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ORGANIC GEOCHEMISTRY OF A HYDROCARBON-RICH CALCARENITE FROM THE CHICXULUB SCIENTIFIC DRILLING PROGRAM

I. Gilmour¹, M.A. Sephton and J.V. Morgan², ¹ Planetary and Space Sciences Research Institute, The Open University, Milton Keynes MK7 6AA, U.K. (I.Gilmour@open.ac.uk), ² Department of Earth Science and Engineering, Imperial College of Science Technology and Medicine, Prince Consort Road, London SW7 2BP, United Kingdom

Introduction: Terrestrial impact craters appear to be unique in the geological environment in that they contain evidence for a wide variety of carbonaceous phases ranging from shock-produced diamonds [1] to hydrocarbons in fluid inclusions [2]. Some of these materials, such as diamond, are a direct result of the impact process. However, at some craters, carbonaceous material has been incorporated into impactites and other rocks post-impact, possibly as a result of hydrothermal activity [3]. Part of the rationale for the Chicxulub Scientific Drilling Project (CSDP) was to investigate the post-impact environment associated with such a large structure, seismic data indicates the diameter of the transient cavity was around 100 km [4]. The instigation of hydrothermal systems following an impact and the consequent mobilization and migration of organic matter and other biologically important nutrients is one mechanism that has been proposed for the development of potential habitats for primitive organisms on Mars [5].

At around a depth of 1.4 km the CSDP recovered core material that was rich in hydrocarbons. This section of the core consists of a laminated black calcarenite that contains intraclasts, synsedimentary microfaulting and soft sedimentary deformation features. This study examines the organic geochemistry of this hydrocarbon-rich material in an attempt to ascertain whether these hydrocarbons are associated with the migration and emplacement of organic matter by post-impact hydrothermal activity. The sample used for our investigation is number 1756 from core box 419 and comes from a depth of 1405.085 m.

Methods: Crushed and powdered samples of the hydrocarbon-bearing calcarenite were solvent extracted using dichloromethane (10 ml, Distol grade) by sonication for 30 minutes and separated into aliphatic and aromatic-rich fractions using column chromatography. The fractions were concentrated to around 50 μ l under a stream of dry nitrogen and around 1 μ l injected used for organic analysis. Analyses were by splitless injection into a BPX5 capillary column (30 m x 0.25 mm x 0.25 μ m). The GC oven was operated under the following conditions: initial isothermal hold for 2 min at 50°C; temperature programmed at 5°C/min to 300°C and final isothermal hold for 8 min.

For pyrolysis around 30 mg of powdered sample was loaded into a pre-cleaned quartz glass tube. The sample was flash pyrolysed at 610°C using a CDS

1000 pyroprobe (CDS Analytical, Oxford, PA), within 15 s after insertion into the interface, for 15 s in a flow of helium. The heating rate of pyrolysis was 20°C ms⁻¹. The interface was held at 260°C and the GC injector maintained at 250°C.

Compound detection and identification was performed by gas chromatography-mass spectrometry using an Agilent Technologies 5973 GCMS operated in fullscan electron ionization mode (50-500 Da, 1.8 scan s⁻¹, 70 eV electron energy). GC column conditions were the same as for the solvent extracted samples.

Results: The total ion current chromatogram for a pyrolysate from the calcarenite sample is shown in Figure 1. The trace is dominated by a large unresolved complex mixture (UCM), with the main resolved components being alkanes, aromatics (including significant amounts of naphthenic compounds) and sulfur containing thiophenes. Figure 2 shows a selected ion mass chromatogram indicating the distribution of n-alkanes in the pyrolysate of the calcarenite sample. A distribution of n-alkanes from n-C₁₂ to n-C₂₉ is observed together with significant abundances of the isoprenoids pristane and phytane.

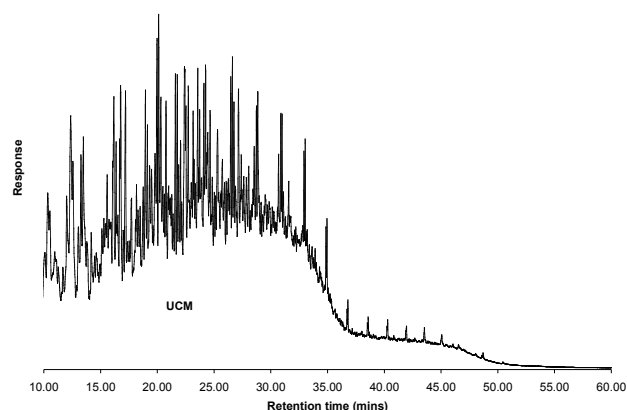


Figure 1 Total ion current chromatogram of pyrolysate from sample 1756, core box 419, a calcarenite from a depth of 1405.085 m

From the total ion current chromatogram it was apparent that there were significant amounts of PAHs present in the calcarenite. Figure 3 shows a reconstructed ion chromatogram of a portion of the TIC where phenanthrene/anthracene and alkyl-substituted phenanthrenes eluted.

Carbon in impact structures: Under 'normal' geological conditions the formation and migration of hydrocarbons is a slow process related to the subsidence of sedimentary basins and the gradual maturation of organic matter. However, in hydrothermal systems the maturation of organic matter, the generation of hydrocarbons, their expulsion and migration effectively take place in an instantaneous geological time frame. Previous studies of hydrothermally generated hydrocarbons [see 6 for a review] suggest that they have a variety of features that can distinguish them from 'normal' petroleum. For example: A broad distribution of n-alkanes with no carbon number predominance, a naphthenic hump, unresolved complex mixture, significant concentrations of pristane and phytane, mature biomarker distributions and high concentrations of PAHs and thio-PAHs. We observe some of these characteristics in the Chicxulub calcarenite: abundant PAHs and thio-PAHs, pristane, phytane and a broad distribution of n-alkanes.

Carbonaceous material has previously been found associated with several impact structures, most notably the Sudbury impact structure in Canada and the Gardnos impact structure in Norway. However, at both these structures the carbon occurs as a severely dehydrogenated graphitic or amorphous carbonaceous material and its method of emplacement has proven problematic to determine. Continued examination of hydrocarbons associated with the Chicxulub structure may indicate the feasibility of hydrothermal generation, expulsion and migration of hydrocarbons as a means of mobilizing, processing and concentrating organic matter on early Earth and Mars.

References: [1] Gilmour I. (1998) *Spec. Pub. Geol. Soc. Lond.* **140**, 205-216. [2] Andersen T. and Burke E. A. J. (1996) *Europ. J. Min.* **8**, 927-936. [3] Gilmour I. et al. (2003) *Geochim. Cosmochim. Acta* In Press. [4] Morgan J.V., Warner M.R., Chicxulub Working Group. (1997) *Nature*, **390**, 472-476. [5] Rathburn J.A. and Squyres S.W.

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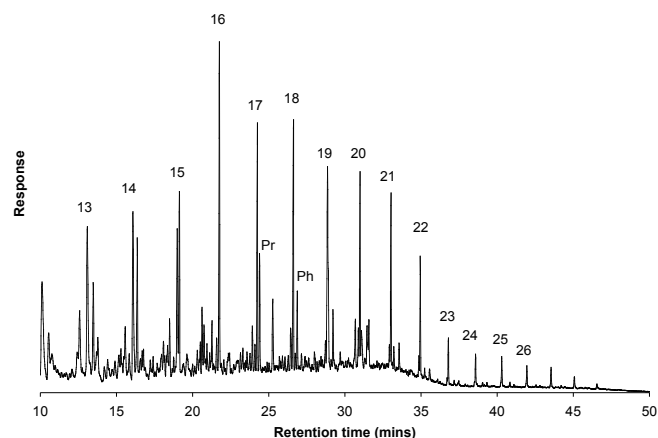


Figure 2 Mass chromatogram (m/z 99) showing the distribution of n-alkanes in sample 1756, core box 419, a calcarenite from a depth of 1405.085 m. Pr = pristane, Ph = Phytane.

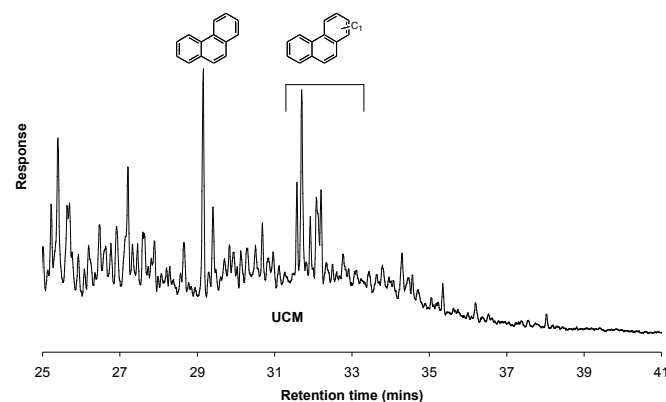


Figure 2 Reconstructed ion chromatogram of the parent and alkyl-phenanthrenes in sample 1756.