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## Hydropyrolysis of insoluble carbonaceous matter in the Murchison meteorite: New insights into its macromolecular structure

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**Abstract**—The major organic component of carbonaceous chondrites is a solvent-insoluble, high molecular weight macromolecular material that constitutes at least 70% of the total organic content in these meteorites. Analytical pyrolysis is often used to thermally decompose macromolecular organic matter in an inert atmosphere into lower molecular weight fragments that are more amenable to conventional organic analytical techniques. Hydropyrolysis refers to pyrolysis assisted by high hydrogen gas pressures and a dispersed catalytically-active molybdenum sulfide phase. Hydropyrolysis of meteorites has not been attempted previously although it is ideally suited to such studies due to its relatively high yields. Hydropyrolysis of the Murchison macromolecular material successfully releases significant amounts of high molecular weight PAH including phenanthrene, carbazole, fluoranthene, pyrene, chrysene, perylene, benzoperylene and coronene units with varying degrees of alkylation. Analysis of both the products and residue from hydropyrolysis reveals that the meteoritic organic network contains both labile (pyrolysable) and refractory (nonpyrolysable) fractions. Comparisons of hydropyrolysis yields of Murchison macromolecular materials with those from terrestrial coals indicate that the refractory component probably consists of a network dominated by at least five- or six-ring PAH units cross-linked together. Copyright © 2004 Elsevier Ltd

### 1. INTRODUCTION

The origin of life on Earth, sometime before 3.5 Ga, was the climax of a lengthy period of chemical evolution with a starting point that may have predated the formation of the Earth and Solar System around 4.6 Ga (e.g., see reviews by Nisbet and Sleep, 2001; Sephton, 2002). The Solar Nebula, from which the Sun and planets formed, contained not only simple carbon-bearing molecules like CO, CO<sub>2</sub> and CH<sub>4</sub> but inherited many more complex organic species from its parent interstellar cloud. Reconstructing how inanimate interstellar organic matter may have been transformed through solar nebula and planetary processing to the raw materials needed for life on Earth is a fundamental goal of organic cosmochemistry. Moreover, even if extraterrestrial organic matter was not directly involved in the origin of life, we can examine it and draw analogies of how natural prebiotic chemical evolution proceeded in the early Solar System and on the primitive Earth.

The Earth-based record of prebiotic chemical evolution has long-since been obliterated by geological processing. However, remains of materials that were involved in the construction of the Earth are preserved in ancient asteroids, fragments of which are naturally-delivered to the Earth as meteorites. Carbonaceous chondrites are a particularly primitive class of meteorite that contain 2 to 5 wt% carbon, most of which is present as organic matter. Much of our current understanding of meteoritic organic matter has come from investigations of the Murchison carbonaceous chondrite, approximately 100 kg of which

fell in Australia in 1969. Over the last three decades Murchison has been the focus of intensive research using the most modern techniques and, consequently, the Murchison organic inventory has become a valuable reference to which all other meteoritic organic matter may be compared. The major organic component in Murchison is a solvent-insoluble, high molecular weight macromolecular material that constitutes at least 70% of the total organic content of the meteorite (Sephton, 2002). As the dominant organic entity, this component is key to understanding the origin of meteoritic organic matter. The macromolecular material consists of an aromatic framework linked and surrounded by short functional groups.

The meteorite macromolecular material in Murchison has been investigated using nondestructive techniques such as infra-red spectroscopy (Hayatsu et al., 1977) and nuclear magnetic resonance (NMR) spectroscopy (Cronin et al., 1987; Gardinier et al., 2000; Cody et al., 2002). More commonly, the macromolecular material has been studied using destructive techniques such as pyrolysis. Pyrolysis thermally decomposes macromolecular organic material in an inert atmosphere. The pyrolysis products (the pyrolysate) are then identified, usually with a mass spectrometer, and carefully studied to reveal the constitution of the parent material. Initially this approach entailed introducing the pyrolysate directly into the mass spectrometer (e.g., Studier et al., 1972). Subsequently, to achieve higher resolution, the pyrolysis products were separated with gas chromatography (GC) before analysis by mass spectrometry (e.g., Levy et al., 1973). Most recently, the meteoritic macromolecular material has been fragmented using hydrous pyrolysis (hereafter H<sub>2</sub>O-pyrolysis), where the sample remains in contact with water for the duration of the experiment (Sep-

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ton et al., 1999). In the case of terrestrial macromolecular materials (kerogens),  $\text{H}_2\text{O}$ -pyrolysis converts more than 55% of the macromolecule to solvent-soluble products that are amenable for further analysis by GC-based systems (e.g., Lewan, 1997). A comprehensive review of the information gleaned from the pyrolysis of meteoritic macromolecular materials is presented in Sephton (2002).

To date, hydrolypyrolysis (hereafter  $\text{H}_2$ -pyrolysis) has not been applied to the study of meteorites.  $\text{H}_2$ -pyrolysis refers to open-system pyrolysis assisted by high hydrogen gas pressures ( $>10$  MPa). When applied to terrestrial kerogens, fixed-bed  $\text{H}_2$ -pyrolysis in the presence of a dispersed catalytically-active molybdenum sulfide phase commonly converts more than 85% of the macromolecule to solvent-soluble hydrocarbons (e.g., Roberts et al., 1995). A continually replenished supply of high speed hydrogen ensures that product rearrangements are minimal, thereby suppressing the recombination of pyrolysis products into a solvent-insoluble char and avoiding alteration to organic structures and stereochemistries (e.g., Love et al., 1995).

Another useful approach involves heating the macromolecular material incrementally in an oxidizing atmosphere to distinguish between carbon phases by their susceptibility to combustion. These stepped heating experiments reveal a number of isotopically-distinct components that make-up the macromolecular material (Kerridge et al., 1987; Alexander et al., 1998; Sephton et al., 2003). Recently stepped combustion-mass spectrometry (stepped combustion-MS) has been used to compare macromolecular materials naturally altered by water on the meteorite parent body with those  $\text{H}_2\text{O}$ -pyrolyzed in the laboratory (Sephton et al., 2003). The progressive loss of  $^{13}\text{C}$ - and  $^{15}\text{N}$ -enrichments during aqueous alteration allows us to recognize the degree of secondary processing for macromolecular materials. A spin-off of this approach is that the efficiency of various pyrolysis methods can be gauged by subjecting the pyrolysis residue to stepped combustion-MS.

In this paper, we present results of a  $\text{H}_2$ -pyrolysis procedure which allows the further characterization of macromolecular material in the Murchison meteorite. In particular, the release of high molecular weight entities by  $\text{H}_2$ -pyrolysis enhances our understanding of this complex organic network. In addition, by comparing stepped combustion-MS data for the residue of the  $\text{H}_2$ -pyrolysis experiment with similar data for previously reported  $\text{H}_2\text{O}$ -pyrolysis residue (Sephton et al., 2003) we can assess the efficiency of the two procedures for extracting organic units from macromolecular materials.

## 2. EXPERIMENTAL

### 2.1. $\text{H}_2$ -Pyrolysis

Crushed whole meteorite was prepared for  $\text{H}_2$ -pyrolysis treatment (Fig. 1). Solvent-extraction which removed any free organic matter and impregnation with an aqueous solution of ammonium dioxodithiomolybdate  $[(\text{NH}_4)_2\text{MoO}_2\text{S}_2]$  gave a nominal 2 wt% loading of molybdenum. Ammonium dioxodithiomolybdate reductively decomposes in situ under  $\text{H}_2$ -pyrolysis conditions above  $250^\circ\text{C}$  to form a catalytically-active molybdenum sulfide phase.  $\text{H}_2$ -pyrolysis runs were performed in an open-system temperature-programmed reactor configura-

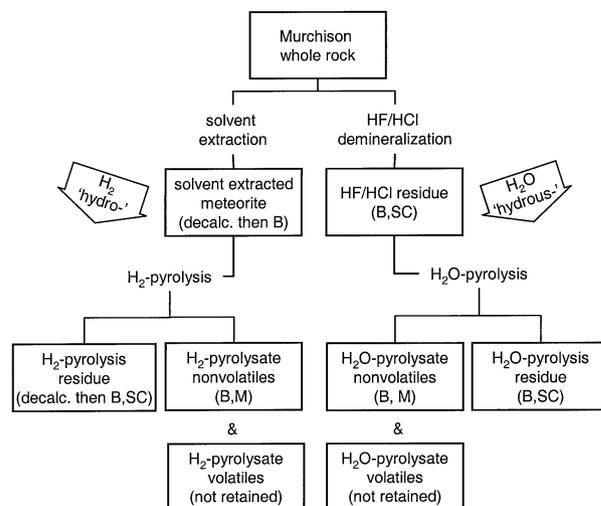


Fig. 1. Experimental flow chart indicating how the Murchison samples were processed. Types of data collected for each fraction are indicated in parentheses as follows: B = bulk C and N abundance and isotopic composition by mass spectrometry; M = molecular data by GC-MS; SC = C and N abundance and isotopic composition by stepped combustion-MS; decalc. = decalcified. For  $\text{H}_2\text{O}$  pyrolysis, GC-MS data can be found in Sephton et al. (1998), and stepped combustion data were reported in Sephton et al. (2003).

tion, which has been described in detail previously (Love et al., 1995). In this investigation, catalyst-loaded samples (50–300 mg of solvent-extracted sample) were initially heated in a stainless steel (316 grade) reactor tube from ambient temperature to  $220^\circ\text{C}$  using a rapid heating rate of  $300^\circ\text{C min}^{-1}$ , then to  $520^\circ\text{C}$  at  $8^\circ\text{C min}^{-1}$ , using a hydrogen pressure of 15 MPa. A constant hydrogen gas flow of  $6 \text{ dm}^3 \text{ min}^{-1}$ , measured at ambient temperature and pressure, through the reactor bed ensured that the residence times of volatiles generated from pyrolysis was of the order of a few seconds. The  $\text{H}_2$ -pyrolysis products (the  $\text{H}_2$ -pyrolysate) were collected in a trap cooled with dry ice and recovered in dichloromethane (DCM). The trap washings were transferred to preextracted and prebaked glass vials (120 mL) and concentrated to a small volume under a stream of nitrogen gas. Preextracted and activated copper turnings were added to the pyrolysate to remove all traces of elemental sulfur, which is formed from disproportionation of the catalyst during  $\text{H}_2$ -pyrolysis.

To reduce levels of background contamination, a cleaning run was performed before the sample run whereby the apparatus was heated to  $520^\circ\text{C}$  using a rapid heating rate ( $300^\circ\text{C min}^{-1}$ ) under high hydrogen pressure conditions. All solvents were predistilled before use and their residue contents were monitored using GC to ensure that trace organic contamination levels were acceptably low.

### 2.2. Gas Chromatography–Mass Spectrometry

Compound detection and identification was performed by gas chromatography-mass spectrometry (GC-MS) using an Agilent Technologies 6890 GC interfaced with a 5973 mass selective detector. Analyses were by splitless injection onto a BPX5 (SGE Ltd.) capillary column (30 m x 0.25 mm x 0.25

$\mu\text{m}$ ). Following a 1 min period at  $50^\circ\text{C}$  the GC oven was programmed from  $50^\circ\text{C}$  to  $300^\circ\text{C}$  at  $5^\circ\text{C min}^{-1}$  and then held at  $300^\circ\text{C}$  for 39 min. Peak identification was based on retention time and mass spectra comparisons with authenticated standards, well-characterized aromatic fractions of a coal tar and crude oil, and by reference to published reports (e.g., Kruge, 2000, and references therein). In this paper, GC-MS data is presented as either total ion chromatograms (TIC) where the complete response of the extract is displayed, or summed ion chromatograms (SIC) where only a small number of ions characteristic of certain compounds are exhibited.

### 2.3. Bulk Measurements by Isotope Ratio Mass Spectrometry

The  $\text{H}_2\text{O}$  pyrolyzed HF/HCl residue from Sephton et al. (1998) was solvent extracted. The  $\text{H}_2$ -pyrolyzed residue from this study was decalcified with increasingly concentrated HCl (0.1 mol/L through 1 mol/L), washed with distilled water until the pH was 7, and dried overnight at  $80^\circ\text{C}$ . The samples were then loaded into clean Sn buckets for combustion and analysis using an Elemental Analyser-Isotope Ratio Mass Spectrometer (PDZ Europa ANCA-SL on a Geo 20-20). The samples were introduced into a furnace containing oxygen at  $1000^\circ\text{C}$ , but where ignition of the Sn bucket subsequently raised the combustion temperature to approximately  $1600^\circ\text{C}$ . Complete sample combustion was assured by passage through chromium oxide at  $1000^\circ\text{C}$ . Any sulfur released from the samples was removed by passing the gases through CuO and Ag wool. Combustion products were entrained in a He carrier gas flowing at  $60\text{ mL min}^{-1}$ . A second furnace at  $600^\circ\text{C}$  containing Cu removed excess oxygen and nitrogen oxides.  $\text{CO}_2$  was removed using Carbosorb;  $\text{H}_2\text{O}$  was extracted with anhydrous magnesium. The abundances of stable isotopes are expressed using the  $\delta$  notation. These indicate the difference, in per mil (‰), between the relevant ratio in the sample and the same ratio in an international standard as follows:  $\delta\% = [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}] \times 1000$ . Where  $R = {}^{13}\text{C}/{}^{12}\text{C}$  for carbon and  ${}^{15}\text{N}/{}^{14}\text{N}$  for nitrogen; standard = PDB for carbon; air for nitrogen.

### 2.4. Stepped Combustion–Mass Spectrometry

The samples were analyzed by stepped combustion using two separate static mass-spectrometer systems. One system, (Finesse) comprises one quadrupole and one magnetic sector mass spectrometer joined to the same extraction line and was used to determine the amounts of carbon (in the form of  $\text{CO}_2$ ), helium, and nitrogen, and the isotopic composition of nitrogen (Wright et al., 1988; Verchovsky et al., 1997). On another instrument (MS86) amounts of carbon and its isotopic composition were measured (Wright and Pillinger, 1989). Both instruments are completely automated and provide a highly reproducible protocol for high-resolution multi-step analysis. One combustion step consists of 30 min heating with an oxygen pressure of 10 mbar followed by a 20 min period in which oxygen is resorbed by CuO. The precision for the isotope analyses was  $\pm 1\%$  for carbon in samples greater than 4 ng and  $\pm 3\%$  for nitrogen in samples greater than 5 ng. Typical sample

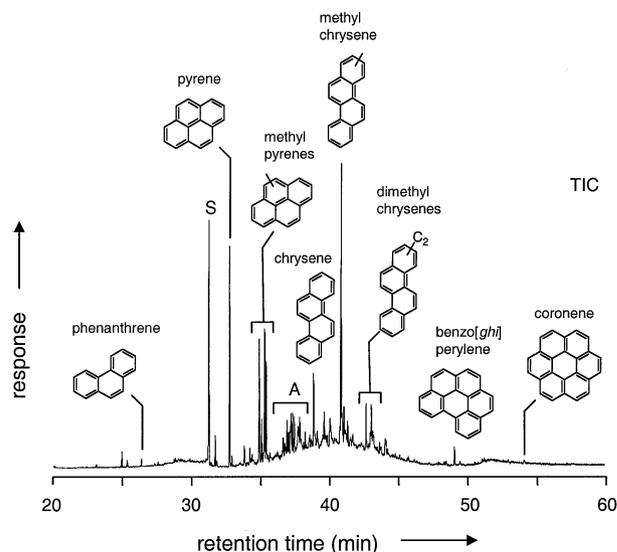


Fig. 2. Total ion chromatogram (TIC) of the  $\text{H}_2$ -pyrolysate from the Murchison meteorite. GC-MS responses labeled by letters are as follows: (S) elemental sulfur, (A) a partly coeluting mixture of dimethylpyrenes, dimethylfluoranthenes, and methylbenzofluorenes.

weight was 1–3 mg. Procedural blank was less than 1 ng for nitrogen and 5–10 ng for carbon.

## 3. RESULTS AND DISCUSSION

### 3.1. GC-MS of $\text{H}_2$ -Pyrolysis Products

Figure 2 displays the TIC of a whole  $\text{H}_2$ -pyrolysate that was recovered in DCM solvent. The majority of the compounds characterized in the Murchison  $\text{H}_2$ -pyrolysate consists of three- to seven-ring polycyclic aromatic hydrocarbons (PAH) and their alkyl homologues. An unresolved complex mixture of aromatic and aliphatic compounds underlies the discrete peaks in the TIC. Long chain aliphatic moieties, either as individual pyrolysis products or as alkyl substituents of PAH are absent. This observation is consistent with several previous pyrolysis studies which indicated that aliphatic moieties exist within or around the aromatic network as hydroaromatic rings and short alkyl substituents or bridging groups (Studier et al., 1972; Levy et al., 1973). Published results from the selective oxidation of Murchison macromolecular material are also consistent with aliphatic carbon being present as hydroaromatic units, bridging groups or short ring substituents (Hayatsu et al., 1977). In addition, earlier NMR studies have also revealed abundant aliphatic units in the form of short, branched groups that link and decorate aromatic centres (Cronin et al., 1987; Gardinier et al., 2000; Cody et al., 2002).

The molecular weight range of the  $\text{H}_2$ -pyrolysis products are noticeably different from the predominantly one- and two-ring aromatics obtained from Murchison using  $\text{H}_2\text{O}$ -pyrolysis (Sephton et al., 1998). However, the  $\text{H}_2\text{O}$ -pyrolysis products were extracted by supercritical fluid extraction (SFE) which allows the retention of components as volatile as benzene and toluene. Compounds this volatile may have been produced by  $\text{H}_2$ -pyrolysis and lost during sample collection to leave behind the higher molecular weight components in Figure 2. Recently,

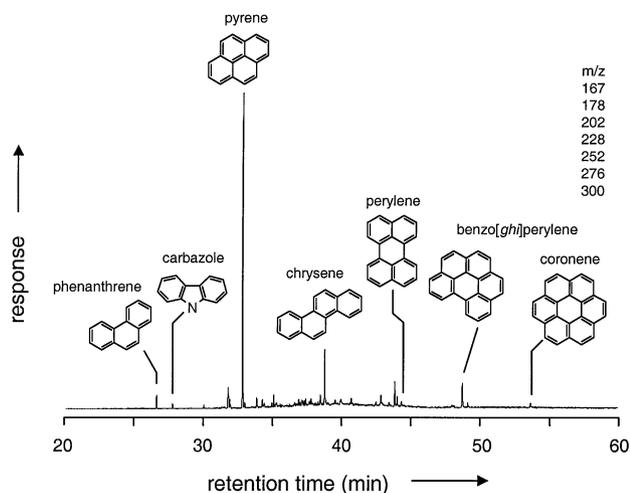


Fig. 3. Summed ion chromatogram ( $m/z$  167 + 178 + 202 + 228 + 252 + 276 + 300) representing the main parental PAH present in the Murchison  $H_2$ -pyrolysate.

methods have been developed to trap volatile  $H_2$ -pyrolysis products more effectively (Meredith et al., 2002).

Figure 3 is a SIC of the Murchison  $H_2$ -pyrolysate that reveals the dominant parent PAH distribution in the extract. As stated, the loss of any volatile aromatic units during the  $H_2$ -pyrolysate collection steps introduces a bias on the data. Yet these PAH units must represent the higher molecular weight region of the aromatic cores within the pyrolysable macromolecular material. The data are consistent with several previous degradation studies in which volatile products were not preserved. For instance, sodium dichromate oxidation has been used to selectively remove aliphatic side chains and isolate a significant amount of two- to four-ring aromatic cores bound to the macromolecular materials by a number of aliphatic linkages (Hayatsu et al., 1977). Two-step desorption/laser ionization has been employed to detect PAH ranging in size from naphthalene to coronene by analyzing HF/HCl residues of Murchison (Kovalenko et al., 1992). We have, therefore, verified the presence of PAH with up to seven-rings (coronene) in the macromolecular organic inventory of Murchison (Fig. 3). Yet such PAH units are still smaller than the 10 to 15 ring PAH recently identified by high resolution transmission electron microscopy (HRTEM) of macromolecular material in Murchison (Derenne et al., 2003) suggesting that not all PAH units present can be accessed by pyrolysis.

Carbazole is the most dominant nitrogen heterocyclic compound in the  $H_2$ -pyrolysate (Fig. 3). Previous work has used dichromate oxidation to release carbazole units from the Murchison macromolecular material, where they appear to be bound by two or three linking bonds, in addition to pyridine ( $m/z$  79) and quinoline/isoquinoline ( $m/z$  129) (Hayatsu et al., 1977). Due to their volatility, and therefore loss during the extraction procedure, pyridine and quinoline/isoquinoline were not detected in our  $H_2$ -pyrolysate and their presence could not be confirmed.

Figure 4 is a SIC of the Murchison  $H_2$ -pyrolysate that reveals the presence of fluoranthene, pyrene, alkyipyrenes, alkyfluoranthenes and alkylbenzofluorenes. Earlier published work

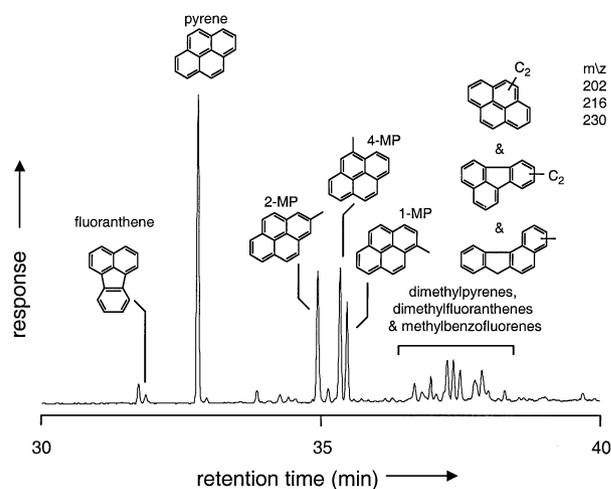


Fig. 4. Summed ion chromatogram ( $m/z$  202 + 216 + 230) representing fluorantheneene, alkyipyrenes, alkyfluoranthenes, dimethylpyrenes, dimethylfluoranthenes, and methylbenzofluoranthenes in the Murchison  $H_2$ -pyrolysate. 2-MP = 2-methylpyrene; 4-MP = 4-methylpyrene; 1-MP = 1-methylpyrene. The exact positions of the methyl substituents on the dimethylpyrenes, dimethylfluoranthenes, and methylbenzofluoranthenes are unknown.

indicates that pyrene (or fluoranthene) can be released from the Murchison macromolecular material by dichromate oxidation and that these units appeared to be bound within the structure by three or four linking bonds. Pyrene (or fluoranthene) has also been detected previously by the thermal decomposition of a trifluoroacetic acid extract of the macromolecular material (Hayatsu et al., 1977). These four-ring units, therefore, must be bound to the organic network by both acid hydrolyzable and thermally-labile bonds. Pyrene has also been released from the Murchison macromolecular material by on-line flash pyrolysis-GC and pyrolysis-GC-MS at  $740^\circ\text{C}$  (Murae, 1995). Molecular ions corresponding to pyrene ( $m/z$  202) were also detected during ramped heating in a thermal analyser-mass spectrometer system (Komiya and Shimoyama, 1996).

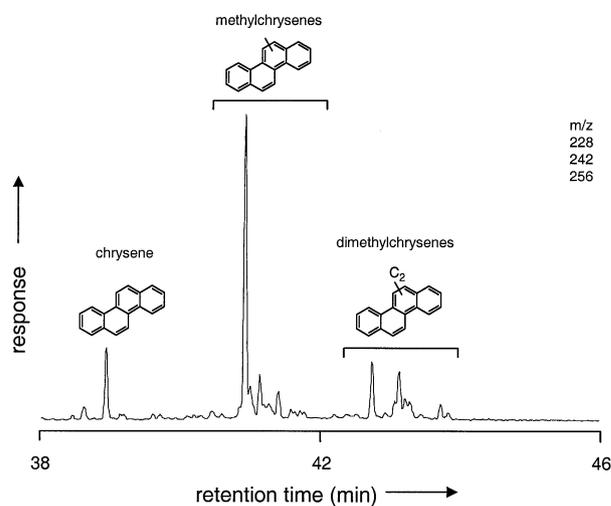


Fig. 5. Summed ion chromatogram ( $m/z$  228 + 242 + 256) representing the alkylchrysenes in the Murchison  $H_2$ -pyrolysate.

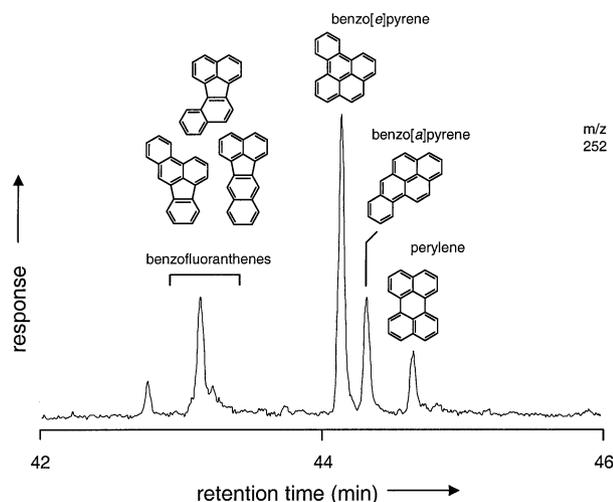


Fig. 6. Summed ion chromatogram ( $m/z$  252) representing the benzo[fluoranthenes], benzopyrenes, and perylene in the Murchison  $H_2$ -pyrolysate.

Figure 5 is a SIC of the Murchison  $H_2$ -pyrolysate, that reveals the presence of chrysene and its alkyl homologues. Earlier work has released chrysene from the Murchison macromolecular material by dichromate oxidation and these units appeared to be bound within the structure by two or three linking bonds (Hayatsu et al., 1977).

Several five-ring PAH are present in the  $H_2$ -pyrolysate (Fig. 6). Two-step desorption/laser ionization of Murchison HF/HCl residue has detected masses of 252 amu which may represent five-ring PAH fragments of the macromolecular material (Kovalenko et al., 1992). Before our study, no pyrolysis-based method had detected PAH with five or more rings in meteorite macromolecular materials.

### 3.2. Carbon and Nitrogen Abundance

The response of the Murchison macromolecular material to  $H_2$ -pyrolysis provides an insight into the nature of its labile and refractory organic contents. Table 1 reveals that the amounts of carbon and nitrogen measured in the Murchison starting material are around twice those in the  $H_2$ -pyrolysis residue indicating a substantial, but not complete, loss of these elements (44

wt% C and 55 wt% N lost) as organic matter. Comparing  $H_2$ - and  $H_2O$ -pyrolysis data (Table 1) reveals that, under the conditions used (320°C, 72 h),  $H_2O$ -pyrolysis releases lesser quantities of organic carbon and nitrogen (26 wt% C, 6 wt% N).

Previous  $H_2$ -pyrolysis work has shown that, for high volatile bituminous coals which typically consist of 50% aromatic carbon present as cross linked two- to four-ring PAH, the majority of carbon is converted to pyrolysis products (Snape et al., 1994). Hence, the unconverted organic residue from  $H_2$ -pyrolysis is likely to contain a refractory organic phase with at least five- or six-ring PAHs bridged by small organic units. Furthermore, if we consider the overall H/C ratio of  $\sim 0.5$  derived by elemental analysis (Cody et al., 2002), then that of the residue must be  $<0.5$  by a significant amount given the  $>0.5$  H/C ratio of the majority of pyrolysis products detected by  $H_2$ -pyrolysis (Fig. 2), and  $H_2O$ -pyrolysis (Sephton et al., 1998).

For purposes of comparison, terrestrial semianthracite coals have H/C ratios of  $\sim 0.5$  and cores of five or six aromatic rings while anthracites have H/C ratios of  $\sim 0.3$  and comprise clusters of greater than 15 aromatic rings. The refractory organic phase in the Murchison macromolecular material, therefore, may be analogous to a terrestrial semianthracite or anthracite coal. The proposal that the nonpyrolysable refractory organic phase in Murchison consists of linked units with at least five- or six-ring PAHs and a H/C ratio of  $<0.5$  is in accord with the detection of 10- to 15-ring PAH units in the Murchison macromolecular material by HRTEM (Derenne et al., personal communication).

### 3.3. Carbon and Nitrogen Stable Isotopes

The organic matter in the Murchison meteorite can be subdivided, operationally, into three types: free organic matter, labile macromolecular material and refractory macromolecular material (Table 2; Sephton et al., 2003). For the two macromolecular components, the labile fraction is relatively enriched, and the refractory fraction relatively depleted, in the heavy isotopes of carbon and nitrogen. Hence, the efficiency of a pyrolysis method can be gauged by establishing how much of the labile  $^{13}C$ - and  $^{15}N$ -enrichments have been removed from the total macromolecular fraction. In other words, the more efficient pyrolysis procedure will produce the isotopically lightest residue.

Table 1. Bulk measurements by isotope ratio mass spectrometry revealing carbon and nitrogen abundance and isotopic composition for the Murchison starting materials, pyrolysates, and pyrolysis residues. Measured values are in plain text; calculated values are in italics.

Sample	C (wt%)	N (wt%)	N/C	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
$H_2$ -pyrolysis					
Solvent-extracted & decalcified	4.39	0.22	0.05	-12.7	+30.0
$H_2$ -pyrolysis residue	2.46	0.10	0.04	-20.7	-23.5
$H_2$ -pyrolysate	—	—	—	-15.4	+9.2
<i><math>H_2</math>-total pyrolysate (by mass balance)</i>				-2.5	+74.6
$H_2O$ -pyrolysis					
HF/HCl residue	8.76	0.33	0.04	-16.6	+23.6
$H_2O$ -pyrolysis residue	6.48	0.31	0.05	-18.8	+4.2
$H_2O$ -pyrolysate	—	—	—	-4.7	—
<i><math>H_2O</math>-total pyrolysate (by mass balance)</i>				-10.4	+343.7

Table 2. Four obvious carbon- and nitrogen-bearing components observed in Murchison HF/HCl residues. Other components combust at higher temperatures (e.g., Sephton et al., 2003).

Component	Characteristic	Combustion temperature (°C)	Stable isotopes
Free organic	Solvent extractable	<250	<sup>13</sup> C and <sup>15</sup> N-rich
Macromolecular organic			
Labile	Readily pyrolysable	250–350	<sup>13</sup> C and <sup>15</sup> N-rich
Refractory	Not readily pyrolysable	350–500	<sup>13</sup> C and <sup>15</sup> N-poor
Diamond		~550	<sup>13</sup> C and <sup>15</sup> N-poor

Carbon and nitrogen isotopic measurements reveal that the H<sub>2</sub>-pyrolysis residue has shifted to lighter values suggesting the release of significant amounts of isotopically-heavy material. Simple mass balance calculations, based on the elemental and isotopic constitution of experiment residues, predict that the total H<sub>2</sub>-pyrolysate should have δ<sup>13</sup>C and δ<sup>15</sup>N values of around −3‰ and +74‰ respectively. Measured values for the H<sub>2</sub>-pyrolysate (δ<sup>13</sup>C = −15.4‰; δ<sup>15</sup>N = +9.2‰) are much lighter indicating that substantial amounts of isotopically heavy volatile material has been lost during H<sub>2</sub>-pyrolysate collection. Comparing H<sub>2</sub>- and H<sub>2</sub>O-pyrolysis data (Table 1) reveals that of the two techniques it is H<sub>2</sub>-pyrolysis which generates the isotopically-lighter residue, confirming that it is the more efficient method under the conditions specified. Mass balance calculations for the H<sub>2</sub>O-pyrolysis samples also reveal the release of significant amounts of isotopically-heavy organic material (Table 1). Pyrolytically-liberated volatiles with <sup>13</sup>C- and, in particular, <sup>15</sup>N-enrichments represent an exciting opportunity for future work on meteoritic macromolecular materials.

For the H<sub>2</sub>-pyrolysis residue, total N/C ratios, δ<sup>13</sup>C and δ<sup>15</sup>N values obtained by stepped combustion-MS (Table 3) are sim-

ilar to those obtained by bulk isotopic measurements (Table 1) indicating the compatibility of the two techniques. When element abundance and isotopic composition are plotted against release temperature, stepped combustion-MS data for HF/HCl residues can be crudely subdivided into three components (Table 2). Two of the components are the macromolecular organic fractions discussed above; the third is diamond. It should be noted that the data presented in Figure 7 are derived from solvent-extracted samples and reflect no contribution from the component termed free organic matter, which is included for completeness in Table 2. The responses of the remaining three components (labile macromolecular material, refractory macromolecular material and diamond) are indicated in Figures 7a,b.

Stepped combustion-MS data of the pyrolysis residues (Fig. 7c-f; Table 3) support the earlier conclusion that, under the conditions specified, H<sub>2</sub>-pyrolysis is more efficient than H<sub>2</sub>O-pyrolysis at removing the <sup>13</sup>C- and <sup>15</sup>N-enriched labile organic matter. The relatively heavy δ<sup>13</sup>C and δ<sup>15</sup>N values close to 300°C in Figures 7a–f reflects the contribution from labile organic matter and the δ<sup>13</sup>C and δ<sup>15</sup>N values for this temperature region of the plot decrease in the order HF/HCl residue >

Table 3. Stepped combustion-MS data reflecting carbon and nitrogen yields and isotopic compositions for two separate experiments performed on the solvent-extracted and decalcified H<sub>2</sub>-pyrolysis residue.

T (°C)	Carbon experiment		Nitrogen experiment			
	C (ppm)	δ <sup>13</sup> C (‰)	N (ppm)	δ <sup>15</sup> N (‰)	C (ppm)	N/C
300	16.27	−19.2	33.57	8.9	1536.30	0.02
325	34.97	−17.8				
350	39.29	−18.0	100.07	−16.5	3417.50	0.03
375	51.80	−18.8				
400	76.56	−12.0	337.67	−47.9	7909.80	0.04
425	117.23	−22.8				
450	166.22	−24.3	181.33	0.9	5159.30	0.04
475	149.39	−23.5				
500	81.26	−18.9	46.26	−41.8	1302.30	0.04
525	43.21	−19.4				
550	32.43	−29.3	14.79	−11.4	110.40	0.13
600	9.03	−21.6	9.47	−3.1	45.23	0.21
650	3.66	−9.2				
700	2.99	−4.9	8.67	3.8	39.00	0.22
800	2.39	−6.8	5.88	5.6	39.47	0.15
900	0.44	2.2	4.57	2.2	27.74	0.17
1000	0.38	10.8	5.86	1.8	27.43	0.21
Total	21727 <sup>a</sup> (2.2%)	−21.4	748.12 <sup>a</sup> (0.8%)	−25.9	19615 <sup>a</sup> (2.0%)	0.04

<sup>a</sup> Weighted average.

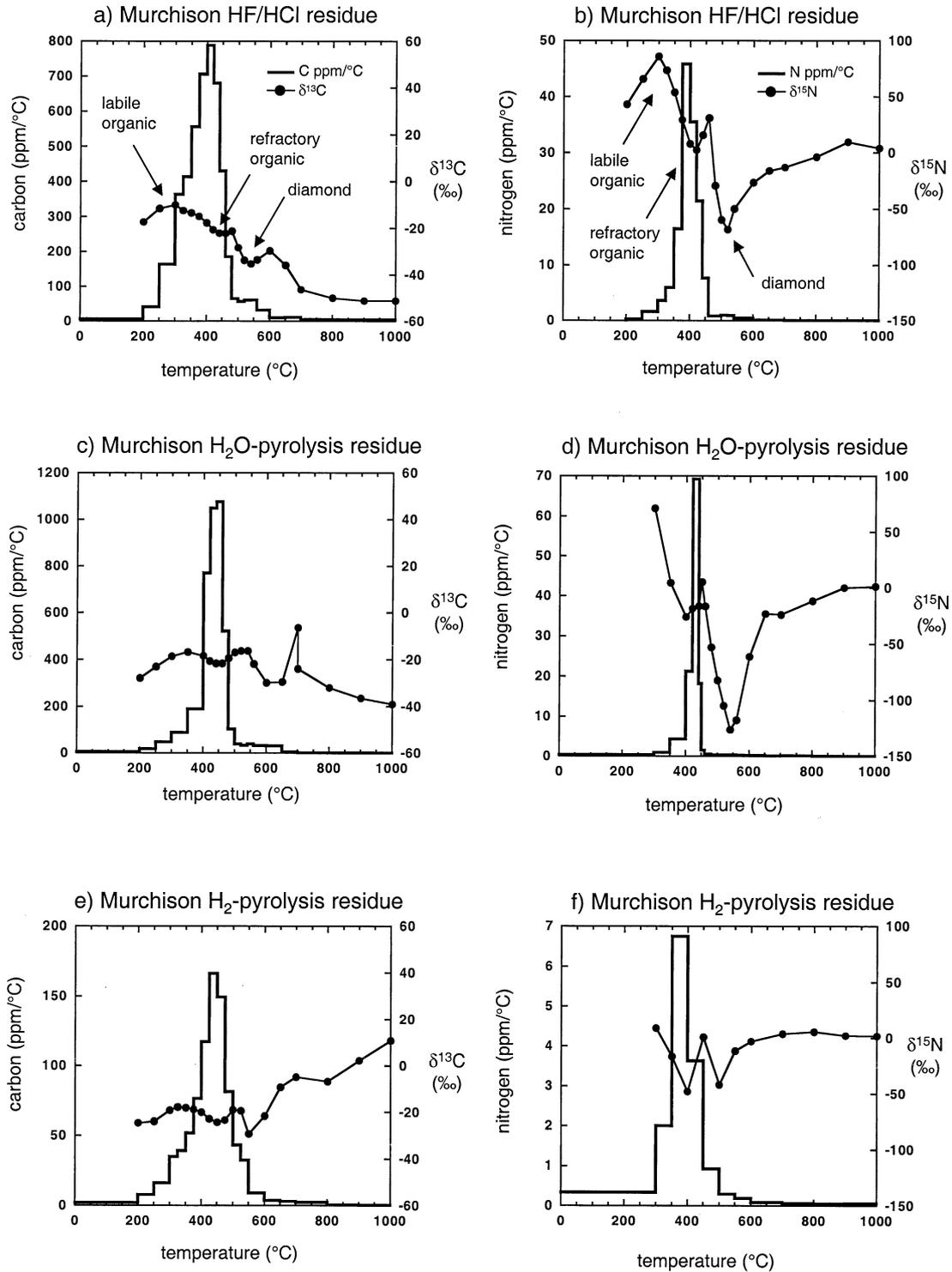


Fig. 7. Element yield (solid line) and isotopic composition (bulleted line) stepped combustion-MS profiles for (a, b) solvent-extracted Murchison HF/HCl residue; (c, d) solvent-extracted 330°C H<sub>2</sub>O-pyrolyzed Murchison HF/HCl residue; and (e, f) solvent-extracted and decalcified H<sub>2</sub>-pyrolysis residue of the Murchison meteorite. (a–d) From Sephton et al. (2003).

H<sub>2</sub>O-pyrolysis residue > H<sub>2</sub>-pyrolysis. The first appearance of isotopically-light values at around 400 to 500°C in the  $\delta^{13}\text{C}$  profiles (Figs. 7a,c,e) and 400 to 450°C in the  $\delta^{15}\text{N}$  profiles (Figs. 7b,d,f) represents refractory organic matter and is lighter

in the H<sub>2</sub>-pyrolysis residue than in the H<sub>2</sub>O-pyrolysis residue reflecting less shielding from portions of the isotopically-heavy labile organic matter. The second appearance of isotopically-light  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values at around 500 to 550°C in Figures

7a–f reveals a contribution from diamond. Combustion of diamond in this temperature range is confirmed by a concomitant release of helium (Sephton et al., 2003). The average diamond in CM meteorites contains around 1000 carbon and 20 nitrogen atoms in its structure; it appears that some originate from supernovae (Clayton et al., 1995) but the majority may be derived from circumstellar environments (Kerckhoven et al., 2002). For the H<sub>2</sub>-pyrolysis residue, the isotopically light  $\delta^{15}\text{N}$  values between 500 to 550°C are not as exaggerated as those seen in the H<sub>2</sub>O-pyrolysis residue. However, this difference is probably due to the fact that the H<sub>2</sub>O-pyrolysis plot displays responses from a HF/HCl residue whereas the H<sub>2</sub>-pyrolysis plot contains data from solvent-extracted and decalcified sample. Hence, some residual <sup>15</sup>N-containing inorganic material may be shielding the light  $\delta^{15}\text{N}$  diamond response at around 550°C in the H<sub>2</sub>-pyrolysis residue.

### 3.4. A Hot or Cold Origin for the Large PAH in Murchison Pyrolysates?

It is often stated that a substantial proportion of the aromatic organic matter in meteorites has a presolar origin, a suggestion supported by deuterium enrichments (Kerridge et al., 1987; Krishnamurthy et al., 1992) and an association with presolar grains (Alexander et al., 1998). Yet the one- to four-ring PAH commonly observed in Murchison extracts contrast sharply with the > 20-ring PAH proposed for the interstellar medium (Pendleton and Allamandola, 2002). The release of up to seven-ring PAH units from the macromolecular material in Murchison, and the deduction that even larger entities must be present in the experimental residue, partly reconciles the apparent disharmony between the meteoritic and interstellar organic inventories. It is appropriate, therefore, to consider some possible presolar source environments for the meteoritic PAH reported in this paper.

As the free and pyrolysable macromolecular aromatic compounds in Murchison share a common origin (Sephton et al., 1998) data for both fractions must be used to constrain their provenance. An adequate explanation for the origin of the free and pyrolysable macromolecular PAH in Murchison must explain the following features: (1) an initial increase and then subsequent decrease in  $\delta^{13}\text{C}$  with increasing molecule size, and (2) large fractionations in carbon isotopes for relatively large compounds which differ by only one or two carbon atoms (Sephton, 2002). Due to the dearth of compound specific isotope data, assigning a source for the refractory, nonpyrolysable PAH is more problematical.

The circumstellar envelopes around carbon stars generate PAHs in gas phase pyrolysis reactions and transfer the products to the interstellar medium. Stellar outflows from carbon stars contain CO and acetylene (C<sub>2</sub>H<sub>2</sub>), the latter of which is reactive and forms PAHs via hydrogen abstraction, radical formation then subsequent polymerization and cyclization with other hydrocarbon species (Frenklach and Feigelson, 1997). The overall reaction proceeds in a temperature window between 900 and 1100 K. PAH formation by acetylene addition has been invoked to explain  $\delta^{13}\text{C}$  values for the four- and five-ring PAH containing sixteen carbon atoms in free organic matter (Gilmour and Pillinger, 1994; Naraoka et al., 2000).

During gas phase pyrolysis, the synthesis of higher molecu-

lar weight compounds from simpler precursors would proceed by the preferential addition of <sup>12</sup>C, and larger PAH will have lighter  $\delta^{13}\text{C}$  values. In carbonaceous chondrites, structural isomers such as pyrene and fluoranthene exhibit different  $\delta^{13}\text{C}$  values (e.g., -13.1 and -5.9‰ respectively for Murchison) that may reflect the relative difficulties of the two different pathways of acetylene addition needed to form the two types of PAH (Gilmour and Pillinger, 1994; Naraoka et al., 2000). However, the relatively large and systematic difference in  $\delta^{13}\text{C}$  values for sizable PAH, which differ by only one or two carbon atoms, suggests that during bond formation isotopic fractionations were at their most extreme. At temperatures of 900 to 1100 K it is doubtful that such large fractionations would have been produced. These constraints based on formation temperature also apply to models proposed for high temperature PAH formation in the solar nebula (e.g., Basile et al., 1984; Morgan et al., 1991).

An alternative formation mechanism is provided by the irradiation of organic mixtures to produce PAH-containing macromolecular residues. Laboratory experiments which subjected methane ices to ion-irradiation have successfully produced polymeric residues which display an increase in <sup>12</sup>C with polymer size (Lecluse et al., 1998). The fractionations were attributed to the preferential evaporation of <sup>13</sup>C-enriched species by sputtering. In this context, it is interesting to note that the compound specific  $\delta^{13}\text{C}$  values for free PAH with identical molecular weights in Murchison reveal a relative increase in <sup>12</sup>C-content for the more stable isomers (Gilmour and Pillinger, 1994). Similar fractionations in individual PAH from several meteorites have also been attributed to simple kinetic isotope effects during the nonthermal, irradiation-induced stepwise synthesis of higher molecular weight PAH from simpler molecules (Sephton and Gilmour, 2000). Such reactions break and form bonds simultaneously, the isotopic consequences of which would explain the rise (bond breaking) and subsequent decline (bond formation) in  $\delta^{13}\text{C}$  with increasing molecule size. Irrespective of the detailed mechanism, irradiation of ices by cosmic rays in low temperature regions appears to be a good candidate for producing the unusual isotopic fractionations observed in meteoritic PAH.

## 4. CONCLUSIONS

1) H<sub>2</sub>-pyrolysis releases significant amounts of high molecular weight PAH from the Murchison macromolecular material

2) The aromatic units in the in the macromolecular material which could be released by H<sub>2</sub>-pyrolysis consists of phenanthrene, carbazole, fluoranthene, pyrene, chrysene, perylene, benzoperylene and coronene units with varying degrees of alkylation.

3) Although H<sub>2</sub>-pyrolysis liberates substantial amounts of organic matter from the macromolecular material, over 50% of macromolecular carbon remains unconverted. Comparisons with experimental yields from terrestrial macromolecular materials indicate that this refractory residue probably consists of a network dominated by at least five- or six-ring PAH cross-linked together. This interpretation is consistent with recently-reported HRTEM data.

4) Stable isotopic investigations of the pyrolysis residue

suggests that H<sub>2</sub>-pyrolysis is more efficient at removing primitive isotopic enrichments than H<sub>2</sub>O-pyrolysis at 320°C

5) Two possible mechanisms for producing the PAH entities observed in the H<sub>2</sub>-pyrolysate are gas phase pyrolysis in circumstellar envelopes or irradiation of interstellar ices. The published data set for Murchison aromatic compounds reveals large carbon isotope fractionations between sizeable PAH units suggesting that irradiation in cold environments may be the more likely source.

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