

**CARBON ISOTOPIC MEASUREMENTS OF FRAGMENTS OF METEORITIC
MACROMOLECULE PRODUCED BY HYDROUS PYROLYSIS; M.A. Sephton, C.T. Pillinger
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Abstract— Meteorites provide us with an excellent opportunity for studying extraterrestrial organic compounds and constitute our only practically available record of pre-biotic evolution and the state of matter 4.5 billion years ago [1]. It now appears that the organic components in meteorites originated from more than one environment and possible source regions include dense interstellar clouds, the solar nebula, planetissimals [2 and refs. therein] and stellar atmospheres [3]. During its complex history the organic fraction has possibly been affected by the hydrothermal alteration that is believed to have created the hydrated silicates in the carbonaceous meteorites[4]. Clues to the origin, synthetic pathways and evidence of aqueous alteration can be found in the structures of organic compounds but more conclusive information is potentially forthcoming from the measurement of isotopic ratios [1].

The majority of the organic matter in meteorites is in the form of a macromolecule which is insoluble in common organic solvents [4]. It is primarily this property which has repulsed attempts at structural elucidation so that it is still only poorly characterised [5]. The macromolecule is believed to be similar to coal and approximates to a condensed aromatic framework with various functional and heteroatomic bridging groups attached [5]. One method, developed over the last 20 years to analyse macromolecules, is hydrous pyrolysis, which involves heating samples at 250 to 360°C for several days under pressure in the presence of water (a hydrogen donor) and an inert atmosphere [6]. The technique relies on components within the macromolecule attempting to attain a more stable molecular configuration. Under high temperatures and pressures the molecule undergoes a progressive elimination of steric hinderances[7]. The process leads to the production of solvent soluble organic fragments which can be analysed by conventional chromatographic means.

The hydrous pyrolysis of solvent extracted Murchison HF/HCl resistant residue was undertaken using a stainless steel high pressure bomb (Parr 4740, 71ml) with a purpose built stainless steel insert (1ml), used to accommodate the small sample size. The residue (136mg) together with 0.4ml high-purity, degassed-water was loaded into the insert which was, in turn, placed into the high pressure bomb surrounded by 19ml of water; both vessels were purged with N₂ to ensure a non-oxidising atmosphere before sealing. The closed bomb was heated in a muffle furnace at 320°C for 72 hours. The fragments produced from the Murchison macromolecule were recovered using super critical fluid extraction (S.F.E., Isco Ltd) to reduce the possibility of losing any compounds with boiling points below 300°C by evaporation [8]. An initial static extraction using pure CO₂ (99.9995%) at 4000psi for 90 mins was followed by a dynamic extraction at 4000psi with a flow rate of 1ml/min for 45mins. The sample was collected by immersing the 50µm fused silica capillary vent in hexane cooled to approx. 0°C and the supercritical CO₂ soluble fraction concentrated down to a less than 200µl, eliminating the need for solvent evaporation by heating. Compounds in the SFE extract were identified by gas chromatography-mass spectrometry (GCMS) and by the comparison of retention times of authentic standards. Carbon isotopic compositions of individual compounds were determined by isotope ratio monitoring-GCMS (GCMS & IRM-GCMS conditions as in [9]).

The most abundant compounds released by hydrous pyrolysis include toluene, naphthalene, methyl naphthalenes, dimethyl naphthalenes, acenaphthene, methyl phenols and dimethyl phenols. The extract is clearly dominated by aromatic compounds but it must be noted that the SFE conditions were designed to only extract relatively non-polar organics.

Table 1. Results of isotopic analyses.

Compound	Macromolecular		Free
	$\delta^{13}\text{C}\text{‰}$	$\pm 1\sigma(n-1)$	$\delta^{13}\text{C}\text{‰}$
naphthalene	-5.7	2.1	-12.5
2-methyl naphthalene	-4.6	1.5	-5.8
1-methyl naphthalene	-7.1	2.3	-11.1
acenaphthene	-5.9	1.7	Undetected

Table 1 shows replicate analyses of the four major components in the extract. The isotopic measurements for the macromolecular fragments confirm their extra-terrestrial origins, as terrestrial contaminants would be expected to be substantially more enriched in ¹²C. In addition the values obtained are significantly enriched in ¹³C than those

for the bulk Murchison macromolecule ($-15.8 \pm 1.4\%$ [10]). The isotopic compositions are close to, but distinct (except for 2-methyl naphthalene) from, previous $\delta^{13}\text{C}$ values obtained for PAHs from total soluble aromatic fractions [11]. Therefore if the fragments represent the isotopic composition of the aromatic portion of the macromolecule, the macromolecule must itself contain a significant amount of an unidentified isotopically light component. As yet, tentative identifications and measurements of pyrolysis fragments in this study, and the work of Yuen *et al.* [12] and Engel *et al.* [13] on soluble compounds, indicate that the light portion is unlikely to be the O and N containing polar material.

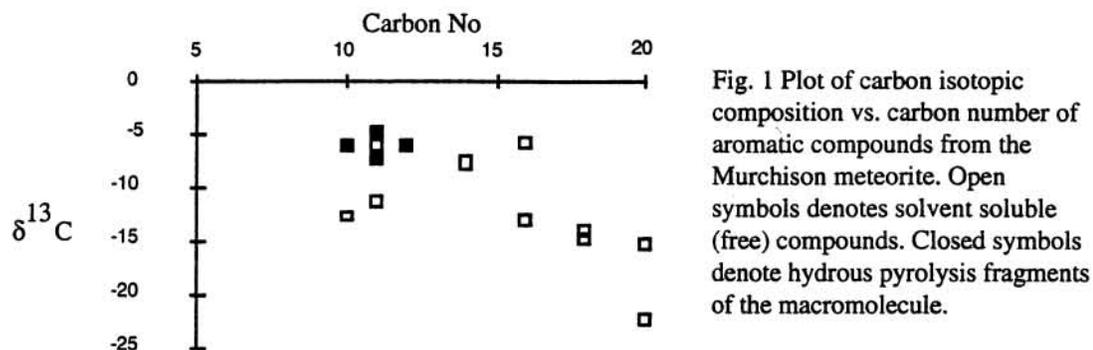


Fig. 1 Plot of carbon isotopic composition vs. carbon number of aromatic compounds from the Murchison meteorite. Open symbols denotes solvent soluble (free) compounds. Closed symbols denote hydrous pyrolysis fragments of the macromolecule.

For a comparison with the results reported above, 1.5g of whole Murchison was extracted and analysed using nearly identical SFE, GCMS and IRGCMS conditions. Qualitatively, the composition of the extract resembled the pattern for the pyrolysis fragments from the macromolecule. It would seem therefore that the macromolecule could have acted as a parent structure which produced the soluble organics following some degradative event. However isotopic measurement of these components showed differences between the $\delta^{13}\text{C}$ values of compounds produced from the macromolecule and those which are free in the meteorite (Table 1, Fig. 1). This difference is most notable with naphthalene where the free form is much lighter than that produced from the macromolecule. One possible explanation is that the naphthalene precursor in the macromolecule has produced isotopically lighter naphthalenes by the preferential breaking of ^{12}C - ^{12}C bonds. As a result the surviving naphthalene would be more refractory and therefore isotopically heavier. Any subsequent naphthalenes produced naturally would be enriched in ^{13}C . A further observation is that acenaphthene, while scarce in its free form, is produced in abundance by hydrous pyrolysis. It seems unlikely that this component could have been preferentially lost by evaporation from the meteorite as its boiling point is higher than the three other major components. Hydrous pyrolysis of the macromolecule, while ideal for producing analysable fragments, possibly does not accurately represent the event which produced the soluble organics assuming the macromolecule is the precursor of the solvent extractable material, and not vice versa. Previous isotopic measurements on soluble aromatics have detected a progressive enrichment in ^{12}C with increasing molecular weight [9], which is consistent with a build up of higher molecular weight species from lower homologues. The value obtained for naphthalene appears not to follow this trend and indicates a more complex picture with perhaps more than one synthetic pathway operating.

References

- Mullie F., Reisse J., 1987, *Topics in current chemistry*. Springer Verlag, Berlin.
- Cronin J.R., Pizzarello S., Cruikshank D. P., 1988, in Kerridge J. F., Matthews M. S., eds, *Meteorites and the early solar system*. Univ. Arizona Press, Tucson, p.879.
- Kroto H.W, Heath J.R., O'Brien S.C., Curl, R.F., Smalley R.E., 1987, *Nature* 326,160-162
- Nagy B.: *Carbonaceous meteorites*, Elsevier Scientific publishing., Amsterdam, 1975.
- Hayatsu R., Winans R.E., Scott R.G., McBeth R.L., Moore L.F., Studier M.H., 1980, *Science*,207,1202.
- Lewan MD, BJORoy M and McDonald J.H., 1979, *Science*,203, 897.
- Tissot B. P., Welte, D. H., 1984, *Petroleum formation and occurrence*, 2nd ed., Springer-Verlag, Heidelberg.
- Gilmour I., Pillinger C. T., 1993, *Lunar. Planet. Sci.*,24,535.
- Gilmour I. and Pillinger C.T., 1994, *Mon. Not. R. Astron. Soc.* 269,235-240.
- Cronin J.R., Chang S., 1993, in Greenburg J.M., Pirronello V., eds, *Chemistry of life's origins*. Kluwer, Dordrecht,p.209.
- Krishnamurthy R. V., Epstein S., Cronin J.R., Pizzarello S., Yuen G. U., 1992, *Geochim.Cosmochim.Acta.* 56,4045.
- Yuen G., Blair N., DesMarias D.J., Chang S., 1984, *Nature* 307,252-254.
- Engel M.H., Macko S.A., Silfer J.A., 1990, *Nature* 348,47-49.