

## Lipids as indicators of paleoclimatic changes, II: Terrestrial biomarkers

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- **Abstract:** Variations in the abundance of specific lipid biomarker compounds derived from terrestrial sources are shown to be closely related to past climatic changes. Despite biodegradation processes, which take place mostly at the water column and sediment water interface, these compounds are found well preserved in oceanic sediments. Here, their relative distribution is employed as a tool to assess changes in terrestrial fluxes to the seabed accompanying climatic variations during glacial and interglacial intervals. These changes in biomarker distribution were estimated in two sediment cores taken from the eastern North Atlantic, covering the past 210,000 years. Comparisons with other paleoclimate proxies showed good agreement and suggest that some specific groups of biomarkers are important indicators of changes in terrestrial inputs to the sea.
  - **Resumo:** A variação na abundância de alguns biomarcadores lipídicos derivados de aportes terrestres pode estar relacionada com mudanças climáticas no passado. Apesar dos processos de biodegradação que, na grande maioria, ocorrem na coluna aquática e na interface sedimento-água, esses compostos são encontrados bem preservados em sedimentos oceânicos. Nesse trabalho, a distribuição relativa desses compostos é empregada como uma ferramenta para avaliar mudanças no transporte de material terrestre para o mar em paralelo às variações climáticas durante os intervalos glaciais e interglaciais. As mudanças na distribuição dos biomarcadores foram estimadas em dois testemunhos coletados ao leste do Atlântico Norte e que correspondem aos últimos 210 mil anos. Os resultados mostraram uma boa correlação entre a distribuição dos biomarcadores e outros parâmetros paleoclimáticos previamente avaliados nos perfis, sugerindo que alguns grupos específicos de compostos orgânicos são importantes indicadores de aporte terrestre para o mar.
  - **Descriptors:** Biomarkers, Marine sediment, Chromatography, North Atlantic.
  - **Descritores:** Biomarcadores, Sedimento marinho, Cromatografia, Atlântico Norte.
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### Introduction

#### Marine and terrestrial biomarkers

Lipid compounds found in deep sea sediments are mainly derived from marine and terrestrial sources. These organic compounds, known as biomarkers, are widely used as indicators of phytoplankton productivity or allochthonous sources. Some groups of biomarkers can also reveal key information about past productivity and climatic changes (Schneider *et al.*, 1995; Madureira *et al.*, 1997; Ohkouchi *et al.*, 1997). Biomarkers may reach the seafloor unaltered or partially altered, so that it is still possible to interpret their occurrence in sediments in terms of

input from a specific source. Groups of marine compounds, for example, phytosterols and the haptophyte-derived long-chain alkenones and alkyl alkenoates are important indicators of overlying surface water productivity and of phytoplankton species composition (Poynter *et al.*, 1989; Farrimond *et al.*, 1990; Madureira *et al.*, 1995). Long-chain alkenones and alkyl alkenonates are also employed as a paleo sea surface temperature (SST) proxy, in stratigraphic records (Zhao *et al.*, 1993 and 1995).

Among the terrestrial biomarkers, straight long-chain (> C<sub>20</sub>) alkanes, alkanols and alkanolic acids are known as the major compounds derived from leaf waxes that may reach the deep sea floor. Their

abundance and within-class distribution may be used to indicate inputs of land-derived material to the sediments (McCaffrey *et al.*, 1991; Jasper and Gagosian, 1993; Madureira *et al.*, 1995). In the North Atlantic, their transport to the open ocean is mainly associated with aerosols from Africa (Simoneit *et al.*, 1977; Huang *et al.*, 1993). However, it is common knowledge that some marine bacteria and algae may also contain such group of compounds, though with a distinct extent of even/odd predominance (Volkman *et al.*, 1981).

In this work, we compared the biomarker data obtained for the sediment core T88-9P taken in 1988, whose results have previously been reported (van Kreveld, 1996; van Kreveld *et al.*, 1996; Madureira *et al.*, 1997), with core T90-2P taken in 1990 in the same region of the eastern North Atlantic (Fig. 1). The same sampling intervals were used in both studies. In order to assess changes in terrigenous input to the seabed, the relative distribution and abundance of three lipid groups - alkanes ( $C_{27}$ ,  $C_{29}$  and  $C_{31}$ ), alkanolic acids ( $C_{24}$ ,  $C_{26}$  and  $C_{28}$ ), and alkanols ( $C_{24}$ ,  $C_{26}$  and  $C_{28}$ ) - were analysed during glacial and interglacial intervals along the two piston cores collected, compiling approximately 210 ka of sediment record.

### Transport of terrestrial material to the ocean

Terrestrial material can be carried to the ocean via three main pathways: aeolian transport, fluvial discharges and, to a lesser extent, ice rafting. River runoff is the major vehicle by which terrestrial material is delivered to estuarine and coastal sediments (Chester, 1990). Land-derived organic matter carried to the ocean in rivers includes recently biosynthesised plant debris and dissolved humic substances, accompanied by older soil humus (Hedges *et al.*, 1986). The average global discharge of river suspended and dissolved organic matter to the west African coast is about 258 million tons per year. In contrast, fluvial discharges in the eastern North Atlantic yield about 18 million tons annually (Chester, *op. cit.*). With respect to lipid compounds, river mouths have been examined and the results indicated significantly higher plant contributions to coastal waters (Farrington *et al.*, 1988; McCaffrey *et al.*, 1991). However, for open oceans it has become increasingly apparent that long-range atmospheric transport is an important route for the delivery of organic material to deep sea sediments (Simoneit, 1977; Simoneit *et al.*, 1977; Gagosian *et al.*, 1981). Atmospheric particles have been extensively studied off the coast of west Africa, particularly pollen (Hooghiemstra, 1989), mineral aerosols (Schultz and Quinn, 1972) and organic compounds (Simoneit,

1978; Huang *et al.*, 1993), showing the importance of both surface and higher altitude zonal winds on the west African coast.

### Indices related to terrestrial inputs

Several indices can be used to assess exogenous input to the sea. For instance, within-class distribution of long-chain ( $> C_{20}$ ) linear alkanes, alkanolic acids, and alkanols is often employed to infer terrestrial input into sediments. Carbon Preference Indices (CPI) based upon the odd/even preferences of these compounds were introduced over twenty years ago (Cooper and Bray, 1963; Kevenvolden, 1966) and, since then, have been extensively used to estimate the extent of land derived input into sediments in a great variety of environments (e.g. Gagosian *et al.*, 1987; Venkatesan and Kaplan, 1987; Rieley *et al.*, 1991). The typical CPI range for each of these three compound classes is 2 - 40 (Rieley *et al.*, *op. cit.*). High values of CPI with a clear terrestrial signature can also be found in aerosol samples, as documented by Simoneit (1978), Gagosian *et al.* (*op. cit.*), and Huang *et al.* (1993). Another index that has been widely used for computing the ratio of the relative concentrations of homologs is the odd/even predominance (OEP) introduced by Scalan and Smith (1970). In our samples, due to the low amounts of several hydrocarbons with even number of carbon atoms, we employed the OEP ratio instead of CPI to assess possible changes in terrestrial sources with core depth (Table 1). This ratio is less sensitive to the general trend in relative abundances but is a more sensitive measure of their local odd/even ratio.

Other indices have been introduced during the last ten years. For example, the Average Chain Length (ACL) index was proposed by Poynter and Eglinton (1990) to discriminate between terrestrial source regions of aerosol inputs from West Africa. This index has not shown clear variations when estimated using surface sediment samples taken in the eastern North Atlantic (Madureira, 1994). These authors also introduced the Alcohol Preservation Index (API), which was proposed in an attempt to measure to what extent alkanes and alkanols may be exposed to degradation while sinking through the water column. Therefore, this index is also associated with variation in the sedimentation rate. Lower values for this ratio should thus be found in sediments deposited in deeper waters, and greater values in shallower waters. We used API to investigate changes in degradation and sedimentation rates with depth in both cores (Table 1).

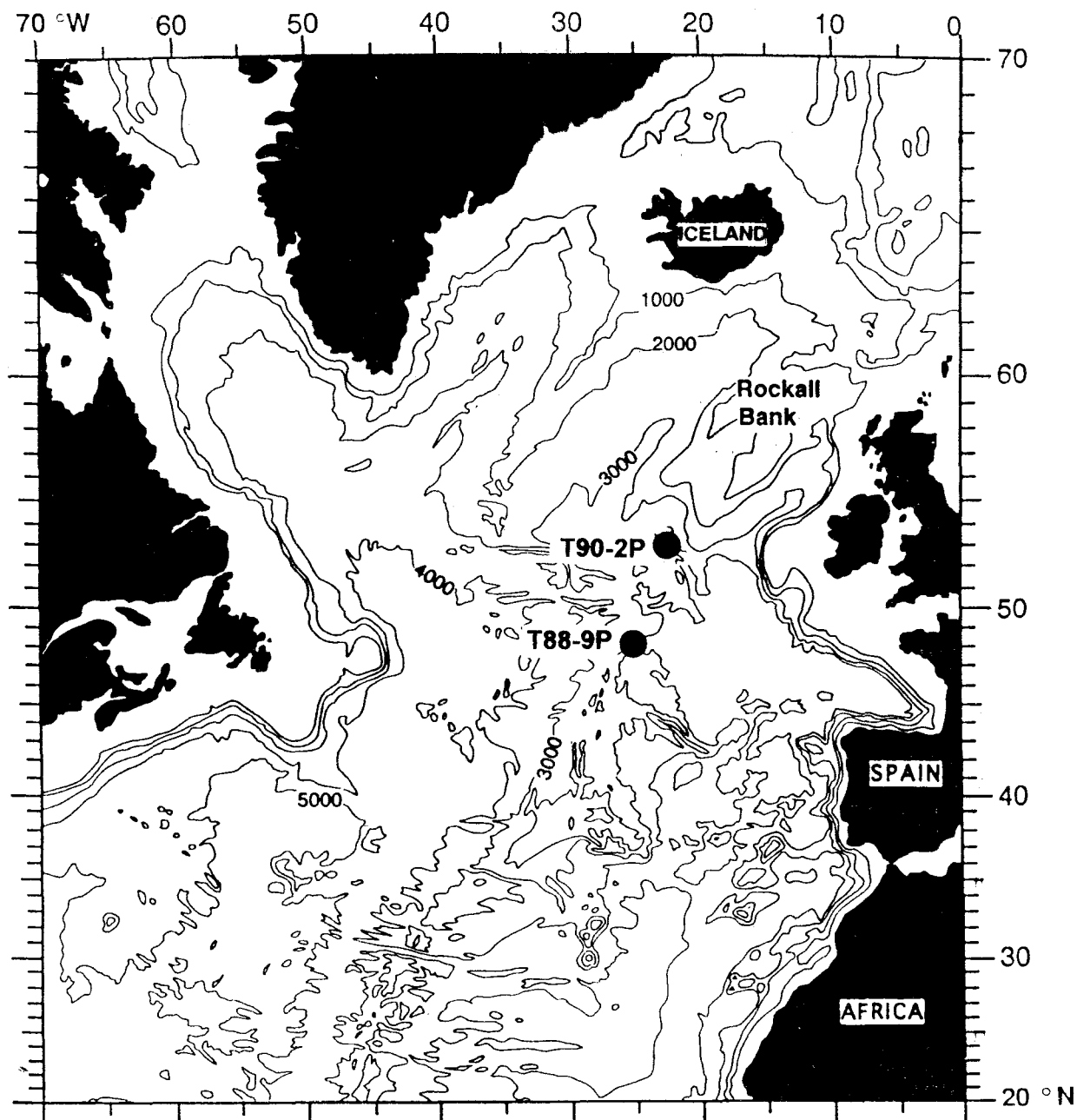


Fig. 1. Physiographic map with locations of both cores T88-9P (48°23'N, 25°05'W, water depth 3193 m, 790 cm long) and T90-2P (52°23'N, 21°05'W, water depth 3200 m, 900 cm long) in the Northeast Atlantic (redrawn from Uchupi, 1971). Core T88-9P was taken on the rising east flank of the Mid-Atlantic Ridge. Core T90-2P was recovered south of the Rockall Plateau.

Table 1. Estimated Alcohol Preservation Index (API) to cores T88-9P and T90-2P and Odd-Even Preference Index (OEP) to core T90-2P during Holocene and Last Glacial intervals.

Period	Depth (cm)	API (T88-9P)	API (T90-2P)	OEP (T90-2P)
Holocene	10	0.54	0.62	0.57
	15	0.56	0.50	0.51
	20	0.57	0.52	0.51
	30	0.58	0.44	0.49
	35	0.63	0.41	0.44
	40	0.63	0.52	0.47
Last	50	0.61	0.54	0.32
	60	0.55	0.50	0.21
	70	0.48	0.50	0.25
Glacial	80	0.58	0.41	0.22
	90	0.59	0.21	0.24
	246	0.58	0.62	0.24
	260	0.67	0.47	0.21

CV < 15% (n=3) for each depth interval of 2.5 cm.

API =  $(C_{24} + C_{26} + C_{28} \text{ alkanols}) / (C_{24} + C_{26} + C_{28} \text{ alkanols}) + (C_{27} + C_{29} + C_{31} \text{ alkanes})$  (Poynter & Eglinton, 1990).

OEP =  $[(C_{27} + 6 \times C_{29} + C_{31} \text{ alkanes}) / (4 \times C_{28} + 4 \times C_{30} \text{ alkanes})]^{-1}$  (Scalan & Smith, 1970)

Ratios of alkanols and alkanes determined from corrected peak areas of gas chromatograms.

In addition to the indices described above, other ratios based on hydrocarbon, alkanol, and fatty acid distribution are widely used to investigate diagenesis, relative contribution of marine versus terrigenous sources of organic matter, and alteration processes taking place at oxic-anoxic interface (e.g. Meyers *et al.*, 1980; Wakeham & Beier, 1991; Bourbonniere & Meyers, 1996). In order to assess possible changes in aquatic-terrestrial contributions over the glacial/interglacial periods, we used a ratio based on the abundance of the alkanolic acid  $C_{16}$  to the hydrocarbon  $C_{29}$  (marine/terrestrial ratio). Short-chain fatty acids ( $C_{12}$ ,  $C_{14}$ , and  $C_{16}$ ) are mainly produced by marine organisms (Cranwell *et al.*, 1987) and the long-chain hydrocarbons are found in epicuticular waxes of land-plants (Rieley *et al.*, 1991).

## Materials and methods

For both cores, sediment sub-samples were taken every 5 cm from the upper 50 cm, and then at about 10 cm intervals for the rest of the core. Samples were also taken at high resolution (2.5 cm intervals, approx. 500 years) across glacial-interglacial transitions (Terminations I and II), which have strong gradients in  $\delta^{18}O$  and microfossil species composition. The depth intervals analysed for terrestrial biomarkers were the same as those for sedimentological analyses described in van Kreveld *et al.* (1996). The extraction technique and sediment analyses for T90-2P by GC and GC-MS followed the same procedure as for T88-9P, and details are given in Madureira *et al.* (1995 and 1997). Briefly, prior to analysis, porewater was removed by evaporation/freeze-drying and the dried sediment homogenised in a mortar and pestle. An internal standard mixture ( $C_{36}$  n-alkane, cholestane, and  $C_{23:1}$

fatty acid) was added before extraction. Lipids were extracted in 1:1  $CH_2Cl_2:CH_3OH$  (2x) and  $CH_2Cl_2$  (1x), using a solvent/sediment ratio of 3:1. The lipid extract was transesterified under  $N_2$  using anhydrous 5% methanolic HCl in toluene. The samples were then trimethylsilylated using BSTFA prior to GC and GC-MS analyses. Gas chromatography was carried out using a model 17A Shimadzu GC, using a 30 m x 0.25 mm, 0.25  $\mu m$  film thickness, CBP1 column. The temperature programme was 50 – 180°C at 10°C  $min^{-1}$  and 180 – 310°C (holding for 20 min) at 4°C  $min^{-1}$ .  $N_2$  was used as a carrier gas. GC-MS analyses (EI mode, 70eV) were carried out on a QP-2000A mass spectrometer interfaced to a model 14B Shimadzu GC. Conditions for GC-MS analyses were as for GC except that He was used as carrier gas. It is important to mention that the T90-2P core was fully extracted and the total lipids analysed at the Chemistry Department of Santa Catarina University, whereas the T88-9P extraction and analysis were carried out at the Biogeochemistry Centre of Geology Department, Bristol University.

The ages shown outside the panels in Figures 2 and 3 are based on three radiocarbon dates, two ash layers and the correlation of the oxygen isotope curves of the planktic foraminiferal *Globigerina bulloides* and *Globorotalia inflata* with the chronostratigraphy of Martinson *et al.* (1987) and van Kreveld *et al.* (1996). These ages were not determined to core T90-2P. The isotopic stage intervals in T90-2P were estimated on the basis of the  $\delta^{18}O$  of *Globigerina bulloides* variation with depth. Analyses of *Globigerina bulloides* specimens in the T90-2P core were performed at the Centre for Marine Earth Sciences, Institute of Earth Sciences, Free University. The foraminiferal tests were ultrasonically cleaned for 1 to 2 minutes in analytical grade methanol and then acidified with 100%  $H_3PO_4$  in vacuum at  $50 \pm 0.5^\circ C$ . The released  $CO_2$  gas was analysed offline with a Finnigan MAT 251 mass spectrometer. All isotopic values are given in the “ $\delta$ ” notation in parts per thousand (‰) and expressed relative to the PDB standard (further details are given in van Kreveld, 1996).

For core T90-2P, a total of 97 bulk samples were analysed in duplicate for weight % carbonate using a Scheibler-type gasometric technique with a  $\pm 2\%$  precision. Duplicate measurements for organic carbon content of 49 bulk samples were carried out in a Carlo Erba NA-1500 elemental analyser and followed the procedure described in van Kreveld (1996). Both cores provided good carbonate production records since they lie above the lysocline and are recovered from an open-ocean environment where coccolithophorid blooms presently occur and where foraminifera are abundant.

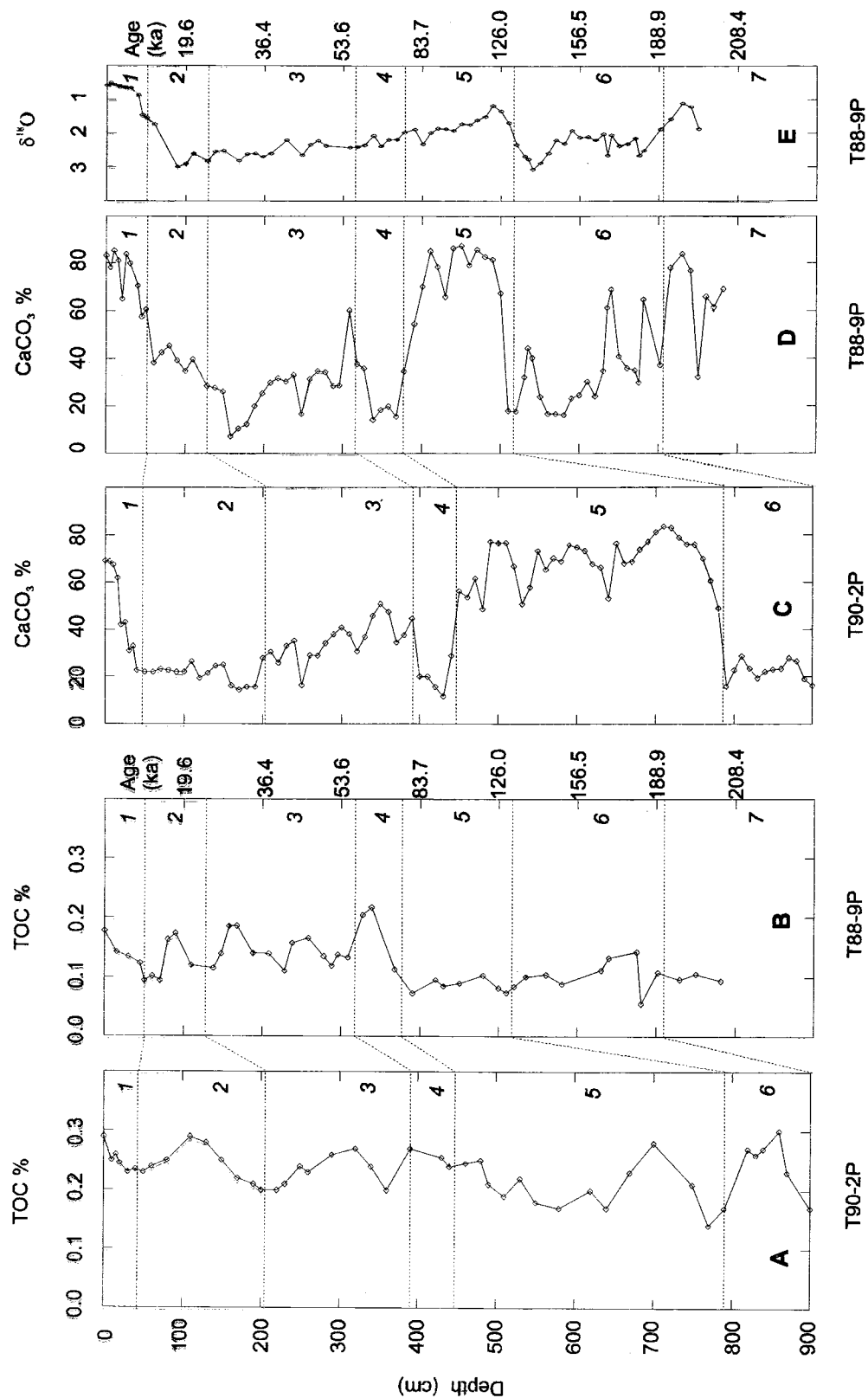


Fig. 2. Downcore profiles in T90-2P and T88-9P cores, respectively, of: weight percentages of total organic carbon, TOC % (A) and (B); %  $\text{CaCO}_3$  of fine fraction ( $< 32 \mu\text{m}$ ) of sediment (C) and (D). The data shown here for oxygen isotopic ratio in *Globigerina bulloides* was estimated to core T88-9P (E) (van Kreveld, 1996). Numbers inside of panels indicate isotopic stages. Ages shown here were only determined to T88-9P core (ka = thousand years).

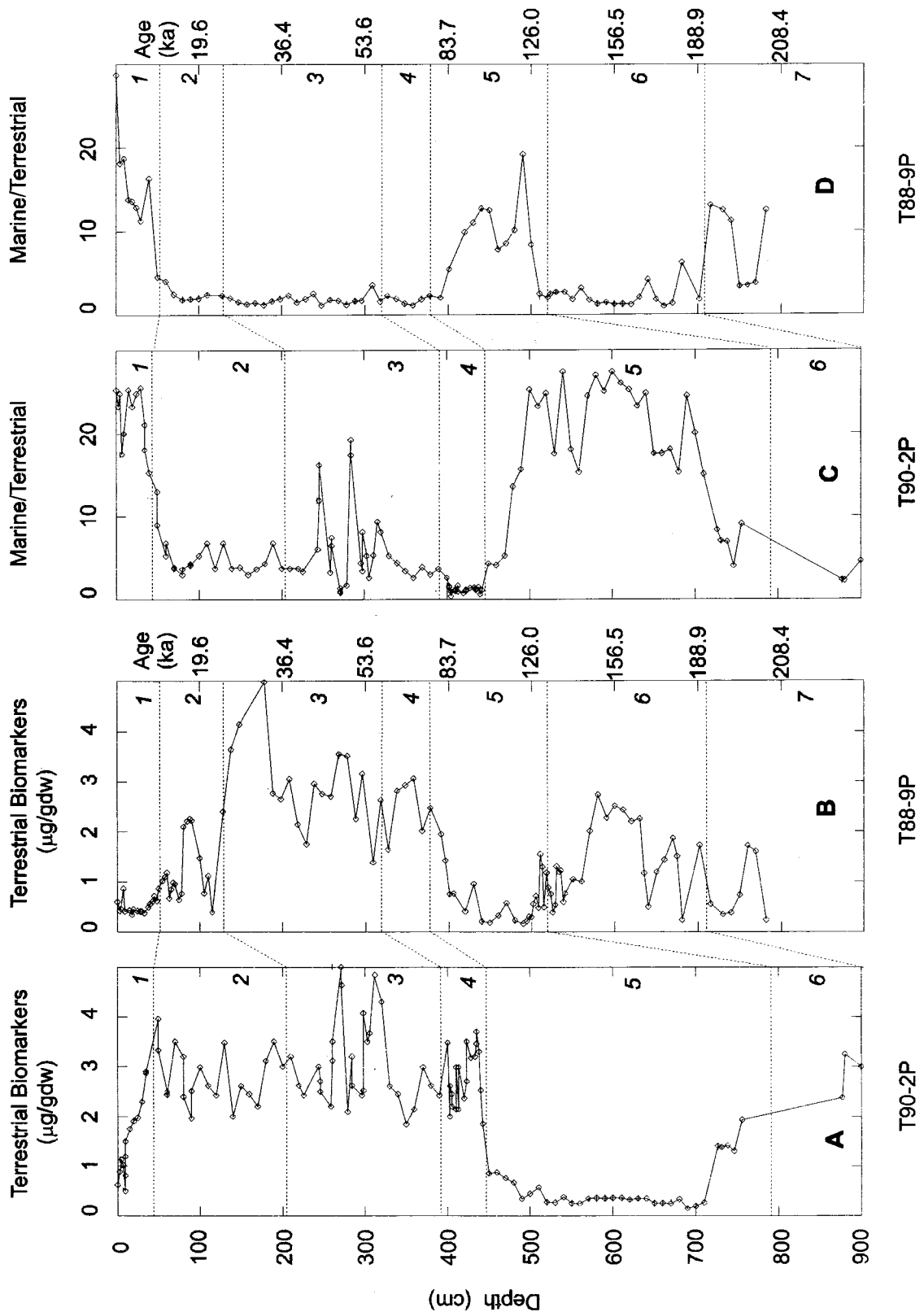


Fig. 3. Downcore profiles in T90-2P and T88-9P cores, respectively, of: sum of terrestrial biomarkers (alkanes  $C_{27}$ ,  $C_{29}$ ,  $C_{31}$ ; alkanolic acids and alkanols  $C_{24}$ ,  $C_{26}$ ,  $C_{28}$  – concentrations in  $\mu\text{g}/\text{gram}$  of dry weight) (A) and (B); marine (hexadecanoic acid  $C_{16}$ ) / terrestrial (hydrocarbon  $C_{29}$ ) ratio (C) and (D). Numbers inside of panels indicate isotopic stages. Ages shown here were only determined to T88-9P core (ka = thousand years).

## Results and discussion

### Bulk parameters

Downcore profiles of total organic carbon (% TOC) varied little with depth at both sites. Most TOC values fell between 0.10 and 0.30 %, with average values for TOC slightly higher for core T90-2P (0.25 %; Fig. 2A) than for core T88-9P (0.12 %; Fig. 2B). These low TOC values were consistent with those of other abyssal sediments measured at nearby stations (Brand & Shimmield, 1992; Santos *et al.*, 1994; Madureira *et al.*, 1995; Manighetti and McCave, 1995; Villanueva *et al.*, 1997). In core T90-2P, TOC values showed no trend along the glacial-interglacial intervals. A clear variation is only seen for core T88-9P, particularly in the transition of isotopic stages 5 – 4, where TOC increased from 0.07 to 0.2%. In Villanueva *et al.* (*op. cit.*), TOC measurements in two cores taken from the North Atlantic also indicated that higher TOC values can be found during glacial periods and lower values during interglacials. According to these authors, most of the TOC present in glacial sediments is of detrital origin, which is a clear indication of higher terrestrial input. As we will discuss later, higher TOC values are associated with higher amounts of terrestrial biomarkers. In contrast with the slight changes of % TOC during the glacial-interglacial transitions, in both cores % CaCO<sub>3</sub> varied quite remarkably in parallel with glacial-interglacial changes in climatic conditions (Fig. 2C and 2D). Values shown here are from the fine carbonate fraction (< 32 µm), which is mainly composed of coccoliths and detrital carbonate with minor contribution from juveniles and fragments of foraminifera (van Kreveld, 1996). Such changes suggest that this carbonate fraction is an important indicator of marine paleo primary productivity for glacial and interglacial intervals. In fact, the boundaries between isotopic stages 6 – 5, 5 – 4, and 2 – 1 are marked by clear changes in the % CaCO<sub>3</sub>. In both sites carbonate increased nearly 50% from the penultimate glacial period (isotopic stage 6) to the last interglacial period (isotopic stage 5). These values remained relatively high along the interglacial interval and began to fall again at the end of this warm period. During the last glacial interval, data from both sites showed that CaCO<sub>3</sub> averaged nearly 30% and only increased again at the beginning of the present interglacial interval (isotopic transition stage 2 - stage 1). The results seen here for the glacial stage are consistent with % CaCO<sub>3</sub> contents found in the Atlantic Ocean bottom sediments during the Last Glacial Maximum (Balsam and McCoy, 1987). Working on T88-9P core, van Kreveld *et al.* (1996)

showed that paleo primary productivity estimates based on biogenic carbonate accumulation rates are generally higher during interglacial periods than in ambient glacials. These authors also identified changes in % CaCO<sub>3</sub> at depth intervals associated with the Heinrich events (see discussion about those events in van Kreveld *et al.*, 1996 and Madureira *et al.*, 1997). Here, the results for both cores stress the importance of fine fraction carbonate as a paleo primary productivity proxy in open ocean sediments dominated by CaCO<sub>3</sub> tests. However, it is important to mention that, apart from changes in sea surface productivity, variability in carbonate contents may result from other factors such as water depth, transport of carbonate material from other areas, and dilution from terrigenous sources (Balsam & McCoy, 1987). For the Atlantic Ocean sediments, water depth is the primary control, as below a certain depth waters become undersaturated in carbonate. Over much of the Atlantic Ocean, the calcium carbonate compensation depth ranges from ca. 4.5 – 5.0 km. At greater depths, dissolution exceeds supply and there is no accumulation of significant amounts of carbonate material. Nevertheless, none of the sites studied here were deeper than 4500 m; thus, water depth does not seem to be a major factor. However, the other two factors mentioned above could be, to some extent, accountable for carbonate shifts. But the sharp carbonate changes following climatic transitions is a strong evidence of sea surface productivity predominance.

### Downcore biomarker profiles

Madureira *et al.* (1997) compared the sum of molecular biomarker and sedimentological data for selected depth intervals of isotopic stages 1 – 6 for core T88-9P. In agreement with previous findings (Madureira *et al.*, *op. cit.*), the results shown here for T90-2P confirmed that glacial stages (2 - 4 and 6) are richer in molecular compounds compared to interglacial stages (Figs 3A and 3B). The molecular based parameter (marine/terrestrial ratio) estimated for both cores showed clear variations with climatic periods (Figs 3C and 3D). This ratio was nearly five times higher for isotopic stages 1 and 5 than for glacial intervals. Such results suggest that interglacial intervals are accompanied by a higher input of marine compounds or that the relative decrease in terrigenous organic matter influx during interglacial intervals could be accountable for the rise in the marine/terrestrial ratio. Figures 3A and 3B seem to support the later statement, as the sum of terrestrial biomarker compounds (alkanes C<sub>27</sub>, C<sub>29</sub>, and C<sub>31</sub>; alkanolic acids and alkanols C<sub>24</sub>, C<sub>26</sub>, and C<sub>28</sub>) was less than one during stages 1 and 5. Our

data agree with the results found in cores SU90/08 and SU90/39, where changes in marine TOC were shown to be independent of glacial-interglacial changes (Villanueva *et al.*, 1997). Unlike marine signals, terrigenous biomarkers showed clear variations in both cores, T90-2P and T88-9P, accompanying climatic changes. However, it is interesting to note that during stage 2 concentrations of terrestrial biomarkers are higher in core T90-2P than T88-9P. This specific feature suggests that in core T90-2P there is a higher contribution of ice-rafted material during this stage, which is consistent with its location, further north than core T88-9P. Significant contributions of terrigenous compounds were also observed in cores SU08/39 and SU90/39 in which alkanes were used to assess continental contributions to organic matter (Villanueva *et al.*, *op. cit.*).

Land derived material is thought to be brought to the open ocean mainly by ice raft, particularly in latitudes higher than 40°N, and to a lesser extent by eolian transport. However, we have recently pointed out that dust material is an important source of exogenous organic matter even in latitudes higher than 40°N (Madureira *et al.*, 1997). Profiles of ion contents originating from aerosols trapped in an ice core from east Antarctica showed that terrestrial aerosol inputs were higher during cold climatic conditions than during the last interglacial and Holocene stages (Legrand *et al.*, 1988; GRIP, 1993). Thus, contributions from eolian dust to marine sediments are also important, and part of the ice-transported material may in fact be dust deposited in ice sheets. Legrand *et al.* (*op. cit.*) used aluminium to show that the increase in inorganic material found trapped in ice cores during glacial intervals could be related to the expansion of arid areas, and that stronger emissions would occur due to increased wind speed over the continents.

A comparison of % CaCO<sub>3</sub> profiles in T88-9P and T90-2P showed good correlation between the carbonate signal and marine/terrestrial changes over glacial-interglacial periods. The plot of % CaCO<sub>3</sub> versus marine/terrestrial ratio summarises this relationship (Fig. 4). Accordingly, high ratio values were found to be related to high % CaCO<sub>3</sub> values and they are associated with interglacial stages. In contrast, low ratio values were found to be related to low % CaCO<sub>3</sub> contents. However, it is important to mention that changes in the marine/terrestrial ratio found in this work seem to be more dependent on variations in the abundance of terrestrial compounds than of marine ones.

The OEP ratio was estimated for a few depth sections in core T90-2P over the last glacial and the present interglacial intervals (Table 1). It is

interesting to note the low OEP values during the last glacial and their slight increase toward the Holocene. Distribution of alkanes without odd/even predominance can be attributed to microbial reworking of the odd C-numbered alkane mixtures (Grimalt *et al.*, 1985; 1986). Thus, such shift in OEP values suggest that the terrestrial biomarkers deposited during those periods may have had distinct origins or that during the glacial period the detrital material deposited was more reworked. Unlike OEP, the API index did not show any trend with depth. It is difficult to establish a clear relationship between oscillations in API values in both sites and either water depth or sedimentation rate. API values could result from a combination of changes involving both parameters.

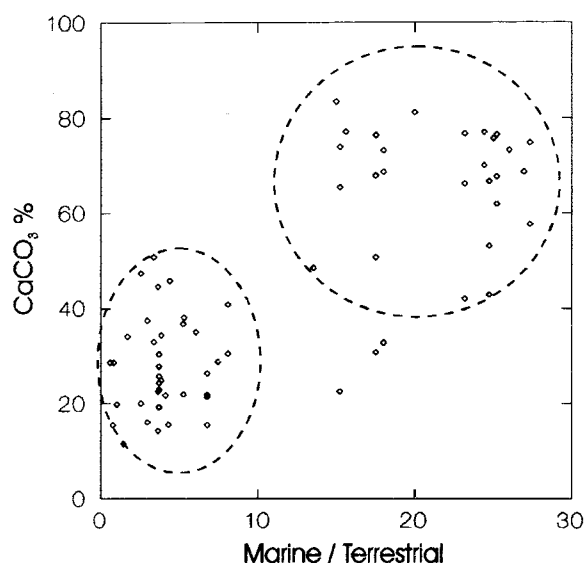


Fig. 4. Core T90-2P plot of % CaCO<sub>3</sub> of fine fraction (< 32 μm) versus marine / terrestrial ratio (hexadecanoic acid C<sub>16</sub>/ hydrocarbon C<sub>29</sub>).

## Conclusions

As we have already mentioned, biomarker compounds have been widely reported to be a valuable tool to assess terrigenous and marine signatures in the sediment record. They can be used with inorganic indicators for paleoceanographic interpretations. Changes in terrigenous inputs to the oceans associated with earth climatic cycles are well documented by some biomarker compounds. Here, we have showed that during glacial stages the extractable fraction of organic matter and TOC are mainly related to terrestrial signatures. However, using some planktonic derived organic compounds, the marine signal observed here was not so evident. Those compounds did not show significant changes



with climatic variations. In fact, the only proxy that showed clear changes was the fine fraction of calcium carbonate analysed in both cores.

Due to the position of T88-9P and T90-2P in the Northeast Atlantic, terrigenous organic matter is believed to be brought mainly by ice raft. However, eolian input cannot be ruled out, and during glacial stages it may have been an additional source of land derived material.

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