International Journal of Astrobiology 3 (2): 107–116 (2004) Printed in the United Kingdom
DOI: 10.1017/S1473550404002046 © 2004 Cambridge University Press

Molecular, isotopic and *in situ* analytical approaches to the study of meteoritic organic material

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Abstract: Organic materials isolated from carbonaceous meteorites provide us with a record of pre-biotic chemistry in the early Solar System. Molecular, isotopic and *in situ* studies of these materials suggest that a number of extraterrestrial environments have contributed to the inventory of organic matter in the early Solar System including interstellar space, the Solar nebula and meteorite parent bodies.

There are several difficulties that have to be overcome in the study of the organic constituents of meteorites. Contamination by terrestrial biogenic organic matter is an ever-present concern and a wide variety of contaminant molecules have been isolated and identified including essential plant oils, derived from either biological sources or common cleaning products, and aliphatic hydrocarbons, most probably derived from petroleum-derived pollutants. Only 25% of the organic matter in carbonaceous chondrites is amenable to extraction with organic solvents; the remainder is present as a complex macromolecular aromatic network that has required the development of analytical approaches that can yield structural and isotopic information on this highly complex material.

Stable isotopic studies have been of paramount importance in understanding the origins of meteoritic organic matter and have provided evidence for the incorporation of interstellar molecules within meteoritic material. Extending isotopic studies to the molecular level is yielding new insights into both the sources of meteoritic organic matter and the processes that have modified it.

Organic matter in meteorites is intimately associated with silicate minerals and the *in situ* examination of the relationships between organic and inorganic components is crucial to our understanding of the role of asteroidal processes in the modification of organic matter and, in particular, the role of water as both a solvent and a reactant on meteorite parent bodies.

Received 1 July 2004, accepted 1 September 2004

Key words: gas chromatography, GC-IRMS, SEM, Murchison, Orgueil, Tagish Lake.

Introduction

The carbonaceous chondrite meteorites are organic-rich fragments of asteroids that have remained relatively unaltered since the Solar System formed. They represent some of the most primitive extraterrestrial material available for scientific investigation and can contain up to 5 wt% organic carbon that includes an array of organic compounds encompassing all classes normally considered to be of biological origin (see Sephton (2002), Gilmour (2004) for reviews). However, with the exception of some terrestrial contamination, there is overwhelming evidence from isotopic and other studies that these organic species are the result of abiotic chemical syntheses (e.g. Smith & Kaplan 1970; Becker & Epstein 1982; Yang & Epstein 1983; Engel *et al*. 1990, Pizzarello *et al*. 1994). The carbonaceous chondrites, therefore, provide natural examples of pre-biotic chemical evolution; understanding the sources of organic molecules in meteorites and the chemical processes that lead to their formation is the primary goal of research into extraterrestrial organic material. Interstellar space, the Solar nebula and asteroids have all been suggested as environments where organic matter (OM) may have formed (Anders 1991).

One meteorite in particular, the Murchison (CM2) carbonaceous chondrite, has been intensively studied since its fall and recovery in 1969, an event that enabled the first systematic analyses to be performed on comparatively pristine samples of extraterrestrial organic material. Much of our detailed knowledge of organic chemistry in the early Solar System has been obtained from Murchison and the wealth of data that has been obtained has led to a sea-change in our understanding of the processes responsible for the synthesis of organic compounds in meteorites (Wright & Gilmour 1990) from largely nebula-based hypotheses (e.g. Anders *et al*. 1973) to one where both the interstellar medium and asteroidal processes are recognized as the principal contributors to the organic inventory of the carbonaceous chondrites (e.g. Cronin & Chang 1993).

Determination of the provenance of meteoritic OM requires detailed structural and isotopic information and developments in its analysis have been largely driven by advances in analytical capabilities. The limited availability of samples, often restricted to a few grams at most, has presented a series of analytical challenges and significant progress was made in the late 1960s and early 1970s when the coupling of gas chromatography with electron impact mass spectrometry (GC-MS) enabled detailed structural information to be obtained on individual compounds (Hayes & Biemann 1968).

Meteoritic OM comprises two principal fractions: a 'free' fraction (up to 25 wt%) that is readily extractable using common solvents (Hayes 1967) and a complex fraction (*ca.* 75 wt%) consisting of a high molecular weight heterogeneous aromatic network, commonly referred to as insoluble macromolecular material (Bandurski & Nagy 1976; Hayatsu *et al.* 1977). The difficulty in analysing such complex macromolecular materials has led to a number of analytical approaches: non-destructive processes such as infra-red spectroscopy (e.g. Hayatsu *et al.* 1977) and nuclear magnetic resonance (NMR) spectroscopy (Cronin *et al.* 1987; Gardinier *et al.* 2000; Cody *et al.* 2002) and destructive techniques such as chemical degradation (Hayatsu *et al.* 1980) and pyrolysis (Simmonds *et al.* 1969; Studier *et al.* 1972; Levy *et al.* 1973; Bandurski & Nagy 1976; Holzer & Oró 1977; Murae 1995; Sephton *et al.* 1999; Sephton & Gilmour 2001b; Sephton *et al.* 2004).

Light element stable isotope measurements of meteoritic OM can provide important information on its origins and the potential of such measurements has long been recognized (Boato 1954). Indeed, meteoritic research has led to significant improvements in stable isotope ratio mass spectrometry (see Pillinger (1984) for a review). The 1970s saw the start of extensive quantitative analysis of solvent extractable compounds from Murchison, together with the first attempts to resolve isotopic heterogeneities in the stable isotopes of carbon, hydrogen and nitrogen, and this work has been the subject of regular detailed reviews (e.g. Anders *et al.* 1973; Mullie & Reisse 1987; Cronin & Chang 1993). More recently, molecular level isotopic analysis (Yuen *et al.* 1984; Engel *et al.* 1990; Gilmour & Pillinger 1994; Sephton *et al.* 1998; Sephton *et al.* 2000) has been employed to constrain the origin of the meteoritic organic phases.

In this paper we review a number of analytical approaches that we have successfully employed to unravel both the complex molecular and the isotopic structure of meteoritic OM.

Assessing the indigeneity of meteoritic organic matter

The difficulties created by terrestrial contamination are a long-standing problem in the analysis and interpretation of organic material in meteorites; one of the earliest chemical analyses of the Cold Bokkeveld meteorite not long after its fall recognized the possibility of terrestrial organic contamination (Faraday 1839). In more recent times, the debate over terrestrial contamination of extraterrestrial samples has taken on a new significance with the reported occurrence of possible biogenic organic remains in the Martian meteorites (Wright *et al.* 1989; McKay *et al.* 1996; Bada *et al.* 1998; Steele *et al.* 2000).

Studies of organic contamination of carbonaceous chondrites (e.g. Cronin & Pizzarello 1990; Sephton *et al.* 2001) have concentrated on contaminants present in the free organic fraction that have previously been interpreted as indigenous compounds, for example *n*-alkanes (Nooner & Oró 1967; Oró & Nooner 1967; Sephton *et al.* 2001), isoprenoids and cycloalkanes (Oró & Nooner 1967; Kvenvolden *et al.* 1970; Oró *et al.* 1971). The potential of molecular level isotopic analyses for the assessment of indigeneity was recognized prior to the development of the analytical capability (Pillinger 1982), and the technique has subsequently been used to demonstrate that *n*-alkanes are largely of terrestrial origin (Sephton *et al.* 2001). Other compounds have isotopic compositions inconsistent with a terrestrial origin and are therefore readily identifiable as indigenous (Yuen *et al.* 1984; Engel *et al.* 1990; Gilmour & Pillinger 1994; Sephton & Gilmour 2001a). Other approaches entailing the use of stable isotopes have also been employed, most notably stepped heating experiments have succeeded in separating organic contamination from other indigenous carbonaceous components in a wide range of meteorites (Swart *et al.* 1983) and in revealing some of the isotopic structure of the macromolecular material (Kerridge *et al.* 1987; Alexander *et al.* 1998).

The Orgueil CI chondrite, which fell in 1864, serves as a useful case study on the extent and nature of terrestrial organic contamination in meteorites. Its comparatively long residence time on Earth combined with historically poor curatorial procedures have resulted in a high level of biogenic terrestrial organic contamination. However, it has not always been recognized as such (Brooks & Shaw 1969; Hodgson & Baker 1969), resulting in an intense debate in the 1960s on the possibility of evidence for extraterrestrial life (see Claus (1968) and Urey *et al.* (1968) for contemporary accounts). Watson *et al.* (2003) undertook a detailed study of the Orgueil free fraction and observed a wide range of largely isoprenoid compounds considered to be terrestrial biogenically-derived contaminants. The majority of compounds identified were C_{10} monoterpenoids (e.g. camphor, borneol, pinenone and terpineol) or C_{15} sesquiterpenoids (e.g. cadalene, calamenene, 5,6,7,8-tetrahydrocadalene and curcumene), which are typical of the biological synthesis of complex molecules from 5-carbon isoprene units by enzymatic condensation reactions (Fig. 1). Cadalene, the most abundant component present, had a concentration of approximately 200 $\mu g\, g^{-1}$ whole meteorite, which was around 9 wt% of the total solvent extractable fraction.

Sesquiterpenoids are common in essential plant oils and fungal antibiotics, whereas monoterpenoids are abundant in higher plants and algae and also essential plant oils. The aromatic nature and narrow molecular weight range of the compounds detected in Orgueil suggests they are not

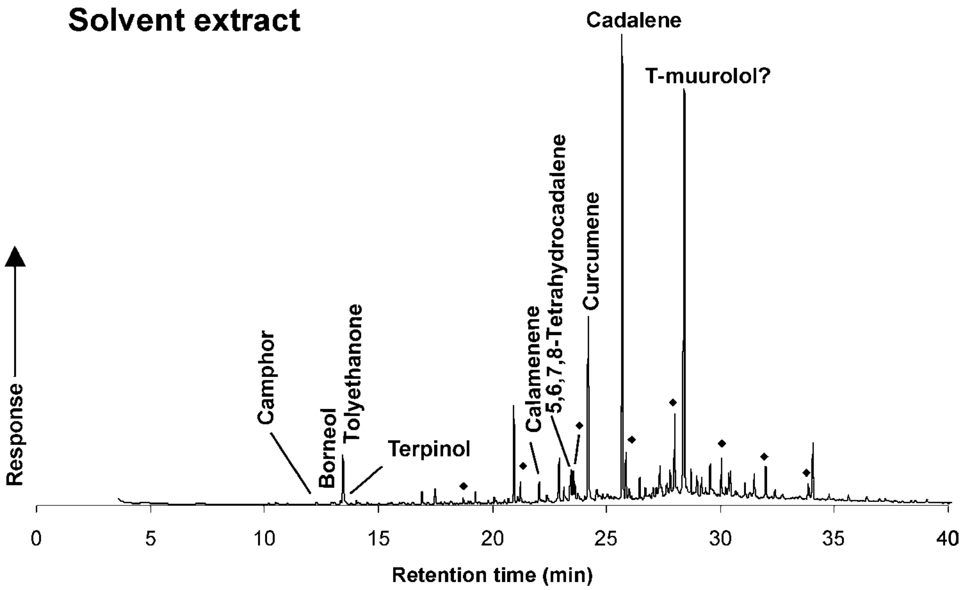

Fig. 1. Gas chromatogram (total ion current) of a solvent extract of a fragment of the Orgueil meteorite showing the presence of contaminant monoterpenoid and sesquiterpenoid compounds.

unaltered plant oils but have in some way undergone a diagenetic change (e.g. aromatization) and/or refinement (e.g. a distillation cut). Diagenesis of sesquiterpenoids can produce cadalene and its derivatives, which are also detected in Orgueil. No such compounds have been detected in pyrolysates of Orgueil macromolecular material (Watson *et al.* 2003), supporting the proposition that these compounds are mobile terrestrial contaminants that have been added to the free fraction.

Essential plant oil derivatives are added to numerous products such as air fresheners, disinfectants and cleaning products, any of which may have come into contact with the meteorite since its fall. However, the actual source of the contamination is unknown; sesquiterpenoids have not been identified in other meteorites although monoterpenoids such as camphor have been previously detected in Orgueil (Studier *et al.* 1968). Camphene was detected in CM2 Murray, which fell in 1950 but was not obtained by the United States National Museum until 6–9 years after its fall and was then stored in open cardboard boxes (Studier *et al.* 1968). The evidence for diagenetic change suggests the contamination is not recent. Therefore, terpenoid contamination is not isolated and may be a previously underestimated problem for certain carbonaceous chondrites and other museum artefacts with long curatorial histories.

Watson *et al.* (2003) also identified a series of *n*-alkanes (C_{13} to C_{20}) together with the long-chain isoprenoids pristane and phytane. Subsequent carbon isotopic analyses of those *n*-alkanes indicates that specimens of Orgueil stored under different conditions for most of their recent history have suffered contamination from apparently different sources (Fig. 2). While three separate stones of Orgueil, one small fragment of material from the Natural History Museum in London and two from the Natural History Museum in Paris, both contain *n*-alkanes, their carbon isotopic compositions are sufficiently different to suggest that the sources of the *n*-alkane contamination are different between stones with different curatorial histories (Fig. 2).

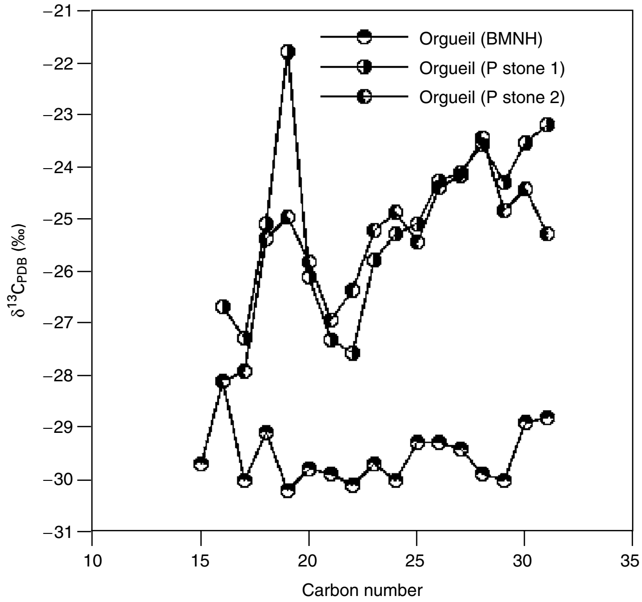

Fig. 2. Carbon isotopic compositions of *n*-alkanes in three stones of the Orgueil CI carbonaceous chondrite. The three stones have different curatorial histories: stone 1 is from the Natural History Museum in London, stones 2a and 2b are from the Natural History Museum in Paris.

Pyrolytic degradation

Pyrolysis, which involves the thermal degradation of high molecular weight macromolecular OM in an inert atmosphere, results in the production of low molecular weight products (pyrolysates) amenable to GC-MS. It provides an effective means of examining the structure of complex macromolecules and has been employed for some time as a means of studying meteorite macromolecular material (e.g. Bandurski & Nagy 1976). Initially, the approach involved introducing the pyrolysates directly into a mass spectrometer (Studier *et al.* 1972). Subsequently, pyrolysis products were separated to a high resolution by the coupling of a pyrolysis furnace directly to a gas chromatograph–mass spectrometer (Py-GC-MS) (Komiya *et al.* 1993). A Py-GC-MS system was successfully employed on the Viking missions (Biemann 1974) and forms part of the scientific payload of Cassini-Huygens (Israel *et al.* 1999).

We have employed flash Py-GC-MS, which allows the uniform heating of small samples at a rapid rate, on solvent extracted, acid treated and untreated carbonaceous chondrites and Martian meteorites (e.g. Sephton & Gilmour 2001b; Sephton *et al.* 2002). These studies suggest that the majority of chondritic organic material is present as one to four aromatic ring species, with one-ring components dominating (Sephton & Gilmour 2001b). Aliphatic groups are present (at times in significant amounts) within the macromolecular aromatic network and appear to exist within or around the network as hydroaromatic rings and short alkyl substituents or bridging groups (Levy *et al.* 1973; Hayatsu *et al.* 1977; Holzer & Oró 1977; Sephton & Gilmour 2001b).

Typical compounds released from carbonaceous chondrites by Py-GC-MS (Fig. 3) include benzene, toluene, alkylbenzenes, naphthalene, alkylnaphthalenes and polycyclic aromatic hydrocarbons with molecular weights up to around 200–300 amu (Simmonds *et al.* 1969; Studier *et al.* 1972; Levy *et al.* 1973; Bandurski & Nagy 1976; Holzer & Oró 1977; Murae 1995; Sephton & Gilmour 2001b).

Pyrolysates from whole-rock Orgueil, Murchison and Mokoia samples are similar except for differences in the mode and range of *n*-alkanes, probable terrestrial contaminants. Pyrolysis of Tagish Lake (an unusual CI2 chondrite) results in a relatively lean trace (Fig. 3) characteristic of a more recalcitrant macromolecule, unyielding even to thermal degradation although small quantities of specific compounds have been positively identified including benzene, toluene, xylenes, C_3 alkylbenzenes, methylthiophenes, benzonitrile, naphthalene and benzothiophene.

There are marked similarities between Py-GC-MS pyrolysates from carbonaceous chondrites and the Martian meteorites EETA79001 and Nakhla (Sephton *et al.* 2002). Given the evidence from ^{14}C studies that in some Martian meteorites a significant proportion of the OM is extraterrestrial in origin (Jull *et al.* 1998, 2000), these similarities may provide evidence that the Martian surface has been subjected to periodic infall of carbonaceous material from space that subsequently became incorporated in Martian igneous rocks.

Considerable additional information can be obtained by undertaking pyrolysis in the presence of water-derived hydrogen atoms (hydrous pyrolysis), which terminate free radical sites produced during pyrolysis, thereby preventing the recombination of pyrolysis products and greatly increasing the pyrolsate yield (Lewan *et al.* 1979; Lewan 1997). We have adapted this off-line technique to examine macromolecular material in Orgueil, Murchison and Cold Bokkeveld (Sephton *et al.* 1999). Hydrous pyrolysates obtained from Orgueil, Murchison and Cold Bokkeveld display a qualitative, although not quantitative, similarity. This implies that the macromolecular OM in different carbonaceous chondrites is composed of essentially the same aromatic structural units including benzene, C_1–C_4 alkyl benzenes, naphthalene, C_1 alkylnaphthalenes, phenols and benzothiophene (Sephton *et al.* 1999). However, differences are observed, most notably in the abundance of volatile aromatic species; for example, Orgueil displays significantly more one-ring species than the CM2 chondrites. Such differences are consistent with the diverse aqueous and thermal histories of the parent asteroids (Brearley 2004) since thermal processing can result in the condensation of macromolecular material by cross linking between aromatic rings; however, in the presence of water this cross linking is hindered resulting in only one- or two-ring aromatic centres (Sephton *et al.* 2004).

Further investigations have employed hydropyrolysis, a process entailing catalysed continuous flow high-pressure hydrogen to fragment the macromolecule in which the products are rapidly flushed from the reactor to limit further transformations (Sephton *et al.* 2004). Hydropyrolysis releases high yields of polycylic aromatic hydrocarbons (Fig. 4) including phenanthrene, carbazole, fluoranthene, pyrene, chrysene, perylene, benzoperylene and coronene units with varying degrees of alklyation. Although hydropyrolysis liberates substantial amounts of OM from the macromolecular material, over 50% of macromolecular carbon remains unconverted.

Molecular-level stable isotope analysis

Stable isotope studies from the 1960s through the early 1980s focused on making isotopic measurements on broad groupings of meteoritic organic compounds, for example HF/HCl acid residues, which concentrated the macromolecular component of the OM, or solvent extracts (e.g. Becker & Epstein 1982). Such studies were successful in establishing that meteoritic OM contained material of probable interstellar origin (Yang & Epstein 1983). Subsequent work began the process of attempting to isolate chemically identifiable components; using chromatographic techniques it was possible to obtain fractions with broadly similar chemical structures. This led to isotopic measurements being obtained on assemblages of compounds, which confirmed that a significant proportion of the solvent extractable OM

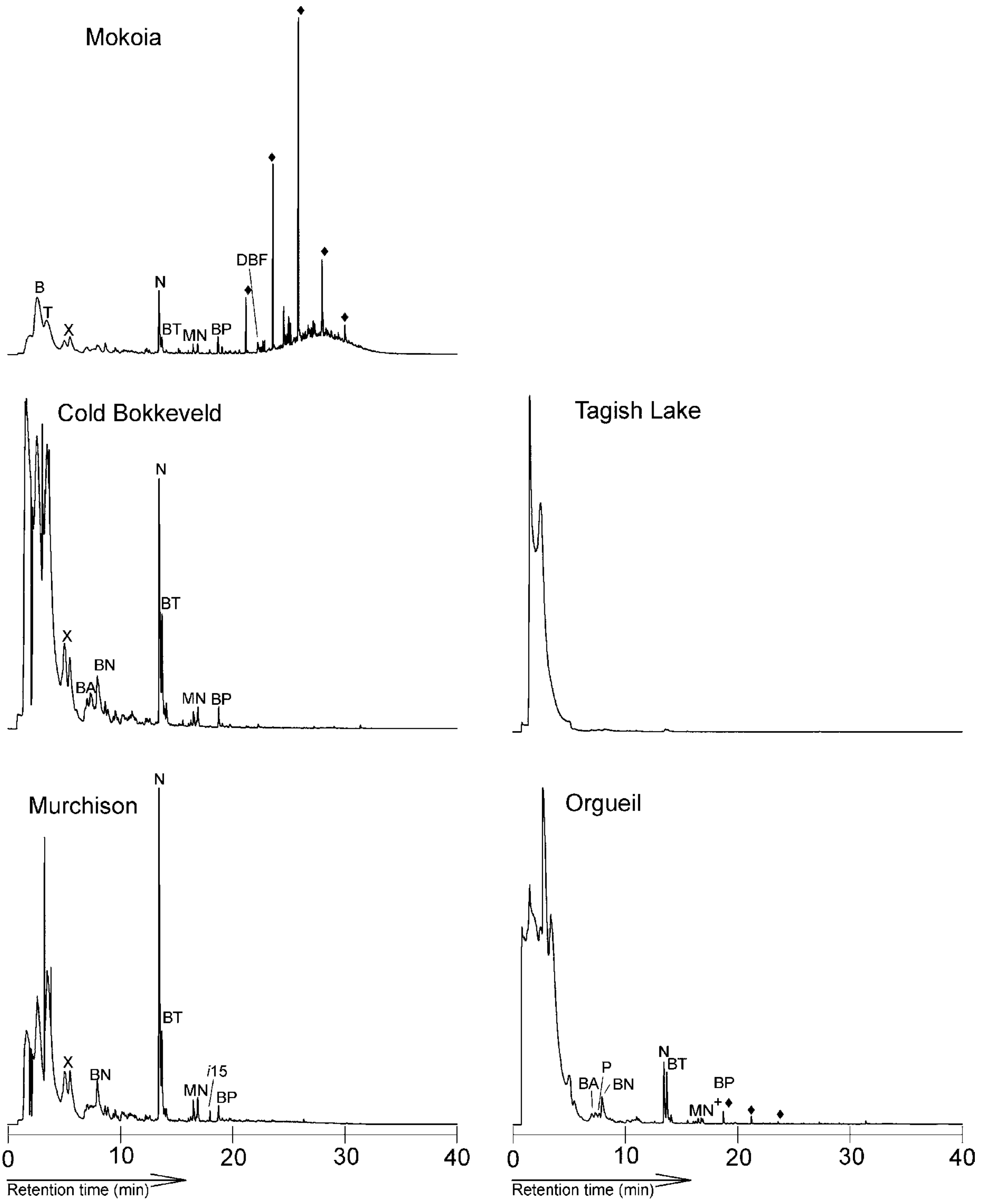

Fig. 3. Pyrolysis-gas chromatograms (total ion current) of Mokoia, Cold Bokkeveld, Murchison, Orgueil and Tagish Lake. B = benzene, T = toluene, X = xylenes, BA = benzaldehyde, P = phenol, BN = benzonitrile, N = naphthalene, BT = benzothiophene, MN = methylnaphthalene, BP = biphenyl, DBF = dibenzofuran, ◆ = *n*-alkane.

was indigenous to meteorites since significant enrichments in ^{13}C, ^{15}N and D were detected and provided strong evidence for the role of interstellar processes in the origin of meteoritic OM (Epstein *et al.* 1987; Pizzarello *et al.* 1991).

The advent of combined gas chromatography–isotope ratio mass spectrometry, GC-IRMS (Hayes *et al.* 1990), has enabled the determination of the isotopic compositions of individual compounds to high levels of precision. Since the approach relies on the ability of analytes to be separated gas chromatographically, volatile meteoritic compounds with hydrocarbon skeletons and relatively few functional groups have been the main focus of investigation to date. Starting with a study by Yuen *et al.* (1984), systematic trends in carbon isotope compositions have been observed for a number

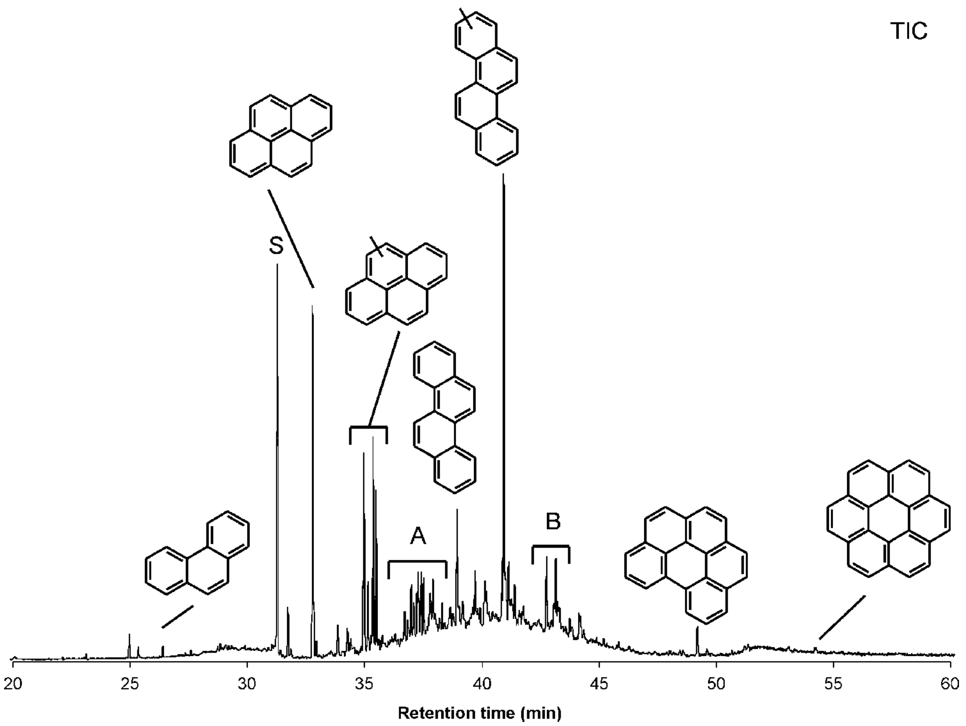

Fig. 4. Total ion chromatogram (TIC) of the hydropyrolysate from the Murchison meteorite. GC-MS responses labelled by letters are as follows: S, elemental sulfur; A, a partly coeluting mixture of dimethylpyrenes, dimethylfluoranthenes and methylbenzofluorenes.

of homologous series in Murchison extracts (Engel *et al.* 1990; Gilmour & Pillinger 1994; Engel & Macko 1997; Naraoka *et al.* 2000). C_1–C_5 aliphatic hydrocarbons, amino acids, carboxylic acids and sulfonic acids from the Murchison meteorite all appear to follow a common trend with $\delta^{13}C$ values generally decreasing as the amount of carbon in the molecules increases. C_6–C_{22} aromatic compounds from the Murchison (CM2) and Asuka-881458 (CM2) meteorites also appear to follow a similar systematic trend with more condensed (lower H/C ratio) PAHs being more depleted in ^{13}C (the open symbols in Fig. 5). These carbon isotopic trends have been interpreted as the consequence of a synthetic process that progressively adds ^{12}C to the carbon skeleton with kinetic isotopic fractionation determining the distribution of carbon isotopes between compounds rather than thermodynamic equilibrium (Gilmour & Pillinger 1994; Naraoka *et al.* 2000). In particular, the $\delta^{13}C$ values obtained for extractable aromatic hydrocarbons in CM2 meteorites display a significant amount of isotopic heterogeneity with a range in $\delta^{13}C$ values of over 20‰. Compounds with relatively high molecular weights, but which differ by only one or two carbon atoms, display significant differences in their $\delta^{13}C$ values. This has led to the suggestion that during the synthetic processes that led to bond formation, isotopic fractionation was at its most extreme, which would imply that synthesis took place in a low-temperature environment such as interstellar space (Sephton & Gilmour 2000).

The combined use of pyrolysis techniques followed by carbon isotopic measurements (both off-line hydrous pyrolysis and on-line pyrolysis-GC-IRMS) enables the isotopic compositions of fragments of the macromolecular material to be determined. We have applied this approach to the study of the stable carbon isotope distribution (the filled symbols in Fig. 5) of macromolecular OM in three carbonaceous chondrites: Orgueil (CI1), Murchison (CM2) and Cold Bokkeveld (CM2) (Sephton *et al.* 1998, 2000; Sephton & Gilmour 2001b). As with the extractable aromatic compounds, large, systematic differences in $\delta^{13}C$ values have been observed for molecules (most notably in Murchison and Cold Bokkeveld) that differ by only one or two carbon atoms, with compounds from Cold Bokkeveld displaying the widest range in $\delta^{13}C$ values (~27‰). Similarities in $\delta^{13}C$ values between free and macromolecular aromatic moieties in Murchison are suggestive of a genetic relationship between the two. This conclusion is supported by the observation of two distinct trends in data from Murchison: $\delta^{13}C$ values for low molecular weight compounds generally become more positive with increasing carbon number (up to around C_{12}) while $\delta^{13}C$ values for high molecular weight PAHs become more negative with increasing carbon number. This is consistent with isotopic fractionation due to both bond formation (synthesis of higher homologs from lower ones) and bond destruction (cracking of higher homologs to form lower ones). For Cold Bokkeveld, a single dominant trend of decreasing $\delta^{13}C$ with increasing carbon number is apparent, while for Orgueil no dominant trend is apparent. It is worth noting that, for the CM2 chondrites, the carbon isotopic compositions correlate more strongly with the number of carbon atoms rather than the extent of cyclization, represented in Fig. 5 by the data plotted against H/C ratio.

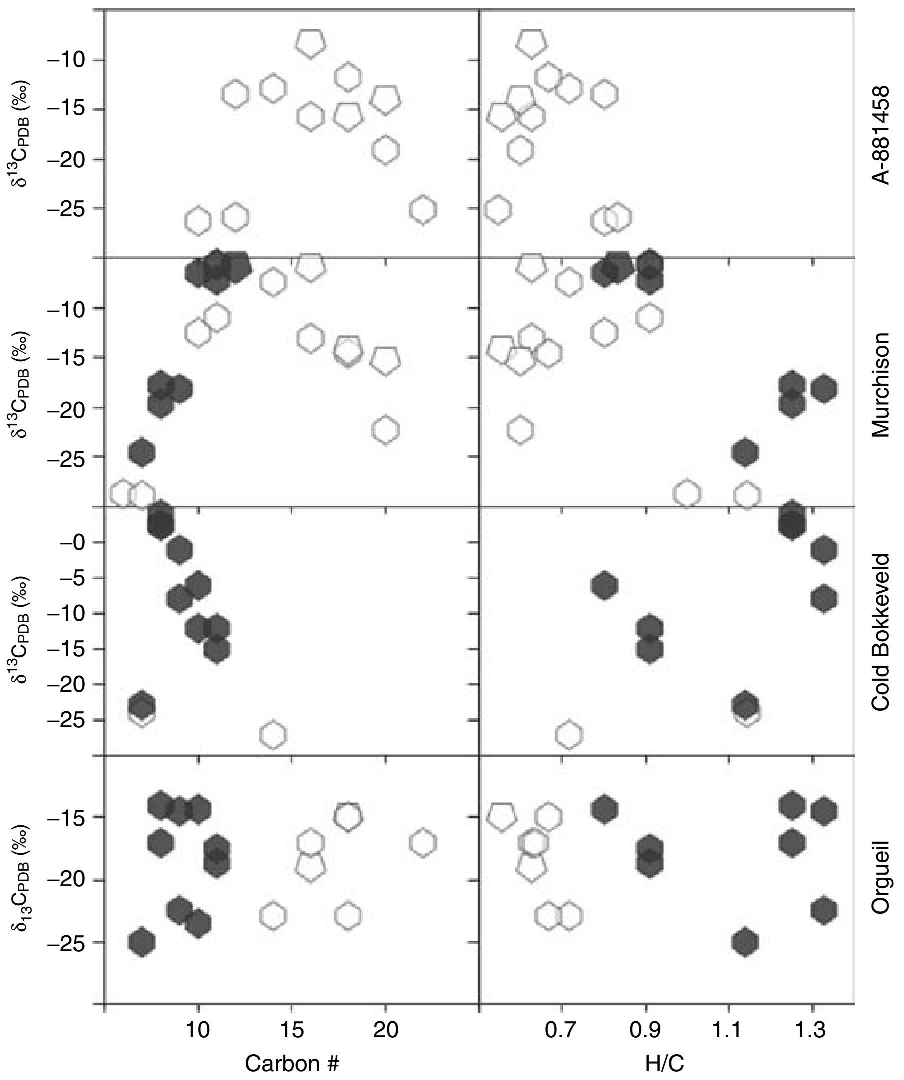

Fig. 5. Carbon isotopic compositions of individual parental and alky-substituted aromatic compounds plotted against carbon number and atomic H/C ratio for the Asuka A-881458 (CM2), Murchison (CM2), Cold Bokkeveld (CM2) and Orgueil (CI1) carbonaceous chondrites. Open symbols represent data obtained on free aromatic compounds isolated using solvent extraction; filled symbols represent data on macromolecular OM fragments released by hydrous pyrolysis. Pentagons represent PAHs containing a five-carbon ring.

This suggests that the addition or removal of C atoms is more important for the isotopic fractionation than cyclization. Such large isotopic fractionations are not observed in the synthesis of PAHs in high-temperature processes such as combustion (O'Malley *et al.* 1997). The restrictive environment of the icy organic-rich mantles of interstellar grains, where radiation-induced reactions could simultaneously create and destroy OM to produce material with an intermediate level of complexity, is a possible setting for the synthesis of precursor material for meteoritic OM (Sandford 1996). However, further experimental work is needed to establish whether the carbon isotopic variations observed are the result of fractionation during (i) the synthesis of organic compounds through processes such as the irradiation of ices, ion-molecule reactions in the gas phase or synthesis in the proto-nebula; or (ii) during hydrothermal episodes, shock-induced chemistry or irradiation on the parent body.

In situ detection

In addition to organic components, carbonaceous chondrites contain anhydrous (e.g. chondrules and mineral aggregates) and hydrous (e.g. matrix) inorganic phases. Aqueous alteration is the most widespread of the secondary processes that have affected the chondritic meteorites and there is evidence of aqueous alteration in all the major chondrite groups, with the exception of the enstatite chondrites. A number of models have been proposed for the aqueous alteration of the chondritic meteorites, reviewed by Brearley (2004). However, textural, chemical and isotopic data, especially for the CI chondrites, provide evidence that is most consistent with

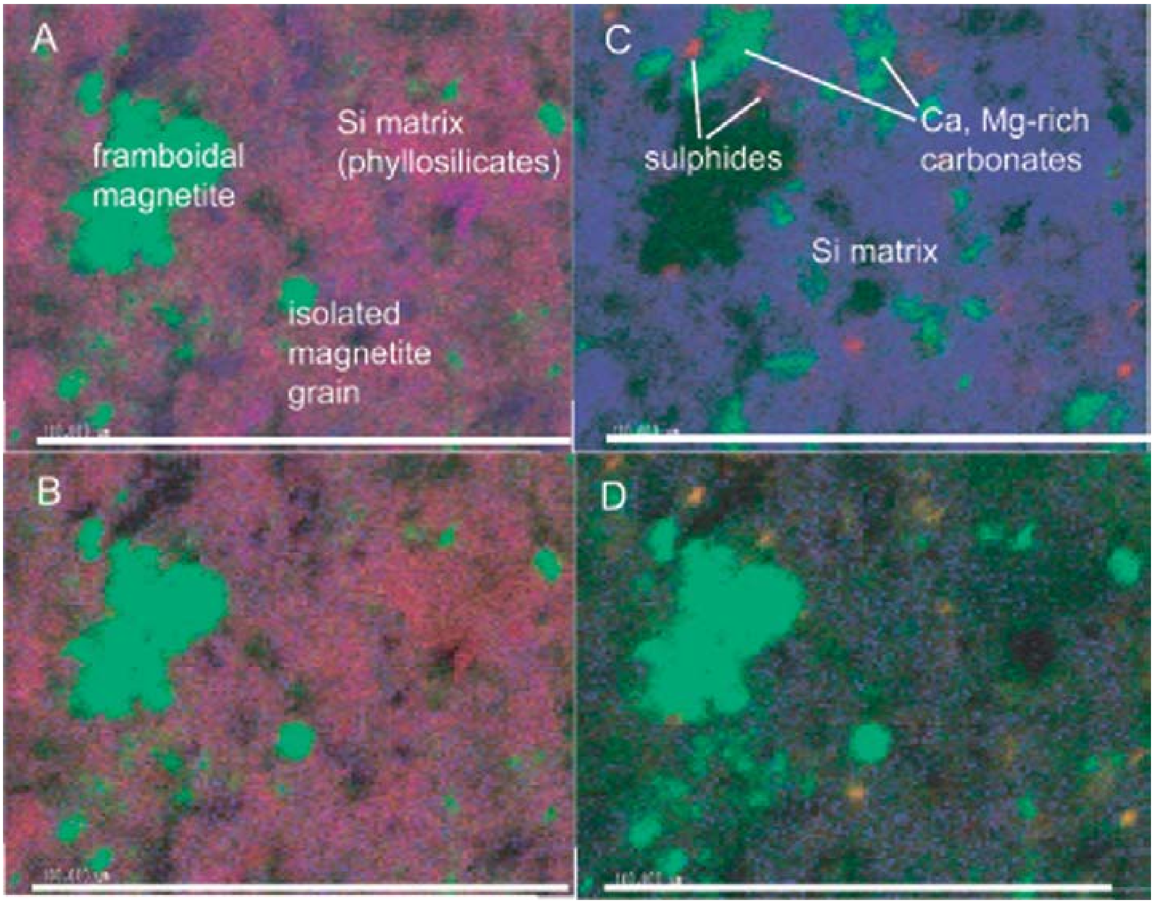

Fig. 6. Colour-coded X-ray maps of Tagish Lake. (a) OsO_4 impregnated surface. Fe is shown as green, S as red and Os as blue. Os deposition is seen within the matrix. (b) OsO_4 impregnated surface showing magnetite and matrix mineralogies. Fe is shown as green, Si as red and Os as blue. The matrix shows enrichment in Os but no presence of Os around magnetite. (c) The surface. S is shown as red, Fe as green and Si as blue. No Os is seen in association with sulphides or carbonates. (d) The surface. Fe is shown as green, Si as red and Mg as blue. The scale bar represents 100 μm.

post-accretion asteroidal alteration. However, in the least altered CM condrites there is evidence of alteration in a pre-accretionary environment; distinguishing these pre-accretionary effects from asteroidal alteration presents a significant challenge.

Understanding the relationships and interdependence of organic and inorganic components is fundamental for understanding the processes and mechanisms involved in the evolution of organic material in the early Solar System. Such relationships can only be adequately investigated using *in situ* analytical techniques. Early attempts to locate organic material employed fluorescence and suggested that OM was present as thin coatings on the surfaces of mineral grains in the Orgueil carbonaceous chondrite (Hahn *et al.* 1988; Kovalenko *et al.* 1991, 1992; Messenger *et al.* 1998). Two-step laser mass spectrometry had also been used to locate PAHs in chondrites and a link between circumstellar grains and PAHs has been inferred (Messenger *et al.* 1998).

We have employed a novel labelling technique to map the distribution of organic material in the Murchison, Ivuna, Orgueil and Tagish Lake carbonaceous chondrites (Pearson *et al.* 2002). By reacting osmium tetroxide (OsO_4) with organic material in whole rock chips of each chondrite, Os is incorporated into the organic network. Scanning electron microscopy can then visually locate the organic material and identify its accompanying mineralogy. Figures 6(a)–(d) show a colour-coded X-ray map of an OsO_4 impregnated surface of a small (*ca.* 5 mm square) fragment of the Tagish Lake (CI2) chondrite. Osmium, shown in blue in Figs 6(a) and 6(b), is observed associated with matrix mineralogies but not magnetite. Earlier studies of the distribution of OM in Orgueil using fluorescence had apparently shown OM in association with magnetite, which had been taken as possible evidence for a catalytic association between the two in the Solar nebula (Alpern & Benkeiri 1973). We have not observed such an association between OM and magnetite in any of the chondrites so far examined (Pearson *et al.* 2002). In Tagish Lake, there is also no apparent association between OM and either sulfide or carbonate mineralogies (Fig. 6(c)). However, Os-labelled organic material has consistently been observed in association with the hydrous mineral matrix.

In terrestrial systems, clay minerals are believed to provide catalytic surfaces for the polymerization of simple organic molecules (Hedges 1980; Collins *et al*. 1995; Salmon *et al*. 2000). It is conceivable therefore that clay minerals may similarly have acted as adsorbents and catalysts for polymerizations of pre-existing interstellar molecules into the macromolecules we see in carbonaceous chondrites in the early Solar System. Trapping between clay layers may have provided a mechanism to protect biologically important molecules from the harsh environment of space.

Provenance of meteoritic organic matter

Hypotheses for the origin of meteoritic organic matter have to account for its molecular and isotopic composition and be consistent with models of meteorite petrogenesis. Consequently, a number of potential environments have been considered:

1. ion–molecule reactions in interstellar clouds;
2. radiation chemistry in interstellar grain mantles;
3. condensation in stellar outflows;
4. equilibrium reactions in the Solar nebula;
5. surface catalysis (Fischer–Tropsch) in the Solar nebula;
6. kinetically controlled reactions in the Solar nebula;
7. radiation chemistry (Miller–Urey) in the nebula;
8. photochemistry in nebular surface regions;
9. liquid-phase reactions on parent asteroids;
10. surface catalysis (Fischer–Tropsch) on asteroids;
11. radiation chemistry (Miller–Urey) in asteroid atmospheres;
12. thermal processing during asteroidal heating events.

However, it has become increasingly apparent that the production of meteoritic organic matter must have involved a combination of different processes taking place in a wide range of environments. The structural, isotopic and *in situ* analysis of meteoritic organic matter reviewed herein has contributed to the development of new models for the origin of organic compounds in meteorites that envisage a distinctly different set of processes from the synthesis models proposed by earlier workers (e.g. Studier *et al*. 1968). The development of the interstellar–parent-body hypothesis based on a combination of petrographic evidence for asteroidal aqueous activity and evidence for interstellar organics has led to the development of a model in which meteoritic organic matter is envisaged as being the product of parent-body aqueous and thermal processing of reactive, volatile precursors such as water, HCN, NH_3 and ^{13}C-, ^{15}N- and D-rich interstellar organics (Cronin & Chang 1993). However, it is worth noting that the majority of our understanding of the origins of organic matter in the Solar System has come from the study of a relatively small number of carbonaceous chondrites and that further studies of different meteorites may provide new insights.

Acknowledgements

This work was supported by PPARC.

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