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Distribution and export of isoprenoid tetraether lipids in suspended particulate matter from the water column of the Western Atlantic Ocean

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ABSTRACT

The TEX_{86} paleotemperature proxy is based on the distribution of archaeal glycerol dibiphytanyl glycerol tetraether (GDGT) lipids preserved in marine sediments, yet both the influence of different physiological factors on the structural distribution of GDGTs and the mechanism(s) by which GDGTs is(are) exported to marine sediments remain(s) unresolved. We investigated the abundance and structural distribution of GDGTs in the South-west and Equatorial Atlantic Ocean in four water column profiles spanning 48 degrees of latitude. The depth distribution was consistent with production by ammonia-oxidizing Thaumarchaeota; maximum GDGT concentration occurred at the base of the NO_2^- maximum, core GDGTs dominated the structural distribution in surface waters above the NO_2^- maximum, and intact polar GDGTs – potentially indicating live cells – were more abundant below the NO_2^- maximum. Between 0 and1000 m, > 98% of the integrated GDGT inventory was present in waters at and below the NO_2^- maximum. Depth profiles of TEX_{86} temperature values displayed local minima at the NO_2^- maximum, while the ratio of GDGT-2:GDGT-3 increased with depth. A model based on the results predicts an average depth of origin for GDGTs exported to sediments between ca. 80–250 m. In the model, exported TEX_{86} values are remarkably insensitive to change in the average depth of origin of GDGTs. However, TEX_{86} values exported from the water column appear to reflect euphotic zone productivity, possibly due to the correlative intensity of organic matter remineralization providing substrates for ammonia oxidation. Predicting the influence of these regional controls on sedimentary TEX_{86} records requires a better understanding of the interaction between GDGT production, particle dynamics, and the depth of origin for exported organic matter.

1. Introduction

Archaeal glycerol dibiphytanyl glycerol tetraether (GDGT) lipids (Supplementary Fig. 1) are ubiquitous in marine sediments and form the basis of the TEX_{86} sea surface temperature (SST) proxy (Schouten et al., 2002). GDGTs in the water column are thought to be sourced primarily from ammonia-oxidizing archaea (AOA) affiliated with the phylum Thaumarchaeota (formerly Marine Group I Crenarchaeota; Brochier-Armanet et al., 2008; Spang et al., 2010). AOA perform the first and rate-limiting step in nitrification, the oxidation of NH_4^+ to NO_2^-, catalyzed by the archaeal ammonia monooxygenase enzyme, *amoA* (Könneke et al., 2005). Accordingly, maximum Thaumarchaeota cell numbers, as well as maximum copies of *amoA* and 16S rRNA genes, occur with the primary NO_2^- maximum near the base of the euphotic zone (Massana et al., 1997; Murray et al., 1999; Karner et al., 2001; Francis et al., 2005; Church et al., 2010; Santoro et al., 2010; Smith et al., 2016). GDGT concentration mirrors the trend in overall thaumarchaeal abundance, with low concentration in surface waters and a maximum concentration near the base of the euphotic zone (Sinninghe Damsté et al., 2002; Turich et al., 2007; Schouten et al., 2012; Basse et al., 2014; Lincoln et al., 2014; Xie et al., 2014; Kim et al., 2016).

Thaumarchaeota produce GDGTs containing from zero to four cyclopentane rings (GDGT-0 to GDGT-4) or four cyclopentane rings and one additional cyclohexane ring (e.g. in crenarchaeol; Sinninghe Damsté, 2002; Supplementary Fig. 1). The ratio between

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GDGTs with one to three cyclizations and the crenarchaeol regioisomer is the basis of the TEX_{86} temperature proxy. TEX_{86} is theoretically based on the concept of homeoviscous membrane adaptation, in which an organism regulates membrane fluidity in response to physical or chemical perturbations (e.g. by incorporation of cyclization in response to increasing temperature). However, TEX_{86} is empirically calibrated using a correlation between the distribution of select GDGT structures in marine sediments and sea surface temperature or subsurface (0–200 m) temperature (Schouten et al., 2002; Kim et al., 2010; Tierney and Tingley, 2015).

Modern TEX_{86} core-top calibrations generally predict SST to within ± 3–5 °C (Kim et al., 2010; Tierney and Tingley, 2014). TEX_{86} paleoclimate records span temporally and geographically diverse events in Earth history, including the Last Glacial Maximum (Huguet et al., 2006b), the Paleocene-Eocene Thermal Maximum PETM (Zachos et al., 2006) and Cretaceous Ocean Anoxic Events (Schouten et al., 2003). TEX_{86} provides an alternative to proxies that cannot be applied for sediments older than the Paleogene (e.g. $U^{k'}_{37}$), or when dissolution or diagenetic processes have impacted the preservation of carbonate-based geochemical signatures (Schouten et al., 2013).

The TEX_{86} proxy rests on the assumptions that temperature is the dominant factor driving lipid composition in planktonic Thaumarchaeota, and that this signal is ultimately preserved in marine sediments. Mesophilic culture and mesocosm studies show that GDGT cyclization can increase at higher temperature (Wuchter et al., 2004; Schouten et al., 2007; Elling et al., 2015; Qin et al., 2015). However, suspended material filtered from the marine water column has TEX_{86} values that do not consistently reflect in situ temperature (Wuchter et al., 2005; Ingalls et al., 2006; Turich et al., 2007; Schouten et al., 2012; Basse et al., 2014; Hernández-Sánchez et al., 2014; Xie et al., 2014; Zhu et al., 2016). In fact, calculated TEX_{86} values often reach a maximum below 200 m, yielding thermocline and sub-thermocline temperatures greater than local sea surface temperatures (Schouten et al., 2012; Basse et al., 2014; Xie et al., 2014; Kim et al., 2016). Therefore, variables other than surface or shallow subsurface temperatures appear to be important additional factors in determining water column TEX_{86} signals.

Recent culture work reveals that ammonia oxidation rate can be a temperature-independent influence on GDGT cyclization in the model thaumarchaeon *Nitrosopumilus maritimus* SCM1 (Hurley et al., 2016). This finding reconciles similar culture experiments with *N. maritimus* that have identified growth stage (Elling et al., 2014) and O_2 availability (Qin et al., 2015) as variables affecting TEX_{86}. In cultures of *N. maritimus*, TEX_{86} correlated negatively with ammonia oxidation rate, resulting in warmer TEX_{86} values at slower oxidation rates and colder values at faster oxidation rates (Hurley et al., 2016). This relationship provides an explanation for why warm upper water columns with lower rates of both primary production and sub-photic zone nutrient regeneration, i.e. lower ammonia oxidation rate, have in situ TEX_{86} temperature values that are too high (e.g. Wuchter et al., 2005), whereas warm upper water columns in high-nutrient upwelling zones have apparent in situ TEX_{86} temperature values that are too low (e.g. Xie et al., 2014).

In order to better understand the environmental factors influencing TEX_{86}, we have examined GDGT distributions in two particle size classes, 0.3–0.7 μm and 0.7–53 μm, between 0 and 1000 m along a transect in the South-west and Equatorial Atlantic Ocean (ca. 40°S to 10°N). We relate the abundance and structural distribution of GDGTs to water column properties. We then model different scenarios to explore how the depth of GDGT export affects the proxy ratio exported to marine sediments.

2. Methods

2.1. Sampling and lipid extraction

Samples were collected from aboard the R/V Knorr during cruise KN210-04 (Fig. 1) in March–May 2013 from 38.0°S 45.0°W (Station 2), 22.5°S 33.0°W (Station 7), 2.7°S 28.5°W (Station 15) and 9.7°N 55.3°W (Station 23). Suspended particulate matter samples were collected between 0 and 1000 m at each station to increase depth resolution in the upper water column, yet full water column depth ranged from 3762 m at Station 23 to 5110 m at Station 2 (Table 1). Samples for inorganic nutrient analysis were collected in HDPE bottles and frozen (−20 °C) immediately after sample collection. All nutrient data have been deposited in the Biological and Chemical Oceanography (BCO) Data System (Kujawinski and Longnecker, 2013).

The CTD rosette system was equipped with a SBE43 oxygen sensor, a Wet Labs FLNTURTD combination fluorometer and turbidity sensor, and a WetLabs C-star transmissometer (operating at a 660 nm with 25 cm path length). The SBE43 O_2 data were calibrated based on the discrete water samples analyzed during the cruise. Fluorescence values from the WET Labs ECO-AFL/FL were converted from volts to mg/m^3 using calibration values from WETLabs. All CTD data are publically accessible in the BCO Data System (Kujawinski and Longnecker, 2014).

Seawater was sequentially filtered in situ via submersible pumps (WTS-LV 08 upright: McLane Research Laboratories, Inc), with total collected volumes between 710 and 10,518 l (mean 3049 l) per depth. Pumps were equipped with three filter tiers, each 142 mm in diameter. The first tier was fitted with a 53 μm mesh Nitex screen, the second with two (stacked) pre-combusted glass fiber filters (Whatman GF/F; 0.7 μm), and the last two (stacked) pre-combusted glass fiber filters (Sterlitech GF-75; 0.3 μm). Filter size was chosen based on ease of comparison to a typical suspended class of particulate organic matter (0.7–53 μm), while the sub-μm class cut off at 0.3 μm represents the smallest available glass fiber filter extractable with organic solvents. All filters were wrapped in pre-combusted Al foil and frozen immediately at −80 °C after recovery.

Filters were extracted in Teflon vessels in 90:10 CH_2Cl_2:CH_3OH using microwave-assisted extraction with a CEM Mars system. This extraction method was the most efficient way to process all 229 filter samples and is reported to have good performance for water column particles (Huguet et al., 2010). Lipid extraction consisted of two steps: a 30 min ramped heating program to 70 °C with a 20 min hold, after which solvent was decanted and fresh solvent added, and then a 30 min ramped heating program to 100 °C with a 20 min hold. The extracts from the successive extraction steps were combined, concentrated under a stream of ultrapure N_2, and stored at −20 °C until measurement. All lipid data have been deposited in the Pangaea database under the DOI https://doi.pangaea.de/10.1594/PANGAEA.861376.

2.2. Intact polar and core lipid analysis

Intact polar lipids (IPLs) and core lipids were analyzed from a 2–10% aliquot of the TLE in MeOH on a Dionex Ultimate 3000RS ultra high performance liquid chromatography (UHPLC) system connected to an ABSciEX QTRAP4500 Triple Quadrupole/Ion Trap mass spectrometry (MS) instrument equipped with a TurboIonSpray ion source operating in positive electrospray (ESI) mode. Separation of core and intact polar lipids was achieved using reversed phase HPLC with an ACE3 C_{18} column (2.1 × 150 mm × 3 μm; Advanced Chromatography Technologies, Aberdeen, Scotland) maintained at 45 °C (Zhu et al., 2013). Target compounds were detected using