

Chapter 6

Temporal and spatial variation in tetraether membrane lipids of marine Crenarchaeota in particulate organic matter:

Implications for TEX₈₆ paleothermometry

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Abstract.

The TEX₈₆ is a new temperature proxy which is based on the number of cyclopentane moieties in the glycerol dialkyl glycerol tetraether (GDGT) lipids of the membranes of Crenarchaeota which occur ubiquitously in oceans and shelf seas. This proxy was calibrated by core top sediments but it is as yet not clear during which season and at which depth in the water column the GDGT signal used for TEX₈₆ paleothermometry is biosynthesized. Here, we analyzed >200 particulate organic matter (POM) samples from 11 different marine settings for TEX₈₆. This revealed that the GDGTs occur seasonally in surface waters and occur in higher abundances during the winter and spring months. The depth distribution showed that GDGTs generally appeared in higher amounts below 100 m depth in the water column. However, the TEX₈₆ values for waters below the photic zone (150-1500 m) did not correlate with the in situ temperature but rather correlated linearly with surface temperature. The TEX₈₆ for POM from the upper 100 m showed a linear correlation with in situ temperature, which was nearly identical to the previously reported core top equation. The correlation of all POM samples with surface temperature was also strikingly similar to the core top correlation. These findings demonstrate that the GDGT signal which reaches the sediment is mainly derived from the upper 100 m of the water column. This may be caused by the fact that GDGTs from the photic zone are much more effectively transported to the sediment by grazing and repackaging in large particles than GDGTs from deeper waters.

6.1 Introduction

Organic components in sediments are useful tools to reconstruct paleo-environments and climates. The most prominent example is sea surface temperature (SST) reconstruction using C_{37} alkenones. Alkenones are produced by marine haptophytes including the cosmopolitan coccolithophorids such as *Emiliana huxleyi* [Volkman *et al.*, 1980] and *Geophyrocapsa oceanica* [Volkman *et al.*, 1994]. In these algae the ratio of di- and tri-unsaturated C_{37} alkenones (expressed in the U_{37}^K ratio) changes as a function of temperature [Brassell *et al.*, 1986].

A new organic geochemical SST proxy, the TetraEther Index of lipids with 86 carbon atoms (TEX₈₆) was recently introduced [Schouten *et al.*, 2002]. This proxy is based on the number of cyclopentane moieties in the tetraether membrane lipids of marine Crenarchaeota. Marine Crenarchaeota are Prokaryotes that belong to the domain of Archaea. Molecular biological work using ribosomal DNA and the analysis of membrane lipids showed that marine Archaea are ubiquitously distributed in the world's ocean and occur in polar as well as in tropical regions [Fuhrman *et al.*, 1992; DeLong, 1992; Hoefs *et al.*, 1997; Sinninghe Damsté *et al.*, 2002a]. Recent molecular biological work revealed that the group of the marine Crenarchaeota comprises ca. 20% of the picoplankton in the world's ocean [Karner *et al.*, 2001]. The membrane lipids of Archaea consist of isoprenoid glycerol dialkyl glycerol diethers and glycerol dibiphytanyl glycerol tetraethers (GDGTs) [DeRosa and Gambacorta, 1988]. Marine Crenarchaeota biosynthesize a specific GDGT, named crenarchaeol, which contains four cyclopentane ring and one cyclohexane ring, in addition to some more generally occurring GDGTs (Fig. 1) [Sinninghe Damsté *et al.*, 2002b]. It has been suggested that marine Crenarchaeota have evolved from hyperthermophilic Crenarchaeota by building an additional “kink” in their membrane lipid, i.e. the cyclohexane ring [Sinninghe Damsté *et al.*, 2002b]. This component is thought to have lowered the transition point of the membrane lipids and allowed the Crenarchaeota to live in temperate environments. Culture experiments and field studies have shown that membrane lipids of hyperthermophilic Archaea change their relative distribution of cyclopentane moieties as a function to temperature [Gliozzi *et al.*, 1983; Ward *et al.*, 1985, DeRosa and Gambacorta, 1988; Uda *et al.*, 2001]. With this mechanism Archaea keep their cytoplasm membrane at a liquid crystalline state and reduce their proton permeation

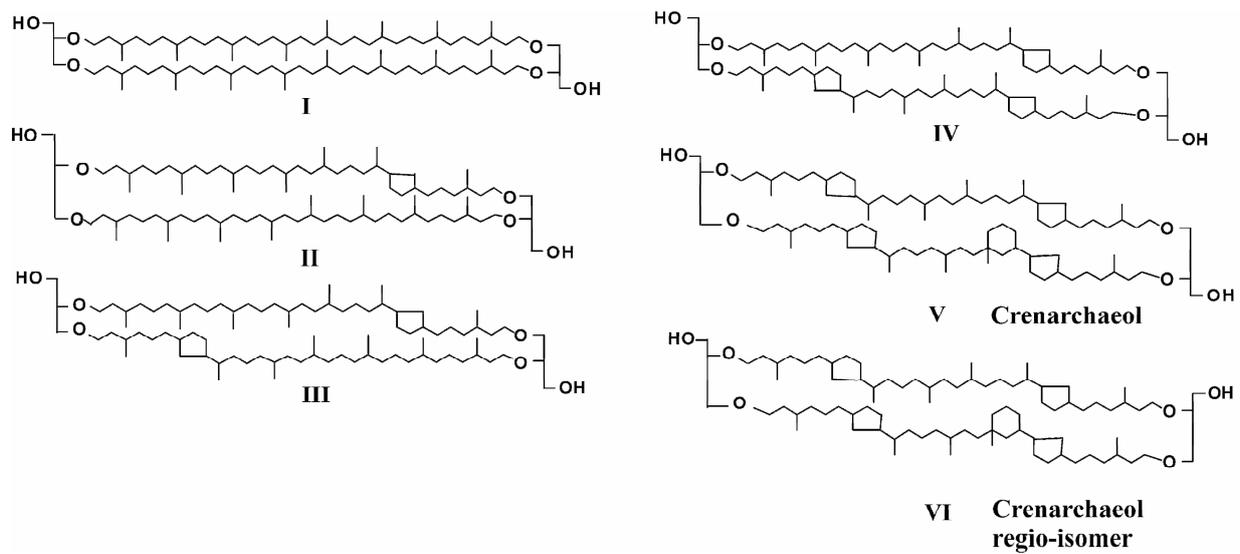


Figure 1. Structures of GDGT membrane lipids of marine pelagic Crenarchaeota.

rate [Albers *et al.*, 2000]. Recent mesocosm studies confirmed that the GDGT composition of marine Crenarchaeota is also determined by temperature [Wuchter *et al.*, 2004]. The membrane lipids of marine Crenarchaeota are relatively stable components, and are found in sediments up to 140 million years old [Kuypers *et al.*, 2001, Carrillo-Hernandez *et al.*, 2003].

Schouten *et al.* [2002] showed that the distribution of crenarchaeotal GDGTs in core top sediments derived from different geographic locations correlate with SST. In cold areas the GDGT distribution is dominated by GDGT I (see Fig. 1 for structures) and crenarchaeol (V). In warmer regions the GDGT distributions differ substantially as crenarchaeol is the most abundant GDGT and higher amounts of 1-3 cyclopentane-containing GDGTs (II-IV) and a regio-isomer of crenarchaeol (VI) are detected (Fig. 2). The relative GDGT distribution can be expressed as an index of GDGT isomers, which was named the TEX₈₆ and is defined as follows:

$$\text{TEX}_{86} = (\text{III} + \text{IV} + \text{VI}) / (\text{II} + \text{III} + \text{IV} + \text{VI}) \quad [1]$$

This index is correlated with the annual mean SST [Schouten *et al.*, 2002]:

$$\text{TEX}_{86} = 0.015 * T + 0.28, (r^2 = 0.92) \text{ with } T = \text{annual mean SST (in } ^\circ\text{C)}. \quad [2]$$

The observed correlation of TEX₈₆ with annual mean SST suggests that marine Crenarchaeota are mainly present in surface waters throughout the whole year. However, this seems in contradiction to ribosomal DNA work from Massana *et al.* [1997] and Murray *et al.* [1998 and

1999], who observed a seasonal occurrence of marine Crenarchaeota in Santa Barbara Channel surface waters and coastal Antarctic surface waters. In addition, cell counts at the tropical Pacific revealed that marine crenarchaeotal cell numbers are relatively invariant throughout the water column during the annual cycle and cell numbers only drop below 250 m [Karner *et al.*, 2001]. In contrast, crenarchaeotal GDGT concentrations are actually higher below the photic zone in the Arabian Sea [Sinninghe Damsté *et al.*, 2002a].

These different observations show that it is as yet not clear when and at which depth in the water column the GDGT signal for TEX₈₆ paleothermometry is produced. To answer this question, we investigated the GDGT composition of particulate organic matter (POM) from different oceanic regimes. We analyzed surface water time series and depth profiles to shed more light on the seasonal and spatial distribution of the marine crenarchaeotal GDGTs and how this affects TEX₈₆ values.

6.2 Material and Methods

To study the seasonal GDGT abundance in surface waters we analyzed particulate organic matter (POM) from time series of two different locations, i.e. Bermuda Atlantic Time Series (BATS) and shallow coastal North Sea waters. The vertical GDGT distribution was studied by analyzing POM from depth profiles from three different locations, i.e. the Equatorial Pacific, eastern North Pacific (VERTEX 5) and Santa Monica Basin. In addition, TEX₈₆ values were calculated for depth profiles from Arabian Sea and Cariaco Basin which were investigated previously [Sinninghe Damsté *et al.*, 2002a, Wakeham *et al.*, 2004]. Finally, a number of surface and depth samples from Peru upwelling region, Seychelles, Southern Ocean and Mediterranean Sea (collected at the French DYFAMED site) were analyzed. For further detailed information about the collection of the samples, see Figure 2 and Table 1.

6.2.1 Sampling and extraction

POM was collected by large volume filtration systems through extracted 50 µm Nitex screen and pre-combusted glass fiber filters (GF) with a nominal pore size of 0.7 µm. The filters were wrapped in clean aluminum foil and kept frozen at -20°C until extraction. Filters were Soxhlet extracted with dichloromethane (DCM) and methanol (2:1 by volume) at Skidaway Institute of Oceanography.

Coastal North Sea surface waters were sampled for POM at about 1 m depth in weekly intervals from August 2002- July 2003 at the NIOZ jetty. 20 l of water collected at high tide were filtered through ashed 3 µm and 0.7 µm GF filters. The filters were wrapped in clean aluminum foil and stored at -20°C until further analyses. The GF filters were freeze-dried and ultrasonically extracted with methanol, methanol/DCM (1:1 by volume) and three times with DCM at NIOZ.

6.2.2 Lipid analysis

An aliquot of the total lipid extract was cleaned over an activated Al₂O₃ column by eluting with methanol/DCM (1:1 by volume). For analysis of intact GDGTs, the solvent was removed under a stream of nitrogen and the residue was dissolved by sonication (5 min) in hexane/propanol (99:1 by volume). The resulting suspension was filtered through a 0.45-µm-pore-size, 4 mm diameter Teflon filter prior to injection. The intact GDGTs were analyzed by high performance liquid chromatography (HPLC) - atmospheric pressure positive ion chemical ionization mass spectrometry (APCI-MS) by applying conditions slightly modified from *Hopmans et al.* [2000]. Analyses were performed using an HP (Palo Alto, CA, USA) 1100 series LC-MS equipped with an auto-injector and Chemstation chromatography manager software. Separation was achieved on a Prevail Cyano column (2.1 x 150 mm, 3 µm; Alltech, Deerfield, IL, USA), maintained at 30°C. Injection volumes were 15 µl. GDGTs were eluted isocratically with 99% A and 1% B for 5 min, followed by a linear gradient to 1.8% B in 45 min, where A = hexane and B = propanol. Flow rate was 0.2 ml/min. After each analysis the column was cleaned by back-flushing hexane/propanol (90:10, by volume) at 0.2 ml/min for 10 min. Detection was achieved using APCI-MS of the eluent. Conditions for APCI-MS were as follows: nebulizer pressure 60 psi, vaporizer temperature 400 °C, drying gas (N₂) flow 6 l/min and temperature 200 °C, capillary voltage -3 kV, corona 5 µA (~ 3.2 kV). GDGTs were detected by single ion monitoring of their [M+H]⁺ ions (dwell time 237 ms). For TEX₈₆ calculation the peak areas of GDGTs I-VI were integrated and TEX₈₆ values were calculated according to Equation I. For the temperature correlation only TEX₈₆ values were used where all isomers of GDGTs could be detected and accurately quantified.

sampling site	area/station	sampling intervals	cruise/ cruise no.	sampling depth	sampling size (l)	number of samples	references
(1) Northeastern Pacific (VERTEX 5)	V5A: 33.3°N, 139.2°W; V5C: 36.1°N, 122.6°W.	June 1984	R/V <i>Wecoma</i>	10-1500m	900-5000	12	<i>Wakeham and Camel, 1988</i> <i>Silver and Gowing 1991</i>
(2) Santa Monica Basin	33°75'N, 119°08'W	March 1991- April 1992	R/V <i>Sea Watch</i> (6 cruises)	25-850m	250-4000	15	<i>Biggare et al., 1997</i>
(3) Equatorial Pacific	Station 6: 140°W, 2°N; Station 15: 140°W, 12°S.	February-March and August- September 1992	R/V <i>Thomas G. Thompson</i> TT007 and TT011	25-840m	2000-17000	32	<i>Murray et al., 1995</i> <i>Sheridan et al., 2002</i>
(4) Peru upwelling region	Transect 12°S and 13.5°S	October, 1992	R/V <i>Seward Johnson</i>	surface	70-190	20	<i>Pancost et al., 1997</i>
(5) Bermuda Atlantic Time Series (BATS)	32°10'N, 64°30'W (Hydrostation S)	November 1991 till January 1996	R/V <i>Weatherbird II</i> BATS 38-88	surface	1000-3000	50	<i>Steinberg et al., 2001,</i> <i>Conte et al., 2001</i>
(6) Cariaco Basin	10° 40'N, 65°36'W	February- March 1986	R/V <i>Isetin</i>	10-1150m	500-5000	10	<i>Wakeham et al., 1990</i> <i>Wakeham et al., 2004</i>
(7) Shallow coastal North Sea waters	53°00'25"N, 4°78'27"E (NIOZ Jetty)	August 2002- July 2003	-----	surface	20	33	This manuscript
(8) MedFlux (DYFAMED)	43°20'N, 7°40'W	September 2002	R/V <i>Tethys II</i>	3-150m	550-800	6	http://alpha.msrc.sunysb.edu/MedFlux/ <i>Liu et al., in press</i>
(9) Arabian Sea Process Study	Sta. 2: 15°58'N, 61°29'E; Sta. 4: 17°12'N, 59°35'E; Sta. 5: 17°24'N, 58°49'E; Sta. 6: 17°41'N, 57°50'E; Sta. 7: 17°40'N, 57°41'E; Sta.10: 17°44'N, 57°29'E; Sta.13: 19°13'N, 58°31'E.	May 1995	R/V <i>Thomas G. Thompson</i> TN047	30-1500m	2400-3000	19	<i>Smith et al., 1998</i> <i>Simmings Damsté et al., 2002</i>
(10) Seychelles	6°12'S, 52°7'E	November 2003	R/V <i>Darwin</i>	surface	20	1	This manuscript
(11) Southern Ocean	Transect along 170°W	Nov-Dec.1996, Feb-March 1998	R/V <i>Nathaniel B. Palmer</i> ; NBP 96-5, NBP 98-2.	surface	1000-1100	22	This manuscript

Table 1. Sampling information and related references of the POM samples investigated in this study.

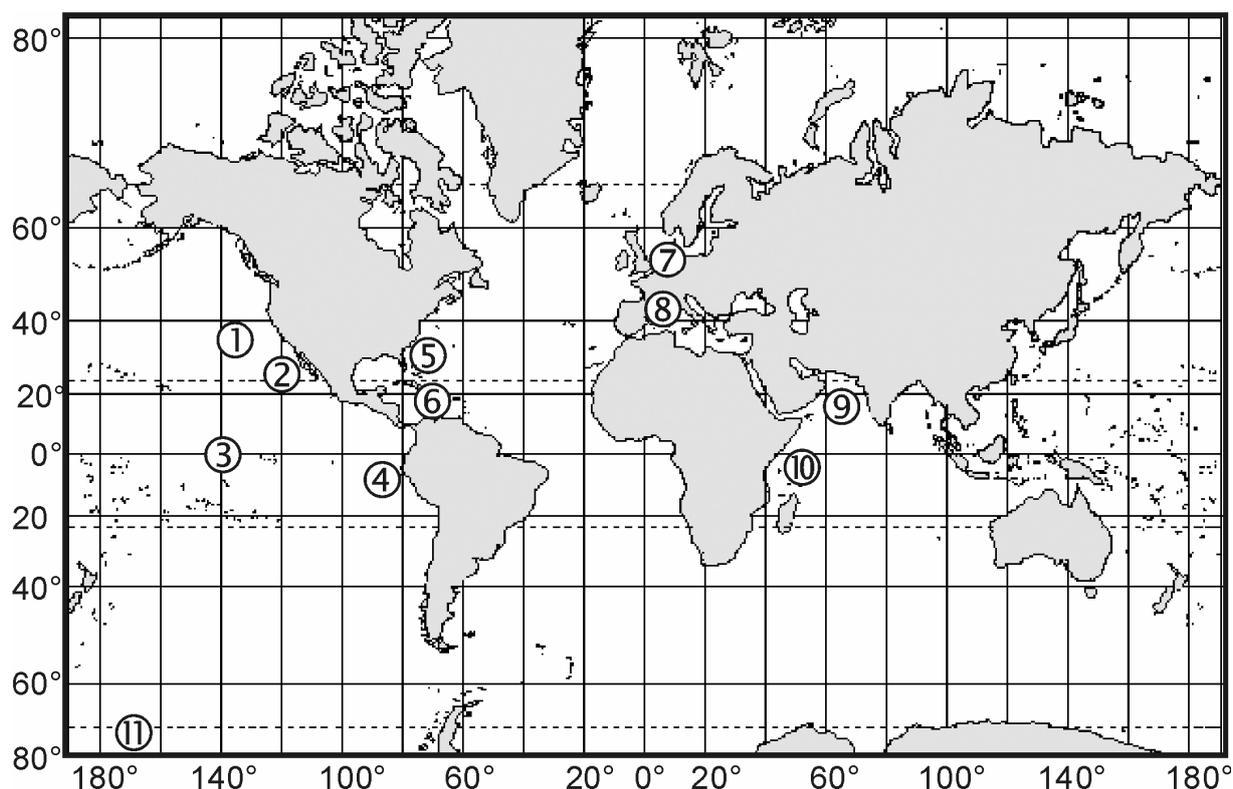


Figure 2. Sampling location of particulate organic matter (POM) analyzed in this study. 1: Northeastern Pacific (VERTEX 5); 2: Santa Monica Basin; 3: Equatorial Pacific; 4: Peru upwelling region; 5: Bermuda Atlantic Time Series (BATS); 6: Cariaco Basin; 7: Shallow Coastal North Sea waters; 8: Mediterranean Sea (DYFAMED); 9: Arabian Sea, 10: Seychelles and 11: Southern Ocean. See Table 1 for further sampling details.

6.3 Results

We analyzed 220 POM samples from different oceanic regimes to determine the GDGT occurrence and distribution with depth and with time. Of these, 118 POM samples contained sufficient amounts of GDGTs for reliable TEX_{86} calculation. The sampling locations ranged from shallow coastal North Sea waters to open ocean samples such as Arabian Sea, Equatorial Pacific, and the Southern Ocean (see Fig. 2).

6.3.1 Surface time series

Both time series, the Bermuda Atlantic Time series (BATS) and the shallow coastal North Sea water, showed a seasonal occurrence of GDGTs during the annual cycle. At the

shallow coastal North Sea water site the GDGTs were most abundant during the winter and early spring seasons (Fig. 3a). In late spring, summer and autumn the concentration of GDGTs was <10% of that in winter. The GDGT distribution was dominated by GDGT I and, to a lesser extent crenarchaeol (V) and a relatively low amount of cyclopentane-containing GDGTs (Fig. 4a). The TEX₈₆ values ranged between 0.39 and 0.51 for shallow coastal North Sea waters during winter and spring (Fig. 3a).

At the BATS site, surface water POM samples were collected monthly [Conte *et al.*, 2001] but GDGTs were only detected in the winter and spring months (Fig. 3b). During the rest of the year the GDGT concentration was near the detection limit (ca. 1 pg/l). The GDGT distribution was dominated by crenarchaeol and relatively high amounts of cyclopentane-containing GDGTs (Fig. 4b). TEX₈₆ values ranged between 0.56 and 0.73 (Fig. 3b).

6.3.2 Depth profiles

All three studied depth profiles had a similar GDGT distribution throughout the water column. POM from different depths of the Santa Monica Basin were obtained in August and October 1991 and in February 1992 at 4 depths ranging between 25 m and 850 m. Apart from the October samples, the GDGT abundance was highest between 100 to 850 m water depths (Fig. 5a). The GDGT distribution was dominated by GDGT I and to a lesser extent crenarchaeol with a relatively low amount of cyclopentane-containing GDGTs. The TEX₈₆ values ranged between 0.42-0.53 (Fig. 5a).

Depth profiles were obtained from POM taken in February/March 1992 and August/September 1992 at two Equatorial Pacific sampling sites at 8 sampling depths ranging from 10 to 842 m in the water column. In all instances GDGTs were more abundant below 100 m (Fig. 5b) The GDGT distribution was dominated by crenarchaeol and relatively high amounts of cyclopentane-containing GDGTs and the obtained TEX₈₆ values ranged between 0.63-0.85 (Fig. 5b).

The two depth profiles of the northeast Pacific setting were obtained from POM at 5 different depths ranging from 10 to 1500 m. The highest GDGT concentrations were again measured below 100 m (Fig. 5c). GDGT I and crenarchaeol were present in equal amounts and substantial amounts of cyclopentane-containing GDGTs were detected. The obtained TEX₈₆ values ranged between 0.47-0.59 (Fig. 5c).

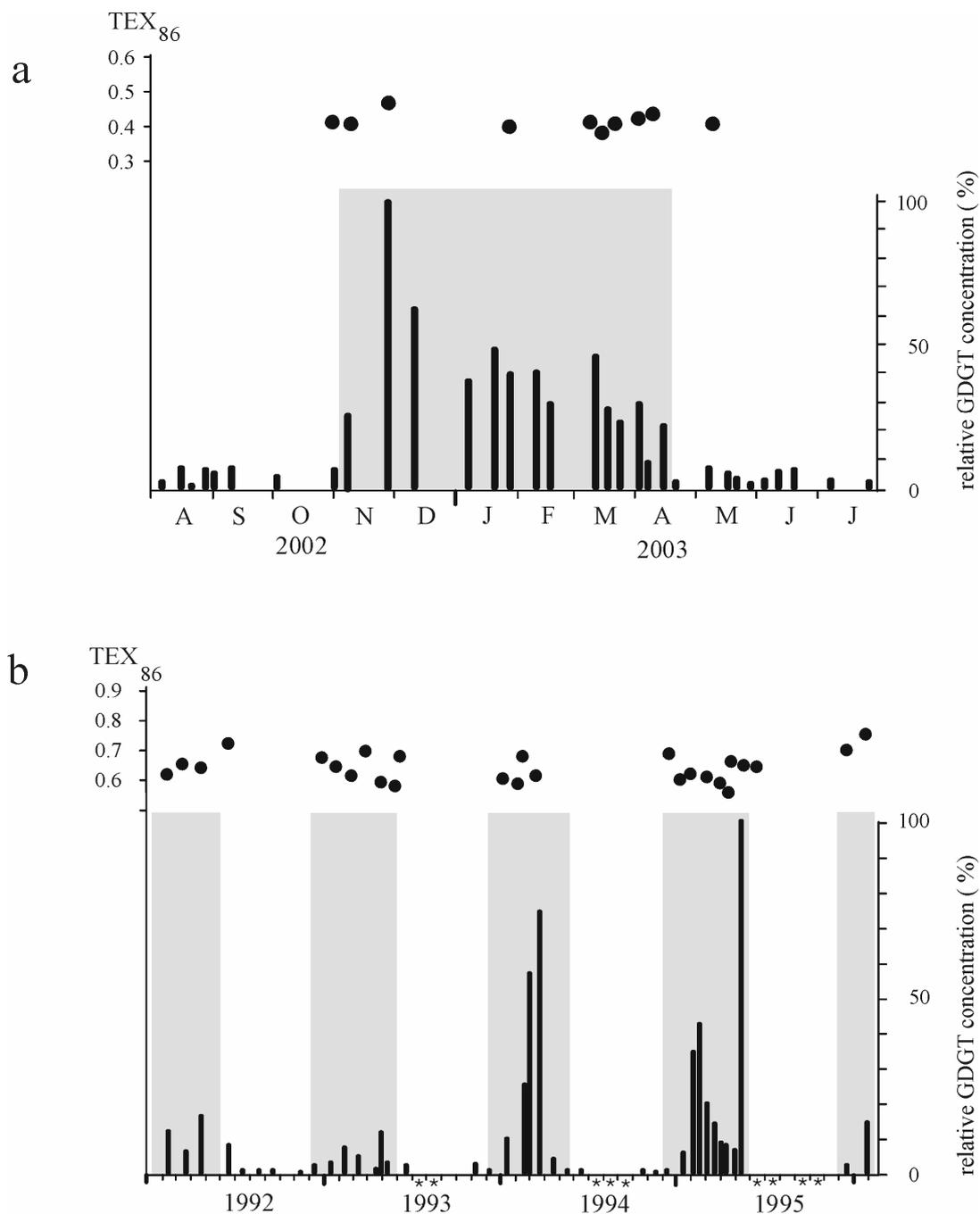


Figure 3. Relative GDGT concentrations and TEX_{86} values measured in POM of time series at two different settings. (a) Shallow coastal North Sea waters time series from August 2002 till July 2003 and (b) Bermuda Atlantic Time Series starting from winter 1991 till winter 1995. Grey shaded areas correspond to winter and spring seasons. Month marked with an asterisk indicate that water samples were analysed but GDGTs were not detected.

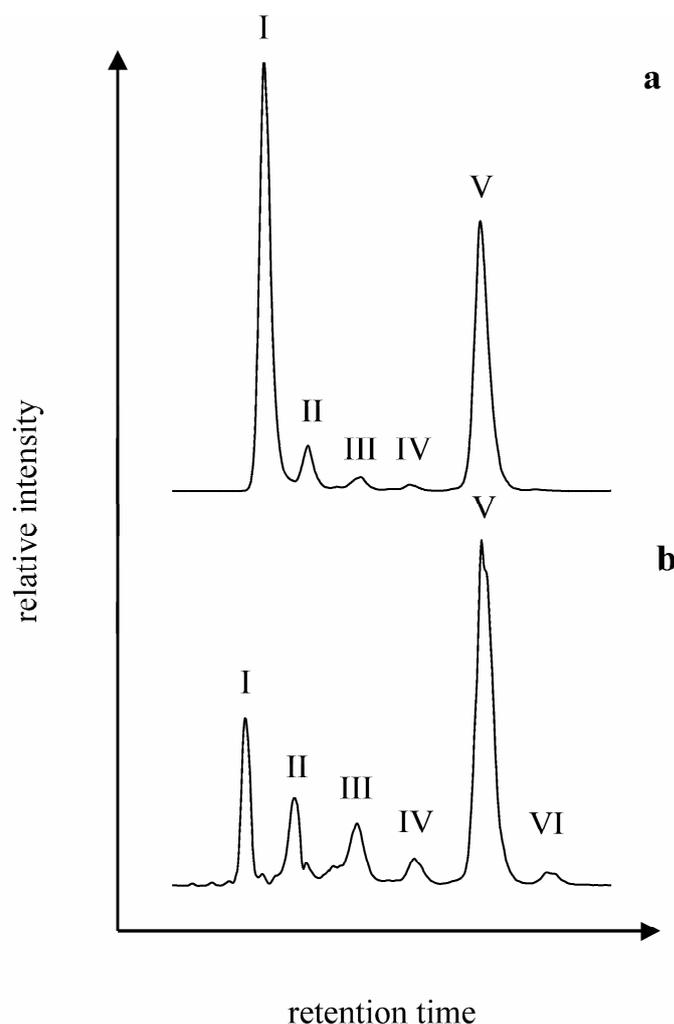


Figure 4. Partial HPLC-APCI/MS base peak chromatograms of POM derived from (a) shallow coastal North Sea waters and (b) Surface water sampled in the Bermuda Atlantic Time Series. Numbers indicate structures shown in Fig. 1.

6.4. Discussion

6.4.1 Seasonality of GDGT abundance

Our data show that there is a strong seasonal contrast in the abundance of GDGTs in surface waters at the BATS and the coastal North Sea sampling station (Fig. 3). GDGT concentrations peak during the spring and winter seasons, respectively. Marine Crenarchaeota are the dominant Archaea in coastal North Sea surface waters during winter (November-February) as revealed by 16S rDNA work [Wuchter et al., unpublished data]. In contrast, chlorophyll-*a* concentrations were high during late spring and early summer over the last 30 years in this area [Cadée and Hegeman, 2002, Colijn and Cadée, 2003]. This seasonal cycle

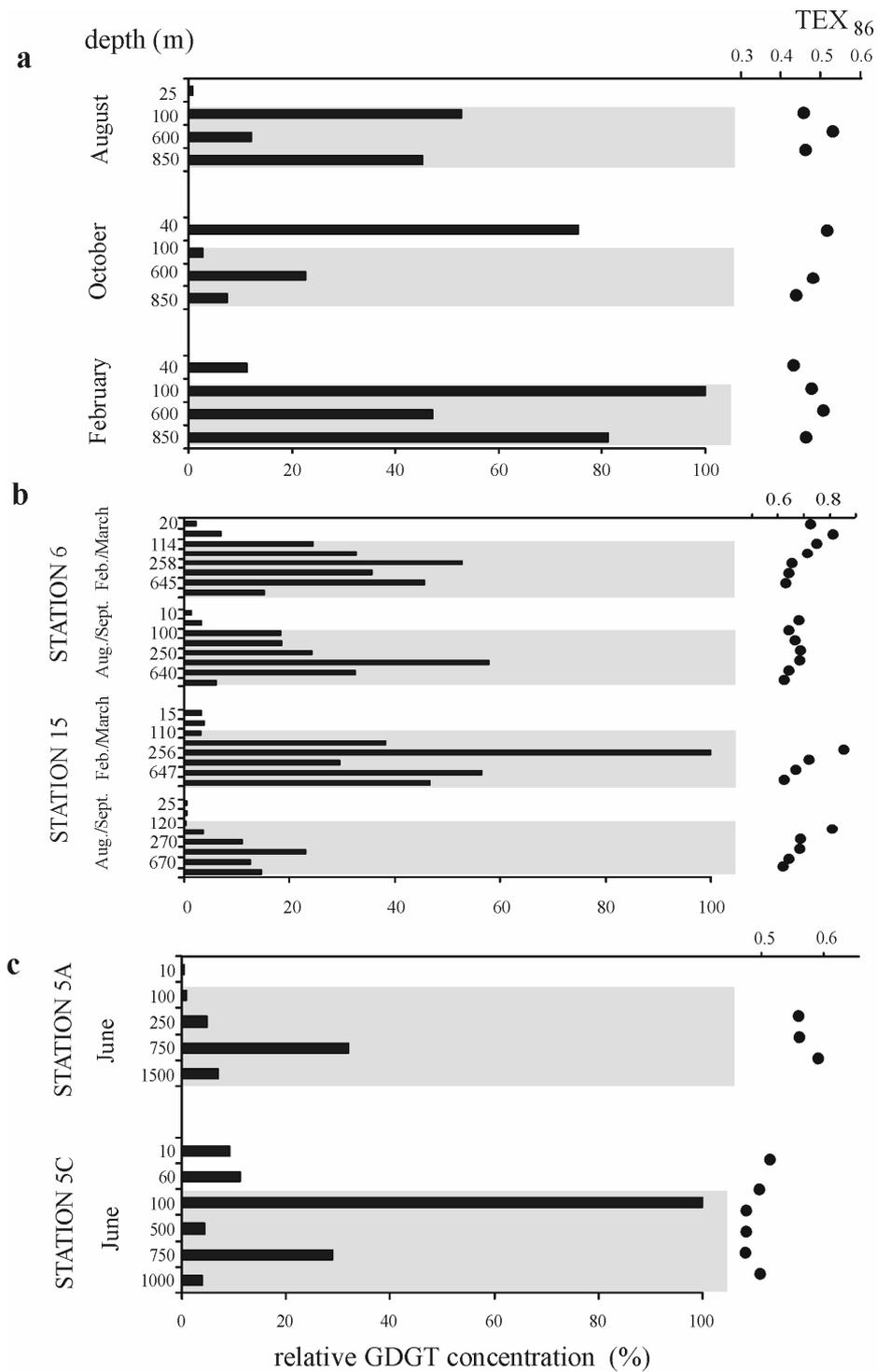


Figure 5. Relative GDGT concentrations (in %) and TEX_{86} values measured in POM of three depth profiles. (a) Santa Monica Basin; (b) Equatorial Pacific and (c) Northeastern Pacific (VERTEX 5). Grey shaded areas correspond to water depths below 100 m.

was also observed in 2002-2003. The GDGT and the chlorophyll-*a* concentration thus show a strong negative correlation during the annual cycle in coastal North Sea waters. This indicates that archaea are not abundant during periods of high primary production. This is consistent with previous 16S rDNA findings in the Antarctic Peninsula region and Santa Barbara Channel which showed that archaeal abundance in surface waters is negatively correlated with chlorophyll-*a* concentrations [Murray *et al.*, 1998 and 1999].

At the BATS site, however, a positive correlation between chlorophyll *a* and archaeal lipids in surface waters is observed. In this region the passage of cold fronts erodes the seasonal thermocline and forms subtropical water during the winter season at the BATS station [Steinberg *et al.*, 2001]. Convective mixing caused by the winds results in mixed layers at 150-300 m depth and associated nutrient enrichment of the surface layers [Steinberg *et al.*, 2001]. High chlorophyll-*a* concentrations in the late winter, early spring season in surface waters are associated with convective deep mixed water layers but are not sustained throughout the year [Steinberg *et al.*, 2001]. The nutrient enrichment in surface waters may also support growth of marine Crenarchaeota. Alternatively, the higher archaeal lipid abundance may be due to the water mixing when the GDGT signal originally derived from deeper waters is upwelled to the surface layer. Deeper waters generally contain higher concentrations of GDGTs (see discussion below).

6.4.2 Depth distribution of GDGTs

The GDGT depth distribution at the Equatorial Pacific, northeast Pacific and Santa Monica Basin sampling sites show a similar pattern (Fig.5). GDGT concentrations increase with depth and have maxima generally below 100 m. These findings are consistent with previous findings of GDGT depth distributions in the Arabian Sea [Sinninghe Damsté *et al.*, 2002a] where the authors reported higher GDGT concentrations below the photic zone and the Cariaco Basin [Wakeham *et al.*, 2004] with maximum GDGT concentrations at 250 m depth. However, there is a discrepancy between the lipid data and 16S rDNA studies. While fluorescence in situ hybridization (FISH) data show that the marine crenarchaeotal absolute abundance in the tropical Pacific Ocean is relatively invariant throughout the upper 250 m of the water column and decreases at lower depth [Karner *et al.*, 2001], our lipid data show maximum GDGT concentrations generally below 100 m at the sampling sites. The FISH

technique detects only living cells whereas our lipid analysis does not discriminate between living and dead crenarchaeotal cell material. Thus, a substantial percentage of the GDGTs encountered at greater depth may be derived from suspended or sinking dead cell debris. This is likely due to the generally more refractory nature of lipids compared to other cell material such as DNA. GDGTs are themselves not more refractory than other membrane lipids as studies have shown that they degrade, under oxic conditions, at similar rates as other phytoplanktonic lipids [Sinninghe Damsté *et al.*, 2002c, Schouten *et al.*, 2004].

6.4.3 TEX₈₆ and temperature

As GDGTs are found throughout the water column, it may be expected that the TEX₈₆ values would reflect a large range of temperatures from surface to deep waters. However, compared to the large range of in situ temperatures, the TEX₈₆ values showed only minor variation with depth (e.g., the Equatorial Pacific and Cariaco Basin sites, Fig. 6). Indeed, when TEX₈₆ values from all sampling locations are compared with in situ temperatures only a weak correlation is observed (Fig. 7a). The TEX₈₆ in surface sediment correlates best with annual mean SST [Schouten *et al.*, 2002], and this suggests that the TEX₈₆ in POM probably also reflects mainly temperatures of the photic zone. To investigate this hypothesis, we splitted the POM TEX₈₆ data into two sets, those derived from the upper 100 m of the water column and those from below 100 m. The correlation of TEX₈₆ for POM in the upper 100 m of the water column with in situ temperature was high, with an r^2 of 0.80 (Fig. 7b), and is nearly identical to the core top equation (Fig. 7f). In contrast, a weak correlation is found between TEX₈₆ values of POM from below 100 m depth with in situ temperature (Fig. 7c). Instead, TEX₈₆ values of POM below 100 m depth correlated well with surface temperatures at the time of sampling (Fig. 7d). When TEX₈₆ values of all POM samples are compared with actual surface temperature, a correlation is obtained (Fig. 7e) that is strikingly similar to the TEX₈₆ core top correlation (Fig. 7f). These findings indicate that the GDGT signal in POM at all depth is mainly reflecting the temperature of the upper 100 m of the water column. Growth of marine Crenarchaeota in deeper waters may influence the TEX₈₆ in POM to a minor degree as observed, for example, in the Equatorial Pacific (Fig. 6) where the TEX₈₆ values slightly decrease with depth. It is most likely that the TEX₈₆ values of deep water POM reflect a mixed GDGT signal from living but slowly growing crenarchaeotal cells, since

microorganisms living in the deep ocean have a slow metabolic rate [Tamburini *et al.*, 2003], and sinking, dead crenarchaeotal cell material in which GDGTs may become enriched through their refractory nature. This is consistent with our depth profile data where GDGTs are enhanced in abundance in deeper water layers and are probably derived for a large part of dead cell material.

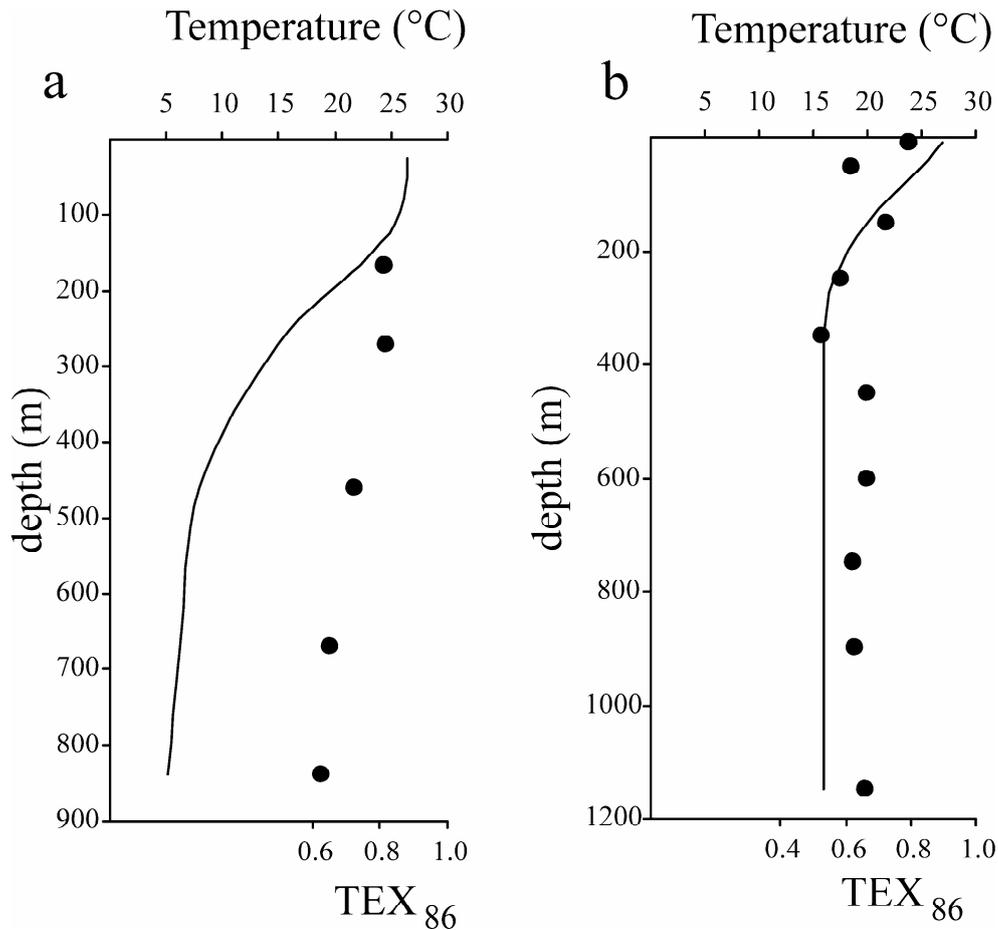


Figure 6. TEX₈₆ values and in situ temperature versus depth for (a) Equatorial Pacific and (b) Cariaco Basin.

6.4.4 Origin of sedimentary GDGT signal

The similarity of the TEX₈₆ POM and the TEX₈₆ core top equations (cf. Figs. 7e and 7f) suggests that the temperature signal that is found in the sediment must be mainly derived from the upper 100 m of the water column. The GDGTs that are found in sediments thus seems to be mainly derived from crenarchaeotal cell material derived from the photic zone and

transported with fast sinking aggregates that reaches the sea floor. These findings are supported by previous work done on the Black Sea [Wakeham *et al.*, 2003]. We analyzed POM, sediment traps and surface sediment samples to investigate the GDGT distribution and isotopical signature of the biphytane skeletons contained in these GDGTs. We found high amounts of ¹³C-depleted biphytanes in POM of the deep anoxic zone of the Black Sea (>1000 m) but could not find the corresponding ¹³C-depleted biphytanes in the sediment traps or the underlying sediments. This led us to suggest that due to the absence of grazing in the deep anoxic zone of the Black Sea, the GDGTs from deeper waters may lack transport mechanisms (e.g. by fecal pellets) to the sea floor and that, therefore, the dominant flux of GDGTs to the surface sediments was derived from the upper part of the water column where particle packaging through grazing can occur. A distinct compositional difference between suspended and sinking particles was also observed for other lipid classes in the Black Sea [Wakeham and Beier 1991] and in oceanic settings like the eastern tropical North Pacific Ocean [Wakeham and Canuel, 1988, Wakeham and Lee, 1993]. Sediments are mainly derived from fast-sinking large particles [McCave, 1984] which are produced by biologically-mediated aggregation (e.g. grazing), and laboratory and field observations showed that fecal pellets and marine snow may sink at rates of tens to hundreds of meters per day [e.g. Small *et al* 1979]. Thus, due to these mechanisms the sedimentary signal is primarily derived from the upper part of the water column where an active food web exists.

Marine crenarchaeota are generally abundant in the surface water during times when the majority of the phytoplankton is not blooming [Murray *et al.*, 1998 and 1999, this study]. Therefore, the GDGT signal which is biosynthesized in the upper 100 m of the water column probably reflects the temperatures at this time interval in the seasonal cycle. The TEX₈₆ temperature signal which is preserved in the sedimentary record may thus mainly reflect a seasonal signal, which may explain some of the scatter in the correlation of the TEX₈₆ with annual mean SST in core tops. Indeed, for surface sediments of the eastern Southern Atlantic Schouten *et al.* [2002] observed that the best correlation of TEX₈₆ is with austral winter SST.

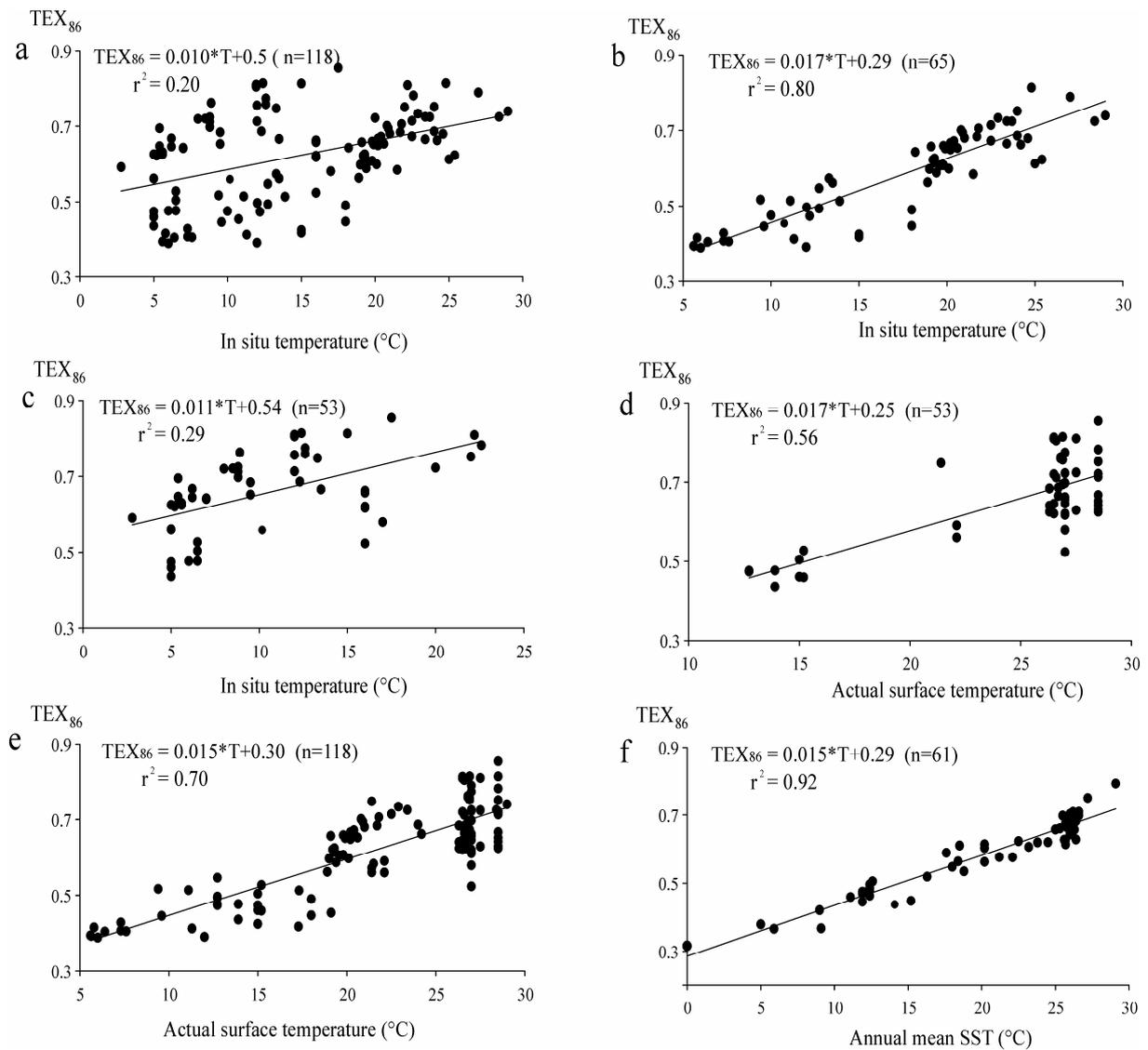


Figure 7. Cross plots of TEX_{86} and temperature for POM (a-e) and sediments (f). The best linear fit is shown. (a) TEX_{86} of POM from all depth versus the in situ temperature, (b) TEX_{86} of POM from the upper 100 m of the water column versus in situ temperature, (c) TEX_{86} of POM from below 100 m depth versus in situ temperature, (d) TEX_{86} of POM from below 100 m depth versus surface temperature, (e) TEX_{86} of POM from all depth versus surface temperature, and (f) Updated TEX_{86} correlation line from surface samples versus annual mean sea surface temperature [Wuchter *et al.*, 2004].

6.5. Conclusion

Our data show that the TEX₈₆ of POM from different oceanic regimes correlates well with temperature at depths shallower than 100 m. TEX₈₆ values of POM from deeper waters (>100 m) do not correlate with in situ temperature but with surface temperature. Thus, these findings suggest that the GDGT signal which reaches the sediment must be mainly biosynthesized in the upper 100 m of the water column. Packaging of small GDGT-containing crenarchaeal cells into fecal pellets and marine snow aggregates probably results in rapid transportation from the photic zone to the sediment. Living suspended deep sea Crenarchaeota do not substantially influence the sedimentary GDGT signal probably due to the lack of aggregation processes and transport mechanisms to the sea floor. Marine Crenarchaeota appear seasonally in surface waters and the GDGT signal accumulating in the underlying sediment may mostly reflect these periods of elevated GDGT biosynthesis. The data presented here, in combination with previous studies on core tops [Schouten *et al.*, 2002], diagenetic stability [Schouten *et al.*, 2004], and mesocosm experiments [Wuchter *et al.*, 2004], show that the TEX₈₆ may be used to reconstruct upper water column temperatures in ancient environments.

6.6. Acknowledgements

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6.7 Supplementary information

Table 1 TEX₈₆ values and corresponding temperature used for the validation of the temperature proxy TEX₈₆ in particulate organic matter. Grey shaded temperature values for some sampling locations are monthly mean temperatures obtained from the world ocean atlas (<http://www.nodc.noaa.gov/OC5/WOA01F/tsearch.html>). All other temperature data were measured at the time of sampling.

sampling location	sampling date	sampling depth (m)	in situ temp.(°C)	SST(°C)	TEX ₈₆
Bermuda Atlantic Time Series					
cruise no. 41	12.02.92	surface	19.3	19.3	0.63
cruise no. 42	10.03.92	surface	19.8	19.8	0.66
cruise no. 43	21.04.92	surface	19.9	19.9	0.65
cruise no. 45	17.06.92	surface	23.4	23.4	0.73
cruise no. 52	12.01.93	surface	21	21	0.68
cruise no. 53	11.02.93	surface	20.2	20.2	0.65
cruise no. 54	10.03.93	surface	19.3	19.3	0.62
cruise no. 55	16.04.93	surface	20.8	20.8	0.70
cruise no. 55a	27.04.93	surface	20.1	20.1	0.60
cruise no. 56	10.05.93	surface	21.5	21.5	0.58
cruise no. 57	19.06.93	surface	24	24	0.69
cruise no. 65	18.02.94	surface	20.4	20.4	0.67
cruise no. 65a	28.02.94	surface	19.6	19.6	0.61
cruise no. 66	21.03.94	surface	19.4	19.4	0.59
cruise no. 67	19.04.94	surface	21.7	21.7	0.68
cruise no. 73	19.10.94	surface	24.2	24.2	0.66
cruise no. 74	15.11.94	surface	22.9	22.9	0.73
cruise no. 75	09.12.94	surface	22.5	22.5	0.71
cruise no. 76	11.01.95	surface	20.9	20.9	0.69
cruise no. 76a	01.02.95	surface	19.8	19.8	0.61
cruise no. 77	14.02.95	surface	19.2	19.2	0.62
cruise no. 77a	01.03.95	surface	19.3	19.3	0.61
cruise no. 78	16.03.95	surface	19	19	0.60
cruise no. 78a	29.03.95	surface	18.9	18.9	0.56
cruise no. 79	10.04.95	surface	20.2	20.2	0.67
cruise no. 79a	27.04.95	surface	20.6	20.6	0.65
cruise no. 80	10.05.95	surface	19.1	19.1	0.66
cruise no. 88	30.01.96	surface	21.8	21.8	0.71

North Sea Time Series					
	04.11.02	surface	11.1	11.1	0.51
	07.11.02	surface	11.3	11.3	0.41
	28.11.02	surface	7.6	7.6	0.41
	28.01.03	surface	5.6	5.6	0.39
	12.03.03	surface	5.8	5.8	0.42
	18.03.03	surface	6.0	6.0	0.39
	24.03.03	surface	6.4	6.4	0.40
	03.04.03	surface	7.3	7.3	0.41
	07.04.03	surface	7.3	7.3	0.43
	07.05.03	surface	12	12.0	0.39
MedFlux (DYFAMED)					
	Sep-02	50	13.5	21.4	0.56
	Sep-02	100	13.3	21.4	0.57
	Sep-02	150	13.3	21.4	0.75
Peru upwelling region					
12S, #109	Oct-92	surface	18	18	0.45
13.5S #014	Oct-92	surface	18	18	0.49
Southern Ocean					
NBP 98-02 #35	29.03.98	surface	9.6	9.6	0.45
NBP 98-02 #37	30.03.98	surface	9.4	9.4	0.52
Seychellen					
	13.11.03	surface	29	29	0.74
Cariaco basin					
	Mar-86	10	27	27	0.79
	Mar-86	50	25	27	0.61
	Mar-86	150	20	27	0.72
	Mar-86	250	17	27	0.58
	Mar-86	350	16	27	0.52
	Mar-86	450	16	27	0.66
	Mar-86	600	16	27	0.66
	Mar-86	750	16	27	0.62
	Mar-86	900	16	27	0.62
	Mar-86	1150	16	27	0.66
Equatorial Pacific					
station 6 survey 1	10.03.92	44	28.4	28.4	0.72
	10.03.92	114	24.8	28.5	0.81
	10.03.92	161	22	28.5	0.75
	10.03.92	258	12	28.5	0.71
	10.03.92	456	9.5	28.5	0.65
	10.03.92	645	7	28.5	0.64

station 6 survey 2	10.03.92	838	5.6	28.5	0.63
	26.08.92	35	24.6	26.7	0.68
	26.08.92	100	18.2	26.7	0.64
	26.08.92	150	13.5	26.7	0.67
	26.08.92	250	12.3	26.7	0.69
	26.08.92	450	9.5	26.3	0.68
	26.08.92	640	7	26.3	0.64
	26.08.92	840	5.6	26.3	0.63
station 15 survey 1	07.03.92	158	22.6	28.5	0.78
	07.03.92	256	17.5	28.5	0.85
	07.03.92	452	8.5	28.5	0.72
	07.03.92	647	6.2	28.5	0.67
	07.03.92	842	5	28.5	0.63
station 15 survey 2	14.09.92	168	22.2	26.5	0.81
	14.09.92	270	15	26.5	0.81
	14.09.92	460	8.0	26.5	0.72
	14.09.92	670	6.2	26.5	0.65
	14.09.92	840	5	26.5	0.62
Northeastern Pacific					
VERTEX 5A	Jun-84	250	10.2	22.1	0.56
	Jun-84	750	5	22.1	0.56
	Jun-84	1500	2.8	22.1	0.59
VERTEX 5C	Jun-84	10	12.7	12.7	0.55
	Jun-84	10	12.7	12.7	0.49
	Jun-84	60	12	12.7	0.50
	Jun-84	100	10	12.73	0.48
	Jun-84	500	6	12.7	0.48
	Jun-84	750	5	12.7	0.47
Santa Monica Basin					
cruise no 3	07.08.91	100	10.8	19.1	0.45
cruise no 3	07.08.91	600	6.5	15.2	0.53
cruise no 3	07.08.91	850	5	15.2	0.46
cruise no 4	31.10.91	40	13.9	17.3	0.51
cruise no 4	31.10.91	600	6.5	13.9	0.48
cruise no 4	31.10.91	850	5	13.9	0.44
cruise no 5	06.02.92	40	15	15	0.42
cruise no 5	06.02.92	100	12.2	15	0.47
cruise no 5	06.02.92	600	6.5	15	0.50
cruise no 5	06.02.92	850	5	15	0.46
cruise no 6	15.04.92	40	15	17.3	0.42
Arabian Sea Process Study					
station 2	May-95	500	12	27	0.81
	May-95	1000	8.8	27	0.72
	May-95	1500	5.4	27	0.63

station 4	May-95	70	23.7	27.5	0.72
	May-95	500	12.6	27.5	0.77
	May-95	1000	8.8	27.5	0.70
	May-95	1500	5.4	27.5	0.65
station 5	May-95	90	22.5	26.9	0.67
	May-95	500	12.4	26.9	0.81
	May-95	1500	5.4	26.9	0.69
station 6	May-95	500	12	26.6	0.80
	May-95	1000	8.8	26.6	0.71
station 7	May-95	85	23.4	26.6	0.67
station 10	May-95	80	24	26.9	0.75
	May-95	450	12	26.9	0.76
station 13	May-95	35	25.4	26.8	0.62
	May-95	500	12.6	26.8	0.76
	May-95	1000	8.9	26.8	0.76

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