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Application of organic geochemistry to detect signatures of organic matter in the Haughton impact structure

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Abstract–Organic geochemistry applied to samples of bedrock and surface sediment from the Haughton impact structure detects a range of signatures representing the impact event and the transfer of organic matter from the crater bedrock to its erosion products. The bedrock dolomite contains hydrocarbon-bearing fluid inclusions which were incorporated before the impact event. Comparison of biomarker data from the hydrocarbons in samples inside and outside of the crater show the thermal signature of an impact. The occurrence of hydrocarbon inclusions in hydrothermal mineral samples shows that organic matter was mobilized and migrated in the immediate aftermath of the impact. The hydrocarbon signature was then transferred from bedrock to the crater-fill lacustrine deposits and present-day sediments in the crater, including wind-blown detritus in snow/ice. Separate signatures are detected from modern microbial life in crater rock and sediment samples. Signatures in Haughton crater samples are readily detectable because they include hydrocarbons generated by the burial of organic matter. This type of organic matter is not expected in crater samples on other planets, but the Haughton data show that, using very high resolution detection of organic compounds, any signature of primitive life in the crater rocks could be transferred to surface detritus and so extend the sampling medium.

INTRODUCTION

Organic geochemistry is most widely used in the fields of petroleum geology, environmental geology, and paleoenvironmental reconstruction. However, there are diverse ways in which organic geochemistry may be helpful in describing and understanding organic matter associated with impact craters, including the identification of the source of organic matter, the current composition of the organic matter, and its degree of alteration (e.g., Avermann 1994; French et al. 1997; Gilmour et al. 2003; Hode et al. 2003). Most previous work on this topic has been focused on location-specific aspects, e.g., identifying a specific source of organic matter for a particular crater. Here, we use the Haughton impact structure to demonstrate generic aspects of the use of organic geochemistry, i.e., the types of signature that can be determined in an impact crater containing organic matter. Five types of signature are described: (i) the thermal effect of impact on the target rocks, (ii) a signature of hydrocarbons in the impact-induced hydrothermal system, (iii) organic signatures in post-impact sedimentary crater-fill deposits, (iv) a signature in modern sediments in and around the crater, and (v) a signature of contamination by later life.

The Haughton impact structure (Fig. 1) was formed ~23 Ma in a ~1880 m series of Lower Paleozoic sedimentary rocks dominated by platform carbonate facies overlying a Precambrian crystalline basement (Thorsteinsson and Mayr 1987; Osinski et al. 2005a). The crater is filled with carbonate-rich impact melt rocks (Osinski and Spray 2001; Osinski et al. 2005b), which contain clasts of crystalline basement material, indicating a depth of penetration of over 2 km. Limited occurrences of Tertiary lacustrine sediments lie unconformably upon the melt rocks. The target rocks within the central part of the crater contain hydrothermal mineral veins of quartz and calcite (Osinski et al 2001, 2005c). Exposure is generally excellent at Haughton. The site has not experienced geological events that would complicate interpretation or impair detailed analysis of its hydrocarbon

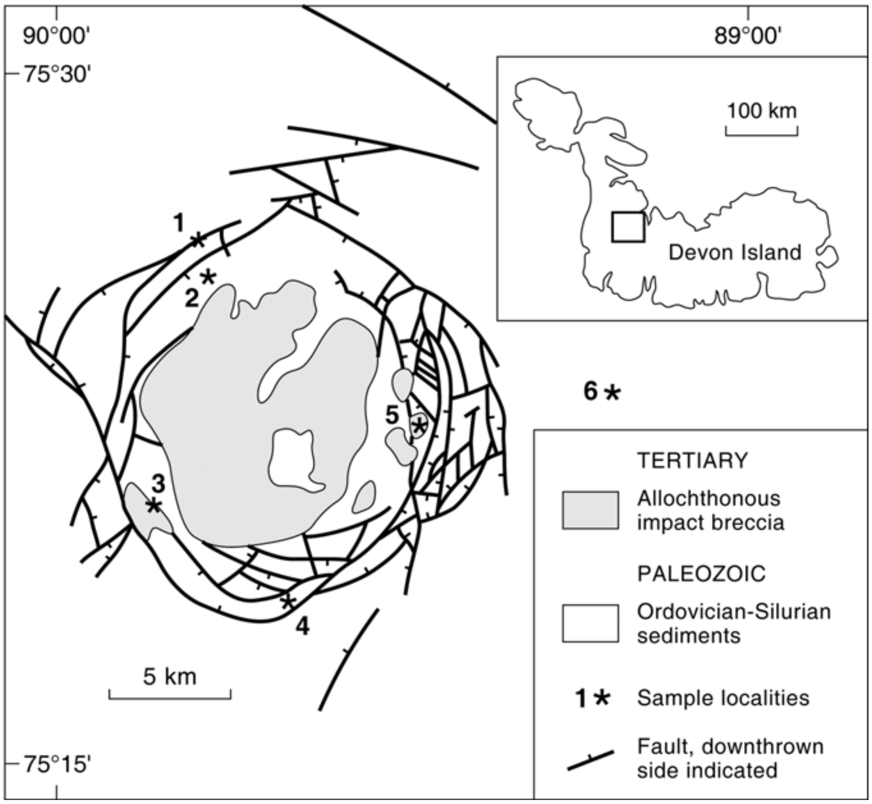

Fig. 1. Map of the Haughton impact structure, Devon Island, Canada, showing location of samples discussed in text. Insert shows site on Devon Island.

system. The present-day Haughton structure lies entirely within the dolomite-rich Allen Bay Formation of Ordovician-Silurian age. These country rocks are predominantly brown dolomites with a sucrosic, porous texture, and are generally unveined.

Hydrocarbons were first recorded in the Haughton impact structure through a fluid inclusion study of the hydrothermal mineral veins (Parnell et al. 2003). A fluid inclusion study of the Allen Bay Formation dolomites shows that inclusions of liquid hydrocarbon also occur within dolomite crystals of the target rocks. These inclusions fluoresce yellow and appear to be primary, i.e., they were trapped during crystal growth. The source of the hydrocarbons lies in Lower Paleozoic mudrock facies, from which migration took place laterally/updip into the porous dolomite facies before entrainment by later hydrothermal activity (Parnell et al. 2003).

METHODOLOGY

Samples of bedrock and sediment (5 g to 50 g) in the Haughton structure were extracted using dichloromethane, then separated using thin layer chromatography, and hydrocarbon fractions were analyzed by gas chromatography-mass spectrometry for n-alkanes (m/z 85), hopanes (m/z 191), and steranes (m/z 217). Analyses were performed using a Hewlett Packard HP5970 MSD instrument attached to a HP5890 gas chromatograph. A 30-m SGE BPX5 column was used with 0.5-micron film thickness and 0.32-mm internal diameter. The gas chromatography temperature programme was 80 °C for 2 min, heating at 4 °C/min up to 290 °C, then holding for 30.5 min. Standard thermal maturity parameters were calculated from biomarker distributions (Waples and Machihara 1991; Peters and Moldowan 1993). Hopane ratios were calculated from the C_{31} $\alpha\beta$ 22S and 22R peaks.

ORGANIC GEOCHEMICAL SIGNATURES

Thermal Signature of Impact

Impact events can impart heat into the target rocks in a number of ways, including energy deposited by the passage of the shock wave, and subsequent conductive heating by impact-melted materials and through post-impact hydrothermal activity. The thermal maturity imparted to the target rocks by impact can be detected by the use of organic geochemical parameters that are sensitive to thermal alteration. A wide range of parameters is available, used routinely to measure thermal maturity during petroleum exploration (Peters and Moldowan 1993; Waples and Machihara 1991). Parameters mostly use ratios between similar molecules that are destroyed or formed at different

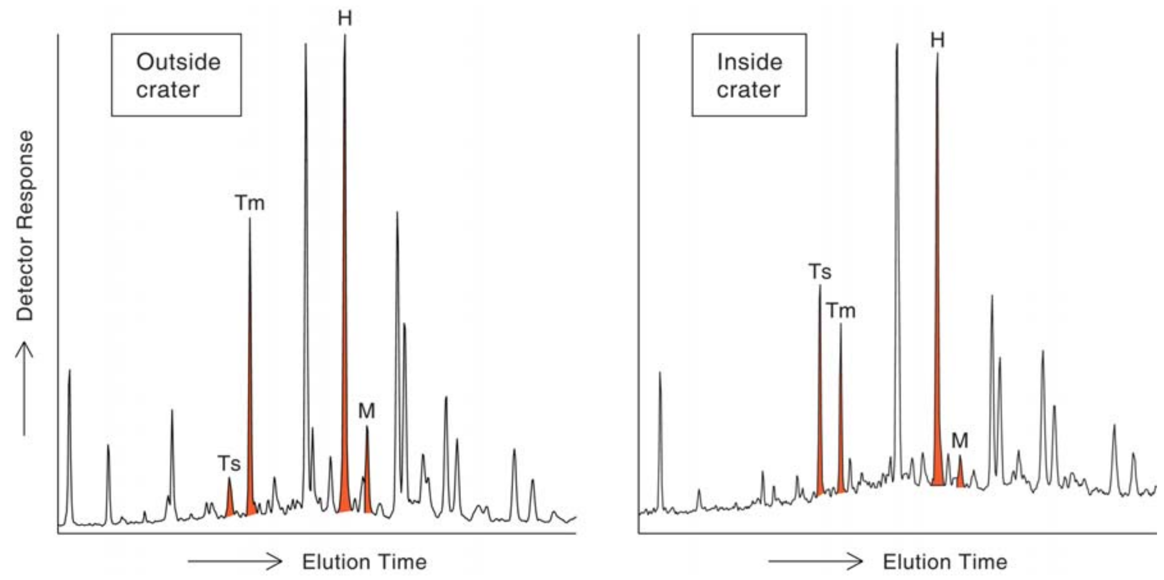

Fig. 2. Hopane profiles for dolomite bedrock samples from within the Haughton crater (locality 4) and from 7 km beyond the crater margin (locality 6), highlighting the four compounds Ts, Tm, and the C_{30} hopane and moretane. Respective ratios of 1.25 and 13.1 for the intra-crater sample and 0.14 and 5.5 for the extra-crater sample demonstrate the enhanced thermal maturity of the intra-crater sample.

rates with increases in temperature. Two types of molecule used widely are hopanes and steranes, which represent the breakdown products of bacterial and eukaryotic membranes, respectively (Tissot and Welte 1984; Brocks et al. 2003). Hopanes are considered to have a potentially valuable role in astrobiology as they have long-term stability (Maule et al. 2003; Parnell et al. 2004).

Figure 2 shows hopane profiles for dolomite bedrock samples from within the crater and from 7 km beyond the crater margin, highlighting the four compounds Ts (C_{27} 18α(H)-22, 29, 30-trisnorneohopane), Tm (C_{27} 17α(H)-22, 29, 30-trisnorhopane), and the C30 hopane and moretane. The ratios Ts/Tm and C30 hopane/moretane both increase with thermal maturity (Waples and Machihara 1991). The respective ratios of 1.25 and 13.1 for the intra-crater sample and 0.14 and 5.5 for the extra-crater sample demonstrate the enhanced thermal maturity of the intra-crater sample. This data cannot be directly calibrated to temperature, because the reactions which alter the molecules are kinetically controlled, so time of heating is also important. However, there is future potential for the estimation of heating time using detailed data sets and independent measurements of temperature.

Signature in Impact-Induced Hydrothermal Systems

Possibly the most interesting setting within impact craters for astrobiologists is in the hydrothermal systems that develop immediately following the impact event. Indeed, in recent years, it has become clear that hydrothermal activity is commonplace after the impact of an asteroid or comet into water-rich solid planetary surfaces. The heat to drive hydrothermal circulation could be supplied by both the energy transferred by impact and the uplift of the central region of the crater from a deeper (hotter) level in the crater (Daubar and Kring 2001). Hydrothermal fluids, including hot springs emerging at the land surface, are envisaged as a likely setting for the evolution of primitive life (Farmer and des Marais 1999; Newsom et al. 2001).

In the Haughton crater, hydrothermal activity is evident as mineral veins and vugs, particularly around the periphery of the central uplift (Osinski et al. 2001, 2005c). Calcite vein samples examined as doubly polished wafers (see Osinski et al. 2005c) show fluorescing hydrocarbon fluid inclusions (Fig. 3). It is apparent that the hydrocarbon-rich fluids become incorporated in the hydrothermal system from a pre-existing source (Parnell et al. 2003, 2004). A similar incorporation of hydrocarbon fluid inclusions in hydrothermal veins has been recorded in other impact craters, including Siljan (Hode et al. 2003) and Lockne (Sturkell et al. 1998).

The significance of this preservation of a hydrocarbon signature is in the demonstration of stability of organic molecules in impact-associated hydrothermal systems. Although we do not expect a petroleum system on Mars, the occurrence of petroleum derivatives in the Haughton hydrothermal system gives us encouragement that biomarkers in putative hydrothermal deposits on Mars would survive, and that such deposits deserve high priority in the exploration for evidence of life.

Organic Signature in Sedimentary Crater-Fill Deposits

Fresh impact craters form a topographic depression that may subsequently be infilled with sediments. The sediment could be simply mass waste or, if water is ponded in the

Fig. 3. Hydrocarbon inclusions fluorescing under UV light in hydrothermal vein calcite, Haughton crater (locality 5). Each inclusion 5–10 microns in size.

crater, lacustrine deposits. These deposits could contain two types of organic signature: a signature conferred from the bedrock that has been eroded to contribute sediment, and a signature from life inhabiting the lacustrine environment. At Haughton, the crater was infilled by a lacustrine deposit, the Miocene Haughton Formation (Hickey et al. 1988), following erosion of impact melt breccias and an earlier phase of crater-fill deposits (Osinski and Lee 2005).

The signature of the biota in the Haughton Formation deposits is the subject of work elsewhere (Lim et al. 2004), but it is also possible to detect the signature derived from the crater bedrock. The Haughton Formation is a mixture of dolomitic silts and muds with subordinate fine-grained dolomitic sands and rare sandstones, in which the latter consist largely of detrital dolomite grains. Therefore, organic geochemical analysis of the sandstone yields a signature comparable to that of the bedrock, showing the same range of biomolecules and at the same levels of thermal maturity (Fig. 4). Thus, although the Haughton Formation is a young deposit that has not been buried except by glacial deposits, its signature is that of the thermally mature Lower Paleozoic bedrock. In other words, the signature of the crater target rocks can be extracted from the crater infill. This may have implications for sampling strategies on Mars where robotic missions will want to sample as broad a spectrum of lithologies as possible, but where the range of the rovers is limited.

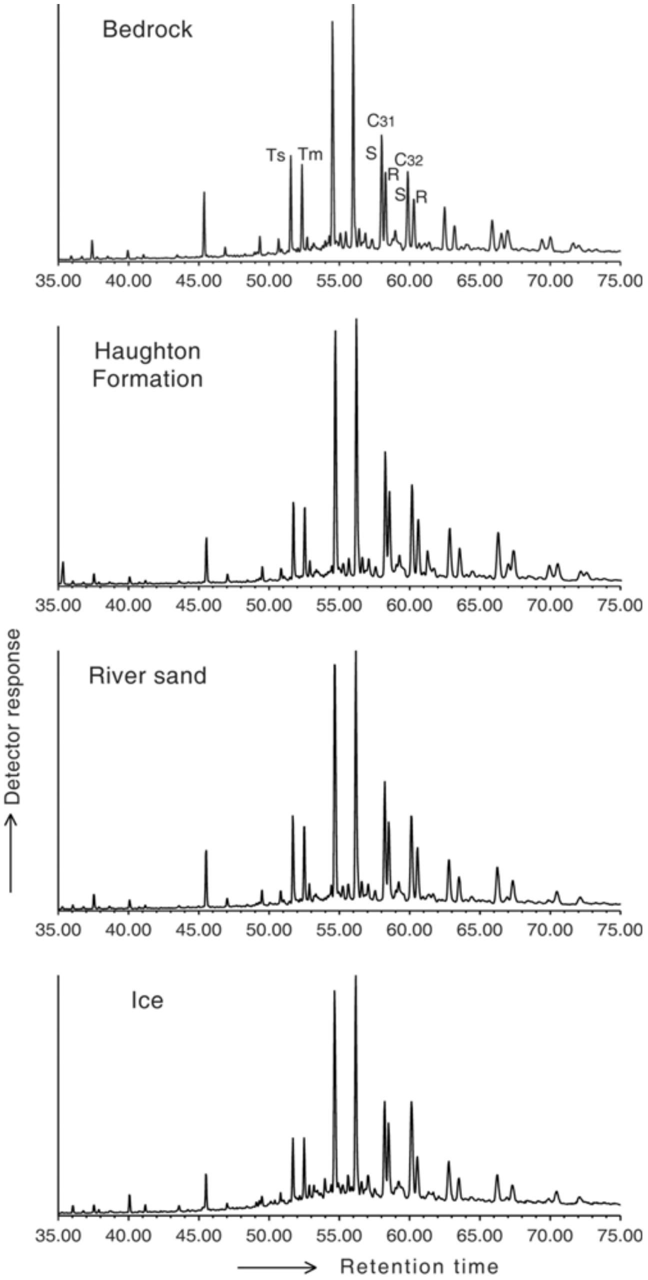

Fig. 4. Mass fragmentograms (m/z 191) showing distribution of hopanes extracted from dolomite bedrock (locality 1), Haughton Formation sands (locality 2), river sand, and sand extract from ice (both locality 1), Haughton crater. The distributions are remarkably similar. The hopanes in the bedrock yield a $C_{31}\alpha\beta$ S/S+R ratio typical of generation within the oil window. Samples enter the oil window due to heating, usually due to burial, on a geological time scale. The corresponding hopane ratios for Haughton Formation sand, river sand, and ice sand are almost identical, despite the fact that these are unconsolidated materials that have not been heated by burial since sedimentation, and in any case are very young. The Ts/Tm ratio is also consistent. The oil window signatures in the sand samples reflect the derivation of the sand from the bedrock.

Organic Signature beyond the Crater

Just as the post-impact crater-fill sediments preserve the signature of the target rocks, so too do the present-day sediments within and around a crater. At Haughton, this includes wind-blown sediment, stream sediment and snow/ice-bound detritus. These deposits may be transient, but represent an important and easy sampling medium. In the Haughton crater, this is exemplified by samples of river sand, and silt/snow extracted from ice. Again, these samples yield the same profiles of biomarkers, reflecting the same level of

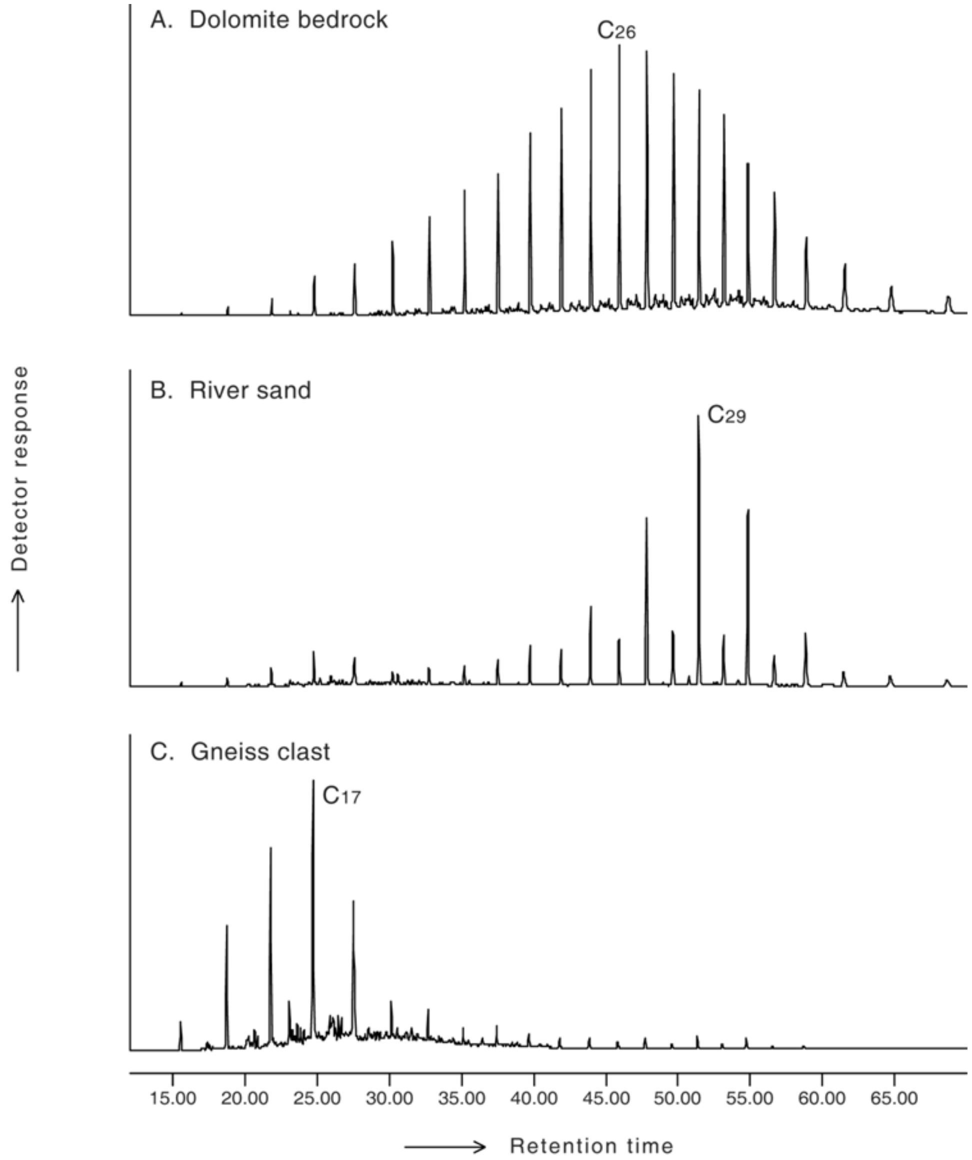

Fig. 5. Mass fragmentograms (m/z 85) showing distribution of n-alkanes extracted from dolomite bedrock, river sand (both locality 1), and gneiss clast in melt breccias (locality 3), Haughton crater. River sand shows a suite of n-alkanes with a marked odd-even predominance (OEP) in the range C_{25} to C_{33}. The OEP is indicative of low thermal maturity and is not evident in bedrock sample, but is typical of non-marine algae. Gneiss sample is dominated by C_{17}, reflecting the cyanobacterium *Gloeocapsa*.

thermal maturity, as the bedrock (Fig. 4). The measurement of the bedrock signature in these sediments demonstrates that the signature extends significantly beyond the crater.

Signature of Contamination by Later Life

In addition to the chemical signature derived from geological organic matter it is very plausible, indeed likely, that rock samples will contain a component of modern organic matter due to the abundant microbial life that colonizes all land surfaces. Where they are large enough, rock samples are trimmed of their outer surface to reduce the non-geological component, but this is not always possible. This modern component could be viewed as either contamination by modern biology that is not related to the crater setting and so is not helpful, or a signature of life that is able to colonize the crater rocks. Components of both could be recorded together. Microbes inhabiting river sediment, for example, are equally likely to be encountered inside or outside the crater. On the other hand, microbes in endolithic or chasmolithic habitats on rock surfaces may be more abundant inside the crater. The shocked nature of crater rocks, particularly from the crater-fill impact melt breccias which have experienced higher pressure, makes them more susceptible to colonization by cyanobacteria (Cockell et al. 2001, 2002).

Samples from the Haughton crater show evidence for both components. Samples of river sediment show a suite of n-alkanes with a marked odd-even predominance (OEP) in the range C_{25} to C_{33} (Fig. 5a). The OEP is indicative of low thermal maturity (Tissot and Welte 1984) and is not evident in samples with a solely geological component (Fig. 5b). This distribution of n-alkanes is typical of non-marine algae (Gelpi et al. 1970; Moldowan et al. 1985). A pure endolithic component can be distinguished by analysis of gneiss samples, which occur in the melt breccias (Metzler et al. 1988). The gneiss should contain no geological organic matter, but is conspicuously colonized by cyanobacteria (Cockell et al. 2002). The n-alkane signature from the cyanobacteria is dominated by C_{17} (Fig. 5c). The predominant cyanobacterium is *Gloeocapsa*, the modern equivalent of *Gloeocapsomorpha* in the geological record, which also yields a distinctive C_{17}-dominated signature (Reed et al. 1986, Jacobsen et al. 1988). Other dolomite rock samples contaminated with endolithic cyanobacteria show variable mixtures of the C_{17}-rich component derived from the cyanobacteria and a C_{23}-C_{31} component derived from the geological organic matter.

DISCUSSION

The detection of organic signatures in the Haughton crater has been made relatively easy by the abundance of naturally generated hydrocarbons and their preservation within fluid inclusions in the dolomite bedrock. The biomarkers at Haughton are present in concentrations far in excess of what one would expect on other planets, including Mars. However, the measurements serve to show that a range of organic signatures can be detected and that, in particular, the bedrock signature can be transferred to later deposits. During planetary exploration, organic signatures that might be sought in an impact crater would include either fossilized or extant “microbial” life. A much higher resolution of organic analysis than that undertaken in this study, involving smaller samples or detecting several orders of magnitude lower concentrations of biomolecules, should detect these signatures. A range of methodologies at very high resolution is already available for such analyses (e.g., Beegle et al. 2001; Keir et al. 2002). As this study shows that organic matter within the crater bedrock can be traced into subsequent deposits, strategies in the search for evidence of life should include these deposits. The study also adds to existing data showing that organic matter can survive impact events (French et al. 1997; Gilmour et al. 1993), and high-temperature processes in general (Wycherley et al. 2004).

The combination of organic-rich target rocks, the preservation of hydrocarbons, and excellent exposure in and around the Haughton crater makes it a good site for studies of organic signatures in impact settings. Accordingly, this is the first record using organic geochemistry to demonstrate the effect of impact on thermal maturity. This success at Haughton suggests that at other sites where impact occurred in Lower Paleozoic platform carbonate-shale sequences, including Siljan (Sweden) (Hode et al. 2003), Lockne (Sweden) (Lindström and Sturkell 1992) and Ames (Oklahoma) (Carpenter and Carlson 1992), organic geochemical studies may also yield valuable information about the effects of impact.

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