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Application of the TEX_{86} temperature proxy to the southern North Sea

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Abstract

A novel temperature proxy, the tetraether index of lipids with 86 carbon atoms (TEX_{86}), was applied to the suspended particulate organic matter (POM) and sediment core tops from eight sites in the southern North Sea in different seasons. The TEX_{86}-derived temperatures in many samples did not correlate with mean annual sea surface temperature (SST), but were shifted toward winter SST, apparently because Crenarchaeota are more abundant and metabolically active during periods of low primary production. This indicates that TEX_{86}-derived SST estimates do not necessarily reflect annual mean SST and may provide essential information about seasonal SST palaeoreconstruction. High TEX_{86}-derived SSTs were measured in the water of the river Rhine and in the sediment core tops and seawater from several stations in the southern North Sea. These sites were all characterised by important input of organic matter from soil and peat, as revealed by the relatively high values obtained with the new terrestrial proxy, the branched and isoprenoid tetraether (BIT) index. These data demonstrate that to reconstruct palaeotemperatures it is essential to estimate both TEX_{86} and BIT indices to check that TEX_{86} temperatures are not biased as a result of large terrestrial input. Important seasonal variations in TEX_{86}-derived SST were also evident for the surface sediments of several stations characterised by extremely low sedimentation rates, indicating temporary settlement of laterally transported organic matter with a warmer temperature signal. This implies that sediment core top correlations between TEX_{86} and mean annual SST should not be carried out in areas characterised by transient sediment deposition.

1. Introduction

The rise in atmospheric CO_2 levels since pre-industrial times makes accurate prediction of future climate change an absolute necessity. To do so, a proper understanding of past climate is required and reconstruction of past sea surface temperatures (SSTs) using geochemical proxies is an essential component of this. The most commonly used temperature proxies are the $\delta^{18}O$ and Mg/Ca ratios of planktonic foraminifera (Chave, 1954; Nurnberg et al., 1996) and the $U_{37}^{K'}$ index derived from the alkenones synthesised by haptophyte algae (Brassell et al., 1986). In contrast to the others, the $U_{37}^{K'}$ index is not directly influenced by seawater chemistry and is thus often considered as the most robust proxy for SST reconstruction (Herbert, 2003). Several problems are, however, inherent in this approach:

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why the degree of saturation of these storage lipids is adjusted according to growth temperature is unknown (Eltgroth et al., 2005); the effects of oxic degradation and shifts in species distribution through time are still undetermined; alkenone-producing organisms are not evenly distributed throughout the surface of the oceans (Herbert, 2003).

Recently, Schouten et al. (2002) introduced a novel SST proxy, the tetraether index of lipids with 86 carbon atoms (TEX_{86}). This is based on the temperature adaptation ability of the membrane lipids of non-thermophilic Crenarchaeota that are made up of isoprenoid glycerol dialkyl glycerol tetraethers (GDGTs; Fig. 1). Schouten et al. (2002) analysed these GDGTs in sediment core tops sampled from different geographical regions and observed that their relative distribution, expressed as the TEX_{86}, correlated best with mean annual SST. Wuchter et al. (2004) have experimentally demonstrated that marine Crenarchaeota synthesize isoprenoid GDGTs with varying numbers of cyclopentane rings according to the ambient seawater temperature. Analysis of suspended particulate organic matter (POM) from several locations distributed worldwide showed that the TEX_{86} signals obtained below and above 100 m depth correlated best with mean annual SST (Wuchter et al., 2005). These

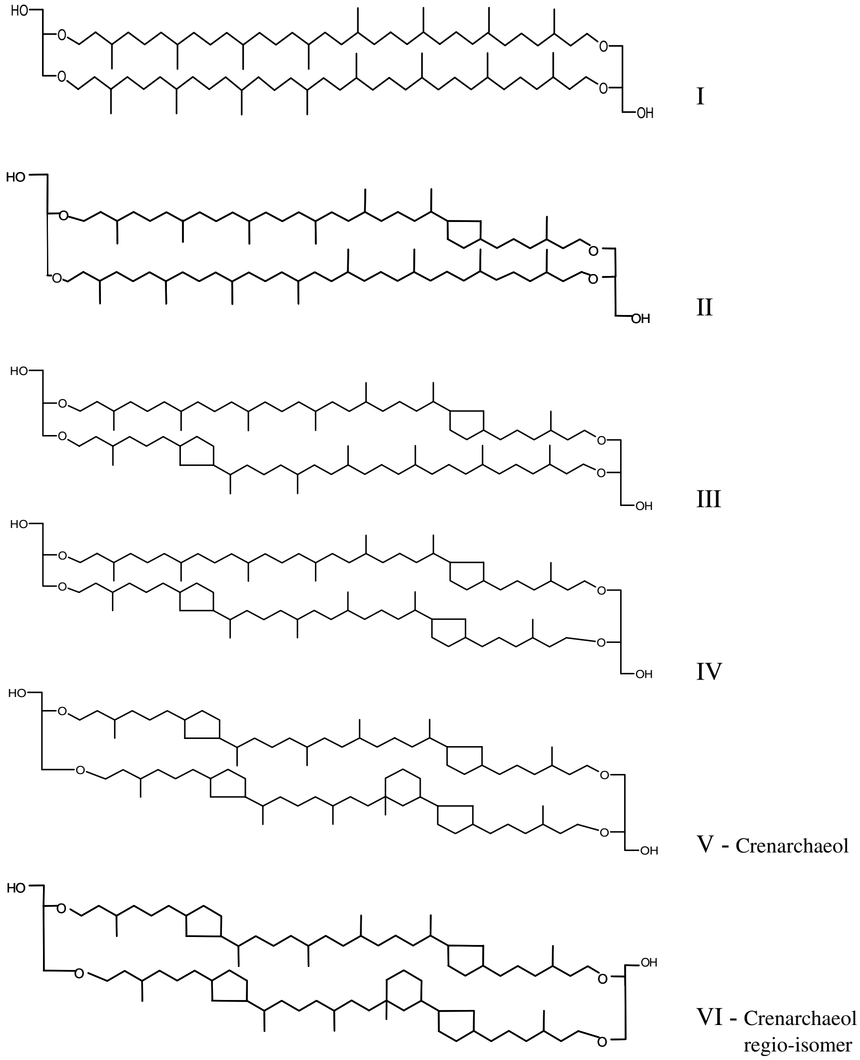

Fig. 1. Structures of GDGTs synthesized by marine Crenarchaeota. GDGT-0 (I) and crenarchaeol (V) are the most abundant membrane lipids and are accompanied by smaller amounts of other isoprenoidal GDGTs (II–IV, VI), used to determine TEX_{86} values.

correlations were in good agreement with those of the original sediment core top calibration computed by Schouten et al. (2002), indicating that, in these settings the sedimentary TEX_{86} signal primarily predicts the temperature of the upper 100 m (Wuchter et al., 2005).

Until recently it was unclear how the temperature signal, originating from the surface, reaches the deeper water layers and eventually arrives unchanged in the sediments, yet bypasses the degradation processes in the water column. This was especially puzzling considering that in the open ocean organisms producing these components are also abundant below the photic zone (Karner et al., 2001; Sinninghe Damsté et al., 2002). Recently, however, Wuchter et al. (2006b) analysed the TEX_{86} signal of POM in sediment traps deployed at different depths in the Pacific Ocean and the Arabian Sea and showed that at all sites and depths TEX_{86}-derived temperatures reflected the SST. In the Arabian Sea, the shallow traps at 500 m gave in situ SST with a 3 weeks offset owing to the sinking speed of particles, while deeper traps provided mean annual SST due to lateral transport of particles that created an integrated signal for the whole area. This supports the idea proposed by Wakeham et al. (2003) of a tight coupling between active food web (and thus particles and faecal pellet sinking) and GDGT transport. So, all sediment core top and POM data gathered thus far have indicated that the TEX_{86} is a good proxy for mean annual SST. This was further supported by recent data obtained by Schouten et al. (2004), which demonstrated that the TEX_{86} signal is not affected by water redox conditions.

Two recent palaeoceanographic studies conducted in widely different locations have suggested, however, a seasonal bias in the TEX_{86} signal. During the recent Arctic Coring Expedition, sediments from the Palaeocene-Eocene thermal maximum interval were retrieved and gave high TEX_{86} values corresponding to temperatures ranging from 15 to 22 °C, thus indicating a potential summer bias in TEX_{86} (Sluijs et al., 2006). Similarly, reconstruction of palaeotemperature using TEX_{86} in the western Arabian Sea clearly identified the Antarctic cold reversal (Huguet et al., 2006). Since the South Pole climatic influence in this region is related to the South West Monsoon that occurs from June to September, this again suggests a seasonal bias in TEX_{86}. In addition, a sediment core top study carried out in the Angola Basin (Eastern South Atlantic) pointed towards a seasonal temperature signal, as TEX_{86} values correlated best with austral winter SST (Schouten et al., 2002).

In the present study, we have applied the TEX_{86} to the seawater and sediment core tops of eight sites in the southern North Sea at different seasons to determine if, in an environment characterized by strong seasonal contrasts and low sedimentation rates, this new proxy gives an annual or seasonal temperature signal. As the Rhine/Meuse is the most important river system flowing into the area (de Kok, 1996), TEX_{86} was also applied to suspended POM collected from the Rhine.

2. Materials and methods

2.1. Study area

The southern North Sea is a shallow shelf sea (max. depth 50 m, except for a few deeper parts) bordered in the east and south by the European continent and in the west by the British Isles. To the South, it is connected to the North East Atlantic Ocean through the Dover Strait, while the Dogger Bank forms the northern boundary (Fig. 2). Since the southern North Sea is located in a temperate region, strong seasonal contrasts prevail, with SSTs ranging from 6.5 °C in winter to 15 °C in summer (World Ocean Atlas, 1998). It is also a highly dynamic area where several water masses converge (Lee, 1980) creating, as a result of geomorphology, tidal motion and predominant westerly winds and an overall anticlockwise current. The interaction between hydrography and topography leads to a lack of net sedimentation and associated burial in the area (Eisma, 1981; de Haas et al., 1997). In addition, the southern North Sea is strongly influenced by coastal run off, with high freshwater inputs supplied by the main West European (essentially Rhine, Meuse and Scheldt) and British (Thames, Humber, Tees and Tyne) rivers. The Rhine, together with the Meuse in a mixed estuary, enters the southern North Sea through the Rotterdam Waterway (Nieuwe Waterweg) and the Haringvliet. With an average annual discharge of 2300 $m^3 s^{-1}$ (de Kok, 1996), it is the most important river flowing into the southern North Sea.

2.2. Sampling

Sampling in the southern North Sea was conducted at eight stations (Fig. 2) during three cruises, with the R.V. *Pelagia* in February 2003 and April

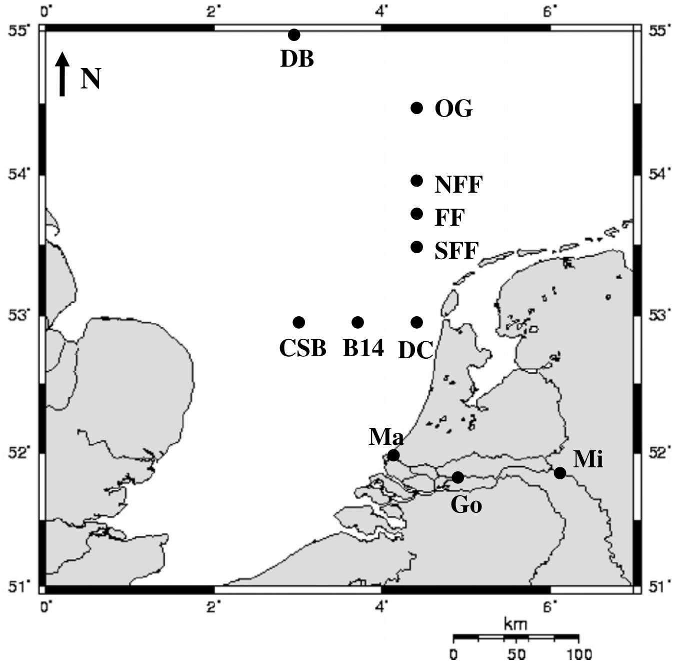

Fig. 2. Map showing location of sites in southern North Sea and river Rhine. Abbreviations: DC, Dutch coast; CSB, Central southern bight; B14, Breeveertien; SFF, South Frisian front; FF, Frisian front; NFF, North Frisian front; OG, Oyster grounds; DB, Dogger bank; Ma, Maassluis; Go, Gorinchem; Mi, Millingen. The geographical position of Breeveertien was slightly modified to 52°:48′N and 3°:33′E during the spring and summer cruises to ensure sampling in the correct water mass.

2004, and with the R.V. *Alkor* in August 2004. During the first cruise, seawater was sequentially filtered on to a 0.7 μm glass fibre filter and a 0.2 μm cellulose acetate filter. This showed that < 5% of the total amount of lipids was recovered with the 0.2 μm filter. Hence, given that cellulose acetate filters tend to cause problems with analysis using high pressure liquid chromatography/mass spectrometry (HPLC/MS) analysis, the 0.2 μm filtration stage was subsequently omitted. Seawater was sampled at 2 or 5 m below surface waters and suspended POM was collected by filtering 40 l of seawater on to pre-ashed 0.7 μm glass fibre filters. These were kept frozen at −20 °C until analysis. In situ temperatures were measured using a conductivity temperature depth sensor. Depth profiles were always analysed before sampling to ensure that in situ temperatures of sampled seawater were similar to surface temperatures. Surface sediments (top 1 cm) were obtained using a cylindrical box corer (max. length: 55 cm, diameter: 50 cm) equipped with a closing lid. Overlaying bottom water was removed by siphoning and sub-samples were taken by inserting three plastic liners (diameter 7 cm). These were stored upright at −20 °C pending analysis.

Sampling from the river Rhine was carried out in February 2005, midway between each bank, at three locations in The Netherlands: Maassluis (Nieuwe Waterweg, estuary of the Meuse/Rhine), Gorinchem (Boven-Merwede) and Millingen (Rhine, at the Dutch-German border; Fig. 2). Suspended POM was collected by filtering 5 l of river water on to pre-ashed 3 and 0.7 μm glass fibre filters. These were kept frozen at −20 °C until analysis.

2.3. GDGT analysis

Freeze-dried filters were ultrasonically extracted three times with MeOH, three times with dichloromethane (DCM)/MeOH (1:1, v/v) and three times with DCM. The extracts were combined and water-soluble material removed by shaking against water. Finely powdered and freeze-dried surface sediment (top 1 cm) was extracted three times with an accelerated solvent extractor (ASE 200, DIONEX) using a mixture of DCM/methanol (9:1, v/v) at high temperature (100 °C) and pressure (7.6×10^6 Pa). The extracts were combined to form the total extract. All samples (seawater and sediments) subsequently underwent similar treatment.

Following a drying procedure over a Na_2SO_4 column using DCM, total extracts were divided into apolar and polar fractions over an Al_2O_3 column using a mixture of hexane/DCM (9:1, v/v) and MeOH/DCM (1:1, v/v), respectively, as eluent. Polar fractions were dried under N_2 flow and re-dissolved by sonication in hexane/propanol (99:1, v/v). The solution was filtered through an Alltech 0.45 μm PTFE filter (diameter 4 mm). GDGTs were measured using HPLC/atmospheric pressure positive ion chemical ionization (APCI)/MS according to Hopmans et al. (2004) except for a modification in the scanning procedure, as the single ion monitoring (SIM) mode was used to increase sensitivity and reproducibility (*m*/*z* 1302.3, 1300.3, 1298.3, 1296.3, 1292.3, 1050.0, 1036.0 and 1022.0 for the different GDGT isomers). A large number of measurements carried out in our laboratory have shown that the analytical error has been considerably improved from 2 °C with the full scan mode used by Schouten et al. (2002) to 1 °C or less using the new SIM method.

2.4. Calculation of TEX_{86} and temperature

TEX_{86} quantifies the relative distribution of GDGTs and is described by Eq. (1):

$$TEX_{86} = (III + IV + VI)/(II + III + IV + VI) \quad (1)$$

where II–VI refer to the GDGT structures in Fig. 1. Peak areas that were at least one order of magnitude greater than the background noise were integrated and used directly to determine TEX_{86}. The annual mean SST (T in °C) was calculated according to Eq. (2) (Schouten et al., 2002):

$$T = (TEX_{86} - 0.28)/0.015 \quad (2)$$

3. Results

3.1. TEX_{86} in seawater

The GDGTs used for calculating TEX_{86} were detected in suspended POM at most stations and seasons (Table 1). In February, GDGTs were found at all stations. The resulting TEX_{86} ranged from 0.32 to 0.47 and gave low SSTs, with values from 2.5 °C to 12.6 °C. In contrast, in April and even more so in August, GDGT concentrations were much lower and, in some instances, below detection limit. TEX_{86} values and the associated temperatures were only computed when all GDGT isomers could

Table 1
Concentrations of GDGTs used for calculating TEX_{86}, TEX_{86}-derived SSTs, in situ temperatures and BIT indices of suspended POM collected at different sites and seasons in southern North Sea (station abbreviations in caption of Fig. 2)

	GDGT II (pg l^{-1})			GDGT III (pg l^{-1})			GDGT IV (pg l^{-1})			GDGT VI (pg l^{-1})			TEX_{86}			Calculated SST (°C)			In situ SST (°C)			BIT index[a]		
	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.
Stations																								
DC	439	31	56	159	16	26	73	7	7	25	6	5	0.37	0.49	0.40	5.9	13.8	8.3	3.9	8.9	18.8	0.25	n.d.	0.17
B14	n.a.	63	27	n.a.	22	10	n.a.	8	3	n.a.	6	n.d.	n.a.	0.36	n.d.	n.a.	5.6	n.d.	5.0	8.5	18.6	n.a.	n.d.	n.d.
CSB	463	302	96	137	107	35	61	41	13	35	22	10	0.33	0.36	0.38	3.6	5.3	6.5	5.0	7.7	17.6	0.04	0.02	0.06
SFF	69	99	53	23	38	18	11	11	5	3	n.d.	n.d.	0.35	n.d.	n.d.	4.7	n.d.	n.d.	3.2	8.1	17.2	0.18	0.03	0.13
FF	196	264	128	67	81	42	30	31	18	13	13	n.d.	0.36	0.32	n.d.	5.2	2.7	n.d.	3.4	7.8	17.6	0.16	0.03	0.10
NFF	45	34	37	16	21	12	5	5	5	3	6	3	0.35	0.48	0.35	4.9	13.5	5.0	4.8	9.5	17.5	n.d.	n.d.	n.d.
OG	161	11	5	48	3	4	16	n.d.	n.d.	11	n.d.	n.d.	0.32	n.d.	n.d.	2.5	n.d.	n.d.	5.7	7.7	16.9	0.07	n.d.	n.d.
DB	41	14	26	28	n.d.	27	5	2	3	3	n.d.	n.d.	0.47	n.d.	n.d.	12.6	n.d.	n.d.	5.3	7.8	16.3	0.08	n.d.	n.d.

n.a., sample not available.
n.d., GDGT concentration below detection limit, so no TEX_{86} and associated temperature.
[a] Data from Herfort et al. (2006).

be accurately quantified. TEX_{86} and TEX_{86}-derived SSTs obtained in April were within similar ranges to those measured in February, with respective values spanning from 0.32 to 0.48 and 2.7 °C to 13.8 °C. In August, TEX_{86} and TEX_{86}-derived SSTs were less scattered, with respective values ranging from 0.35 to 0.40 and 5.0 °C to 8.3 °C.

Fig. 3 presents a plot of the in situ and TEX_{86}-derived SSTs obtained for surface seawater at each site and season. In February, in situ and TEX_{86}-derived SSTs were rather similar, with respective means of 4.5 °C and 5.7 °C, corresponding to an average difference of 1.1 °C, which is near the analytical reproducibility of 1 °C. In April, the average in situ and TEX_{86}-derived SSTs were the same (8.2 °C) with a non-significant difference of 0.1 °C, but as stated above not all TEX_{86}-derived SSTs could be estimated because of the low GDGT concentrations. The discrepancy between in situ and TEX_{86}-derived SSTs was far more pronounced in August, with an average difference of 11 °C. The TEX_{86}-derived SSTs were still low, with an average of 6.6 °C, while the in situ values averaged 17.6 °C. It is also important to note the large decrease in GDGT concentration; TEX_{86} could consequently only be computed for 3 out of 8 stations.

3.2. TEX_{86} in sediments

The GDGTs used for calculating the TEX_{86} were detected in surface sediments (top 1 cm) in the southern North Sea at all stations and seasons

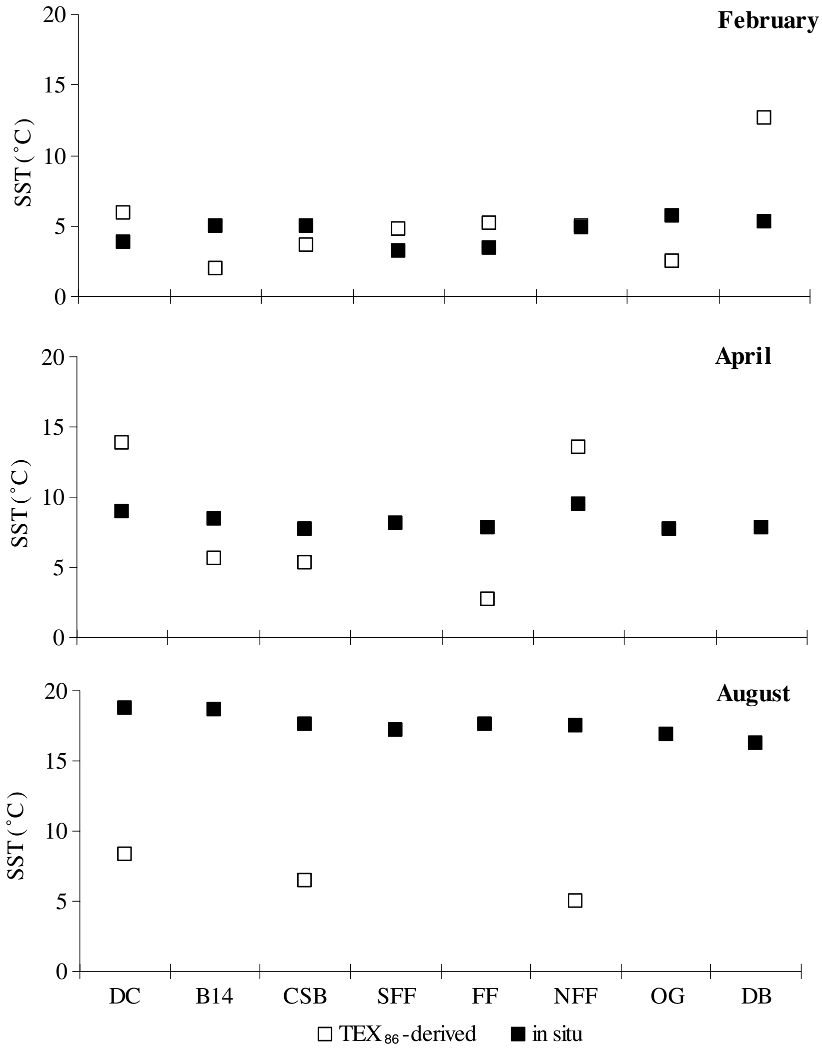

Fig. 3. In situ and TEX_{86}-derived SSTs for surface seawater at different sites and seasons in southern North Sea. Station abbreviations given in caption of Fig. 2.

Table 2
Concentrations of GDGTs used for calculating TEX_{86}, TEX_{86}-derived SSTs and BIT indices of sediment core tops collected at different sites and seasons in southern North Sea (station abbreviations in caption of Fig. 2)

	GDGT II ($pg\ g^{-1}$ dw)			GDGT III ($pg\ g^{-1}$ dw)			GDGT IV ($pg\ g^{-1}$ dw)			GDGT VI ($pg\ g^{-1}$ dw)			TEX_{86}			SST (°C)			BIT index[a]		
	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.	Feb.	Apr.	Aug.
Stations																					
DC	114.2	19.1	57.6	38.6	6.7	27.8	14.8	2.3	10.2	8.4	1.2	8.3	0.35	0.35	0.45	4.8	4.4	11.0	0.10	0.11	0.14
B14	95.5	73.2	139.5	33.4	26.5	56.3	12.4	9.4	19.2	6.0	4.4	10.0	0.35	0.35	0.38	4.7	5.0	6.6	0.07	0.08	0.09
CSB	3.2	2.7	3.3	1.4	1.3	1.4	0.5	0.5	0.5	0.2	0.2	0.2	0.39	0.42	0.40	7.6	9.5	7.7	0.26	0.29	0.25
SFF	80.6	61.3	91.5	30.2	21.8	46.8	11.1	7.9	14.0	6.6	3.7	10.7	0.37	0.35	0.44	6.1	4.8	10.6	0.08	0.09	0.11
FF	4.1	4.2	5.0	1.7	1.7	2.2	0.6	0.6	0.7	0.3	0.4	0.4	0.38	0.39	0.40	6.6	7.5	7.9	0.08	0.07	0.11
NFF	1.8	2.4	1.9	0.7	0.9	0.8	0.3	0.3	0.3	0.2	0.2	0.2	0.37	0.38	0.40	6.2	6.5	7.8	0.11	0.10	0.12
OG	1.8	1.9	1.5	0.6	0.7	0.5	0.2	0.3	0.2	0.1	0.1	0.1	0.35	0.36	0.37	4.5	5.4	6.2	0.10	0.11	0.13
DB	92.3	3.9	2.8	37.6	1.7	1.6	14.5	0.6	0.5	7.4	0.5	0.4	0.39	0.43	0.47	7.5	9.8	12.6	0.19	0.13	0.19

[a] Data from Herfort et al. (2006).

(Table 2) and gave TEX_{86}-derived SSTs ranging from 4.4 to 12.6 °C, with an average of 7.1 °C (Table 2 and Fig. 4). Each TEX_{86}-derived SST represents an average of duplicate measurements of the same sample. Important seasonal variations were measured, with higher values almost always detected in August. This was particularly pronounced for the stations Dutch Coast, South Frisian Front and the Dogger Bank with, for instance, up to 6.2 °C difference between February and August at the Dutch Coast. In addition, at two stations, Central Southern Bight and Dogger Bank, the TEX_{86}-derived SSTs obtained for the different seasons ranged from 7.5 to 12.6 °C with, when considering the analytical error of 1 °C, some values above the overall average TEX_{86}-derived SST value of 7.1 °C.

3.3. TEX_{86} in river water

The GDGTs used for calculating TEX_{86} were detected in suspended POM at all three locations in the river Rhine (Table 3), with concentrations ranging from 0.2 to 2.8 $ng\ l^{-1}$. The resulting TEX_{86} and TEX_{86}-derived temperatures averaged 0.50 and 14.4 °C, respectively.

4. Discussion

4.1. Seasonality in crenarchaeotal abundance and TEX_{86} values

In February, the TEX_{86}-derived SSTs of suspended POM were in good agreement, while in August they underestimated the in situ SST by 11 °C (Fig. 3). This discrepancy may be explained by the strong seasonality in the occurrence of marine Crenarchaeota. Fingerprinting analysis of archaeal 16S rDNA and quantification of crenarchaeotal cells by catalyzed reported deposition fluorescence, in situ hybridization have revealed that Crenarchaeota are abundant in the coastal southern North Sea during winter, but are essentially not detectable during spring and summer (Wuchter et al., 2006a). This is consistent with our data, since higher concentrations of the GDGTs used for calculating the TEX_{86} were found in February (Table 1). This seasonal occurrence of Crenarchaeota may be related to the strong negative correlation between crenarchaeotal abundance and chlorophyll *a* reported for surface seawater in other areas (Murray et al., 1998, 1999). Indeed, the southern North

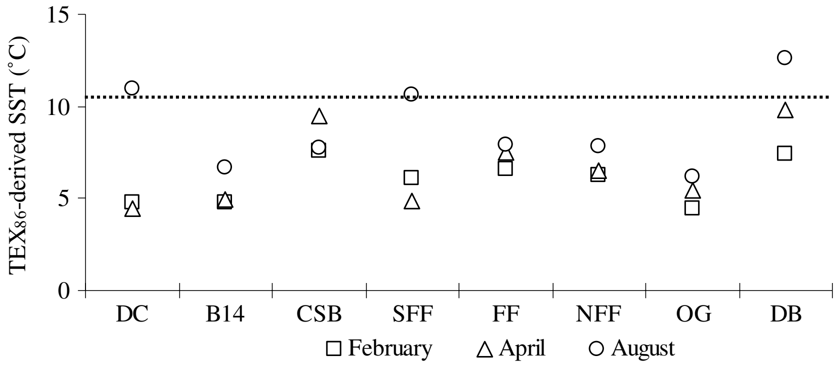

Fig. 4. TEX_{86}-derived SSTs for sediment core tops at different sites and seasons in southern North Sea. Dotted line represents mean annual SST of region (10.5 °C) reported in World Ocean Atlas (1998). Station abbreviations given in caption of Fig. 2.

Table 3
Concentrations of GDGTs used for calculating TEX_{86}, TEX_{86}-derived temperatures, in situ temperatures (T) and BIT indices of suspended POM collected at three different sites in river Rhine and estuary (station abbreviations in caption of Fig. 2)

	GDGT II (ng l^{-1})	GDGT III (ng l^{-1})	GDGT IV (ng l^{-1})	GDGT VI (ng l^{-1})	TEX_{86}	TEX_{86}-derived T (°C)	In situ T (°C)	BIT index[a]
Stations								
Maassluis	1.8	1.0	0.4	0.2	0.46	12.2	5.0	0.71
Gorinchem	2.8	1.9	0.7	0.4	0.52	16.0	4.9	0.88
Millingen	2.8	1.7	0.6	0.5	0.50	14.9	4.9	0.79

[a] Data from Herfort et al. (2006).

Sea is a highly eutrophic environment characterised by the presence of large phytoplankton blooms in spring and summer that may outcompete the marine Crenarchaeota, especially as nitrification has recently been identified among members of this group, at least some of which oxidize ammonia to nitrite (Könneke et al., 2005; Wuchter et al., 2006a), and crenarchaeotal genes for putative ammonia monooxydases are prevalent (Francis et al., 2005). These prokaryotes were thus abundant during periods of low primary production and adapted their membrane lipids to low in situ temperatures. Since lipid adaptation to temperature is a rapid process (within a few weeks; Wuchter et al., 2004), this implies that Crenarchaeota were metabolically active in February. In contrast, the GDGTs analysed in April and August were probably derived from dead, inactive or re-suspended organisms, which had been metabolically active during the previous winter and had thus preserved membrane lipid signatures characteristic of winter SSTs. Accordingly, the temperature stratification observed in August at the Oyster Grounds (16.9 °C and 13.4 °C for surface and bottom seawater, respectively) was not detected with the TEX_{86}-derived temperatures because the TEX_{86} signal was biased towards winter temperatures throughout the water column (data not shown). Since the TEX_{86}-derived temperatures of surface and bottom seawater were similar during all seasons, only the data from surface seawater are presented.

Clearly, the bias towards colder temperatures observed for suspended POM was also transported to the sediments, as the average TEX_{86}-derived SST calculated for all sediments (7.1 °C) was 3.4 °C lower than the mean annual SST of the region (10.5 °C) reported in World Ocean Atlas (1998). This is in contrast with previous studies that suggested an excellent correlation between TEX_{86}-derived SSTs of sediment core tops and mean annual SST (Schouten et al., 2002). As discussed above, the membrane lipids of marine Crenarchaeota living in the water column in the southern North Sea impart a cold temperature signal to the overlaying sediments. Hence, in the southern North Sea the TEX_{86} proxy does not correlate with mean annual SST, but is biased toward winter SSTs when Crenarchaeota are metabolically active. This seasonal pattern may also apply to other areas with high primary production and may thus provide essential information on seasonal SST palaeoreconstruction. It is important, however, to remember that, although a winter temperature signal was detected for the southern North Sea and the Angola Basin (this study; Schouten et al., 2002), a summer temperature bias has been reported for the Arctic and the Arabian Sea (Sluijs et al., 2006; Huguet et al., 2006). A better understanding of crenarchaeotal ecology and physiology thus seems necessary in order to accurately use this temperature proxy as a palaeothermometer. It should be noted that these requirement also hold for many other SST proxies. Nevertheless, the extensive TEX_{86} calibration with sediment core tops of Schouten et al. (2002) did accurately predict SST in a large number of marine environments.

4.2. Effect of terrestrial input on TEX_{86}

The GDGTs used for calculating the TEX_{86} have also been detected in peat bogs and soils, albeit in relatively low concentrations (Weijers et al., 2004; Weijers et al., 2006a) and, when transported to the marine environment, may alter the TEX_{86} signal. The GDGT composition of soils is, however, dominated by another type of GDGT (i.e., branched GDGTs) produced by anaerobic bacteria (Weijers et al., 2006b). A possible allochthonous contribution of isoprenoid GDGTs can be readily estimated while carrying out TEX_{86} measurements by using the newly introduced proxy, the branched and isoprenoid tetraether (BIT) index, which is based on the relative abundance of crenarchaeol (V; Fig. 1), the isoprenoidal GDGT considered as a specific biomarker for the marine Crenarchaeota group I and the three main branched GDGTs produced by anaerobic soil bacteria (Hopmans et al., 2004). According to Weijers et al. (2006a), the BIT index should be determined before carrying out any TEX_{86} analyses in marine settings to make sure that TEX_{86}-derived temperatures are not biased as a result of a large terrestrial input. In fact, the concentrations of the GDGT used for calculating the TEX_{86} were on average 20–40 times greater in the water of the river Rhine than in the seawater of the southern North Sea (Tables 1 and 3). Despite being much lower than that of branched GDGTs, the concentration of crenarchaeol was also greater than the average concentration found in the southern North Sea (Herfort et al., 2006), but molecular analysis of our samples revealed low Crenarchaeota abundance (6000 cells ml^{-1}) in the Rhine (Herfort et al., unpublished results). This suggests that in our study the high concentrations of crenarchaeol, and thus also of the GDGTs used for calculating TEX_{86}, may be essentially derived from dead material from soil and peat erosion. The high concentrations of GDGTs from a terrestrial origin gave rise to unrealistic TEX_{86}-derived temperatures (average 14.4 °C) 9.5 °C higher than the in situ river water temperatures (Table 3). These high TEX_{86}-derived temperatures were also associated with high BIT indices (Table 3; Herfort et al., 2006), which clearly indicate input of GDGTs from soil and peat into river water. This confirms that high soil and peat bog input can bias the TEX_{86} signal of river water and that a high BIT index may be a good signal for this artefact.

In February, relatively elevated BIT indices were measured for suspended POM at the stations Dutch Coast, South Frisian Front and Frisian Front (Table 1; Herfort et al., 2006). The Dutch Coast is located within the river Rhine coastal jet, while strong westerly winds shifted the position of the East Anglian Turbidity Plume that carries materials from the rivers Thames and Humber, toward the South Frisian Front and Frisian Front (Herfort et al., 2006). This input of river material into seawater probably slightly affected TEX_{86}, since TEX_{86}-derived SSTs were 1.5 °C to 2 °C warmer than the in situ SSTs.

The TEX_{86}-derived SSTs obtained from the surface sediments of the stations Central Southern Bight and the Dogger Bank at the different seasons ranged from 7.5 °C to 12.6 °C with, when considering the analytical error of 1 °C, some values above the overall average TEX_{86}-derived SST value of 7.1 °C. The Central Southern Bight is located directly in the path of the East Anglian Turbidity Plume, while the Dogger Bank receives freshwater from the rivers Tees and Tyne (Kröncke and Knust, 1995), and relatively high BIT indices (0.27 and 0.17, respectively) were measured for the surface sediment at both sites (Table 2; Herfort et al., 2006). Hence, terrestrial input probably generated the elevated TEX_{86}-derived SSTs detected at these two stations. Other factors, such as lateral transport or resuspension, may also be involved in producing such high estimated SSTs. Nevertheless, the data presented here confirm that, to reconstruct paleotemperatures in marine environments, it is essential to estimate both TEX_{86} and BIT index to ascertain that TEX_{86}-derived temperatures are not influenced by large freshwater discharge.

4.3. TEX_{86} seasonality in sediment core tops

Important seasonal variations in TEX_{86}-derived SSTs were measured for sediment core tops, with higher values almost always detected in August. This was particularly pronounced at the stations Dutch Coast, South Frisian Front and Dogger Bank. Such seasonal variations were unexpected as sediment core top correlations between TEX_{86} and mean annual SST are based on the assumption that surface sediments give an integrated annual SST value. Vertical transport of a high temperature signal from the overlaying seawater cannot explain the observed seasonal sedimentary differences because, as discussed above, in the southern North Sea Crenarchaeota are more abundant and metabolically active during periods of low primary production and the TEX_{86} in POM is consequently biased toward winter temperatures. In addition, large seasonal variations in terrestrial input did not give rise to these seasonal differences in temperature, since the BIT indices for the sediments did not substantially differ between seasons (Table 2; Herfort et al., 2006). Instead, the dynamic hydrography and extremely low sedimentation rates found at these sites (Eisma, 1981; de Haas et al., 1997) gave rise to substantial small scale variation in TOM deposition in the southern North Sea (Herfort et al., 2006) that probably resulted in these seasonal differences in TEX_{86}-derived SSTs. All the sites are indeed characterized by low sedimentation rates, but lower concentrations of isoprenoid and branched GDGTs and lower silt and total organic carbon content were measured for the surface sediments of the Dutch Coast, Breeveertien, South Frisian Front and Dogger Bank than at the other stations (Herfort et al., 2006). The shallow sandy sea bed (24–26 m) and the strong overlaying tidal current (e.g., 1 m s^{-1} at the Dutch Coast; Visser et al., 1991) for the sediments of the Dutch Coast, Breeveertien, South Frisian Front and Dogger Bank essentially prevent any deposition of suspended matter at these sites, creating an environment characterised by extremely transient settling of laterally transported organic matter with a warmer temperature signal. Clearly, the other group of stations give a more time-integrated temperature signal. So, sediment core top correlations between TEX_{86} and mean annual SST should not be carried out for areas characterised by transient sediment deposition, as sediment resuspension and transport probably have an important effect on TEX_{86} temperature reconstruction.

5. Conclusions

The TEX_{86}-derived SSTs of suspended POM and sediment core tops did not correlate with the mean annual SST of the southern North Sea, but were shifted towards winter SSTs, probably because Crenarchaeota are more abundant and metabolically active during periods of low primary production. This suggests that a similar seasonal impact on TEX_{86} may occur in other settings. This may provide essential information on seasonal SST palaeoreconstruction. Elevated TEX_{86}-derived SSTs were measured for the sediment core tops and suspended POM from several stations in the southern North Sea, which were influenced by terrestrial organic matter input, as revealed by relatively high BIT indices. In addition, TEX_{86}-derived temperatures almost 10 °C warmer than the in situ temperature were also found in the water of the river Rhine. These data demonstrate that to reconstruct palaeotemperatures, it is essential to determine both TEX_{86} and BIT index to certify that TEX_{86} temperatures are not influenced by large freshwater discharges. Important seasonal variations in TEX_{86}-derived SSTs were evident for the surface sediments of several stations characterised by extremely low sedimentation rates, suggesting that sediment core top correlations between TEX_{86} and mean annual SST should not be carried out in areas with transient sediment deposition because of important resuspension and transport of organic matter.

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