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SEA SURFACE TEMPERATURES RECONSTRUCTION OF THE LAST 16,000 YEARS IN THE EASTERN MEDITERRANEAN SEA.

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Riassunto. È stato svolto uno studio dettagliato su due box cores provenienti dal Mediterraneo orientale (BC02 e BC06) e su una carota a pistone proveniente dall'Adriatico meridionale (AD91-17), sul rapporto di sotto-saturazione degli alkenoni, un approccio molecolare per la ricostruzione delle temperature marine superficiali (SST) del passato. Lo scopo è stato di identificare gli eventi climatici degli ultimi 16 Ka, con particolare attenzione alle condizioni durante la formazione del sapropel S1. Un attento confronto delle tre curve della temperatura ha rivelato l'assenza di un raffreddamento nell'evento stadiale Younger Dryas e di un riscaldamento negli eventi interstadiali Boelling/Alleroed. Subito prima della base del sapropel S1, le SST calano per poi aumentare di circa 5°C durante l'intervallo di deposizione del sapropel. All'interno del sapropel S1, le SST mostrano un marcato riscaldamento seguito da un chiaro raffreddamento. Negli intervalli più alti le temperature sono per lo più costanti, sebbene si osservi sempre un evento caldo. Questa fase di riscaldamento potrebbe corrispondere al "Optimum Climatico Alto Medioevale" (nella carota AD91-17) e al "Optimum Romano" (nei box cores).

Abstract. A detailed study has been performed on two eastern Mediterranean box cores (BC02 and BC06) and on a southern Adriatic piston core (AD91-17) on the alkenone unsaturation ratio, a molecular proxy for past sea surface temperatures. The aim was to identify climatic events of the last 16 Ky, with particular attention on the conditions during formation of sapropel S1. All three temperature curves lack evidence for cooling in the Younger Dryas stadial and warming in the Boelling/Alleroed interstadial events. Just prior to the sapropel S1 base, SST cooled and increased by about 5°C during the sapropel deposition interval. Within sapropel S1, SST show a marked warming followed by a clear cooling. In the topmost intervals of the cores SST are mostly constant, but a warming event is always observed. This warming phase may correspond to the "Medieval climatic Optimum" (in the AD91-17 core) and to the "Roman Optimum" (in the box cores).

Introduction

Alkenones are organic molecules that are produced by a group of haptophyte algae, most notably the coccolithophorid *Emiliania huxleyi* (Volkman et al. 1980; Brassell et al. 1986a, b; Westbroeck et al. 1993).

Field sampling and culture experiments with various species of haptophytes suggest a relationship between water temperature and the number of double bonds of alkenones with 37 carbon atoms (Brassell et al. 1986a, b). The unsaturation ratio is expressed as:

$$U^{k'}_{37} = [C_{37:2} - C_{37:4}] / [C_{37:2} + C_{37:3} + C_{37:4}]$$

It was later modified by removing the term corresponding to the 37:4Me alkenone, because this compound was rarely found in open-sea sediments or water-column particles (Brassell et al. 1986a; Prahl & Wakeham 1987):

$$U^{k'}_{37} = [C_{37:2}] / [C_{37:2} + C_{37:3}]$$

$U^{k'}_{37}$ has been shown to vary linearly with the ambient water temperature (at least over the range 8-25°C) of cultured organisms (Prahl & Wakeham 1987; Prahl et al. 1988). In open-sea environments, Uk'37 covaries with sea-surface temperature of the euphotic zone where the alkenones are biosynthesized by specific haptophytes (e.g. *Emiliania huxleyi, Gephyrocapsa oceanica*) (e.g. Volkman et al. 1980, 1995; Müller et al. 1998). This correlation between $U^{k'}_{37}$ and sea surface temperatures has been the basis to reconstruct past SST from sedimentary alkenones and has been applied in paleoceanographic studies of marine environments (e.g. Jasper & Gagosian 1989; Eglinton et al. 1992; Chapman et al. 1996; Müller et al. 1998).

The advantage of alkenones is the possibility to reconstruct absolute temperature values, with a relative small analytical error (Prahl & Wakeham 1987; Rosell Melé et al. in press). Only small amounts of sediment material are needed for the analyses (1-2 g). Together with an increasingly automated methodology, this permits to study a large number of samples resulting in high-resolution SST records (Madureira et al. 1997; Cacho et al. 1999a, b). Alkenone-based SST reconstruc-

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tions have been used to reconstruct short and relatively small temperature variations. In NW African cores, for example, climatic changes of 200 to 500 years duration were registered during the last 80 Kyr (Zhao et al. 1995), or of 70 to 200 year duration during glacial terminations I, II, IV (Eglinton et al. 1992; Zhao et al. 1993), with temperature oscillations of about 1-3°C.

Another advantage in using alkenones as paleotemperature reconstructions to use them for temperature correction of oxygen isotope values in order to reconstruct paleosalinity records. This is particularly interesting for the Mediterranean Sea, where changes in salinity have strongly influenced the isotopic signal in the past (Rohling & De Rijk 1999).

Recent studies in the eastern Mediterranean Sea (Emeis et al. 2000; Emeis et al. submitted) reconstructed the temperature and salinity history of the surface water during the last 16,000 years to recognize the physical factors that contribute to sapropel formation. The authors find that sapropel S1 began to form at the same time, when a significant salinity and density decrease occurred in the Ionian Sea.

Aside from the molecular thermometer, $\delta^{18}O$ and sea surface temperature records derived from census data of planktonic foraminifera were used from Kallel et al. (2000) to estimates the oxygen isotopic composition of surface water (δw), during the last 200,000 years in the Tyrrhenian Sea and Levantine basin. The authors shows strong δw/salinity decrease in both basins associated with each sapropel, reflecting a drastic change in local freshwater input comparable to that observed during the sapropel S1 (Negri & Giunta 2001; Giunta 2001), here studied. The temperature range obtained by Kallel et al. (2000) from foraminifer census data agrees well with those obtained by Emeis et al. (submitted) from $U^{k'}_{37}$, although the detailed patterns differ significantly.

On the other hand, the alkenone-based method of SST reconstruction has some limitations. Rossel-Melé et al. (1995) observed some disagreement between water samples temperature and Atlantic surface sediment $U^{k'}_{37}$, possibly because the alkenone producing organisms were not correctly identified. In fact, although different species can inhabit similar ecological and geographical niches (i.e. *E. huxleyi* and *G. oceanica*, within coccolithophores) (McIntyre 1967) their bloom period could be different (autumn-winter for *G. oceanica*, spring-summer for *E. huxleyi*), and therefore $U^{k'}_{37}$ can registered different SST periods (Herbert et al. 1998).

Some systematic studies were performed on suspended matter and surface sediments also in the Mediterranean Sea (Cacho et al. 1999a; Ternois et al. 1996, 1997), with the aim to elucidate the relationship between SST and $U^{k'}_{37}$ for this marginal sea.

An apparent systematic difference in slope of the $U^{k'}_{37}$ - temperature relationship between column particulates (Ternois et al. 1997) and core tops sediments (Müller et al. 1998) is observed especially in the western Mediterranean Sea (Cacho et al. 1999a). The authors found spring suspended particulate $U^{k'}_{37}$ values in agreement with water column temperatures, according to the regional calibration of Ternois et al. (1997). However, surface sediments show $U^{k'}_{37}$ values closely in agreement with annual average near-surface temperature obtained with Müller et al. (1998) core top calibration.

For reasons given elsewhere (Emeis et al. 2000), we chose the Müller et al. (1998) calibration instead of the Ternois calibration for the Eastern Mediterranean Sea; Emeis et al. (2000) also discuss possible errors introduced by this choice.

Although alkenones are relatively stable compounds, a further error in alkenone SST estimates may arise, for some authors, from a variable overprint of the alkenone unsaturation patterns by diagenesis under oxic and anoxic conditions (Gong & Hollander 1999; Hoefs et al. 1998; Prahl et al. 1989). Gong & Hollander (1999) found systematic offset between SST estimates from coeval laminated and neighboring non-laminated sediments. The SST estimates of anoxic sediments were found to be colder by 2.5°C, attributed to bioturbation mixing and possible preferential degradation of the tri-unsaturated C_{37} methyl ketones relative to the di-unsaturated C_{37} methyl ketones under oxic conditions. Their interpretation are in line with arguments presented by Hoefs et al. (1998), but contradict earlier studies (Prahl et al. 1989) that found no evidence for preferential degradation.

Recently, Grimalt et al. (2000, 2001) shed light on possible analytical causes for seeming preferential degradation of tri- versus di-unsaturated C_{37} alkenones. They found higher absorption of $C_{37:3}$ than $C_{37:2}$ on capillary columns at low alkenone concentrations in the injected sample volume. The absorption effect will shift the $U^{k'}_{37}$ indices toward higher values (warmer temperatures), and is of concern to many of our samples. In the work presented here, oxic sediment often shows alkenone concentrations near and even below these critical values. Should a systematic chromatographic artifact have caused raised $U^{k'}_{37}$ and higher calculated SST of oxic sediments, then the temperature difference between oxic mud deposited during glacials and sapropel S1 become even greater and thus confirm our main conclusions. However, this analytical error must be considered in interpreting short SST oscillations of about 1 - 2°C in sample intervals with low alkenone concentrations.

In spite of possible problems that require additional work, the SST reconstructions based on alkenone unsaturation give coherent SST estimates and permits to reconstruct SST gradients, if several coeval cores are investigated. No attempt has yet been made to investigate the patterns of SST in the course of the deglacial

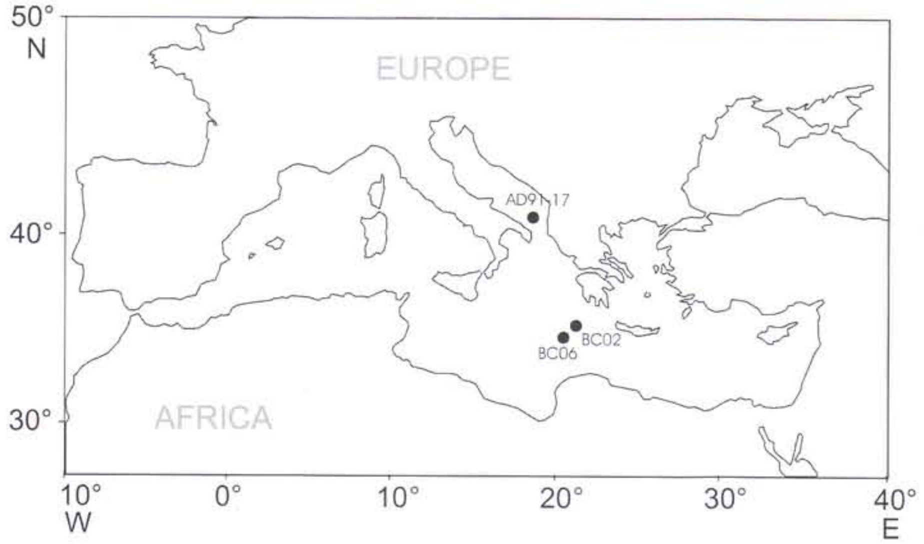


Fig 1 - Location of the studied core and box cores.

Site	Lat.	Long.	Depth	Length	Location
BC 02	35° 17' 09.33"	21° 24' 55.17"	3349m	55cm	Plateau between Urania and l'Atlante basins
BC 06	34° 52' 30"	21° 07' 08"	2539m	49cm	Mediterranean Ridge Crest
AD91-17	40°52.17'	18°38.15'	844	331cm	Southern Adriatic Sea

and Holocene on the important North-South gradients of SST in the eastern Mediterranean Sea. This paper aims to establish SST from alkenones in the Adriatic Sea and Central Mediterranean area and to identify climatic events of the last 16 Ky. Our aim is to reconstruct the general course of sea surface temperatures in this area at the transition from glacial to Holocene conditions. Particular attention is given to the climatic optimum, which in the eastern Mediterranean Sea corresponds to an anoxic event, resulting in the deposition of sapropel S1.

Materials and methods

Alkenones

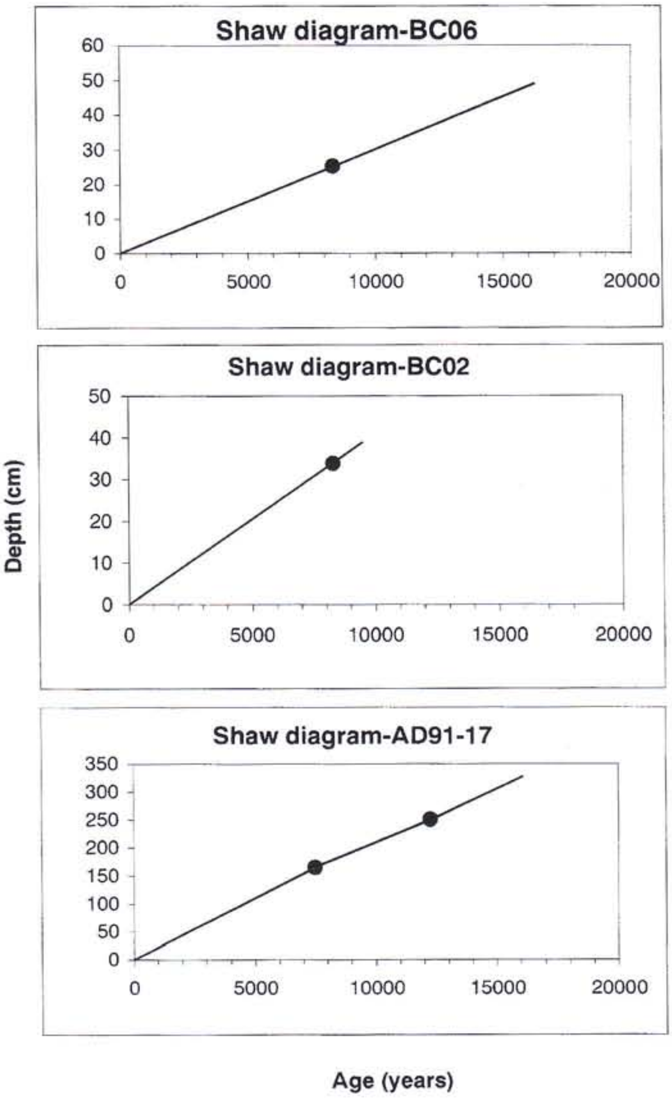
Detailed alkenone analyses were performed on two eastern Mediterranean box cores (BC 02 and BC06) and on a southern Adriatic piston core (AD91-17) (Fig.1). BC02 and BC06 were collected during the R/V Urania Cruise (17/11-12/12 1997), while AD91-17 was recovered during the cruise AD91 performed by the R/V Minerva. Visual description and on board speed geochemical analyses reveals that all cores have a preserved organic-rich layer (sapropel S1) (Della Vedova et al. 1997). The two box cores show also a successive oxidized interval containing two levels enriched in Fe and Mn, respectively (van Santvoort et al. 1987). A more detailed description of the cores is given in Capotondi & Morigi (1996) and Giunta (2001).

In the AD91-17 core, chronology is assessed by ^{14}C AMS datings and by correlation to oxygen isotopic record performed on *G. bulloides* by Capotondi et al. (1999). This correlation allows to identify a warming phase which Capotondi et al. (1999) made correspond to the First Meltwater Event in Termination TIa (FME), dated 12.300 years, and the beginning of the Younger Dryas cold event. A ^{14}C AMS dating was performed at 170-171 cm with a corresponding age of 7750±60 years. The two dated points permit the reconstruction of the sedimentation rate of the core and to estimate an age of 16.1 Kyr for its bottom (Fig. 2).

In the two box cores, chronology is reconstructed assuming an age of 8300 year ($^{14}C_{nc}$BP) for the sapropel S1 base (Rohling et al. 1997) and a constant sedimentation rate. This allows extrapolating an age of 16.3 Kyrs for the base of BC 06, while the base of BC02 has an age of 9.5 Kyr (Fig. 2).

Samples from half of each box core were taken every cm in the hemipelagic intervals and every 0.5 cm where the sapropel S1 and its oxidized part were present. Due to the higher sedimentation rate in core AD91-17 from the Adriatic sea, samples were taken every 5 cm in the hemipelagic interval between 2 and 128 cm, every 2 cm between 128 and 211 cm where the sapropel was recognized (except a gap between 186 and 201 cm, due to the presence of a tephra layer and an erosion gap at the sapropel bottom). Sample spacing was wider - every 10 cm - from 211 to 322 cm.

For alkenone analyses, samples were freeze-dried, homogenized and 30 ml of distilled CH_2Cl_2 was added to a weighted sub-sample. Soluble organic matter was ultrasonically extracted (2x10 min); after each extrac-



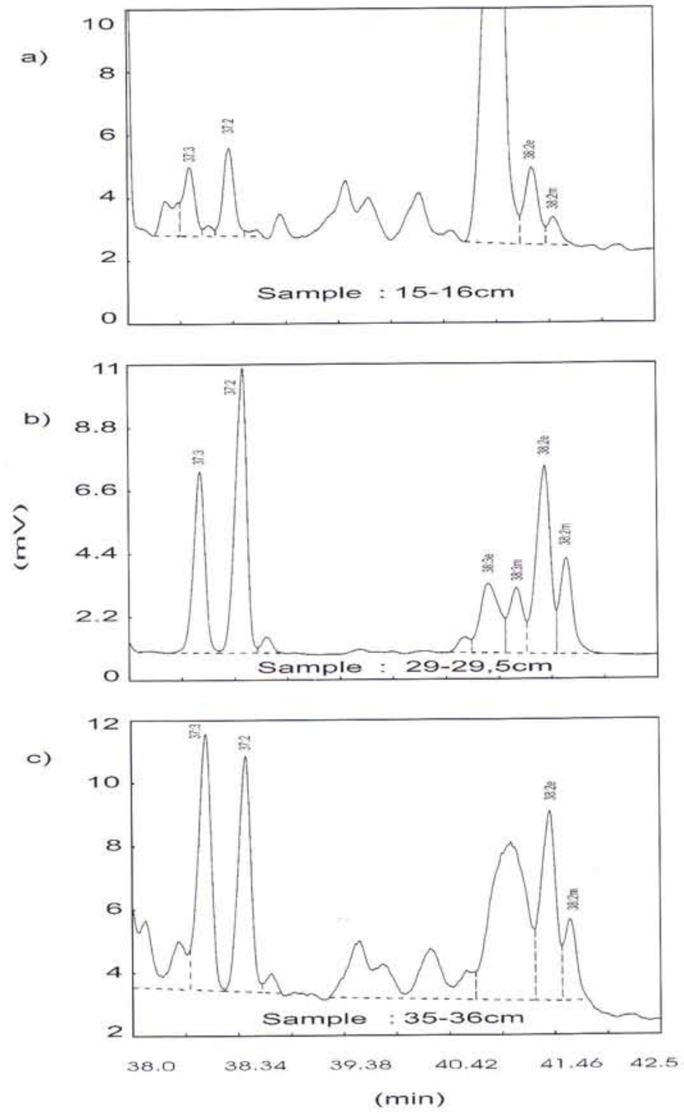


Fig. 2 - Shaw diagrams showing the sedimentation rates of the box cores and the gravity core, considering an age of 8300 year ($^{14}C_{nc}$BP) for the sapropel S1 base (Rohling et al., 1997) and the dated ages for the AD91-17 core.

Fig. 3 - Chromatographic quality of alkenone peaks in box core BC02, in the interval above (a), within (b) and below (c) the sapropel interval.

tion step, samples were centrifuged and the solution (CH_2Cl_2+ extractable lipids) was collected by pipette and dried in a rotary evaporator to remove CH_2Cl_2.

The dried extracts were dissolved again in CH_2Cl_2 and cleaned by column-chromatography in packed silica gel columns (conditioned with at least 30 ml CH_2Cl_2). Eluates were then dried again in a rotary evaporator and taken up in 100 to 200 µl n-hexane, of which 1-2 µl were injected.

GC analyses were carried out on an HR 8000 Fisons gas chromatograph (FID, cold on column injection) equipped with 30 m fused silica capillary column (DB5HT, JandW Scientific, 0.32 mm i.d., 0.25 mm film thickness). Hydrogen was used as carrier gas (column head pressure 110 kPa). In core BC02 oven temperature programming conditions were from 45°C to 200°C at 15°C min^{-1} followed by an isothermal period of 10 min at 200°C, from 200°C to 285°C at 15°C min^{-1} (elution of alkenones) to 330°C at 15°C min^{-1} followed by an isothermal period of 10 min at 330°C. Due to good separation of alkenones in core BC06 and AD91-17, a different temperature program was used: from 45°C to 300°C at 15°C min^{-1} followed by 15 min isothermal, and to 330°C at 15°C min^{-1} followed by 10 min isothermal. Alkenones were recognized by comparing retention times with those of synthetic standards (37:3Me and 37:2Me alkenones, provided by A. Rosell-Melé, Newcastle), and those of an in-house standard (sapropel from Mediterranean Sea).

Peak areas were integrated to calculate the unsaturation index ($U^{k'}_{37}$), and subsequently the sea surface temperature: SST = ($U^{k'}_{37}$ - 0.044)/0.033 according to

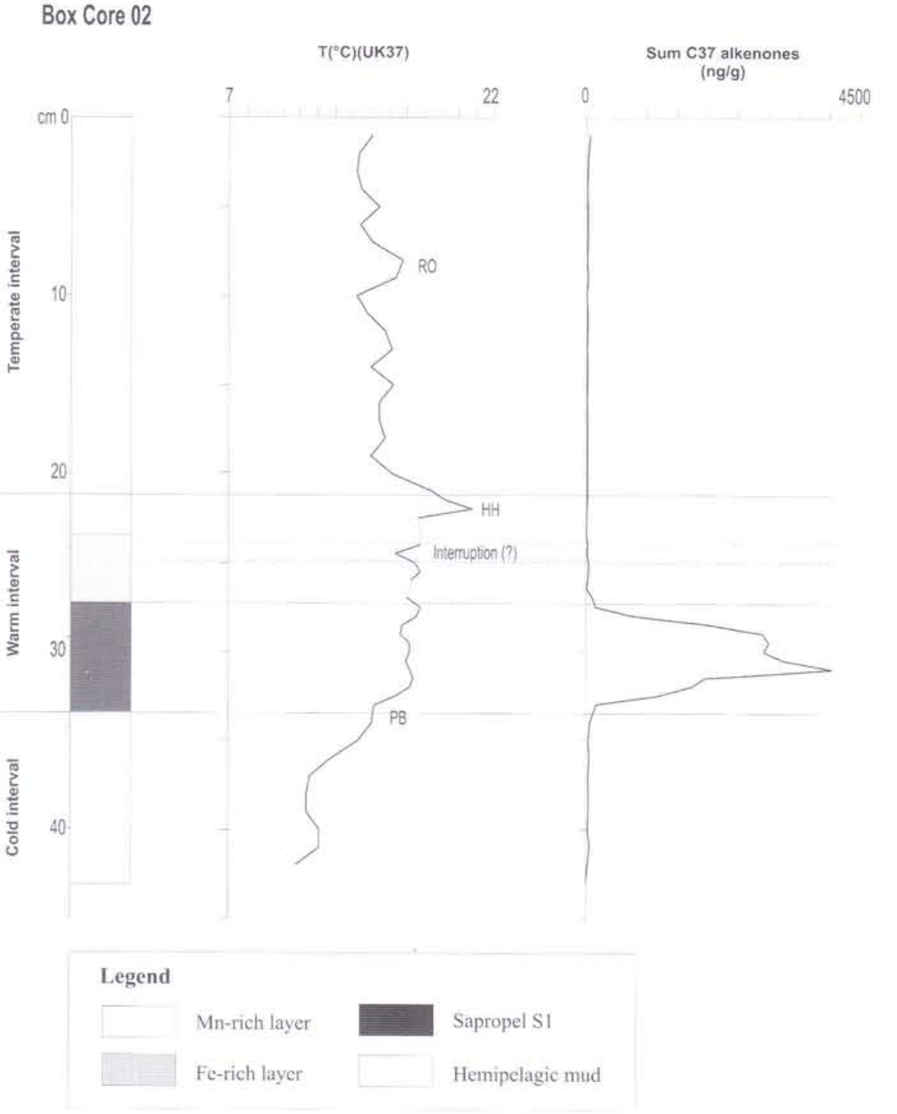


Fig. 4 - Temperature curve, obtained using the alkenone unsaturation index ($U^{k'}_{37}$) and alkenone concentrations in box core BC02. (RO = Roman Optimum; HH = Holocene Hypsithermal; PB = Preboreal event).

Müller et al. (1998).

Alkenone concentrations were determined based on detector responses relative to 5α-cholestane injected as an external standard.

TC (Total Carbon) and TOC (Total Organic Carbon)

In box core BC02, sub-samples of about 100mg were taken and total carbon concentrations were determined measuring the quantity of CO_2 emitted after combustion at 1200°C in a Heraeus Elemental Analyzer. Inorganic carbon was analyzed in a Eltra Carbon Analyzer after the addition of 5ml of 50% phosphoric acid (H_3PO_4). As for total carbon, results are registered automatically in percentage of C_{inorg} in the sediment; organic carbon was calculated as the difference between C_{tot} and C_{inorg} (Tab. 1).

Results

Alkenones

BC02 - A total of 55 samples were studied in this core and alkenones were found in all samples, but total amount differed significantly.

Alkenones are less abundant between 43 and 33 cm and between 21 and 1 cm (hemipelagic mud intervals), with concentrations between 62 and 22 ng/g and between 29 and 10 ng/g respectively (with the exception of the first superficial sample where values are 50 ng/g) (Tab. 2, Fig. 4).

In these intervals, the peaks of $C_{37:2}$ and $C_{37:3}$ alkenones, although always recognizable in the chromatograms, are not well defined and overlain by peaks of other organic compounds (Fig. 3a, c). These coelutions made a correct integration and estimation of the real alkenone quantity difficult. For some samples the proper estimate of peaks areas was impossible, because of peak overlaps (samples 23, 23.5, 26.5, 43).

The chromatograms improved considerably in the interval between 33 and 27 cm (preserved S1 interval), where high quantities of alkenones were found (from 4056 to 103 ng/g) (Fig. 4). The good definition of peaks permitted a precise estimation of the peak areas and alkenone quantity within the samples (Fig. 3b). Concentrations were lower in the interval between 27 and 21.5 cm (oxidized S1 interval), with values between 37 and 9 ng/g, showing again some peak overlapping by other substances.

The temperature curve (Fig. 4) shows a continuous increase of temperature in the interval between 42 and 33 cm from 10.8°C to 15.2°C, with a pronounced warming at 40-41 cm to around 12°C. Temperature increased from 32.5 cm and were more constant to approximately 20 cm with values between 16.2°C and 17.8°C. At 24.5 cm the temperature dropped slightly to 16.4°C, rising to 20.8-18.5°C at 21-22 cm. SST were rather uniform in the 20-1 cm interval, with values between 15.8°C and 14.2°C and a small excursion to

16.3°C to 16.8°C between 9 and 8 cm.

BC06 - We analyzed 55 samples in this box core and found alkenones in all samples, but in variable quantity. Alkenone concentrations were low in the intervals between 46 to 26 cm and 20.5 to 0 cm (hemipelagic mud + oxidized S1 intervals), with values between 79 and 12 ng/g and 15 to 8 ng/g respectively (Tab. 3, Fig. 5). In these intervals of low concentrations, the chromatographic peaks, although always recognizable, were not well defined and often overlain and partially hidden by peaks of other organic compounds. In samples from 19 cm and 47 cm, proper estimate of peak areas was not possible. Much higher quantity of alkenones characterized the interval between 25.5 and 21 cm (S1 interval), with concentrations between 952 to 91 ng/g and good peak resolution (Fig. 5).

The temperature curve (Fig. 5) shows a continuous increase in the interval between 46 and 25.5 cm from 7.3°C to 15.2°C, with some minor oscillations. A sudden decrease of temperature at 25 cm by 14.4 °C interrupts the warming trend. Resumption of increasing temperatures characterized the interval between 24.5 and 19.5 cm, reaching a maximum of 21.8°C, values varies little upward to 16 cm. At 20 cm the temperature drops slightly to 20.2°C. From the SST maximum, temperature decreases gradually in the 16-0 cm interval. A brief warming between 6 and 4 cm, where SST reaches 18.1-17.4°C, coincides with a thin sediment layer rich in pteropods. The youngest sediment had a temperature of 14.5°C.

AD91-17 - As in the other two cores, all 61 samples studied contained alkenones, but again the quantity varied. Alkenone concentrations were low in the intervals between 322 and 201 cm and 118 and 0 cm (hemipelagic mud intervals), with values around 32 and 8 ng/g and between 50 and 17 ng/g, respectively (Tab. 4, Fig. 6). Peak integration was difficult in these samples, but nevertheless it was possible to integrate the peaks of all samples. Gradually higher quantity of alkenones characterized the interval between 186 and 123 cm (S1 interval), with values between 384 to 63 ng/g and good peak quality.

The temperature curve (Fig. 6) shows a rather homogeneous trend in the interval between 322 and 201 cm, characterized by values around 10°C. A small decrease of temperature at 203 cm (9.7°C) precedes a sudden increase by 5°C to warmer temperatures that characterize the rest of the interval. Within this warming we can distinguish an interval with variable temperatures around 15°C (186-167 cm); a positive excursion to 16°C (163-157 cm) followed by a decrease to 14.4-14.1°C (153-151 cm). Temperature returned to 15°C in the interval between 147-128 cm with some oscillations. The interval from 123 to 93 cm had rather constant temperatures around 16.6°C. Towards the top (88-2 cm) temperatures decreased from 16.1 to 14.1°C even if some oscillations were present. A marked one was between 33 and 2 cm with 15.9°C.

Carbon

Inorganic carbon concentrations in box core BC02 show major changes in the interval between 43 and 22.5 cm, with two isolated small peaks at 33 cm (5.8%) and at 30.5 cm (5.6%). A marked increase is seen between 26 and 23 cm (6-6.7%),while values were around 4.7 and 5.5% in the remainder of the record. TIC dropped at 28 cm (4.5%) and 22.5 cm (5.7%). Little change is seen in the interval between 22.5 and 1 cm (Tab. 1; Fig. 7) with concentrations from 5.8 to 4.9% in the first 15 cm and a gradual small increase from 21 to 17 cm with maximum value of 6.2%. The C_{org} curve has only one interval in which values reached between 0.8 and 4.3% (34-27 cm) and outline a broad peak. The rest of the curve has values that are constant between 0.4-0.9%.

Discussion

Previous paleoclimatic reconstructions of the glacial to Holocene transition in the study area have mainly been based on faunal assemblage and stable oxygen isotope data (Vergnaud-Grazzini et al. 1977, 1988; Capotondi & Morigi 1996; Capotondi et al. 1999). In this study we define the paleoclimatic conditions during the studied period by alkenone unsaturation ratios and SST calculated from that ratio. In addition to information on SST, the alkenone concentration curves (Fig. 4, 5, 6) clearly marked the extension of the organic-rich interval of the S1 sapropel.

a) Ionian Sea

The alkenone-based temperature curves of the box cores BC02 and BC06 (Fig. 4, 5) suggest a clear distinction of three principal intervals. These are from the bottom: a first cold interval (11-12°C in BC02; constantly warming with values between 7.1° and 15.2°C in BC06), a second warming interval starting just at the base of the sapropel S1 (about 17°C in BC02 and 16.9-21.8°C in BC06) and a last temperate and more constant interval, with temperature around 15°C in BC02 and 16°C in BC06, above the sapropel.

The temperature increase below S1 in the two cores is from as low as 7°C to 15°C just before the onset of sapropel deposition. It is of note that the SST increase is very uniform, and lacks structure seen in other cores from the western Ionian Sea (Emeis et al. 2000). Using the onset of S1 as an isochronous stratigraphic marker in both cores, the SST evolution both in structure of the curve, and in absolute temperatures, is virtually the same at both locations in the eastern Ionian Sea. Minor fluctuations are seen in both cores, but the SST reconstructions in the basal colder interval have remarkably little structure and lack clear temperature signals of stadials and interstadials during the deglaciation, such as the

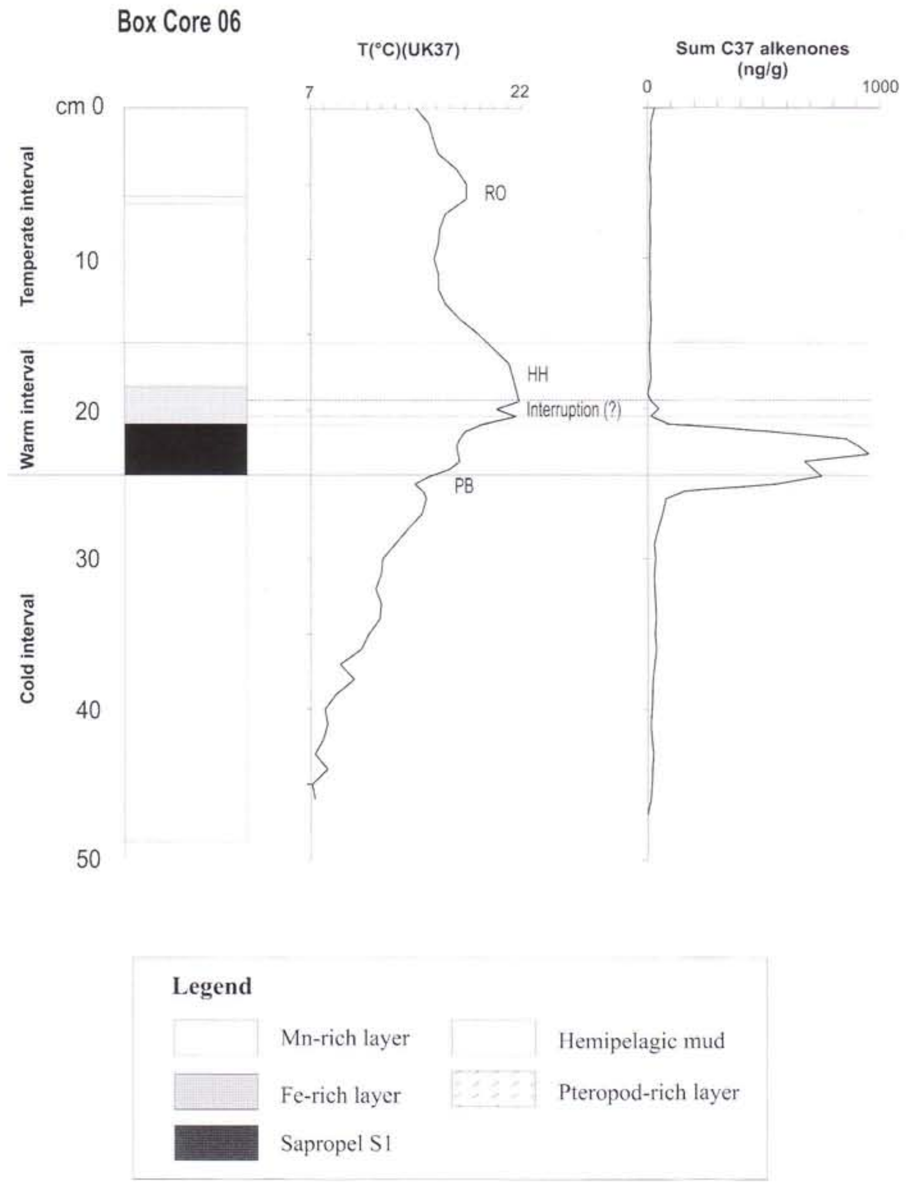


Fig. 5 - Temperature curve, obtained using the alkenone unsaturation index ($U^{k'}_{37}$) and alkenone concentrations in box core BC06. (RO = Roman Optimum; HH = Holocene Hypsithermal; PB = Preboreal event).

Younger Dryas (YD) and the Boelling/Alleroed (B/A) events. The sapropel is always preceded by a more or less marked cooling that could correspond to the Preboreal oscillation, recognized in some eastern Mediterranean cores (Emeis et al. 2000).

Transition to the sapropel and the middle part of the SST curves is always characterized by a warming trend by about 5°C and high SST characterize sapropel S1. Warm SST persist to the dark layer associated with the two oxidized intervals (Fe and Mn-rich), that were proposed to represent the oxidation of the sapropel after re-oxygenation of the deep water (De Lange et al. 1989; van Santvoort et al. 1997). The presence of constant temperature in the entire interval suggests that depositional conditions remained the same during sapropel deposition up to the oxidation front. The burning down of the upper part of the sapropel was confirmed by nannofossil analyses (Negri & Giunta 2001) and by the benthic foraminiferal assemblage (Morigi pers. comm.) showing persisting anoxic conditions in the interval above the present-day sapropel top.

Within the middle interval and precisely in the oxidized Fe rich level, we can distinguish a warming phase (at 25.5 cm in BC02 and 20.5 cm in BC06) immediately followed by a cooling of about 1.4°C (at 24.5 cm in BC02 and 20 cm in BC06). This slight cooling event may correspond to a short period of sapropel interruption (de Rijk et al. 1999), although evidence of repopulation by deep benthic fauna have not been found (Principato pers. comm.). In BC02 and BC06, highest SST (18.5°-20.8°C) occur within the oxidized Mn-rich part above sapropel S1. This interval probably represent the peak of the Holocene Hypsithermal at about 6 Ky. The SST curves suggest that warm conditions, that contributed to water column stratification before the sapropel deposition, continued until the end of the sapropel period. The warming trend ended at 19 cm in BC02, and at 12 cm in BC06. At the same levels in the cores, Negri & Giunta (2001) observed changes within the coccolithophorid assemblage: the last common occurrence of the species *Braarudosphaera bigelowii*, corresponding to the end of the low salinity water event that characterized the upper part of the sapropel deposition, was recognized just above the Mn-rich oxidized layer. This suggests the presence of a transitional period between anoxic and oxic conditions, with still warm and low salinity waters. The only period when the two Ionan Sea records differ significantly is in the interval just above the preserved sapropel: samples from BC06 are 4°C warmer than those from BC02.

Temperate and more constant sea surface temperatures characterize the post-sapropel period. In this

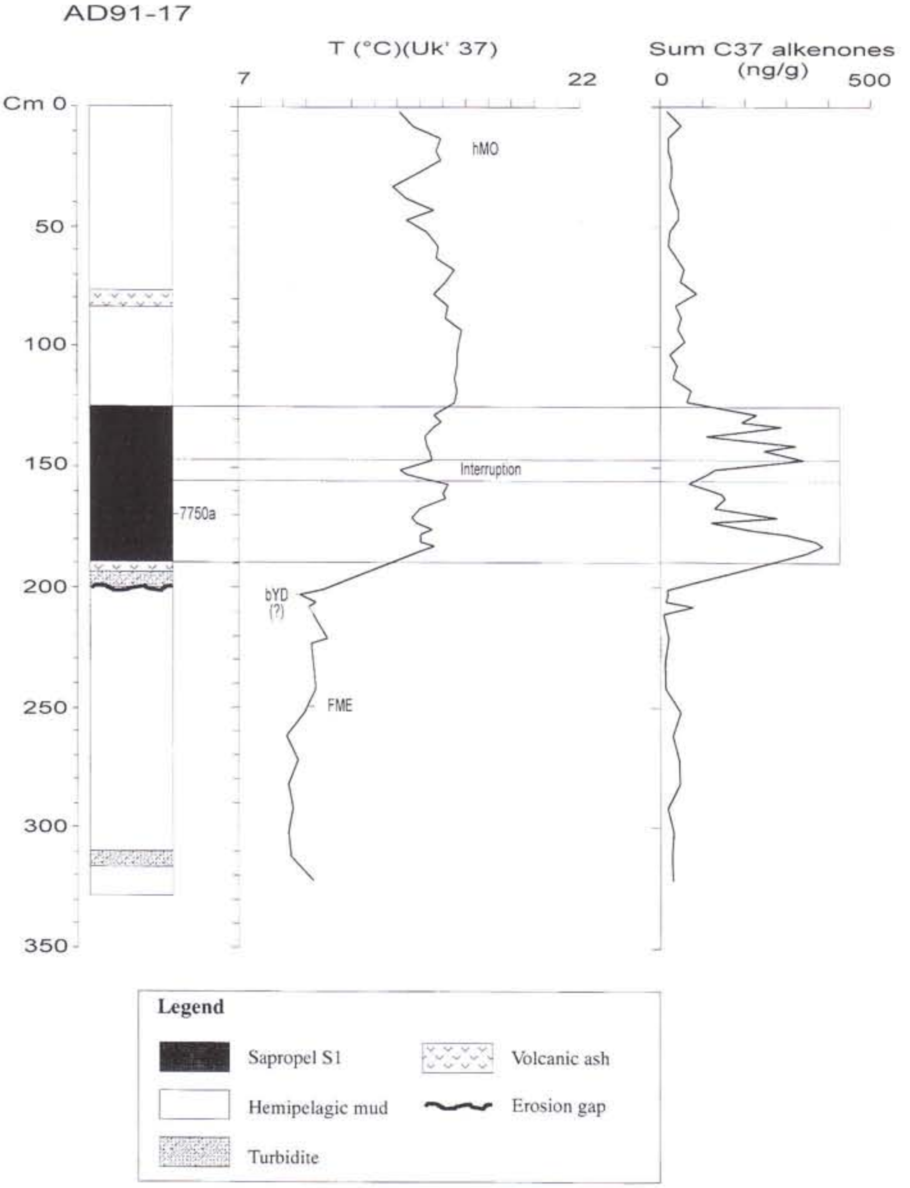


Fig. 6 - Temperature curve, obtained using the alkenone unsaturation index ($U^{k'}_{37}$) and alkenone concentrations in core AD91-17; (hMO = high Medieval Optimum; bYD = Younger Dryas beginning; FME = First Melt-water Event in termination Ia, according to Capotondi et al. 1999).

period, a phase of warmer SST (16.4-16.8°C in BC02 and 18.1°C in BC06) is present. Assuming a linear sedimentation rate, the age calculated for this warming phase is between 1700-1900 yr B.P. If we assume a constant sedimentation rate from the sapropel bottom (assumed of 8300 yr from Rohling et al. 1997) to the core top, the event may represent the "Roman Optimum" which occurred between 1 and 140 a. D. (Veggiani 1986, 1994). This will be tested by dating (Corselli pers. comm., 2000).

Although both SST profiles are very similar, such short and small SST oscillations (about 1 - 2°C) recorded in core sections with low alkenone concentrations in the post-sapropel period may be analytical artifacts (Grimalt et al. 2000, 2001) and must not be over-interpreted.

b) Adriatic Sea

The temperature curve obtained for the AD91-17 core (Fig. 6) shows more detail, thanks to the high sedimentation rate. Uniform SST characterize the interval between 322-252 cm that represents the late glacial (on average 10°±0.9°C). A small warming of 2°C follows the Capotondi et al. (1999) "First-melt Water Event" in Termination Ia, identified at 250 cm.

A small cooling of 2°C is noted at 203 cm and corresponds to the beginning of the Younger Dryas. The entire YD is not represented, because a stratigraphic gap is present in the core (Capotondi & Morigi 1996). A sudden increase of 5°C is observed at the bottom of sapropel S1 (to 15°C). SST oscillate around this value in the entire organic rich level S1.

Both sea surface temperature and benthic faunal assemblage data suggest that sapropel S1 deposition was interrupted during a brief period, represented in this core at 153 to 151 cm, although no clear colour changes or organic carbon variations are observed. In this interval we notice a cooling of about 2°C at a time when deep infauna repopulated the sea floor (Morigi pers. comm.). Both observations are consistent with a rapid re-oxygenation of the bottom environment due to surface water cooling (de Rijk et al. 1999).

After the sapropel interruption, SST increase again by about 2.5°C (147-128 cm), and maintain constant values above S1 all through the middle Holocene interval (123-93 cm). Maximum SST were around 17°C. Towards the top, SST fluctuate between 14 and 16°C during the last few thousand years (88-2 cm). The general decrease is interrupted by a warm period between 33 and 2 cm. The interpolated age of this warming period is approximately 1000 yr B.P. and may thus correspond to the "high-Medieval climatic Optimum" or "little climatic optimum" (Veggiani 1986, 994; Marabini & Veggiani 1993) that occurred between 800 and 1200yr a.D. How-

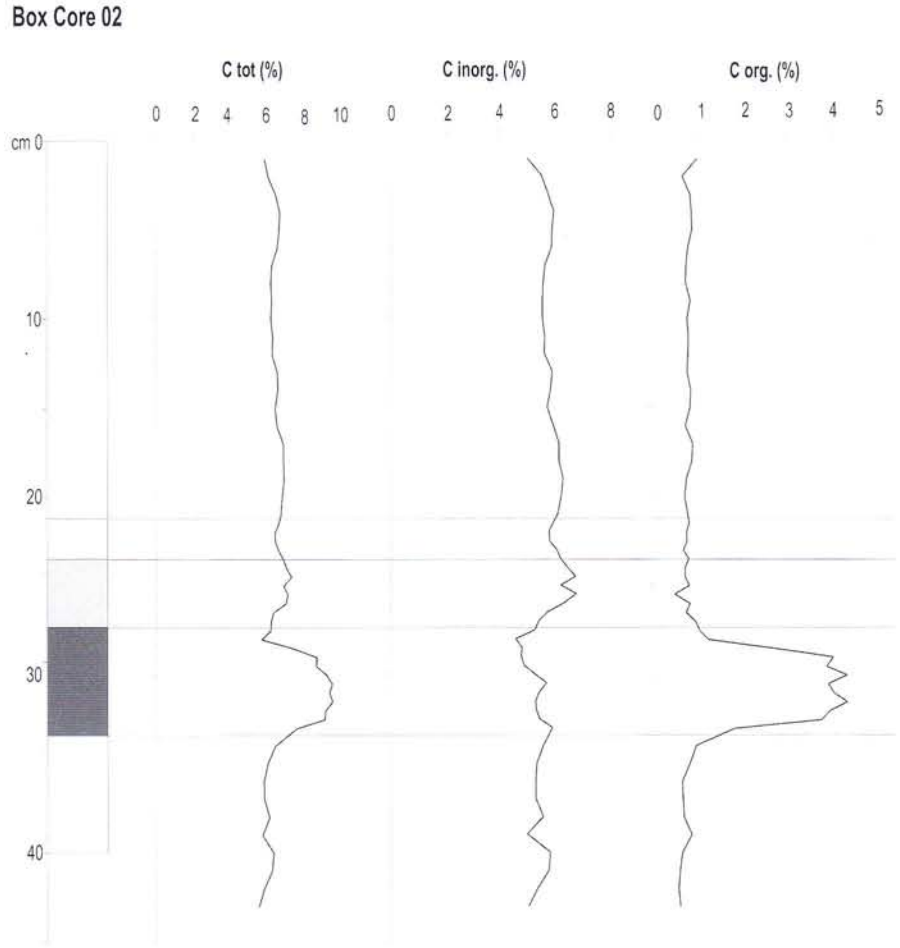


Fig. 7 - Distribution of total, organic and inorganic carbon in box core BC02.

ever, in order to confirm this speculation, new AMS ^{14}C dating will be necessary.

A comparison of the two records (Ionian versus Adriatic Sea) reveals some remarkable differences:

1. A temperature gradient developed between the Ionian Sea and Adriatic during the deglacial. Whereas the Adriatic Sea record shows consistently low (between 9°C and 11°C) SST, the Ionian Sea became increasingly warmer. This gradient steepended during S1 formation: at the onset of S1 deposition, it was 2°C and reached 5°C at the end of S1. A similar SST range as that found in the sapropel from two eastern Ionian Sea records, was found in the central Ionian Sea by Emeis et al. (1998), with average temperature fluctuating around 17.1 ± 1.1°C in the Ionian Sea. At the same time, SST in the Eastern Mediterranean Sea were 2°C warmer. The SST gradient in our records diminished in the post-S1 period, where temperature varied around 15-16°C in the Ionian Sea and around 14-15°C in the Adriatic. Our results suggest a significantly steeper N-S than E-W temperature gradient prior to and during S1 deposition in the Eastern Mediterranean Sea; the gradient seen in the post-S1 intervals approximately corresponds to the climatic differences observed in modern times.

2. The difference between minimum glacial SST and maximum interglacial values exceeds 14°C in the Ionian Sea (BC06), whereas the Adriatic core show a warming of only about 7°C. Although AD91-17 did not recover the full glacial SST minimum, it appears that Holocene warming in the northern periphery of the Mediterranean Sea was less pronounced than in the central Mediterranean. The Ionian warming is also considerably larger also than that described by Cacho et al. (2001) for the Alboran and Tyrrhenian Seas. In the western basin, the difference between minimum glacial and maximum interglacial SST is around 8-9°C. This is in agreement with the authors hypothesis that SST oscillations were larger towards more intra-Mediterranean locations.

3. The Holocene SST trend is very similar to that described by Cacho et al. (2001) for different sites of the Western Mediterranean Sea. The authors recognized a general cooling trend, briefly interrupted by some short cooling events (1-2°C), that are more intense in the Tyrrhenian Sea. This short-term variability was probably in part transmitted through the inflowing North Atlantic Water. The larger Tyrrhenian SST variatio indicates a Mediterranean amplification, probably induced by changes in the wind regime that could be related to processes in the North Atlantic.

Conclusions

A careful comparison of three sea surface temperature curves reveals several common features, but also some differences:

· In the studied area, the Younger Dryas cooling and Boelling/Alleroed warming phases are not recognized in any of the three records.

· All curves show a short cooling event just before the sapropel S1 base, which probably represents the Preboreal oscillation at 9600 yr.

· The sapropel is always characterized by warming SST (on average an increase of 5°C).

Depth (cm)	C TOT (%)	C inorg. (%)
1	5.9	5
2	6.1	5.5
3	6.5	5.7
4	6.7	5.9
5	6.7	5.9
6	6.6	5.8
7	6.3	5.6
8	6.2	5.5
9	6.3	5.5
10	6.2	5.5
11	6.3	5.6
12	6.3	5.6
13	6.6	5.8
14	6.6	5.8
15	6.4	5.7
16	6.5	5.9
17	6.9	6.1
18	6.9	6.1
19	6.9	6.2
20	6.8	6.2
21	6.8	6
21.5	6.6	5.9
22	6.4	5.7
22.5	6.4	5.7
23	6.6	6
23.5	6.9	6.1
24	7	6.4
24.5	7.3	6.7
25	6.9	6.1
25.5	7.1	6.7
26	7	6.3
26.5	6.3	5.7
27	6.2	5.3
27.5	6.2	5.2
28	5.7	4.5
28.5	7.4	4.7
29	8.7	4.7
29.5	8.7	4.8
30	9.2	5.2
30.5	9.5	5.6
31	9.4	5.3
31.5	9.5	5.2
32	9.2	5.2
32.5	9.1	5.4
33	7.6	5.8
34	6.4	5.5
35	6	5.3
36	5.8	5.2
37	5.8	5.2
38	6.1	5.5
39	5.7	4.9
40	6.3	5.8
41	6.2	5.7
42	5.8	5.3
43	5.5	5

Tab. 1 - Results of the carbon analyses (total, organic and inorganic carbon) on box core BC02.

BC 02- depth (cm)	Area 37:3	Area 37:2	Uk37	T[°C]	Sum C37 alkenones (ng/g)
1	186403	221844	**0.543**	**15.1**	50
2	463089	491780	**0.515**	**14.3**	29
3	196655	205100	**0.511**	**14.2**	15
4	219463	240437	**0.523**	**14.5**	12
5	177310	220190	**0.554**	**15.5**	14
6	193446	207932	**0.518**	**14.4**	13
7	174383	207000	**0.543**	**15.1**	13
8	147620	220912	**0.599**	**16.8**	12
9	270288	379500	**0.584**	**16.4**	23
10	58098	60650	**0.511**	**14.2**	4
11	195014	221035	**0.531**	**14.8**	15
12	155149	201651	**0.565**	**15.8**	14
13	176969	244081	**0.58**	**16.2**	12
14	217456	255033	**0.54**	**15**	15
15	133061	186361	**0.583**	**16.3**	13
16	172310	214299	**0.554**	**15.5**	10
17	160666	201468	**0.556**	**15.5**	13
18	149880	194104	**0.564**	**15.8**	13
19	197267	230979	**0.539**	**15**	16
20	209304	286979	**0.578**	**16.2**	15
21	138739	264722	**0.656**	**18.5**	13
21.5	89050	190761	**0.682**	**19.3**	18
22	38761	105564	**0.731**	**20.8**	11
22.5	65112	109259	**0.627**	**17.7**	12
23	-	-	-	-	-
23.5	-	-	-	-	-
24	132321	227339	**0.632**	**17.8**	28
24.5	58647	82727	**0.585**	**16.4**	9
25	135058	222474	**0.622**	**17.5**	30
25.5	122685	211069	**0.632**	**17.8**	37
26	107520	172115	**0.615**	**17.3**	22
26.5	-	-	-	-	-
27	245441	379402	**0.607**	**17.1**	103
27.5	242154	413295	**0.631**	**17.8**	151
28	793394	1314771	**0.624**	**17.6**	733
28.5	500378	748926	**0.599**	**16.8**	2010
29	389795	569712	**0.594**	**16.7**	2906
29.5	498202	786875	**0.612**	**17.2**	3008
30	194628	305692	**0.611**	**17.2**	2928
30.5	248348	382276	**0.606**	**17**	3247
31	183388	289238	**0.612**	**17.2**	4056
31.5	246695	401031	**0.619**	**17.4**	1957
32	212774	337441	**0.613**	**17.2**	1742
32.5	186796	262107	**0.584**	**16.4**	1148
33	63831	76183	**0.544**	**15.2**	160
34	141692	167245	**0.541**	**15.1**	56
35	108448	115233	**0.515**	**14.3**	33
36	738137	646213	**0.467**	**12.8**	50
37	568462	422272	**0.426**	**11.6**	35
38	741720	537529	**0.42**	**11.4**	42
39	712752	513517	**0.419**	**11.4**	38
40	608269	485659	**0.444**	**12.1**	22
41	954116	763152	**0.444**	**12.1**	62
42	627481	422347	**0.402**	**10.8**	26
43	-	-	-	-	-

Tab. 2 - Results of the alkenones analyses on box core BC02.

BC 06-depth (cm)	Area 37:3	Area 37:2	Uk37	T[°C]	Sum C37 alkenones (ng/g)
0	143363	162063	0.531	14.5	30
1	124471	160568	0.563	15.4	13
2	163500	218962	0.573	15.7	14
3	133073	187502	0.585	16.1	13
4	91179	154828	0.629	17.4	10
5	71678	135369	0.654	18.1	14
6	134436	253951	0.654	18.1	14
7	79028	119538	0.602	16.6	9
8	111314	160252	0.59	16.2	11
9	120231	169463	0.585	16.1	12
10	93190	126079	0.575	15.8	10
11	111627	158034	0.586	16.1	11
12	94513	134354	0.587	16.1	10
13	101497	155655	0.605	16.6	11
14	116141	205890	0.639	17.6	15
14 duplicate	129772	216579	0.625	17.2	16
15	73189	155418	0.68	18.9	10
16	51098	126820	0.713	19.8	8
17	54254	167605	0.755	21.1	11
18	46455	153847	0.768	21.4	12
19	-	-	-	-	-
19.5	50535	179138	0.78	21.8	16
20	115958	309539	0.727	20.2	47
20.5	18036	61681	0.774	21.6	13
21	75848	169793	0.691	19.2	91
21 duplicate	91201	200802	0.688	19.1	110
21.5	165140	306720	0.65	18	522
22	266500	466452	0.636	17.6	856
22.5	295886	504741	0.63	17.4	910
23	184777	336272	0.645	17.8	952
23.5	204800	357297	0.636	17.6	675
24	192515	305275	0.613	16.9	711
24.5	260111	335404	0.563	15.4	750
25	171735	191639	0.527	14.4	556
25.5	65364	79332	0.548	15	159
26	64806	81435	0.557	15.2	79
27	57103	68117	0.544	14.9	64
28	42519	44586	0.512	13.9	45
29	88371	81912	0.481	13	29
30	106904	88199	0.452	12.1	33
31	98113	79415	0.447	12	29
32	70065	53793	0.434	11.6	30
33	74900	60668	0.448	12	33
34	81287	64377	0.442	11.9	36
35	53748	38429	0.417	11.1	31
36	65345	43135	0.398	10.6	37
37	60132	32257	0.349	9.1	31
38	40104	25036	0.384	10.1	22
39	28328	14380	0.337	8.8	21
40	25626	11589	0.311	8	19
41	19180	8897	0.317	8.2	14
42	26459	11657	0.306	7.9	19
43	35669	14445	0.288	7.3	25
44	28546	13248	0.317	8.2	21
45	27119	10584	0.281	7.1	19
46	17554	7043	0.286	7.3	12
47	-	-	-	-	-

Tab. 3 - Results of the alkenones analyses on box core BC06.

AD91-17 depth (cm)	Area 37:3	Area 37:2	Uk37	T[°C]	Sum C37 alkenones (ng/g)
2	90338	96688	0.517	14.1	17
8	262548	307274	0.539	14.7	49
13	90720	125306	0.58	15.9	21
18	96851	129182	0.572	15.7	19
22	88898	122122	0.579	15.9	26
28	129562	153720	0.543	14.8	28
33	135973	141115	0.509	13.8	23
38	213907	240042	0.529	14.4	33
43	217948	286377	0.568	15.6	43
47	234240	262593	0.529	14.4	42
52	111556	142132	0.56	15.3	24
52 duplicate	127857	159519	0.555	15.2	14
58	83717	113739	0.576	15.8	20
63	201862	272180	0.574	15.7	38
68	244400	365575	0.599	16.5	55
73	180401	256659	0.587	16.1	48
78	347655	460804	0.57	15.6	85
83	195953	283699	0.591	16.2	36
88	252796	357405	0.586	16.1	50
93	135480	211400	0.609	16.8	41
98	309187	479824	0.608	16.7	58
103	223264	342343	0.605	16.6	24
108	348551	534666	0.605	16.6	39
113	263103	392939	0.599	16.5	29
118	654785	990527	0.602	16.6	72
123	130327	195062	0.599	16.5	63
123 duplicate	135125	199613	0.596	16.4	33
128	265441	352096	0.57	15.6	227
131	207276	284202	0.578	15.9	193
133	293333	386997	0.569	15.6	287
137	124243	155099	0.555	15.2	108
141	358529	456738	0.56	15.3	320
143	227133	294230	0.564	15.4	244
147	440904	574715	0.566	15.5	339
151	181318	194368	0.517	14.1	130
153	120412	135204	0.529	14.4	113
157	154874	223417	0.591	16.2	68
157 duplicate	241187	342628	0.587	16.1	161
161	322203	451709	0.584	16	144
163	386430	546814	0.586	16.1	153
167	339680	413716	0.549	15	127
171	714721	827153	0.536	14.6	277
173	271697	320954	0.542	14.8	119
176	318709	417291	0.567	15.5	216
176 duplicate	329081	454009	0.58	15.9	213
178	302368	369441	0.55	15	301
181	521653	637211	0.55	15	368
183	446652	595441	0.571	15.6	384
186	556735	654519	0.54	14.7	342
201	132267	89353	0.403	10.7	17
203	158153	92573	0.369	9.7	17
206	134218	86714	0.392	10.4	14
208	344585	211945	0.381	10.1	78
211	49953	31742	0.389	10.3	8
221	129279	89077	0.408	10.9	20
231	77347	48694	0.386	10.2	11
242	83352	54282	0.394	10.4	13
252	351181	210139	0.374	9.9	48
262	211126	113258	0.349	9.1	29
272	540267	308881	0.364	9.6	44
282	593526	322629	0.352	9.2	47
292	225015	126470	0.36	9.4	18
302	396909	216916	0.353	9.2	32
312	346605	189853	0.354	9.3	28
322	359538	227530	0.388	10.3	29

Tab. 4 - Results of the alkenones analyses on core AD91-17.

· A short cooling event can be distinguished within the organic-rich or oxidized sapropel sequence. It may correspond to an interruption of the sapropels (best defined only in the AD91-17 south Adriatic core).

· In the topmost core interval, characterized by more constant temperatures (higher frequency oscillations are recognized in the AD91-17 core, probably due to higher temporal resolution) a warming is always observed, possibly corresponding to the "high-Medieval climatic Optimum" (in the AD91-17 core) and to the "Roman Optimum" (in the box cores).

· The Ionian Sea was considerably warmer (>5°C) during the sapropel S1 period than the Adriatic. In the late Holocene, this difference was only 1-2°C (15-16°C in the Ionian Sea; 14-15°C in the Adriatic) and corresponds to the modern difference.

· Comparing our results with those of other author for eastern Mediterranean, stronger than modern temperature gradients existed in the Mediterranean Sea during sapropel S1 deposition, with more pronounced N-S than E-W gradient.

· The post sapropel SST trend is similar to that observed in the western Mediterranean Sea, with a general cooling trend and short term oscillations.

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REFERENCES

Brassell S. C., Brereton R.G., Eglinton G., Grimalt J., Liebezeit G., Marlow I. T., Pflaumann U. & Sarnthein M. (1986a) - Paleoclimatic signals recognized by chemometric treatment of molecular stratigraphic data. *Org. Geochem.*, 10: 649-660, Amsterdam.

Brassell S. C., Eglinton G., Marlow I. T., Pflaumann U. & Sarnthein M. (1986b) - Molecular stratigraphy: a new tool for climatic assesment. *Nature*, 320: 129-133, London.

Cacho I., Pelejero C., Grimalt J.O., Calafat A.M. & Canals M. (1999a) - C37 alkenone measurements of sea surface temperature in the Gulf of Lions (NW Mediterranean). *Org. Geochemistry*, 33: 557-566, Amsterdam.

Cacho I., Grimalt J.O., Pelejero C., Canals M., Sierro F.J., Flores J.A. & Shackleton N. (1999b) - Dansgaard. Oeschger and Heinbrich event imprints in Alboran Sea paleotemperatures. *Paleoceanography*, 14(6): 698-705, Washington DC.

Cacho I., Grimalt J.O., Canals M. Sbaffi L. Shackleton N.J., Schoenfeld J. & Zahn R. (2001) - Variability of the western Mediterranean Sea surface temperature during the last 25,000 years and its connection with the Northern Hemisphere climatic changes. *Paleoceanography*, 16(1):40-52, Washington DC.

Capotondi L. & Morigi C. (1996) - The last deglaciation in the souht Adriatic sea: biostratigraphy and paleoceanography. *It. J. Quat. Sci.*, 9(2): 1-7, Verona.

Capotondi L., Borsetti A.M. & Morigi C. (1999) - Foraminiferal ecozones, a high resolution proxy for the Quaternary biochronology in the central Mediterranean Sea. *Marine Geology*, 153: 253-274, Amsterdam.

Chapman M. R., Shackleton N. J., Zhao M. & Eglinton G. (1996) - Faunal and alkenone reconstruction of subtropical North Atlantic surface hydrography and paleotemperature over the last 28kyr. *Paleoceanography*, 11(3): 343-357, Washington DC.

Della Vedova B. & Urania crew (1997) - Urania 15/97 report (Formia, 18 Nov.- Messina, 11 Dec., 1997). *Internal report.*

De Lange G. J., Middelburg J.J. & Pruysers P.A. (1989) - Discussion. Middle and Late Quaternary depositional sequences and cycles in the eastern Mediterranean. *Sedimentology*, 36: 151-158, Oxford.

De Rijk S., Rohling E.J. & Hayes A. (1999) - Onset of climatic deterioration in the eastern Mediterranean around 7 ky BP; micropalaeontological data from Mediterranean sapropel interruptions. *Marine Geology*, 153: 337-343, Amsterdam.

Eglinton G., Bradshaw S.A., Rosell A., Sarnthein M., Pflaumann U. & Tiedemann R. (1992) - Molecular record of secular sea surface temperature changes on 100-year timescales for glacial terminations I, II and IV. *Nature*, 356: 423-426, London.

Emeis K.C., Schulz H.M, Struck U., Sakamoto T., Doose H., Erlenkeuser H., Howell M., Kroon D. & Paterne M. (1998) - Stable isotope and alkenone temperature records of sapropels from sites 964 and 967: constraining the physical environment of sapropel formation in the eastern Mediterranean Sea. In: Robertson A.H.F., Emeis K.C., Richter C. & Camerlenghi A. (eds.)- *Proc. ODP, Sci. Results*, 160: College Station, TX (Ocean Drilling Program), 309-331.

Emeis K.C., Struck U., Schulz H., Rossignol-Strick M., Erlenkeuser H., Howell M.W., Kroon D., Mackensen H., Ishizuka S., Oba T., Sakamoto T. & Koizumi I. (submitted) - Eastern Mediterranean surface water temperatures and $\delta^{18}O$ composition during deposition of sapropels in the late Quaternary. *Paleoceanography*, Washington DC.

Emeis K.C., Struck U., Schulz H.-M., Rosenberg R., Bernasconi S., Erlenkeuser H., Sakamoto T. & Martinez-Ruiz F. (2000) - Temperature and salinity of Mediterranean Sea surface water over the last 16.000 years from records of planktonic stable oxygen isotopes and alkenone unsaturation ratios. *Paleogeogr., Paleoclim., Paleoecol.*, 158: 259-280, Amsterdam.

Giunta S. (2001) - I coccolitoforidi ed i loro derivati geochimici (alkenoni): un valido strumento per l'interpretazione paleoclimatica e paleoceanografica degli ultimi 18.000 anni. (Mediterraneo centro-orientale e Oceano Indiano). PHD. Dissertation. Bologna Univ., Bologna.

Gong C. & Hollander D.J. (1999) - Evidence for differential degradation of alkenones under contrasting bottom water oxygen conditions: implication for paleotemperature reconstructions. *Geochim. Cosmochim.Acta*, 63(3/4): 405-411, Amsterdam.

Grimalt J.O., Rullkoetter J., Sicre M.A., Summons R., Farrington J., Harvey H.R., Goni M. & Sawada K. (2000) - Modifications if the C37 alkenone and alkenoate composition in the water column and sediment: possible implications for sea surface temperature estimates in paleoceanography. *Geochemistry, Geophysics and Geosystems*, 1(November 10). Web site: http://146.201.254.53/

Grimalt J.O., Calvo E. & Pelejero C. (2001) - Sea surface paleotemperature errors in $U^{k'}_{37}$ estimation due to alkenone measurements near the limit of detection. *Paleoceanography*, 16(2): 226-232, Washington DC.

Herbert T.D., Schuffert J.D., Thomas D., Lange CC., Weinheimer A., Peleo-Alampay A. & Herguera J.C. (1998) - Depth and seasonality of alkenone production along the California margin inferred from a core top transect. *Paleoceanography*, 13(3): 263-271, Washington DC.

Hoefs M.J.L., Versteegh G.J.M., Rijpstra W.I.C., de Leeuw J.W. & Sinninghe Darusté J.S. (1998) - Postdepositional oxic degradation of alkenones: implications for the measurement of paleo sea surface temperatures. *Paleoceanography*, 13(1):42-49, Washington DC.

Jasper J. P. & Gagosian R.B. (1989) - Alkenone molecular stratigraphy in an oceanic environment effected by glacial freshwater events. *Paleoceanography*, 4(6): 603-614, Washington DC.

Kallel N., Duplessy J.-C., Labeyrie L., Fontugne M., Paterne M. & Montacer M. (2000) - Mediterranean pluvial periods and sapropel formation over the last 200.000 years. *Palaeogeogr., Palaeoclim., Palaeoecol.*, 157: 45-58, Amsterdam.

Madureira L.A.S., van Kreveld S.A., Eglinton G., Conte M.H., Ganssen G., van Hinte J.E. & Ottens J.J. (1997) - Late Quaternary high resolution biomarker and other sedimentary climate proxies in a northeast Atlantic core. *Paleoceanography*, 12(2): 255-269, Washington DC.

Marabini F. & Veggiani A. (1993) - Evolutional Trends of the Coastal Zone and the Influence of Climatic Fluctuations. In: Phyllis M. Grifman, James A. Fawcett (eds.) - International perspectives on Coastal Ocean Space Utilization. *Sea Grant Progr. Southern California Univ.*: 459-474, Los Angeles.

McIntyre A. (1967) - Coccolith as paleoclimatic indicators of Pleistocene Glaciations. *Science*, 158: 1314-1317, Washington DC.

Müller P.J., Kirst G., Ruhland G., von Storch I. & Rosell-Melé A. (1998) - Calibration of the alkenone paleotemperature index $U^{k'}_{37}$ based on core-tops from eastern South Atlantic and the global ocean (60°N-60°S). *Geochim. Cosmochim. Acta*, 62(19): 1757-1772, Amsterdam.

Negri A. & Giunta S. (2001) - Calcareous nannofossil paleoecology in the sapropel S1 of the eastern Ionian sea: paleoceanographic implications. *Palaeogeogr., Palaeoclim., Palaeoecol.*, 169: 101-112, Amsterdam.

Prahl F.G., Muehlhausen L. A. & Zahne D.L. (1988) - Further evaluation of long-chain alkenones as indicators of paleoceanographic conditions. *Geochim. Cosmochim. Acta*, 52: 2303-2310, Amsterdam.

Prahl F.G., de Lange G. J., Lyle M. & Sparrow M. A. (1989) - Post depositional stability of long-chain alkenones under contrasting redox conditions. *Nature*, 341:434-437, London.

Prahl F.G. & Wakeham, S.G. (1987) - Calibration of unsaturation patterns in long-chain ketone composotions for paleotemperature assesment. *Nature*, 330: 367-369, London.

Rohling, E.J., Jorissen F.J. & De Stigter H.C. (1997) - 200 year interruption of Holocene sapropel formation in the Adriatic sae. *J. Micropaleontol.*, 16(2): 97-108, London.

Rohling E.J. & De Rijk S. (1999) - Holocene Climate Optimum and Last Glacial Maximum in the Mediterranean: the marine oxygen isotope record. *Marine Geology*, 153: 57-75, Amsterdam.

Rosell-Melé A., Eglinton G., Pflaumann U. & Sarnthein M. (1995) - Atlantic core-top calibration of the $U^{k'}_{37}$ index as a sea-surface paleotemperature indicator. *Geochim. Cosmochim. Acta*, 59(15): 3099-3107, Amsterdam.

Rosell-Melé A., Bard E., Emeis K.-C., Grimalt J., Müller P., Schneider R., Bouloubassi I., Epstein B., Fahl K., Fluegge A., Freeman K., Goni M., Güntner U., Hartz D., Hellebust S., Herbert T., Ikehara M., Ishiwatari R., Kawamura K., Kenig F., de Leeuw J., Lehman S., Ohkuchi N., Pancost R.D., Prahl F., Quinn J., Rontani J.-F., Rostek F., Rullkötter J., Sachs J., Sanders D., Sawada K., Schulz-Bull D., Sikes E., Ternois Y., Versteegh G., Volkman J. & Wakeham S. (2001) - Inter-laboratory comparison of the quantification of the relative (Uk´37) and absolute abundance of alkenones. *Geochemistry, Geophysics, Geosystems*, 2:2000GC000141.

Ternois Y., Sicre M.-A., Boireau A., Conte M.H. & Eglinton G. (1997) - Evaluation of long-chain alkenones as paleotemperature indicators in the Mediterranean Sea. *Deep-Sea Res.*, 1 (44): 271-286, Oxford.

Ternois Y., Sicre M.-A., Boireau A., Marty J.-C. & Mique, J.-C. (1996) - Production patterns of alkenones in the Mediterranean Sea. *Geophysical Res. Lett.*, 23: 3171-3174, Washington DC.

Van Santvoort P.J.M., de Lange G.J., Langereis C.G., Dekkers M.J. & Paterne M. (1997) - Geochemical and paleomagnetic evidence for the occurrence of "missing" sapropels in the eastern Mediterranean sediments. *Paleoceanography*, 12(6): p. 773-786, Washington DC.

Veggiani A. (1986) - L'ottimo climatico medievale in Europa. Testimonianze lungo la fascia costiera padano-adriatica. *Studi Romagnoli*, XXXVII : 3-26, Bologna.

Veggiani A. (1994) - I deterioramenti climatici dell'età del ferro e dell'Alto Medioevo. In: - Torricelliana. *Boll. Soc. Torr. Sc. Lett.*, 45: 1-80, Faenza.

Vergnaud-Grazzini C., Ryan W.B.F. & Cita M.B. (1977) - Stable isotopic fractionation, climate change and episodic stagnation in the eastern Mediterranean during the late Quaternary. *Marine Micropaleontology*, 2: 353-370, Amsterdam.

Vergnaud-Grazzini C, Borsetti A.M., Cati F., Colantoni P., D'Onofrio S., Saliege J.F., Sartori R. & Tampieri R. (1988) - Paleoceanographic record of the last deglaciation in the strait of Sicily. *Marine Micropaleontology*, 13: 1-21.

Volkmann J.K., Eglinton G., Lorner E.D.S. & Forsberg T.E.V. (1980) - Long-chain alkenes and alkenones in the marine coccolithophorid Emiliana huxleyi. *Phytochemistry,* 19: 2619-2622, Oxford.

Volkmann J.K., Barret S.M., Blackburn S. I. & Sikes E.L. (1995) - Alkenones in Gephyrocapsa oceanica: implications for studies of paleoclimate. *Geochim. Cosmochim. Acta,* 59(3): 513-520, Amsterdam.

Westbroeck P., Brown C. W., von Bleijswijk J., Brownlee C., Brummer G. J., Conte M., Egge J, Fernandez E., Jordan R., Knappertsbusch M., Stefels J., Veldhuis M., van der Wal P. & Young J. (1993) - A model system approach to biological climate forcing. The example of *Emiliana huxleyi. Global Planet. Change*, 8: 27-46, Amsterdam.

Zhao M., Beveridge N.A.S., Shackleton N.J., Sarnthein M. & Eglinton G. (1995) - Molecular stratigraphy of cores of northwest Africa: sea surface temperature history over the last 80 ka. *Paleoceanography*, 10(3): 661-675, Washington DC.

Zhao M., Rossel A. & Eglinton G. (1993) - Comparison of two $U^{k'}_{37}$ -sea surface temperature records for the last climatic cycle at ODP Site 658 from the sub-tropical Northeast Atlantic. *Palaeogeogr., Palaeoclimat., Palaeoecol,* 103: 57-65, Amsterdam.