HYDROPYROLYSIS OF HIGH MOLECULAR WEIGHT ORGANIC MATTER IN MURCHISON.

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Introduction: The Earth-based record of pre-biotic chemical evolution has long-since been obliterated by geological processing. However, remains of materials 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, such as the Murchison meteorite, are particularly primitive and contain 2 to 5 wt. % carbon, most of which is present as organic matter [1]. At least 70% of the organic matter in Murchison is a solvent-insoluble, high molecular weight macromolecular material. 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 [1].

Pyrolysis-based techniques are probably the most common means of analysing the macromolecular material in meteorites. Analytical pyrolysis involves thermally decomposing macromolecular organic matter in an inert atmosphere into lower molecular weight fragments that are more amenable to conventional organic analytical techniques. Hydropyrolysis, which refers to pyrolysis assisted by high hydrogen gas pressures and a dispersed sulphided molybdenum catalyst, has not been previously applied to the study of high molecular weight meteoritic organic matter.

Methods: Crushed whole meteorite was solvent-extracted and impregnated with an aqueous solution of ammonium dioxydithiomolybdate $[(NH_4)_2MoO_2S_2]$ to give a 2 wt% nominal loading of molybdenum. Hydropyrolysis runs were performed in an open-system, temperature-programmed reactor configuration, which has been described in detail elsewhere [2].

Compound detection and identification was performed by gas chromatography-mass spectrometry (GC-MS) using an Agilent Technologies 6890 gas chromatograph interfaced with a 5973 mass selective detector. Analyses were by splitless injection onto a BPX5 capillary column (30 m x 0.25 mm x 0.25 μm). Following a 1 min period at 50 °C the gas chromatograph oven was programmed from 50 °C to 300 °C at 5 °C min-1 and then held at 300 °C for 39 min.

Carbon and nitrogen abundance and isotopic composition of samples were determined using an Elemental Analyser-Isotope Ratio Mass Spectrometer (PDZ Europa ANCA-SL on a Geo 20-20) as in [3]. A hydrous pyrolysis (pyrolysis in the presence of water) residue from a previous study [4] was analysed for comparison. The results are expressed using the δ notation as follows: $\delta\ (‰) = [(R_{sample} - R_{standard}) / R_{standard}]$ x 1000. Where $R = {}^{13}C/{}^{12}C$ for carbon and ${}^{15}N/{}^{14}N$ for nitrogen; standard = PDB for carbon; air for nitrogen.

Results and discussion: Hydropyrolysis of the Murchison macromolecular material successfully releases significant amounts of high molecular weight polyaromatic hydrocarbons (PAH) (Figure 1). The majority of the carbon in the Murchison hydropyrolysate appears to be present as three- to seven-ring PAH including phenanthrene, carbazole, fluoranthene, pyrene, chrysene, perylene, benzoperylene and coronene units with varying degrees of alklyation. The absence of long-chain alkyl substituents indicates that aliphatic moieties exist within or around the aromatic network as hydroaromatic rings and short alkyl substituents or bridging groups. The molecular weight range of the hydropyrolysis products are noticeably different from the predominantly one- and two-ring aromatics obtained from Murchison using hydrous pyrolysis [4]. However, the hydrous pyrolysis products were extracted by supercritical fluid extraction which allows the retention of components as volatile as benzene and toluene. Compounds this volatile may have been produced by hydropyrolysis and lost during sample collection to leave behind the higher molecular weight components in Figure 1. A summed mass chromatogram of the Murchison hydropyrolysate (Figure 2) reveals the dominant parent PAH distribution in the extract. It is apparent that the higher molecular weight PAH within the pyrolysable macromolecular material extend up to coronene. Carbazole is a dominant nitrogen heterocyclic compound in the hydropyrolysate.

Although hydropyrolysis liberates substantial amounts of organic matter from the macromolecular material, over 50% of macromolecular carbon remains unconverted. Hence, the meteoritic organic network contains both labile (pyrolysable) and refractory (non-pyrolysable) fractions. Comparisons with experimental yields from bituminous coals (over 85%) indicates that this refractory residue probably consists of a network dominated by at least five- or six-ring PAH moieties cross-linked together.

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It has been established that the labile fraction is relatively enriched, and the refractory fraction relatively depleted, in the heavy isotopes of carbon and nitrogen [5]. 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. Stable isotopic investigations suggests that the hydropyrolysis residue ($\delta^{13}C$ -20.7‰, $\delta^{15}N$ -23.5‰) has had its primitive isotopic enrichments removed more efficiently than the residue from hydrous pyrolysis ($\delta^{13}C$ -18.8‰, $\delta^{15}N$ +4.2‰).

References: [1] Sephton M. A. (2002) *Nat. Prod. Rep.* 19, 292-311. [2] Love G. D. et al. (1995) *Org. Geochem.* 23, 981-986. [3] Sephton M. A. et al. (2002) *Geology* 30, 1119-1122. [4] Sephton M. A. et al. (1998) *Geochim. Cosmochim. Acta* 62, 1821-1828. [5] Sephton M. A. et al. (2002) *Geochim. Cosmochim. Acta*. in press.

Figure 1. Total ion chromatogram (TIC) of the hydropyrolysate from the Murchison meteorite. (S) elemental sulfur.
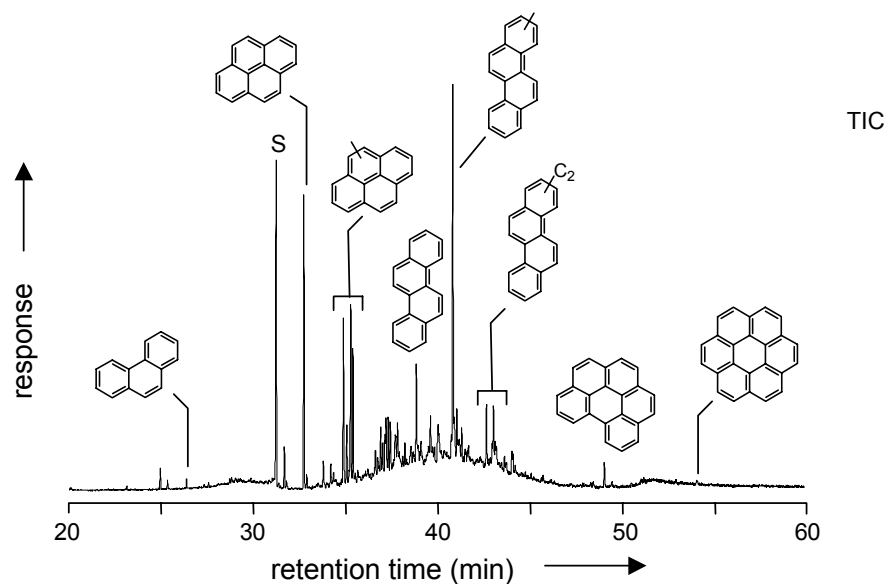

Figure 2. Summed mass chromatogram representing the main parental PAH present in the Murchison hydropyrolysate.