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Hydropyrolysis: A new technique for the analysis of macromolecular material in meteorites

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Abstract

The carbonaceous chondrite meteorites are fragments of asteroids that have remained relatively unprocessed since the formation of the Solar System 4.56 billion years ago. The major organic component in these meteorites is a macromolecular phase that is resistant to solvent extraction. The information contained within macromolecular material can be accessed by degradative techniques such as pyrolysis. Hydropyrolysis refers to pyrolysis assisted by high hydrogen gas pressures and a dispersed sulphided molybdenum catalyst. Hydropyrolysis of the Murchison macromolecular material successfully releases much greater quantities of hydrocarbons than traditional pyrolysis techniques (twofold greater than hydrous pyrolysis) including significant amounts of high molecular weight polyaromatic hydrocarbons (PAH) such as phenanthrene, carbazole, fluoranthene, pyrene, chrysene, perylene, benzoperylene and coronene units with varying degrees of alkylation. When hydropyrolysis products are collected using a silica trap immersed in liquid nitrogen, the technique enables the solubilisation and retention of compounds with a wide range of volatilities (i.e. benzene to coronene). This report describes the hydropyrolysis method and the information it can provide about meteorite macromolecular material constitution.
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1. Introduction

Meteorites are overwhelmingly dominated by fragments of asteroids coerced into Earth-crossing orbits by relatively recent collisions in the asteroid belt and the perturbing effect of gravitational interactions with Jupiter (Wetherill and Chapman, 1988). Meteorites have escaped many of the geological processes experienced on the planets and as a result preserve some of the most primitive materials in the Solar System. In particular, the low petrographic type carbonaceous chondrites have elemental abundances similar to those of the Sun and contain substantial amounts (up to ca. 5%) of H, C and N in the form of organic matter (Sephton, 2002). Meteoritic organic matter is, at present, our only available record of natural pre-biotic chemical evolution and, based on deuterium enrichments appears to contain some exceedingly ancient matter which is only partially transformed from pre-solar materials (Kolodny et al., 1980; Robert and Epstein, 1982). The organic matter in meteorites is present as three solubility classes; around 25% is present as solvent-soluble or free organic matter but the majority is in the form of a

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complex solvent-insoluble macromolecular material (Sephton, 2002 and refs therein). The macromolecular material itself can be operationally defined into pyrolysable (i.e. breaks down under thermal stress) and non-pyrolysable (i.e. does not break down under thermal stress) fractions. These two macromolecular fractions are termed labile organic matter and refractory organic matter, respectively (Sephton et al., 2003). As the dominant organic entity, the macromolecular material is key to understanding the origin of meteoritic organic matter as a whole.

The macromolecular material in Murchison has been investigated using non-destructive techniques such as infra-red spectroscopy (Hayatsu et al., 1977) and nuclear magnetic resonance spectroscopy (NMR) (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 stepwise heating and pyrolysis. Stepwise heating experiments distinguish between different carbon phases in the meteoritic macromolecular material by their susceptibility to combustion or pyrolysis (thermal decomposition) and have revealed significant isotopic heterogeneity (e.g. Robert and Epstein, 1982; Kerridge et al., 1987). However, stepwise heating experiments provide little or no structural information.

Pyrolysis thermally decomposes macromolecular organic material and the 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) prior to analysis by mass spectrometry (e.g. Levy et al., 1973).

Recently, the meteoritic macromolecular material has been fragmented using hydrous pyrolysis where the sample remains in contact with water for the duration of the experiment (Sephton et al., 1999). In the case of terrestrial macromolecular materials (kerogens), hydrous pyrolysis converts more than 55% of the macromolecular phase to solvent-soluble products that are amenable to 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).

Most recently, hydropyrolysis has been applied to the study of meteorites (Sephton et al., 2004). Hydropyrolysis refers to open-system pyrolysis assisted by high hydrogen gas pressures (>10 MPa). When applied to terrestrial kerogens, fixed-bed hydropyrolysis in the presence of a dispersed sulphided molybdenum catalyst 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 of the organic structures and stereochemistries (e.g. Love et al., 1995). Indeed for petroleum source rocks and coals, char yields are less than 20%; for coals the char is dominated by intractable intertinite macerals (Snape et al., 1994; Roberts et al., 1995). In this paper, we describe in detail the highly efficient hydropyrolysis method and the information it reveals about the constitution of meteoritic macromolecular materials.

2. Experimental

2.1. Hydropyrolysis

Crushed whole meteorite was prepared for hydropyrolysis treatment by performing solvent-extraction (ultrasonication with a solvent mixture of 93:7 dichloromethane(DCM)/methanol followed by removal of the supernatant, $\times 3$), a process which removes any free organic matter (Sephton et al., 1998, 2000). Subsequently, the sample was impregnated with an aqueous solution of ammonium dioxydithiomolybdate $[(NH_4)_2MoO_2S_2]$ to give a nominal loading of molybdenum of 2 wt%. $(NH_4)_2MoO_2S_2$ reductively decomposes in situ under hydropyrolysis conditions above 250 °C to form a catalytically active sulphided molybdenum phase. Hydropyrolysis runs were performed in an open-system, temperature-programmed reactor configuration, which has been described in detail previously (Love et al., 1995) (Fig. 1). 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 °C at 300 °C min^{-1}, then to 520 °C at 8 °C min^{-1}, using a hydrogen pressure of 15 MPa. A constant hydrogen sweep gas flow of 6 dm^3 min^{-1}, measured at ambient temperature and pressure, through the reactor bed ensured that the residence times of volatiles generated from pyrolysis was extremely short, of the order of a few seconds.

The hydropyrolysis products (the hydropyrolysate) were collected in a trap cooled with dry ice and recovered in DCM. In an attempt to retain volatile products more efficiently, a second analysis was performed using silica as a trap adsorbent and liquid nitrogen as a coolant. This procedure has been shown to improve the recovery of volatile molecules such as benzene and heptane from 0% to over 40%, while molecules with higher molecular masses than decane are almost completely retained (Meredith et al., 2004). The silica trap was washed ($\times 3$) with DCM and the extracts
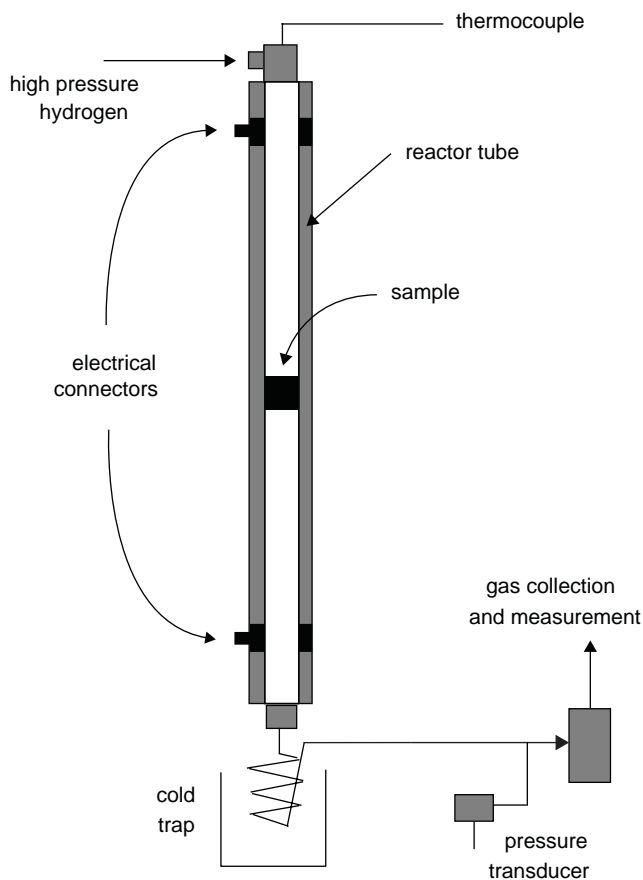
Fig. 1. Schematic of the hydropyrolysis equipment.

were transferred to pre-extracted and pre-baked glass powder rounds (120 ml), concentrated to a small volume and (pre-extracted) activated copper turnings were added to remove all traces of elemental suphur, which is formed from disproportionation of the catalyst during hydropyrolysis.

To reduce levels of background contamination, a cleaning run was performed prior to the sample run whereby the apparatus was heated to 520 °C using a rapid heating rate (300 °C min^{-1}) under high hydrogen pressure conditions. All solvents were pre-distilled 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). For the hydropyrolysate trapped without silica, an Agilent Technologies 6890 gas chromatograph interfaced with a 5973 mass selective detector was employed (Sephton et al., 2004). Analyses were by splitless injection onto a BPX5 capillary column (30 m × 0.25 mm × 0.25 μm). Following a 1 min period

at 50 °C, the gas chromatograph oven was programmed from 50 to 300 °C at 5 °C min^{-1} and then held at 300 °C for 39 min. Peak identification was based on retention time and mass spectra comparisons with authenticated standards, well-characterised aromatic fractions of a coal tar and crude oil and by reference to published reports (e.g. Kruge, 2000 and references therein). For the silica-trapped hydropyrolysate, GC-MS analyses were performed on a Fisons Instruments 8000 gas chromatograph interfaced to a MD 800 mass spectrometer (ionising energy 70 eV, source temperature 280 °C). Separation was performed on a fused silica capillary column (DB5, 30 m × 0.25 μm) with helium as the carrier gas and an oven programme of 50 °C (2 min) to 300 °C (28 min) at 5 °C min^{-1}.

3. Results and discussion

3.1. Pyrolysis yield

Following hydropyrolysis, analysis of the experimental residue (Sephton et al., 2004) indicates that the procedure liberates substantial amounts of carbon- and nitrogen-containing (44 wt% C and 55 wt% N lost) organic matter. The efficacy of hydropyrolysis relative to other off-line pyrolysis methods can be ascertained by comparisons with published hydrous pyrolysis data (Sephton et al., 2003). The data reveal that, under the conditions used (320 °C, 72 h), hydrous pyrolysis releases lesser quantities of organic carbon and nitrogen (26 wt% C, 6 wt% N).

3.2. Pyrolysis products

Fig. 2a displays the total ion chromatogram (TIC) of a whole hydropyrolysate that was trapped using dry ice as a coolant and without silica adsorbent. The lack of a response for molecules more volatile than phenanthrene implies that a significant loss of volatile pyrolysis products may have occurred. The majority of carbon in the Murchison hydropyrolysate appears to be present within aromatic ring systems. Significant numbers of aliphatic and aromatic compounds in the hydropyrolysate form an unresolved complex mixture which underlies the more discrete peaks. Identifiable organic entities in hydropyrolysate consists primarily of three- to seven-ring polyaromatic hydrocarbons (PAH) and their alkyl homologues. The absence of long-chain alkyl substituents is consistent with previous work; several pyrolysis studies have indicated that these moieties exist within or around the aromatic network as hydroaromatic rings and short alkyl substituents or bridging groups (Studier et al., 1972; Levy et al., 1973). Previous results from the selective oxidation of Murchison macromolecular material were also consistent with aliphatic carbon being

Comparisons with hydropyrolysis responses of terrestrial macromolecular materials such as coals containing inertinite macerals (Snape et al., 1994) indicate that the unconverted organic residue from Murchison is likely to contain at least five- or six-ring PAHs bridged by small organic units, comparable to a terrestrial semi-anthracite or anthracite coal. This assertion is supported by published elemental analysis data for the macromolecular material which give an average value of 0.5 (Cody et al., 2002). As the majority of pyrolysis products have much greater H/C ratios, the unconverted residue must consist of more hydrogen-poor compact and condensed PAH units.

Fig. 2b displays the TIC of a whole hydropyrolysate that was trapped with silica adsorbent and recovered in DCM. Substantial amounts of more volatile entities are evident. Once again the majority of carbon is present in aromatic ring structures and a noticeable unresolved complex mixture elutes as a hump containing aliphatic and aromatic units in the centre of the chromatogram.

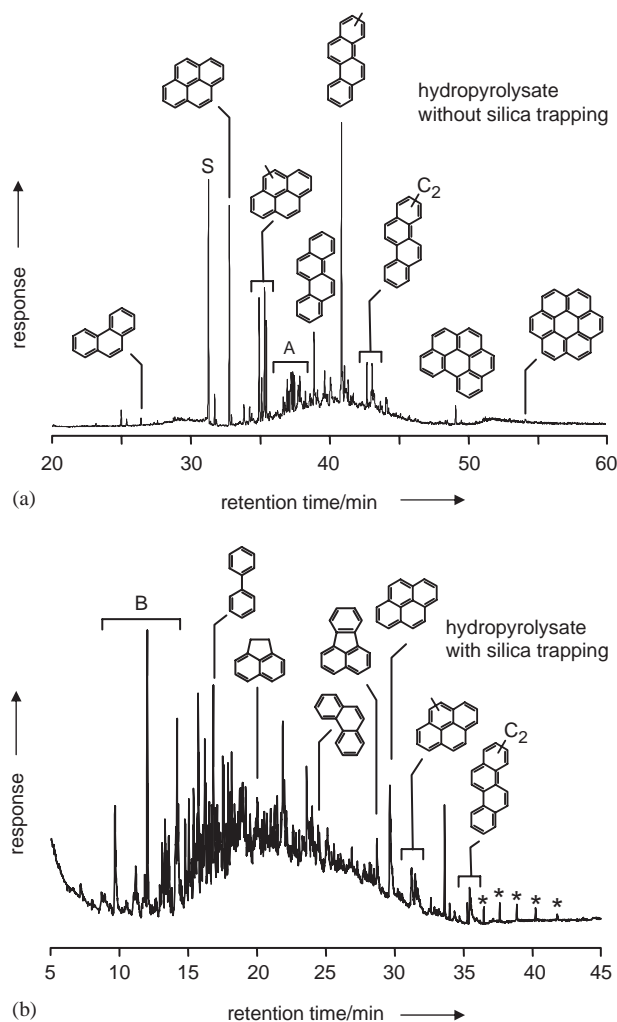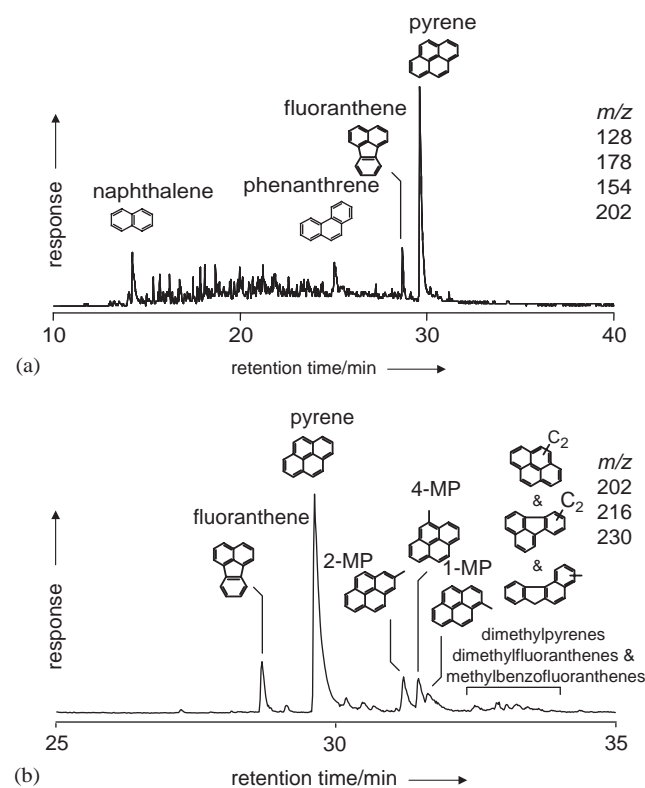Fig. 3a highlights parental PAH from the silica trapped hydropyrolysate with volatilities equal to and

Fig. 2. GC-MS (total ion chromatograms) traces for (a) hydropyrolysate of the Murchison meteorite trapped with dry ice and recovered in DCM (Sephton et al., 2004), and (b) hydropyrolysate of the Murchison meteorite trapped onto a silca adsorbent cooled by liquid nitrogen and recovered in DCM. GC-MS responses labelled by letters and symbols are as follows: (S) elemental sulphur, (A) a partly coeluting mixture of dimethylpyrenes, dimethylfluoranthenes and methylbenzofluorenes, (B) volatile hydrocarbons including alklybenzenes and short chain aliphatic compounds, (*) column bleed.

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). Selected ion monitoring of m/z 167 reveals that carbazole is a dominant nitrogen heterocyclic compound in the hydropyrolysate.

Although significant amounts of carbon and nitrogen are solubilised from the macromolecular materials by hydropyrolysis, analysis of the hydropyrolysis residue indicates that a substantial amount of carbon and nitrogen is not liberated (66 wt% C and 45 wt% N).

Fig. 3. Summed ion chromatograms representing (a) parental PAH present in the Murchison hydropyrolysate (m/z 128 + 154 + 178 + 202) and (b) fluoranthene, alkylpyrenes, alkylfluoranthenes, dimethylpyrenes, dimethylfluoranthenes and methylbenzofluoranthenes in the Murchison hydrouspyrolysate (m/z 202 + 216 + 230). (2-MP) 2-methylpyrene. (4-MP) 4-methylpyrene. (1MP) 1-methylpyrene. The exact positions of the methyl substituents on the dimethylpyrenes, dimethylfluoranthenes and methylbenzofluoranthenes are unknown.

less than pyrene. Using the silica trapping method negligible loss of these molecular mass entities must have occurred (Meredith et al., 2004). The GC-MS response of the parental PAH should be very similar and therefore peak height reflects relative abundance. Clearly, larger PAH are more dominant in the portion of the macromolecular material accessible by hydropyrolysis.

Fig. 3b is a summed ion chromatogram which shows fluoranthene, pyrene, alkylpyrenes, alkylfluoranthenes and alkylbenzofluoranthene. The relative responses for these four ring entities are remarkably similar to those in a previous hydropyrolysate of Murchison (Sephton et al., 2004). The similarity highlights both the reproducibility of the technique and the homogeneous macromolecular architecture of the meteorite macromolecular material.

3.3. Comparisons of hydrocarbon distribution with other pyrolysis methods

A previous *off-line* pyrolysis method used to investigate the constitution of macromolecular materials in meteorites is hydrous pyrolysis. Degradation of macromolecular material in meteorites by hydrous pyrolysis has involved subjecting samples to heating at 320 °C for 72 h in the presence of water (Sephton et al., 1998, 1999, 2000). The hydrous pyrolysis products were extracted by supercritical fluid extraction (SFE) which allows the retention of components as volatile as benzene and toluene. The lower molecular mass limit of the hydropyrolysis products trapped onto silica is similar to that for combined SFE and hydrous pyrolysis, i.e. one- and two-ring aromatics (Sephton et al., 1998). Differences are apparent, however, at the higher molecular mass limit where the hydropyrolysate contains many larger components that were not detected in previous hydrous pyrolysis experiments.

A common *on-line* pyrolysis method used to investigate macromolecular material structure is pyrolysis-gas chromatography mass spectrometry (Pyrolysis-GC-MS). In a similar fashion to hydrous pyrolysis, pyrolysis-GC-MS releases predominantly one- and two-ring aromatic compounds (Sephton and Gilmour, 2001). However, larger entities have been detected and pyrene has been released from the Murchison macromolecular material by pyrolysis-GC-MS at 740 °C (Murae, 1995). Furthermore, molecular ions corresponding to pyrene (m/z 202) were detected during ramped heating in a thermal analyser-mass spectrometer system (Komiya and Shimoyama, 1996). Yet, prior to our study, no pyrolysis-based method had detected five-, six- and seven-ring PAH in meteorite macromolecular materials, even though up to seven-ring units have been detected in soluble fractions (Sephton, 2002, and refs therein).

3.4. Comparisons with other degradative methods

Sodium dichromate oxidation has been used to selectively remove aliphatic side chains and therefore release any aromatic cores present. This procedure liberated a significant amount of two- to four-ring aromatic entities bound to the Murchison macromolecular materials by a number of aliphatic linkages (Hayatsu et al., 1977). Pyrene (or fluoranthene) was also released by this method and these units appeared to be bound within the structure by three or four linking bonds. Chrysene, bound within the structure by two or three linking bonds, was the highest molecular mass PAH compound released by sodium dichromate oxidation (Hayatsu et al., 1977).

Sodium dichromate oxidation has also released 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 the hydropyrolysate and their presence could not be confirmed. All of the components released by sodium dichromate oxidation, in addition to some higher molecular mass *products*, have been liberated by hydropyroysis.

3.5. Significance of the hydropyrolysis products

Established theories of meteorite macromolecular material structure point to condensed aromatic cores connected to various functional groups and heteroatomic rings, all cross-linked by aliphatic, ether and sulphide linkages (e.g. Anders et al., 1973; Bandurski and Nagy, 1976; Hayatsu et al., 1977). Because hydropyrolysis removes exocyclic heteroatoms, pyrolysis products of units with hydroxyl groups and thiophene rings are transformed to the corresponding hydrocarbon skeleton. Therefore, the release of pyrolysates containing aromatic compounds, a number of which have aliphatic side chains, is consistent with generally accepted hypotheses of macromolecular material structure.

With the release of hitherto unobserved organic units (PAH with > 5 rings) from the macromolecular material, it is interesting to consider that meteoritic organic matter is often compared with that observed in the interstellar medium. It is generally accepted that the molecular cloud which collapsed to form the Solar System bequeathed a significant amount of interstellar organic matter, aliquots of which are preserved in primitive asteroids and the meteorites derived from them (e.g. Alexander et al., 1998). An interstellar origin for the macromolecular material in Murchison is supported by noticeable deuterium enrichments (Robert and Epstein, 1982; Yang and Epstein, 1983; Kerridge

et al., 1987). For many years, only one- to four-ring PAH were commonly observed in Murchison macromolecular material break-down products, which contrasted sharply with the greater than 20-ring PAH proposed for the interstellar medium (Pendleton and Allamandola, 2002). During hydropyrolysis, up to seven-ring PAH units have been liberated from the macromolecular material in Murchison. Furthermore, as stated above, 66 wt% C and 45 wt% N remains behind after hydropyrolysis and must reside in at least five- or six-ring PAHs. Such an interpretation is in accord with recent high-resolution transmission electron microscopy data which has detected 10- to 15-ring PAH units in the Murchison macromolecular material (Derenne et al., 2003). These discoveries partly reconcile the apparent incongruence between the meteoritic and interstellar organic inventories.

3.6. Implications for research into meteoritic organic material

The success of hydropyrolysis in solubilising sizeable aromatic units from Murchison has important implications for the analysis of carbonaceous chondrites in general. The greater the molecular mass of a pyrolysis product, the more it reveals about the internal molecular architecture of its organic parent. The ideal product of pyrolysis methods is just large enough to pass through GC-based systems thereby combining maximum information with analytical amenability. This, combined with the high yields associated with hydropyrolysis, ensures that the technique can provide more comprehensive information on complex extraterrestrial macromolecular materials than traditional pyrolysis methods.

4. Conclusions

(1) Hydropyrolysis releases substantial amounts of PAH from the Murchison macromolecular material. The yield is greater than previously applied pyrolysis techniques (e.g. a twofold increase over hydropyrolysis, Sephton et al., 1998). Generally, the liberated compounds are similar to those produced by previous degradative techniques.
(2) Combining hydropyrolysis with a new silica trap immersed in liquid nitrogen enables the solubilisation and then retention of compounds with a wide range of volatilities (i.e. benzene to coronene).
(3) The aromatic units in the in the macromolecular material which can be released by hydropyrolysis consists of benzene, toluene, naphthalene, phenanthrene, carbazole, fluoranthene, pyrene, chrysene, perylene, benzoperylene and coronene units with varying degrees of alklyation.

(4) The release of up to seven-ring PAH units during hydropyrolysis, in conjunction with interpretations that the experimental residue must contain further amounts of large PAH, decreases the apparent incongruence between meteoritic PAH and the greater than 20-ring PAH proposed for the interstellar medium (Pendleton and Allamandola, 2002).

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