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# **1. DATA REPORT: ORGANIC GEOCHEMICAL** SCREENING OF A BERMUDA RISE SAMPLE FROM SITE **1063**<sup>1</sup>

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# INTRODUCTION

A subsample from the Bermuda Rise (Ocean Drilling Program Sample 172-1063B-38X-5, 40–50 cm) was submitted by Lloyd Keigwin (Woods Hole Oceanographic Institution) for organic geochemical screening. The sample is comprised of a small, thin fragment (7.5 mm × 4 mm × <1 mm) of medium brown colored waxy material that was taken from a thin flexure plain within the sediment interval. The material was presumed to be organic in origin based on its odor and appearance. The goal of this project was to characterize the material to determine whether the fragment is organic and, specifically, whether it is related to petroleum-derived products.

# **MICROSCOPE SCREENING**

A subsample was strew-mounted on a glass slide. The sample was analyzed using a Zeiss Axiophot II microscope functioning in transmitted light ( $400\times$ ). The sample showed no discernible cellular structure at this magnification and was characterized as amorphous.

# **CURIE POINT FLASH PYROLYSIS**

Flash pyrolysis is a thermal technique used to break down larger macromolecules into simpler monomers. This technique helps reconstruct the chemical composition of complex substances that are often difficult

<sup>1</sup>Eglinton, L.B., and Whelan, J.K., 2000. Data report: Organic geochemical screening of a Bermuda Rise sample from Site 1063. In Keigwin, L.D., Rio, D., Acton, G.D, and Arnold, E. (Eds.), Proc. ODP, Sci. Results, 172, 1–9 [Online]. Available from World Wide Web: <http://wwwodp.tamu.edu/publications/172\_SR/ VOLUME/CHAPTERS/SR172\_01.PDF>. [Cited YYYY-MM-DD] <sup>2</sup>Department of Marine Chemistry and Geochemistry, MS 4, Woods Hole Oceanographic Institution, Woods Hole MA 02543-1543, USA. Correspondence author: Leglinton@WHOI.edu

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to analyze by conventional spectroscopic and chromatographic techniques such as gas chromatography and gas chromatography–mass spectrometry. Based on the microscope observations and because of the limited sample size available, we proceeded to geochemically screen the sample without any other preparative extraction by on-line flash pyrolysis gas chromatography mass spectrometry (Py-GCMS).

## **METHODS**

A Horizon Instruments' Curie point pyrolysis unit was fitted to the head of a Hewlett Packard 6890 gas chromatograph with dual mass specific detection (MSD) (operated in scan mode over a range of 50–550 a.m.u.) and flame ionization detection (FID). A small amount of sample material was cold pressed onto a 610°C Curie point wire and flash pyrolyzed for 10 s. Products were directly transferred by a stream of helium onto a 60-m DB-5 capillary gas chromatography column and separated using the following temperature program: 50°C for 5 min ramped at 3°C/min to 350°C then held for 20 min. Resolved pyrolysis products were then split to the FID and MSD. Compound identification was confirmed by their mass spectra.

## RESULTS

The sample represents organic material comprised mainly of straightchain lipid components that yield suites of a homologous series of pyrolysis products, notably the long-chain alkenes (Fig. F1) that are possibly derived from the breakdown of bound fatty acids that are a common component of algal biomass. In addition, there is a separate small suite of pyrolysis products comprising longer chain (C<sub>30</sub>) cyclic and branched alkenes (also biological in origin), possibly squalene derivatives. Mass chromatograms for triterpanes, m/z 191 and steranes, m/z 217 (Fig. F2A, F2B, respectively) show distributions that are not typical of hydrocarbons derived from petroleum (Fig. F2C, F2D, respectively). Additionally, the m/z 91 mass chromatogram for a petroleum from a Kazakhstan well (Fig. F3A) shows the regular distributions of nalkanes commonly associated with oil-derived hydrocarbons. A mass chromatogram for m/z 91 for Sample 172-1063B-38X-5, 40-50 cm, however, does not show this regular distribution (Fig. F3B) and is, therefore, considered to be nonrelated to mature petroleum. Minute traces of longer chain *n*-alkanes are present but are insignificant when compared to the bulk of the pyrolysis products. Evidence for a series of nitrogen-bearing compounds as shown by the 115 (Fig. F4A) and 117 ions (Fig. F4B) possibly indicate the presence of proteins that may be biologically derived. The total ion current clearly shows the presence of a significant amount of contaminant, identified as silicone material on the basis of the prominent m/z 207 and 281 ions (not shown).

## CONCLUSIONS

In conclusion, this Py-GCMS study clearly demonstrates that the sample is not derived from petroleum or related geochemically to thermally mature materials. Rather, it has the characteristics of immature biologically derived material, possibly a fragment of an algal mat.

**F1.** Mass chromatogram of m/z 83 diagnostic of alkenes, p. 4.



**F2.** Mass chromatograms of m/z 191 and m/z 217 in a sample from Site 1063 compared to a typical distribution in an oil from Kazakhstan, p. 5.



**F3.** Mass chromatograms of m/z 91 for petroleum hydrocarbons from a Kazakhstan oil well compared to a sample from Site 1063, p. 7.



F4. Mass chromatograms showing distributions commonly associated with nitrogen containing compounds, p. 9.



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**Figure F1.** Mass chromatogram of m/z 83 diagnostic of alkenes. Note the presence of a homologous series of *n*-alkenes marked by the solid circles. A short series of longer chain  $C_{30}$  branched and cyclic alkenes are marked with the double-headed arrow. These are biological in origin.



**Figure F2.** Comparison of mass chromatograms for (A) m/z 191 triterpanes, (B) m/z 217 steranes in a sample from Site 1063 compared to a typical distribution for (C) triterpanes and (D) Steranes in an oil from the JV Armaan Well, Caspian Sea, Kazakhstan. (Continued on next page.)



Figure F2 (continued).



**Figure F3.** Comparison of mass chromatograms (m/z 91) for typical petroleum hydrocarbons from (A) a Kazakhstan oil well and (B) a sample supplied from Site 1063. The Site 1063 sample does not show the typical distributions of *n*-alkanes commonly associated with a mature petroleum origin. (Continued on next page.)



Figure F3 (continued).



**Figure F4.** Mass chromatograms for (A) m/z 115 and (B) m/z 117 showing distributions commonly associated with nitrogen containing compounds that may possibly be derived from proteins indicative of recent biological material.

