Coherent millennial-scale patterns in U$_{37}^{k'}$ and TEX$_{86}^{H}$ temperature records during the penultimate interglacial-to-glacial cycle in the western Mediterranean

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[1] The TEX$_{86}^{H}$ temperature proxy is a relatively new proxy based on crenarchaeotal lipids and has rarely been applied together with other temperature proxies. In this study, we applied the TEX$_{86}^{H}$ on a sediment core from the Alboran Sea (western Mediterranean, core ODP-977A) covering the penultimate climate cycle, that is, from 244 to 130 ka, and compared this with previously published sea surface temperatures derived from the U$_{37}^{k'}$ of alkenones of haptophyta and Mg/Ca records of planktonic foraminifera. The TEX$_{86}^{H}$ temperature record shows remarkably similar stadial-interstadial patterns and abrupt temperature changes to those observed with the U$_{37}^{k'}$ palaeothermometer. Absolute TEX$_{86}^{H}$ temperature estimates are generally higher than those of U$_{37}^{k'}$, though this difference ($<3°C$ in 81% of the data points) is mainly within the temperature calibration error for both proxies, suggesting that crenarchaeota and haptophyta experienced similar temperature variations. During occasional events ($<5\%$ of the analyzed time span), however, the TEX$_{86}^{H}$ exhibits considerably higher absolute temperature estimates than the U$_{37}^{k'}$. Comparison with Mg/Ca records of planktonic foraminifera as well as other Mediterranean TEX$_{86}$ and U$_{37}^{k'}$ records suggests that part of this divergence may be attributed to seasonal differences, that is, with TEX$_{86}^{H}$ reflecting mainly the warm summer season while U$_{37}^{k'}$ would show annual mean. Biases in the global calibration of both proxies or specific biases in the Mediterranean are an alternative, though less likely, explanation. Despite differences between absolute TEX$_{86}^{H}$ and U$_{37}^{k'}$ temperatures, the correlation between the two proxies ($r^2 = 0.59$, 95% significance) provides support for the occurrence of abrupt temperature variations in the western Mediterranean during the penultimate interglacial-to-glacial cycle.

1. Introduction

[2] Reconstructions of past seawater temperatures, particularly sea surface temperature (SST), is a key parameter for paleoceanographic studies and a range of proxies are used. Among the most widely used proxies are the $\delta^{18}O$ and Mg/Ca of planktonic foraminifera and the U$_{37}^{k'}$ based on the distribution of diunsaturated and triunsaturated alkenones ($C_{37:2}/C_{37:2} + C_{37:3}$) synthesized by haptophyta algae. Although these proxies have resulted in a wealth of information on past SST variations, uncertainties exists as many temperature records are constrained by a single proxy which can be influenced by factors like diagenesis or respond to factors other than temperature such as salinity and nutrient concentration. Therefore, there is a strong need for additional SST proxies as well as a multiproxy approach to constrain uncertainties in SST reconstructions.

[3] A more recently developed molecular temperature proxy, the TEX$_{86}$, is based on lipids from marine crenarchaeota [*Schouten et al.*, 2002]. Marine crenarchaeota occur ubiquitously in marine environments and are one of the dominant prokaryotes in today's oceans [*Karner et al.*, 2001]. A number of studies have shown that most of the marine crenarchaeota are autotrophic nitrifiers [e.g., *Könneke et al.*, 2005; *Wuchter et al.*, 2006a; *Park et al.*, 2010], although some studies indicate that they also take up amino acids [e.g., *Herndl et al.*, 2005] or may have a mixotrophic metabolism [*Ingalls et al.*, 2006]. Marine crenarchaeota biosynthesize different types of isoprenoid glycerol dialkyl glycerol tetra-

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ether (GDGT) membrane lipids containing 0 to 3 cyclo-pentane moieties and crenarchaeol which, in addition to 4 cyclopentane moieties has a cyclohexane moiety [*Schouten et al.*, 2000; *Sinninghe Damsté et al.*, 2002]. Core top studies showed that marine Crenarchaeota change this composition according to temperature, that is, higher temperatures result in an increase in the relative amounts of GDGTs with two or more cyclopentane moieties. *Schouten et al.* [2002] proposed the use of the TEX_{86} to quantify this change in the distribution of GDGTs:

$$TEX_{86} = \frac{[GDGT-2]+[GDGT-3]+[Cren\,regio-isomer]}{[GDGT-1]+[GDGT-2]+[GDGT-3]+[Cren\,regio-isomer]}, \quad (1)$$

where crenisomer is the regio-isomer of crenarchaeol. Core top calibrations show that the TEX_{86} correlates well with annual mean SST [*Schouten et al.*, 2002; *Kim et al.*, 2008, 2010]. Mesocosm experiments confirmed that marine cre-narchaeota change their membrane composition with growth temperature and showed that changes in salinity and nutrients do not substantially affect the temperature signal recorded by the TEX_{86} [*Wuchter et al.*, 2004]. Analysis of particulate organic matter and of core tops showed that TEX_{86} values correlated well with in situ temperature at depths <100 m [*Wuchter et al.*, 2005; *Kim et al.*, 2008, 2010]. However, it was also shown that soil organic matter often contains small amounts of isoprenoid GDGTs with 0–4 cyclopentane moieties and, thus, TEX_{86} values in sediments receiving large amounts of soil organic matter may be biased [*Weijers et al.*, 2006]. This effect can be evaluated using the BIT index which is the relative amount of soil-derived branched GDGTs, derived from soil bacteria [*Weijers et al.*, 2006], compared to crenarchaeol [*Hopmans et al.*, 2004]:

$$BIT\,index = \frac{[GDGT-I]+[GDGT-II]+[GDGT-III]}{[Crenarchaeol]+[GDGT-I]+[GDGT-II]+[GDGT-III]}. \quad (2)$$

The BIT index can range between 0 and 1 with low values corresponding to low amounts of soil organic matter input.

[4] Although the TEX_{86} proxy has been applied in a range of cores spanning the Cretaceous to the late Quaternary, it remains uncertain how well this proxy reconstructs annual mean SST. For example, *Huguet et al.* [2007a], *Lee et al.* [2008], and *Lopes dos Santos et al.* [2010] showed that TEX_{86} is not reflecting SST but subsurface temperatures, while *Menzel et al.* [2006], *Castañeda et al.* [2010], and *Leider et al.* [2010] showed that TEX_{86} in the Eastern Mediterranean and the Adriatic Sea may be skewed toward summer temperatures. One way of constraining potential issues with SST proxies is to apply multiple proxies on the same sediment record. Therefore, in this study we analyzed GDGT lipids in core ODP-977A from the Alboran Sea and compared this with previously published proxy-based tem-perature records from the same core. *Martrat et al.* [2004] previously reconstructed SST for the Alboran Sea based on the $U^{k'}_{37}$ from this core and showed a good correlation (up to $r^2 = 0.77$) with climatic changes reconstructed from Greenland $\delta^{18}O_{ice}$ profiles [*Cacho et al.*, 1999; *Martrat et al.*, 2004, 2007]. During the penultimate glacial (Marine Isotope Stage 6 (MIS 6)) there were less frequent SST changes reflecting stadial-interstadial patterns than those of the last ice age (from MIS 2 to 4) and the most prominent events occurred after relatively warm and largely ice-free periods, that is, MIS 5 and 7 [*Martrat et al.*, 2004, 2007]. In addition, Mg/Ca values of planktonic foraminifera from selected parts of the MIS 6 and 7 showed similar patterns as those of the $U^{k'}_{37}$ record [*Gonzalez-Mora et al.*, 2008]. Thus, we generated a TEX_{86} temperature record from ODP-977A for MIS 6 and 7 and compared it with previously published temperature records from the same core. This multiproxy comparison allowed us to evaluate the coherency and potential differences in SST reconstructions during a period of both long- and short-term climatic changes in the Alboran Sea.

2. Material and Methods

2.1. Study Area

[5] Core ODP-977A was retrieved from the eastern sub-basin of the Alboran Sea during Leg 161 of the Ocean Drilling Program in 1996 [*Comas et al.*, 1996] (Figure 1a). The Alboran Sea (western Mediterranean) is a transitional area between the Atlantic and the Mediterranean. The area has a complex water column structure with deep Mediter-ranean and surface Atlantic water masses (Figure 1b). SST in the area, computed from satellite data, presently ranges from 14°C in February to 25°C in August [*Garcia-Gorriz and Garcia-Sanchez*, 2007; *Parada and Canton*, 1998]. Sea surface temperatures at 0 m from more than 3,000 hydro-graphical stations from the Alboran Sea yielded an average annual value of 18.0°C ± 0.4°C, with lowest averages recorded in winter (15.3°C), highest during summer (22.0°C) and intermediate values during spring (17.7°C) and autumn (18.4°C) (MEDAR Group, Mediterranean Targeted Project, Mass Transfer and Ecosystem Response, 2002, http://www.ieo.es) (Figure 1b).

[6] The Alboran Sea is one of the most productive areas, not directly associated to the influence of major river flow, within the western Mediterranean [*Fabres et al.*, 2002]. In the eastern Alboran basin, nonbiogenic fluxes remain roughly constant, while the biogenic flux responds strongly to sea-sonal variations throughout the water column, which is under the influence of the Almeria-Oran front (AOF)] [*Sanchez-Vidal et al.*, 2004, 2005]. Westerly driven upwelling of cool subsurface waters contributes to the fertilization of this region because water upwelled by wind is rich in nutrients [*Garcia-Gorriz and Carr*, 1999; *Sanchez-Vidal et al.*, 2005; *Sarhan et al.*, 2000]. Two regimes occur: an autumn-to-winter bloom (November to March) and a nonbloom period (May to September) [*Garcia-Gorriz and Carr*, 1999]. Transition periods occur in April to May, when thermal stratification begins. A less strong peak in chlorophyll can be noted in October to November, coinciding with maximum wind var-iability and a breakup of the stratification within the basin [*Baldacci et al.*, 2001; *Garcia-Gorriz and Carr*, 1999]. Export production in the eastern Alboran Sea is higher than in other Mediterranean sites, with 0.5–0.9% of the carbon fixed during photosynthesis transferred down the water column and buried in the deep sediments [*Sanchez-Vidal et al.*, 2004, 2005]. At the core site ODP-977A, pelagic particle settling is steady because it is located far from the direct influence of resuspension and downslope transfer from the shallow margins [*Masque et al.*, 2003].
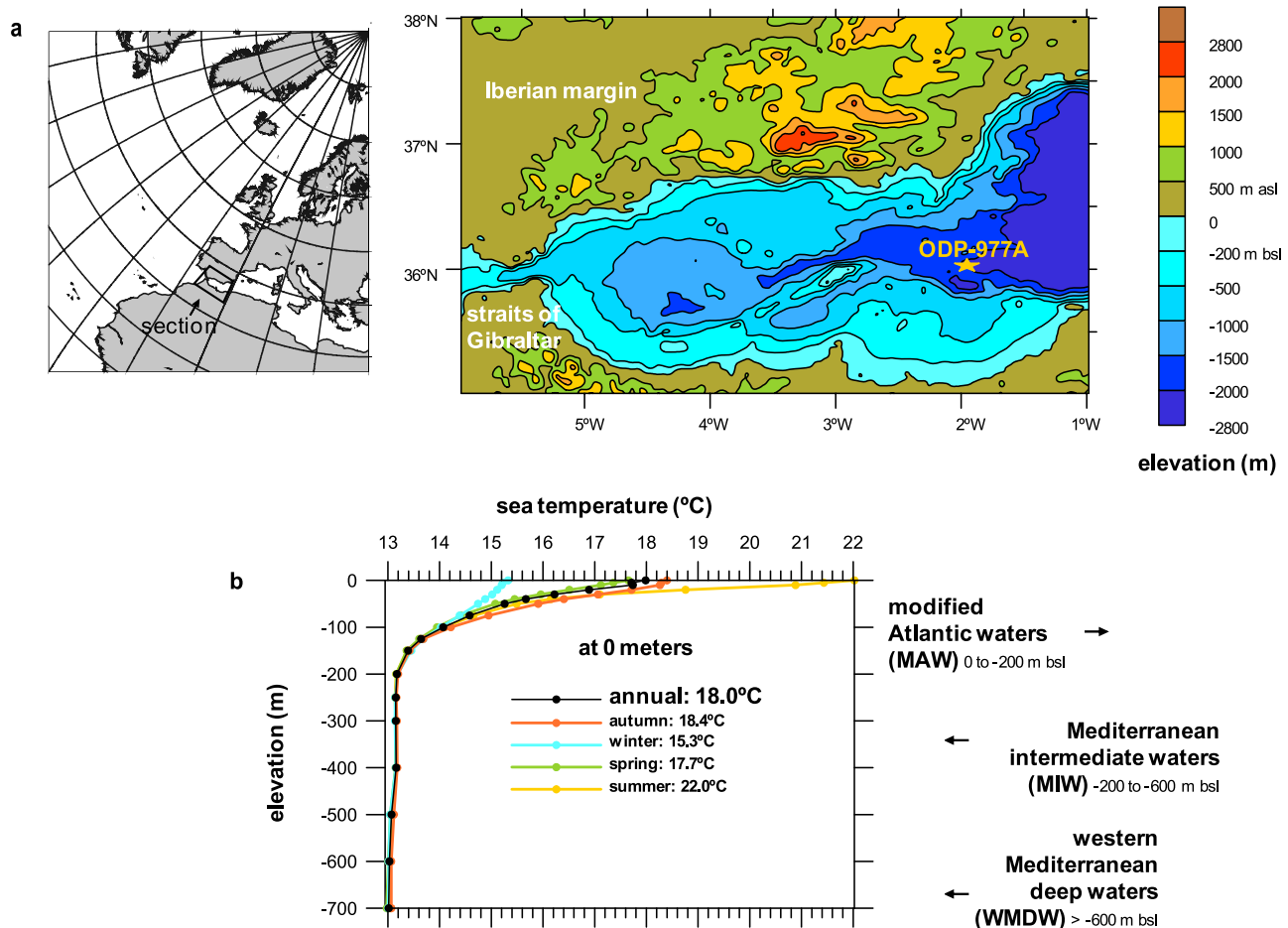
Figure 1. (a) Map of the study area showing the location of core ODP-977A (36°1.907′N, 1°57.319′W, −1984 m below sea level). (b) Oceanographic patterns in the Alboran basin. In this basin there is an interface layer between the relatively warm and light modified Atlantic waters (MAW; between 0 and −200 m below sea level (bsl)) and outflowing intermediate and deep Mediterranean waters (MIW between −200 and −600 m bsl; WMDW deeper than 600 m bsl). The temperature at the upper water column (0 m) is 18.0°C ± 0.4°C in average annual value. The seasonal variability ranges from the lowest averages recorded in winter (15.3°C), highest during summer (22.0°C) and intermediate values during spring (17.7°C) and autumn (18.4°C) (MEDAR Group, Mediterranean Targeted Project II, Mass Transfer and Ecosystem Response, 2002, http://www.ieo.es).

2.2. Sampling Strategy

[7] In a previous study, analysis of the first 3967 cm of core ODP-977A allowed high-resolution reconstruction of the climatic history along the past 250 kyr, using stable isotopes (n = 794 samples) and SST derived from the alkenone index (n = 655 samples) [*Martrat et al.*, 2004]. In the present study, GDGT lipid analyses of the section between 3967 and 2731 cm (from 244 to 145 ka; n = 199 samples) are performed with an average temporal resolution at centennial scale throughout. The age model of this section was constructed by comparing the $\delta^{18}O_{cc}$ profile of *Globigerina bulloides* with ten defined orbital tuned isotopic events assuming constant sedimentation rates between control points (see *Martrat et al.* [2004, 2007] for details).

2.3. GDGT Analysis

[8] Freeze-dried sediment samples were extracted using an Accelerated Solvent Extractor 200 (ASE 200, DIONEX)

with a mixture of dichloromethane (DCM) and methanol (MeOH) (9:1; vol:vol) at 100°C and 7.6 × 10⁶ Pa. An aliquot of each total extract was divided into an apolar and a polar fraction, using a glass pipette column filled with activated alumina, and sequentially eluting with hexane/DCM (1:1; vol:vol) and DCM/MeOH (1:1; vol:vol), respectively.

[9] The polar fraction was analyzed for GDGTs according to the procedure described by [*Hopmans et al.*, 2000] and [*Schouten et al.*, 2007]. Analyses were performed in triplicate with an HP 1100 Series Liquid Chromatography–Mass Spectrometer (LC-MS) equipped with an autoinjector and ChemStation chromatography manager software. Separation was achieved on a Prevail Cyano column (2.1 × 150 mm, 3 μm; Alltech, Deerfield, Illinois, USA), maintained at 30°C. GDGTs were eluted isocratically first with hexane/isopropanol (99:1%; vol:vol) for 5 min, then using a linear gradient up to 1.8% volume of isopropanol over 45 min. Flow rate was 0.2 mL/min. After each analysis the column was cleaned

by back flushing hexane/isopropanol (90:10; vol:vol) at 0.2 mL/min for 10 min. Detection was achieved using atmospheric pressure chemical ionization–mass spectrometry (APCI-MS) of the eluent with the following conditions; nebulizer pressure 60 psi, vaporizer temperature 400°C, N$_2$ drying gas flow 6 L/min at 200°C, capillary voltage −3kV, corona 5μA (~3.2kV). Single Ion Monitoring (SIM) was used instead of full mass scanning because SIM increases the signal-to-noise ratio and thus improves reproducibility [*Schouten et al.*, 2007]. SIM was set to scan the five [M+H]$^+$ ions of the GDGTs and the [M+H]$^+$ ions of the three major branched GDGTs derived from soil bacteria with a dwell time of 237 ms for each ion. The TEX$_{86}$ was calculated according to equation (1) [*Schouten et al.*, 2002] and the BIT index was calculated according to equation (2) [*Hopmans et al.*, 2004]. Samples were run in triplicate. The average standard deviation was 0.004 (~0.3°C) for TEX$_{86}$ and 0.01 for the BIT index.

[10] The TEX$_{86}$ values were related to temperature according to the following empirical relationship based on globally distributed core top sediments with annual mean SST [r^2 = 0.87; n = 255, p < 0.0001] [*Kim et al.*, 2010]:

$$SST = +38.6 + 68.4 \times (\log TEX_{86}). \quad (3)$$

This calibration introduces a nonlinear term (TEX$_{86}^{H}$, which is defined as the logarithmic function of TEX$_{86}$), improving accuracy in the estimation of warm temperatures with a calibration error of 2.5°C [*Kim et al.*, 2010].

[11] The $U_{37}^{k'}$ temperatures [*Martrat et al.*, 2004] were derived from a global core top calibration providing annual mean estimates at surface level ranging from 0° to 29°C [r^2 = 0.96; n = 370, 95% significance] with a calibration error of 1.5°C [*Müller et al.*, 1998]:

$$U_{37}^{k'} = 0.033 \times SST + 0.044. \quad (4)$$

3. Results

[12] The TEX$_{86}$ ranged between 0.36 and 0.65 or 8.4 and 25.9°C when translated to SST using the recent temperature calibration of *Kim et al.* [2010] (Figure 2a). The average TEX$_{86}^{H}$ temperature estimate was lower in the glacial (17.7°C) than during the interglacial complex (21°C). Most of the changes in TEX$_{86}^{H}$-derived temperatures (Figure 2a) were synchronous with the known cold events (Iberian Margin Stadials, IMS; areas shaded gray and horizontal numbers in Figure 2b) and warm events (Iberian Margin Interstadials, IMI; vertical numbers) previously reported for the $U_{37}^{k'}$ record [*Martrat et al.*, 2004] (Figure 2b). These events are listed from more to less recent and include in their nomenclature the number of the climate cycle to which they belonged (e.g., 2IMS-7 is the seventh cooling stage of limited duration within the second climate cycle) [cf. *Martrat et al.*, 2007]. The $U_{37}^{k'}$ and TEX$_{86}^{H}$-derived temperatures show great variability in the glacial (2IMI and 2IMS events 1 to 9), whereas only six stadials and interstadials are observed during the interglacial complex, when longer periods of stability at high temperatures are observed (2IMI and 2IMS events 10 to 15). The BIT values are low, ranging from 0.01 to 0.17 with average BIT values nearly identical for MIS 6 (0.05) and MIS 7 (0.06) (Figure 2e). Concentrations

of the marine isoprenoid GDGTs varied between 54 and 150 μg/g sediment (Figure 2a) while those of C$_{37}$ alkenones varied between 5 and 45 μg/g sediment (Figure 2a).

4. Discussion

4.1. Comparison of SST Estimates in Stadials and Interstadials

[13] The trends in TEX$_{86}^{H}$ temperatures (Figure 2a) are in line with both the $U_{37}^{k'}$ temperatures (Figure 2b) and the δ^{18}O record of the planktonic foraminifer *G. bulloides* (Figure 2f), suggesting that the TEX$_{86}^{H}$ proxy also records temperature changes in the Alboran Sea. No temporal offset of the temperature proxy records derived from crenarchaeota, coccolithophores and foraminifera are observed indicating that dissimilar sedimentation processes of these organisms did not play a major role [e.g., *Mollenhauer et al.*, 2005], at least not on the time scale investigated here. This agrees with previous observations in the nearby northwest African margin where large age offsets occur under specific depositional conditions only, that is, at sites where lateral advection was predominant or TOC content was at its highest [*Mollenhauer et al.*, 2005, 2007]. Importantly, the TEX$_{86}^{H}$ record shows that crenarchaeota like the haptophyta experienced major variations in temperature in stadial-interstadial episodes. The events recorded with the paleothermometers exhibited equivalent and persistently repeated saw-tooth morphology, that is, oscillations commenced with an abrupt warming in just a few centuries, immediately followed by a gradual cooling trend (Figure 2c). The coherent patterns in temperature change can be illustrated by cross-plotting TEX$_{86}^{H}$ and $U_{37}^{k'}$ temperatures, showing the detrended difference between the two proxies over time (Figure 2d, left axis), that is, normalizing each value for the period studied by subtracting the sample mean and dividing the result for the sample standard deviation, and their scatter. Nearly sixty percent of total variability in the TEX$_{86}^{H}$ can be explained by the linear relationship between the TEX$_{86}^{H}$ and $U_{37}^{k'}$ SST estimates (r^2 = 0.59; n = 199; Figure 3a).

[14] Although the patterns in temperature change are the same, the absolute temperature ranges are different for the two molecular proxies. The TEX$_{86}^{H}$-derived temperatures are generally higher than those estimated by the $U_{37}^{k'}$, although this difference is less than 3°C in 81% of the record (Figure 2d). The analytical error in both the TEX$_{86}^{H}$ and $U_{37}^{k'}$ indices is <0.5°C and the calibration error is ~2.5°C for TEX$_{86}^{H}$ [*Kim et al.*, 2010] and 1.5°C for $U_{37}^{k'}$ [*Müller et al.*, 1998]; thus, deviations of less than ±3°C could be considered within the error of the estimate. However, during certain periods, particularly during warm IMS events within the MIS6 glacial, TEX$_{86}^{H}$ temperatures are much higher than $U_{37}^{k'}$ temperatures, up to 10°C (Figure 2). Possible reasons to explain why the TEX$_{86}^{H}$ temperatures are generally higher than $U_{37}^{k'}$ temperatures and even more during certain time periods are discussed in detail below.

4.2. Terrigenous Influence

[15] The Alboran Sea area is strongly influenced by the surrounding landmasses [*Fabres et al.*, 2002] and, thus, large amounts of soil organic matter may be present in the sediment which, due to an influx of soil-derived isoprenoid GDGTs, can bias TEX$_{86}^{H}$ temperature estimates [*Weijers*
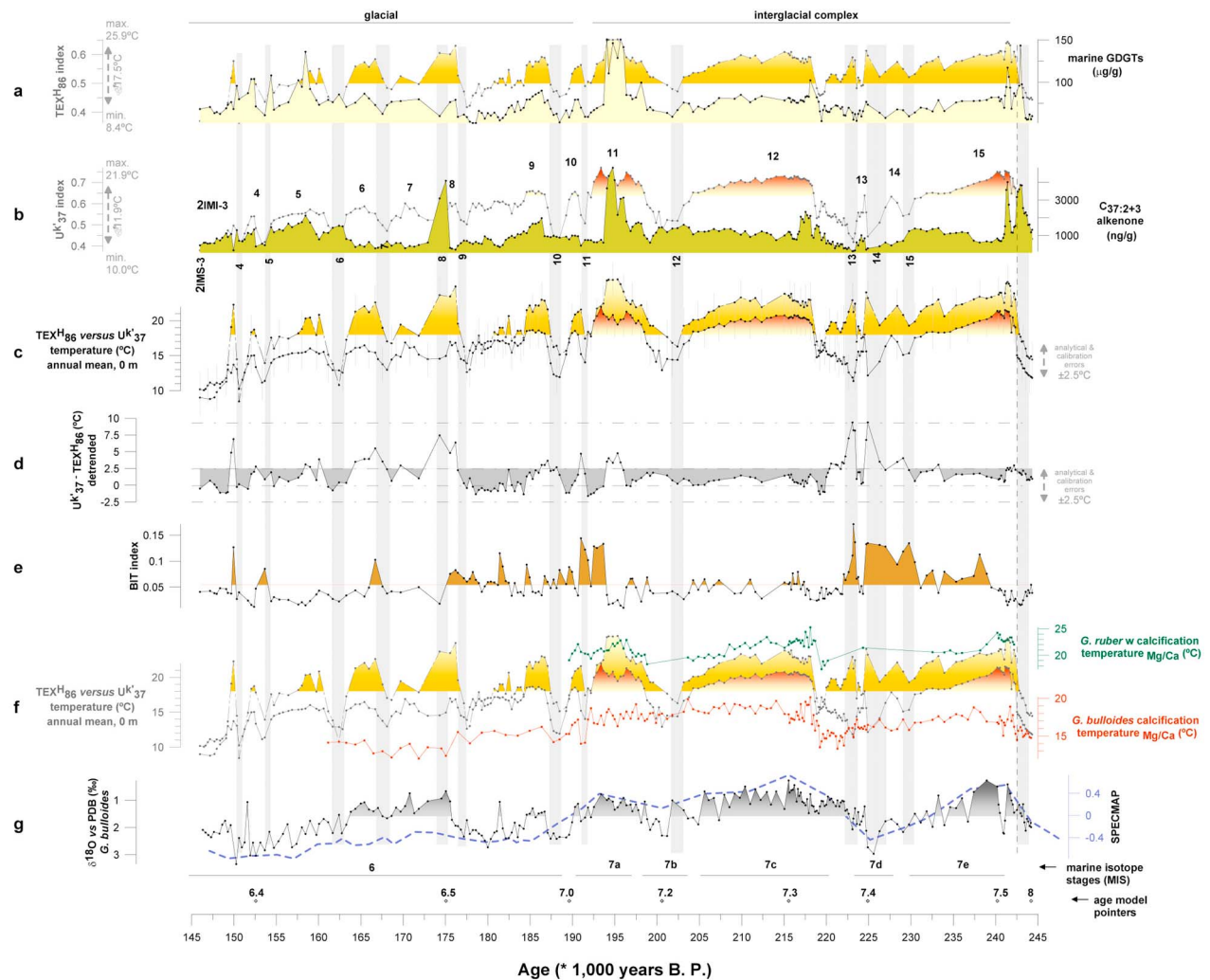
Figure 2. Temperature estimations in core ODP-977A during the penultimate interglacial-to-glacial cycle. They are based on (a) the tetraether index TEX_{86}^{H} (this study) and (b) the alkenone unsaturation index $U_{37}^{k'}$ [*Martrat et al.*, 2004]; values above present annual SST (18.0°C) are shaded yellow and red, respectively. The warm events (Iberian margin interstadials, IMI) and cold spells (Iberian margin stadials, IMS; areas shaded gray) were reported by *Martrat et al.* [2004, 2007]. The nomenclature of these events includes the number of the climate cycle to which they belonged (e.g., 2IMS-7 is the seventh cooling stage of limited duration within the second climate cycle) [*Martrat et al.*, 2007]. In addition, the concentration of marine GDGTs (i.e., those used in the TEX_{86}^{H}) as well as alkenones are plotted. (c) TEX_{86}^{H} (dashed profile) (this study) and $U_{37}^{k'}$ (solid profile) [*Martrat et al.*, 2004] temperatures plotted on the same axis. Vertical gray bars indicate the combined analytical and calibration error. (d) Detrended difference between TEX_{86} and $U_{37}^{k'}$ temperatures. (e) BIT index as a tracer of soil-sourced organic matter. (f) TEX_{86}^{H} (dashed profile) and $U_{37}^{k'}$ (solid profile) temperatures plotted on the same axis together with Mg/Ca temperatures derived from *G. ruber* and *G. bulloides* [from *Gonzalez-Mora et al.*, 2008]. (g) Marine isotope stages (MISs) 6 and 7 are roughly defined on the $\delta^{18}O_{cc}$ of *G. bulloides* [*Martrat et al.*, 2004] by comparison with the SPECMAP standard isotope curve (dotted line), which provides the control points (diamonds) used for the age model [*Martinson et al.*, 1987].

et al., 2006]. Minor peaks in the BIT record (Figure 2e), a tracer for soil-derived organic matter, are observed during the glacial (e.g., 2IMI-3, 2IMS-7, 2IMS-11) and a colder period around 225 ka (2IMS-13, 2IMS-14, 2IMS-15). However, there is no correlation between TEX_{86}^{H} and BIT index ($r^2 = 0.015$, 95% significance; Figure 3c) and BIT values are always low (<0.17; Figure 2e), indicating only a small input of riverine soil organic matter [cf. *Hopmans et al.*, 2004; *Weijers et al.*, 2006; *Huguet et al.*, 2007b; *Walsh et al.*, 2008], consistent with the absence of a large river system in the area and the relatively small and irregular fluvial input in the Alboran Sea [*Fabres et al.*, 2002]. Thus, a substantial impact of soil organic matter input on the TEX_{86}^{H} values is unlikely.
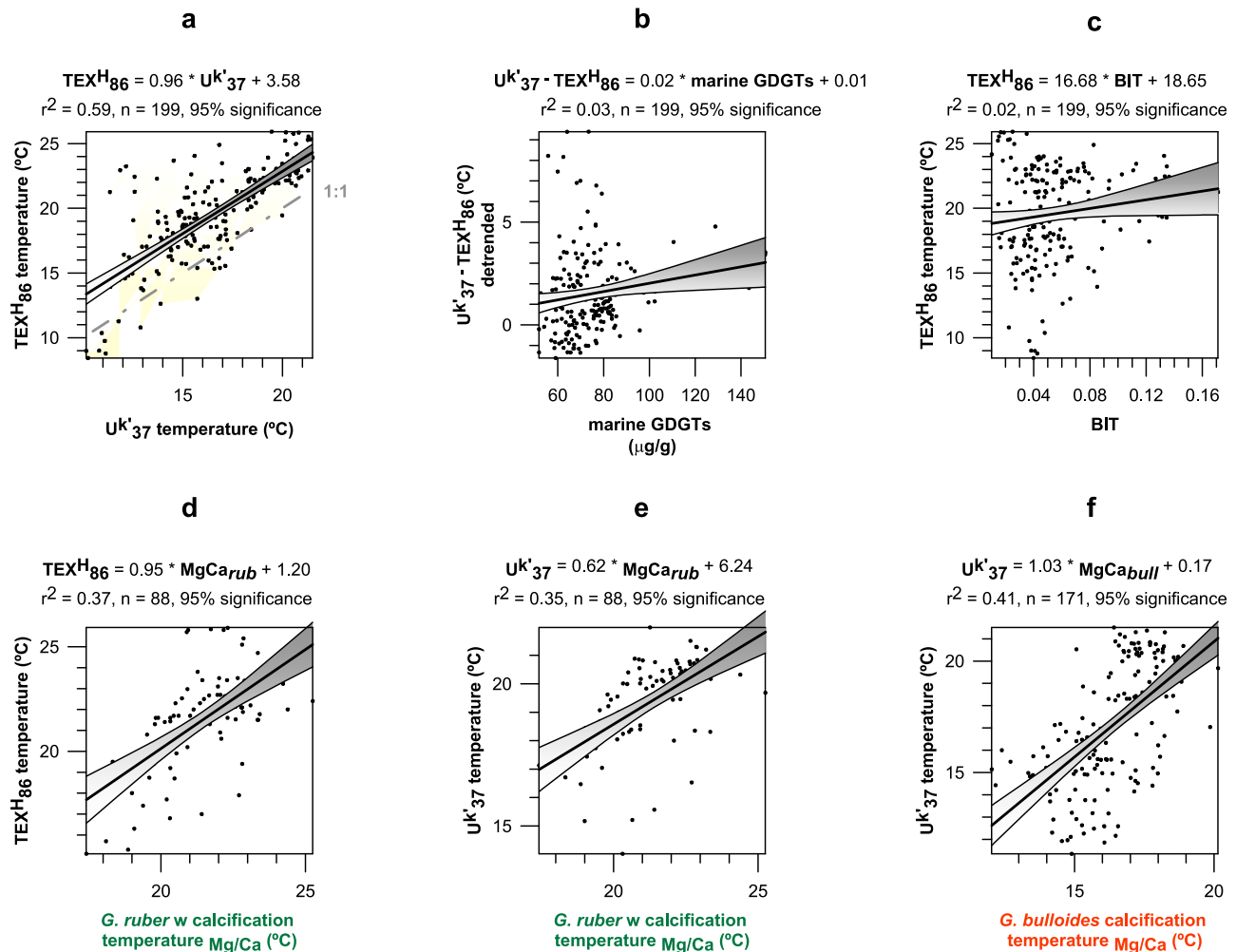
Figure 3. Correlations between different parameters in the ODP-977A core during MIS6 and MIS7. (a) TEX^{H}_{86} and $U^{k'}_{37}$, (b) difference between TEX^{H}_{86} and $U^{k'}_{37}$ and concentrations of marine isoprenoid GDGTs, (c) TEX^{H}_{86} and BIT, (d) TEX^{H}_{86} and Mg/Ca ratio of *G. ruber* [from *Gonzalez-Mora et al.*, 2008], (e) $U^{k'}_{37}$ and Mg/Ca ratio of *G. ruber* [from *Gonzalez-Mora et al.*, 2008], and (f) $U^{k'}_{37}$ and Mg/Ca ratio of *G. bulloides* [from *Gonzalez-Mora et al.*, 2008].

4.3. Vertical SST Distributions and Upwelling

[16] The agreement in pattern and, to some extent, absolute temperature estimates between TEX^{H}_{86} and $U^{k'}_{37}$ temperatures for a large part of the record suggests that the organisms producing the lipids on which these proxies are based are reflecting mostly temperatures of the same depth. Haptophyta are light-dependent, which restricts them to the photic zone in the western Mediterranean [*Ternois et al.*, 1997]. Due to their resistance to microbial or chemical degradation, alkenone distributions exported to the bottom waters trace temperatures corresponding to surface level, where maximum production occurs [*Bentaleb et al.*, 1999]. In contrast, marine crenarchaeota are thought to be mostly chemoautotrophs [*Könneke et al.*, 2005; *Herndl et al.*, 2005; *Wuchter et al.*, 2003, 2006a], are not light-dependent as they use ammonia as their energy source and can thrive deeper in the water column as has been shown in numerous studies [e.g., *Massana et al.*, 1998; *Murray et al.*, 1999; *Karner et al.*, 2001; *Herndl et al.*, 2005]. However, previous studies have also shown that the TEX_{86} correlates well with surface water temperatures (depths < 100 m) and that the signal in the deeper water layers and sediments is primarily derived from these surface waters because of preferential transport of GDGTs from these layers compared to deeper waters [*Wakeham et al.*, 2003; *Wuchter et al.*, 2006b; *Huguet et al.*, 2006a]. Nevertheless, some studies have noted that TEX_{86} records subsurface (between ~40 and 100 m) temperatures rather than SST [e.g., *Menzel et al.*, 2006; *Huguet et al.*, 2007a; *Lopes dos Santos et al.*, 2010]. Since TEX^{H}_{86} derived temperatures generally agree or are higher than $U^{k'}_{37}$ derived temperatures, migration of crenarchaeota to deeper, colder waters is unlikely to explain the generally higher TEX^{H}_{86} temperatures compared to those of the $U^{k'}_{37}$ (Figure 2).

[17] It has been suggested that contributions of pelagic Euryarchaeota can cause SST overestimation in areas affected by upwelling [*Turich et al.*, 2007] although this hypothesis has been disputed [*Schouten et al.*, 2008; *Turich et al.*, 2008]. Upwelling is a distinctive feature in the Alboran Sea, which

may also have been the case in the past. Over the last glacial cycle, waters from this area were more productive during the interstadials than in stadials, as shown by studies of coccoliths [*Colmenero-Hidalgo et al.*, 2004], calcium carbonate, barium excess, total organic carbon and alkenone concentration [*Moreno et al.*, 2004]. However, TEX$^{H}_{86}$ measurements from upwelling areas show temperature estimates consistently lower than expected [*Kim et al.*, 2008; *Huguet et al.*, 2007a; *Lee et al.*, 2008]. Furthermore, there is no correlation between the offset of TEX$^{H}_{86}$ with $U^{k'}_{37}$ and the concentration of marine isoprenoid GDGTs (Figure 3b). Hence, at this point it seems unlikely that upwelling intensity has resulted in TEX$^{H}_{86}$ values yielding higher SST estimates than $U^{k'}_{37}$.

4.4. Seasonal Differences

[18] The core top calibrations used to derive the TEX$^{H}_{86}$ and $U^{k'}_{37}$ temperatures in principle provide annual mean temperature estimates at surface level [*Kim et al.*, 2008, 2010; *Müller et al.*, 1998]. Alkenone unsaturation index measurements in surface sediments of core ODP-977A ($U^{k'}_{37}$-SST = 18.2°C; 0–2 cm representing the average of past 130 years) [*Martrat et al.*, 2004] show a good correspondence with present average annual SST data (18.0 ± 0.4°C) (MEDAR Group, Mediterranean Targeted Project II, Mass Transfer and Ecosystem Response, 2002, http://www.ieo.es). Furthermore, the $U^{k'}_{37}$-derived SST estimate for the last glacial maximum in the Alboran Sea ($U^{k'}_{37}$-SST = 12°C, 21 kyr ago) [*Cacho et al.*, 1999; *Martrat et al.*, 2004] also compares well with other reconstructions of annual mean SST based on a comprehensive set of foraminifera calibration data for the Mediterranean Sea [*Hayes et al.*, 2005; *Pérez-Folgado et al.*, 2003; 2004]. *Bárcena et al.* [2004] showed, using sediment traps, that coccolith fluxes of the alkenone producing species *Geophyrocapsa oceanica* and *Emiliania huxleyi* are particularly high after turbulent winter conditions. However, at Mediterranean latitudes, productivity is not limited by light or nutrients and these species albeit less abundant, are always present.

[19] The in general higher temperature of the TEX$^{H}_{86}$ compared to the $U^{k'}_{37}$ specifically during some events could suggest that the GDGTs of the crenarchaeota are at that time derived from a different and warmer period, that is, the summer season. Several studies in other areas have shown crenarchaeotal abundance to be negatively correlated with phytoplankton abundance, probably due to competition for nutrients [e.g., *Murray et al.*, 1999; *Wuchter et al.*, 2006a]. It has been shown that Crenarchaeota can thrive at ammonia concentrations well below those needed by ammonium oxidizing bacteria [*Martens-Habbena et al.*, 2009], thus, declining nutrients would give crenarchaeota a competitive advantage. Unfortunately, studies on the seasonality of marine crenarchaeota in the Alboran Sea are, to the best of our knowledge, presently lacking. Recent sediment studies in the Mediterranean suggest, however, that there may be a seasonality bias in the TEX$_{86}$. *Castañeda et al.* [2010] found that TEX$_{86}$ derived SST from the core top of a sediment core in the eastern Mediterranean was in agreement with local summer SST while $U^{k'}_{37}$ derived SST reflected annual mean SST. Furthermore, *Leider et al.* [2010] showed that TEX$_{86}$ in core tops from the Adriatic Sea tend to reflect summer

temperatures rather than annual mean. Indeed, TEX$^{H}_{86}$ derived SST estimates from core tops in the Alboran Sea are higher than annual mean SST (V. Nieto Moreno et al., unpublished data, 2010) also suggesting that it mainly reflects the summer season in the Mediterranean. The reason that TEX$_{86}$ is skewed toward summer temperatures in most of the Mediterranean may not have to do with a preferred growth season of marine crenarchaeota. Instead, the summer season might simply be the time of largest export flux of GDGTs from the surface waters [cf. *Wuchter et al.*, 2006b]. Indeed, *Sanchez-Vidal et al.* [2005] observed that the time of largest particle and organic carbon export in the eastern subbasin of the Alboran Sea was during the summer season of 1997. This preferential export of GDGTs would not need to affect the export of alkenones as these are tied to coccolith fluxes which can be independent of the main particle fluxes due to the mineral ballast. This preferred timing of export could thus explain the generally higher TEX$^{H}_{86}$ temperatures compared to the $U^{k'}_{37}$ SST estimates.

[20] To further investigate the seasonality hypothesis, we compared the TEX$^{H}_{86}$ and $U^{k'}_{37}$ SST estimates with Mg/Ca derived temperatures for the planktonic foraminifera *Globigerinoides ruber* and *Globigerina bulloides* [*Anand et al.*, 2003; *Elderfield and Ganssen*, 2000] from core ODP-977A for the same time interval as studied here [*Gonzalez-Mora et al.*, 2008]. At the Iberian margin, the more stenotopic species *G. ruber* (white) (a "warm" indicator species) yields a discontinuous record of temperature change, while *G. bulloides* (an "upwelling" indicator species) exhibits a relatively continuous Mg/Ca record [*Skinner and Elderfield*, 2005] (Figure 2f). This is different in other environments: for example, in the Arabian Sea, *G. ruber* thrives throughout the year and *G. bulloides* occurs mainly when surface waters contain high nutrients during upwelling or convective mixing [*Anand et al.*, 2008]. In core ODP-977A, the Mg/Ca–*G. ruber* temperatures (from 17.4°C to 25.2°C) are in a similar range as those of TEX$^{H}_{86}$ derived temperatures and generally higher than those of $U^{k'}_{37}$ (Figure 2f). Furthermore, Mg/Ca–*G. ruber* (white) temperatures correlate reasonably well with TEX$^{H}_{86}$ derived temperatures ($r^2 = 0.37$, n = 88; Figure 3d) although also with $U^{k'}_{37}$ derived temperatures ($r^2 = 0.35$, n = 88; Figure 3e). In contrast, Mg/Ca–*G. bulloides* calcification temperatures (from 12°C to 20.2°C) are more similar to $U^{k'}_{37}$ derived temperatures (Figure 2f) and also covary ($r^2 = 0.41$, n = 171; Figure 3f). These data tentatively suggest that TEX$^{H}_{86}$ indeed reflects temperatures during warmer seasons, as does *G. ruber* (white). Alternatively, though less likely, the observed differences between TEX$^{H}_{86}$ and $U^{k'}_{37}$ derived temperatures are due to certain biases in the global calibration of both proxies relative to each other or caused by local biases specific for the Mediterranean thereby requiring local calibrations. To properly evaluate the effect of seasonality on the temperature proxies a local Mediterranean calibration between TEX$^{H}_{86}$ and summer SST would be needed as well as the study of seasonality in crenarchaeota and haptophyta ecology as well as lipid fluxes in the Alboran Sea.

5. Conclusions

[21] The TEX$^{H}_{86}$ record of the Alboran Sea shows trends coherent with that of the $U^{k'}_{37}$ and confirms the previously

inferred stadial and interstadial episodes detected with the $U_{37}^{k'}$ in the study area [*Martrat et al.*, 2004]. The absolute temperature estimates of TEX$_{86}^{H}$ and $U_{37}^{k'}$ agree reasonably well, that is, a large part is within the estimation error of these proxies. However, in some part of the records TEX$_{86}^{H}$ is consistently higher than $U_{37}^{k'}$ predominantly during interstadials. Soil organic matter input, changes in depth habitat or other archaeal sources of GDGTs are unlikely to explain why differences between the two proxies increase during warming events. More likely, core top studies and comparison with Mg/Ca of planktonic foraminifera suggests that the offset may in part be due to seasonality effects on TEX$_{86}^{H}$ where the latter is more reflective of the warmer, summer season rather than annual mean SST. Alternatively, the global calibrations of both proxies contain certain biases compared to each other or are locally biased in the Mediterranean.

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