

EXTRACTION AND ISOTOPIC ANALYSIS OF MEDIUM MOLECULAR WEIGHT
HYDROCARBONS FROM MURCHISON USING SUPERCRITICAL CARBON DIOXIDE: Iain
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The large variety of organic compounds present in carbonaceous chondrites poses particular problems in their analysis not the least of which is terrestrial contamination. Conventional analytical approaches employ simple chromatographic techniques to fractionate the extractable compounds into broad classes of similar chemical structure. However, the use of organic solvents and their subsequent removal by evaporation results in the depletion or loss of semi-volatile compounds as well as requiring considerable preparative work to assure solvent purity. Supercritical fluids have been shown to provide a powerful alternative to conventional liquid organic solvents used for analytical extractions [1]. Besides their strong solvating ability, supercritical fluids have several characteristics that make them useful for the quantitative recovery of organic compounds from carbonaceous chondrites. The solvent strength of a supercritical fluid is directly related to its density so that modification of the extraction pressure and temperature enables species of different solubility to be extracted. The polarity of a supercritical fluid can also be controlled by the addition of solvent modifiers such as methanol. The low critical temperature of a supercritical fluid such as carbon dioxide (31°C) can be used to avoid the decomposition of thermally labile components. Finally, although liquid when in the supercritical state fluids such as carbon dioxide retain the low viscosity and subsequent penetration of the sample matrix of a gas; after the extraction the use of a gas makes sample recovery much simpler.

A sample of Murchison from the Field Museum (courtesy E.Olsen) was used for these analysis. Two interior fragments were used; the first (2.85 g) was crushed in an agate pestel and mortar to a grain size of ca. 50-100 µm, the second (1.80 g) was broken into chips 3-8 mm in size. Each sample was loaded into a stainless steel bomb and placed in the extraction chamber of an Isco supercritical fluid extractor maintained at 35°C. High purity (99.9995%) carbon dioxide was used and was pressurised using an Isco syringe pump. The samples were extracted dynamically by flowing CO₂ under pressure through the bomb and venting via a 50 µm fused silica capillary into 5 mls of hexane used as a collection solvent. The hexane was maintained at a temperature of 0-5°C. A series of extractions were done on each sample (Table 1) using CO₂ of increasing density.

Pressure (psi)	Density CO ₂ g/ml	Solubility (Hildebrand)	Time (mins)	Principal Components extracted
1927	0.801	6.828	30	Aliphatic hydrocarbons + mono and di-aromatics
3000	0.878	7.486	30	Polycyclic aromatics + S
5000	0.958	8.160	10	Trace Polycyclic aromatics
7000	1.022	8.708	90	No detectable compounds

The principal components extracted in each fraction are summarized in the table. Fig 1 shows the GCMS results for the 1927 psi fraction. The extractable organics are dominated by naphthalene and by straight chain hydrocarbons, isoprenoid hydrocarbons, and a homologous series of alkyl cyclohexanes and a broad hump due to cycloalkanes. With the exception of the relatively high abundance of naphthalene the results are very similar to those obtained in benzene-methanol extracts by Cronin and Pizzarello [2]. The 3000 psi extract was dominated by phenanthrene, fluoranthene and pyrene, the three most abundant PAH in Murchison, and by a large peak due to S₈. The minor components were thiophene, dibenzothiophene, methyl dibenzothiophenes, methyl phenanthrenes, and methyl pyrenes. No traces of higher molecular weight PAH were found. The 5000 psi extract contained very few compounds, those that were detectable were apparently trace quantities of PAH similar to the 3000 psi extract. No compounds were found in the 7000 psi extract. It would appear that supercritical CO₂ by itself is an efficient means of separating polar from non-polar compounds.

The alkanes, isoprenoid alkanes and alkyl cyclohexanes (all common petroleum hydrocarbons) were identified by Cronin and Pizzarello [2] as terrestrial contaminants as they were found at higher abundances in exterior compared to interior samples. Their presence here in interior chips of Murchison highlights the susceptibility of carbonaceous chondrites to atmospheric hydrocarbon contamination. We

have previously confirmed the indigeneity of PAH from measurements on the $\delta^{13}\text{C}$ values of individual compounds (3), however, volatile PAH like naphthalene and methyl naphthalenes are also common petroleum hydrocarbons. Isotopic measurements of these compounds will be necessary to confirm their indigeneity, however, the use of supercritical carbon dioxide at 35°C greatly reduces the possibility that these and other free PAH in Murchison are cracking products of the macromolecular material produced either during extraction with organic solvents at elevated temperatures or by rigorous ultrasonication.

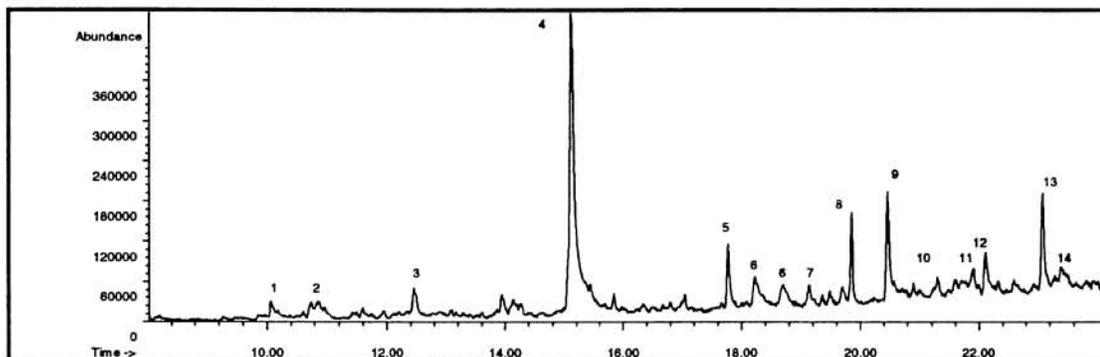


Fig 1. Partial Total Ion Chromatogram (C_{10} to C_{15} of 1972 psi supercritical CO_2 extract of 3-8 mm chips of Murchison. The numbered compounds were tentatively identified by comparison of their mass spectra with reference spectra and standards. (1) n-decane, (2) Dichlorobenzene, (3) n-undecane, (4) naphthalene, (5) n-tridecane, (6) Methyl naphthalenes, (7) Alkylcyclohexane, (8) 2,6,10-trimethyl dodecane, (9) n-tetradecane, (10) Dimethyl naphthalenes, (11) Octyl cyclohexane (?), (12) 2,6,10-trimethyl tridecane, (13) n-pentadecane, (14) Acenaphthene.

Table 2. lists the carbon isotopic compositions determined by isotope-ratio-monitoring GCMS for the hydrocarbons in the 1927 psi chip fraction. As can be seen the majority have terrestrial $\delta^{13}\text{C}$ of -26 to -33‰. However, by backflushing helium through the combustion interface of the irm-GCMS it is possible to determine the $\delta^{13}\text{C}$ value of a background hump. This was done several times in the molecular weight range C_{15} to C_{20} and gave $\delta^{13}\text{C}$ values ranging from -9 to -6‰. This confirms the indigeneity of the highly structurally diverse suite of cycloalkanes.

Compound	$\delta^{13}\text{C}$ (‰)	Compound	$\delta^{13}\text{C}$ (‰)
n- C_{13}	-28.5	cycloalkane hump C_{16}	-8.5
n- C_{14}	-33.2	cycloalkane hump C_{18}	-8.5
n- C_{15}	-28.2	cycloalkane hump C_{20}	-6.0
n- C_{16}	-30.6	cycloalkane hump C_{20}	-6.0

Supercritical carbon dioxide offers an effective low contamination risk means of separating non-polar from polar hydrocarbons in the extraction of organic compounds from meteorites. Perhaps the greatest promise of this technique comes from the ability to directly couple SFE systems to the front-end of a GCMS thereby enabling direct extraction and analysis of considerably smaller samples than conventional methods allow.

References

- (1) Hawthorne S.B. and Miller D.J. (1987) *J. Chromatogr.* **403**, 63-76; (2) Cronin J.R. and Pizzarello S. (1990) *Geochim. Cosmochim. Acta* **54**, 2859-2868; (3) Gilmour I. and Pillinger C.T. (1992) *Meteoritics* **27**, 224-225.