomers predominate,

v) there is a structural preference in the order $\alpha > \gamma > \beta$,

vi) an exponential decline in amount with increasing carbon number, and

vii) enantiomers occur in approximately equal amounts although evidence is growing that there may be small excesses of L-enantiomers in protein and non-protein amino acids (see below).

To date, over seventy amino acids have been detected in Murchison (CM2), only eight of which are found in terrestrial proteins and 11 more have a restricted occurrence on Earth.[120] The remaining amino acids appear unique to carbonaceous chondrites.

Recently, amino acid analyses using high performance liquid chromatography of the CI1 carbonaceous chondrites, Orgueil and Ivuna, have found that the amino acid distribution in CI1s is distinct from that in CM2s.[121] Relative to glycine (assigned a concentration of 1.0), β-alanine is more abundant in Orgueil (CI1) (2.9) and Ivuna (CI1) (2.3) than in Murchison (CM2) and Murray (CM2) (~0.5) and α-aminoisobutyric acid and isovaline, which are abundant in Murchison and Murray are present only in trace amounts in Orgueil and Ivuna. Ehrenfreund *et al.* [121]used these data to suggest that the CI1 meteorites came from a different type of parent body than the CM2s, possibly an extinct comet.

4.3.2 Enantiomeric excesses

Initially, solvent and water extracts of Cold Bokkeveld (CM2),[122] Haripura (CM2) and Mokoia (CV3)[123] and other chondrites[97] were found to be optically neutral. The first positive result was obtained on a saponified extract of Orgueil (CI1) which was found to be laevorotatory.[124–126] Earlier negative results were attributed to the use of low sensitivity polarimeters and unfractionated organic matter. Other workers criticised these results and suggested that they were analytical artefacts;[127–129] no consensus was achieved.[1]

In 1969, Murchison (CM2) fell and was analysed soon thereafter by Kvenvolden *et al.*[28, 102] Four chiral protein amino acids (all of which could be separated into D- and L-isomers) and seven chiral non-protein amino acids (four of which could be separated into D- and L-isomers) were found. It was discovered that the four non-protein amino acids were racemic.[102] Pollock *et al.*[109] confirmed that the racemic mixtures were likely to be primary characteristics by establishing that isovaline, which is resistant to secondary racemisation, had a ratio of D- to L-isomers (D/L) of approximately 1. These results were consistent with the lack of optical rotation in extracts from other

carbonaceous chondrites observed by many earlier workers (with the exception of Nagy and co-workers) and with the amino acids being the products of abiotic chemical reactions.

The detection of racemic mixtures of amino acids was extended to the Antarctic carbonaceous chondrites by Shimoyama *et al.*[113,115] Racemic alanine, aspartic acid and glutamic acid was found in Yamato-74662 (CM2)[113] and racemic alanine and α-amino-*n*-butyric acid in Yamato-791198 (CM2).[115]

Engel and Nagy[130] considered that early determinations of amino acid D/L values had been hampered by small sample sizes. Using improved analytical techniques they detected an L-excess (0.029 to 0.682%) in five protein amino acids (alanine, glutamic acid, proline, aspartic acid and leucine) from three different extracts: aqueous extract, hydrolysed aqueous extract and acid extract. The authors dismissed the possibility of terrestrial contamination because some protein amino acids were missing (*e.g.* tyrosine and methionine) but these results were criticised and attributed to an overprint of terrestrial molecules.[131] Subsequently, Engel *et al.*[132] bolstered their argument by measuring similar non-terrestrial δ^{13}C values for L- and D-alanine at +27 and +30‰ respectively. Engel and Macko[133] obtained more supporting isotopic data by measuring similar δ^{15}N values for L- and D-enantiomers of alanine and glutamic acid. Both had significantly heavier δ^{15}N values (approx. +60‰) than their terrestrial counterparts (approx. −10 to +20‰). On this basis, they argued that the excess of L-forms over D-forms (33 and 54% for alanine and glutamic acid respectively) is an extraterrestrial feature and not the result of terrestrial contamination. Pizzarello and Cronin[134] questioned this work, however, and believed that other meteoritic amino acids were coeluting with L-alanine and contributing to the L-excess and δ^{15}N determinations.

An alternative approach to establishing indigeneity of enantiomeric excess was taken by Cronin and Pizzarello.[134–136] They looked at the enantiomers of non-protein amino acids and discovered an L-excess in the α-methyl-α-amino acids in Murchison (CM2)[135] (2–9%) and discovered a similar but smaller excess in the same compounds in Murray (CM2)[134, 136] (1–6%). This contrasted with the previous work of Pollock *et al.*[109] who believed that the α-methyl-α-amino acid isovaline was racemic.

Pizzarello and Cronin[136] believed this L-excess to be indigenous because:

i) there was no correlation between L-excess and relative terrestrial abundance for the amino acids,

ii) the four amino acids have never been reported in nature,

iii) the terrestrially ubiquitous protein amino acids alanine and valine were racemic (Murray) or showed small enantiomeric excesses (Murchison), and

iv) reversed phase preparative chromatography prior to GC removed potentially-coeluting compounds.

Pizzarello and Cronin[136] proposed that the absence of an enantiomeric preference for the protein α-H-α-amino acids but its presence in the non-protein α-methyl-α-amino acids was a result of either a resistance to racemization for the former or different origins for the two types of amino acid.

4.3.3 Origin of enantiomeric excess

Engel *et al.*[132] favoured the Vester–Ulbricht hypothesis as a mechanism for producing the L-excess observed in the Murchison (CM2) amino acids. This hypothesis involves the β-decay of cosmic ray produced ^{14}C which is accompanied by circularly polarized photons that selectively destroy the D-enantiomers. Cronin and Pizzarello[135] and Engel and Macko[133] proposed an alternative explanation where it is the irradiation of amino acids by ultraviolet circularly polarised light (UVCPL) that induces the preferential destruction of the D-enantiomer. The location for this process would be in the presolar cloud and the source of UVCPL would be a nearby neutron star.

An explanation involving presolar processes accords with a number of lines of evidence that suggest a presolar origin for a number of components in carbonaceous chondrites. For example, D-enrichments in meteoritic amino acids suggest an interstellar origin for these compounds or their precursors.[76] Moreover, interstellar grains such as graphite, SiC and Si_3N_4 originate from supernovae and are present in carbonaceous chondrites.[137] Supernovae directly precede the formation of a neutron star and are often implicated in the collapse of molecular clouds to form solar systems. In this way, meteoritic organic matter may have been subjected to neutron star radiation at an early stage in its history. However, Bailey[138] has stated that neutron stars are not good sources of UVCPL and, in addition, that light from the most common astronomical sources of UVCPL (magnetic white dwarf and magnetic white dwarf binaries) would rarely encounter the organic molecules in molecular clouds. Consequently, Bailey[138] believed that reflection nebulae in star forming regions could produce UVCPL "when and where it is needed".

4.3.4 Amino acid precursors

Acid hydrolysis can increase the yield produced from hot water extracts of carbonaceous chondrites by over 100%.[103,107] This increase in yield indicates the presence of amino acid precursors. Glycine, for example, was found in the Murchison (CM2) and Murray (CM2) extracts at concentrations of 3.4 and 1.5 μg g^{-1} respectively, whereas the acid hydrolysed extracts contain 6.1 and 3.0 μg g^{-1} respectively.[103] These observations raised questions concerning the nature of the water-extractable material which liberates amino acids on acid hydrolysis, the state of the amino acids prior to extraction, and possible chemical reactions occurring during extraction.[103]

To study the chemistry of amino acid precursor hydrolysis, Lawless and Peterson[106] extracted a sample of the Murchison (CM2) meteorite with D_2O. In addition to free amino acids, showing no D incorporation, some amino acids contained D suggesting either the production of amino acids from precursors or simply hydrogen–deuterium exchange. A later study, however, concluded that all the carbon–deuterium bond formation, observed after extraction of the meteorite with D_2O, results from hydrogen–deuterium exchange in existing carbon–hydrogen bonds, rather than from the synthesis of carbon–deuterium bonds during the extraction procedure.[139]

To investigate the nature of amino acid precursors, the acid-labile compounds in a Murchison (CM2) hot water extract were fractionated by column chromatography on a cation exchange resin by Cronin.[140] Seventy per cent behaved as neutral or acidic compounds.[140] Subsequently, these compounds were partly identified as linear and cyclic aliphatic amides, including monocarboxylic acid amides, dicarboxylic acid monoamides, hydroxy acid amides, lactams, carboxylactams, lactims, *N*-acetylamino acids and substituted hydantoins.[141] Carboxylactams, lactims, *N*-acetylamino acids and hydantoins all convert to amino acids during acid hydrolysis and therefore qualify as precursors. Of the remaining basic molecules, 9% may be peptides and amino acyl amides.[142]

With the working hypothesis that the enantiomeric ratios of amino acid precursors would not be affected by terrestrial contamination, Pizzarello and Cooper[143] determined the enantiomeric excess and carbon isotopic composition of these compounds. Free alanine (1.2% to 58%) and glutamic acid (19% to 45.8%) both showed L-excess in Murchison (CM2), while free glutamic acid was racemic in Murray (CM2). *N*-Acetylalanine was racemic in both Murchison and Murray, while *N*-acetylglutamic acid had an L-enantiomeric excess in Murchison (41%) and Murray (8.6%). Hence, there was no consistent relationship between an L-excess of the free amino acids and a

Table 7 Results from carbon, nitrogen and hydrogen isotopic measurements performed on individual amino acids, from the Murchison (CM2) meteorite. Parenthetical values are corrected for hydrogen exchange during the water extraction procedure

Compound	δ^{13}C (‰)	Ref.	δ^{15}N (‰)	Ref.	δD (‰)	Ref.
Murchison						
Glycine	+22	132	+37			
Alanine			+61	133		
D-Alanine	+30	132	+60	133		
L-Alanine	+27	132	+57	133		
Glycine + alanine	+41	77			+1072(+2448)	77
Methylglycine (sarcosine)			+129	133		
α-Aminoisobutyric acid	+5	132	+184	133	+67(+149)	77
α-Aminoisobutyric acid + α-amino-*n*-butyric acid	−1	77				
Isovaline	+17	132	+66	133		
Isovaline + valine	+30	77			+713(+1014)	77
Aspartic acid	+4	77			+214(+630)	77
DL-Aspartic acid			+61	133		
L-Leucine			+60	133		
DL-Proline			+50	133		
Glutamic acid					+523(+1013)	77
D-Glutamic acid			+60	133		
L-Glutamic acid	+6	132	+58	133		
Orgueil						
Glycine	+22	121				
β-Alanine	+18	121				

similar excess in the precursors of those amino acids. Additionally, δ^{13}C values appeared to be shifted to terrestrial values and indicated that free glutamic acid and its precursor contain some terrestrial contamination. These results did not confirm the working hypothesis of Pizzarello and Cooper[143] and a complex contamination history of both free amino acids and precursors was implied.

4.3.5 Stable isotopes and amino acids

Unusually high δD values (1370‰) and δ^{15}N values (90‰) for a Murchison (CM2) amino acid fraction were unlike any observed on the Earth and were characteristic of known interstellar molecules[76] (Table 3). Later isotopic measurements of individual amino acids confirmed that they contained a D-enrichment and, hence, these molecules or their precursors predated the solar system[77] (Table 7). Compound-specific δ^{13}C values for amino acids in Murchison (CM2)[77,132] and Orgueil (CI1)[121] indicate a non-terrestrial origin although a contribution from terrestrial contamination has affected the isotopic composition of the amino acids and their precursors to some extent.[134,136] When δ^{13}C values are plotted against carbon number, they suggest an origin for the hydrocarbon skeleton of the amino acids *via* a kinetically controlled synthesis of higher molecular weight compounds from simpler precursors.[77,132]

δ^{15}N measurements for individual amino acids in Murchison (CM2) reveal that most have δ^{15}N values around +60‰, but variations do exist[133] (Table 7). Glycine is relatively ^{15}N-depleted (+37‰), while δ^{15}N values for α-aminoisobutyric acid and sarcosine are more extreme (+129‰ and +184‰ respectively). Compound-specific isotopic measurements for both enantiomers of alanine (δ^{13}C D-alanine +30‰, L-alanine +27‰, δ^{15}N D-alanine +60‰ L-alanine +57‰) and glutamic acid (δ^{15}N D-alanine +60‰ L-alanine +58‰) display similar non-terrestrial values supporting proposals that the L-excess is indigenous.[132,133]

4.4. Carboxylic acids

4.4.1 Monocarboxylic acids

4.4.1.1. Short chain monocarboxylic acids

Yuen and Kvenvolden[144] detected low molecular weight (<C_9) monocarboxylic acids in a methanolic potassium hydroxide extract of Murchison (CM2) by GC-MS. Attempts to find the long chain even number dominant fatty acids found in the Orgueil (CI1) meteorite in the 1960s failed. Subsequently, Lawless and Yuen[30] quantified the Murchison monocarboxylic acids using deuterated analogues. By the end of the 1970s, it was apparent that the indigenous carboxylic acids in Murchison were structurally distinct and displayed the following characteristics:

i) complete structural diversity, with all C_2 to C_5 isomers present,

ii) a general decrease in amount with increasing carbon number, and

iii) an equal concentration of branched and straight-chain isomers.

Interestingly, the monocarboxylic acids in Murchison (CM2) were present in a much higher concentration than the amino acids and are the most abundant solvent extractable compounds. For instance, the concentration of the most abundant monocarboxylic acid (propanoic acid 135 μg g^{-1}) was around 50 times greater than the most abundant amino acid (glycine 3 μg g^{-1}). Yuen *et al.*[27] used a freeze–thaw disaggregation technique to release volatile hydrocarbons and C_2 to C_5 carboxylic acids that displayed a decrease in abundance with increasing carbon number.

GC analyses of methanolic potassium hydroxide extracts of Antarctic carbonaceous chondrites have detected aliphatic and aromatic monocarboxylic acids in Yamato-791198 (CM2), Yamato-74662 (CM2) and Asuka-881458 (CM2).[67,145,146] In all three meteorites, most of structural isomers of the C_4, C_5, and C_6 acids were present and in Asuka-881458, 14 of the 17 possible C_7 acid isomers were identified. One interesting observation was the increasing predominance of straight chain over branched monocarboxylic acids in Yamato-74662 and Asuka-881458.[67,146]

The amounts of monocarboxylic acids in Yamato-791198 (CM2) (9.5 μg g^{-1}) and Yamato-74662 (CM2) (14.1 μg g^{-1}) were much less than in Asuka-881458 (CM2) (191.2 μg g^{-1}) and Murchison (CM2) (332 μg g^{-1}) and three other meteorites (Yamato 793321 (CM2), Asuka-88120 (CM2), Asuka-881334 (CM2)) contained none, raising the possibility that these water soluble compounds have been leached by the Antarctic ice or destroyed by pre-terrestrial parent body alteration.[67,146]

4.4.1.2. Long chain monocarboxylic acids

Observations of long chain fatty acids in meteorites were reported during the 1960s. UV and IR spectroscopy suggested the presence of acid groups in water extracts of Mokoia.[147] GC[148] and IR spectroscopy[127] of solvent extracts confirmed their presence in Orgueil (CI1). However, concentrations of these compounds in the surface portions of the meteorites analysed and a dominance of the terrestrially most common chain lengths (C_{16}, C_{18}) suggested an origin by terrestrial contamination.[11,53] Recently, long chain monocarboxylic acids have been found in Murchison (CM2)[63] and Asuka-881458 (CM2)[146] though their indigeneity is uncertain.

4.4.2 Dicarboxylic acids

Lawless *et al.*[31] identified a large suite of aliphatic dicarboxylic acids by GC-MS of acidified hot water extracts of Murchison (CM2). This suite included many of the branched and straight chained isomers with up to nine carbon atoms. The dicarboxylic acids were found to be one or two orders of magnitude higher in abundance than amino acids. Seventeen dicarboxylic acids were identified including 15 saturated and two unsaturated aliphatic compounds (fumaric and/or maleic acid). These compounds exhibited almost complete structural diversity. The chiral methylsuccinic acid was present as a racemic mixture. Cronin *et al.*[78] extended the number of dicarboxylic acids identified to at least forty species with chains through C_9. It is likely that the dicarboxylic acids are present in the meteorite as carboxylate dianions.[5] The calcium salt of oxalic acid was detected by Lawless *et al.*[31]

4.4.3 Hydroxycarboxylic and hydroxydicarboxylic acids

Peltzer and Bada[149] reported the presence of seven α-hydroxycarboxylic acids (hydroxy acids) in the Murchison (CM2) meteorite. These compounds were racemic and corresponded in structure to the more abundant amino acids. Peltzer and Bada[149] concluded that the amino acids in meteorites are formed by the Strecker synthesis, that is, the reaction of hydrogen cyanide, aldehydes and ammonia in aqueous solution, to produce amino nitriles, which yield amino acids following acid hydrolysis. In such a reaction, in addition to amino acids, the corresponding α-hydroxycarboxylic acids are also produced by the reaction of hydrogen cyanide and aldehydes (the cyanohydrin synthesis). Furthermore, the ammonia concentration determines the ratio of hydroxy (low ammonia) to amino acids (high ammonia) produced in the reaction. Therefore, if decomposition of the α-hydroxy carboxylic acids during extraction is avoided[150] the ratio of hydroxy to amino acids can provide some indication as to the ammonia content of the environment in which these compounds were synthesised.[32]

Cronin *et al.*[78] detected α-hydroxycarboxylic and, for the first time, α-hydroxydicarboxylic acids in Murchison (CM2). Carbon chains ranged up to C_8 or C_9 and many, if not all, structural isomers were represented at each carbon number. The α-hydroxycarboxylic acids and α-hydroxydicarboxylic acids corresponded structurally to many of the known meteoritic α-aminocarboxylic acids and α-aminodicarboxylic acids.

4.4.4 Stable isotopes and carboxylic acids

The carboxylic acid fraction from Murchison (CM2) gave non-terrestrial $\delta^{13}C$ (+6.7‰) values indicating indigeneity (Table 3). δD values for the same fraction (+357‰) suggested a contribution from interstellar molecules. Non-terrestrial $\delta^{13}C$ values for individual compounds (+22.7 to +4.5‰) also indicated indigeneity (Table 8).

CO_2 was more enriched (+29.1‰) than the heaviest carboxylic acid (acetic acid, +22.7‰) but, when treated as a C_1 carboxylic acid, $\delta^{13}C$ values plotted smoothly with carbon number (Fig. 3). The data implied the kinetically controlled synthesis of higher molecular weight carboxylic acids from lower ones. Furthermore, aliphatic hydrocarbons are consistently lighter than their acid counterparts. Hence, the $\delta^{13}C$ of the carboxy group appeared to be heavier than the aliphatic group, suggesting that the carboxy and aliphatic groups were derived from isotopically-distinct precursors.

Table 8 Results from carbon isotopic measurements performed on individual carboxylic acids, CO and CO_2 from the Tagish lake (CI2) and Murchison (CM2) meteorite

Compound	Tagish Lake (CI2) $\delta^{13}C$ (‰)	Murchison (CM2) $\delta^{13}C$ (‰)	Ref.
Monocarboxylic acids			
CO		−32.0±2.0	27
CO_2		+29.1±0.2	27
Acetic acid		+22.7±0.2	27
Propionic acid		+17.4±0.2	27
Isobutyric acid		+16.9±0.2	27
Butyric acid		+11.0±0.3	27
Isovaleric acid		+8.0±0.2	27
Valeric acid		+4.5±0.2	27
Dicarboxylic acids			
Succinic acid	+22.5±0.6	+28.1±1.1	39
Methylsuccinic acid	+15.4±3.0	+26.5±0.7	39
Glutaric acid	+22.9±1.5	+26.8±0.3	39
Methylglutaric acid	+18.6±0.7	+27.9±1.0	39

The carbon and hydrogen isotopic composition of the dicarboxylic acids was measured in a fraction shared with the hydroxydicarboxylic acids (Table 3). δD values reveal a D-enrichment, though $\delta^{13}C$ values were unexpectedly light. The data of Yuen *et al.*[27] suggested that the carboxylic acid group was isotopically heavy. Therefore, the presence of the extra carboxylic acid group on the dicarboxylic acids should have shifted them to more positive values. Cronin *et al.*[78] invoked different sources for the carbonyl carbon in mono and dicarboxylic acids. Isotopic analyses of the hydroxy acids indicate non-terrestrial $\delta^{13}C$ values (−6‰) and δD values (+573‰) indicating the presence of interstellar material. Compound-specific carbon isotope measurements of dicarboxylic acids in Murchison (CM2) and Tagish Lake (CI2) also reveal non-terrestrial values (Table 8).

Hence, it is clear that the marked structural correspondence between the α-amino acids and α-hydroxy acids implied their formation during Strecker-cyanohydrin reactions on the meteorite parent body. The high D contents indicate that many of the aldehydes, ketones, ammonia, and hydrogen cyanide starting materials have originated in interstellar space.[120]

4.5 Sulfonic and phosphonic acids.

Sulfonic acid esters were identified for the first time by IR spectra of solvent extracts of the Orgueil (CI1) meteorite[54] although it was subsequently suggested that Studier had simply misidentified silicon oil contamination.[151] Much later, Cooper *et al.*[44] detected a homologous series of C_1 to C_4 alkyl phosphonic acids and alkanesulfonic acids in water extracts of the Murchison (CM2) meteorite. As with the amino acids in Murchison, the sulfonic and phosphonic acids display an exponential decline in amount with increasing carbon number and complete structural diversity. Five of the eight possible alkyl phosphonic acids and seven of the eight possible alkanesulfonic acids through C_4 were identified.

Cooper *et al.*[43] measured intramolecular carbon, hydrogen, and sulfur isotope ratios on a homologous series of organic sulfonic acids discovered in Murchison (CM2) (Table 9). D-Enrichments indicated the formation of the hydrocarbon portion of these compounds in a low-temperature interstellar

Table 9 Results of carbon, hydrogen and sulfur isotopic measurements performed on individual sulfonic acids from the Murchison (CM2) meteorite

Compound	δ^{13}C (‰)	δD (‰)	δ^{33}S (‰)	δ^{34}S (‰)	δ^{36}S (‰)	Δ^{33}S	Ref.
Methanesulfonic acid	+29.8	+483	+7.63	+11.27	+22.5	+2	43
Ethanesulfonic acid	+9.1	+787	+0.33	+1.13	+0.8	−0.24	43
Propanesulfonic acid	−0.4	+536	+0.20	+1.20	+2.1	−0.40	43
1-Methylethanesulfonic acid	−0.9	+852	+0.32	+0.68	+2.9	−0.02	43

environment. Because sulfur contains four stable isotopes, it was possible to construct a three-isotope plot on which normal mass-dependent fractionations lie on a line of $\delta^{33}S = 0.5\ \delta^{34}S$. Deviations from this line indicate mass-independent fractionations (expressed as $\Delta^{33}S = \delta^{33}S - 0.5\ \delta^{34}S$). It was discovered that the sulfur isotopic composition of methanesulfonic acid from Murchison implied a mass-independent enrichment in ^{33}S. These isotopic features were attributed to the interstellar gas-phase UV-irradiation of the symmetrical CS_2 molecule, leading to the production of the methanesulfonic acid precursor.

4.6 Alcohols, aldehydes, ketones and sugars

Alcohols were detected in carbonaceous chondrites by Studier *et al.*[54] who analysed Murray (CM2) and Orgueil (CI1) by thermal extraction mass spectrometry, although a similar analysis of Murray (CM2) by Hayes and Biemann[56] did not confirm the earlier results. In 1976, Jungclaus *et al.*[33] positively identified methanol (5 μg g^{-1}), ethanol (3 μg g^{-1}), isopropanol (2 μg g^{-1}) and butyl alcohols (1 μg g^{-1}) in water extracts and headspace gases of Murchison using colorimetry, GC and GC-MS.

Carbonyl compounds were first detected by IR spectroscopy of solvent extracts of Murray (CM2)[152] and Orgueil (CI1).[47] Later, thermal extraction of Murray (CM2) revealed the presence of small amounts of aldehydes and ketones.[56] Breger *et al.*[153] reported the presence of formaldehyde in Allende (CV3) using a colorimetric technique. Jungclaus *et al.*[33] identified acetone (6 μg g^{-1}), butan-2-one (2 μg g^{-1}), pentan-3-one (3 μg g^{-1}) and pentan-2-one (5 μg g^{-1}) using GC and GC-MS of Murchison water extracts and headspace gases.

Aromatic ketones were detected in a solvent extract of Murchison (CM2) using GC-MS.[62] Fluoren-9-one, anthracenedione, phenenthrenedione, benzanthracen-7-one and anthracen-9(10*H*)-one were identified. Aromatic ketones may have been generated from aromatic hydrocarbons *via* oxidation reactions occurring in interstellar space[154] or during aqueous alteration on the meteorite parent body.

Using paper chromatography, Degens and Bajor[96] reported the presence of free sugars in an 80% ethanol extract of the Murray (CM2) meteorite. Kaplan *et al.*[97] confirmed this result and extended this work to detect sugars in Orgueil (CI1). Much later, Cooper *et al.*[34] detected sugar-related compounds (sugars, sugar alcohols and sugar acids), in Murchison (CM2) by GC-MS of trimethylsilyl and/or *tert*-butyl(dimethylsilyl) derivatives. These polyhydroxylated compounds or "polyols", were present in similar abundances to the amino acids (Table 2). The Murchison (CM2) polyols displayed many of the features of extraterrestrial compounds. Progressively larger polyols became less abundant and, in addition, they displayed almost complete structural diversity and contain some terrestrially-rare compounds. Further evidence of indigeneity came from isotopic measurements on a combined fraction of neutral polyols which suggested that most were indigenous (δ^{13}C −5.89‰ and δD +119‰; Table 3).

4.7 Amines and amides

Hayatsu *et al.*[37] detected aliphatic amines in a hydrolysed water extract of Murchison (CM2) by paper chromatography and mass spectrometry. Subsequently, Jungclaus *et al.*[36] identified 10 aliphatic amines in a water extract of Murchison (CM2) by ion exchange chromatography and mass spectrometry. Primary amines through C_4 showed complete structural diversity. Pizzarello *et al.*[35] isolated volatile bases from an acid hydrolysed hot water extract and identified a series of aliphatic amines by GC-MS of pentafluoropropionyl derivatives. Almost all primary and secondary amine isomers through C_5 were present.

The amines in Murchison (CM2) displayed the following characteristics:

i) concentration was doubled by acid hydrolysis,
ii) amounts decreased with increasing carbon number,
iii) branched chains > straight chains, and
iv) almost all isomers through C_5 show complete structural diversity.

Stable isotope analyses of the volatile bases revealed a significant enrichment in the heavy isotopes (δD +1221‰, δ^{13}C +22‰, δ^{15}N +93‰; Table 3) consistent with the amines or their precursors originating in an interstellar environment.[35]

Pizzarello *et al.*[35] considered two possible sources of the amines in Murchison (CM2). Firstly they may be directly inherited from the presolar molecular cloud as methylamine has been detected in interstellar space. Secondly the amines may be the products of the thermal decarboxylation of the α-amino acids. Sixteen of the 20 aliphatic amines can be accounted for by the decarboxylation of known Murchison (CM2) α-amino acids.

Hayatsu *et al.*[155] detected the amides guanylurea and possibly urea, substituted urea and phenylurea in a 6 M HCl extract of Murchison (CM2) by paper chromatography and mass spectrometry. Later, Cooper and Cronin[141] used GC-MS to detect a series of linear and cyclic amides in a hydrolysed water extract of Murchison. The compounds identified included monocarboxylic acid amides, dicarboxylic acid monoamides, hydroxyacid amides, lactams, carboxylactams, lactims and small amounts of *N*-acetylamino acids and hydantoins. These compounds were characterised by:

i) structural diversity through C_8,
ii) a decline in abundance with carbon number, and
iii) the presence of many compounds with no terrestrial source.

4.8 Nitrogen heterocycles

The possible presence of the purine and pyrimidine bases in water extracts of carbonaceous meteorites was first reported in the early 1960s. Calvin[152] and Briggs[147] reported the spectroscopic evidence of purine and pyrimidine bases in water extracts of carbonaceous chondrites. However, Oró[156] suggested that the substances detected were laboratory contamination from ion exchange resins and Kaplan *et al.*[97] could not find convincing evidence for the presence of nucleic acid bases in the UV spectra of carbonaceous chondrites.

Hayatsu *et al.*[155,157] made an attempt to resolve earlier problems by applying analytical techniques which did not include the use of ion exchange resins but involved solvent extraction followed by acid hydrolysis. Hayatsu *et al.*[155,157] established the presence of the purines (adenine and guanine) and guanylurea in the Orgueil (CI1) meteorite and the triazines, melamine and ammeline, which have no known biological significance, were also identified. Folsome *et al.*[158,159] used GC-MS to analyse

charcoal adsorbates of water and formic acid extracts of the Murchison (CM2), Murray (CM2) and Orgueil (CI1) carbonaceous chondrites. In direct contrast to previous work, Folsome *et al.*[158,159] failed to find any purines, triazines or guanylurea but, instead, detected some unusual and exclusively non-biological pyrimidines, in particular 4-hydroxypyrimidine. Hayatsu *et al.*[37] subjected Murchison to extractions of different severity and discovered that water and formic acid extracts produce aliphatic amines and alkyl pyridines while HCl and trifluoroacetic acid extractions produce adenine, guanine and melanin, cyanuric acid, urea and guanylurea. They concluded that purines and triazines are present as macromolecular entities which require drastic extraction conditions to coax them out of the meteorite. Hayatsu *et al.*[37] believed that different extraction methods were the cause of the discrepancy between previously published studies. Hayatsu *et al.*[37] failed, however, to detect 4-hydroxypyrimidine.

Using high performance liquid chromatography (HPLC) van der Velden and Schwartz[160] identified xanthine, hypoxanthine and guanine in a formic acid extract of Murchison (CM2). No pyrimidines were detected. 4-Hydroxypyrimidine appeared after silylation of the water extract and was shown to be an experimental artefact.[160] Stoks and Schwartz[40] reinvestigated the possible occurrence of pyrimidines in the Murchison (CM2), Murray (CM2) and Orgueil (CI1) carbonaceous meteorites using specific fractionation techniques and high sensitivity analysis. This led to the positive identification of uracil in water and formic acid extracts of all three meteorites. Stoks and Schwartz[41] used reverse phase chromatography to detect the purines reported previously by Hayatsu *et al.*[37] and van der Velden and Schwartz.[160] Neither the 4-hydroxypyrimidine nor the *s*-triazines (melamine, ammeline, ammelide and cyanuric acid) were detected raising the possibility that the *s*-triazines may also be experimental artefacts.[161] Stoks and Schwartz[38] investigated Murchison (CM2) and identified two types of basic N-heterocyclic compounds by GC and GC-MS. The first was a series of alkylpyridines containing 3 to 5 carbon atoms as methyl or ethyl side chains; the detection of these compounds supported the earlier observation of Hayatsu *et al.*[37] The second was a series of quinolines and isoquinolines with 0 to 4 carbon atoms present exclusively as methyl side chains. GC-MS of solvent extracts of Murchison (CM2) have tentatively identified 9*H*-carbazole and biphenyldicarbonitrile[62] and benzoquinoline isomers.[64]

In summary, Murchison (CM2) contains several classes of basic and neutral N-heterocycles, including:

i) purines (xanthine, hypoxanthine, guanine, and adenine),
ii) pyrimidines (uracil),
iii) quinolines/isoquinolines, and
iv) pyridines.

All of the purines and pyrimidines found are biologically common and together account for 1.3 μg g^{-1} in Murchison. The quinolines, isoquinolines and pyridines. are structurally diverse and contain a large number of isomeric alkyl derivatives.

Recently carboxylated pyridines were found in a water extract of the Murchison (CM2) meteorite. Nicotinic acid, its two isomers and 12 methyl and dimethyl homologs were identified by GC-MS.[39]

Isotopic analyses of the nitrogen heterocycles are restricted to the polar fractions in which they elute (Table 3). With the exception of the amino acid and volatile base fractions, the polar hydrocarbons have the heaviest δD, δ^{13}C and δ^{15}N values.

4.9 Sulfur heterocycles

Prior to 1968 there was a reluctance to investigate sulfur compounds in meteorites because of the possibility that they were the result of secondary reactions between elemental sulfur and hydrocarbons during extraction.[1] During the thermal extraction-mass spectrometry of sulfur compounds in Murray (CM2), however, the lack of evolved hydrogen sulfide indicated that this problem was overstated.[56] Thermal extraction and GC-MS of Murray (CM2) showed thiophenes and alkyl thiophenes that increased in abundance with increasing extraction temperature.[55] Thermal extraction-mass spectrometry and GC-MS of Murray (CM2)[56] and Murchison (CM2)[60,61] revealed the presence of small amounts of parental and alkylated thiophenes, benzothiophenes and dibenzothiophenes. Basile *et al.*[62] detected the high molecular weight dibenzothiophene and benzonaphthothiophene in a solvent extract of Murchison (CM2). Shimoyama *et al.*[42] analysed Murchison (CM2) for polynuclear aromatic thiophenes in a solvent extract. Benzothiophene, dibenzothiophene and their methyl derivatives, and benzonaphthothiophenes were detected at concentration levels of 0.3 μg g^{-1} (Table 2). The abundance pattern of these thiophenes in the chondrite was markedly different from those in the two kinds of terrestrial sediments, indicating the abiotic origin of these thiophenes.

4.10 Macromolecular material

The macromolecular materials are generally assumed to be completely indigenous due to their high molecular weight and immobility. However it is these attributes which create analytical difficulties and consequently the macromolecular materials are less often studied than the free compounds. This is regrettable, as an understanding of the origins of meteoritic organic matter *in toto* requires an appreciation of the major organic component. Nagy[162] compared this situation to trying to understand the internal structure of a house by intensively studying a few bricks. Established theories of macromolecular material structure point to condensed aromatic cores, connected by aliphatic and ether linkages and with various functional groups attached.[163,164]

4.10.1 Elemental composition

The elemental composition of the Murchison (CM2) macromolecular material has been determined as $C_{100}H_{71}N_3O_{12}S_2$ based on elemental analysis[163] and revised to $C_{100}H_{48}N_{1.8}O_{12}S_2$ based on pyrolytic release studies.[165] Such large macromolecules are difficult to study and analytical approaches primarily attempt to break the structure down into fragments that are easier to deal with, using techniques such as pyrolysis or chemical degradation.

4.10.2 Aromatic and aliphatic hydrocarbons

The majority of the carbon in meteoritic macromolecular materials is present within aromatic ring systems. This aromatic nature has been revealed by a series of pyrolysis studies on previously solvent-extracted, thermally-extracted or acid demineralised samples of Allende (CV3),[166,167] Murchison (CM2),[60,61,168–171] Orgueil (CI1)[172] and a number of Antarctic carbonaceous chondrites.[170,173] The macromolecular materials were thermally fragmented to produce aromatic hydrocarbons such as benzene, toluene, alkylbenzenes, naphthalene, alkylnaphthalenes, indenes, acenaphthene, fluorene, phenanthrene, biphenyl and pyrene.

Further identification of the aromatic units in the macromolecular materials was achieved by Hayatsu *et al.*,[163] who used sodium dichromate oxidation to selectively remove aliphatic side chains in the Murchison (CM2) macromolecular materials and, thereby, isolate and release the aromatic cores present. These studies have revealed a dominance of single-ring aromatic entities but also indicated a significant amount of two- to four-ring aromatic cores bound to the macromolecular materials by a number of aliphatic linkages.

Cross polarisation–magic angle spinning ^{13}C nuclear magnetic resonance (CP/MAS NMR) spectroscopy was used by Cronin *et al.*[164] to detect aromatic carbon within the Orgueil

Table 10 Estimations of functional group abundance by NMR from ref. 176

Functional group	Intensity
Aromaticity	60% (of total intensity)
Carbonyl	5% (of total intensity)
Carboxy	6% (of total intensity)
Aromatic OH	12% (of aromatic intensity)
Methyl	31% (of aliphatic intensity)
Methylene	44% (of aliphatic intensity)
Methine	10% (of aliphatic intensity)
Aliphatic–O	15% (of aliphatic intensity)

(CI1), Murchison (CM2) and Allende (CV3) macromolecular materials and indicated aromaticities of 47 and 40% for the Orgueil (CI1) and Murchison (CM2) macromolecular materials respectively. As CP/MAS does not detect carbon distant from protons, Cronin *et al.*[164] believed the technique was underestimating the aromaticity of the macromolecular materials and invoked the presence of extensive polycyclic aromatic sheets significantly larger than the one- to four-ring aromatic entities isolated by Hayatsu *et al.*[163] When the different meteorites were compared, the Orgueil (CI1) and Murchison (CM2) macromolecular materials had relatively greater amounts of hydrogenated aromatic/olefinic and aliphatic groups than Allende (CV3). Gardinier *et al.*[174] re-examined the Murchison (CM2) and Orgueil (CI1) macromolecular materials and determined the amount of aromatic carbon to be between 69 and 78% in Orgueil (CI1) and 61 and 67% in Murchison (CM2) and favoured the presence of highly substituted rather small aromatic units. Cody *et al.*[175] refined estimates of aromaticities for the Murchison (CM2) macromolecular material to between 61 and 66% and concurred that aromatic units were highly substituted (Fig. 4; Table 10). NMR of Tagish Lake (CI2) has revealed an exclusively aromatic character.[39]

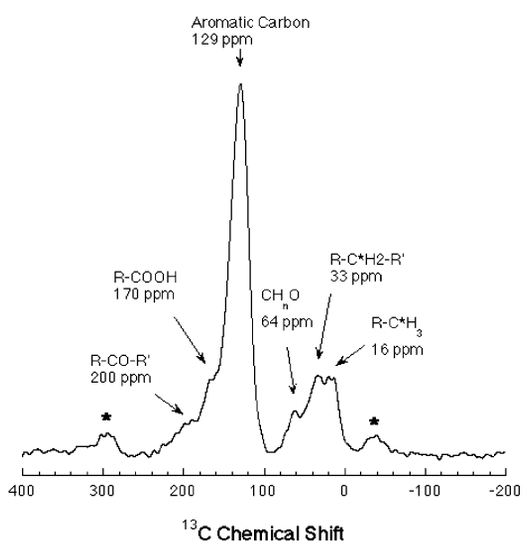

Fig. 4 Variable amplitude cross polarisation spectrum (12 KHz MAS) of the Murchison (CM2) macromolecular material. Prominent peaks and shoulders are assigned to probable functional groups identified by their respective chemical shifts in ppm (ref. 175)

Recently, Sephton *et al.*[68,82,177] investigated the composition of the Murchison (CM2), Cold Bokkeveld (CM2) and Orgueil (CI1) macromolecular materials using hydrous pyrolysis followed by SFE. The retention of volatile components in the hydrous pyrolysate such as toluene, alkylbenzenes, naphthalene and alkylnaphthalenes indicated that the amounts of small aromatic units had been underestimated in previous work that used solvent extraction techniques (*e.g.* ref. 163). The remarkable qualitative similarity between the hydrous pyrolysates of

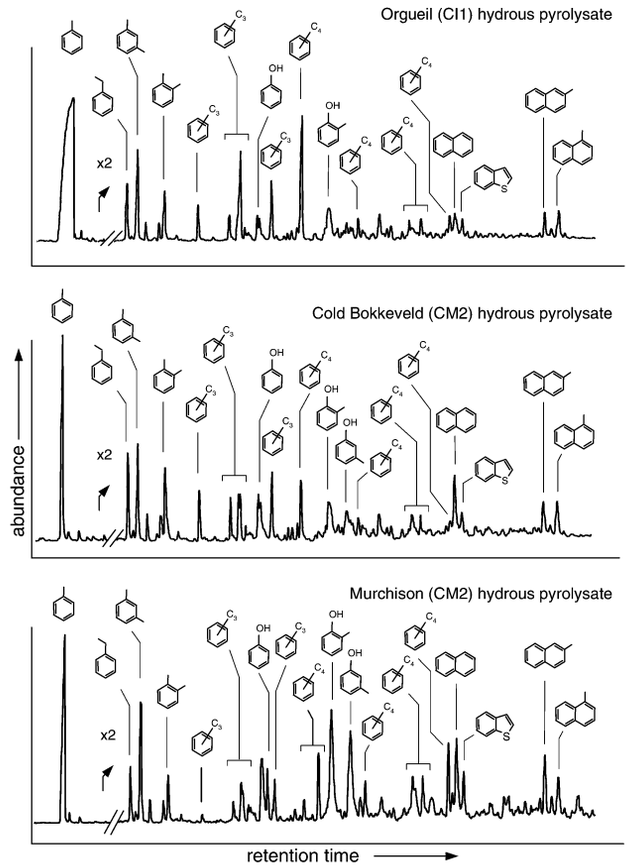

Fig. 5 GC-MS analyses of SFE extracts of the hydrous pyrolysates from Orgueil (CI1), Cold Bokkeveld (CM2) and Murchison (CM2). (//) represents a portion of condensed baseline (ref. 82).

Orgueil (CI1), Murchison (CM2) and Cold Bokkeveld (CM2) indicated that macromolecular materials in different meteorites are made up of essentially the same units[82] (Fig. 5). Quantitative differences, however, were apparent and appeared to be related to levels of parent body aqueous alteration. The general similarity between the major organic components in the CI and CM meteorites appears inconsistent with the interpretation of Ehrenfreund *et al.*,[121] based on amino acid data, that the CI and CM meteorites come from different types of parent bodies (comets and asteroids respectively).

Aliphatic hydrocarbon moieties are present in significant amounts within the meteoritic macromolecular materials. Several pyrolysis studies have indicated that these moieties exist within or around the aromatic network as hydroaromatic rings and short alkyl substituents or bridging groups.[60,61,166–173] NMR studies have also revealed abundant aliphatic units in the form of short, branched groups that link and decorate aromatic centres[164,174,175] (Table 10).

4.10.3 Oxygen, sulfur and nitrogen-containing moieties

Several pyrolysis experiments have released oxygen-containing moieties such as phenols, benzenecarboxylic acids, aldehydes, ketones, furans, benzofurans, dibenzofurans and their alkylated forms from the macromolecular materials in carbonaceous chondrites.[56,60,61,68,82,163,168,169,177] Sodium dichromate oxidation of the macromolecular materials liberated the cyclic diaryl ether dibenzofuran and aromatic ketones such as fluorenone, benzophenone and anthraquinone. Each of these organic units appears to be bound into the macromolecular network by two to four aliphatic linkages.[163] Hayatsu *et al.*[178] used alkaline cupric oxide to selectively cleave organic moieties incorporated into the Murchison (CM2) macromolecular materials by ether groups. These authors established the presence of a significant

Table 11 Stable carbon isotopic values for individual free aromatic molecules released by the pyrolysis of macromolecular materials in carbonaceous chondrites

	Orgueil (CI1)		Cold Bokkeveld (CM2)		Murchison (CM2)	
Compound	δ^{13}C (‰)	Ref.	δ^{13}C (‰)	Ref.	δ^{13}C (‰)	Ref.
Toluene	−25±1.1	82	−22.9±2.3	82	−24.6 ±0.2	68
					−1.3 ±2.0	179
					−5.4	179
Ethylbenzene	−10±0.6	82	2.5±2.3	82	−21.9 ±1.4	179
m-Xylene	−17±0.5	82	4.0±3.8	82	−19.6	68
					−21.7 ±0.4	179
					−20.3	179
p-Xylene	−14±1.5	82	2.4±0.3	82	−17.8	68
C_3-Alkylbenzene	−22.5±0.7	82	−1.0±2.0	82	−18.1	68
Benzaldehyde					−23.7 ±0.6	179
					−24.0 ±0.3	179
Phenol			−14.0±1.5	82	−24.1	68
C_3-Alkylbenzene	−14.5±1.8	82	−8.0±0.4	82		
C_4-Alkylbenzene	−23.6±1.1	82	−12.2±1.1	82		
2-Methylphenol	−12.8±0.9	82	−3.9±2.2	82	−10.3	68
3-Methylphenol			−3.4	82	−10.4	68
					−13.9 ±0.9	179
					−18.5 ±1.9	179
Naphthalene	−14.3±1.4	82	−6.1±1.3	82	−6.5 ±2.5	68
					−5.5 ±0.5	179
					−6.4 ±0.8	179
Benzothiophene					−15.8	68
2-Methylnaphthalene	−17.5±1.5	82	−12.1	82	−5.6 ±2.1	68
					−6.4 ±0.8	179
1-Methylnaphthalene	−18.7±0.4	82	−15.1	82	−7.2 ±2.0	68
					−7.1	179
Acenaphthene					−5.9 ±1.7	68

amount of phenols bound to the macromolecular materials by ether linkages. NMR studies also indicate significant amounts of hydroxy and ether bonds (Table 10).

Thiophenes are common pyrolysis products of meteoritic macromolecular materials and thiophenes, benzothiophenes, dibenzothiophenes and their alkylated forms have been detected using pyrolysis.[60,61,68,82,166–173,177] Sodium dichromate oxidation has revealed the presence of substituted benzothiophene and dibenzothiophene moieties within the macromolecular materials.[178]

Pyrolysis has also led to the identifications of nitrogen-containing compounds. Acetonitrile and benzonitrile are common pyrolysis products (*e.g.* ref. 61, 169). Cyanuric acid[60] and alkylpyridines[163] have been detected in the Murchison (CM2) macromolecular materials. Substituted pyridine, quinoline and carbazole were observed in sodium dichromate oxidation of the macromolecular materials.[163]

4.10.4 Stable isotopes and macromolecular materials

Detailed isotopic analysis of the macromolecular material represents a formidable challenge. In its natural state the macromolecular material will not yield combined structural and isotopic information at the molecular level by either combustion-IRMS or GC-IRMS methods. Consequently, much work has investigated the macromolecular material as a bulk entity. A more incisive approach is to use stepwise heating experiments, which distinguish between carbon phases by their susceptibility to combustion or pyrolysis. This method has revealed several distinct components in the Murchison (CM2) macromolecular material and significant isotopic variability.[79] Recently, the intractable nature of the macromolecular material has been overcome by the use of off-line hydrous pyrolysis to liberate C_7 to C_{11} aromatic and alkyl aromatic fragments of the macromolecular material for carbon isotopic analysis by GC-IRMS.[68] However, although the small-scale nature of these experiments reduced the conventional hydrous pyrolysis sample size requirements from several hundred grams to one or two grams,[177] this is still too demanding for many of the meteorite samples available for analysis. Recently, in an attempt to accommodate this restriction, on-line pyrolysis-GC-IRMS has been used effectively on milligram-sized samples of the Murchison (CM2) meteorite, providing carbon isotopic measurements for C_7 to C_{11} aromatic and alkyl aromatic fragments of the macromolecular material.[179] The combination of pyrolysis-based techniques and of compound-specific isotope analysis has generated a significant data set for the structural units which make up the macromolecular materials in meteorites (Table 11). These data provide important clues as to the origin of the macromolecular materials.

δ^{13}C values for the aromatic molecules liberated from the macromolecular material exhibit the following characteristics, some of which are shared by the free aromatic molecules.

i) δ^{13}C values of low molecular weight compounds increase with increasing carbon number while δ^{13}C values for high molecular weight compounds decrease. This indicates that bond formation and destruction was important during the formation of the macromolecular material.

ii) There are relatively large and systematic differences in δ^{13}C values for sizeable compounds which differ by only one or two carbon atoms reflecting acute fractionation during bond formation and destruction.

iii) δ^{13}C values for 1-methylnaphthalene in the meteorite pyrolysates are consistently lighter than 2-methylnaphthalene reflecting the greater reactivity of the ^{12}C-enriched reactants and the 1-position on the naphthalene molecule during bond formation.[82]

iv) A noticeable feature of the aromatic compounds in Murchison (CM2), and to some extent Cold Bokkeveld (CM2)(Fig. 3), is the similarity in δ^{13}C values for both free and macromolecular moieties suggesting a genetic relationship. Close inspection of the cases where δ^{13}C values are available for both free and macromolecular compounds reveals a consistent enrichment in ^{12}C in the free compounds. This indicates that the free aromatic compounds have been released from the macromolecular material in a pre-terrestrial generation event.[68]

5 Origin and evolution of organic matter in meteorites

5.1 Soluble compounds

When considering the origin of the majority of the free molecules (amino acids, carboxylic acids, sulfonic and phosphonic acids) in carbonaceous chondrites the following common features must be accommodated:

i) Complete structural diversity, a predominance of branched chain isomers, and an exponential decline in amount with increasing carbon number, all of which indicate an abiotic reaction mechanism with random chain synthesis.

ii) $\delta^{13}C$ values that decrease with increasing carbon number indicating stepwise synthesis of higher molecular weight compounds from lower homologues (Fig. 3).

iii) D-enrichments suggesting an ultimate origin in interstellar space.

As a result of these features it is becoming widely considered that significant amounts of meteoritic organic matter, or its precursor materials, are synthesised in an interstellar environment.[5] Yet, it is also becoming clear that, although the feedstock for meteoritic organic matter may predate the solar system, the final molecular architecture of meteoritic organic matter is strongly determined by the effects of aqueous alteration on the meteorite parent body. Organic precursors synthesised in interstellar space are hydrolytically transformed to water-soluble polar organic compounds.[91] The influence that the interstellar and asteroidal environments appear to exert on the final constitution of meteoritic organic matter has led to this model being called "the interstellar-parent body hypothesis".[5] The free aromatic compounds display trends of $\delta^{13}C$ values with carbon number that are distinct from other soluble molecules and are more closely related to the macromolecular material (Fig. 3). Free and macromolecular aromatic units seem to have a common origin (see below).

The *n*-alkanes in meteorites exhibit none of the features outlined above and are isotopically and structurally similar to common biologically-derived terrestrial molecules.[83] Hence, it appears that following the arrival of a meteorite at the Earth's surface, its organic assemblage may be compromised by the addition of terrestrial contaminants.

5.2 Macromolecular materials

Various environments and reaction mechanisms have been proposed for the macromolecular material in carbonaceous chondrites. The macromolecular materials in carbonaceous chondrites are D-rich and it has been suggested that this enrichment is a result of the formation of the macromolecular materials from interstellar molecules.[14,180] Interstellar clouds contain simple gaseous compounds, such as CH_4, CH_2O, H_2O, N_2, and NH_3. Some of these molecules are ionized and fragmented by cosmic radiation. These ions may then combine with neutral molecules resulting in D-enriched reaction products. Such ion–molecule interactions produce increasingly D-enriched and complex organic matter that condenses on to dust grains.[14] Within interstellar clouds simple gas-phase molecules condense as icy mantles around silicate dust grains.[181] Increased temperatures or periods of UV radiation lead to thermally- or photolytically-driven polymerization reactions in these mantles. This process results in complex organic products that may also be D-enriched.[182] The large carbon isotope fractionations reflected by the range in $\delta^{13}C$ values for aromatic units in the macromolecular materials and a D-enrichment for these entities suggest that these reactions occurred in a dense interstellar cloud. The juxtaposition of the synthesis and cracking products implies that the reactions occurred in a restricting medium, the most likely candidate for which is the icy organic mantles of interstellar grains. During radiation-induced reactions, organic matter is simultaneously formed and destroyed to achieve an intermediate level of organic complexity.[183] The term "circle reaction" has been proposed for this process and such reactions may have produced and/or modified aromatic hydrocarbons, resulting in the coexisting synthesis and cracking features evident in meteoritic aromatic compounds.[80] Once formed by reactions in the gas phase, solid phase or combinations of both, these D-enriched complex organic residues would be available to participate in the formation of the carbonaceous chondrites following the collapse of the interstellar cloud.

Hayatsu *et al.*[163] proposed that the macromolecular materials are the result of the thermally-induced polymerization and aromatization of aliphatic hydrocarbons produced by the Fischer–Tropsch reaction in the solar nebula. The Fischer–Tropsch reaction involves the production of *n*-alkanes from CO and H_2 on the surfaces of mineral catalysts. Supporting evidence for this theory includes an apparently similar carbon isotopic fractionation between the macromolecular materials and coexisting carbonates in the meteorite to that seen in Fischer–Tropsch syntheses,[28,89] the occurrence of the macromolecular materials as coatings on the surfaces of mineral nuclei[184] and the presence of aliphatic moieties within the macromolecular materials as revealed by photochemical oxidation.[163]

However, as a means of producing macromolecular materials, the Fischer–Tropsch theory encounters the same problems discussed for the free *n*-alkanes (section 4.2.2). Isotopic measurements reveal that the proposed CO source gas is substantially ^{13}C-depleted relative to the macromolecular material[27] and petrographic evidence indicates that the catalysts necessary to trigger the reaction in the primitive solar nebula were formed much later on the meteorite parent body.[90,91] The aliphatic species present in the macromolecular materials can be accounted for by alkyl substitution, hydroaromatic rings, and bridging groups between aromatic units, none of which are characteristic of Fischer–Tropsch reactions.

It has also been proposed that the macromolecular materials were produced in the solar nebula by the gas-phase pyrolysis of simple aliphatic hydrocarbons such as acetylene (C_2H_2) and methane (CH_4) at temperatures of 900 to 1100 K.[185] The addition of acetylene molecules by a free radical mechanism leads to polymerization and the formation of high molecular weight aromatic structures. Acetylene and methane are believed to be present in interstellar clouds and would have been inherited by the solar nebula following cloud collapse.[185] In fact, it is suggested that 1 to 10% of the initial gaseous carbon in the solar nebula was present as small aliphatic hydrocarbons.[185]

Peltzer *et al.*[32] proposed that following the formation of the meteorite parent body, electric discharges and UV light may have acted on transient atmospheres leading to the production of organic matter by Miller–Urey reactions. Miller–Urey reactions are known to be efficient processes for the production of complex organic matter.[186]

The internal heating of the meteorite parent body is thought to have initiated periods of aqueous alteration, as liquid water was present at temperatures of less than 20 °C.[187] Organic synthesis could have occurred as hot fluids reacted on the surfaces of mineral catalysts during transport from the interior of the parent body. Similar processes have been proposed for the Earth[188] and Mars.[189] Alternatively, pre-existing organic matter in cometary ices may have been transformed by hydrolytic reactions.[91]

Overall, theories that rely on *de novo* synthesis of the macromolecular materials (and the genetically-related free aromatic molecules) in the solar nebula or on the meteorite parent body suffer from major flaws, namely the inability to produce the D-enrichment seen in the macromolecular materials and the large and systematic fractionations in $\delta^{13}C$ exhibited by its constituents (Fig. 3). These features suggest that events in the solar nebula and on the meteorite parent body are more likely to amount to the secondary processing of pre-existing interstellar organic matter rather than primary synthesis.

6 Meteoritic organic matter and the origin of life

All known life is based on organic compounds and water and both of these have been present in the carbonaceous chondrites. As a result, these meteorites constitute a valuable "natural laboratory" of prebiotic chemical evolution. Analyses of the organic matter in meteorites can provide an inventory of the types of chemical reactions and organic products which could have been significant on the prebiotic Earth. This inventory substitutes our terrestrial record which has been obliterated by biological and geological activity. In addition, a plausible model has been proposed in which the feedstock for the development of life was supplied by the arrival of meteoritic and cometary organic matter at the surface of the Earth.[190–192]

The amounts of organic matter extraterrestrial objects can deliver to the Earth's surface are considerable. For example, the following calculation can be performed for comet Halley:[193]

$$M_{org} = f_{org}\, M_{com} = 0.19(4\pi/3)\, \rho_C\, R_C^3 = 3 \times 10^{16}\ \text{g}$$

where M_{org} is the mass of organic matter, f_{org} is the organic refractory fraction, M_{com} is the mass of the comet, ρ_c is the comet density (0.26 g cm^{-1}), and R_c is the comet radius (5 km). This answer is equal to approximately 10% of the current biomass of the Earth. Even if only a small fraction of the molecules are biologically relevant they would have had a significant impact on the prebiotic chemistry of the Earth.

7 References

1 J. Hayes, *Geochim. Cosmochim. Acta*, 1967, **31**, 1395.
2 R. Hayatsu and E. Anders, *Top. Curr. Chem.*, 1981, **99**, 1.
3 F. Mullie and J. Reisse, *Top. Curr. Chem.*, 1987, **139**, 85.
4 J. R. Cronin, S. Pizzarello, and D. P. Cruikshank, in *Organic matter in carbonaceous chondrites, planetary satellites, asteroids and comets*, ed. J. F. Kerridge and M. S. Matthews, University of Arizona Press, Tucson, AZ, 1988.
5 J. R. Cronin and S. Chang, in *Organic matter in meteorites: Molecular and isotopic analyses of the Murchison meteorite*, ed. J. M. Greenburg and V. Pirronello, Kluwer Academic Publishing, Dordrecht, 1993.
6 R. T. Dodd, *Meteorites: A chemical and petralogical synthesis*, Cambridge University Press, Cambridge, 1981.
7 G. W. Wetherill and C. R. Chapman, in *Asteroids and meteorites*, ed. J. F. Kerridge and M. S. Mathews, University of Arizona Press, Tucson, 1988.
8 C. M. O. Alexander, S. S. Russell, J. W. Arden, R. D. Ash, M. M. Grady and C. T. Pillinger, *Meteorit. Planet. Sci.*, 1998, **33**, 603.
9 E. Anders, *Circumstellar material in meteorites; noble gases, carbon and nitrogen*, ed. J. F. Kerridge and M. S. Matthews, University of Arizona, Tucson, 1988.
10 J. F. Kerridge, *Geochim. Cosmochim. Acta*, 1985, **49**, 1707.
11 J. W. Smith and I. R. Kaplan, *Science*, 1970, **167**, 1367.
12 J. W. Smith and D. Rigby, *Earth Planet. Sci. Lett.*, 1981, **54**, 64.
13 P. K. Swart, M. M. Grady and C. T. Pillinger, *Nature*, 1982, **297**, 381.
14 F. Robert and S. Epstein, *Geochim. Cosmochim. Acta*, 1982, **46**, 81.
15 J. Yang and S. Epstein, *Geochim. Cosmochim. Acta*, 1983, **47**, 2199.
16 M. M. Grady, I. P. Wright, P. K. Swart and C. T. Pillinger, *Geochim. Cosmochim. Acta*, 1988, **52**, 2855.
17 A. Virag, E. Zinner, R. S. Lewis and M. Tang, *Lunar Planet. Sci.*, 1989, **20**, 1158.
18 S. S. Russell, J. W. Arden and C. T. Pillinger, *Meteorit. Planet. Sci.*, 1996, **31**, 343.
19 V. K. Pearson, M. A. Sephton, I. Gilmour and I. A. Franchi, *Lunar Planet. Sci.*, 2001, **32**, CD #1861.
20 A. A. Penzias, *Science*, 1980, **208**, 663.
21 M. L. Fogel and L. A. Cifuentes, in *Isotope fractionation during primary production*, ed. M. H. Engel and S. A. Macko, Plenum Press, New York, 1993.
22 D. E. Mathews and J. M. Hayes, *Anal. Chem.*, 1978, **50**, 1465–1473.
23 M. A. Sephton and I. Gilmour, *Mass Spectrom. Rev.*, 2001, **20**, 111.
24 J. Oró, J. Gibert, H. Lichtenstein, S. Wikstrom and D. A. Flory, *Nature*, 1971, **230**, 105.
25 P. G. Brown, A. R. Hildebrand, M. E. Zolensky, M. Grady, R. N. Clayton, T. K. Mayeda, E. Tagliaferri, R. Spalding, N. D. MacRae, E. L. Hoffman, D. W. Mittlefehldt, J. F. Wacker, J. A. Bird, M. D. Campbell, R. Carpenter, H. Gingerich, M. Glatiotis, E. Greiner, M. J. Mazur, P. J. A. McCausland, H. Plotkin and T. R. Mazur, *Science*, 2000, **290**, 320.
26 S. Chang, R. Mack and K. Lennon, *Lunar Planet. Sci.*, 1978, **9**, 157.
27 G. Yuen, N. Blair, D. J. DesMarias and S. Chang, *Nature*, 1984, **307**, 252.
28 K. Kvenvolden, J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnamperuma, I. R. Kaplan and C. Moore, *Nature*, 1970, **228**, 928.
29 K. L. Pering and C. Ponnamperuma, *Science*, 1971, **173**, 237.
30 J. G. Lawless and G. U. Yuen, *Nature*, 1979, **282**, 396.
31 J. G. Lawless, B. Zeitman, W. E. Pereira, R. E. Summons and A. M. Duffield, *Nature*, 1974, **251**, 40.
32 E. T. Peltzer, J. L. Bada, G. Schlesinger and S. L. Miller, *Adv. Space Res.*, 1984, **4**, 69.
33 G. A. Jungclaus, G. U. Yuen, C. B. Moore and J. G. Lawless, *Meteoritics*, 1976, **11**, 231.
34 G. Cooper, N. Kimmich, W. Belisle, J. Sarinana, K. Brabham and L. Garrel, *Nature*, 2001, **414**, 879.
35 S. Pizzarello, X. Feng, S. Epstein and J. R. Cronin, *Geochim. Cosmochim. Acta*, 1994, **58**, 5579.
36 G. Jungclaus, J. R. Cronin, C. B. Moore and G. U. Yuen, *Nature*, 1976, **261**, 126.
37 R. Hayatsu, E. Anders, M. H. Studier and L. P. Moore, *Geochim. Cosmochim. Acta*, 1975, **39**, 471.
38 P. G. Stoks and A. W. Schwartz, *Geochim. Cosmochim. Acta*, 1982, **46**, 309.
39 S. Pizzarello, Y. S. Huang, L. Becker, R. J. Poreda, R. A. Nieman, G. Cooper and M. Williams, *Science*, 2001, **293**, 2236.
40 P. G. Stoks and A. W. Schwartz, *Nature*, 1979, **282**, 709.
41 P. G. Stoks and A. W. Schwartz, *Geochim. Cosmochim. Acta*, 1981, **45**, 563.
42 A. Shimoyama and H. Katsumata, *Chem. Lett.*, 2001, **3**, 202.
43 G. W. Cooper, M. H. Thiemens, T. L. Jackson and S. Chang, *Science*, 1997, **277**, 1072.
44 G. W. Cooper, W. M. Onwo and J. R. Cronin, *Geochim. Cosmochim. Acta*, 1992, **56**, 4109.
45 W. G. Meinschein, *Nature*, 1963, **197**, 833.
46 W. G. Meinschein, *Space Sci. Rev.*, 1963, **2**, 653.
47 W. G. Meinschein, B. Nagy and D. J. Hennessy, *Ann. N. Y. Acad. Sci.*, 1963, **108**, 553.
48 A. P. Vinogradov and G. P. Vdovykin, *Geochem. Int.*, 1964, **1**, 831.
49 G. P. Vdovykin, *Geochem. Int.*, 1964, **1**, 693.
50 B. T. Commins and J. S. Harington, *Nature*, 1966, **212**, 273.
51 R. J. Olson, J. Oró and A. Zlatkis, *Meteorites and tektites*, 1967, **31**, 1935.
52 D. W. Nooner and J. Oró, *Geochim. Cosmochim. Acta*, 1967, **31**, 1359.
53 J. Han, B. R. Simoneit, A. I. Burlingame and M. Calvin, *Nature*, 1969, **222**, 364.
54 M. H. Studier, R. Hayatsu and E. Anders, *Science*, 1965, **149**, 1455.
55 M. H. Studier, R. Hayatsu and E. Anders, *Geochim. Cosmochim. Acta*, 1968, **32**, 151.
56 J. M. Hayes and K. Biemann, *Geochim. Cosmochim. Acta*, 1968, **32**, 239.
57 D. W. Muenow, S. J. Steck and J. L. Margrave, *Geochim. Cosmochim. Acta*, 1971, **35**, 1047.
58 T. Belsky and I. R. Kaplan, *Geochim. Cosmochim. Acta*, 1970, **34**, 257.
59 R. L. Levy, C. J. Wolf, M. A. Grayson, J. Gilbert, E. Gelpi, W. S. Updegrove, A. Zlatkis and J. Oró, *Nature*, 1970, **227**, 148.
60 M. L. Studier, R. Hayatsu and E. Anders, *Geochim. Cosmochim. Acta.*, 1972, **36**, 189.
61 R. L. Levy, M. A. Grayson and C. J. Wolf, *Geochim. Cosmochim. Acta*, 1973, **37**, 467.
62 B. P. Basile, B. S. Middleditch and J. Oró, *Org. Geochem.*, 1984, **5**, 211.
63 D. W. Deamer and R. M. Pashley, *Origins Life Evol. Biosphere*, 1989, **19**, 21.
64 R. V. Krishnamurthy, S. Epstein, J. R. Cronin, S. Pizzarello and G. U. Yuen, *Geochim. Cosmochim. Acta*, 1992, **56**, 4045.
65 I. Gilmour and C. T. Pillinger, *Mon. Not. R. Astron. Soc.*, 1994, **269**, 235.
66 H. Naraoka, A. Shimoyama, M. Komiya, H. Yamamoto and K. Harada, *Chem. Lett.*, 1988, 831.
67 A. Shimoyama, H. Naraoka, M. Komiya and K. Harada, *Geochem. J.*, 1989, **23**, 181.
68 M. A. Sephton, C. T. Pillinger and I. Gilmour, *Geochim. Cosmochim. Acta*, 1998, **62**, 1821.
69 M. A. Sephton, C. T. Pillinger and I. Gilmour, *Planet. Space Sci.*, 2001, **49**, 101.
70 J. H. Hahn, R. Zenobi, J. L. Bada and R. N. Zare, *Science*, 1988, **239**, 1523.

71 M. R. Wing and J. L. Bada, *Geochim. Cosmochim. Acta*, 1991, **55**, 2937.
72 M. R. Wing and J. L. Bada, *Origins Life Evol. Biosphere*, 1992, **21**, 375.
73 T. N. Tingle, C. H. Becker and R. Malhotra, *Meteoritics*, 1991, **26**, 117.
74 M. S. De Vries, K. Reihs, H. R. Wendt, W. G. Golden, H. E. Hunziker, R. Fleming, E. Peterson and S. Chang, *Geochim. Cosmochim. Acta*, 1993, **57**, 933.
75 R. H. Becker and S. Epstein, *Geochim. Cosmochim. Acta.*, 1982, **34**, 257.
76 S. Epstein, R. V. Krishnamurthy, J. R. Cronin, S. Pizzarello and G. U. Yuen, *Nature*, 1987, **326**, 477.
77 S. Pizzarello, R. V. Krishnamurthy, S. Epstein and J. R. Cronin, *Geochim. Cosmochim. Acta*, 1991, **55**, 905.
78 J. R. Cronin, S. Pizzarello, S. Epstein and R. V. Krishnamurthy, *Geochim. Cosmochim. Acta*, 1993, **57**, 4745.
79 J. F. Kerridge, S. Chang and R. Shipp, *Geochim. Cosmochim. Acta*, 1987, **51**, 2527.
80 M. A. Sephton and I. Gilmour, *Astrophys. J.*, 2000, **540**, 588.
81 H. Naraoka, A. Shimoyama and K. Harada, *Earth Planet. Sci. Lett.*, 2000, **184**, 1.
82 M. A. Sephton, C. T. Pillinger and I. Gilmour, *Geochim. Cosmochim. Acta*, 2000, **64**, 321.
83 M. A. Sephton, C. T. Pillinger and I. Gilmour, *Precambrian Res.*, 2001, **106**, 47.
84 B. Nagy, W. G. Meinschein and D. J. Hennessy, *Ann. N. Y. Acad. Sci.*, 1961, **93**, 25.
85 J. Oró, D. W. Nooner, A. Zlatkis and S. A. Wisktrom, *Life Sci. Space Res.*, 1966, **4**, 63.
86 J. Oró and D. W. Nooner, *Nature*, 1967, **213**, 1085.
87 J. Oró, E. Gelpi and D. W. Nooner, *J. Br. Interplanet. Soc.*, 1968, **21**, 83.
88 E. Gelpi and J. Oró, *Geochim. Cosmochim. Acta*, 1970, **34**, 981.
89 M. S. Lancet and E. Anders, *Science*, 1970, **170**, 980.
90 J. F. Kerridge, A. L. Mackay and W. V. Boynton, *Science*, 1979, **205**, 395.
91 T. E. Bunch and S. Chan, *Geochim. Cosmochim. Acta*, 1980, **44**, 1543.
92 E. F. Du Fresne and E. Anders, *Geochim. Cosmochim. Acta*, 1962, **26**, 1085.
93 B. Nagy, W. G. Meinschein and D. J. Hennessy, *Ann. N. Y. Acad. Sci.*, 1963, **108**, 534.
94 J. R. Cronin and S. Pizzarello, *Geochim. Cosmochim. Acta*, 1990, **54**, 2859.
95 G. Claus and B. Nagy, *Nature*, 1961, **192**, 594.
96 E. T. Degens and M. Bajor, *Naturwissenschaften*, 1962, **49**, 605.
97 I. R. Kaplan, E. T. Degens and J. H. Reuter, *Geochim. Cosmochim. Acta*, 1963, **27**, 805.
98 E. Anders, A. Cavaille, A. DuFresne, E. R. DuFresne, F. W. Fitch and R. Hayatsu, *Science*, 1964, **3648**, 1157.
99 P. B. Hamilton, *Nature*, 1965, **205**, 284.
100 J. Oró and H. B. Skewes, *Nature*, 1965, **207**, 1042.
101 J. R. Vallentyne, in *Two aspects of the geochemistry of amino acids*, ed. S. W. Fox, Academic Press, New York, 1965.
102 K. A. Kvenvolden, J. G. Lawless and C. Ponnamperuma, *Proc. Natl. Acad. Sci. U. S. A.*, 1971, **68**, 86.
103 J. R. Cronin and C. B. Moore, *Science*, 1971, **172**, 1327.
104 J. G. Lawless, K. A. Kvenvolden, E. Peterson, C. Ponnamperuma and C. Moore, *Science*, 1971, **173**, 626.
105 J. G. Lawless, K. A. Kvenvolden, E. Peterson, C. Ponnamperuma and E. Jarosewich, *Nature*, 1972, **236**, 66.
106 J. G. Lawless and E. Peterson, *Origins Life*, 1975, **6**, 3.
107 J. R. Cronin and C. B. Moore, *Geochim. Cosmochim. Acta*, 1976, **40**, 853.
108 K. A. Kvenvolden, E. Peterson and F. S. Brown, *Science*, 1970, **169**, 1079.
109 G. E. Pollock, C.-N. Cheng, S. E. Cronin and K. E. Kvenvolden, *Geochim. Cosmochim. Acta*, 1975, **39**, 1571.
110 J. G. Lawless, *Geochim. Cosmochim. Acta*, 1973, **37**, 2207.
111 R. K. Kotra, A. Shimoyama, C. Ponnamperuma and P. E. Hare, *J. Mol. Evol.*, 1979, **13**, 179.
112 J. R. Cronin, S. Pizzarello and C. B. Moore, *Science*, 1979, **206**, 335.
113 A. Shimoyama and C. Ponnamperuma, *Nature*, 1979, **282**, 394.
114 A. Shimoyama and K. Harada, *Geochem. J.*, 1984, **18**, 281.
115 A. Shimoyama, K. Harada and K. Yanai, *Chem. Lett.*, 1985, 1183.
116 J. R. Cronin and S. Pizzarello, *Adv. Space Res.*, 1983, **3**, 5.
117 J. R. Cronin, W. E. Gandy and S. Pizzarello, *J. Mol. Evol.*, 1981, **17**, 265.
118 J. R. Cronin, S. Pizzarello and G. U. Yuen, *Geochim. Cosmochim. Acta*, 1985, **49**, 2259.
119 J. R. Cronin and S. Pizzarello, *Geochim. Cosmochim. Acta*, 1986, **50**, 2419.
120 J. R. Cronin, G. W. Cooper and S. Pizzarello, *Adv. Space Res.*, 1995, **15**, 91.
121 P. Ehrenfreund, D. P. Glavin, O. Botta, G. Cooper and J. L. Bada, *Proc. Natl. Acad. Sci. U. S. A.*, 2001, **98**, 2138.
122 G. Mueller, *Geochim. Cosmochim. Acta*, 1953, **4**, 1.
123 M. H. Briggs and G. Mamikunian, *Space Sci. Rev.*, 1963, **1**, 647.
124 G. Nagy, T. J. Murphy, V. E. Modzeleski, G. E. Rouser, G. Claus, D. J. Hennesy, U. Colombo and F. Gazzarini, *Nature*, 1964, **202**, 228.
125 B. Nagy, *Science*, 1965, **150**, 1846.
126 B. Nagy, *Proc. Natl. Acad. Sci. U. S. A.*, 1966, **56**, 389.
127 R. Hayatsu, *Science*, 1965, **149**, 443.
128 R. Hayatsu, *Science*, 1966, **153**, 859.
129 W. G. Meinschein, C. Frondel, P. Laur and K. Mislow, *Science*, 1966, **154**, 377.
130 M. H. Engel and B. Nagy, *Nature*, 1982, **296**, 837.
131 J. L. Bada, J. R. Cronin, M.-S. Ho, K. A. Kvenvolden, J. G. Lawless, S. L. Miller, J. Oró, S. Steinberg, M. H. Engel and B. Nagy, *Nature*, 1983, **301**, 494.
132 M. H. Engel, S. A. Macko and J. A. Silfer, *Nature*, 1990, **348**, 47.
133 M. H. Engel and S. A. Macko, *Nature*, 1997, **389**, 265.
134 S. Pizzarello and J. R. Cronin, *Nature*, 1998, **394**, 236.
135 J. R. Cronin and S. Pizzarello, *Science*, 1997, **275**, 951.
136 S. Pizzarello and J. R. Cronin, *Geochim. Cosmochim. Acta*, 2000, **64**, 329.
137 S. Amari, E. Anders, A. Virag and E. Zinner, *Nature*, 1990, **345**, 238.
138 J. Bailey, *Origins Life Evol. Biosphere*, 2001, **31**, 167.
139 W. E. Pereira, R. E. Summons, T. C. Rindfleisch, A. M. Duffield, B. Zeitman and J. G. Lawless, *Geochim. Cosmochim. Acta*, 1975, **39**, 163.
140 J. R. Cronin, *Origins Life*, 1976, **7**, 337.
141 G. W. Cooper and J. R. Cronin, *Geochim. Cosmochim. Acta*, 1995, **59**, 1003.
142 J. R. Cronin, *Origins Life*, 1976, **7**, 343.
143 S. Pizzarello and G. Cooper, *Meteorit. Planet. Sci*, 2001, **36**, 897.
144 G. U. Yuen and K. A. Kvenvolden, *Nature*, 1973, **251**, 40.
145 A. Shimoyama, H. Naraoka, H. Yamamoto and K. Harada, *Chem. Lett.*, 1986, 1561.
146 H. Naraoka, A. Shimoyama and K. Harada, *Origins Life Evol.Biosphere*, 1999, **29**, 187.
147 M. H. Briggs, *Nature*, 1961, **191**, 1137.
148 B. Nagy and M. C. Bitz, *Arch. Biochem. Biophys.*, 1963, **101**, 240.
149 E. T. Peltzer and J. Bada, *Nature*, 1978, **272**, 443.
150 H. Mizutani, *Nature*, 1978, **276**, 738.
151 A. L. Burlingame and H. K. Schnoes, *Science*, 1966, **152**, 104.
152 M. Calvin and S. K. Vaughn, in *Extraterrestrial life : some organic constituents of meteorites and their significance for possible extra-terrestrial biological evolution*, ed. Kallmann-Bijl, North-Holland, Amsterdam, 1960.
153 I. A. Breger, P. Zubovic, J. C. Chandler and R. S. Clarke Jr., *Nature*, 1972, **236**, 155.
154 M. P. Bernstein, S. A. Sandford, L. J. Allamandola, J. S. Gillette, S. J. Clemett and R. N. Zare, *Science*, 1999, **283**, 1135.
155 R. Hayatsu, *Science*, 1964, **146**, 1291.
156 J. Oró, *Nature*, 1963, **197**, 756.
157 R. Hayatsu, M. H. Studier, A. Oda, K. Fuse and E. Anders, *Geochim. Cosmochim. Acta*, 1968, **32**, 175.
158 C. E. Folsome, J. G. Lawless, M. Romiez and C. Ponnamperuma, *Nature*, 1971, **232**, 108.
159 C. E. Folsome, J. G. Lawless, M. Romiez and C. Ponnamperuma, *Geochim. Cosmochim. Acta*, 1973, **46**, 455.
160 W. van der Velden and A. W. Schwartz, *Geochim. Cosmochim. Acta*, 1977, **41**, 961.
161 P. G. Stoks and A. W. Schwartz, in *Nitrogen compounds in carbonaceous meteorites: A reassessment*, ed. Y. Wolman, D. Reidel, Dordrecht, 1981.
162 B. Nagy, *Carbonaceous meteorites*, Elsevier, Amsterdam, 1975.
163 R. Hayatsu, S. Matsuoka, E. Anders, R. G. Scott and M. H. Studier, *Geochim. Cosmochim. Acta*, 1977, **41**, 1325.
164 J. R. Cronin, S. Pizzarello and J. S. Frye, *Geochim. Cosmochim. Acta*, 1987, **51**, 299.
165 E. Zinner, in *Interstellar cloud material in meteorites*, ed. J. F. Kerridge, and M. S. Mathews, University of Arizona Press, Tucson, 1988.
166 P. G. Simmonds, A. J. Bauman, E. M. Bollin, E. Gelpi and J. Oró, *Proc. Natl. Acad. Sci. U. S. A.*, 1969, **64**, 1027.
167 R. L. Levy, C. J. Wolf and J. Oró, *J. Chromatogr. Sci.*, 1970, **8**, 524.
168 K. Biemann, *Origins Life*, 1974, **5**, 417.
169 G. Holzer and J. Oró, *Org. Geochem.*, 1977, **1**, 37.

170 T. Murae, *J. Anal. Appl. Pyrolysis*, 1995, **32**, 65.
171 M. Komiya and A. Shimoyama, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 53.
172 E. L. Bandurski and B. Nagy, *Geochim. Cosmochim. Acta*, 1976, **40**, 1397.
173 M. Komiya, A. Shimoyama and K. Harada, *Geochim. Cosmochim. Acta*, 1993, **57**, 907.
174 A. Gardinier, S. Derenne, F. Robert, F. Behar, C. Largeau and J. Maquet, *Earth Planet. Sci. Lett.*, 2000, **184**, 9.
175 G. D. Cody, C. M. O. Alexander and F. Tera, *Geochim. Cosmochim. Acta*, 2001, in the press.
176 G. D. Cody, C. M. O. Alexander and F. Tera, *Lunar Planet. Sci.*, 1999, **30**, CD #1582.
177 M. A. Sephton, C. T. Pillinger and I. Gilmour, *Planet. Space Sci.*, 1999, **47**, 181.
178 R. Hayatsu, R. E. Winans, R. G. Scott, R. L. McBeth, L. P. Moore and M. H. Studier, *Science*, 1980, **207**, 1202.
179 M. A. Sephton and I. Gilmour, *Planet. Space Sci.*, 2001, **49**, 465.
180 Y. Kolodny, J. F. Kerridge and I. R. Kaplan, *Earth Planet. Sci. Lett.*, 1980, **46**, 149.
181 J. M. Greenberg, *Sci. Am.*, 1984, **250**, 96.
182 S. A. Sandford, *Meteorit. Planet. Sci.*, 1996, **31**, 449.
183 K. Roessler, *Nucl. Instrum. Methods Phys. Res. A*, 1992, **65**, 55.
184 B. Alpern and Y. Benkheiri, *Earth Planet. Sci. Lett.*, 1973, **19**, 422.
185 W. A. Morgan, E. D. Feigelson, H. Want and M. Frenlach, *Science*, 1991, **252**, 109.
186 C. Sagan and B. N. Khare, *Nature*, 1979, **277**, 102.
187 R. N. Clayton and T. K. Mayeda, *Earth Planet. Sci. Lett.*, 1984, **67**, 151.
188 E. L. Shock and M. D. Schulte, *J. Geophys. Res.-Planets*, 1998, **103**, 28513.
189 M. Zolotov and E. Shock, *J. Geophys. Res.-Planets*, 1999, **104**, 14033.
190 J. Oró, *Nature*, 1961, **190**, 389.
191 C. F. Chyba, P. J. Thomas, L. Brookshaw and C. Sagan, *Science*, 1990, **249**, 366.
192 C. Chyba and C. Sagan, *Nature*, 1992, **355**, 125.
193 J. M. Greenberg, in *Physical and chemical composition of comets – from interstellar space to the Earth*, ed. J. M. Greenburg and V. Pirronello, Kluwer Academic Publishing, Dordrecht, 1993.