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TEX_{86} paleothermometer as an indication of bottom water temperature in the Yellow Sea

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A B S T R A C T

The TEX_{86} paleothermometer was applied for reconstructing sea surface temperature (SST) from glycerol dialkyl glycerol tetraethers (GDGTs) in marine sediments. It has become clear that GDGT-producing archaea live throughout the water column, with maximum concentration usually well below the surface mixed layer of the ocean. Why the TEX_{86} parameter correlates well with SST remains poorly understood. Here we evaluate the fidelity of the TEX_{86} thermometer using surface sediments and suspended particles from the Yellow Sea (YS), a shallow marginal sea between China and the Korean peninsula. The highest concentration of GDGTs in the water column at a site (A02) from the middle of the YS occurred in the bottom layer, at 70 m. This contrasts with phytoplankton lipids, which were most abundant near the surface. Consistent with the maximum abundance of GDGTs in bottom water, TEX_{86} values in surface sediments correlated better with mean annual bottom water temperature (BWT, R^2 0.81) than with mean annual SST (R^2 0.74). Moreover, TEX^H_{86} temperature derived from a global core top calibration gave values 0.1–9.4 °C colder than mean annual SST but much closer to mean annual BWT (2.7–4 °C). Lastly, TEX_{86} and $U^{K'}_{37}$ paleotemperature values displayed distinctly different trends over the last 12 kyr for sediments from the shelf between the YS and the East China Sea (ECS), consistent with the notion that TEX_{86} and $U^{K'}_{37}$ reflect different temperature signals. This preponderance of evidence supports the use of TEX_{86} as a proxy for BWT in the YS. Therefore, we propose a local calibration of TEX^L_{86} for reconstructing mean annual BWT (TEX^L_{86} = 0.03 BWT-0.94; R^2 0.86, n = 22, P < 0.0001). The combination of alkenone ($U^{K'}_{37}$) derived SST with TEX^L_{86} BWT yielded a quantitative reconstruction of the vertical thermal gradient in the YS, and an insight into understanding the impact of the Kuroshio Current and East Asian monsoon on the YS.

1. Introduction

The TEX_{86} paleothermometer, based on the relative abundance of cyclopentane rings in membrane glycerol dialkyl glycerol tetraether (GDGT) lipids from *Thaumarchaeota*, has been increasingly revealed to indicate mean annual surface temperature (SST) values in marine (Schouten et al., 2002; Kim et al., 2008, 2010) and lacustrine settings (Powers et al., 2010). As more becomes known about the habitat of *Thaumarchaeota*, the environmental conditions to which they respond, and the species most responsible for producing the GDGTs included in the TEX_{86} index, it should become possible to refine the interpretation of TEX_{86} derived temperature values. For example, recent work has demonstrated that GDGT production occurs primarily in subsurface waters of the ocean (Nakanishi et al., 2012; Basse et al., 2014). Subsurface growth of chemoautotrophic *Thaumarchaeota* is thought to result from the greater availability of NH_4^+ generated from remineralization of particulate organic matter (POM) sinking out of the euphotic zone (Karner et al., 2001; Wuchter et al., 2006a; Schouten et al., 2013). Growth of GDGT-producing archaea below the euphotic zone may also be promoted by light inhibition (Merbt et al., 2012) and the absence of competition for NH_4^+ by photoautotrophs (Murray et al., 1998,1999; Wuchter et al., 2005; Herfort et al., 2006). Much lower TEX_{86}–derived temperatures than mean annual SST were found

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(Wei et al., 2011) for sediments from depths < 100 m in the South China Sea (SCS). Further study indicated that surface sediment TEX_{86}^{H} values reflected a deeper and cooler subsurface temperature than surface or mixed layer temperature in the SCS (Jia et al., 2012) and sediment records revealed that TEX_{86} temperature values were consistently lower than $U_{37}^{K'}$ ones over the past 356 kyr, providing further support for TEX_{86} as a proxy for subsurface temperature (Li et al., 2013).The difference between TEX_{86}^{H} temperature and $U_{37}^{K'}$ temperature was also used to reconstruct variation in thermocline depth, revealing an uplifted local thermocline during glacial times in the southern SCS (Dong et al., 2015).

Any seasonality in the production of archaeal GDGTs has the potential to influence the temperature reflected in sedimentary TEX_{86} values (Schouten et al., 2013 and references therein). Analysis of GDGTs in surface sediments from the Angola Basin revealed that TEX_{86} values correlated best with winter SST (Schouten et al., 2002), while those in the Mediterranean Sea correlated best with summer SST (Menzel et al., 2006; Leider et al., 2010), except at nearshore sites where they reflected winter SST (Leider et al., 2010). In a study of sedimentary GDGTs from the coastal northern SCS, TEX_{86}^{H} was found to reflect winter SST (Ge et al., 2013; Zhang et al., 2013), which may result from the highest *Thaumarchaeota* abundance occurring during the cold season (Zhang et al. 2013). In addition, TEX_{86} derived temperature in suspended POM and core top sediments from the North Sea closely co-varied with winter SST, but not with annual mean SST, implying greater *Thaumarchaeota* production during the winter period of low primary production (Herfort et al., 2006).

Elsewhere, sediment traps from 500–3000 m in the Arabian Sea revealed a GDGT flux that co-varied with the flux of phytol, an indicator of photoautotrophic production (Wuchter et al., 2006b). This was interpreted to mean that the flux of GDGTs to the seafloor was modulated by the flux of sinking particles, itself controlled by primary production in the surface water (Wuchter et al., 2006b). Lastly, a correlation between chlorophyll *a* and archaeal lipids in surface waters was observed at the Bermuda Atlantic Time-series Study site (Wuchter et al., 2005). This was ascribed to either NH_4^+ concentration being sufficient to support high surface Thaumarchaeal production when phytoplankton production was high, or to the upward mixing of GDGTs from the subsurface during winter and early spring mixing events (Wuchter et al., 2005).

TEX_{86} derived temperature values are still commonly used as indicative of annual mean surface temperature. This stems from the observation that GDGTs in suspended POM from both the shallow (< 100 m) and deep (150–1500 m) ocean from a variety of settings gave TEX_{86} temperature values that correlated highly with SST values (R^2 0.56–0.8; Wuchter et al., 2005). TEX_{86} values for surface sediments also tend to be highly correlated with SST values (Schouten et al., 2002; Kim et al., 2008, 2010). These empirical relationships have supported the interpretation of TEX_{86} as a proxy for SST in most studies, even though the available evidence indicates that *Thaumarchaeota* reach their highest concentration in the ocean at a depth of 150–500 m (Karner et al., 2001) and GDGT concentration generally peaks below 100 m water depth (Wuchter et al., 2005). For example, vertical distributions of GDGTs in sinking particles from the oligotrophic water of the northeastern Pacific and the upwelling area near the California coast revealed that the maximum GDGT abundance occurred at 750 m and 200–300 m, respectively (Wuchter et al., 2006b). In coastal waters, such as the slope and shelf of the northern ECS GDGT concentration in suspended particles also peaked below the euphotic zone, at 74–99 m (Nakanishi et al., 2012). This contrasted with alkenone concentration, also used for $U_{37}^{K'}$ paleo-SST reconstruction, that peaked in the upper 25 m (Nakanishi et al., 2012).

Consistent with the production of GDGTs in the subsurface, several studies have reported that TEX_{86} derived temperature values from surface sediments and particulate material correlated better with subsurface water temperature than with SST. Huguet et al. (2007) found that GDGTs in sinking particles collected in a sediment trap at ca. 490 m depth from the Santa Barbara Basin reflected subsurface (100–150 m) water temperature. Lee et al. (2008) analyzed core top sediments from the Benguela upwelling system and found that TEX_{86} values reflected water temperature below the mixed layer. Jia et al. (2012) came to a similar conclusion from their study of core top GDGTs in the SCS. In lake sediments as well, such as those from Lake Lucerne, TEX_{86} values in surface sediments reflected subsurface water temperature, consistent with the subsurface habitat of *Thaumarchaeota* in the lake (Blaga et al., 2011). Based on these observations, several researchers have applied the TEX_{86} paleothermometer to reconstruct subsurface or thermocline temperatures, as Rommerskirchen et al. (2011) did for the Benguela upwelling region, Lopes dos Santos et al. (2010) did for the tropical North Atlantic and Li et al. (2013) did for the SCS.

In addition to depth and season of production, the process of GDGT sinking and preservation in sediments also has the potential to impact the TEX_{86} signal. Even if no seasonality in GDGT production exists, but the sinking flux of particles from the euphotic zone varies seasonally, then it is possible that GDGTs are preferentially transported to the seafloor during the season of highest phytoplankton export flux. This could occur if fecal pellets and other fast sinking particles that transport a significant fraction of the phytoplankton export flux to the seafloor also incorporate archaeal biomass. A related way in which phytoplankton and zooplankton dynamics might impact sedimentary TEX_{86} values is if the packaging of fast sinking particles preferentially incorporates those GDGTs that were produced in the surface (Yamamoto et al., 2012). In that case, even if archaeal production of GDGTs occurred primarily in subsurface water, sedimentary GDGTs would be expected to reflect surface temperature, as was proposed by Yamamoto et al. (2012) for the western North Pacific.

Few studies have explored the use of the TEX_{86} palaeothermometer in semi-enclosed marginal seas. These settings can provide excellent high resolution paleoclimate records owing to the high accumulation rate of sediments adjacent to continents. Their proximity to land also provides the opportunity to reconstruct both marine and continental climate from a single archive. One such location is the Yellow Sea (YS). Located between the West Pacific Ocean and the East Asia continent, it is influenced by both the Kuroshio Current and the East Asian monsoon (Fig. 1). In winter, due to the strong northerly wind, the water column is well mixed in the shallow regions and is only weakly stratified in the deep regions. In summer, owing to reduced wind speed, there is a sharp thermocline between 10 and 30 m, except in certain coastal areas with significant tidal mixing (Wei et al., 2010). Up to 5 m thick sequences of Holocene mud (Yang et al., 2003) have provided several detailed records of oceanographic, ecological and climatic change in the YS since the end of the last glacial period (Kong et al., 2006; Xiang et al., 2008; Xing et al., 2012). Some studies indicated a correlation of TEX_{86}^{H} and annual mean SST (R^2 0.61) in the ECS (Zhu et al., 2011) and a better correlation with annual mean summer SST (R^2 0.84) in the east coastal seas of China (Lü et al., 2014), but we know little about the relationship between subsurface temperature and TEX_{86} proxy and vertical distribution of GDGTs in the YS. We therefore report on the abundance of GDGTs and the TEX_{86} index in surface sediment from 31 sites and in suspended particles from one site of the YS, with the aim of better understanding this temperature proxy so that it can be applied to reconstructing Holocene temperature changes.