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The impact of ice-sheet dynamics in western Mediterranean environmental conditions during Terminations. An approach based on terrestrial long chain n-alkanes deposited in the upper slope of the Gulf of Lions

Aleix Cortina [a,*], Joan O. Grimalt [a], Andrés Rigual-Hernández [c], Anne-Marie Ballegeer [c], Belen Martrat [a], Francisco Javier Sierro [b], José Abel Flores [b]

[a] Department of Environmental Chemistry, IDAEA-CSIC, 08034 Barcelona, Spain
[b] Department of Geology, University of Salamanca, 37008 Salamanca, Spain
[c] Department of Biological Sciences, Macquarie University, North Ryde, NSW 2109, Australia

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ABSTRACT

During the PROMESS campaign (summer 2004) a borehole (PRGL1) was drilled in the upper slope of the Gulf of Lions. Previous studies showed that the deposition of the sedimentary units at borehole PRGL1 was determined by changes in the discharge of the Rhone river, induced by sea level and climate variability with a strong 100 ka imprint. However, there are no detailed studies that focus on the glacial/interglacial transitions (i.e. Terminations) that define 100 ka Quaternary ice-age cycles. Here we present a high-resolution record of terrestrial long chain n-alkanes (C_{21} to C_{33}) from MIS 3 to MIS 11 in order to monitor changes in the sediments deposited on the upper slope of the Gulf of Lions with the aim to provide new insight into the climatic events occurring during Terminations in the western Mediterranean Sea.

Principal component analysis grouped n-alkane on the basis of the degree of maturation of organic matter (fresh/degraded) that allowed to monitor past variability in the source of the sediment deposited in the upper slope as a consequence of sea level and climate change. This information was used to estimate the impact that northern ice-sheet variability had on the western Mediterranean basin. As sea level started to fall, fresh terrestrial organic matter increased owing to the seaward migration of Rhone's mouth. Simultaneously, the decrease in sea level exposed old and reworked organic material from the Rhone's catchment, including the delta plain and the continental shelf, that was eroded and transported into our study site. This resulted in an increase in the proportion of degraded terrestrial organic matter together with sea level decrease. Aside from sea level changes, the proportion of fresh vs degraded organic matter seems to be affected by the amount of continental runoff, with an increasing proportion of fresh terrestrial organic matter occurring at times of reduced continental runoff. During the last glacial, the increase of fresh terrestrial organic matter was contemporaneous with Heinrich events (HEs), suggesting dry and cold conditions on the western Mediterranean basin. These dry and cold millennial-scale episodes were reproduced during Terminations II, III and IV preceding flood events, most probably due to weakening/reinforcement of Atlantic Meridional Overturning Circulation (AMOC) that caused dry/humid conditions in western Mediterranean.

1. Introduction

The Gulf of Lions is a stable and micro-tidal continental margin located in the northwestern sector of the Mediterranean Sea, south of the Rhone delta. It comprises a wide and crescent-shaped shelf and a continental slope indented by numerous submarine canyons (Fig. 1). Previous studies in this region have allowed the reconstruction of the architecture and stratigraphy of the Gulf of Lions continental margin over the Late Pleistocene and Holocene (Tesson et al., 1990; Berne et al., 1998; Jouet et al., 2006; Bassetti et al., 2008; Sierro et al., 2009 among others). The sedimentary units deposited on this continental shelf during the Late Pleistocene and Holocene were the result of changes in the accommodation space, which is defined as the volume available to store sediment and water on the shelf. Drops in sea level during periods of maximum glaciation over the last 400 ka (i.e. MIS 2, 6, 8 and 10) resulted in the reduction of the accommodation space and in a consequent increase of the sedimentation rate on the shelf. This process produced a rapid progradation of the deltaic system and a subsequent formation of forced regressive deposits (Posamentier

* Corresponding author.
E-mail address: acortina@usal.es (A. Cortina).

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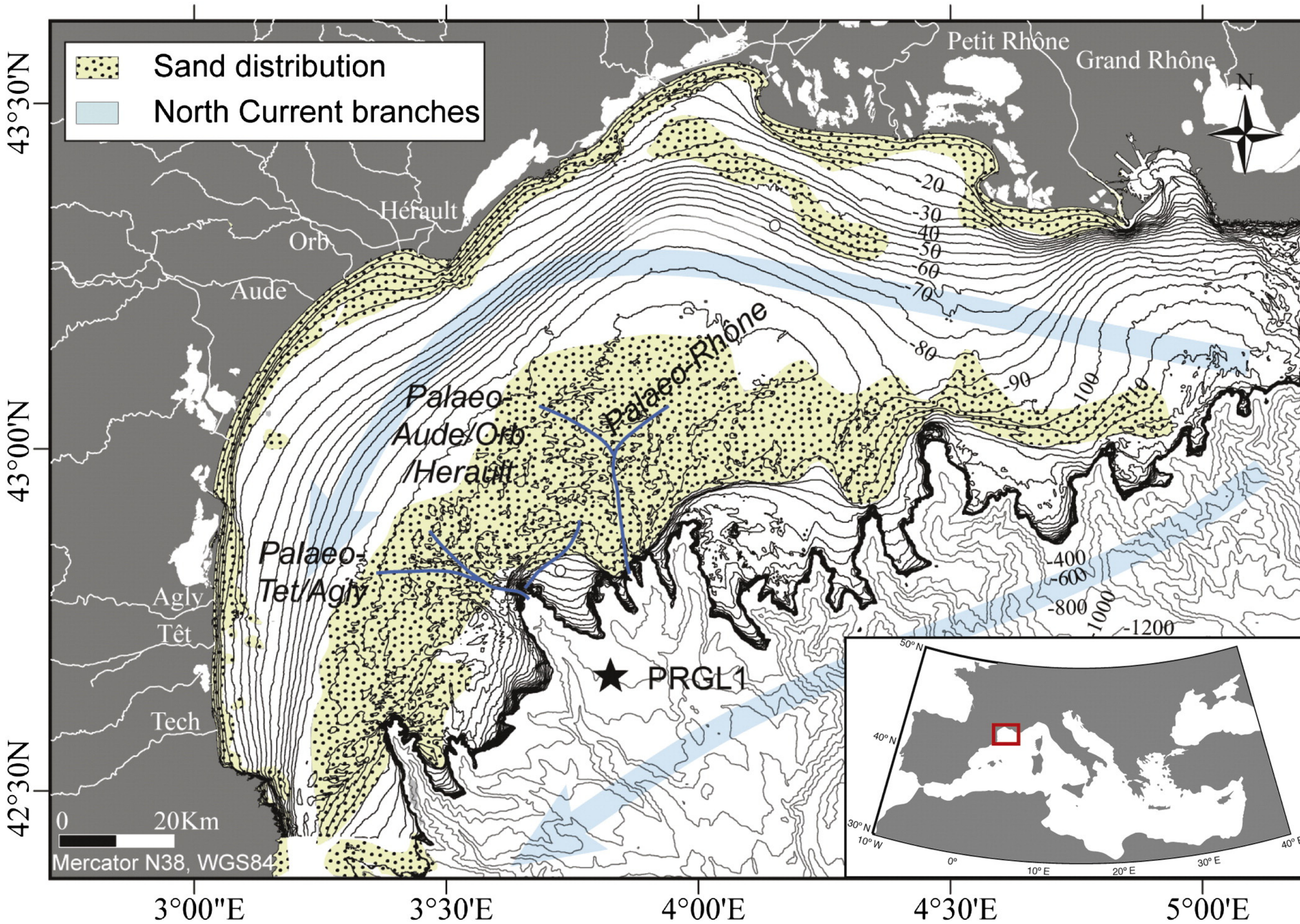

Fig. 1. Map of the Gulf of Lions. The present-day morphology and the sand distribution on the continental shelf (Aloïsi, 1986) illustrating the Last Glacial sea level rise. Blue arrows depict the two North Current branches. Core site PRGL1 is indicated by a black star. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Map taken from Jouet et al. (2006).

et al., 1992), which are characterized by fine-grained pelitic sediments (Bassetti et al., 2006). In contrast, sea level rises during deglaciation periods (e.g. Holocene) were associated with a rapid retrogradation of the deltaic system from the outer to the inner shelf, as indicated by the series of transgressive parasequences overlying the regressive parasequence sets (Berne et al., 2007). The transgressive parasequences were characterized by pelagic coarse-grained skeletal sediments and low sedimentation rates (Bassetti et al., 2006).

Due to its location, the Gulf of Lions plays an important role in the general circulation of the Mediterranean Sea as Western Mediterranean Deep Water (WMDW) is formed. These water masses are formed when Modified Atlantic Water cools and sinks (Millot, 1999). Past climate changes in its source area have had an impact on WMDW formation (Cacho et al., 2002; Sierro et al., 2005; Frigola et al., 2008; Nieto-Moreno et al., 2011, among others), which highlights the importance of performing paleoclimate studies in this region.

The last glacial period was imprinted by major cooling episodes known as Heinrich events (HEs), which involved massive iceberg discharges into the North Atlantic (Bond et al., 1993). Each of these events marked the end of a series of cold and warm oscillations (stadials and interstadials respectively), which began with a prominent warming. During HE, drifting North Atlantic icebergs led to the entrance of meltwater in the western Mediterranean basin producing brief, yet pronounced, negative isotope anomalies which coincided with a large increase in the polar species *Neogloboquadrina pachyderma* (sin) (Sierro et al., 2005). H-like events were also present during Terminations II, III and IV (T-II, T-III, T-IV) when prominent Ice Rafted Debris (IRD) discharges were reported in the North Atlantic (McManus et al., 1999).

Sediments deposited in the upper slope of the Gulf of Lions successfully monitored the nature of HE during MIS 3. Sierro et al. (2009) demonstrated that a sea level rise had occurred after the HE by studying the formation of condensed layers (CLs) in the upper slope of the Gulf of Lions. The CLs, rich in biogenic material, were deposited during times of slow sedimentation rates with high sea levels, when the coastline was very distant from the shelf break, accommodating the prodeltaic muds and coastal sediments supplied by the river in the continental shelf. Frigola et al. (2012) also achieved similar results by using a silt/clay ratio on carbonate free sediments (Ca-free silt/clay ratio). A high Ca-free silt/clay ratio after HE was interpreted as a consequence of Dense Shelf Water Cascading (DSWC) reinforcement due to a greater water volume at the continental shelf during periods of high sea level. However, these granulometric proxies (Sierro et al., 2009; Frigola et al., 2012) need a water mass threshold lying at the continental shelf, making time a critical aspect for monitoring climate effects. For this reason, the development of a new approach independent of either CL formation or DSWC activation with the aim to assess the impact of rapid H-stadial events during Terminations is needed.

The study of Terminations is crucial for understanding Quaternary ice-age cycles with a predominant 100 ka periodicity because they define the saw-toothed character of glacial to interglacial transitions (Broecker and van Donk, 1970) with gradual buildup and rapid collapse of ice-sheets. However, the explanation of this 100 ka period has been problematic because, even though it dominates the ice-volume power spectrum, its power is small in the insolation spectrum. Furthermore, a high-resolution study in the Alboran Sea (i.e. close to our area) on Terminations has revealed rapid warm/cold transitions, highlighting the intricate nature of these periods (Martrat et al., 2014). Therefore, further research needs to be carried out for these periods in order to unveil the climate processes occurring at the centennial-to millennial-scale periodicities, allowing for a better understanding of the mechanisms triggering 100 ka ice-age cycles.

The sediments carried by the Rhone were deposited on the upper slope during the past five climate cycles (Tesson et al., 1990; Berne et al., 1998; Jouet et al., 2006; Bassetti et al., 2008; Sierro et al., 2009; Frigola et al., 2012; Cortina et al., 2013) suggesting that the use of terrestrial biomarkers could be advantageous to understand past climate variability. A previous study at the same site (Cortina et al., 2013), using benthic foraminifer assemblages and the proportion between Sr and Ca in the sediments, identified an increase of $CaCO_3$ associated to a detrital source during lowstands. These results revealed that this site precisely monitors the Rhone's mouth position as a function of the degree of sediment maturation; increasing its detrital component associated to fine-grained pelitic sediments (Bassetti et al., 2006) at times of low sea level.

Long chain n-alkanes concentration and the relative abundance of even/odd carbon preference vary as a function of the degree of organic matter maturity (Bray and Evans, 1961). Hence, the study of long chain n-alkane concentration and distribution could be used at PRGL1 to monitor changes in the Rhone's mouth position deriving from changes in climate and sea level. Contrary to the granulometric proxies previously presented (Sierro et al., 2009; Frigola et al., 2012) a time threshold is not needed in order to monitor past climate oscillations, implying that biomarker analyses could be extremely useful to assess climate oscillation during short periods (e.g. Terminations) when measured at high resolution.

Here we present a new approach based on biomarker analyses including long chain n-alkane and alkenone compounds. The central objectives of our study are to characterize the sedimentary units deposited during the last 440 ka and to assess the impact of the H-like events during Terminations II, III and IV on the climatic conditions of the northwestern Mediterranean region.

2. Study area

The study site is located on the upper slope of the Gulf of Lions, on the interfluve of the Boucart and Herault canyons at a water depth of 298 m (Fig. 1). The location of this site, which is not far from the shelf-break, provides the potential for recording glacial-to-interglacial changes in sediment supply from the Rhone. This area is very suitable for the preservation of continuous sedimentary records because of the balance between the sedimentation rates and the accommodation space. Furthermore, it is not strongly influenced by the Rhone deltaic system and is very distant from the Catalonian Margin, where erosive processes have been documented (Rabineau et al., 2005).

The general oceanographic circulation in the Gulf of Lions is governed by the Northern Current (NC), which is divided into two branches: the principal branch flowing through the continental slope and a secondary branch that penetrates the continental shelf (Millot, 1990) (Fig. 1). Due to seasonal stratification and changing wind regimes, the current oscillates in magnitude and direction over the year, doubling its magnitude during winter in comparison with the summer months (Béthoux, 1984).

3. Material and methods

During the PROMESS1 campaign (summer 2004), a borehole (PRGL1) was drilled in the Gulf of Lions (42.690 N, 3.838 E) (Fig. 1) in order to study the sea level changes and climatic variability of the western Mediterranean Basin. In the laboratory, 1-cm-thick slices were taken for every 10 cm. In this study we analyzed samples from 19.25 to 230.90 mbsf (meter below sea floor), representing material aged from 23 ka to 440 ka.

3.1. Age model and *Globigerina bulloides* $\delta^{18}O$ record

The age model used in this paper was derived from two previous studies on borehole PRGL1: for 19.25 to 157.10 mbsf the age model published by Sierro et al. (2009) was used, whereas for 157.10 to 230.90 mbsf, the age model published by Frigola et al. (2012) was applied. In both cases the age model was mainly based on comparison of the *G. bulloides* $\delta^{18}O$ record with the LR04 benthic stack (Lisiecki and Raymo, 2005). The calculated sedimentation rates resulted in an average sampling resolution of 1150 years during interglacials and 160 years during glacial stages.

3.2. Biomarker analysis

A total of 700 samples were analyzed. Biomarker extraction was based on the Villanueva et al. (1997b) procedure. Samples were freeze-dried. An internal standard (n-nonadecan-1-ol, n-hexatriacontane and n-dotetracontane) of about 2.5 g of sediment that was extracted with dichloromethane in an ultrasonic bath was included. The extract was saponified with 10% potassium hydroxide in methanol to clean up the interferences with carboxylic acids and ester wax. The phase with the neutral lipids was extracted with hexane which was completely evaporated under an N_2 atmosphere. Finally, the compounds were re-dissolved with toluene and derivatized with bis(trimethylsilyl) trifluoroacetamide and analyzed with gas chromatography. The samples were analyzed with a Varian 3800 equipped with a Zebron Phenomenex ZB-1HT INFERNO column coated with 100% dimethylpolysiloxane (film thickness of 0.12 mm; 50 mL ∗ 0.32 mm ID). Hydrogen was the carrier gas (2.5 mL/min). The oven was programmed from 90 °C (holding time of 1 min) to 170 °C at 20 °C/min, then to 280 °C at 6 °C/min (holding time 25 min), to 320 °C at 10 °C/min (holding time 12 min). The injector was programmed from 90 °C (holding time 0.5 min) to 350 °C at 200 °C/min (holding time was 20 min) (holding time of 1 min). The detector was maintained with a constant temperature of 320 °C.

From chromatograms, the long chain n-alkane (C_{21} to C_{33}) where identified by direct comparison of retention times of known standards and samples. The area of each compound was then integrated and converted to concentration taking into consideration sample weight and internal standard concentration.

3.3. Biomarker proxies

Long chain di- and tri-unsaturated alkenones (C_{37}) are produced by few phytoplankton species belonging to the class of Prymnesiophyceae. Thus, the concentration of alkenones in the sedimentary record can be used as a proxy for productivity (Prahl et al., 1993; Villanueva et al., 1998; Zhao et al., 2006). In this study, alkenone concentrations from a previous study (Cortina et al., 2015) were used to monitor past productivity in the area.

Sediments also receive allocthonous organic compounds from continental vascular plants, e.g. long chain n-alkanes, which are terrestrial plant waxes easily removed from leaf surfaces especially by sandblasting during dust storms (Eglinton and Hamilton, 1967; Eglinton and Eglinton, 2008). The n-alkanes analyzed in this study comprise series from C_{21} to C_{33} odd/even carbon numbered. Long chain C_{23}–C_{33} n-alkanes with a strong predominance of homologs with an odd carbon number are derived from fresh terrestrial organic matter (Eglinton and Hamilton, 1967). On the contrary, degraded organic matter typically displays a distribution of n-alkanes without an odd carbon number preference. In order to quantify n-alkane distribution and to assess the degree of maturation of terrestrial organic matter two indexes were used: (1) Carbon Preference Index (CPI), and (2) Alkane Reworked (A_{rew}).

The CPI (Bray and Evans, 1961) of n-alkanes was used to examine the odd over even carbon number predominance as follows:

$$\mathrm{CPI} = \frac{\sum_{i=0}^{4} C_{(25+2i)}}{\sum_{i=0}^{4} C_{(24+2i)}}$$

where C_i is the measured concentration of each n-alkane. CPI values close to 1 indicate either a contribution from petroleum contamination or degraded organic matter (Bouloubassi et al., 1997), whereas CPIs > 3 indicate input from terrestrial plants (Bray and Evans, 1961).

In order to differentiate the odd numbered higher plant n-alkanes from the reworked n-alkanes we used the following expression (Villanueva et al., 1997a):

$$A_{odd} = \sum_{i=1}^{6} C_{(21+2i)} - \sum_{i=1}^{5} C_{(22+2i)} - \frac{C_{22} + C_{32}}{2}$$
$$A_{rew} = C_t - A_{odd}$$

where C_i is the measured concentration of each n-alkane and C_t is the sum if all n-alkane homologs between C_{21} and C_{33}. Higher values would be indicative of a source of degraded organic matter.

3.4. Statistical analysis

In order to assess the relationship and a common source of both n-alkanes and alkenones, we applied a Q-mode principal component analysis (PCA) performed by STATISTICA (StatSoft, Inc., version 7, 2004). We considered long-chain n-alkanes (C_{21}–C_{33}) and alkenone concentrations ($ng*g^{-1}$) as input variables. On the factors obtained, we applied a varimax-normalized rotation with the aim to maximize the sum of the variances of the squared factor loadings (e.g. increase correlation between variables belonging the same factor).

4. Results

4.1. Changes in the organic matter source inferred from its degree of maturation

Glacial-to interglacial stages are well defined in the δ^{18}O *G. bulloides* profile of site PRGL1 (Fig. 2A). The general interglacial–glacial trend of the CPI (Fig. 2B) shows a decrease from maximum values during interglacials to minimum values at times of Glacial Maxima (GM) 2, 6, 8 and 10. Superimposed to this general trend, short-term oscillations are also noticed along the whole record with increases of the CPI at times of heavy *G. bulloides* δ^{18}O values (Fig.2A). The A_{rew} index (Fig. 2C) showed an inverse long-term relationship with CPI, with higher values at times of lower sea level during the GM (e.g. 2, 6, 8, and 10). After that, the A_{rew} index started to decrease at the beginning of the subsequent Terminations reaching its lowest values at the onset of interglacials.

4.2. The evolution of the biomarker concentration at the upper slope of the Gulf of Lions during the last 440 ka

The PCA identified three major components that accounted for 82% of the total variance (Table 1). The sum of the concentrations of the compounds that defines each PCA component was used to monitor changes in the composition of the sediments deposited on the upper slope of the Gulf of Lions.

For Factor 1 (41% of the variance), the main compounds were long chain n-alkane from C_{21} to C_{26}. The sum of their concentrations (Fig. 2D) tended to increase at the end of glacial stages, reaching the highest values prior to Terminations, during GM 2, 6, 8 and 10. Throughout the rest of the record, its values remained comparatively low.

Factor 2, explaining 28% of the variance, is mainly composed of long chain odd n-alkane compounds from C_{27} to C_{33}. The sum of their concentrations (Fig. 2E) shows high variability during the entire record, increasing during the glacial stages (MIS 2, 6, 8 and 10) and MIS 5b, 5d, 7b, 7d, 9b, 9d, 11b, in line with heavy *G. bulloides* δ^{18}O values (Fig. 2A).

Factor 3, with an explained variance of 13% was mainly comprised of long chain di- and tri-unsaturated C_{37} alkenones. The sum of the alkenone compounds concentration (Fig. 2F) indicated significant peaks from 160 ka to 180 ka (MIS 6), at MIS 7d and the interval around 250 to 265 ka (MIS 8). Alkenone concentration remained low for the rest of the record, generally exhibiting relatively higher values during warmer periods of the interglacial stages (i.e. 5a, 5c and 5e).

Total n-alkane concentration (Fig. 2G) mainly oscillated accordingly with the long chain odd n-alkane compounds from C_{27} to C_{33} (Fig. 2E), with a correlation of 0.91 ($p < 0.001$). Correlation decreased to 0.50 ($p < 0.001$) when comparing total n-alkane concentration with the sum of the concentration of the main compounds of factor 1 (long chain n-alkane from C_{21} to C_{26}) (Fig. 2D).

5. Discussion

5.1. Sedimentation processes in the upper slope of the Gulf of Lions over the past 440 ka

The n-alkane distribution along the PRGL1 together with the biomarker indexes described in the present work recorded changes in the source of sediments deposited on the upper slope of the Gulf of Lions. In order to explain these changes we should take into account that first, the Rhone is the main source of sediments for the Gulf of Lions shelf although other rivers account for minor contributions along the coastline (Pont et al., 2002) and second, the shelf accommodation space in the Gulf of Lions (i.e. the volume available to store sediment and water on the shelf) has changed over the Late Pleistocene (Jouet et al., 2006; Bassetti et al., 2008; among others) in response to sea level oscillations. High sedimentation rates (Sierro et al., 2009; Frigola et al., 2012) and a decreased Ca-free silt/clay ratio have been documented at PRGL1 during periods of maximum glaciation MIS 2, 6, 8 and 10. These events were the result of a rapid progradation of the deltaic system towards the shelf edge, as the deltaic system could no longer be accommodated in the shelf during periods of limited accommodation space due to the drop in sea level (Sierro et al., 2009). On the contrary, during interglacial periods the sea level increase resulted in the retrogradation of the deltaic system. During these times there was enough space on the shelf to accommodate the prodeltaic muds and coastal sediments supplied by the Rhone. The outcome was a decrease of the sedimentation rates and the formation of CLs, rich in biogenic material (Sierro et al., 2009).

During glacial stages (MIS 2, 6, 8 and 10) and substages (5b, 5d, 7b, 7d, 9b, 9d, 11b), when the sea level started to fall, an increase in the total amount of n-alkanes (Fig. 2G) with a strong signature of the odd n-alkanes from C_{27} to C_{33} (Fig. 2E) was monitored. Sedimentological studies in the modern Gulf of Lions identified an inverse relationship between n-alkanes concentration and the distance of the Rhone's mouth (Bouloubassi et al., 1997; Kim et al., 2006). Consistent with these studies, our results suggest that the increased Rhone input caused by a seaward migration of its mouth led to an increased supply of terrestrial organic matter to the upper slope. These results are in line with previous studies where these compounds are extensively used as a measure to supply fresh vascular waxy plant matter to the environment (Eglinton and Hamilton, 1963). Therefore, the sum of odd n-alkanes from C_{27} to C_{33} could be used as a reliable proxy of fresh terrestrial organic matter.

As glacial stages further developed, the sea level continued to fall leading to changes in the organic matter composition. An increasing importance of the n-alkanes from C_{21} to C_{26} (Fig. 2D) with a reworked nature (Fig. 2C) and without an odd carbon preference (low CPI) (Fig. 2B) was observed at the PRGL1 location. Usually, the n-alkane

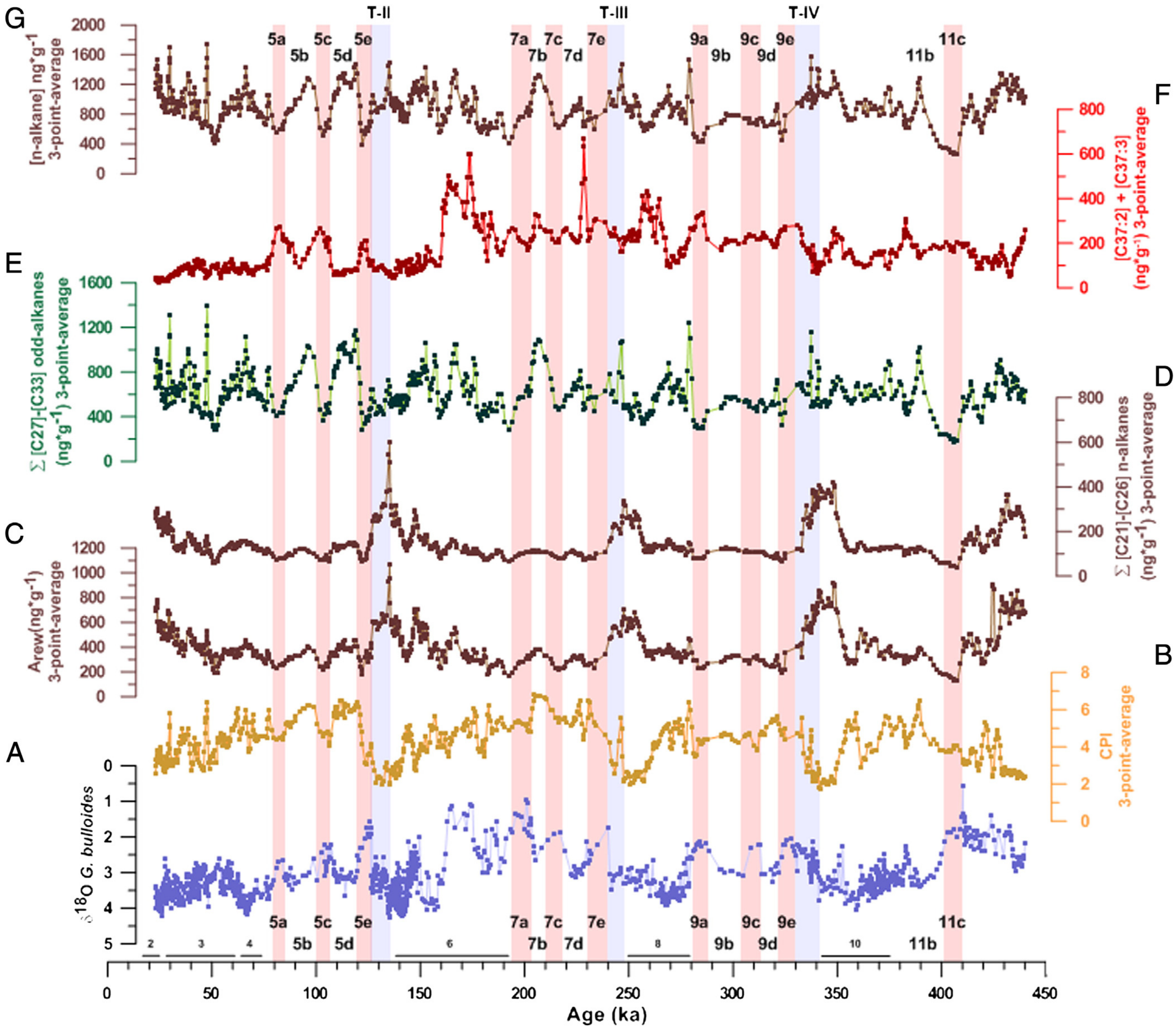

Fig. 2. Biomarkers in sediment core PRGL1. A. *Globigerina bulloides* $\delta^{18}O$ values. B. Three-point-average of the Carbon Preference Index (CPI). C. Three-point-average of the alkane reworked concentration ($ng*g^{-1}$). D. Three-point-average of the sum of the concentrations of C_{21} to C_{26} n-alkanes ($ng*g^{-1}$). E. Three-point-average of the sum of the concentrations of odd-alkanes from C_{27} to C_{33} ($ng*g^{-1}$). F. Three-point-average of the sum of the concentrations of C_{37} di and tri unsaturated alkenone ($ng*g^{-1}$). G. Three-point-average of the total n-alkane concentration ($ng*g^{-1}$). Red bars represent warmer substages. Blue bars indicate Terminations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
A, values from 23 ka to 265 ka were taken from Sierro et al. (2009), values from 266 ka to 440 ka were taken from Frigola et al. (2012); F, alkenone concentrations were taken from Cortina et al. (2015).

distributions predominated by a mixture of C_{25} to C_{33} n-alkanes with high odd-to-even CPI constitute the typical distribution of hydrocarbons originated from higher plants (Eglinton and Hamilton, 1967). Their occurrence is consistent with the predominant inputs observed in deltaic environments (Albaiges et al., 1984, 1987).

Hydrocarbons in aerobic and anaerobic bacteria generally consist of n-alkanes with no preference for odd or even carbon number homologs in the C_{23} to C_{31} range (Davis, 1968; Jones, 1969; Jones and Young, 1970; Bird and Lynch, 1974; Naccarato et al., 1974). Some fungal (Jones, 1969; Jones and Young, 1970) and yeast (Baraud et al., 1967; Fabre-Joneau et al., 1969) species also synthesize these mixtures.

Microbial modification of originally sedimented organic matter can also be considered as a possible source of these n-alkane distributions in the C_{23} to C_{31} range without odd or even carbon number preference. Johnson and Calder (1973) observed rapid changes brought by in situ microbial activity breaking down the higher plant alkanes with resynthesis of a distribution lacking odd-to-even predominance. In other studies, growing experiments performed with fungal species (*Cladosporium resinae*) using n-C_{16} as substrate showed that a modal n-alkane distribution ranging between C_{19} and C_{30} maximized at n-C_{28} with no odd-to-even carbon number preference is formed (Walker and Cooney, 1973). Studies of bacterial reworking of sedimentary lipids have also led to these distributions (Grimalt et al., 1985, 1988).

Typically, land-derived organic matter is often reported as a mixture of modern and reworked material that has been eroded from sedimentary deposits or paleo-soils. This erosion can be influenced by climate as well as relative changes in base sea level. A detailed study by Bassetti et al. (2008) on the prograding sediment wedges recovered in the vicinity of our core site demonstrated that during general sea level fall our study area was sourced by deposits of reworked material from the entire emerged shelf. Furthermore, a decrease of the sea level would

Table 1
Factor loadings and explained variance of n-alkanes and alkenones resulting from Q-mode principal component analysis. Three factors were extracted explaining a total variance of 82%.

Components	Factor 1	Factor 2	Factor 3
	Loadings		
C21	**0.96**	−0.04	0.14
C22	**0.92**	−0.09	0.00
C23	**0.96**	0.09	0.17
C24	**0.96**	0.10	0.11
C25	**0.86**	0.42	0.16
C26	**0.95**	0.21	0.14
C27	0.30	**0.86**	0.07
C28	0.50	0.32	0.06
C29	0.08	**0.96**	0.12
C30	0.53	0.44	0.06
C31	−0.04	**0.96**	0.07
C32	0.48	0.49	−0.22
C33	0.06	**0.91**	0.02
C37:2	−0.21	−0.17	**−0.91**
C37:3	−0.11	0.00	**−0.95**
Explained variance	41%	28%	13%

Components were listed in a factor if factor loading was higher than 0.7 (bold numbers).

make older sediments available for erosion from the entire Rhone catchment area, including the continental shelf and the delta plain, with a more reworked nature. Consequently, we hypothesize that as sea level falls, a major proportion of old and reworked material from the Rhone catchment area was eroded increasing the proportion of reworked n-alkanes reaching the upper slope. Consequently, the sum of n-alkanes from C_{21} to C_{26} seems to be a reliable tool to monitor degraded terrestrial organic matter.

The variation of n-alkane concentration over the past 440 ka, as shown in Fig. 3A–B, corroborates our sedimentation model. These data suggest a high supply of fresh terrestrial organic matter (odd C_{27} to C_{33}) along the entire record, with a partial substitution of degraded terrestrial organic matter (C_{21} to C_{26}) during GMs. A histogram of the n-alkane concentrations during GM at MIS 10 (Fig. 3D) and MIS 7b (Fig. 3C) allowed us to corroborate the preference for odd carbon number during periods with a predominant deposition of fresh terrestrial organic matter compared to periods with a higher supply of degraded terrestrial organic matter. Despite the changes in composition during glacial stages, the total n-alkane concentrations (Fig. 2G) increased from the beginning to the end of these periods as a result of seaward migration of the shoreline. Our sedimentation

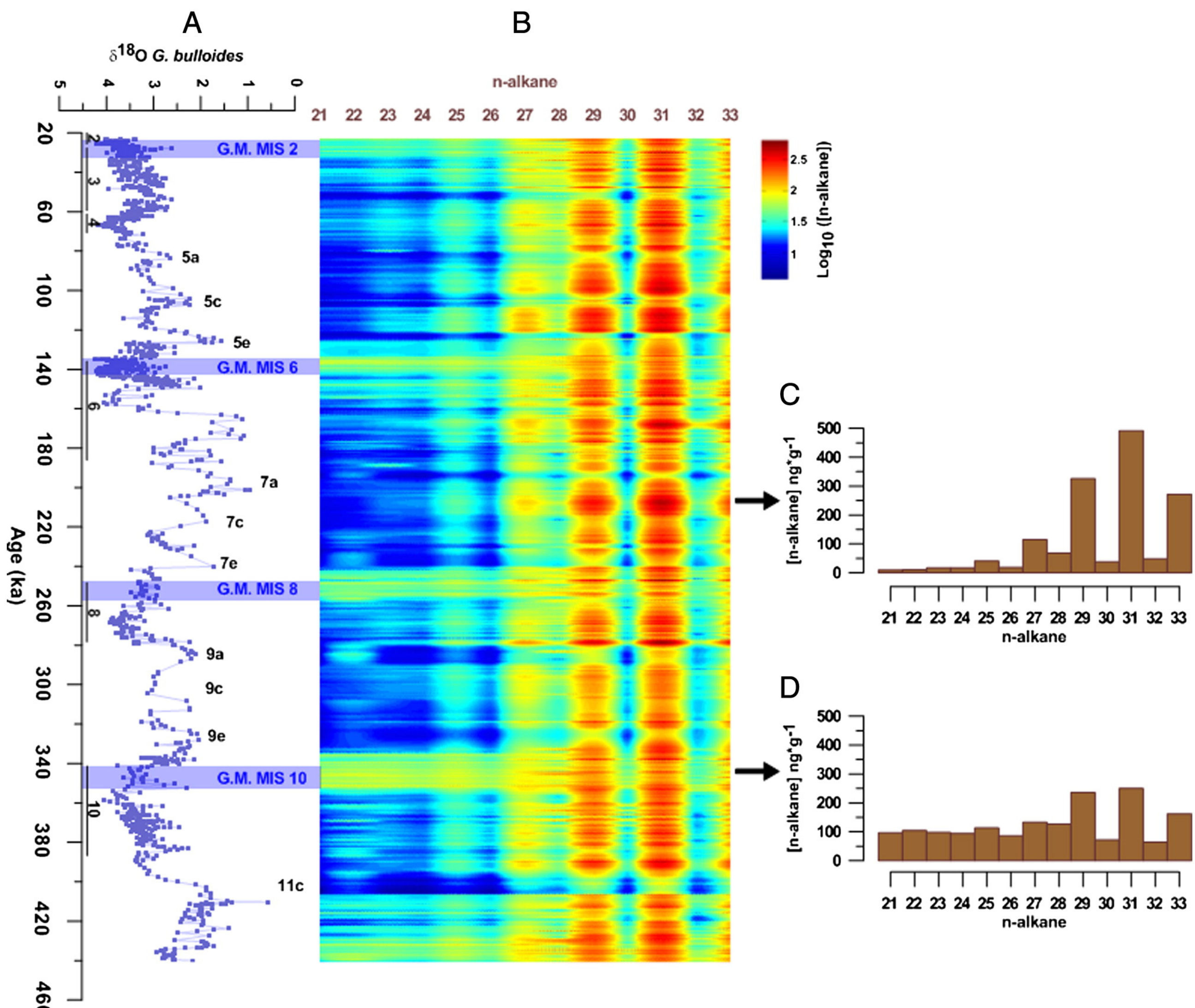

Fig. 3. The n-alkane concentrations in sediment core PRGL1. A. *Globigerina bulloides* $\delta^{18}O$ values. B. Evolution of n-alkane concentration ($ng{*}g^{-1}$) between 23 ka and 440 ka. C. The n-alkane concentration of one sample taken during glacial substage 7b (mbsf: 156.36 m, age: 207 ka). D. The n-alkane concentration of one sample taken during MIS 10 Glacial Maximum (mbsf: 203.46 m, age: 350 ka).
A, values from 23 ka to 265 ka were taken from Sierro et al. (2009), values from 266 ka to 440 ka were taken from Frigola et al. (2012).

model based on n-alkane concentration is in line with previous studies at PRGL1 (Sierro et al., 2009; Cortina et al., 2011, 2013; Frigola et al., 2012) that monitored an increase of the Rhone input as sea level decrease.

In order to ascertain the change in the nature of organic matter (fresh vs degraded), the percentage of both the fresh (Fig. 4H) and degraded terrestrial organic matter was calculated (Fig. 4I). The biogenic carbonate index (Cortina et al., 2013) measures the proportion of biogenic carbonate derived mainly from foraminifera and coccolith shells in relation with detrital carbonate from Dolomite Alps associated fine-grained prodeltaic sediments. This index was calculated from XRF data by subtracting the standardized Ca value from the standardized Sr value (Sr–Ca) (see more details in Cortina et al. (2013)) (Fig. 4E). The sediment deposited during the onset of glacials (Fig. 4A, B) is characterized by the high percentage of fresh terrestrial organic matter (Fig. 4H), which is in agreement with an elevated proportion of biogenic carbonate (Fig. 4E), high values of Ca-free silt/clay ratio (Fig 4F) and benthic foraminifer test concentration (Cortina et al., 2013) (Fig. 4G). As the Rhone's mouth migrated seaward in response to the sea level drop, sedimentation rates at the upper slope increased (Fig. 4C). This occurred because the accommodation space in the continental margin was not sufficient enough to accommodate the sedimentary particles of the Rhone and the fine-grained pelitic sediments associated with the prodeltaic system were deposited at the upper slope (Bassetti et al., 2006). The benthic foraminifer microfauna switched from mesotrophic (highstands) to eutrophic (GM) (Cortina et al., 2013) decreasing the benthic foraminifer test concentration and therefore the proportion of biogenic carbonate owing to elevated Rhone input. The sediments

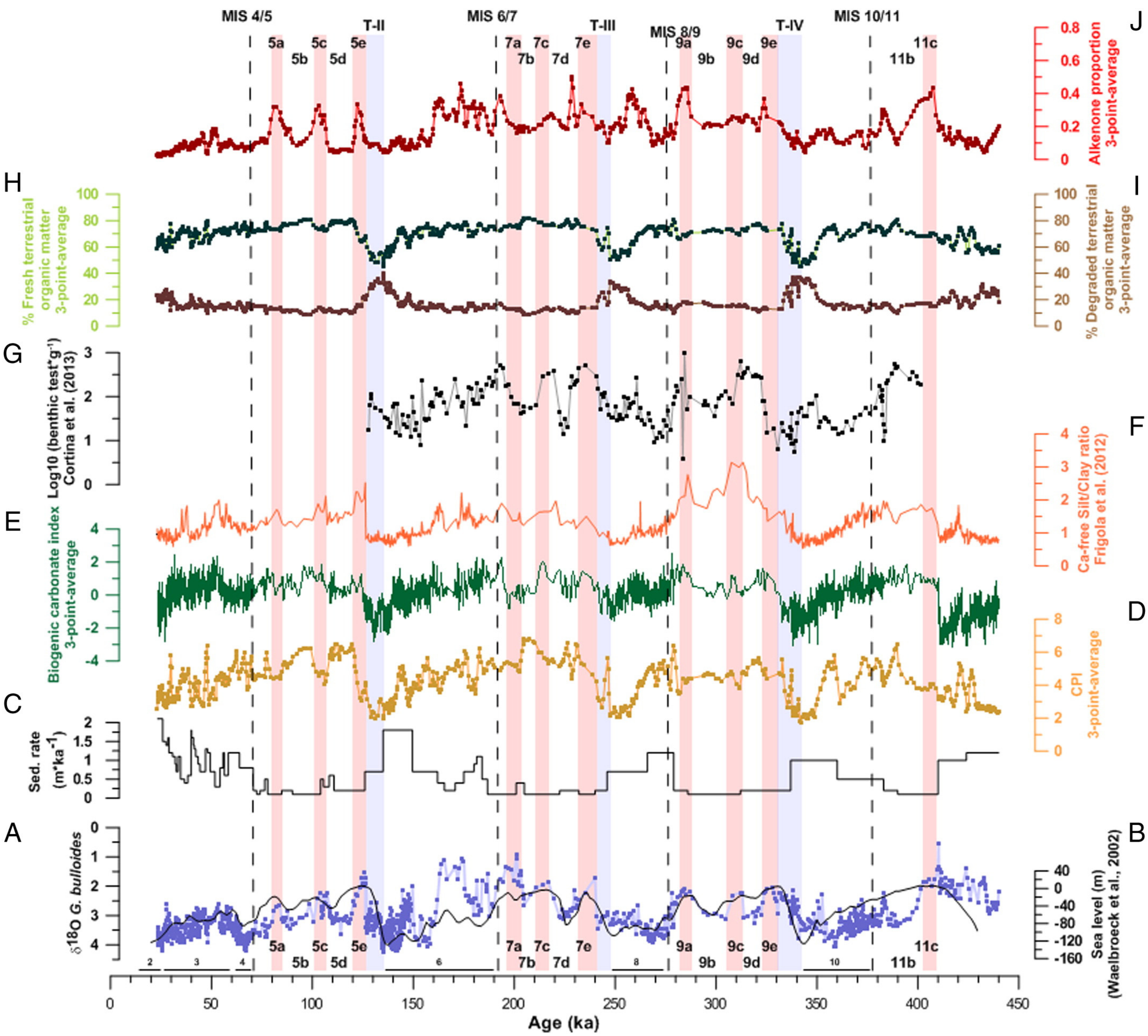

Fig. 4. Fresh vs degraded terrestrial organic carbon deposition at the Gulf of Lions. A. *Globigerina bulloides* δ^{18}O values. B. Sea level reconstruction (Waelbroeck et al., 2002). C. Sedimentation rates ($m*ka^{-1}$). D. Three-point-average of the Carbon Preference Index (CPI). E. Three-point-average of the biogenic carbonate index, see details of calculation in Cortina et al. (2013). F. Silt/clay ratio on carbonate free sediment (Frigola et al., 2012). G. Log10 benthic foraminifer test$*g^{-1}$ (Cortina et al., 2013). H. Three-point-average of the percentage of fresh terrestrial organic matter. I. Three-point-average of the percentage of degraded terrestrial organic matter. J. Three-point-average of the alkenone proportion that was calculated as follows: [alkenones] / ([alkenones] + [n-alkanes]). Red bars represent warmer substages. Blue bars indicate Terminations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
A, values from 23 ka to 265 ka were taken from Sierro et al. (2009), values from 266 ka to 440 ka were taken from Frigola et al. (2012).

deposited on the upper slope during GMs had a higher proportion of degraded terrestrial organic matter with low CPI values (Fig. 4D) associated with fine particles that resulted in a decreased Ca-free silt/clay ratio. These results corroborated the general idea that the decrease in sea level exposed old and reworked material from the Rhone catchment area, including the continental shelf and the delta plain, making these sediments available to erosion. Such conditions led to an increase of the proportion of terrestrial degraded organic matter in the sediments deposited at the upper slope as Rhone input increased due to sea level drop.

5.2. The productivity events recorded by alkenones in the Gulf of Lions during the last 440 ka

Marine biosynthesized alkenones (Table 1, Factor 3) remained relatively low compared with terrestrial derived n-alkanes (Fig. 2G), suggesting the importance of Rhone input in the sediments deposited on the upper slope of the Gulf of Lions. The proportion of alkenones in relation to n-alkanes (i.e. [alkenones] / ([n-alkanes] + [alkenones])) was calculated to evaluate periods with elevated oceanic producers contribution to the sediments (i.e. high ratio values) (Fig. 4J).

Based on planktic foraminifer assemblages (Cortina et al., 2013) it has been demonstrated at PRGL1 from MIS 6 to 11 that productivity in the mixed layer increased during glacial stages (i.e. MIS 6, 8 and 10) and cold substages (i.e. 7b, 7d, 9b, 9d). However, alkenone-based productivity estimates generally showed low values during glacials and no-significant increases at times of cold substages (Fig. 2F). The most plausible explanation for this seems to be the seaward migration of Rhone's mouth as a response to sea level drop and the ensuing increase of Rhone input that diluted oceanic signal (i.e. low alkenone proportion) (Fig. 4J). On the contrary, high alkenones concentrations and proportions were found during warmer periods (i.e. MIS 5a, 5c, 5e, 7a, 7c, 7e, 9a, 9c, 9e and 11c). At these times the increase in sea level caused an increase in the accommodation space in the continental shelf where Rhone sediments where deposited. Hence, the sediments deposited in the upper slope were predominantly of oceanic origin leading to an increase of alkenone concentration and CL formation (Sierro et al., 2009). These results indicated that the record of alkenone-based productivity on the upper slope was highly influenced by Rhone's mouth migration as a response to sea level variability. Moreover, the fact that the proportion of alkenones in relation to n-alkanes decreased simultaneously with CPI values supports the idea that low CPI values were the result of an increase in the proportion of terrestrial degraded organic matter rather than to the increase of low-chain marine-sourced biomarkers (Rosell-Melé and McClymont, 2007).

Very high and distinctive productivity values recorded during cold MIS 8 and 7d periods appear also to have a sea level component, as corroborated by low n-alkane concentrations (Fig. 2G). The MIS 8 productivity event occurred during the glacial period with the highest sea level (Cortina et al., 2013), and the 7d productivity event occurred during a warmer interval (Fig. 4A) with higher temperatures (Cortina et al., 2015) and therefore, a probable sea level rise. The third productivity maximum took place around 170 ka. Interestingly, increased rainfall both in the eastern (Ayalon et al., 2002) and western (Plagnes et al., 2002) Mediterranean basins has been reported during this interval. Furthermore, high percentages of *Neogloboquadrina pachyderma* (dex.) linked to increased annual stratification in the water column have been monitored in the Gulf of Lions, leading to the formation of a deep chlorophyll maximum (Cortina et al., 2013). Taken together, all these evidences suggest that enhanced productivity conditions in the western Mediterranean basin were coetaneous with increased precipitation in the whole Mediterranean Sea around 170 ka. Moreover, the fact that this interval coincides with the deposition of the singular cold Sapropel 6 in the eastern Mediterranean Sea (Cita et al., 1977) suggests a possible link between these two events. However, further research needs to be carried out in order to unveil possible connections.

5.3. The impact of HE on the sediments deposited in the Gulf of Lions during the last glacial period

The granulometric proxies (Sierro et al., 2009; Frigola et al., 2012) require a water mass threshold lying at the continental shelf, making the variable of time a critical aspect for monitoring climate effects. On the contrary, the continuous interplay between fresh and degraded terrestrial organic matter is not time-dependent and therefore can be used to monitor H-like events occurring at millennial scales during Terminations. Hence we propose (1) to assess the impact of HE on terrestrial organic matter deposition (fresh vs degraded) during the last glacial period and, (2) to characterize the H-like events during T-II, T-III and T-IV and its ensuing impact on the western Mediterranean climate.

Light isotope signature (Fig. 5A), and in the case of the strongest events the presence of *N. pachyderma* sin (Fig. 5G), marks the HE during the last glacial period (Sierro et al., 2005). The H3, H4 and H5 in the upper slope of the Gulf of Lions are defined by an increase of the percentage of fresh terrestrial organic matter (Fig 5C) with high CPI (Fig. 5B), and a decrease of the proportion of the degraded terrestrial organic matter (Fig. 5D). Considering the results discussed in Section 5.1, the partial substitution of degraded terrestrial organic matter (associated with low CPI) by fresh terrestrial organic matter (associated with a high CPI) could be taken as an indicator of changes in the source of terrestrial organic matter to the upper slope. Furthermore, granulometric proxies, the CL's formation (Fig. 5E) (Sierro et al., 2009) and the increase of the Ca-free silt/clay ratio via DSWC activation (Fig. 5F) (Frigola et al., 2012) suggest the occurrence of flooding events posterior to HE, or at least restricted to the last phase of HE (Flückiger et al., 2006).

The mechanism behind this variability could be as follows: during the HEs there was a collapse of the Atlantic Meridional Overturning Circulation (AMOC) (Broecker, 1994) concurrent with Northern Hemisphere (NH) coolings owing to reduced inter-hemispheric heat exchange and conspicuous warmings in Antarctica (Blunier and Brook, 2001). During these times the Mediterranean climate was cool and dry (Cacho et al., 1999; Shackleton et al., 2000; Sánchez-Goñi et al., 2002; Combourieu-Nebout et al., 2002; de Abreu et al., 2003; Pérez-Folgado et al., 2003) and rainfall and runoff from continents was reduced (Cacho et al., 1999; Sánchez-Goñi et al., 2002; Combourieu-Nebout et al., 2002; Bartov et al., 2003; Jiménez-Espejo et al., 2007; Rodrigo-Gámiz et al., 2011). The reduction of the runoff from the continents could weaken the erosional processes in Rhone catchment area, plunging the amount of degraded terrestrial organic matter reaching the upper slope and therefore raising the proportion of fresh terrestrial organic matter with elevated odd carbon preference. The rapid AMOC resumption after HE linked with Greenland (Blunier and Brook, 2001) and Mediterranean (Martrat et al., 2004, 2007) warming favored the increase of the Rhone's flow enhancing erosion of old and reworked sediments and thus, the arrival of degraded terrestrial organic matter to the upper slope.

This process finished with a sea level rise during the warmest temperatures in Greenland and both, the formation of the CL in the upper slope of the Gulf of Lions (Fig. 5E) (Sierro et al., 2009) and the increase of Ca-free silt/clay ratio owing to DSWC activation (Frigola et al., 2012). These patterns, although recognizable, are not as apparent in HE5a and HE6 maybe a consequence of higher sea level that prevented the upper slope to monitor clearly the changes in the source of the terrestrial organic matter.

5.4. The impact of the northern ice sheets dynamics on the western Mediterranean climate during T-II, T-III and T-IV

HEs were described as marine sediment layers containing a large concentration of IRD and a scarcity of foraminifera at particular northeast Atlantic mid-latitudes (Broecker et al., 1992) and these IRD were

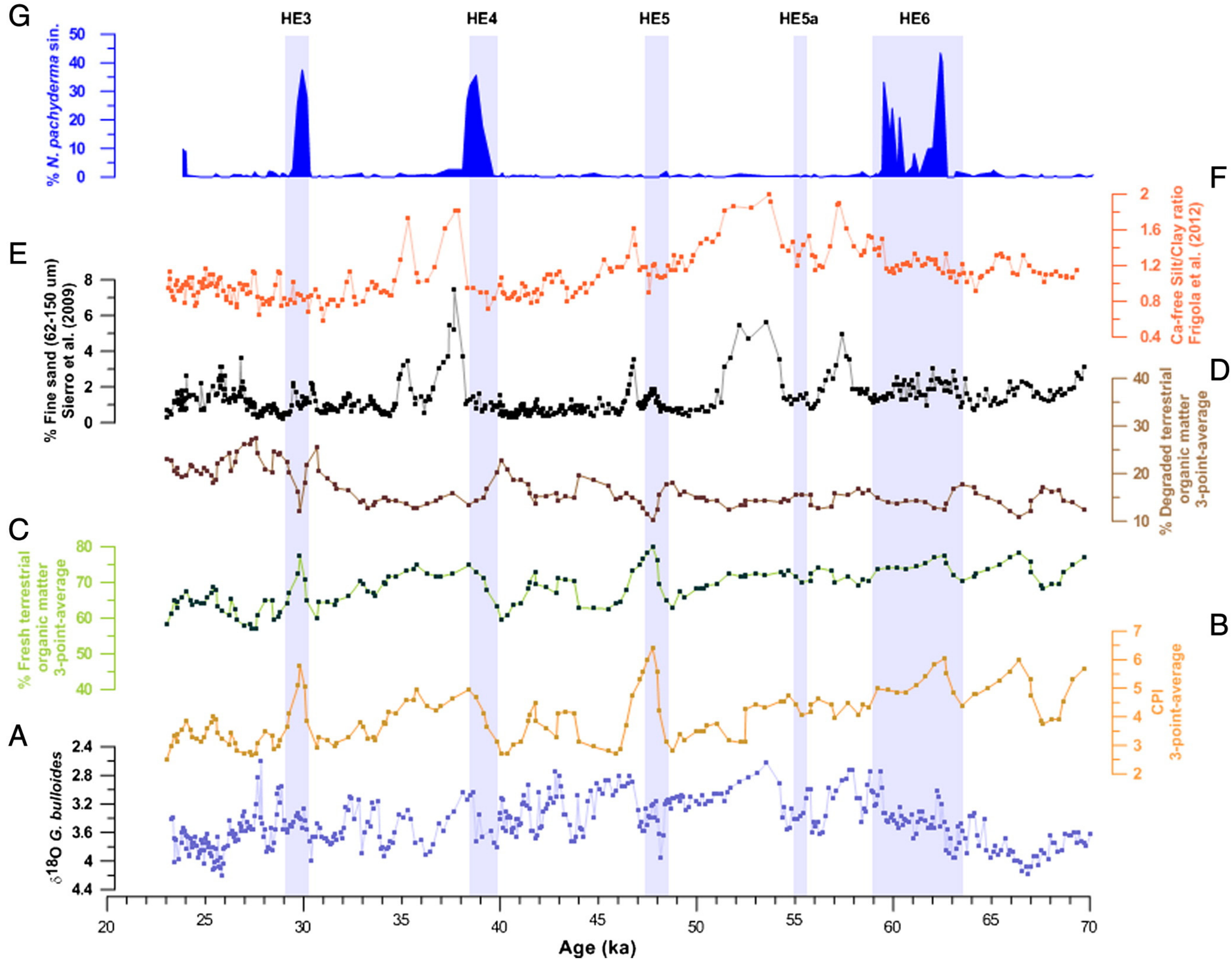

Fig. 5. Impact of Heinrich events on northwestern Mediterranean environmental conditions. A. *Globigerina bulloides* $\delta^{18}O$ values (Sierro et al., 2009). B. Three-point-average of the Carbon Preference Index (CPI). C. Three-point-average of the percentage of fresh terrestrial organic matter D. Three-point-average of the percentage of degraded terrestrial organic matter. E. Percentage fine sand (62–150 μm) (Sierro et al., 2009). F. Silt/clay ratio on carbonate free sediment (Frigola et al., 2012). G. Percentage of *Neogloboquadrina pachyderma* (sin). Blue bands depict Heinrich events (HEs). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

recorded over each of the rapid Terminations during the past 500 ka (McManus et al., 1999).

Fig. 6 shows that in the Gulf of Lions (PRGL1) similar patterns regarding terrestrial organic carbon deposition are monitored during the last glacial period and Terminations. Rapid fresh/degraded oscillations of terrestrial organic matter were monitored (Fig. 6C, D). The mechanisms behind these rapid cold–warm (fresh/degraded terrestrial organic matter) transitions should be similar than those described during last glacial period (Section 5.3), and are probably related to ice rafting and meltwater events in the North Atlantic region (Bond and Lotti, 1995) and its ensuing impact on the climate of the Mediterranean region. Starting from the GM (lower CPI values), rising summer insolation triggered initial disintegration of a massive, isostatically compensated ice sheet (Cheng et al., 2009). The associated injection of fresh water at northern latitudes reduced the North Atlantic Deep Water (NADW) formation, reducing AMOC (Dixon et al., 1999; Wiebe and Weaver, 1999) and initiating a cooling in the North Atlantic region (Barreiro et al., 2008). This AMOC weakening would result in a increase of the atmospheric pressure gradient in the North Atlantic (Ganopolski and Rahmstorf, 2001), which resulted in arid and cold conditions in western Mediterranean (Moreno et al., 2005). Cooling in North Atlantic reduced melt rate and reestablished NADW, causing warming in northern high latitudes. Such conditions would result in decreased atmospheric gradient (Ganopolski and Rahmstorf, 2001), enhancing humid and warm conditions in western Mediterranean (Moreno et al., 2005). The temperature increase at northern latitudes then again led to a freshwater input into the North Atlantic and the gradual shutdown of NADW formation. These rapid cold/warm ended when the interglacial conditions were achieved.

We hypothesize that the changes in the proportion of fresh/degraded terrestrial organic matter are intimately linked to these rapid cold/warm episodes. Cold and arid conditions would lead to a decrease of the Rhone's input. The flow reduction would result in the reduction of old and reworked material erosion that was exposed since sea level is still increasing. Such conditions favored the deposition of fresh terrestrial organic matter in the upper slope. In contrast, during rapid warm and humid events the Rhone's input would increase due to both, a precipitation enhancement and the melting of the continental ice accumulated. Hence, the increase in Rhone's input would enhance the erosion of old and reworked material increasing the proportion of degraded terrestrial organic matter sedimenting on the upper slope. Our model is in line with a previous study in the Gulf of Mexico (Meckler et al., 2008) that described a similar increase in the deposition of reworked material at times of flood events during last deglaciation. These warm episodes, probably associated to flooding events, were analogous to flooding events recorded during last glacial (Sierro et al., 2005; Frigola et al.,

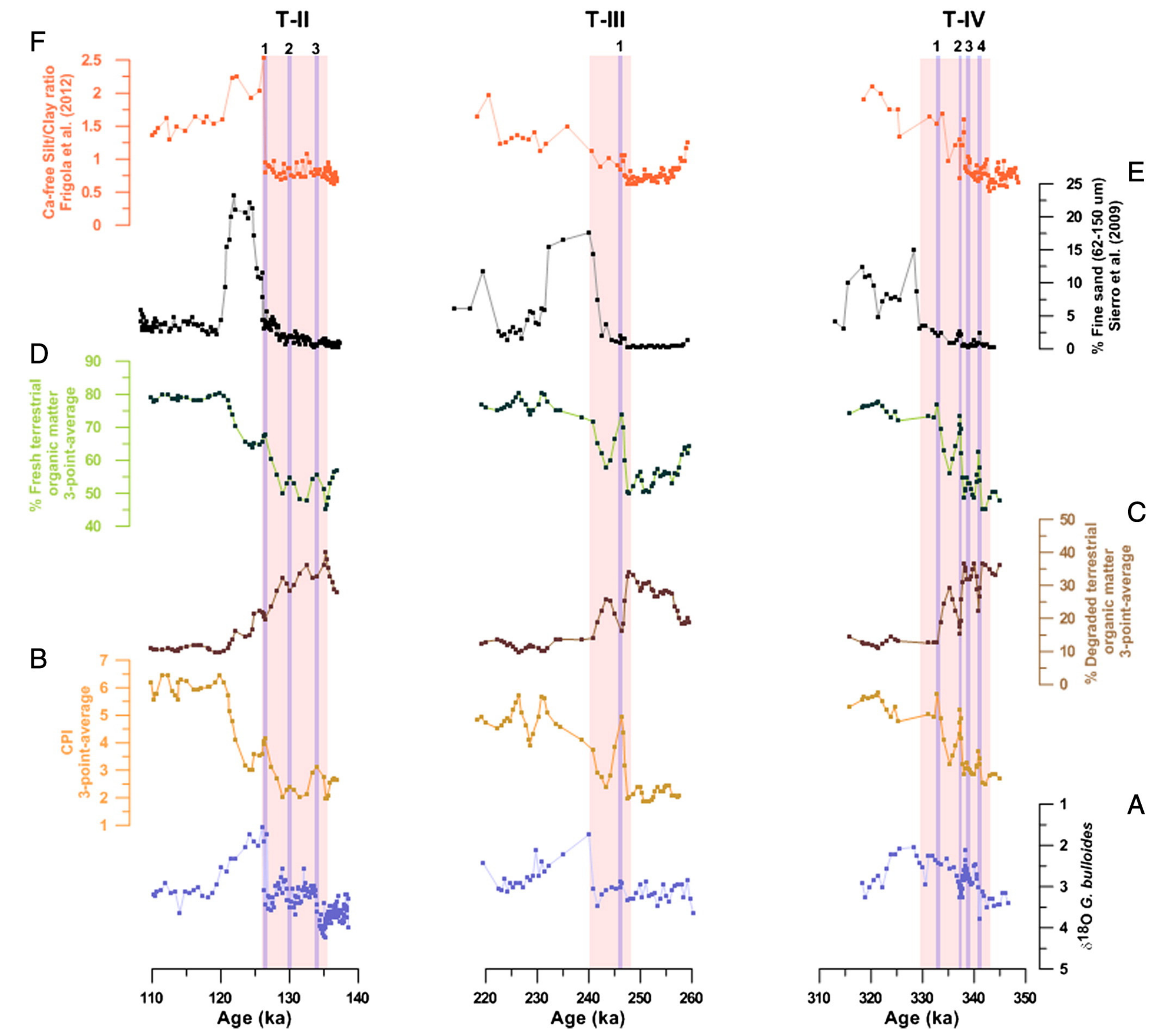

Fig. 6. Impact of H-like events during Terminations on northwestern Mediterranean environmental conditions. A. *Globigerina bulloides* $\delta^{18}O$ values. B. Three-point-average of the Carbon Preference Index (CPI). C. Three-point-average of the percentage of degraded terrestrial organic matter. D. Three-point-average of the percentage of fresh terrestrial organic matter. E. Percentage fine sand (62–150 μm) (Sierro et al., 2009). F. Silt/clay ratio on carbonate free sediment (Frigola et al., 2012). Orange bars depict Terminations. H-like events are numbered and represented by blue bands.
A, values from 23 ka to 265 ka were taken from Sierro et al. (2009), values from 266 ka to 440 ka were taken from Frigola et al. (2012).

2012). However, unlike granulometric proxies (i.e. % fine sand, Ca-free silt/clay ratio) (Fig. 6E, F), our proxy based on n-alkanes responded quickly to change in the Rhone's source monitoring similar patterns during Terminations. These results highlight the usefulness of n-alkane-based proxies to monitor rapid climate oscillations during Terminations.

During T-II and T-IV the increase in the proportion of fresh terrestrial organic matter was most likely linked to cold/arid conditions and reduced runoff coinciding with heavy ^{18}O values in the western Mediterranean region (Fig. 6A). Interestingly, during T-III high fresh terrestrial organic matter input was linked to light ^{18}O values (Fig. 6A). The exact source of the isotope signal during massive IRD discharges in the Mediterranean remains unclear. Sierro et al. (2005) claimed that during the last glacial interval, the meltwater pulses into Mediterranean produced light isotope excursions during HE. However, a new high-resolution record by Martrat et al. (2014) has showed that western Mediterranean region experienced a high climate variability during T-II where massive IRD occurred as well. The former authors documented warm periods within T-II that could be associated to light ^{18}O values inside stadials not previously recorded due to the low-resolution of previous studies. This observation raises corresponding caution with the interpretation of ^{18}O records in the Mediterranean during periods of high IRD discharge in the North Atlantic.

Accordingly, two mechanisms could explain the anomalous light ^{18}O values during T-III. First, as proposed by Sierro et al. (2005) and analogous to HE occurring in last glacial, the input of freshwater in Mediterranean Sea from melted icebergs could produce an anomalous decrease of ^{18}O isotope values during cold periods. Secondly, this behavior could be a consequence of the amount and rate of insolation rise. Speleothem studies at Sambao Cave (China) (Cheng et al., 2009) during Terminations, demonstrated that contrary to T-II and T-IV, T-III was interrupted by a long interstadial that could be a response to a low amount and rate of insolation rise. The warm signature of this interstadial could imprint ^{18}O isotope values hiding the effect of cold and arid climate, as monitored in H-like events at T-II and T-IV. The exact mechanism remains unclear, however, the fact that regarding ^{18}O isotope values uninterrupted Terminations (T-II and T-IV) had similar pattern and different to the interrupted (T-III) Termination lets us assume that this interstadial plays an important role in the ^{18}O isotope signature.

Regarding the intensity, global sea level reconstructions (Waelbroeck et al., 2002) (Fig. 4B), isotope studies in benthic foraminifera (Shackleton, 1987) and previous studies in the Gulf of Lions (Cortina et al., 2013) have indicated MIS 6 and MIS 10 as similar glacial stages, and MIS 8 as a less intense glaciation. The fact that T-II and T-IV had a greater number of steps (3 H-like and 4 H-like respectively) than T-III (1 H-like) could be the result of differences in the quantity of ice melted until reaching an interglacial state. Therefore, MIS 8 would be a less intense deglaciation associated to a less intense glacial. This can also be corroborated by the recorded percentage of IRD that were 63.66%, 43.59% and 79.77% for MIS 6, MIS 8 and MIS 10 respectively (McManus et al., 1999). Regardless the number of steps, all the Terminations studied showed a strong millennial component transmitted from high latitudes to the northwestern Mediterranean basin, highlighting the strong interconnection between northern and middle North Atlantic latitudes.

6. Conclusions

The proportion of degraded/fresh terrestrial organic matter arriving to the upper slope of the Gulf of Lions varies mainly at glacial/interglacial scales as a function of sea level changes. As sea level decreases an increase of both total n-alkanes and fresh terrestrial organic matter is monitored in the upper slope owing to the seaward migration of the Rhone's mouth. As glacial stages further developed, the sea level continued to fall exposing to erosional processes the older and reworked sediments from the Rhone catchment area, including the continental shelf and the delta plain. The outcome was an increase of the proportion of degraded terrestrial organic matter arriving to the upper slope that was associated to the fine-grained prodeltaic sediments. On the contrary, during episodes of extremely high sea level river-borne sediments barely arrived to the upper slope, enhancing the proportion of marine-derived components (e.g. alkenones). A pronounced productivity event occurred around 170 ka, a period characterized by enhanced precipitation in the whole Mediterranean Sea. During this interval the deposition of the singular cold Sapropel 6 took place in the eastern Mediterranean Sea. Therefore, further research is needed to unveil possible links between the two basins during this period.

During last glacial, as the sea level fell the progressive decrease of fresh terrestrial organic matter was punctuated by several increases during HE. We interpreted these increases as a consequence of the cold and dry conditions prevailing at these times that caused a decrease in Rhone's flow. These short cold events were followed by short flooding events that caused an increase of the proportion of the degraded terrestrial organic matter. We interpret that both precipitation and meltwater of the continental ice led to increased continental runoff enhancing the erosion of old and reworked material from Rhone catchment area.

Analogous to last glacial, rapid cold/warm oscillations were identified during T-II, T-III and T-IV, where the cold episodes shared some similarities with HE. These rapid cold/warm oscillations detected in the western Mediterranean basin, responded most probably to a collapse/resumption of the AMOC. During a collapse, increased atmospheric gradient in the North Atlantic induced dry and cold conditions in the western Mediterranean region, reducing runoff and enhancing the proportion of fresh terrestrial organic matter. However, the AMOC resumption produced a decrease in the atmospheric gradient in the North Atlantic, which resulted in warm and more humid conditions in the western Mediterranean. Such conditions led to increased continental runoff and the ensuing erosion of old and reworked material from the Rhone catchment area that imprinted sediments deposited in the upper slope.

Our high-resolution record showed that climate conditions during Terminations were more dynamic than thought, identifying 3 (T-II), 1 (T-III) and 4 (T-IV) rapid stadial events during these short periods of strong sea level increase. Moreover, it was demonstrated that the western Mediterranean climate responded quickly to both northern icesheets and AMOC dynamics. As the western Mediterranean is a key region in deep-water production, the impact of these rapid oscillations is expected to spread in the whole basin affecting the Mediterranean ocean circulation and land climate.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2016.03.015.

References

Albaiges, J., Grimalt, J., Bayona, J.M., Risebrough, R., De Lappe, B., Walker, W., 1984. Dissolved, particulate and sedimentary hydrocarbons in a deltaic environment. Org. Geochem. 6, 234–248.

Albaiges, J., Algaba, J., Arambarri, P., Cabrera, F., Baluja, G., Hernandez, L.M., Castroviejo, J., 1987. Budget of organic and inorganic pollutants in the Doñana National Park (Sevilla, Spain). Sci. Total Environ. 63, 13–28.

Aloïsi, J.C., 1986. Sur un modèle de sédimentation deltaïque: contribution à la conaissance des marges passives. Université de Perpignan, Perpignan, p. 162.

Ayalon, A., Bar-Matthews, M., Kaufman, A., 2002. Climatic conditions during marine oxygen isotope stage 6 in the eastern Mediterranean region from the isotopic composition of speleothems of Soreq Cave, Israel. Geology 30 (30330), 3.

Baraud, J., Cassagne, C., Genevois, L., Joneau, M., 1967. Presence d'hydrocarbures dans l'insaponifiable des lipides de levures. CR Acad. Sci. Paris 265 (D), 83–85.

Barreiro, M., Fedorov, A., Pacanowski, R., Philander, S.G., 2008. Abrupt climate changes: how freshening of the Northern Atlantic affects the thermohaline and wind-driven oceanic circulations. Annu. Rev. Earth Planet. Sci. 36, 33–58.

Bartov, Y., Goldstein, S.L., Stein, M., Enzel, Y., 2003. Catastrophic arid episodes in the Eastern Mediterranean linked with the North Atlantic Heinrich events. Geology 31, 439–442.

Bassetti, M.A., Jouet, G., Dufois, F., Berné, S., Rabineau, M., Taviani, M., 2006. Sand bodies at the shelf edge in the Gulf of Lions (Western Mediterranean): deglacial history and modern processes. Mar. Geol. 234, 93–109.

Bassetti, M.A., Berné, S., Jouet, G., Taviani, M., Dennielou, B., Flores, J.A., Gaillot, A., Gelfort, R., Lafuerza, S., Sultan, N., 2008. The 100-ka and rapid sea level changes recorded by prograding shelf sand bodies in the Gulf of Lions (western Mediterranean Sea). Geochem. Geophys. Geosyst. 9, Q11R05.

Berne, S., Lericolais, G., Marsset, T., Bourillet, J.F., De Batist, M., 1998. Erosional offshore sand ridges and lowstand shorefaces; examples from tide- and wave-dominated environments of France. J. Sediment. Res. 68, 540–555.

Berne, S., Jouet, G., Bassetti, M.A., Dennielou, B., Taviani, M., 2007. Late glacial to preboreal sea-level rise recorded by the Rhone deltaic system (NW Mediterranean). Mar. Geol. 245, 65–88.

Béthoux, J.P., 1984. Paleoceanographic changes in the Mediterranean-Sea in the last 20,000 years. Oceanol. Acta 7, 43–48.

Bird, C.W., Lynch, J.M., 1974. Formation of hydrocarbons by micro-organisms. Chem. Soc. Rev. 3, 309–328.

Blunier, T., Brook, E.J., 2001. Timing of millennial-scale climate change in Antarctica and Greenland during the last glacial period. Science 291, 109–112.

Bond, G.C., Lotti, R., 1995. Iceberg discharges into the North Atlantic on millennial time scales during the Last Glaciation. Science 267, 1005–1010.

Bond, G., Broecker, W., Johnsen, S., McManus, J., Labeyrie, L., Jouzel, J., Bonani, G., 1993. Correlations between climate records from North Atlantic sediments and Greenland ice. Nature 365, 143–147.

Bouloubassi, I., Lipiatou, E., Saliot, A., Tolosa, I., Bayona, J.M., Albaigés, J., 1997. Carbon sources and cycle in the western Mediterranean—the use of molecular markers to determine the origin of organic matter. Deep-Sea Res. II Top. Stud. Oceanogr. 44, 781–799.

Bray, E.E., Evans, E.D., 1961. Distribution of n-paraffins as a clue to recognition of source beds. Geochim. Cosmochim. Acta 22, 2–15.

Broecker, W.S., 1994. Massive iceberg discharges as triggers for global climate change. Nature 372, 421–424.

Broecker, W.S., van Donk, J., 1970. Insolation changes, ice volumes, and the O18 record in deep-sea cores. Rev. Geophys. 8, 169–198.

Broecker, W., Bond, G., Klas, M., Clark, E., McManus, J., 1992. Origin of the northern Atlantic's Heinrich events. Clim. Dyn. 6, 265–273.

Cacho, I., Grimalt, J.O., Pelejero, C., Canals, M., Sierro, F.J., Flores, J.A., Shackleton, N., 1999. Dansgaard–Oeschger and Heinrich event imprints in Alboran sea paleotemperatures. Paleoceanography 14, 698–705.

Cacho, I., Grimalt, J.O., Canals, M., 2002. Response of the Western Mediterranean Sea to rapid climatic variability during the last 50,000 years: a molecular biomarker approach. J. Mar. Syst. 33–34, 253–272.

Cheng, H., Edwards, R.L., Broecker, W.S., Denton, G.H., Kong, X., Wang, Y., Zhang, R., Wang, X., 2009. Ice Age Terminations. Science 326, 248–252.

Cita, M.B., Vergnaud-Grazzini, C., Robert, C., Chamley, H., Ciaranfi, N., d'Onofrio, S., 1977. Paleoclimatic record of a long deep sea core from the eastern Mediterranean. Quat. Res. 8, 205–235. http://dx.doi.org/10.1016/0033-5894(77)90046-1.

Combourieu-Nebout, N., Turon, J.L., Zahn, R., Capotondi, L., Londeix, L., Pahnke, K., 2002. Enhanced aridity and atmospheric high-pressure stability over the western Mediterranean during the North Atlantic cold events of the past 50 k.y. Geology 30, 863–866.

Cortina, A., Sierro, F.J., González-Mora, B., Asioli, A., Flores, J.A., 2011. Impact of climate and sea level changes on the ventilation of intermediate water and benthic foraminifer assemblages in the Gulf of Lions, off South France, during MIS 6 and 7. Palaeogeogr. Palaeoclimatol. Palaeoecol. 309, 215–228.

Cortina, A., Sierro, F.J., Filippelli, G., Flores, J.A., Berné, S., 2013. Changes in planktic and benthic foraminifer assemblages in the Gulf of Lions, off south France: response to climate and sea level change from MIS 6 to MIS 11. Geochem. Geophys. Geosyst. 14, 1258–1276.

Cortina, A., Sierro, F.J., Flores, J.A., Martrat, B., Grimalt, J.O., 2015. The response of SST to insolation and ice sheet variability from MIS 3 to MIS 11 in the northwestern Mediterranean Sea (Gulf of Lions). Geophys. Res. Lett. 42 (23), 10,366–10,374. http://dx.doi.org/10.1002/2015GL065539.

Davis, J.B., 1968. Paraffinic hydrocarbons in the sulfatereducing bacterium *Desulfovibrio desulfuricans*. Chem. Geol. 3, 155–160.

de Abreu, L., Shackleton, N.J., Schönfeld, J., Hall, M., Chapman, M., 2003. Millennial-scale oceanic climate variability off the Western Iberian margin during the last two glacial periods. Mar. Geol. 196, 1–20.

Dixon, K.W., Delworth, T.L., Spelman, M.J., Stouffer, R.J., 1999. The influence of transient surface fluxes on North Atlantic overturning in a coupled GCM climate change experiment. Geophys. Res. Lett. 26, 2749–2752.

Eglinton, T.I., Eglinton, G., 2008. Molecular proxies for paleoclimatology. Earth Planet. Sci. Lett. 275, 1–16.

Eglinton, G., Hamilton, R.J., 1963. The distribution of alkanes. In: Swain, T. (Ed.), Chemical Plant Taxonomy. Academic Press, pp. 187–217.

Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. Science 156, 1322–1335.

Fabre-Joneau, M., Baraud, J., Cassagne, C., 1969. Nature et repartition des hydrocarbures chez la levure *Candida utilis*. CR Acad. Sci. Paris 268 (D), 2282–2285.

Flückiger, J., Knutti, R., White, J.W.C., 2006. Oceanic processes as potential trigger and amplifying mechanisms for Heinrich events. Paleoceanography 21, PA2014.

Frigola, J., Moreno, A., Cacho, I., Canals, M., Sierro, F.J., Flores, J.A., Grimalt, J.O., 2008. Evidence of abrupt changes in Western Mediterranean Deep Water circulation during the last 50 kyr: a high-resolution marine record from the Balearic Sea. Quat. Int. 181, 88–104.

Frigola, J., Canals, M., Cacho, I., Moreno, A., Sierro, F.J., Flores, J.A., Berné, S., Jouet, G., Dennielou, B., Herrera, G., Pasqual, C., Grimalt, J.O., Galavazi, M., Schneider, R., 2012. A 500 kyr record of global sea-level oscillations in the Gulf of Lion, Mediterranean Sea: new insights into MIS 3 sea-level variability. Clim. Past 8, 1067–1077.

Ganopolski, A., Rahmstorf, S., 2001. Rapid changes of glacial climate simulated in a coupled climate model. Nature 409, 153–158.

Grimalt, J., Albaiges, J., Al-Saad, H.T., Douabul, A.A.Z., 1985. n-Alkane distributions in surface sediments from the Arabian Gulf. Naturwissenschaften 72, 35–37.

Grimalt, J.O., Torras, E., Albaiges, J., 1988. Bacterial reworking of sedimentary lipids during sample storage. Org. Geochem. 13, 741–746.

Jiménez-Espejo, F.J., Martínez-Ruiz, F., Finlayson, C., Paytan, A., Sakamoto, T., Ortega-Huertas, M., Finlayson, G., Iijima, K., Gallego-Torres, D., Fa, D., 2007. Climate forcing and Neanderthal extinction in Southern Iberia: insights from a multiproxy marine record. Quat. Sci. Rev. 26, 836–852.

Johnson, R.W., Calder, J.A., 1973. Early diagenesis of fatty acids and hydrocarbons in a salt marsh environment. Geochim. Cosmochim. Acta 37, 1943–1955.

Jones, J.G., 1969. Studies on lipids of soil micro-organisms with particular reference to hydrocarbons. J. Gen. Microbiol. 59, 145–152.

Jones, J.G., Young, B.V., 1970. Major paraffin constituents of microbial cells with particular references to *Chromatium* sp. Arch. Mikrobiol. 70, 82–88.

Jouet, G., Berné, S., Rabineau, M., Bassetti, M.A., Bernier, P., Dennielou, B., Sierro, F.J., Flores, J.A., Taviani, M., 2006. Shoreface migrations at the shelf edge and sea-level changes around the Last Glacial Maximum (Gulf of Lions, NW Mediterranean). Mar. Geol. 234, 21–42.

Kim, J.-H., Schouten, S., Buscail, R., Ludwig, W., Bonnin, J., Sinninghe Damstt, J.S., Bourrin, F., 2006. Origin and distribution of terrestrial organic matter in the NW Mediterranean (Gulf of Lions): exploring the newly developed BIT index. Geochem. Geophys. Geosyst. 7, Q11017.

Lisiecki, L.E., Raymo, M.E., 2005. A Pliocene–Pleistocene stack of 57 globally distributed benthic d18O records. Paleoceanography 20, PA1003.

Martrat, B., Grimalt, J.O., Lopez-Martinez, C., Cacho, I., Sierro, F.J., Flores, J.A., Zahn, R., Canals, M., Curtis, J.H., Hodell, D.A., 2004. Abrupt temperature changes in the Western Mediterranean over the past 250,000 years. Science 306, 1762–1765.

Martrat, B., Grimalt, J.O., Shackleton, N.J., de Abreu, L., Hutterli, M.A., Stocker, T.F., 2007. Four climate cycles of recurring deep and surface water destabilizations on the Iberian Margin. Science 317, 502–507.

Martrat, B., Jimenez-Amat, P., Zahn, R., Grimalt, J.O., 2014. Similarities and dissimilarities between the last two deglaciations and interglaciations in the North Atlantic region. Quat. Sci. Rev. 99, 122–134.

McManus, J.F., Oppo, D.W., Cullen, J.L., 1999. A 0.5-million-year record of millennial-scale climate variability in the North Atlantic. Science 283, 971–975.

Meckler, A.N., Schubert, C.J., Hochuli, P.A., Plessen, B., Birgel, D., Flower, B.P., Hinrichs, K.-U., Haug, G.H., 2008. Glacial to Holocene terrigenous organic matter input to sediments from Orca Basin, Gulf of Mexico exiccombined optical and biomarker approach. Earth Planet. Sci. Lett. 272 (251), 263.

Millot, C., 1990. The Gulf of Lions' hydrodynamics. Cont. Shelf Res. 10, 885–894.

Millot, C., 1999. Circulation in the Western Mediterranean Sea. J. Mar. Syst. 20, 423–442.

Moreno, A., Cacho, I., Canals, M., Grimalt, J.O., Sánchez-Goni, M.F., Shackleton, N., Sierro, F.J., 2005. Links between marine and atmospheric processes oscillating on a millennial time-scale, a multi-proxy study of the last 50,000 yr from the Alboran Sea (Western Mediterranean Sea). Quat. Sci. Rev. 24, 1623–1636. http://dx.doi.org/10.1016/j.quascirev.2004.06.018.

Naccarato, W.F., Gilbertson, J.R., Gelman, R.A., 1974. Effects of different culture media and oxygen upon lipids of *Escherichia coli* K-12. Lipids 9, 322–327.

Nieto-Moreno, V., Martínez-Ruiz, F., Giralt, S., Jiménez-Espejo, F., Gallego-Torres, D., Rodrigo-Gámiz, M., García-Orellana, J., Ortega-Huertas, M., de Lange, G.J., 2011. Tracking climate variability in the western Mediterranean during the Late Holocene: a multiproxy approach. Clim. Past 7, 1395–1414.

Pérez-Folgado, M., Sierro, F.J., Flores, J.A., Cacho, I., Grimalt, J.O., Zahn, R., Shackleton, N., 2003. Western Mediterranean planktonic foraminifera events and millennial climatic variability during the last 70 kyr. Mar. Micropaleontol. 48, 49–70.

Plagnes, V., Causse, C., Dominique, G., Paterne, M., Blamart, D., 2002. A discontinuous climatic record from 187 to 74 ka from a speleothem of the Clamouse Cave (south of France). Earth Planet. Sci. Lett. 201 (87), 87.

Pont, D., Simonnet, J.P., Walter, A.V., 2002. Medium-term changes in suspended sediment delivery to the ocean: consequences of catchment heterogeneity and river management (Rhône River, France). Estuar. Coast. Shelf Sci. 54, 1–18.

Posamentier, H.W., Allen, G.P., James, D.P., Tesson, M., 1992. Forced regressions in a sequence stratigraphic framework: concepts, examples, and exploration significance. Aapg Bull. Am. Assoc. Pet. Geol. 76, 1687–1709.

Prahl, F.G., Collier, R.B., Dymond, J., Lyle, M., Sparrow, M.A., 1993. A biomarker perspective on prymnesiophyte productivity in the northeast pacific ocean. Deep-Sea Res. I Oceanogr. Res. Pap. 40, 2061–2076.

Rabineau, M., Berné, S., Aslanian, D., Olivet, J.L., Joseph, P., Guillocheau, F., Bourillet, J.F., Ledrezen, E., Granjeon, D., 2005. Sedimentary sequences in the Gulf of Lion: a record of 100,000 years climatic cycles. Mar. Pet. Geol. 22, 775–804.

Rodrigo-Gámiz, M., Martínez-Ruiz, F., Jiménez-Espejo, F.J., Gallego-Torres, D., Nieto-Moreno, V., Romero, O., Ariztegui, D., 2011. Impact of climate variability in the western Mediterranean during the last 20,000 years: oceanic and atmospheric responses. Quat. Sci. Rev. 30, 2018–2034.

Rosell-Melé, A., McClymont, E.L., 2007. Biomarkers as paleoceanographic proxies. In: Hillaire-Marcel, C., de Vernal, A. (Eds.), Proxies in Late Cenozoic Paleoceanography. Elsevier Science, Amsterdam (pp. 441).

Sánchez-Goñi, M., Cacho, I., Turon, J., Guiot, J., Sierro, F., Peypouquet, J., Grimalt, J., Shackleton, N., 2002. Synchroneity between marine and terrestrial responses to millennial scale climatic variability during the last glacial period in the Mediterranean region. Clim. Dyn. 19, 95–105.

Shackleton, N.J., 1987. Oxygen isotopes, ice volume and sea level. Quat. Sci. Rev. 6, 183–190.

Shackleton, N.J., Hall, M.A., Vincent, E., 2000. Phase relationships between millennial-scale events 64,000–24,000 years ago. Paleoceanography 15 (6), 565–569.

Sierro, F.J., Hodell, D.A., Curtis, J.H., Flores, J.A., Reguera, I., Colmenero-Hidalgo, E., Bárcena, M.A., Grimalt, J.O., Cacho, I., Frigola, J., Canals, M., 2005. Impact of iceberg melting on Mediterranean thermohaline circulation during Heinrich events. Paleoceanography 20, PA2019.

Sierro, F.J., Andersen, N., Bassetti, M.A., Berne, S., Canals, M., Curtis, J.H., Dennielou, B., Flores, J.A., Frigola, J., Gonzalez-Mora, B., Grimalt, J.O., Hodell, D.A., Jouet, G., Perez-Folgado, M., Schneider, R., 2009. Phase relationship between sea level and abrupt climate change. Quat. Sci. Rev. 28, 2867–2881.

Tesson, M., Gensous, B., Allen, G.P., Ravenne, C., 1990. Late Quaternary deltaic lowstand wedges on the Rhône continental shelf, France. Mar. Geol. 91, 325–332.

Villanueva, J., Grimalt, J.O., Cortijo, E., Vidal, L., Labeyriez, L., 1997a. A biomarker approach to the organic matter deposited in the North Atlantic during the last climatic cycle. Geochim. Cosmochim. Acta 61, 4633–4646.

Villanueva, J., Pelejero, C., Grimalt, J.O., 1997b. Clean-up procedures for the unbiased estimation of C37 alkenone sea surface temperatures and terrigenous n-alkane inputs in paleoceanography. J. Chromatogr. A 757, 145–151.

Villanueva, J., Grimalt, J.O., Labeyrie, L.D., Cortijo, E., Vidal, L., Louis-Turon, J., 1998. Precessional forcing of productivity in the North Atlantic Ocean. Paleoceanography 13, 561–571.

Waelbroeck, C., Labeyrie, L., Michel, E., Duplessy, J.C., McManus, J.F., Lambeck, K., Balbon, E., Labracherie, M., 2002. Sea-level and deep water temperature changes derived from benthic foraminifera isotopic records. Quat. Sci. Rev. 21, 295–305.

Walker, J.D., Cooney, J.J., 1973. Aliphatic hydrocarbons of *Cladosporium resmae* cultured on glucose, glutamic acid, and hydrocarbons. Appl. Microbiol. 26, 705–708.
Wiebe, E.C., Weaver, A.J., 1999. On the sensitivity of global warming experiments to the parametrisation of sub-grid scale ocean mixing. Clim. Dyn. 15, 875–893.
Zhao, M., Huang, C.-Y., Wang, C.-C., Wei, G., 2006. A millennial-scale U37K′ sea-surface temperature record from the South China Sea (8°N) over the last 150 kyr: monsoon and sea-level influence. Palaeogeogr. Palaeoclimatol. Palaeoecol. 236, 39–55.