Climate conditions in the westernmost Mediterranean over the last two millennia: An integrated biomarker approach

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A B S T R A C T

Climate conditions in the westernmost Mediterranean (Alboran Sea basin) over the last two millennia have been reconstructed through integration of molecular proxies applied for the first time in this region at such high resolution. Two temperature proxies, one based on isoprenoid membrane lipids of marine Thaumarchaeota (TEX86, tetraether index of compounds consisting of 86 carbons) and the other on alkenones produced by haptophytes (U37C index) were applied to reconstruct sea surface temperature (SST). Both records reveal a progressive long term decline in SST over the last two millennia and an increased rate of warming during the second half of the 20th century. This is in accord with previous temperature reconstructions for the Northern Hemisphere. TEX86 temperature values are higher than those inferred from U37C, probably due to differences in the bloom season of haptophytes and Thaumarchaeota, and reflect summer SST. The branched vs. isoprenoid tetraether index (BIT index) suggests a low contribution of soil organic matter (OM) to the sedimentary OM. The stable carbon isotopic composition of long chain n-alkanes indicates a predominant C3 plant contribution, with no major change in vegetation over the last 2000 yr. The distribution of long chain 1,14-diols (most likely sourced by Proboscia spp. in this setting) provides insight into variation in upwelling conditions during the last 2000 yr and depicts a correlation with the North Atlantic Oscillation (NAO) index, providing evidence of enhanced wind induced upwelling during periods of a persistent positive mode of the NAO.

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1. Introduction

Beyond the instrumental record, the reconstruction of natural climate variability requires reliable proxies for a better understanding of the climate system at longer timescales and a trustworthy prediction of climate change scenarios (Jansen et al., 2007). Sea surface temperature (SST) is one of the most important variables for deciphering past climate. Hence, several lipid-based proxies have been developed over the last few decades for temperature reconstruction (e.g. Eglinton and Eglinton, 2008). The first proxy based on biomarkers to infer palaeo-SST was the U37C index (Brassell et al., 1986). It uses the ratio of di- and tri-unsaturated C37 long chain ketones (alkenones) biosynthesized by haptophyte algae and is used as a proxy for average annual SST (Prahl and Wakeham, 1987; Müller et al., 1998). In 2002, Schouten et al. proposed a new proxy for reconstructing past SST, based on archaeal isoprenoid membrane lipids, the TEX86 index (tetraether index of compounds consisting of 86 carbons), an expression of the number of cyclopentane moieties in the marine dihydroxyketyl tetraethers (GDGTs) in the membrane lipids of marine Thaumarchaeota. The latter are prokaryotic single cell microorganisms occurring ubiquitously in the marine environment where they act mainly as nitrifiers (e.g. Wuchter et al., 2006). The TEX86 index correlates well with water temperature in the upper water column (0–100 m) and is suitable for reconstructing SST. Higher temperature results in an increase in the relative amount of GDGTs with two or more cyclopentane moieties (Wuchter et al., 2004, 2005; Kim et al., 2008). Recently, a new TEX45 calibration was proposed by Kim et al. (2010), which is based on a logarithmic function of TEX45 (TEX86) and reconstructs SST more reliably.

Sedimentary lipids may also be used to reconstruct changes in the relative contribution from plants to marine sediments,
fluctuating in parallel with climatic conditions (e.g. Rosell-Melé and McClymont, 2007). Long chain n-alkanes are major lipid components of the epicuticular wax of terrestrial higher plant leaves (Eglinton and Hamilton, 1967), which is transported to the ocean by wind (Scheufler et al., 2003) or fluxurally run off (Castaheda et al., 2007), being deposited and well preserved in marine sediments. The BIT index (branched vs. isoprenoid tetraether index) allows reconstruction of past fluxual input of soil organic matter (OM) to the marine environment (Hopmans et al., 2004; Weijers et al., 2006). Further information on past climate conditions can be obtained from long chain 1,14-diols, biosynthesized mainly by diatoms of the genus Proboscia, and often abundant in upwelling regions (Sinninghe Damsté et al., 2003; Rampen et al., 2007). They have been applied as a proxy for reconstructing intensity in upwelling during the last 90 kyr in the Arabian Sea (Rampen et al., 2008). Recently, Rampen et al. (2011) extended the biological occurrence of long chain 1,14-diols to a second group of marine microalgae (Apedinella radians), which occurs globally, although predominantly in estuarine waters. This finding might have potential implications for the use of long chain 1,14-diols as biomarkers of Proboscia diatoms and as an indicator of upwelling conditions.

Using these organic proxies, we have performed a detailed biomarker study of the western Mediterranean (Alboran Sea basin), a key area for palaeoclimate and palaeoceanographical reconstruction due to its high sensitivity to climate variability (Nieto-Moreno et al., 2011; Moreno et al., 2012). The Mediterranean area has been identified as a highly vulnerable region for climate change, with projected alteration and environmental impact much more severe than in other territories in the world (Durrieu de Madron et al., 2011). SST reconstruction in the region was based mostly on alkane and naphthenic and focussed on the last deglacial cycle at millennial timescales (Cacho et al., 1999, 2001; Emeis et al., 2000, 2002; Marchal et al., 2002; Martrat et al., 2004, 2007). TEX$_{86}$ has also been applied, together with U$_{C36}$, to confirm the abrupt temperature variation during the penultimate interglacial to glacial cycle, where the latter reflected mainly the warmer summer season rather than annual mean SST (Huguet et al., 2011). Moreover, the n-hexadecanol/n-nonadecane index has been applied in the Alboran Sea to record enhanced OM oxidation and well ventilated deep seawater during cold abrupt events (Cacho et al., 2000). All the records revealed the sensitivity of the region to short term climate change (Dansgaard/Oeschger cycles, Heinrich events and Holocene cold events, Hidalgo et al., 2004), and a possible role of the North Atlantic Oscillation (NAO) as a driving mechanism of natural climate variability during the Holocene was suggested (Rimbu et al., 2003, 2004). Nevertheless, high resolution marine records focussing on the last few millennia are comparatively scarce. In this regard, the Late Holocene is an important reference period for evaluating the significance of future climate change and impact, because forcing factors and climate boundary conditions have been similar to those of the present day (e.g. Mayewski et al., 2004).

Hence, palaeoclimatic reconstruction carried out for this time period may significantly contribute to our overall understanding of Earth’s climate at regional and global scales. Recent work on the westernmost Mediterranean has reported climate fluctuation during the last 4000 yr, allowing characterisation of dry and humid periods based on variation in chemical and mineralogical composition, as well as grain size distribution (Martín-Puertas et al., 2010; Nieto-Moreno et al., 2011). We studied two marine box cores recovered from the westernmost Mediterranean at high resolution and have performed TEX$_{86}$ and U$_{C36}$ palaeothermometry, complemented by the information gathered from other proxies such as the BIT index, the diol index and the carbon isotope composition of n-alkanes.

2. Modern climatic setting

The western Mediterranean is in a transitional zone between the mid-latitude westerlies system and the subtropical high pressure belt, linked to the North Atlantic climate system through the Strait of Gibraltar and under the influence of the dominant mode of winter climate variability in the North Atlantic region; the NAO (Trigo et al., 2002).

The downward flux of particles in the westernmost Mediterranean region is predominantly controlled by fluvial discharge and upwelling-induced primary production at the northern edge of the western Alboran Gyre (WAG; Fabres et al., 2002) (Fig. 1a). Maximum flux of haptophytes takes place during March and October, before the most productive period (Bárcena et al., 2004). According to García-Gorriz and Carr (1999, 2001), in the present-day Alboran Sea basin, phytoplankton blooms occur predominantly from November to March at SST < 17.4 °C (Fig. 1c and d) whereas the non-bloom period is from May to September with SST > 19.5 °C (Fig. 1b and e) and light is not a growth limiting factor throughout the year. A transition period occurs in April–May, when thermal stratification starts, and in October–November, coinciding with maximum wind variability and loss of stratification within the basin. Presently, SST in the Alboran Sea basin (Santoleri et al., 1994) ranges between 13 and 16 °C in winter, 19 and 21 °C in the fall and 23 and 25 °C in summer; the annual average SST ranges between 18 and 20 °C (Fig. 1b–e).

At Site 384B exchange of water between the Mediterranean and the eastern Atlantic takes place. The site is ca. 110 km east of the Strait of Gibraltar and close to the influence of the upwelling cell associated with the northern edge of the WAG (Fig. 1a). This geostrophic front, the so-called Málaga Front, is associated with high productivity (Bárcena and Abrantes, 1998). The upwelling is induced via two main mechanisms: the southward drifting of the Atlantic Jet, and more importantly, the wind driven upwelling when westerlies blow (Saran et al., 2000). The location of core 436B, close to the influence of the upwelling cell associated with the northern edge of the WAG, makes it suitable for studying upwelling intensity in the Alboran Sea using long chain diols.

3. Material and methods

3.1. Core material and sampling

Two box cores, 384B (35°59.161′N, 4°44.976′W, 1022 m below sea level (m.b.s.l.) and 436B (36°12.318′N, 4°18.800′W, 1108 m.b.s.l.), recovered from the southwestern Alboran Sea basin in 2002 using a KP 1.5 box corer (50 × 50 × 50 cm) during the Training-Through-Research Cruise 17 (Sagas-08 Cruise), Leg 1, on R/V Professor Logachev, were selected (Fig. 1a). On retrieval, they were sub-sampled using PVC pipes (50 cm × 11.8 cm i.d.) inserted into the sediment. One core from each box core was immediately frozen on board at −18 °C and sampled in 1 cm slices in the laboratory to provide a high resolution record. The sediments consisted mainly of water-saturated brownish mud in the upper part and quite homogeneous greyish clay with foraminifera and some shell fragments in the lower part.

3.2. Age-depth model

The model is based on the activity-depth profiles of $^{210}$Pb and $^{137}$Cs, together with 14C dating (Fig. 2). Determination of $^{210}$Pb activity was accomplished through the measurement of its daughter nuclide, $^{210}$Po, following the methodology described by Sánchez-Cabeza et al. (1998). Samples were dried at 50 °C to
constant wt., and dry bulk density and water content were calculated. Briefly, after addition of a given amount of $^{209}$Po as internal tracer, an aliquot (200–300 mg) of each sample was dissolved in acid by using an analytical microwave oven. Po isotopes were plated onto pure Ag discs in HCl (1 N) at 70°C, with stirring for 8 h. Po emission was subsequently counted with $\alpha$-spectrometers equipped with low-background silicon surface barrier (SSB) detectors for $4 \times 10^3$ s. $^{226}$Ra (via $^{214}$Pb through its 351 keV gamma emission line) and $^{137}$Cs were determined by way of $\gamma$-spectrometry using a high purity well-type Ge detector. Excess $^{210}$Pb activity ($^{210}$Pb$_{ex}$) was determined by subtracting the $^{226}$Ra activity (assumed to equal the supported $^{210}$Pb activity) from the total $^{210}$Pb activity (Fig. 2a and b).

$^{14}$C AMS dating was performed on picked planktonic foraminifera ($Globigerina bulloides$) obtained from the >125 µm fraction and analysed by way of accelerator mass spectrometry (Poznan Radiocarbon Laboratory). Radiocarbon ages were calibrated to calendar years (yr AD) using the CALIB 6.0 software (Stuiver and Reimer, 1993) and the MARINE09 curve (Reimer et al., 2009), assuming a marine reservoir age correction of 400 yr. Data are reported with $2\sigma$ uncertainty (Fig. 2c and d). One post-modern sample was converted to yr AD using the CaliBomb software (Reimer et al., 2004) and the calibration dataset of Levin and Kromer (2004), updated by Levin et al. (2008).

3.3. Lipid extraction and fractionation

Ca. 5 g of sediment (dry mass) was freeze dried, homogenised with an agate mortar and extracted with an accelerated solvent extractor (DIONEX 200) using dichloromethane (DCM) and MeOH (9:1 v/v) at 100°C and 7.6 × 10⁶ Pa. An aliquot of the extract was separated into apolar, ketone and polar fractions using a Pasteur pipette column filled with activated Al₂O₃ and eluted with hexane/DCM (9:1 v/v), hexane/DCM (1:1 v/v) and DCM/MeOH (1:1 v/v), respectively.

3.4. Determination of TEX$_{86}^{11}$ and BIT index

An aliquot of the polar fraction containing the GDGTs was eluted using hexane/isopropanol (99:1 v/v) to a concentration of
2 mg ml⁻¹ and filtered through a 0.45 μm PTFE filter attached to a 1 ml syringe. Analysis was performed using high performance liquid chromatography–mass spectrometry (HPLC–MS; Agilent 1100 with an auto-injector and Chemstation software) according to the procedure described by Hopmans et al. (2000) and Schouten et al. (2007). Detection was achieved using atmospheric pressure chemical ionisation (APCI). Identification and quantification of the different GDGT isomers were carried out via single ion monitoring (SIM, [M+H]+ ions at m/z 1300, 1298, 1296, 1292, 1050, 1036 and 1022, with a dwell time of 234 ms each; Schouten et al. (2007)). TEX86 was calculated on the basis of the relative abundance of branched and crenarchaeol following Hopmans et al. (2004), where in Eq. (2) roman numbers 5–7 correspond to terrestrial branched GDGTs from anaerobic bacteria with 4–6 methyl branches and 4 is crenarchaeol with four cyclopentane rings and one cyclohexane ring:

\[
\text{BIT} = \frac{[\text{GDGT-5}] + [\text{GDGT-6}] + [\text{GDGT-7}]}{([\text{GDGT-5}] + [\text{GDGT-6}])}
\]

Replicate analyses of Alboran Sea sediments have indicated a mean value of the standard deviation of 0.008 in the TEX86 index (Rodrigo-Gámiz, 2012).

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\[
\text{TEX86} = \frac{[\text{GDGT-2}] + [\text{GDGT-3}] + [\text{GDGT-4}]}{([\text{GDGT-1}] + [\text{GDGT-2}] + [\text{GDGT-3}])} \cdot \frac{[\text{GDGT-5}] + [\text{GDGT-6}] + [\text{GDGT-7}]}{([\text{GDGT-5}] + [\text{GDGT-6}])} + [\text{GDGT-4}]
\]

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The BIT index was calculated from the relative abundance of branched GDGTs and crenarchaeol following Hopmans et al. (2004), where in Eq. (2) roman numbers 5–7 correspond to terrestrial branched GDGTs from anaerobic bacteria with 4–6 methyl branches and 4 is crenarchaeol with four cyclopentane rings and one cyclohexane ring:

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\]

Replicate analyses of Alboran Sea sediments have indicated a mean value of the standard deviation of 0.024 in the TEX86 index (Rodrigo-Gámiz, 2012).

The ketone fraction was dissolved in ca. 30 μl hexane and injected under conditions described by Schouten et al. (1998, 2000). Samples were measured using a Hewlett Packard 6890 GC instrument provided with an on-column injector and flame ionisation detector and equipped with a fused silica column (50 m × 0.32 mm i.d.) coated with CP Sil-5 (0.12 μm thickness), with He as mobile phase. \( U'_{\text{C37}} \) was calculated from the relative abundance of long chain unsaturated ketones (di- vs. tri-unsaturated C37 ketones) following the definition by Prahl and Wakeham (1987):

\[
U'_{\text{C37}} = \frac{[\text{C37}_2]}{([\text{C37}_2] + [\text{C37}_3])}
\]

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\[
U'_{\text{C37}} = \frac{[\text{C37}_2]}{([\text{C37}_2] + [\text{C37}_3])}
\]
and annual mean atlas sea surface temperature (SST, 0–29°C) from 0 m water depth:

\[ U^E_{37} = 0.033 \cdot \text{SST} + 0.044 \] (5)

The calibration has been applied for the reconstruction of SST in the western Alboran Sea, showing good agreement with average annual mean SST (Cacho et al., 1999, 2002; Martrat et al., 2004, 2007).

3.6. Diol index

An aliquot of the polar fraction was eluted on a Pasteur pipette column filled with Al2O3 impregnated with AgNO3 and using pyridine, and heating at 60°C for 20 min. The calibration was prepared in EtOAc to a concentration of 2 mg ml⁻¹ and analysed using a Thermo Finnigan TRACE GC instrument equipped with a fused silica column (50 m × 0.32 mm i.d.) coated with CP-Sil-5 (0.12 µm film thickness), using He as mobile phase and the GC conditions as above for alkene analysis (Schouten et al., 1998, 2000). The gas chromatogram was coupled to a Thermo Finnigan DSQ quadrupole mass spectrometer. Identification and quantification of the different diol isomers was carried out via SIM at m/z 299, 313, 327 and 341 (Versteegh et al., 1997). The diol index was calculated using the relative abundances of the two dominant Proboscia diols (C28 and C30 14-diol) vs. the C30 15-diol (Rampen et al., 2008):

\[ \text{Diol index} = \left( \frac{[C_{28} \cdot 1.4-diol] + [C_{30} \cdot 1.4-diol]}{[C_{30} \cdot 1.4-diol]} \right) \] (6)

3.7. Alkane average chain length and weight average mean \( ^{13} \text{C} \) values

The apolar fraction was further separated using a Pasteur pipette column filled with Al2O3 impregnated with AgNO3 and using hexane as eluent. The carbon isotopic composition of the alkane fraction was determined using a Thermo Electron DELTA Plus XL isotope ratio monitor in a 19R–19S–19D–19M–19F system. GC conditions were similar to those described above for alkenone analysis. The average chain length (ACL) was calculated as the average number of carbons per molecule based on the abundance of the odd numbered n-alkanes as follows (Poynter and Eglinton, 1990):

\[ \text{ACL} = \Sigma \left( i \cdot X_i \right) / \Sigma X_i \] (7)

where \( X_i \) is the fraction of individual odd n-alkane abundance and \( i \) designates odd-numbered compounds in the range C27 to C32.

The carbon isotopic composition of the n-alkanes was determined using a Thermo Electron DELTA Plus XL isotope ratio monitor (irm)-GC–MS system. GC conditions were similar to those described above for alkene analysis (Schouten et al., 1998, 2000). The calibration has been applied for the reconstruction of SST in the western Alboran Sea, showing good agreement with average annual mean SST (Cacho et al., 1999, 2002; Martrat et al., 2004, 2007).

4. Results and discussion

4.1. Age-depth model and sedimentation rate

The calibration has been applied for the reconstruction of SST in the western Alboran Sea, showing good agreement with average annual mean SST (Cacho et al., 1999, 2002; Martrat et al., 2004, 2007).

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where \( X_i \) is the fraction of individual odd n-alkane abundance and \( i \) designates odd-numbered compounds in the range C27 to C32.

The carbon isotopic composition of the n-alkanes was determined using a Thermo Electron DELTA Plus XL isotope ratio monitor (irm)-GC–MS system. GC conditions were similar to those for GC analysis except that the film thickness of the CP-Sil-5 column was 0.4 µm and that a constant flow of He was used at 1.5 ml min⁻¹. Compounds were pyrolysed at 1450°C in an empty ceramic tube, which was pre-activated by a CH₄ flow of 0.5 ml min⁻¹ for 5 min as described by Poynter and Eglinton (1990) and Schouten et al. (1998, 2000). CO₂ of known isotopic composition was used as reference and a mixture of C16–C32 n-alkanes, each of known isotopic composition (~42‰ to ~25.6‰ vs. Vienna standard mean oceanic water (VSMOW)) was used to monitor the performance of the system. The stable carbon isotope composition is reported in the δ notation versus the Vienna Pee Dee belemnite PDB standard. The weighted mean isotopic composition of the odd n-alkanes (δ¹³CWMAS27–33) was determined as follows (Collister et al., 1994):

\[ \delta^{13}C_{WMAS27–33} = \sum X_i \cdot \delta_i \] (8)

where Xi is fraction of individual odd n-alkane abundance, δi is individual odd n-alkane δ value and i ranges from C27 to C33.
Holocene (18–20 °C). This is in good agreement with our reconstruction of 18.5–20 °C based on $^{13}$C (Fig. 3). The relatively high TEX$^{86}$ SST suggests that this reflects SST during the summer season. Although it is unknown when marine Thaumarchaeota thrive in the western Mediterranean, studies at other sites showed that they are generally abundant in surface waters when the majority of the phytoplankton is not blooming (Murray et al., 1998, 1999; Wuchter et al., 2005; Pitcher et al., 2011), which is summer for the western Mediterranean. The hypothesis that TEX$^{86}$-derived SST reflects summer SST is in agreement with other studies of the Mediterranean. Castañeda et al. (2010) reported TEX$^{86}$-derived SST of ca. 23–25 °C throughout the Holocene in eastern Mediterranean marine records and Leider et al. (2010) concluded that, for the most offshore sites, TEX$^{86}$ values in core tops (0–2 cm) from the Adriatic Sea reflect summer temperature. Furthermore, in the Alboran Sea basin, Huguet et al. (2011) showed higher TEX$^{86}$ SST than estimated from $^{13}$C during the MIS7 interglacial in core 977 ODP (21 °C), and Jiménez-Espejo et al. (2008) found average summer SST of 22 °C during the Middle Holocene, inferred from the modern analogue technique (MAT). Likewise, according to the MEDATLAS/2002 data base (MEDAR Group, 2002), the present average summer SST and annual mean SST of the upper water column (0 m) at the study sites is around 21 °C and 18 °C, respectively (Fig. 1b–e). Hence, we suggest that the TEX$^{86}$ temperature signal in the western Mediterranean sedimentary record reflects summer SST during the last two millennia. It is unlikely that our TEX$^{86}$ records are biased by the influence of soil-derived OM (cf. Weijers et al., 2006) since the BIT index is always low (<0.05; Fig. 3).

For both cores, TEX$^{86}$ and $^{13}$C SST progressively dropped from the highest values at the end of the DA (core 436B) and from the beginning of the MCA (core 384B) until the end of the LIA, where minimum values were attained (Fig. 3). $^{13}$C SST shows a sharp increase during the Industrial Period (IP), which is not mirrored in TEX$^{86}$-derived values, where SST depicts only a slight increase. The MCA has been described as the most recent pre-industrial warm period noted in Europe and over the Northern Hemisphere, warmer than the subsequent LIA, and also with temperature values comparable to those of the 20th century (Mann et al., 2008, 2009).
During the MCA and the LIA, an average temperature of 24 and 19 °C was recorded from TEX186 and U137, respectively, for both cores, although during the LIA the values are slightly lower in both cores. During the DA, TEX186 SST reached higher values than during the MCA, with a mean temperature of 24 °C (Fig. 3).

In summary, a progressive long term decline in SST is apparent during the last two millennia (Fig. 3), in accord with the reconstructed cooling due to solar irradiance forcing in the Northern Hemisphere during the last millennium (Fig. 4) (Mann et al., 1999; Jones et al., 2001). Annual mean temperature (based on U137) provides evidence for the LIA as the coldest period of the last two millennia, the MCA being the warmest pre-industrial period.

4.2.2. Terrestrial input fluctuation: land–ocean correlation

The BIT index reflects the relative fluvial input of soil OM to marine environments (Hopmans et al., 2004; Weijers et al., 2006). It varies between 0 and 1, representing marine and soil-devoid OM end members, respectively. BIT values are low in both cores, ranging from 0.02 to 0.04, with a mean of 0.03 (Fig. 3). The low values suggest only a minor input of soil OM to the basin and a mainly marine provenance for the OM. A slightly decreasing trend is observed during the DA and the MCA, with a slightly increasing trend during the LIA in both cores. Values were higher during the LIA than during the MCA for both cores. The riverine influence is slightly higher during wet periods (higher values during the LIA) than during dry periods (lower values during the MCA).

The n-alkanes exhibit a unimodal distribution between C27 and C33, peaking at C31, and with a strong odd/even preference, which indicates a typical origin from the epicuticular wax of terrestrial higher plant leaves (Eglinton and Hamilton, 1967). The ALO does not reveal any considerable fluctuation over the last two millennia, varying between 30.0 and 30.3 (Fig. 5), suggesting that the higher plant input has not undergone major fluctuation due to climate variability.

The stable carbon isotopic composition of the odd n-alkanes (C27 to C33) ranges from −31.2‰ to −29.6‰ for C27, −32.9‰ to −31.0‰ for C29, −32.6‰ to −31.4‰ for C31 and −32.5‰ to −30.4‰ for C33 in core 436B, i.e. it shows a rather uniform pattern. The δ13C values of the most abundant n-alkanes, C29 and C31, run essentially in parallel with a difference of <1‰, C31 being slightly more depleted in 13C, as observed for higher plant leaf wax (Collister et al., 1994; Bird et al., 1995; Zhao et al., 2000). The weighted average of the δ13C values of the long chain n-alkanes (δ13CWM27–33) can be used to track changes in the source and the relative contribution from plants using a different carbon fixation pathway during photosynthesis (i.e. C2 vs. C4 plants) and thus to establish the palaeohydrological conditions and vegetation composition through time (e.g. Schefuß et al., 2005). In general, C3 plants are the most 13C depleted and common, whereas C4 plants are found predominantly in tropical savannas, salt marshes and semi-deserts. C4 plants have leaf tissue δ13C values between −10‰ and −16‰ and C3 plants between −25‰ and −30‰ (Collister et al., 1994). The average δ13C values of leaf wax derived n-alkanes are depleted in 13C by ca. 8‰ and 4‰ in C3 and C4 plants, respectively (Rieley et al., 1993). The δ13CWM27–33 value of n-alkanes in core 436B fluctuates between −32.4‰ and −30.8‰ (Fig. 5). With reported end-member values of −36‰ for C3 and −21‰ for C4 vegetation (e.g. Castañeda et al., 2009), this indicates a predominant C3 plant contribution over the last two millennia.

Regarding the provenance of the n-alkanes, the Alboran Sea basin receives riverine and aeolian inputs deriving from both the Iberian margin and the African margin, so both sources might provide plant wax. A persistent positive mode in the NAO during the MCA and a negative one during the LIA has been proposed as the dominant mode of atmospheric circulation over Europe (Trouet et al., 2009, 2012), and enhanced aeolian transport of Saharan dust to the Mediterranean Sea has been evidenced during positive NAO phases (Moulin et al., 1997). Indeed, in the western Mediterranean region, an increase in fluvial input depicts the LIA, while drier environmental conditions are recognised during the MCA (a decrease in fluvial input and enhanced dust transport; Nieto-Moreno et al., 2011). There is no study on disentangling fluvial vs. aeolian plant wax n-alkanes contribution to hemipelagic sediments in the region. Nevertheless, fluvial sediment transport from the northern African margin to the basin seems negligible (Fabres et al., 2002) and aeolian transport of dust from the Sahara over the western Mediterranean represents 10–20% of the recent deep sea sedimentation (Guerzoni et al., 1997). Thus, an increase in fluvial input

![Fig. 5. Fluctuation in land plant input and upwelling intensity conditions during the last two millennia (500–2000 yr AD) for site 436B: NAO (blue line) and diol index, ACL, and the δ13CWM27–33 of odd n-alkanes (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).](image-url)
should promote a greater contribution from C$_3$ plants during wet periods. However, slightly lower $\delta^{13}$C$_{\text{VMA27-33}}$ values are found during the MCA, when stronger winds, greater aeolian input and a decline in fluvial elements are evident (Nieto-Moreno et al., 2011). In contrast, partly higher $\delta^{13}$C$_{\text{VMA27-33}}$ and BIT values are evident during the LIA when more humid conditions prevailed, thus suggesting that fluvial input from the Iberian margin mainly provides plant wax instead of aeolian input from the African margin, although the relationship is not altogether clear. Additional studies are required to support this hypothesis.

4.2.3. Upwelling and palaeoproductivity indicators

The diol index is high during the entire DA and the MCA, ranging between 0.35 and 0.5, followed by a decrease starting at the beginning of the LIA, reaching the lowest values around 1950 yr AD (diol index 0.2; Fig. 5). As shown by Rampen et al. (2007) for sediment traps from the Arabian Sea, the diol index may be a useful indicator to provide evidence for periods of enhanced intensity of upwelling, since their inferred source, mainly diatoms of the genus Proboscia, is often abundant in upwelling regions.

On the other hand, Vargas-Yáñez et al. (2008) showed a positive correlation between the NAO index and westerly wind-induced upwelling in the Alboran Sea. This enhanced wind-induced upwelling during periods of persistent positive NAO index, such as during the MCA, might have caused the slightly colder TEX$_{86}$-based SST values recorded for core 436B in relation to core 384B throughout the MCA until the beginning of the LIA due to upwelling of nutrient-rich cold water up into the photic zone. In the same way, during the wetter LIA, the sharp decrease in this index might be due to a turn into a negative mode of the NAO and thus weakened westerly wind-induced upwelling at this time interval.

4.3. Climate conditions since 1950 AD

Reconstruction shows a warming trend of TEX$_{86}$-based SST from 23.5 to 25.0 °C for both cores during the last century. This warming trend is not such apparent in the $U_37^c$-derived SST, possibly because the analytical error for $U_37^c$-derived SST is higher than for TEX$_{86}$-derived SST (0.024 and 0.008 respectively). The highest TEX$_{86}$-derived SST values are reached from 1980 onwards in both cores and the lowest between 1950 and 1980 (Fig. 3). These changes are of the same order of magnitude as the cooling trend over the last two millennia (25–23 °C for TEX$_{86}$). It is, however, not entirely known to what extent this is affected by bioturbation occurring in the surface mixed layer of the sediment cores. The constant activity of $^{210}$Pb$_{\text{ex}}$ in the upper 5 cm (Fig. 2a and b) indicates that bioturbation has occurred. The observed warming trend in the TEX$_{86}$ record is in accordance with other Northern Hemisphere multi-proxy temperature reconstructions (Rayner et al., 2003; Trenberth et al., 2007; Wahl et al., 2010) (Fig. 4).

Concerning marine productivity, the diol index shows a sharp increase in 436B, with values from 0.2 at 1950 yr AD to 0.4 at and after 1980 yr AD (Fig. 5). The NAO index shows a persistent trend to a positive mode during the last 25 yr (Fig. 5). The lowest values of the diol index suggest the absence of upwelling conditions, which coincides with a more negative mode of the NAO (less intense winds) and higher BIT values (greater input of fluvial-derived nutrients). During the last 30 yr, higher values of the diol index, a persistent positive mode of the NAO and a slightly lower influence of riverine input (BIT index), evoke intensification of the upwelling conditions in the area under the influence of the WAG. Therefore, based on the results obtained from the diol index, local upwelling events were occurring during the MCA and during the last century, when higher values are registered (Fig. 5). However, during these time intervals, SST based on TEX$_{86}$ is higher rather than lower, as would be expected from increased upwelling (Fig. 3). So our SST reconstruction is in accordance with other Northern Hemisphere temperature reconstructions (Fig. 4), even though SST reconstruction may have been influenced by changes in local upwelling.

5. Conclusions

A multi-proxy high resolution record based on organic fossil remains in two marine box cores from the Alboran Sea basin was obtained to further advance the reconstruction of climate variability during the last two millennia in the westernmost Mediterranean region. A progressive long term decline in SST was observed during the last two millennia (between 1.5 and 2 °C) and a sharp increase in SST took place during the second half of the 20th century (between 0.5 and 1.8 °C), with higher temperature during the MCA and lower temperature during the LIA in the western Mediterranean, in accord with previous Northern Hemisphere multi-proxy temperature reconstructions (Wahl et al., 2010). Both cores showed similar overall trends, although TEX$_{86}$-derived summer SST values were higher than those inferred from the $U_37^c$ ratio, which reflects annual mean SST or autumn SST. BIT values were low for both cores (<0.05), suggesting a predominant marine provenance for the OM and a low influence of riverine derived soil OM in the basin, which is higher during wet periods (LIA) than during dry periods (MCA). The stable carbon isotopic composition of odd $n$-alkanes suggested a predominantly C$_3$ plant contribution over the last two millennia and fluvial input as the main provenance source of the higher plants. The highest values of the diol index coincided with a more positive mode of the NAO and lower riverine influence (BIT index), and vice versa, suggesting a bloom of Proboscia spp. diatoms due to nutrient-rich upwelled cold water carried into the photic zone. This was caused by an intensification in the wind-induced upwelling conditions during positive NAO phases, such as those prevailing during the MCA or during the second half of the 20th century.

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