

INVESTIGATING PAST METHANE CYCLE PERTURBATIONS THROUGH THE LENS OF NOVEL POLYFUNCTIONALISED HOPANOIDS

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Introduction

Methane (CH₄) is a potent greenhouse gas, second only to carbon dioxide in its importance to climate change. Highly resolved ice-core records indicate that atmospheric CH₄ concentrations have oscillated on orbital timescales. However, we do not understand how the methane cycle operates beyond the reach of ice core records (>800,000 years ago). Enhanced aerobic methanotrophy has been inferred in wetland environments during past warm climates, notably the Paleocene-Eocene Thermal Maximum (PETM; ~56 Ma). This is based on a negative carbon isotope excursion in bacterial-derived hopanes ($\delta^{13}\text{C}_{\text{hop}}$)¹. However, these compounds have multiple source organisms (*e.g.*, methanotrophs, photoautotrophs, and heterotrophs), and $\delta^{13}\text{C}_{\text{hop}}$ can also reflect changes in the metabolic pathway used to assimilate carbon.

In contrast, bacteriohopanepolyols (BHPs) are polyfunctionalised hopanoids that may be a more diagnostic tracer of methane oxidation. For example, complex BHPs with an amine functionality at the terminal C-35 position (amino-BHPs) are associated with aerobic methanotrophs³. Although these compounds were initially thought to be unstable, rapidly losing their functional groups during the earliest stages of diagenesis, they were reported in one PETM-aged deposit, extending the application of BHPs into the geologic past⁴. Since this discovery, methodological advancements have allowed the separation of a diverse suite of previously undetected BHPs, with novel side chain structures⁵. The preservation potential of these novel BHPs in the geologic record is less clear. In this study, we use ultra-high-performance liquid chromatography coupled with high-resolution mass spectrometry to: (i) determine the preservation of novel BHPs during the PETM; and (ii) explore the potential of BHPs as a proxy to reconstruct past methane cycle dynamics. Samples are obtained from Otaio River, a mixed terrestrial-marine PETM-aged deposit that exhibits a ~-60‰ excursion in $\delta^{13}\text{C}_{\text{hop}}$ values during the PETM².

Results and Discussion

We identify sixteen BHPs (Figure 1), six of which are reported for the first time in sedimentary deposits beyond 50 million years ago. The detection of a wide array of BHPs at Otaio River has been possible due to analytical developments. Yet, the prevalence of complex structures also show that BHPs can be found well-preserved in the geologic record. However, in general, anhydro BHPs (thought to be diagenetic products) are the most dominant, and are especially found in samples with high TOC (>20%). Crucially, a peak in 35-aminobacteriohopane-30,31,32,33,34-pentol (aminopentol) coincides with the most negative $\delta^{13}\text{C}_{\text{hop}}$ value during the PETM. An increase in aminopentol during the PETM was also previously observed⁴, further

supporting the utility of aminopentol as a complementary tracer for methanotrophs in the past. Overall, this study demonstrates the opportunity for BHPs to not only reconstruct methane cycling during transient warming events, but possibly a range of other environmental controls.

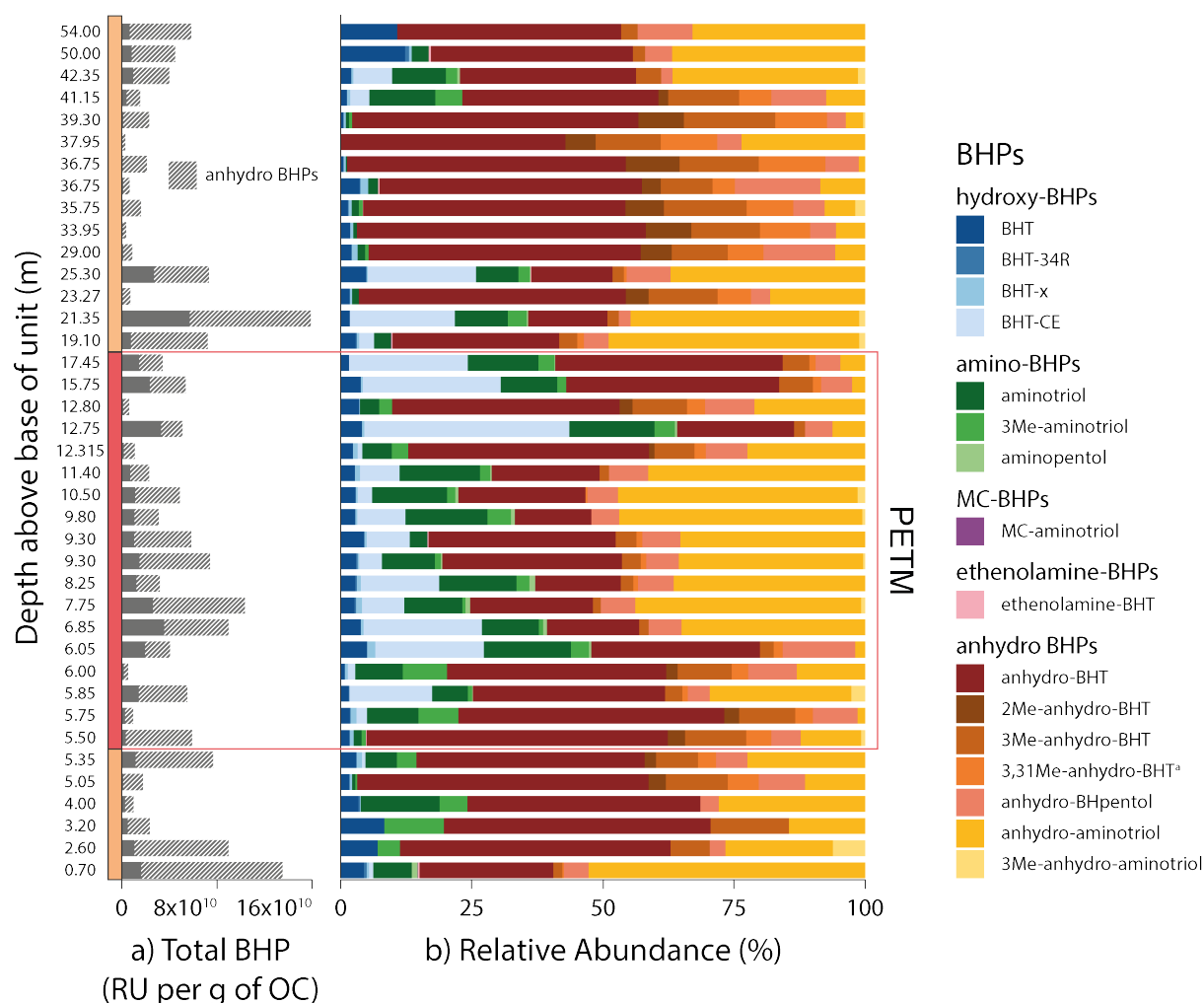


Figure 1 The abundance of total BHPs in response unit (RU) per g of OC and relative abundances (%) of individual BHPs within each sample.

References

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