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HOPANE BIOMARKERS TRACED FROM BEDROCK TO RECENT SEDIMENTS AND ICE AT THE HAUGHTON IMPACT STRUCTURE, DEVON ISLAND: IMPLICATIONS FOR THE SEARCH FOR BIOMARKERS ON MARS.

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Summary: Hopanoid biomarkers have been successsfully traced from Palaeozoic target bedrock to Miocene impact-processed rocks, post-impact sediments, and Quaternary ice at the Haughton impact Structure, Devon Island, High Arctic, suggesting that similar biomarkers and techniques to detect them might provide a promising strategy in the search for biomarkers in rocks, sediments and ice on Mars.

Biomarkers and the Search for Life: Living organisms on Earth produce diverse compounds that are not known from inorganic origins, and therefore are regarded as biomarkers. Many proposed techniques for the detection of life during planetary exploration depend upon the identification of specific biomarkers. However, while these may be potential signatures for extant life, most do not have long-term stability and are therefore not good targets when searching for evidence of fossil life. DNA and RNA degrade over time, and except in special circumstances (e.g. at very low temperatures in ice, or preserved in amber) will not survive on time scales greater than a few million years [1]. Other biomarkers common in recent sediments, including amino acids, sugars and alcohols, also degrade relatively quickly. This low survivability of many biomarkers is an important limiting factor in the search for life on planets such as Mars where environmental conditions have changed over time and life might not have been present at the surface recently.

Hopanes on Earth: However, experience in petroleum geochemistry shows that hopanes and steranes, which are derived from prokaryotic and eukaryotic membranes respectively, have much greater stability and are routinely sought in samples of age hundreds of millions of years or even billions of years [2,3]. Hopanes in particular are ubiquitous on Earth. Our widespread life and lengthy fossil record mean that hopanes are readily detected in many rocks in the geological record. They are encountered in rocks such as shales where microbial remains are fossilized, and also in porous rocks where oil derived from microbial remains is reservoired. Specific antibodies have been developed for hopanes [4], making them valuable targets in ancient samples. But even if hopane-like biomarkers were present on Mars, how might they be found? Would source rocks need to be analyzed, or might sediments, and especially ice, be adequate as has been proposed [5,6,7]?

Analog study at the Haughton Impact Structure: The Haughton impact structure, Devon Island, Arctic Canada, was formed ~23 Ma in a ~1750m series of Lower Palaeozoic sedimentary rocks dominated by carbonate facies overlying a Precambrian crystalline basement [8]. The crater is filled with impact melt rocks [9], which contain clasts of basement, indicating an excavation depth of 2km+. Limited Tertiary lacustrine sediments and Quaternary fluvio-glacial deposits lie upon the melt rocks. Country rocks are predominantly dolomites. Exposure is generally excellent. Ground ice, surface ice and snow deposits are present.

We conducted a search for hopanoid biomarkers at Haughton in each of bedrock, sediment and ice samples to assess their survivability through time and geologic processing. The dolomitic limestone bedrock at Haughton has experienced oil generation-migration [10], so hopanes and other organic compounds are abundant in it. Hopanes were measured from the m/z 191 mass fragment using GC-MS, following DCM extraction of crushed samples and TLC to separate the saturates fraction. Surface sediments in the region derived by erosion of the bedrock, and ice deposits protected from melting within gullies were also sampled. Both sediments and ice contain sandy-silty detritus incorporated from wind and surface run-off.

Organic Compounds in Ice and Snow: There is widespread evidence from terrestrial samples of ice and snow, including ice cap cores, that organic compounds can be determined in them. Specific studies include measurement of polycyclic aromatic hydrocarbons [11, 12, 13], carboxylic acids [14], PCBs [15] and DNA [16]. Some input to this can be attributed to anthropogenic emissions (fossil fuels, other industry), but contributions are also related to natural wildfires [14], and bacteria incorporated with wind-blown dust particles [17]. In some cases, organisms actually inhabit ice and snow, and hence can contribute to its organic content [16]. These records show that ice can be a valuable record of surface chemistry. Where winds are strong enough surface particles and any biosignature they carry may become entrapped in ice by adhesion [18].

Hopanes in the Haughton Impact Structure:

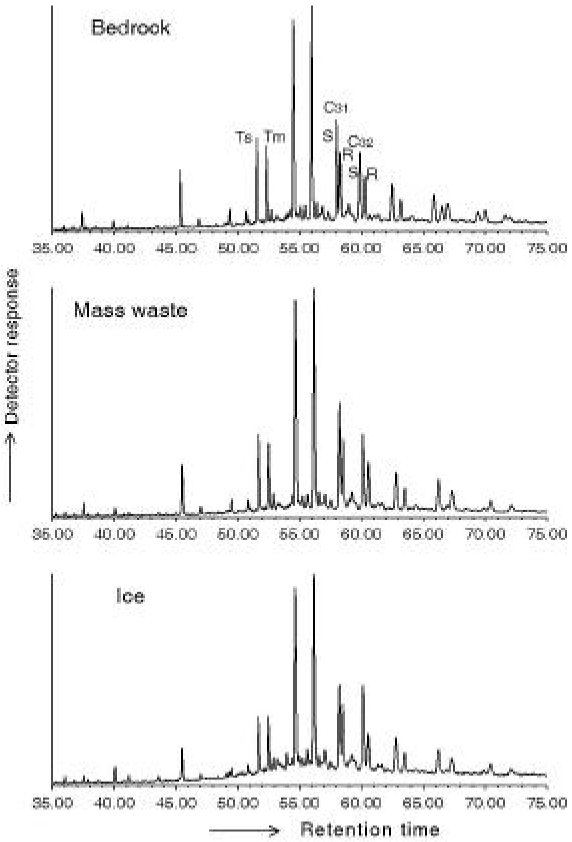

Fig. 1. m/z 191 fragmentograms for hopanes extracted from bedrock, mass waste and sand extract from ice, Haughton Impact Structure, Devon Island.

The m/z 191 fragmentograms for hopanes from different substrates at Haughton are shown in Fig. 1. They are remarkbly similar. The hopanes in the bedrock yield a C_{32}aß 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 timescale. The corresponding hopane ratios for river sand and snow 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.

Micron-scale inclusions of liquid hydrocarbon occur within the dolomite crystals [10]. These inclusions were trapped during crystal growth. During erosion of the bedrock dolomites, inclusions are preserved within individual sand grains, hence the biomolecular signature is retained within the sand.

Implications for Mars: Hopanoids are in principle attractive biomarkers to trace in the search for evidence of past microbial life on Mars because (i) they are a product of simple, prokaryotic biology, (ii) they have high longevity, (iii) we have extensive experience in their interpretation from petroleum geochemistry. They can also be purchased in purified form for experimentation. While the biomarkers at Haughton are present in concentrations far in excess of what one would expect on Mars, where they might occur in residues in rocks or as traces in H_2O (e.g. included in surface mineral precipitates [19]), this study shows the potential for biosignatures to be transferred intact from bedrock to surface sediment and ice, which increases the chance of detecting a signature.

A search for biomolecular evidence of life on Mars would target bedrock, surface sediment and surface fluids. Liquid water is not known to be available for sampling at the surface at present, but ice could be at relatively shallow depth or at the surface in polar regions. In fact, the polar ice caps of Mars are suggested to be strong candidates for the preservation of a biomolecular record [5], and biotechnology is being developed for the detection of biomolecules in Martian ice [6, 7]. With a rich record of microbial biosignatures, the Haughton site provides further opportunities for analog studies in Mars-relevant astrobiology.

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