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Core-top calibration of the lipid-based $U^{K'}_{37}$ and TEX_{86} temperature proxies on the southern Italian shelf (SW Adriatic Sea, Gulf of Taranto)

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ABSTRACT

The Mediterranean Sea is at the transition between temperate and tropical air masses and as such of importance for studying climate change. The Gulf of Taranto and adjacent SW Adriatic Sea are at the heart of this region. Their sediments are excellently suited for generating high quality environmental records for the last millennia with a sub-decadal resolution. The quality of these records is dependent on a careful calibration of the transfer functions used to translate the sedimentary lipid signals to the local environment. Here, we examine and calibrate the $U^{K'}_{37}$ and TEX_{86} lipid-based temperature proxies in 48 surface sediments and relate these to ambient sea surface temperatures and other environmental data. The $U^{K'}_{37}$ -based temperatures in surface sediments reflect winter/spring sea surface temperatures in agreement with other studies demonstrating maximum haptophyte production during the colder season. The TEX_{86}-based temperatures for the nearshore sites also reflect winter sea surface temperatures. However, at the most offshore sites, they correspond to summer sea surface temperatures. Additional lipid and environmental data including the distribution of the BIT index and remote-sensed chlorophyll-*a* suggest a shoreward increase of the impact of seasonal and spatial variability in nutrients and control of planktonic archaeal abundance by primary productivity, particle loading in surface waters and/or overprint by a cold-biased terrestrial TEX_{86} signal. As such the offshore TEX_{86} values seem to reflect a true summer signal to the effect that offshore $U^{K'}_{37}$ and TEX_{86} reconstruct winter and summer temperature, respectively, and hence provide information on the annual temperature amplitude.

1. Introduction

A valid and powerful method to better understand short-term environmental and climate change is to study the past. The interactions between atmosphere and ocean are complex so deciphering them requires quantitative and reliable proxies for key environmental parameters such as temperature, air pressure, sea level and the precipitation–evaporation budget. This is also valid for the Mediterranean climate, which is especially sensitive to climate change due to its location between the subtropical high-pressure belt and mid-latitude westerlies (e.g., Trigo et al., 1999; Xoplaki et al., 2003, 2004).

As sea surface temperature (SST) is an important factor in the Earth's climate, its reconstruction is essential for an understanding of past climate change. The commonly used geochemical temperature proxies include $\delta^{18}O$ and Mg/Ca ratios of planktonic foraminifera (Elderfield and Ganssen, 2000; Erez and Luz, 1983; Nürnberg et al., 1996), the $U^{K'}_{37}$ from alkenones synthesized by haptophytes (Prahl and Wakeham, 1987) and the TEX_{86} based on archaeal isoprenoidal tetraether lipids (Kim et al., 2008; Schouten et al., 2002).

The $U^{K'}_{37}$ exploits the observation that the abundance of the diunsaturated C_{37} methyl alkenone, relative to the total of di- and triunsaturated C_{37} methyl alkenones in surface waters and algal cultures increases with increasing water temperature. These alkenones are produced by a small group of haptophyte algae thriving in the mixed layer: the coccolithophore *Emiliana huxleyi* and related species (Brassell et al., 1986; Conte et al., 1998; Marlowe et al., 1984; Prahl and Wakeham, 1987; Volkman et al., 1980). Global calibrations of marine core-top $U^{K'}_{37}$ values with mean annual SSTs show a consistent linear relationship with an uncertainty of 1.1 °C (Conte et al., 2006; Müller et al., 1998). This led to the establishment of the $U^{K'}_{37}$ index as a reliable paleoceanographic tool to estimate SSTs in a variety of oceanic settings (Haug et al., 2005; Herbert et al., 2003 and references therein; Sachs and Anderson, 2005).

Nevertheless, some studies reveal clear discrepancies between the $U^{K'}_{37}$ signal in sediments and annual mean SST (e.g., Volkman, 2000). Factors suggested to cause these discrepancies include preferential degradation of the triunsaturated alkenone (Gong and Hollander, 1999; Hoefs et al., 2002; Kim et al., 2009b; Rontani et al., 2006, 2009; Sun and Wakeham, 1994), influence of nutrients and light (Epstein et al., 1998; Prahl et al., 2003; Versteegh et al., 2001), input of

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alkenones from remote regions (Benthien and Müller, 2000; Goñi et al., 2001; Mollenhauer et al., 2007; Ohkouchi et al., 2002), differences in species composition (Conte et al., 1998; Volkman et al., 1995), production at greater depths within the euphotic zone (Bentaleb et al., 1999; Prahl et al., 2005; Ternois et al., 1997) or strong blooming of haptophytes in periods with water temperatures that are significantly different from the annual mean (Bentaleb et al., 1999; Popp et al., 2006 and references therein; Prahl et al., 2001; Sikes et al., 1997; Versteegh et al., 2007). In spite of these deviations from the global calibration the utility of site-specific calibrations between the environment and $U^{K'}_{37}$ is contentious.

The TEX_{86} temperature proxy is based on archaeal glycerol dialkyl glycerol tetraethers (GDGT), which are abundant in marine sediments (Schouten et al., 2000, 2002). The biological sources are non-hyperthermophilic cren- and euryarchaeota, a major group of prokaryotes in today's oceans and lakes (Karner et al., 2001; Powers et al., 2004). The relative distribution of these isoprenoidal GDGTs varies with growth temperature and (similar to the $U^{K'}_{37}$) linear regressions of core-top TEX_{86} values to SST enable the use of the TEX_{86} as a temperature proxy (Kim et al., 2008, 2010; Schouten et al., 2002, 2007a; Wuchter et al., 2005). The TEX_{86} is considered to reflect the annual mean temperatures of the upper mixed layer (Kim et al., 2008; Schouten et al., 2002). Although, the TEX_{86} is increasingly used for reconstructing ancient SSTs, a number of issues remain unresolved (Huguet et al., 2006; Pearson et al., 2007). It appears that the TEX_{86} can be biased due to additional production of GDGTs below the mixed layer (Huguet et al., 2007; Lee et al., 2008; Pearson et al., 2001), by seasonality in crenarchaeotal growth (Herfort et al., 2006; Huguet et al., 2006, 2007; Menzel et al., 2006; Schouten et al., 2002; Wuchter et al., 2006) and by the ecology of planktonic cren-and euryarchaeota due to their presence in different water depths of the ocean and the theoretical possibility of GDGT synthesis by marine euryarchaeota (DeLong, 2006; Turich et al., 2007; Wuchter et al., 2005). Additionally, archaea living in sediments of continental margins and the deep-sea may contribute to the GDGT pool and thus influence the TEX_{86} value (Lipp and Hinrichs, 2009; Lipp et al., 2008; Shah et al., 2008; Sorensen and Teske, 2006).

In coastal settings, fluvial input of terrestrial isoprenoidal GDGTs may bias the TEX_{86} (Herfort et al., 2006). Fortunately, this latter bias can be determined by using the Branched and Isoprenoid Tetraether (BIT) index (Hopmans et al., 2004), a ratio between the abundance of branched GDGTs (presumably derived from anaerobic soil bacteria) and crenarchaeol indicating the relative importance of terrestrial organic matter input (Herfort et al., 2006; Kim et al., 2006; Weijers et al., 2006a,b).

Diagenetic overprints of the TEX_{86} due to changing redox conditions seem to be less important than for other biomarkers (Kim et al., 2009b; Schouten et al., 2004; Sinninghe Damsté et al., 2002a). However, selective degradation during resuspension, transport and redeposition may be significant in some cases and has to be considered for the reliable application of the TEX_{86} as a SST proxy (Kim et al., 2009a; Mollenhauer et al., 2007). Considering these factors, careful assessment of site-specific relations between $U^{K'}_{37}$ values, TEX_{86} and SST is vital to arrive at reliable SST reconstructions.

At the Gallipoli shelf (Gulf of Taranto, southern Italy) the influence of the mid-latitude westerlies, represented by the seasonal modes of the Northern Atlantic Oscillation (NAO), has a significant effect on the region causing for example maxima in precipitation during winter and arrival of Atlantic storm tracks in southern Italy (e.g., Hurrell and Van Loon, 1997; Xoplaki et al., 2004). Sediments at the shelf are suitable for high-resolution environmental reconstruction (e.g., Cini Castagnoli et al., 1999b; Versteegh et al., 2007) (Fig. 1). Shallow-water cores revealed the unique potential for high-resolution down-core studies of the past two centuries based on radiometric dating and tephroanalysis (Bonino et al., 1993; Cini Castagnoli et al., 1990). Furthermore, carbonate contents (Cini Castagnoli et al., 1992a,b), thermoluminescence (Cini Castagnoli et al., 1997) and the stable carbon and oxygen isotope compositions of the planktonic foraminfer *G. ruber* show significant decadal to centennial components, assumed to be related to solar forcing (Cini Castagnoli et al., 1999a,b, 2000, 2002, 2005). An

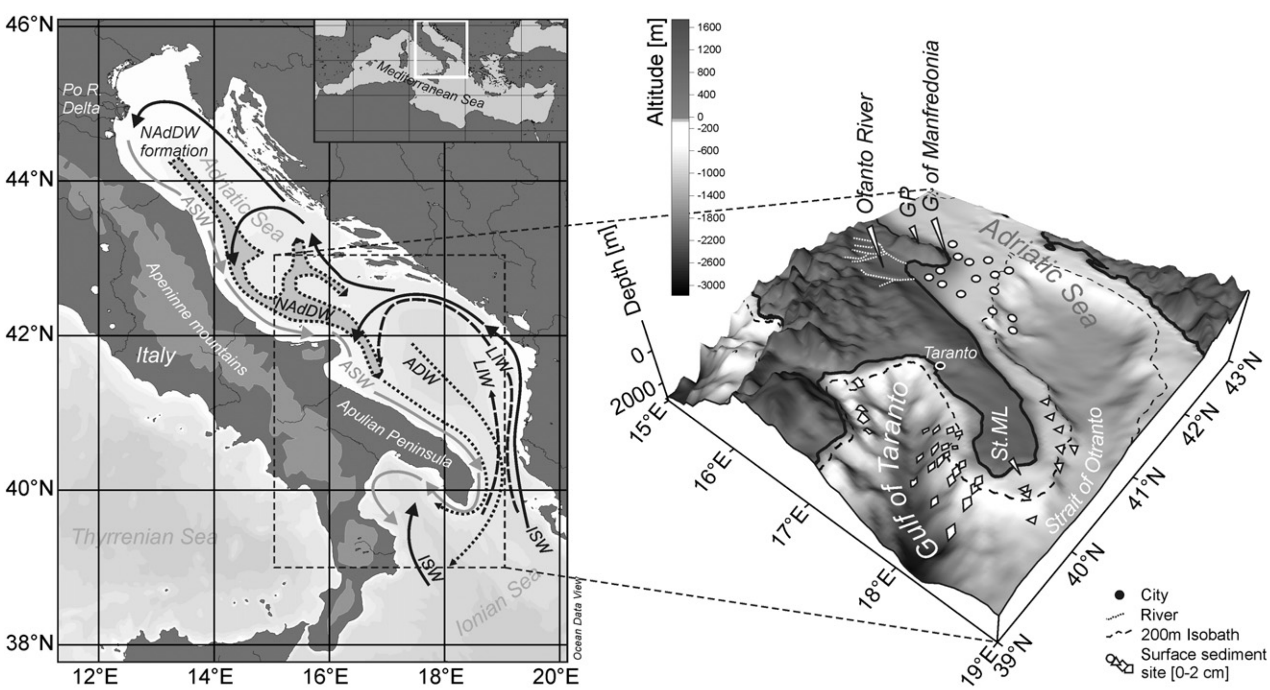

Fig. 1. Map of the Adriatic and Ionian Sea indicating the study area and general circulation pattern (ISW: Ionian Surface Water, ASW: Adriatic Surface Water, LIW: Levantine Intermediate Water, NAdDW: Northern Adriatic Deep Water, and ADW: Adriatic Deep Water, redrawn from Artegiani et al., 1997b; Poulain, 2001; Vilibić and Supić, 2005). Right zoom in 3D-map showing the locations of the surface sediment analyzed in this study (GP: Gargano Promontory; G. of Manfredonia: Gulf of Manfredonia; St.ML: Cape Santa Maria di Leuca). Samples were grouped in accordance to their spatial distribution within the southern Adriatic Sea (circles: GP and G. of Manfredonia, triangles: Strait of Otranto) and Gulf of Taranto (diamonds: E Gulf of Taranto, squares: W Gulf of Taranto).