



Distribution of intact and core tetraether lipids in water column profiles of suspended particulate matter off Cape Blanc, NW Africa



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ARTICLE INFO

Article history:

Received 9 April 2014

Accepted 9 April 2014

Available online 24 April 2014

Keywords:

GDGT

Archaea

TEX₈₆

Suspended particulate matter

NW-Africa

Upwelling

Intact polar lipids

Oxygen minimum zone

Nepheloid layers

In situ production

ABSTRACT

In the reconstruction of sea surface temperature (SST) from sedimentary archives, secondary sources, lateral transport and selective preservation are considered to be mainly negligible in terms of influencing the primary signal. This is also true for the archaeal glycerol dialkyl glycerol tetraethers (GDGTs) that form the basis for the TEX₈₆ SST proxy. Our samples represent four years variability on a transect off Cape Blanc (NW Africa). We studied the subsurface production, vertical and lateral transport of intact polar lipids and core GDGTs in the water column at high vertical resolution on the basis of suspended particulate matter (SPM) samples from the photic zone, the subsurface oxygen minimum zone (OMZ), nepheloid layers (NL) and the water column between these. Furthermore we compared the water column SPM GDGT composition with that in underlying surface sediments. This is the first study that reports TEX₈₆ values from the precursor intact polar lipids (IPLs) associated with specific head groups (IPL-specific TEX₈₆). We show a clear deviation from the sea surface GDGT composition in the OMZ between 300 and 600 m. Since neither lateral transport nor selective degradation provides a satisfactory explanation for the observed TEX-derived temperature profiles, with a bias towards higher temperatures for both core- and IPL-specific TEX₈₆ values, we suggest that subsurface in situ production of archaea with a distinct relationship between lipid biosynthesis and temperature is a responsible mechanism. However, in the NW-African upwelling system the GDGT contribution of the OMZ to the surface sediments did not seem to affect the sedimentary TEX₈₆ as it showed no bias and still reflected the signal of the surface waters between 0 and 60 m.

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1. Introduction

Marine planktic Thaumarchaeota produce glycerol dibiphytanyl glycerol tetraethers (GDGTs) as their major membrane building blocks. These lipids occur in the natural environment as intact polar lipids (IPLs) with glycosidic and/or phosphate head groups attached to the GDGT core, or as core lipids (CLs) without these head groups. Core lipid GDGTs (CL-GDGTs) have the potential to be preserved in sediments up to hundreds of millions of years (Kuypers et al., 2001; Jenkyns et al., 2012). They may contain one to four cyclopentyl moieties and up to one cyclohexyl moiety in the isoprenoid chains. The relative abundance of the cyclopentyl moieties is expressed in the TEX₈₆ proxy (Schouten et al., 2002).

Since core-TEX₈₆ for surface sediments mainly correlates well with the annual mean sea surface temperature or integrated temperature of the upper water column (Kim et al., 2008, 2010) it has been widely used to reconstruct sea surface temperature (SST) values from ancient sediments. The procedure assumes an accurate transfer of core-TEX₈₆ from the overlying surface water through the water column to the sediment and negligible influence from selective preservation or lateral transport (Mollenhauer et al., 2008; Shah et al., 2008; Kim et al., 2009a) and from other sources of GDGTs from e.g. deep cold water (e.g., Wuchter et al., 2005; Huguet et al., 2006a). The validity of these assumptions has been primarily empirical. It is based on correlations between sediment surface core-TEX₈₆ values with satellite-derived SST data but hardly on the water column analysis required to assess the above modifying processes. There is only a relatively small number of studies providing comprehensive information on GDGTs in suspended particulate matter (SPM) in the water column, especially > 1000 m water depth, available. The SPM data indicate that,

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in the water column > 100 m, neither core-TEX₈₆ (Wuchter et al., 2005; Ingalls, 2006; Turich et al., 2007; Schouten et al., 2012, 2013; Taylor et al., 2013) nor IPL-derived TEX₈₆, considered to reflect bulk IPL-TEX₈₆ (Schouten et al., 2012), correlates with in situ water temperature. This has been explained by the hypothesis that the CL-GDGTs from surface sediments are derived only from non-living matter transported from the upper water column (Wuchter et al., 2005). However, this is debatable, and a “subsurface” GDGT contribution has also been hypothesized (Huguet et al., 2006a; Lee et al., 2008; Schouten et al., 2013; Taylor et al., 2013). Lateral transport, e.g. in nepheloid layers, may introduce an allochthonous component to the sediment. As this material may originate up to several hundred km from the site of sedimentation (Ohkouchi et al., 2002; Nowald et al., 2006), this component might differ completely from the autochthonous signal and thus potentially cause strong bias. However, some evidence exists that transport processes do not affect GDGTs to the same extent as other lipids like, e.g. alkenones (Mollenhauer et al., 2008; Shah et al., 2008).

Studies have shown that marine picoplankton communities change with depth: While the photic zone is primarily dominated by bacteria, archaea contribute up to 50% or more to the total microbial community in deep water (Karner et al., 2001; Teira et al., 2004). Changes in archaeal ecotypes in deep vs. shallow water have been observed (Francis et al., 2005; Hallam et al., 2006; Mincer et al., 2007). Variation in O₂ concentration may also have an influence on the archaeal community (Herndl et al., 2005; Labrenz et al., 2010; Loescher et al., 2012). This is consistent with observations of anoxic or suboxic environments where the TEX₈₆ signal in the water column correlates neither with in situ nor with surface temperature (Schouten et al., 2012).

In general, intact polar GDGTs with head groups (IPL-GDGTs) were thought to be degraded rapidly after cell death (Harvey et al., 1989) and thus could be used as biomarkers for living microbes (Sturt et al., 2004; Biddle, 2006; Biddle et al., 2006; Lipp and Hinrichs, 2009; Schubotz et al., 2009). However, more recently the predominant glycosidic IPL-GDGTs have been suggested to be affected by a fossil contribution, especially in anoxic environments such as sediments, and may even be preserved on geological timescales (Schouten et al., 2010). It is still under discussion whether differences in the lability of IPL-GDGTs with different head groups can significantly influence core-GDGT composition in the water column and sediments (Lengger et al., 2012a,b; Schouten et al., 2012).

To obtain a better insight into the potential modification of the GDGT composition and TEX₈₆ by lateral transport, in situ production and differential degradation, we collected SPM from the water column at different depths at multiple stations along an onshore-offshore transect off the upwelling area near Cape Blanc (Fig. 1a) in

four consecutive years. For the first time not only core-TEX₈₆ values but also TEX₈₆ values from IPL groups associated with specific head groups (IPL-specific TEX₈₆) were systematically examined in organic matter (OM) from different water depths by applying a new high performance liquid chromatography–mass spectrometry (HPLC–MS) protocol (Zhu et al., 2013). This allowed us to constrain the influences of (i) productivity along the onshore–offshore gradient, (ii) lateral transport by comparison with samples from nepheloid layers, (iii) degradation by comparing samples from different water depths, (iv) in situ production through differences in IPL composition and (v) low O₂ concentrations within the local oxygen minimum zone (OMZ).

2. Material and methods

2.1. Study area

The northwest African upwelling system is one of the four largest eastern boundary upwelling systems in the world and is characterized by high productivity (Carr, 2001). A considerable part of the biomass produced in the photic zone sinks to the deep sea in the form of aggregates, fecal pellets and marine snow (Nowald et al., 2006; Fischer and Karakas, 2008, 2009). On its way, the sinking OM undergoes degradation and remineralization, whereby microorganisms degrade up to 13% of the organic carbon (OC) per day (Iversen et al., 2010). As a result, the concentration of lipids generally decreases exponentially with water depth (Martin et al., 1987; Sarmiento, 1993). Nevertheless, a relevant amount of OM still reaches the seafloor and is buried in the deep-sea sediments, which contain 0.4–2% OC (Seiter et al., 2004). Long term observations (Ratmeyer et al., 1999; Nowald et al., 2006) with sediment traps and particle cameras (ParCa) as well turbidity sensors show that transport is not only vertical. Particles are also transported laterally (Karakas et al., 2009), mainly in nepheloid layers (NLs) containing a significantly higher concentration of particles than the water column in between. In particular, an intermediate nepheloid layer (INL) at ca. 250–600 m water depth and a bottom layer (BL) at 50–100 m above the seafloor could be detected during several years of observation (Müller and Fischer, 2001; Karakas et al., 2006; Fischer and Karakas, 2009). The INL seems to originate at the shelf break and seems to be derived at least partly from re-suspended shelf material. The BL generates particle “clouds” detaching from the slope at 1900–2800 m.

2.2. Sampling

Samples were taken from an east–west transect off Cape Blanc at three main stations (CB, CBi and Slope) during four cruises: MSM

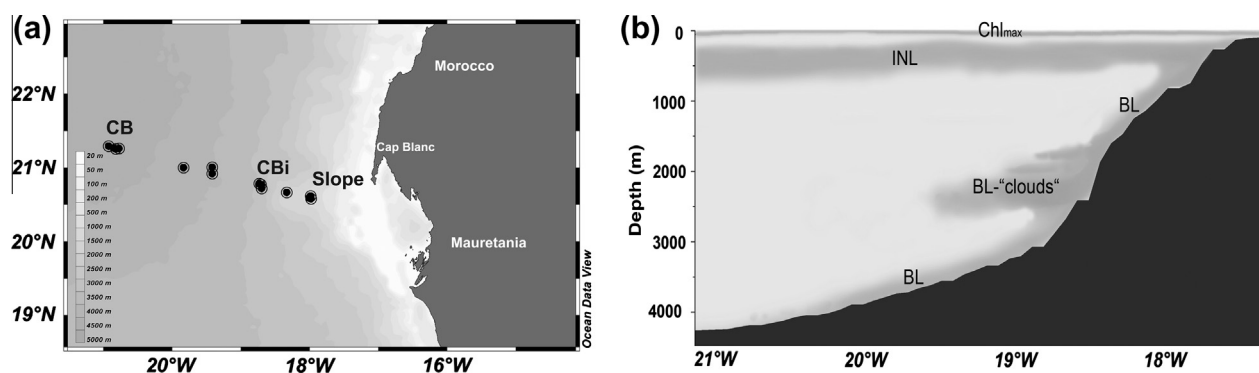


Fig. 1. Map of study area off Cape Blanc with sampling stations (dark gray circles) on the offshore transect (a) and general distribution of chlorophyll maximum (Chl_{max}), intermediate nepheloid layer (INL) and bottom near layer (BL) in the water column along the offshore transect derived from CTD–turbidity-sensor data (b). Note: horizontal scales are not identical in (a) and (b).

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