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Recognition of Early Eocene global carbon isotope excursions using lipids of marine Thaumarchaeota

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ABSTRACT

The Paleocene–Eocene Thermal Maximum (PETM; ~56 Ma) and Eocene Thermal Maximum 2 (ETM2; ~53 Ma) are geological short (< 200,000 years) episodes of extreme global warming and environmental change. Both the PETM and ETM2 are associated with the injection of ^{13}C-depleted carbon into the ocean–atmosphere system as revealed through a globally recognized carbon isotope excursion (CIE) and massive dissolution of deep sea carbonate. However, the magnitude of these CIEs vary with the type of fossil matter, i.e. multiple carbonate phases, bulk organic matter, and terrestrial and marine biomarker lipids, making it difficult to constrain the actual CIE in atmospheric and oceanic carbon pools. Here we analyzed the stable carbon isotopic composition (δ^{13}C) of glycerol dibiphytanyl glycerol tetraether lipids (GDGTs) derived from marine Thaumarchaeota in sediments deposited during the PETM in the North Sea Basin and ETM2 in the Arctic Ocean. The δ^{13}C values of these lipids are potentially directly recording variations in δ^{13}C dissolved inorganic carbon (DIC) and can thus provide a record of marine δ^{13}C DIC across both these Eocene carbon cycle perturbations. Reconstructed pre-CIE $\delta^{13}C_{DIC}$ values are slightly lower (0.5–1‰) than modern day values, possibly because Thaumarchaeotal lipids are not only derived from surface waters but also from ^{13}C-depleted subsurface waters. Their values decrease by ~3.6 (± 0.3)‰ and ~2.5 (± 0.7)‰ during the PETM and ETM2, respectively. The CIE in crenarchaeol for ETM2 is higher than that in marine calcite from other locations, possibly because of the admixture of deep water ^{13}C-depleted CO_2 generated by the euxinic conditions that developed occasionally during ETM2. However, the reconstructed PETM CIE lies close to the CIE inferred from marine calcite, suggesting that the δ^{13}C record of crenarchaeol may document changes in marine DIC during the PETM in the North Sea Basin. The δ^{13}C of thaumarchaeotal lipids may thus be a novel tool to reconstruct the δ^{13}C of DIC in sediments that are devoid of carbonates, but relatively rich in organic matter, such as shallow marine coastal settings.

1. Introduction

The Paleocene–Eocene Thermal Maximum (PETM) is characterized by a rapid large decrease in stable carbon isotope ratios (δ^{13}C) in marine and terrestrial carbonates and organic matter and massive dissolution of seafloor carbonates, providing evidence for the massive and rapid injection of ^{13}C-depleted carbon in the oceans and atmosphere (Dickens et al., 1997; Zachos et al., 2005; McInerney and Wing, 2011). Several mechanisms have been proposed to explain the global negative carbon isotope excursion (CIE), amongst others the release of thermogenic methane due to contact metamorphism (Svensen et al., 2004), rapid burning of terrestrial organic matter (Kurtz et al., 2003), the release of carbon stored in permafrost soils at high latitudes triggered by orbital forcing (DeConto et al., 2012), and the dissociation of methane hydrates (Dickens et al., 1995). Several of these hypotheses provide mechanisms that not only explain the CIE of the PETM, but also offer an explanation for the several smaller CIEs that have occurred after the PETM, such as the Eocene Thermal Maximum 2 (ETM2) and H2 event (Cramer et al., 2003; Lourens et al., 2005; Nicolo et al., 2007; Sluijs et al., 2009; Stap et al., 2010; Westerhold et al., 2009; Slotnick et al., 2012). However, authentication of the sources of the ^{13}C-depleted carbon strongly depends on the

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magnitude of the actual CIE recorded in the PETM sediments (e.g., Pagani et al., 2006; Dickens, 2011). Unfortunately, the reported magnitude of the CIEs vary widely between different marine and terrestrial carbon records, such as carbonate shells, bulk organic matter and specific terrestrial and marine biomarkers (see Table 1 in McInerney and Wing, 2011). These variations in shape and magnitude of individual carbon isotope records are often caused through changes in: (1) the relative abundance of mixed components with different $\delta^{13}C$ values within a measured substrate, (2) change in isotope fractionation through physiological change, and (3) the isotope composition of the carbon source, or combinations of these (Sluijs and Dickens, 2012 and references cited therein). Although the magnitude of the biases generated by these factors is relatively well known, assessing the magnitude of these biases for any individual $\delta^{13}C$ record remains a challenge (Sluijs and Dickens, 2012).

In this study, we investigate the potential use of the stable carbon isotopic composition ($\delta^{13}C$) of the biomarker lipid crenarchaeol, which exclusively occurs in ammonia-oxidizing Thaumarchaeota (Pitcher et al., 2011 and references cited therein), to reconstruct the variations in $\delta^{13}C$ of marine dissolved inorganic carbon (DIC), the largest carbon reservoir in the global exogenic carbon pool, during the Eocene hyperthermals. Several studies using ^{13}C-labeling experiments and cultivation studies showed that Thaumarchaeota have a chemoautotrophic lifestyle (Jung et al., 2011; Park et al., 2010; Wuchter et al., 2003), using ammonium as electron donor, which is oxidized to nitrite (Hallam et al., 2006; Könneke et al., 2005; Wuchter et al., 2006). Based on the relatively ^{13}C-enriched isotopic composition of crenarchaeol, and the isoprenoidal ether-bound lipids (biphytanes) derived thereof, compared to algal biomarkers, it was suggested that Thaumarchaeota take up bicarbonate as a carbon source (Hoefs et al., 1997; Pearson et al., 2001a; Kuypers et al., 2001). Furthermore, Kuypers et al. (2001) found that the ^{13}C of the crenarchaeol was enriched by 3‰ compared to modern values during the mid-Cretaceous oceanic anoxic event 1b and attributed this to the 2–3‰ $\delta^{13}C$ offset between modern and mid-Cretaceous DIC. Confirmation came from Berg et al. (2007), showing that Thaumarchaeota assimilate carbon through the 3-hydroxypropionate/4-hydroxybutyrate biochemical pathway, which involves the direct utilization of bicarbonate.

The active uptake of HCO_3^- by Thaumarchaeota suggests that the $\delta^{13}C$ composition of Thaumarchaeal lipids may be independent to variations in CO_2 concentrations, unlike phytoplankton (e.g. Laws et al., 1995), and predominantly depend on the $\delta^{13}C$ of HCO_3^-. This is supported by labeling studies with enrichment cultures of marine Thaumarchaeota, which showed no limitation on growth rates of the Thaumarchaeota in response to increased aqueous HCO_3^- -levels (Park et al., 2010). Importantly, Könneke et al. (2012) found that the $\delta^{13}C$ composition of both biomass as well as crenarchaeol of the Thaumarchaeote *Nitrosopumilus maritimus* was indeed independent of DIC concentrations, and the carbon isotopic fractionation between crenarchaeol and DIC was a consistent −19.7 ± 0.5‰. Interestingly, reported $\delta^{13}C$ values of crenarchaeol in modern marine sediments range from −18‰ to −23‰, average around −21 ± 1‰ (Schouten et al., 2013). Assuming that DIC of marine surface waters at the studied sites is roughly between −1‰ and 1.5‰ (Kroopnick, 1985) and sedimentary crenarchaeol is mainly derived from pelagic sources (e.g. Schouten et al., 2010; Lengger et al., 2012), the $\delta^{13}C$ values of crenarchaeol are thus fairly consistent with a fractionation of ~20‰ as observed in *N. maritimus*. The $\delta^{13}C$ composition of biphytanes derived from GDGTs produced by Thaumarchaeota may thus reflect changes in past $\delta^{13}C$ values of marine DIC. This is a major advantage compared to other biomarker proxies reconstructing the CIE because bicarbonate comprises the largest carbon reservoir in the global exogenic carbon pool. Furthermore,

Table 1
Stable carbon isotope values of TOC and biphytanes for three PETM sections in Denmark and for the ETM2 section (IODP 302) from the Lomonosov Ridge, Arctic Ocean.

Sample code	Location	Age	Depth	Stable carbon isotope composition ($\delta^{13}C$) in ‰ VPDB				
			(m)	TOC	BP-0	BP-1	BP-2	BP-3
PS090785	Fur, Denmark	CIE PETM	30.51	−27.1 ± 0.1	−22.7 ± 0.1	−22.9 ± 0.3	−21.9 ± 0.3	−21.3 ± 0.4
PS090784	Fur, Denmark	CIE PETM	20.51	−29.8 ± 0.1	−25.2 ± 0.1	−24.4 ± 0.2	−22.8 ± 0.5	−22.5 ± 0.4
PS090783	Fur, Denmark	CIE PETM	17.51	−31.5 ± 0.0	−27.1 ± 0.1	−26.2 ± 0.3	−24.0 ± 0.0	−23.8 ± 0.1
PS090782	Fur, Denmark	CIE PETM	2.51	−30.8 ± 0.1	−28.3 ± 0.3	−25.9 ± 0.2	−25.5 ± 0.2	−25.1 ± 0.2
PS090781	Fur, Denmark	CIE PETM	1.06	−30.9 ± 0.2	−27.2 ± 0.6	−24.3 ± 0.1	−23.7 ± 0.2	−23.8 ± 0.3
PS090751	Fur, Denmark	CIE PETM	0.15	−31.0 ± 0.1	−27.2 ± 0.5	−24.5 ± 0.2	−23.5 ± 0.2	−23.4 ± 0.1
PS090750	Fur, Denmark	CIE PETM	0.08	−30.8 ± 0.0	−25.3 ± 0.2	−24.5 ± 0.3	−23.2 ± 0.2	−23.2 ± 0.1
PS090749	Fur, Denmark	Latest Paleocene	−0.08	−25.9 ± 0.2	−25.7 ± 0.2	−31.5 ± 0.1	−22.1 ± 0.3	−21.1 ± 0.3
PS090748	Fur, Denmark	Latest Paleocene	−0.16	−25.8 ± 0.0	−30.4 ± 0.2	−31.4 ± 0.4	−22.5 ± 0.1	−21.7 ± 0.4
PS090747	Fur, Denmark	Latest Paleocene	−0.29	−26.7 ± 0.0	−26.2 ± 0.1	−26.6 ± 0.2	−22.4 ± 0.3	−21.6 ± 0.2
PS090790	Ølst-Hinge, Denmark	Earliest Eocene	9.27	−26.4 ± 0.0	−23.1 ± 0.2	−24.7 ± 0.5	−22.5 ± 0.3	−22.9 ± 0.5
PS090788	Ølst-Hinge, Denmark	Earliest Eocene	6.84	−27.2 ± 0.0	−22.3 ± 0.3	−22.6	−21.7 ± 0.2	−21.5 ± 0.3
PS090787	Ølst-Hinge, Denmark	Earliest Eocene	4.52	−26.5 ± 0.0	−24.0 ± 0.3	−22.5 ± 0.2	−22.9 ± 0.1	−22.5 ± 0.2
PS090786	Ølst-Hinge, Denmark	Earliest Eocene	0.02	−27.0 ± 0.0	−24.3 ± 0.3	−20.0 ± 0.2	−21.0 ± 0.1	−20.4 ± 0.2
PS090789	Ølst-Hinge, Denmark	CIE PETM	−1.20	−31.0 ± 0.1	−27.4 ± 0.0	−25.6 ± 0.2	−24.3 ± 0.1	−24.3 ± 0.2
PS090746	Store Bælt, Denmark	CIE PETM	128.45	−29.5 ± 0.1	−27.8 ± 0.4	−24.0 ± 0.3	−22.7 ± 0.2	−22.5 ± 0.1
PS105882	Store Bælt, Denmark	CIE PETM	129.27	−28.6 ± 0.1	−26.3 ± 0.0	−25.7 ± 0.3	−23.2 ± 0.0	−22.5 ± 0.2
PS090745	Store Bælt, Denmark	CIE PETM	130.89	−31.3 ± 0.1	−26.8 ± 0.3	−24.2 ± 0.1	−23.2 ± 0.5	−23.1 ± 0.4
PS103458	Store Bælt, Denmark	CIE PETM	131.85	−30.7 ± 0.1	−26.1 ± 0.3	−24.6 ± 0.2	−23.8 ± 0.3	−23.7 ± 0.2
302-4-27 × 1-59-60	Lomonosov Ridge, Arctic Ocean	Post-ETM2	367.99	−29.1	−25.7 ± 0.1	−28.3 ± 0.8	−23.8 ± 0.2	−22.7 ± 0.1
302-4-27 × 1-118-120	Lomonosov Ridge, Arctic Ocean	CIE ETM2	368.58	−29.3	−26.1 ± 0.1	−27.3 ± 1.4	−25.4 ± 0.9	−22.7 ± 0.0
302-4-27 × 1-122-124	Lomonosov Ridge, Arctic Ocean	CIE ETM2	368.62	−29.8	−25.6 ± 0.1	n.d.	n.d.	−22.7 ± 0.2
302-4-27 × 1-132-134	Lomonosov Ridge, Arctic Ocean	CIE ETM2	368.72	−30.8	−24.7 ± 0.0	−25.5	−24.9 ± 0.0	−23.0 ± 0.4
302-4-27 × 1-139-141	Lomonosov Ridge, Arctic Ocean	CIE ETM2	368.79	−31.2	−22.6 ± 0.3	−20.8 ± 0.2	−21.3 ± 0.0	−20.2 ± 0.1
302-4-27 × 2-12-14	Lomonosov Ridge, Arctic Ocean	CIE ETM2	369.00	−27.5	−23.3 ± 0.2	−19.0 ± 0.2	−21.4 ± 0.3	−20.9 ± 0.1
302-4-27 × 2-31-32	Lomonosov Ridge, Arctic Ocean	Pre-ETM2	369.21	−27.5	−23.0 ± 0.4	−21.0 ± 0.1	−20.4 ± 0.2	−19.5 ± 0.3

n.d. = not detected.