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Polyfunctionalised bio- and geohopanoids in the Eocene Cobham Lignite

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ABSTRACT

We investigated the bacteriohopanepolyol (BHP) distribution in the Cobham Lignite sequence (SE England) deposited across the Palaeocene–Eocene boundary, including part of the Palaeocene–Eocene Thermal Maximum (PETM) as shown previously by a negative carbon isotope excursion (CIE). A variety of BHPs were identified, including the commonly occurring and non-source specific biohopanoid, bacteriohopanetetrol (BHT), and 32,35-anhydroBHT which was the most abundant polyfunctionalised geohopanoid in the majority of samples. BHPs with a terminal amine functionality, diagnostic biomarkers for methanotrophic bacteria, were found throughout the sequence, with similar distributions in both the lower laminated and upper blocky lignite except that 35-aminobacteriohopanepentol (aminopentol), indicative of Type I methanotrophs (gammaproteobacteria), was generally more abundant in the upper section within the CIE. The diagenetic fate of these compounds is currently poorly constrained; however, we also identified the recently reported N-containing transformation product, anhydroaminotriol, and several tentatively assigned novel N-containing structures potentially containing ketone functionalities. Although present throughout the section, there was a sharp peak in the occurrence of these novel compounds, which correlated with the onset of the CIE and highly isotopically depleted hopanes in the upper part of the laminated lignite, both also correlating well with aminopentol peak abundance. The significant abundance of these compounds suggests that 35-aminoBHPs have their own specific diagenetic pathway, potentially providing an alternative method allowing methanotroph activity to be traced in older samples even if the original biohopanoid markers are no longer present.

At this time we cannot preclude the possibility that some or all of these BHPs have been produced by more recent subsurface activity, post deposition of the lignite; however, this would not be expected to generate the observed stratigraphic variability and we suggest that unprecedented observations of a range of highly functionalised biohopanoids in samples of this age could significantly extend the window of their known occurrence.

1. Introduction

Bacteriohopanepolyols (BHPs) are highly functionalised pentacyclic triterpenoids derived from a wide range of prokaryotes (e.g. Rohmer et al., 1984; Pearson et al., 2007, 2009). In their biological form (biohopanoids), they comprise a diverse suite of structures (e.g. Rohmer, 1993; see Appendix for examples) which have been linked to cellular membrane adaptation, regulating fluidity and permeability in response to environmental stress (e.g. Kannenberg and Poralla, 1999; Welander et al., 2009; Sáenz et al., 2012; Kulkarni et al., 2013). Typically, they contain four, five or six functional groups (termed tetra-, penta- and hexafunctionalised respectively) at C-30 to 35 in the side chain although cyclised side chains are also known. For example, adenosylhopane (**Ip**) is the precursor for all other side chain extended BHPs (Bradley et al., 2010) via a pathway involving the intermediate ribosylhopane (Liu et al., 2014; Bodlenner et al., 2015). Biohopanoids are also the precursors of the ubiquitous geohopanoids (hopanols, hopanoic acids and hopanes) found in geological materials (e.g. Ourisson et al., 1987; Ourisson and Albrecht, 1992; Farrimond et al., 2004).

Biohopanoids can provide useful information about certain source organisms, biogeochemical processes and environmental conditions (e.g. Talbot and Farrimond, 2007). One such group are BHPs with an amine functionality at C-35 (collectively termed aminoBHPs herein; e.g. Talbot et al., 2014; Wagner et al., 2014; Spencer-Jones

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et al., 2015), which include 35-aminobacteriohopane-32,33, 34-triol (aminotriol from hereon, **If**), 35-aminobacteriohopane-31, 32,33,34-tetrol (aminotetrol, **Ig**) and 35-aminobacteriohopane-30, 31,32,33,34-pentol (aminopentol, **Ih**). Sources of aminopentol are thought to be restricted to Type I aerobic methane oxidising bacteria (Gammaproteobacteria; e.g. Neunlist and Rohmer, 1985; Cvejic et al., 2000; van Winden et al., 2012a), whilst aminotetrol is produced by both Type I and II (Alphaproteobacteria) methanotrophs. The only known additional source of the penta- and hexafunctionalised compounds is some species of *Desulfovibrio* sulfate reducing bacteria (SRB; Blumenberg et al., 2006, 2009), although aminopentol was only reported from one species at trace level (Blumenberg et al., 2012). Further, when observed in *Desulfovibrio* spp., the ratio of aminotriol to aminotetrol (**If/Ig**) was in the range 20–100 (Blumenberg et al., 2006, 2009, 2012), whilst it is significantly lower in most methanotrophs, with the pentafunctionalised compound often more abundant (e.g. Jahnke et al., 1999; Talbot et al., 2001). Aminotriol is less diagnostic as it is produced by a range of other prokaryotes (including other proteobacteria and some cyanobacteria; Talbot et al., 2008 and references therein) in addition to all Type II and some Type I methanotrophs (Talbot et al., 2001; van Winden et al., 2012a; Banta et al., 2015).

AminoBHPs have been reported from a wide range of environments including soils (e.g. Cooke et al., 2008a; Xu et al., 2009; Pearson et al., 2009; Rethemeyer et al., 2010; Kim et al., 2011; Zhu et al., 2011), peat (e.g. van Winden et al., 2012a,b), and marine, river and lacustrine sediments (e.g. Talbot et al., 2003a; Talbot and Farrimond, 2007; Coolen et al., 2008; Blumenberg et al., 2010, 2013; Zhu et al., 2010, 2011). Aminotetrol (**Ig**) and aminopentol (**Ih**) are therefore of particular interest and have been used to identify material sourced from sites of intense aerobic methane oxidation, such as river estuaries (Zhu et al., 2010), tropical wetlands (Talbot et al., 2014; Wagner et al., 2014; Spencer-Jones et al., 2015) and water columns (e.g. Blumenberg et al., 2007; Wakeham et al., 2007; Berndmeyer et al., 2013). Other markers for Type I aerobic methanotrophs include hopanoids methylated at C-3 (e.g. Cvejic et al., 2000), but non-methanotrophs can also be potential sources of this structural feature (e.g. Welander and Summons, 2012). Typically, therefore, these studies also rely on analysis of compound specific carbon isotope ratios with the strong isotopic depletion expected for methanotroph-derived lipids (e.g. Collister et al., 1992). However, the absence of C-3 methylated pseudohomologues of these aminoBHP compounds does not preclude either the Type II methanotrophs or Type I organisms such as *Methylomonas* sp. or *Methylovulum* sp. (e.g. Rohmer et al., 1984; van Winden et al., 2012a), which do not produce the methylated homologues (see discussion by Talbot et al., 2014).

Originally considered to be rapidly transformed to geohopanoids at the earliest stages of diagenesis (both free and bound), evidence is now growing that polyfunctionalised biohopanoids may be more stable than originally thought. The oldest reported polyfunctionalised biohopanoid is bacteriohopane-32,33, 34,35-tetrol (BHT; **Ic**) in a sample from marine Palaeogene cores from Tanzania dating to 50.4–49.7 million years ago (Ma; van Dongen et al., 2006). It is the most frequently reported BHP structure, facilitated by the fact that it is amenable to analysis using gas chromatography mass spectrometry (GC–MS), as well as liquid chromatography-mass spectrometry (LC–MS; e.g. Talbot et al., 2003a). It has a wide range of potential prokaryotic sources, meaning that it cannot be considered as indicative of any particular group of bacteria or set of environmental conditions (e.g. Talbot et al., 2008). Additional early degradation products retaining multiple functional groups derived from BHT or more complex precursors such as BHT cyclitol ether (**Im**) or BHT glucosamine (**In**) include 32,35-anhydrobacteriohopane-32,33,34,35-tetrol (anhydroBHT; **Ia**) and its C-2 methylated homologue (**IIa**; Schaeffer et al., 2008, 2010) and they have been reported in samples up to Jurassic in age (Bednarczyk et al., 2005). Multiple isomers of the related compound derived from a pentafunctionalised precursor i.e. anhydrobacteriohopanepentol (anhydroBHPentol; **Id**) have been reported from geothermal sinters (Talbot et al., 2005; Gibson et al., 2014).

Recently, we identified aminoBHPs including aminopentol (**Ih**) in samples from the Congo deep-sea fan aged up to 1.2 Ma and the source of the material was proposed as continental wetland environments (Talbot et al., 2014; Spencer-Jones et al., 2015; Spencer-Jones, 2016). Burhan et al. (2002) reported aminotriol from the Be'eri sulfur deposit (Pleistocene age sandstones of the Southwestern Mediterranean Coastal Plain of Israel); however, it is uncertain if it represents a Pleistocene age signal or one from sub-contemporary bacteria feeding on seeping methane. The findings suggest that BHP compounds produced in aerobic systems can be preserved in the geological record when conditions are favourable and could therefore be useful in examining methane cycling in more ancient settings.

To explore the potential for BHP preservation in ancient sediments, we investigated the BHP signature of a well preserved, immature lignite sequence from southern England. The Cobham Lignite is an exceptional example of a terrestrial lacustrine/mire deposit associated with the Palaeocene–Eocene Thermal Maximum (PETM; Collinson et al., 2003, 2007, 2009). Previously, a negative carbon isotope excursion (CIE) indicated by a sharp depletion in $\delta^{13}C$ of ca. 1‰ in the bulk organic carbon within the section has been interpreted as being the negative CIE characteristic of the PETM onset, although its magnitude is markedly lower than the total extent of the CIE in other terrestrial settings (McInerney and Wing, 2011). Furthermore, isotopically depleted hopanoids have also been reported from this section, suggesting an increase in the methanotroph population resulting from enhanced methane production, likely driven by hydrological changes towards a warmer and wetter climate (Pancost et al., 2007). These changes are also manifested as a lithological change from laminated to blocky lignite. Hopanoids at the site are present in exceptional abundance relative to other biomarkers and are relatively immature, based on observation of the biological 17β,21β(*H*) configuration and lack of compounds with 22*S* stereochemistry (Pancost et al., 2007). We therefore considered this site favourable for investigation of the potential for preservation of polyfunctionalised biohopanoids.

2. Methods

2.1. Site and samples

The ca. 2 m thick early Paleogene Cobham Lignite sequence was sampled from a temporary exposure, which became available near Cobham, Kent, southern England, when a cutting was made through a hill for construction of the Channel Tunnel Rail Link during 1999–2000. In order to procure a complete sequence of the lignite with intact stratigraphy, surrounding sediment was excavated to produce pillars (10–15 cm in depth and width) free on three sides. The three exposed sides were enclosed in a plaster jacket to prevent breakage and pillars were removed from the exposure at the fourth side using spades. The fourth side was not enclosed. These plaster-jacketed pillars were stored in ambient room conditions whilst attempts were made to obtain funding for their study.

Prior to sub-sampling, sediment was removed and discarded from the surface of the exposed side to a depth of ca. 3 cm until sediment with original appearance (e.g. colour, degree of integrity) was reached. Sub-sampling of each cleaned pillar was completed within one day. Cleaning and sub-sampling were undertaken using sharp single-edged razor blades that had been rinsed in alcohol