

INVESTIGATING THE CONSTITUTION OF MACROMOLECULAR MATERIAL IN METEORITES USING HYDROUS PYROLYSIS

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ABSTRACT

Carbon content analyses of hydrous pyrolysis residues of macromolecular material from the Murchison meteorite reveal that more than 55 % of macromolecular carbon is solubilised by this pyrolysis method. GC-MS analyses indicate that the majority of products are volatile one or two ring aromatic compounds.

Pyrolysis-GC-MS analyses of hydrous and anhydrous pyrolysis residues reveal that the macromolecular material contains a nitrogen-containing moiety. This organic entity is liberated by hydrous pyrolysis. It follows therefore that nitrogen-containing moieties may have been released from the macromolecular material during the aqueous alteration event known to have affected the Murchison meteorite parent body.

INTRODUCTION

Most meteorites are fragments of asteroids propelled into Earth-crossing orbits by relatively recent collisions in the asteroid belt (1). Asteroids, and therefore the meteorites derived from them, have escaped the extensive geological processing experienced on the planets. Due to this quiescent history meteorites contain primitive materials relatively unchanged since their formation of the solar system. The carbonaceous chondrites are especially primitive meteorites and excepting the most volatile elements, have a bulk composition similar to the Sun (2). These meteorites are particularly interesting to the organic cosmochemist as they contain up to several percent carbon which is present as organic matter.

Approximately 25 % of this organic matter is present as solvent-soluble or free molecules while the remaining 75 % is present as a solvent-insoluble macromolecular material (3). The soluble organic matter has been the most intensively studied of the two solubility classes and contains aliphatic hydrocarbons, aromatic hydrocarbons, amides, amines, nitrogen heterocycles, amino acids, carboxylic acids, sulphonic acids, phosphonic acids, alcohols and carbonyl compounds (3).

By comparison, the insoluble macromolecular material has been neglected. Pyrolytic release studies have revealed an empirical formula of $C_{100}H_{48}N_{1.8}O_{12}S_2$ for this organic component in the Murchison meteorite (4). It consists of condensed aromatic cores, connected by aliphatic and ether linkages and with various functional groups attached (5,6). Several techniques have been used to study the macromolecular material including infrared spectroscopy, nuclear magnetic resonance spectroscopy and pyrolysis (5,6).

Pyrolysis thermally dissociates macromolecular material in an inert atmosphere into lower molecular weight moieties. For meteorite research, most analyses of this type have utilised an on-line anhydrous pyrolysis unit directly coupled to a gas chromatograph or mass spectrometer (e.g. 5). Off-line hydrous pyrolysis requires that the heated samples are in contact with liquid water for the duration of the experiment and is used to simulate oil-generation from terrestrial rocks (7). This technique is conventionally performed on several hundred grams of sample (7,8) but has recently been scaled down to accommodate less than two grams of extraterrestrial sample (9).

As hydrous pyrolysis transforms the insoluble macromolecular material into free molecules, an obvious application of this technique is to investigate the relationships between the two organic solubility classes in meteorites. Previous authors have suggested that the free molecules in meteorites cannot be related to the macromolecular material because of the large isotopic differences between these two organic components (10). However isotopic measurements of individual free aromatic hydrocarbons and their structurally identical counterparts, released from the macromolecular material in the Murchison meteorite by hydrous pyrolysis, have revealed that they are related by an extraterrestrial degradative event (11). Whether more polar organic moieties are transferred between solubility classes in the extraterrestrial environment has not previously been established.

Here we report pyrolysis-gas chromatography-mass spectrometry (pyrolysis-GC-MS) and carbon content analyses of meteoritic macromolecular material in the Murchison meteorite both before and after hydrous pyrolysis. This information is used to further understand the yields and nature of the organic moieties liberated by the hydrous pyrolysis procedure. Furthermore, the implications of these analyses to reconstructing the extraterrestrial history of meteoritic organic matter are also considered.

EXPERIMENTAL

Hydrous pyrolysis. Full details of the hydrous pyrolysis method can be found in (9). The insoluble organic material in the Murchison meteorite was isolated by digesting the inorganic matrix with hydrofluoric (HF) and hydrochloric (HCl) acids and by removing any free organic compounds with solvent extraction (11). 136 mg of the HF/HCl residue was placed in a 1ml stainless steel insert and 0.4 ml of high purity water was added. The insert was then purged with nitrogen gas, sealed and placed into a 71 ml stainless steel high pressure reactor

(series 4740, Parr Instrument Co.) which was filled with 20 ml water. The whole arrangement was heated to 320 °C for 72 hours.

Supercritical fluid extraction. Hydrous pyrolysis products were extracted by supercritical fluid extraction (SFE). An initial static extraction with pure CO₂ (99.9995 %, 4000 psi) for 90 mins was followed by a dynamic extraction (4000 psi, 1 ml/min) for 45mins. The extract was collected in diethyl ether cooled to approximately 0 °C. These conditions produced an extract of non-polar compounds dissolved in a few 100 µl of solvent ready for immediate analysis.

Gas chromatography-mass spectrometry. Compound detection and identification was performed by gas chromatography-mass spectrometry (GC-MS) using a Hewlett Packard 5890 gas chromatograph interfaced with a 5971 mass selective detector. Analyses were by on-column injection onto a HP5 capillary column (50 m x 0.2 mm x 0.17 µm). Following a 10 min period at 25 °C the GC oven was programmed from 25 °C to 220 °C at 5 °C min⁻¹ and then from 220 to 300 °C at 10 °C min⁻¹. The final temperature was held for 12 min.

Anhydrous pyrolysis. Samples were prepared for comparisons with the pyrolysis-GC-MS analysis of the hydrous pyrolysis residue. Unheated and hydrously pyrolysed Murchison HF/HCl residue were subjected to off-line anhydrous pyrolysis. Samples were loaded into Pyrex glass tubes followed by the removal of air by purging the tube interior with N₂ gas. These tubes were then sealed and heated at 320 °C for 72 hours.

Pyrolysis-GC-MS. Samples were introduced as dry pellets (typically ca. 1 mg) into a quartz lined pyrojector (S.G.E, Ltd) held at 500 °C. Separation of the flash pyrolysis products was performed using a Hewlett Packard 5890 GC fitted with a Ultra2 capillary column (50 m x 0.2 mm x 0.32 µm). During a run, the GC oven was held at 50 °C for 1 min before a ramp was employed of 10 °C min⁻¹ to 100 °C and 5 °C min⁻¹ to 300 °C where it was held for 14 min. Detection and identification products was performed as for GC-MS.

RESULTS AND DISCUSSION

Fig. 1 shows GC-MS analyses of the hydrous pyrolysate from the Murchison HF/HCl residue. The main pyrolysis products are volatile aromatic and heteroatom-containing aromatic compounds with low molecular weights, suggesting that the majority of aromatic centres within the macromolecular material are small and consist of one or two aromatic rings. Sephton *et al.* (11) calculated a yield of 1.36 % of the high molecular weight starting material based on a solvent extract of the pyrolysate. Table 1 illustrates the carbon contents of the HF/HCl residues before and after the hydrous pyrolysis procedure. The values reveal that the amount of Murchison macromolecular carbon solubilised by hydrous pyrolysis is 55.3 %. Therefore, there is an obvious disagreement between the amount of carbon solubilised by hydrous pyrolysis and the amount of product measured by weighing a solvent extract dried under a stream of N₂. Hence, as indicated by the SFE extract, it appears that the majority of hydrous pyrolysis products from the Murchison macromolecular material are more volatile than the tricyclic PAHs. These volatile products are lost during conventional solvent extraction and evaporation steps, but are retained by SFE.

To investigate the change in the organic constitution of the macromolecular material brought about by the hydrous pyrolysis procedure, unheated Murchison HF/HCl residue and hydrous pyrolysis residue were analysed by pyrolysis-GC-MS (Fig. 2). Analyses of the hydrous pyrolysis residue indicate that some aromatic moieties do remain following the hydrous pyrolysis procedure. Although when compared to the pyrolysis-GC-MS trace for the unheated Murchison HF/HCl residue, it is apparent that much structural diversity has been lost.

To further investigate the nature of the process which liberates organic moieties from the macromolecular material during hydrous pyrolysis, pyrolysis-GC-MS analyses were performed for hydrously pyrolysed residues and samples pyrolysed anhydrously under comparable conditions. One noticeable difference between the two types of pyrolysis is the relative abundance of benzonitrile. This compound is present in small amounts in the unheated Murchison residue, is absent in the hydrously heated sample, but is abundant in the anhydrously heated sample. This suggests that the Murchison macromolecular material contains a substantial amount of organic nitrogen. The host of this organic nitrogen becomes more visible to pyrolysis-GC-MS following off-line anhydrous pyrolysis.

To confirm whether this nitrogen bearing organic component is removed by hydrous pyrolysis or simply hidden by a reaction with water, a hydrous pyrolysis residue was subjected to anhydrous pyrolysis. The residue from this process failed to produce benzonitrile during pyrolysis-GC-MS. Therefore it appears that the Murchison macromolecular material contains a nitrile precursor which is removed from the macromolecular material by hydrous pyrolysis. Nitriles in meteoritic organic matter have attracted some attention in the past due to the possibility that they may be the degradation products of amino acids, although other structures may degrade during pyrolysis to give these compounds. Possible candidates for the nitrile precursor include macromolecularly-bound amides (RCONH₂), imines (R₂CNR) and amino acids (RCH(NH₂)COOH).

Therefore, a nitrogen-containing moiety is transferred from the insoluble macromolecular material to soluble organic molecules by hydrous pyrolysis. These observations suggest that a CM macromolecule may release nitrogen-bearing organic compounds during aqueous alteration. As the Murchison macromolecule has already been subjected to pre-terrestrial aqueous alteration (12), it is reasonable to expect that communication of nitrogen containing organic matter between solubility classes occurred on the Murchison meteorite parent body. This suggestion is consistent with previous work which established that aromatic hydrocarbons have been released from the Murchison macromolecular material during a preterrestrial alteration event (11).

CONCLUSIONS

The majority of hydrous pyrolysis products of meteoritic macromolecular material are volatile, consisting of mono or diaromatic organic molecules. This suggests that meteoritic macromolecular material is comprised of one or two ring aromatic cores connected by aliphatic linkages and heteroatomic groups.

Pyrolysis-GC-MS analyses of pyrolysis residues indicate that a nitrogenous organic moiety is present in the Murchison macromolecular material. This organic unit is released by hydrous pyrolysis. Therefore it appears that some low molecular weight nitrogen-containing organic compounds in the Murchison meteorite may have been released from the macromolecular material during the aqueous alteration event that is known to have affected the Murchison parent body. This is further evidence that aqueous alteration on the meteorite parent body can exert a strong control on macromolecular material structure and can lead to interaction between organic solubility classes.

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Table 1

% carbon of Murchison HF/HCl residue before and after hydrous pyrolysis	
Sample	Carbon (%)
Murchison HF/HCl residue	8.5
Hydrous pyrolysis residue	3.8

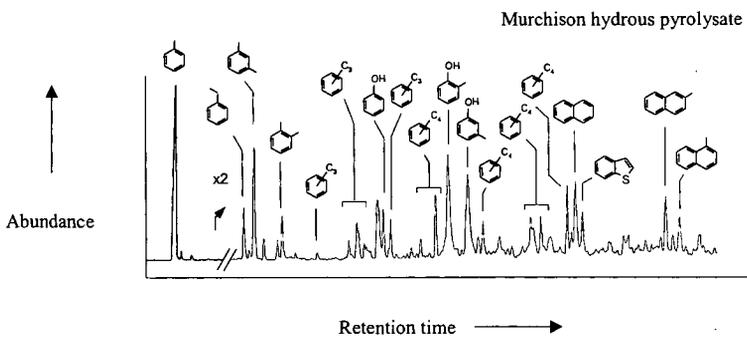


Figure 1. GC-MS analysis of the SFE extract of the hydrously pyrolysed HF/HCl residue from the Murchison meteorite. After Sephton *et al.* (1998).

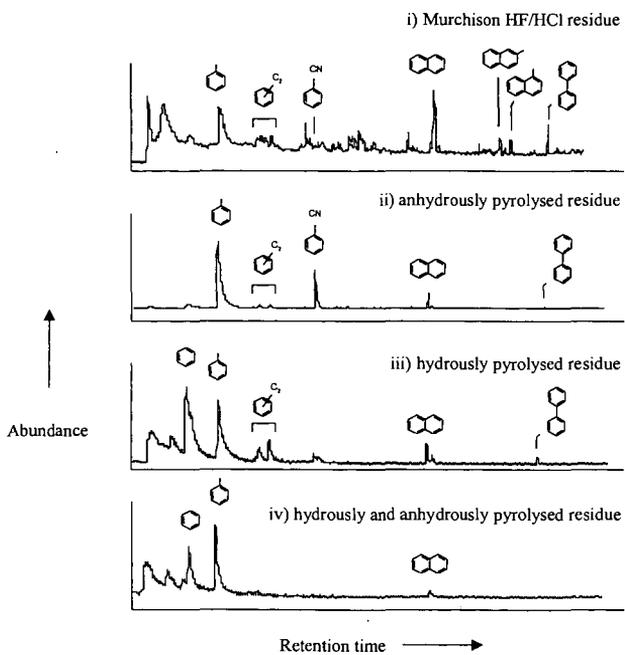


Figure 2. Pyrolysis-GC-MS analyses of i) the unheated Murchison HF/HCl residue, ii) anhydrously pyrolysed residue, iii) hydrously pyrolysed residue, and iv) hydrously and anhydrously pyrolysed residue.