

Alkylation of polycyclic aromatic hydrocarbons in carbonaceous chondrites

JAMIE E. ELSILA,¹ NATHALIE P. DE LEON,¹ PETER R. BUSECK,² and RICHARD N. ZARE^{1,*}

¹Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA

²Departments of Geological Sciences and Chemistry/Biochemistry, Arizona State University, Tempe, AZ 85287-1404, USA

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Abstract—Using microprobe laser-desorption, laser-ionization mass spectrometry ($\mu\text{L}^2\text{MS}$), we measured the distributions of alkylated and unalkylated polycyclic aromatic hydrocarbons (PAHs) in the free organic material of 20 carbonaceous chondrites. These meteorites represent a variety of meteorite classes and alteration histories, including CI, CK, CM, CO, CR, CV, and Tagish Lake. This work provides information on free organic compounds that is complementary to studies of the structure and composition of meteoritic macromolecular content.

For the nine CM2 meteorites analyzed, we observe that higher relative abundances of alkylated PAHs correlate with more intense aqueous activity. We attribute this correlation to the differences in solubility and volatility between unalkylated and alkylated PAHs. Naphthalene and its alkylation series are more susceptible to the effects of aqueous exposure than the less-soluble PAH phenanthrene and its alkylated derivatives. These observations are consistent with the possibility of chromatographic separations on the meteorite parent bodies. We identify six CM2 meteorites with similar PAH distributions that may represent the original, unaltered organic composition of the parent body.

Increased metamorphic intensity reduces the abundance of all PAHs. The thermally metamorphosed CK chondrites had no detectable levels of typical meteoritic PAHs. This observation might be explained either by a loss of PAHs caused by volatilization or by a significantly different organic content of the CK parent body. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

The carbonaceous chondrite meteorites are among the oldest and most primitive solid materials in the solar system. Carbonaceous chondrites contain up to 3% carbon by weight, in the form of a variety of organic compounds (Cronin and Chang, 1993). The majority of meteoritic organic carbon occurs as an insoluble macromolecular material composed largely of aromatic rings cross-linked by aliphatic chains, esters, ethers, sulfides, and other functional groups (Hayatsu et al., 1977). This macromolecular material has been the subject of many recent studies aimed at elucidating its structure and composition (Gardinier et al., 2000; Sephton et al., 2000, 2004; Pizzarello et al., 2001; Cody et al., 2002; Sephton, 2002). Up to 30% of organic material in carbonaceous chondrites, however, is in a solvent-extractable form containing aromatic and aliphatic hydrocarbons, amino acids, and other compounds (Hayes, 1967; Cronin et al., 1988). At least some of this solvent-extractable organic material (referred to as the “free organic material”) appears to be related to the macromolecular material, perhaps deriving from a preterrestrial alteration event (Sephton et al., 1998; Sephton et al., 2003).

Such alteration events, caused by thermal activity and liquid water on meteorite parent bodies, had the potential to modify the original distribution of organics. Based on isotopic evidence, it is clear that at least some meteoritic organic components (both free and macromolecular) are interstellar in origin, indicating that meteoritic organic material may provide a record of the chemistry that occurred in the interstellar medium

and the solar nebula (Robert and Epstein, 1982; Yang and Epstein, 1983; Kerridge et al., 1987; Pizzarello et al., 1991; Messenger et al., 1998). The observed mineralogy of carbonaceous chondrites demonstrates, however, that conditions necessary for aqueous and thermal alteration were present on many parent bodies (McSween et al., 1988; Zolensky and McSween, 1988; Buseck and Hua, 1993). This observation suggests that the final composition of meteoritic organics reflects both interstellar and parent-body environments (Cronin and Chang, 1993). Thus, one might expect a relationship between the chemical and spatial distributions of organics on carbonaceous chondrites and their alteration histories.

The carbonaceous chondrites are subdivided into several classes, each defined by characteristic mineral and chemical properties, as well as by thermal and aqueous alteration histories (Sears and Dodd, 1988). The alteration processes that occurred on meteorite parent bodies had the potential to cause chemical reactions and change the chemical and spatial distributions of organic compounds. Correlations between the structure of macromolecular organic material and aqueous alteration history have been shown for a small number of meteorites (Sephton et al., 2000). Thermal alteration has been correlated with both graphitization of macromolecular material (Kitajima et al., 2002) and the abundance of free organic material in CM chondrites (Naraoka et al., 2004). The spatial distribution of free and macromolecular organic material also correlates with meteoritic features such as chondrules, inclusions, and clay minerals, which indicates a link between parent body history and chemistry (Pearson et al., 2002; Plows et al., 2003).

Polycyclic aromatic hydrocarbons (PAHs) constitute a class of organic compounds composed of two or more fused benzene rings. They are estimated to contain up to 20% of galactic

* Author to whom correspondence should be addressed (zare@stanford.edu).

carbon, and are abundant in the interstellar medium (Allamandola et al., 1989; Puget and Leger, 1989). PAHs are also among the most prevalent meteoritic organics (Mullie and Reisse, 1987), and are important components of both the free and macromolecular organic material. Many meteoritic PAHs are functionalized with aliphatic side chains, hydroxyl groups, or other structures (Oro et al., 1971; Pering and Ponnampereuma, 1971). The structure, position, and number of these side groups, particularly the alkyl chains, may be influenced by the aqueous and thermal conditions experienced by the meteorites (Sephton et al., 2000).

In this paper, we report on the distribution of PAHs measured in the free organic material of 20 carbonaceous chondrites. The analyzed meteorites include representatives of six major classes (CV, CO, CI, CM, CR, and CK), as well as three meteorites with less well-defined classifications (Tagish Lake, Coolidge, and MAC 88107). They range in alteration history from type 1 and 2 (extensive and moderate aqueous alteration, respectively), to type 3 (little thermal or aqueous alteration) and type 4 to 5 (moderate to high thermal alteration).

We measured the relative amounts of the PAHs naphthalene ($C_{10}H_8$) and its alkylated derivatives, phenanthrene ($C_{14}H_{10}$) and its alkylated derivatives, and pyrene ($C_{16}H_{10}$) in these meteorites. Samples were analyzed by microprobe laser-desorption, laser-ionization mass spectrometry (μL^2MS), a sensitive and selective technique that has been used to detect PAHs in a variety of samples, including ancient terrestrial rocks (Mahajan et al., 2001), soils and sediments (Gillette et al., 1999; Ghosh et al., 2000), interplanetary dust particles (Clemett et al., 1993), kerogens (Zhan et al., 1997), and meteorites (Zenobi et al., 1989; McKay et al., 1996; Plows et al., 2003). We observe correlations between the degree of alkylation and the alteration history of the meteorites that suggest a link between the parent body environment and the PAH inventory of a given meteorite. To our knowledge, this work represents the most extensive analysis of aromatic compounds and their distributions across the carbonaceous chondrite classes.

2. EXPERIMENTAL

2.1. Meteorite Samples

Carbonaceous chondrites were obtained from several sources, as detailed in Table 1. All except the Tagish Lake sample were received as chunks no less than 1 cm per side, ranging from 2 g to 40 g in mass. The Tagish Lake sample was obtained as a powder that had been ground from a pristine sample of the meteorite collected without exposure to liquid water.

Fresh interior chips of each sample (excluding Tagish Lake) were removed using a clean chisel. Each chip (~ 10 mg) was enveloped in aluminum foil and crushed to a fine powder using an alumina pestle. Each resulting powder was mixed to provide a homogeneous sample reservoir for mass spectral analysis. Three chips were taken from each meteorite sample and powdered separately to provide replicate measurements. The Tagish Lake powder was used as received, with no additional preparation.

Studies of the Orgueil meteorite indicate exposure to terrestrial contamination (Anders et al., 1964; Sephton et al., 2001; Watson et al., 2003). Contamination of the free organic material by *n*-alkanes, pristane, phytane, and terpenoids has been reported; although PAHs and their alkylated derivatives have been identified in the free organic material of Orgueil, there is no reported evidence that they are terrestrial contaminants (Watson et al., 2003). The PAH distributions from likely sources of terrestrial contamination show a predominance of alkylated PAHs (Gingrich et al., 2001). By contrast, the Orgueil dis-

Table 1. Carbonaceous chondrite samples.

Meteorite	Class	Source ^a
ALH 84039	CM2	UCSC/JSC
ALH 84044	CM2	UCSC/JSC
ALH 85013	CM2	JSC
Cold Bokkeveld	CM2	UCSC/FM
LEW 85311	CM2	UCSC/JSC
Mighei	CM2	UCSC/FM
Murchison	CM2	NMC
Murray	CM2	ASU
Nogoya	CM2	ASU
GRA 95229	CR2	JSC
MAC 88107	C2	UCSC/JSC
Tagish Lake	C2	NASA
Orgueil	CI1	UCSC/FM
Allende	CV3	ASU
Mokoia	CV3	ASU
ALH 83108	CO3	JSC
Coolidge	C4	ASU
ALH 85002	CK4	JSC
EET92002	CK5	JSC
Karoonda	CK4	ASU

^a ASU = Center for Meteorite Studies, Arizona State University; JSC = Antarctic Meteorite Collection, NASA Johnson Space Center; UCSC/JSC = D. Deamer, UC-Santa Cruz, originally from Antarctic Meteorite Collection; UCSC/FM = D. Deamer, UC-Santa Cruz, originally from Field Museum of Chicago; NMC = National Meteorite Collection, Smithsonian Institution; NASA = D. Cruikshank, NASA/Ames Research Center, originally from M. Zolensky.

tributions measured in our work show moderate levels of alkylated PAHs, on the same order as several of the other meteorites in which contamination is not suspected.

2.2. Microprobe Laser-Desorption, Laser-Ionization Mass Spectrometry

Powdered meteorite samples were mounted on brass sample platters using double-sided tape; these platters were then introduced into the vacuum chamber of the μL^2MS instrument for analysis. A detailed description of this instrument is provided elsewhere (Clemett and Zare, 1997). Briefly, in the first step of the technique, a pulsed IR laser beam (10.6- μm wavelength) is focused to a 40- μm spot on the sample surface, releasing constituent sample molecules through thermal desorption. In the second step, a pulsed ultraviolet laser (266 nm) selectively ionizes the desorbed aromatic molecules; compounds such as aliphatic hydrocarbons that do not have an appropriate electronic transition are not ionized and hence are not detected. The resulting ions are analyzed in a reflectron time-of-flight mass spectrometer. The mass spectra consist of the PAHs and their derivatives and show little evidence for fragmentation of the desorbed molecules. Heterocyclic aromatics are detected to varying degrees, as described in section 3.4.

The degree to which the desorption step combines thermal desorption of the free organic material with pyrolysis of the macromolecular material is a key factor in properly interpreting μL^2MS results of meteorite powders. We compared μL^2MS spectra of whole meteorite powders, solvent-extracted powders (Soxhlet extracted for 24 h in toluene), macromolecular material (acid-demineralized and extracted to remove free organics; Cronin et al., 1987), and partially pyrolyzed material (Sephton et al., 2004) from the Allende and Murchison meteorites. Comparison of the analyzed results indicated that more than 90% of the observed PAH signal arose from the free organic material; the samples that had been extracted or pyrolyzed to remove the free component resulted in low signal levels (Fig. 1). We therefore interpret the spectra in this study as essentially representing the free organic components of the carbonaceous chondrites.

The μL^2MS method is not strictly quantitative because its signal intensity is a function of several properties of a given analyte, including

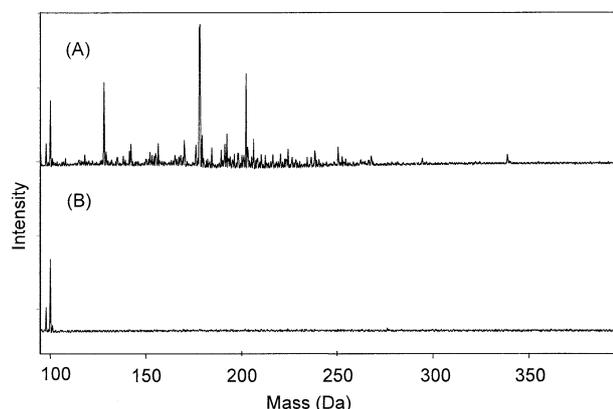


Fig. 1. $\mu\text{L}^2\text{MS}$ spectra of (A) unextracted Murchison powder and (B) solvent-extracted Murchison macromolecular material. The peak at 100 Da is d_8 -toluene, a mass calibrant.

photoionization cross-section, ionization efficiency, the matrix in which the analyte is embedded, and the interaction of the desorption laser with that matrix. The effect of different matrices is seen most clearly when comparing different sample types such as minerals, plastics, metals, and thin films. For the meteorites studied in this work, the matrices are similar enough to cause negligible differences in signal strength.

The photoionization cross-section and ionization efficiency differ from compound to compound, leading to different instrument response factors. Isomers with different aromatic skeletons have response factors in our instrument that differ by nearly a factor of 20 (McGlathlin, 2003). We can therefore assign mass peaks to the more sensitively detected isomer (e.g., 178 Da to phenanthrene rather than anthracene, and 202 Da to pyrene rather than fluorene).

To a first approximation, however, alkylation (replacement of $-\text{H}$ with $-\text{CH}_3$) does not significantly change the photoionization cross-section. This means that the $\mu\text{L}^2\text{MS}$ response to a PAH and its alkylated derivatives (e.g., naphthalene and methylnaphthalene) is roughly equal and their relative concentrations in a sample can be inferred from the ratio of their $\mu\text{L}^2\text{MS}$ peak areas. Conversely, a direct comparison of the peak areas for two structurally different PAHs (e.g., naphthalene and phenanthrene) does not generally correspond to their exact relative concentrations. A *change* in the relative peak areas of these PAHs, however, is significant. For example, a difference in the naphthalene:phenanthrene ratio across several meteorites indicates that different relative amounts of these PAHs are present, although their exact concentrations cannot be calculated. The ratios of these peak areas depend on instrumental parameters such as desorption laser power and ionization laser alignment (Elsila et al., 2004); for this reason, most of the meteorites to be compared in this study were analyzed in 1 d under identical $\mu\text{L}^2\text{MS}$ instrumental conditions. The exceptions to this procedure were the three CK meteorites, which were analyzed one day under identical conditions to the main set of meteorites and with a subset of the other meteorites for comparison.

The $\mu\text{L}^2\text{MS}$ technique produces a complete mass spectrum for each IR desorption shot. In this work, sets of 25 shots were averaged using a digital oscilloscope (Waverunner LT342, LeCroy, Chestnut Ridge, NY, USA). Three 25-shot averages were acquired for each meteorite powder sample, for a total of nine 25-shot-average spectra per meteorite. PAH peak areas for each averaged mass spectrum were integrated using IGOR software (Wavemetrics, Lake Oswego, OR), and the mean and standard deviation of the nine measurements were used as the data point for a given meteorite. Table 2 shows the structures and masses of some of the analyzed PAHs. The structures of the alkylated PAHs are not shown because $\mu\text{L}^2\text{MS}$ is incapable of distinguishing among isomers at a fixed wavelength. Peaks identified as C_2 -naphthalene, for example, represent the addition of two carbons to the parent structure of naphthalene, either as two methyl groups (dimethylnaphthalene) or as an ethyl group (ethylnaphthalene); the position of the substituent group or groups cannot be determined.

Table 2. Masses and structures of PAHs.

Compound	Mass	Structure
Naphthalene	128 Da	
C_1 -naphthalene	142 Da	
C_2 -naphthalene	156 Da	
C_3 -naphthalene	170 Da	
Phenanthrene	178 Da	
C_1 -phenanthrene	192 Da	
C_2 -phenanthrene	206 Da	
C_3 -phenanthrene	220 Da	
Pyrene	202 Da	

3. RESULTS AND DISCUSSION

3.1. Naphthalene Alkylation Series

Figure 2 shows the naphthalene alkylation distribution for 16 of the 20 analyzed carbonaceous chondrites; the three CK meteorites and the Coolidge sample did not contain detectable levels of naphthalene (see discussion below). On these spider graphs, each spoke represents a given alkylated species (increased alkylation proceeding clockwise), and the distance to the spoke corresponds to the integrated peak area for that compound normalized to that of naphthalene. The unalkylated “parent” PAH is represented on the vertical axis. To simplify the graphs, error bars are not displayed, but the relative standard deviations for these measurements are typically 10%–20%. The meteorites are grouped to highlight similarities in distributions and classification.

Figure 2A displays the results for six CM2 meteorites. The naphthalene alkylation distributions for these six meteorites are similar, matching each other within one standard deviation. Unsubstituted naphthalene is more abundant than any of the alkylated naphthalene compounds, and the relative amounts of the compounds decrease with increasing alkylation. This observation matches previous analyses of the Murchison meteorite (Tingle et al., 1991). The three CM2 meteorites represented in Figure 2B, however, do not match this pattern. In the Mighei meteorite sample, increasing alkylation correlates with increasing abundance, with a C_3 -naphthalene peak area that is 85% that of the unalkylated naphthalene. The Cold Bokkeveld meteorite contains more alkylation, with peak areas for the C_1 - to C_3 -naphthalene compounds approximately equal to that of the unalkylated naphthalene. The Nogoya sample reveals the highest level of alkylation in these CM2 meteorites, peaking with a C_3 -naphthalene signal that is greater than twice that of the signal from unalkylated naphthalene.

The CM2 meteorites all underwent moderate aqueous alteration on the meteorite parent body, but the degree of aqueous exposure varies. Studies suggest that the amount of aqueous alteration increases in the order Murchison < Murray < Mighei < Nogoya < Cold Bokkeveld (Browning et al., 1996); there are no data on the relative amounts of aqueous exposure for the Antarctic CM2 meteorites we studied (ALH 84039, ALH 84044, ALH 85013, and LEW 85311). A correlation thus

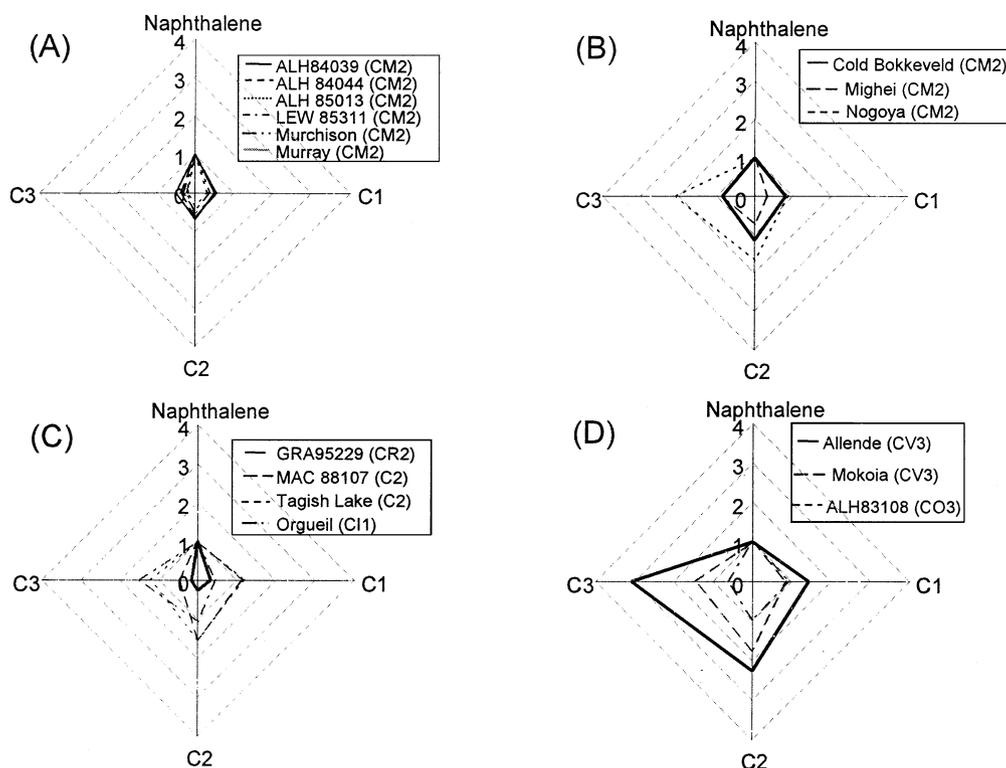


Fig. 2. Naphthalene alkylation distributions for four sets of carbonaceous chondrites. The symbols C1, C2, and C3 represent mono-, di-, and trialkylated naphthalene.

appears between extent of aqueous alteration and naphthalene alkylation pattern in our measurements, at least for those meteorites for which we have information on aqueous exposure; the most aqueously altered CM2 meteorites have the highest amount of naphthalene alkylation.

Figure 2C presents the degree of naphthalene alkylation for four non-CM2 carbonaceous chondrites that also underwent aqueous alteration. The meteorite GRA 95229 shows a degree of naphthalene alkylation similar to that of the meteorites displayed in Figure 2A, with an inverse correlation between abundance and alkylation. This CR2 meteorite has seen moderate aqueous alteration (Weisberg et al., 1993). The ungrouped C2 meteorite MAC 88107 has high abundances of C₁- and C₂-naphthalene, similar to the meteorites in Figure 2B, but low levels of C₃-naphthalene, similar to those in Figure 2A. The Tagish Lake meteorite, also an ungrouped C2 chondrite (Zolensky et al., 2002), has relatively high amounts of alkylation, as does the Orgueil (CI1) meteorite sample, which has been extensively aqueously altered (Tomeoka and Buseck, 1988). As with the meteorites presented in Figure 2A and 2B, increasing degree of naphthalene alkylation appears to correlate with increasing aqueous alteration.

Figure 2D displays the naphthalene alkylation distribution for three meteorites that have undergone less alteration than those in Figures 2A–C. The Allende and Mokoia meteorites are both CV3 carbonaceous chondrites. Studies suggest that Mokoia has seen some amount of aqueous and anhydrous alteration (Tomeoka and Buseck, 1990; Kimura and Ikeda, 1998), while Allende may have experienced slight thermal and hydrothermal alteration (Keller and Buseck, 1991; Guimon et

al., 1995), and both meteorites show evidence of oxidation (McSween, 1977). These two meteorites have high amounts of alkylation, with alkylated naphthalene compounds being more abundant than unalkylated naphthalene. The Allende meteorite contains higher levels of naphthalene alkylation than any other meteorite studied in this work. The third meteorite displayed, ALH 83108, is classified CO3, and reveals moderate amounts of alkylated naphthalene compounds that decrease in concentration with increasing alkylation.

Four analyzed meteorites are not displayed in Figure 2 because they had undetectable levels of naphthalene or its derivatives. The $\mu\text{L}^2\text{MS}$ spectra of the three CK meteorites analyzed (ALH 85002, EET 92002, and Karoonda) are strikingly different from all other carbonaceous chondrites studied, but show similarities to each other (Fig. 3). The PAHs commonly detected in meteorites (e.g., naphthalene, phenanthrene, pyrene) were not observed, although other unidentified peaks were seen at 135 Da, 179 Da, and 250 Da. The presence of odd masses suggests the possible incorporation of nitrogen into these hydrocarbons, either as side chains or as part of the parent skeleton (see Section 3.4 for more discussion). Overall signal intensity was also much lower than in most other analyzed chondrites. The CK meteorites have all undergone thermal metamorphism (Kallemeyn et al., 1991); it is possible that this metamorphism caused the volatilization and loss of PAHs from the free organic material. It is also possible that the CK meteorites, for which there are no reported studies of organic content, originated from a parent body whose organic content is markedly different from the parent bodies of the other carbonaceous chondrites. The Coolidge meteorite, an ungrouped C4

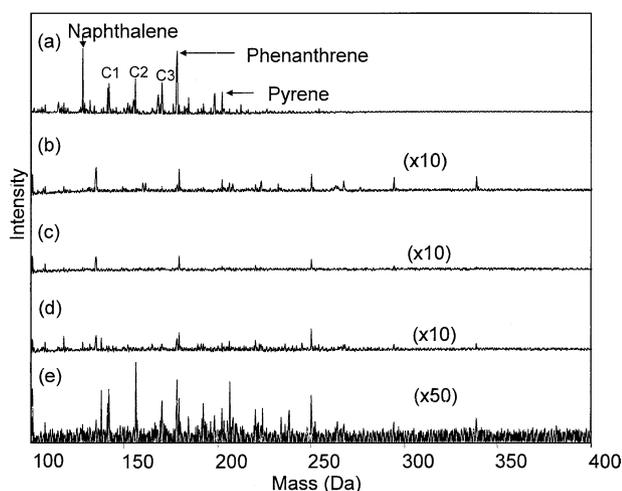


Fig. 3. $\mu\text{L}^2\text{MS}$ spectra for (a) Nogoya, a CM2 chondrite; (b) ALH 85002, a CK4 chondrite; (c) EET 92002, a CK5 chondrite; (d) Kaarooda, a CK4 chondrite; and (e) Coolidge, a C4 chondrite. Traces (b), (c), and (d) are magnified 10 times relative to (a); trace (e) is magnified 50 times. The mass spectra of the CK chondrites do not exhibit the typical PAH peaks shown in Nogoya. Coolidge exhibits typical PAH signals, but with diminished intensity.

meteorite (Kallemeyn and Rubin, 1995), has also been thermally altered. Its mass spectrum has some similarities to those of the CK chondrites, but also exhibits the meteoritic PAHs typically seen in the CM, CO, and CV meteorites, albeit at very low levels. Alkylated naphthalenes are detected, but unalkylated naphthalene is not. It is possible that thermal metamorphism caused the preferential loss of naphthalene, the most volatile PAH, from the free organic material of this meteorite.

The observed naphthalene alkylation distributions for these 20 carbonaceous chondrites reveal information about meteoritic organic content. First, it is clear that, contrary to our previous preliminary report on PAH alkylation in the Allende and Murchison meteorites (Plows et al., 2003), there are differences in the degree of alkylation between these meteorites. This contradiction can be explained by our better understanding of the dependence of PAH ratios on $\mu\text{L}^2\text{MS}$ operating parameters (Elsila et al., 2004), and by our current sample protocol, which takes this dependence into account by measuring all meteorites under identical conditions.

Another key observation is that there exist both similarities and trends in the naphthalene alkylation data; six of the nine CM2 meteorites, as well as the similarly aqueously altered CR2 sample, have matching degrees of alkylation. The other CM2 meteorites, as well as the ungrouped C2 and C1 samples examined, show increased amounts of alkylation corresponding to their greater aqueous alteration. One possible explanation for this observation is that aqueous exposure on the meteorite parent body could lead to chromatographic separation (Wing and Bada, 1991). PAHs are relatively insoluble in water, but naphthalene has a higher solubility than its alkylated derivatives [31 mg/L for naphthalene compared to 25 mg/L for 2-methylnaphthalene and 2.5 mg/L for 2,3-dimethylnaphthalene (Mackay et al., 1992)], and would be more transportable through the parent body. This differential transport would leave behind the less-soluble alkylated naphthalenes, thereby increas-

ing their relative concentrations. The transported naphthalene cannot simply disappear, however, and must ultimately reside somewhere. This suggests either that there are portions of the parent body enriched in naphthalene relative to its alkylated derivatives (creating a mirror image distribution of what is observed here), or that the naphthalene has been lost to space, depleting the entire parent body. Chromatographic transport could move naphthalene outward from the center of the parent body to its edges, where volatilization and loss could occur.

It is also possible that differences in volatility between naphthalene and its alkylated derivatives could account for some of our observations. Although hydrothermal alteration probably occurred at maximum temperatures less than 150°C (Zolensky and McSween, 1988), naphthalene has a significantly higher vapor pressure than some of its alkylated derivatives (Shiua and Mab, 2000), and could be preferentially lost or transported during thermal processing.

It is more difficult to explain the naphthalene distributions in meteorites that appear essentially free of aqueous alteration. Thermal metamorphism appears to remove naphthalene and its derivatives from the free organic material, most likely through volatilization. The relatively high amounts of alkylation in the CV3 and CO3 meteorites are unexpected and may reflect differences in organic content of the meteorite parent bodies. The high degree of alkylation observed in Allende is counterintuitive, given that oxidation appears to have played a role in the chemical history of this meteorite (McSween, 1977), and cannot currently be explained. It is possible that terrestrial contamination of the Allende meteorite may have contributed to the high concentration of alkylated naphthalenes. We obtained similar results (not shown) upon analysis of five separate Allende samples (18 g–30 g in size) from Arizona State University, however, indicating that the high degree of naphthalene alkylation occurs in several portions of the meteorite.

3.2. Phenanthrene Alkylation Series

Figure 4 shows the phenanthrene alkylation distribution for 17 carbonaceous chondrites; they are grouped identically to Figure 2, with the addition of the Coolidge meteorite (Fig. 4D). The degree of phenanthrene alkylation again appears to correlate with meteorite class and alteration history, although there are significant differences from the naphthalene alkylation distribution.

Figure 4A presents the same six CM2 meteorites as Figure 2A; again, the six show degrees of alkylation that agree within experimental uncertainty. The alkylated phenanthrene compounds are less abundant than unalkylated phenanthrene. Figure 4B displays the three CM2 meteorites that exhibit the most aqueous alteration. Cold Bokkeveld again has high levels of alkylation, with C_1 - and C_2 -phenanthrene abundances equal to that of unalkylated phenanthrene. The Mighei meteorite contains moderate amounts of phenanthrene alkylation, and the phenanthrene alkylation distribution of the Nogoya meteorite matches the six meteorites of Figure 4A. It thus appears that aqueous alteration may correlate with increased phenanthrene alkylation in the CM2 meteorites, but to a lesser extent than with naphthalene alkylation. The four aqueously altered meteorites of Figure 4C support this hypothesis. All contain higher relative abundances of alkylated phenanthrenes than the meteorites of Figure 4A, although the degree of alkylation is less

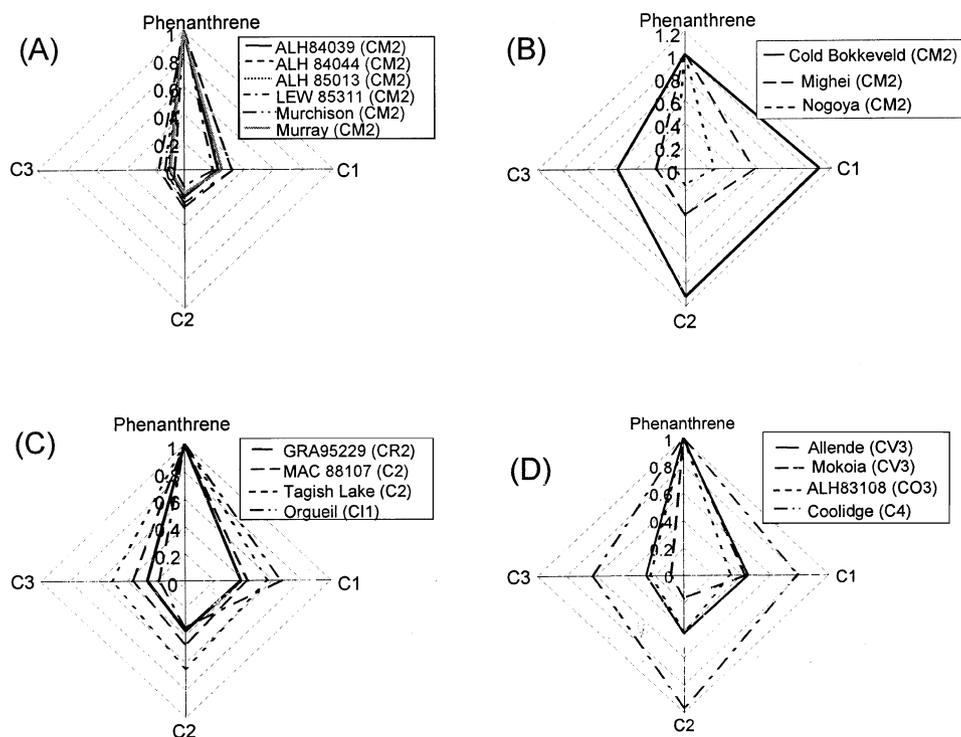


Fig. 4. Phenanthrene alkylation distributions for four sets of carbonaceous chondrites. The symbols C1, C2, and C3 represent mono-, di-, and trialkylated phenanthrene.

than that of the corresponding naphthalene series. In all cases, unalkylated phenanthrene is more abundant than its alkylated derivatives.

Figure 4D presents the data from the CV3, CO3, and C4 meteorites; the three CK meteorites are not included because they contained no detectable levels of phenanthrene or its alkylated derivatives. All these meteorites contain more unalkylated phenanthrene than alkylated compounds. The Coolidge meteorite shows the highest degree of alkylation; Allende, Mokoia, and ALH 83108 are similar to the aqueously altered meteorites of Figure 4C.

The degree of phenanthrene alkylation in these carbonaceous chondrites is not as variable as the corresponding naphthalene alkylation series, but the phenanthrene series still provides useful information. One significant observation is the well-matched distributions in six of the nine CM2 chondrites. Combined with the similarities in their naphthalene distributions, this behavior suggests that the PAH content of these six meteorites represents the original, unaltered organic content of the CM2 parent body. The differences observed in the other three CM2 meteorites may represent localized differences on the parent body caused by varying exposure to hydrothermal alteration.

Aqueous alteration in the non-CM2 meteorites appears to have less effect on phenanthrene alkylation than on naphthalene alkylation, although increased exposure to water still correlates with slightly higher degrees of alkylation. This observation may corroborate the suggestion in the previous section that the relatively high solubility of naphthalene is responsible for the correlation between aqueous alteration and high naphthalene alkylation. The solubility of phenanthrene in water is

much lower than naphthalene [1.1 mg/L vs. 31 mg/L (Mackay et al., 1992)], making it less susceptible to chromatographic separation or hydrothermally induced loss, and accounting for the smaller differences in phenanthrene alkylation distributions among meteorites.

The effect of thermal metamorphism on phenanthrene alkylation is more difficult to discern. The thermally altered CK meteorites do not contain measurable levels of phenanthrene or its derivatives. The Coolidge meteorite, however, which has also been thermally altered, does contain alkylated and unalkylated phenanthrene, in distributions similar to those in other carbonaceous chondrites. This again suggests that either the CK parent body has a significantly different distribution of PAHs than the other meteorite parent bodies, or that more intense thermal exposure in the CK chondrites has caused the volatilization and loss of the free aromatic compounds.

3.3. Parent PAHs

Figure 5 displays the relative peak areas of the unalkylated PAHs naphthalene, phenanthrene, and pyrene for 17 carbonaceous chondrites. To simplify comparison, the meteorites are grouped similarly to their arrangements in Figures 2 and 4.

The six CM2 chondrites with matching naphthalene and phenanthrene alkylation distributions have similar parent PAH distributions, with the exception of the pyrene:phenanthrene ratio in ALH 84039. This similarity supports the suggestion that the PAHs in these meteorites represent the original organic content of the CM2 parent body. The three CM2 chondrites that show differences in alkylation distributions from the other CM2 samples also differ in their

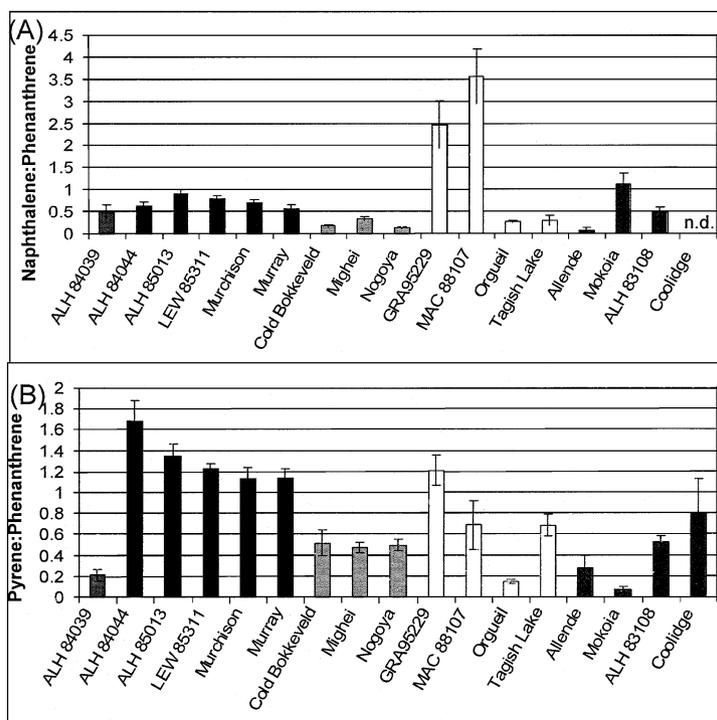


Fig. 5. Comparison of (A) the naphthalene:phenanthrene ratio and (B) the pyrene:phenanthrene ratio for 17 carbonaceous chondrites.

parent PAH ratios. This trend supports the idea that chromatographic separation caused by aqueous alteration affected PAH distribution.

The two CV3 meteorites, Allende and Mokoia, reveal different parent PAH ratios. This variation may be caused by the differences in alteration processes that Allende and Mokoia experienced, as described in the section on naphthalene alkylation. The remaining meteorites are difficult to interpret; there are no immediately apparent trends that may be explained by aqueous exposure or thermal metamorphism. Studies suggest that aqueous alteration correlates with the dominant ring size of PAHs in meteoritic macromolecular material, with increasing alteration causing a larger ratio of small (one-ring) compounds to larger (two-ring) compounds (Sephton et al., 2000). The $\mu\text{L}^2\text{MS}$ measurements do not include one-ring compounds, but we can compare the abundance of two-ring (naphthalene) to three-ring (phenanthrene) compounds as a measure of the relationship between ring size and alteration. The reported macromolecular correlation does not appear to be true for the free organic material in the meteorites we studied. For example, both aqueous alteration and the one-ring:two-ring macromolecular ratio follow the order Murchison < Cold Bokkeveld < Orgueil (Sephton et al., 2000). The $\mu\text{L}^2\text{MS}$ measurements of the free organic component of these same meteorites reveal a naphthalene:phenanthrene ratio that increases in the order Cold Bokkeveld < Orgueil < Murchison. This observation indicates that although the free organic material and the macromolecular material may be closely related, they can have significant compositional differences.

4. HETEROCYCLIC AROMATICS

Although the most prominent mass peaks in the $\mu\text{L}^2\text{MS}$ spectra correspond to parent PAHs and their alkylated derivatives, some peaks arising from heterocyclic aromatics may be present. Such heterocyclic compounds, particularly those containing oxygen, have been identified in previous studies of carbonaceous chondrites (Cronin and Chang, 1993; Pizzarello et al., 2001). It is difficult to quantify these heterocyclics in the present work, however, because they often have very small peak areas and cannot be unambiguously identified. For example, mass peaks at 184 Da and 234 Da may correspond to C_4 -naphthalene and C_4 -phenanthrene, or they may arise from the sulfur-containing compounds dibenzothiophene and benzo-naphthothiophene. These peaks and those corresponding to their alkylated series appear strongly in the Mokoia, Mighei, Cold Bokkeveld, Orgueil, and ALH 83108 spectra, suggesting (but not confirming) the presence of sulfur-containing aromatics.

The odd-mass-number peaks observed in the CK meteorites strongly suggest possible nitrogen-containing aromatics, although it is not possible to ascertain whether the nitrogen atom is part of the skeleton or a side chain on the skeleton. For example, the peak at 179 Da could indicate phenanthridine, a benzoquinoline or benzoisquinoline, or acridine. Similarly, the peak at 135 Da could arise from adenine. Although these peaks may be present in the non-CK meteorites, they are difficult to observe and isolate. The 179 Da peak, for example, directly follows the usually strong 178 Da phenanthrene peak, and may include both *N*-containing aromatic ions and ^{13}C - or deuterium-containing phenanthrene (although preliminary iso-

topic studies by Naraoka et al. (Naraoka et al., 2002) would seem to exclude the latter possibility).

Oxygen-containing aromatics such as aromatic carboxylic acids, their imide derivatives, and carboxylated pyridines were identified in Tagish Lake and other meteorites by previous studies (Cronin and Chang, 1993; Pizzarello et al., 2001). Mass peaks corresponding to these compounds were not observed in the current $\mu\text{L}^2\text{MS}$ work. It is possible that the sensitivity of $\mu\text{L}^2\text{MS}$ to oxygen-containing aromatics is not sufficient for their detection.

5. CONCLUSIONS

Meteoritic organic compounds represent a record of both the synthetic processes that occurred in the interstellar medium and solar nebula out of which the meteorite parent bodies formed and the subsequent synthetic and alteration histories of these parent bodies. Our study of the PAH compositional distribution in the free organic material of 20 meteorites provides information about differences and similarities in organic content across the major carbonaceous chondrite classes. Contrary to previous results (Plows et al., 2003), the relative amounts of alkylated and parent PAHs vary significantly among these meteorites. We identified six CM2 meteorites with nearly identical distributions of naphthalene and its alkylated derivatives, phenanthrene and its alkylated derivatives, and pyrene. We suggest that these represent the original PAH distribution of the CM2 parent body, with different distributions appearing in CM2 meteorites that have been aqueously altered.

Aqueous alteration appears to affect naphthalene alkylation patterns more than phenanthrene alkylation, perhaps because of the higher solubility of naphthalene in water. We believe that this result supports the suggestion that chromatographic separation on the meteorite parent bodies causes the observed link between alkylation distribution and aqueous alteration.

Thermal metamorphism may reduce the overall presence of PAHs in meteorites by volatilizing those aromatics in the free organic component. The thermally altered CK meteorites contain no measurable free PAHs, suggesting either that they lost their free PAHs because of thermal exposure (which we consider the more likely explanation), or that the CK parent body did not contain significant levels of PAHs (which cannot be logically excluded).

Knowledge of the structure and content of meteoritic macromolecular material has been rapidly increasing in recent years, but many carbonaceous chondrite classes have yet to be thoroughly analyzed. A comparison of the observations from the free organic material analyzed in this study with the macromolecular material from these same or related meteorites will provide further insight into the formation, alteration, and distribution of meteoritic organic compounds.

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REFERENCES

- Allamandola L. J., Tielens A. G. G. M., and Barker J. R. (1989) Interstellar polycyclic aromatic hydrocarbons: The infrared emission bands, the excitation/emission mechanism and the astrophysical implications. *Astrophys. J.* **71**, 733–775.
- Anders E., DuFresne E. R., Hayatsu R., Cavaille A., DuFresne A., and Fitch F. W. (1964) Contaminated meteorite. *Science* **146**, 1157–1161.
- Browning L. B., McSween H. Y. Jr., and Zolensky M. E. (1996) Correlated alteration effects in CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* **60**, 2621–2633.
- Buseck P. R. and Hua X. (1993) Matrices of carbonaceous chondrite meteorites. *Annu. Rev. Earth Planet. Sci.* **21**, 255–305.
- Clemett S. J., Maechling C. R., Zare R. N., Swan P. D., and Walker R. M. (1993) Measurement of polycyclic aromatic hydrocarbons (PAHs) in interplanetary dust particles. *Lunar Planet. Sci.* **24**, 309–310.
- Clemett S. J. and Zare R. N. (1997) Microprobe two-step laser mass spectrometry as an analytical tool for meteoritic samples. In *Molecules in Astrophysics: Probes and Processes* (ed. E. F. van Dishoeck), pp. 305–320. Kluwer.
- Cody G. D., Alexander C. M. O. D., and Tera F. (2002) Solid-state (^1H and ^{13}C) nuclear magnetic resonance spectroscopy of insoluble organic residue in the Murchison meteorite: A self-consistent quantitative analysis. *Geochim. Cosmochim. Acta* **66**, 1851–1863.
- Cronin J. R., Pizzarello S., and Frye J. S. (1987) ^{13}C NMR spectroscopy of the insoluble carbon of carbonaceous chondrites. *Geochim. Cosmochim. Acta* **51**, 299–303.
- Cronin J. R., Pizzarello S. and Cruikshank D. P. (1988) Organic matter in carbonaceous chondrites, planetary satellites, asteroids and comets. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 819–857. University of Arizona Press.
- Cronin J. R. and Chang S. (1993) Organic matter in meteorites: Molecular and isotopic analysis of the Murchison meteorite. In *The Chemistry of Life's Origins*, Vol. 416 (eds. J. M. Greenberg, C. X. Mendoza and V. Pirronelle), pp. 209–258. Kluwer.
- Elsila J. E., de Leon N. P., and Zare R. N. (2004) Factors affecting quantitative analysis in laser desorption/laser ionization mass spectrometry. *Anal. Chem.* **76**, 2430–2437.
- Gardiner A., Derenne S., Robert F., Behar F., Largeau C., and Maquet J. (2000) Solid state CP/MAS ^{13}C NMR of the insoluble organic matter of the Orgueil and Murchison meteorites: Quantitative study. *Earth Planet. Sci. Lett.* **184**, 9–21.
- Ghosh U., Gillette J. S., Luthy R. G., and Zare R. N. (2000) Microscale location, characterization and association of polycyclic aromatic hydrocarbons on harbor sediment particles. *Environ. Sci. Technol.* **34**, 1729–1736.
- Gillette J. S., Luthy R. G., Clemett S. J., and Zare R. N. (1999) Direct observation of polycyclic aromatic hydrocarbons on geosorbents at the sub-particle scale. *Environ. Sci. Technol.* **33**, 1185–1192.
- Gingrich S. E., Diamond M. L., Stern G. A., and McCarty B. E. (2001) Atmospherically derived organic surface films along an urban-rural gradient. *Environ. Sci. Technol.* **35**, 4031–4037.
- Guimon R. K., Symes S. J. K., Sears D. W. G., and Benoit P. H. (1995) Chemical and physical studies of type 3 chondrites XII: The metamorphic history of CV chondrites and their components. *Meteoritics* **30**, 704–714.
- Hayatsu R., Matsuoka S., Scott R. G., Studier M., and Anders E. (1977) Origin of organic matter in the early solar system-VII. The organic polymer in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **41**, 1325–1339.
- Hayes J. M. (1967) Organic constituents of meteorites—A review. *Geochim. Cosmochim. Acta* **31**, 1395–1440.
- Kallemeyn G. W., Rubin A. E., and Wasson J. T. (1991) The compositional classification of chondrites: V. The Karoonda (CK) group of carbonaceous chondrites. *Geochim. Cosmochim. Acta* **55**, 881–892.
- Kallemeyn G. W. and Rubin A. E. (1995) Coolidge and Loongana 001: A new carbonaceous chondrite grouplet. *Meteoritics* **30**, 20–27.
- Keller L. P. and Buseck P. R. (1991) Calcic micas in the Allende meteorite: Evidence for hydration reactions in the early solar nebula. *Science* **252**, 946–9.

- Kerridge J. F., Chang S., and Shipp R. (1987) Isotopic characterization of kerogen-like material in the Murchison carbonaceous chondrite. *Geochim. Cosmochim. Acta* **51**, 2527–2540.
- Kimura M. and Ikeda Y. (1998) Hydrous and anhydrous alterations of chondrules in Kaba and Mokoia CV chondrites. *Meteorit. Planet. Sci.* **33**, 1139–1146.
- Kitajima F., Nakamura T., Takaoka N., and Murae T. (2002) Evaluating the thermal metamorphism of CM chondrites by using the pyrolytic behavior of carbonaceous macromolecular material. *Geochim. Cosmochim. Acta* **66**, 163–172.
- Mackay D., Shiu W. Y., and Ma K. C. (1992) *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*. Lewis.
- Mahajan T. B., Plows F. L., Gillette J. S., Zare R. N., and Logan G. A. (2001) Comparison of microprobe two-step laser desorption/laser ionization mass spectrometry and gas chromatography/mass spectrometry studies of polycyclic aromatic hydrocarbons in ancient terrestrial rocks. *J. Am. Soc. Mass Spectrom.* **12**, 975–987.
- McGlothlin D. R. (2003) Polycyclic aromatic hydrocarbon (PAH) response factors for microprobe laser desorption/laser ionization mass spectrometry. Master's thesis. Stanford University.
- McKay D. S., Gibson E. K., Thomas-Keptra K. L., Vali H., Romanek C. S., Clemett S. J., Chillier X. D. F., Maechling C. R., and Zare R. N. (1996) Search for past life on Mars: Possible relic biogenic activity in Martian meteorite ALH84001. *Science* **273**, 924–930.
- McSween H. Y. (1977) Petrographic variations among carbonaceous chondrites of the Vigarano type. *Geochim. Cosmochim. Acta* **41**, 1777–1790.
- McSween H. Y., Sears D. W. G. and Dodd R. T. (1988) Thermal metamorphism. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 102–114. University of Arizona Press.
- Messenger S., Clemett S. J., Amari S., Gao X., Walker R. M., Chillier X. D. F., and Zare R. N. (1998) Indigenous polycyclic aromatic hydrocarbons in circumstellar graphite grains from primitive meteorites. *Astrophys. J.* **502**, 284–295.
- Mullie F. and Reisse J. (1987) Organic matter in carbonaceous chondrites. In *Topics in Current Chemistry*, Vol. 139, pp. 85–117. Springer-Verlag.
- Naraoka H., Mita H., Komiya M., and Shimoyama A. (2002) δD of individual PAHs from Murchison and an Antarctic carbonaceous chondrite. *Geochim. Cosmochim. Acta* **66**, A546.
- Naraoka H., Mita H., Komiya M., Yoneda S., Kojima H., and Shimoyama A. (2004) A chemical sequence of macromolecular organic matter in the CM chondrites. *Meteorit. Planet. Sci.* **39**, 401–406.
- Oro J., Gibert J., Lichtenstein H., Wikstrom S., and Flory D. A. (1971) Amino-acids, aliphatic and aromatic hydrocarbons in the Murchison meteorite. *Nature* **230**, 105–106.
- Pearson V. K., Sephton M. A., Kearsley A. T., Bland P. A., Franchi I. A., and Gilmour I. (2002) Clay mineral-organic matter relationships in the early solar system. *Meteorit. Planet. Sci.* **37**, 1829–1833.
- Pering K. L. and Ponnampereuma C. (1971) Aromatic hydrocarbons in the Murchison meteorite. *Science* **173**, 237–239.
- Pizzarello S., Krishnamurthy R. V., Epstein S., and Cronin J. R. (1991) Isotopic analyses of amino acids from the Murchison meteorite. *Geochim. Cosmochim. Acta* **55**, 905–910.
- Pizzarello S., Huang Y., Becker L., Poreda R. J., Nieman R. A., Cooper G., and Williams M. (2001) The organic content of the Tagish Lake meteorite. *Science* **293**, 2236–2239.
- Plows F. L., Elsilá J. E., Zare R. N., and Buseck P. R. (2003) Evidence that polycyclic aromatic hydrocarbons in two carbonaceous chondrites predate parent-body formation. *Geochim. Cosmochim. Acta* **67**, 1429–1436.
- Puget J. L. and Leger A. (1989) A new component of the interstellar matter: Small grains and large aromatic molecules. *Ann. Rev. Astron. Astrophys.* **27**, 161–198.
- Robert F. and Epstein S. (1982) The concentration and isotopic composition of hydrogen, carbon and nitrogen in carbonaceous meteorites. *Geochim. Cosmochim. Acta* **46**, 81–95.
- Sears D. W. G. and Dodd R. T. (1988) Overview and classification of meteorites. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 3–31. University of Arizona Press.
- Sephton M. A. (2002) Organic compounds in carbonaceous meteorites. *Nat. Prod. Rep.* **19**, 292–311.
- Sephton M. A., Pillinger C. T., and Gilmour I. (1998) $\delta^{13}C$ of free and macromolecular aromatic structures in the Murchison meteorite. *Geochim. Cosmochim. Acta* **62**, 1821–1828.
- Sephton M. A., Pillinger C. T., and Gilmour I. (2000) Aromatic moieties in meteoritic macromolecular materials: Analyses by hydrous pyrolysis and $\delta^{13}C$ of individual compounds. *Geochim. Cosmochim. Acta* **64**, 321–328.
- Sephton M. A., Pillinger C. T., and Gilmour I. (2001) Normal alkanes in meteorites: Molecular $\delta^{13}C$ values indicate an origin by terrestrial contamination. *Precamb. Res.* **106**, 47–58.
- Sephton M. A., Verchovsky A. B., Bland P. A., Gilmour I., Grady M. M., and Wright I. P. (2003) Investigating the variations in carbon and nitrogen isotopes in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **67**, 2093–2108.
- Sephton M. A., Love G. D., Watson J. S., Verchovsky A. B., Wright I. P., Snape C. E., and Gilmour I. (2004) Hydropyrolysis of insoluble carbonaceous matter in the Murchison meteorite: New insights into its macromolecular structure. *Geochim. Cosmochim. Acta* **68**, 1385–1393.
- Shiu W.-Y. and Mab K.-C. (2000) Temperature dependence of physical-chemical properties of selected chemicals of environmental interest. I. Mononuclear and polynuclear aromatic hydrocarbons. *J. Phys. Chem. Ref. Data* **29**, 41–130.
- Tingle T. N., Becker C. H., and Malhotra R. (1991) Organic compounds in the Murchison and Allende carbonaceous chondrites studied by photoionization mass spectrometry. *Meteoritics* **26**, 117–128.
- Tomeoka K. and Buseck P. R. (1988) Matrix mineralogy of the Orgueil CI carbonaceous chondrite. *Geochim. Cosmochim. Acta* **52**, 1627–40.
- Tomeoka K. and Buseck P. R. (1990) Phyllosilicates in the Mokoia CV carbonaceous chondrite: Evidence for aqueous alteration in an oxidizing environment. *Geochim. Cosmochim. Acta* **54**, 1745–54.
- Watson J. S., Pearson V. K., Gilmour I., and Sephton M. A. (2003) Contamination by sesquiterpenoid derivatives in the Orgueil carbonaceous chondrite. *Org. Geochem.* **34**, 37–47.
- Weisberg M. K., Prinz M., Clayton R. N., and Mayeda T. K. (1993) The CR (Renazzo-type) carbonaceous chondrite group and its implications. *Geochim. Cosmochim. Acta* **57**, 1567–1586.
- Wing M. R. and Bada J. L. (1991) Geochromatography on the parent body of the carbonaceous chondrite Ivuna. *Geochim. Cosmochim. Acta* **55**, 2937–2942.
- Yang J. and Epstein S. (1983) Interstellar organic matter in meteorites. *Geochim. Cosmochim. Acta* **47**, 2199–2216.
- Zenobi R., Philippoz J. M., Buseck P. R., and Zare R. N. (1989) Spatially resolved organic analysis of the Allende meteorite. *Science* **246**, 1026–1029.
- Zhan Q., Zenobi R., Buseck P. R., and Teerman S. (1997) Analysis of polycyclic aromatic hydrocarbons in kerogens using two-step laser mass spectrometry. *Energy Fuels* **11**, 144–149.
- Zolensky M. and McSween H. Y. (1988) Aqueous alteration. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 114–143. University of Arizona Press.
- Zolensky M. E., Nakamura K., Gounelle M., Mikouchi T., Kasama T., Tachikawa O., and Tonui E. (2002) Mineralogy of Tagish Lake: An ungrouped type 2 carbonaceous chondrite. *Meteorit. Planet. Sci.* **37**, 737–761.