

# Precessional forcing of productivity in the North Atlantic Ocean

Joan Villanueva, Joan Grimalt, Laurent Labeyrie, Elsa Cortijo, Laurence

Vidal, Jean Louis-Turon

### ▶ To cite this version:

Joan Villanueva, Joan Grimalt, Laurent Labeyrie, Elsa Cortijo, Laurence Vidal, et al.. Precessional forcing of productivity in the North Atlantic Ocean. Paleoceanography, 1998, 13 (6), pp.561-571. 10.1029/98PA02318 . hal-02958592

## HAL Id: hal-02958592 https://hal.science/hal-02958592

Submitted on 12 Oct 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

### Precessional forcing of productivity in the North Atlantic Ocean

Joan Villanueva and Joan O. Grimalt

Department of Environmental Chemistry (CID-CSIC), Barcelona, Catalonia, Spain

Laurent D. Labeyrie,<sup>1</sup> Elsa Cortijo and Laurence Vidal Centre des Faibles Radioactivités, Laboratoire Mixte CNRS-CEA, Gif-sur-Yvette, France

Jean Louis-Turon

Laboratoire de Géologie et Océanographie, Université de Bordeaux I, Talence, France

Abstract. The sedimentary  $C_{37}$  alkenone fluxes in core SU90/08 situated in the North Atlantic (43°N) showed that export productivity related to some Haptophyta was driven by precession (1/23 kyr<sup>-1</sup>) in the last 260 kyr during the glacial periods. In the interglacial stages these alkenones were strongly depleted. This different behaviour is attributed to the displacement of Ekman pumping to lower latitudes and to thermocline stability decreases in the glacial periods. The alkenones were coherent and nearly phased with boreal winter insolation, suggesting a link between productivity and the strength of the westerlies. They were also coherent with the precessionally driven nutriocline minima and winter sea surface temperature in the equatorial Atlantic Ocean. The combination of the measurements at these different latitudes point to a strong coupling in the dynamics of the Hadley and Ferrel cells and to a dominant North Atlantic modulation of marine productivity to precession during the glacial stages.

#### 1. Introduction

Marine productivity has been proposed to be one of the fundamental factors determining CO<sub>2</sub> transport from atmosphere to deep sea waters and sediments [Broecker, 1982; Shackleton et al., 1983; Mix, 1989]. This process has been referred as the "biological pump" by which CO<sub>2</sub> is removed from surface waters by algal intake and transported to deep levels in the form of sinking organic particles. Unfortunately, whereas the atmospheric CO<sub>2</sub> record during the last glacial-interglacial cycles has been well determined from the studies of the ice-trapped air [Neftel et al., 1982; Barnola et al., 1987], the changes in marine productivity are still far from being described with accuracy. Several studies have shown that productivity was higher during the last glacial maximum than in the Holocene [Boyle, 1986; Sarnthein et al., 1987; Berger et al., 1989], but the aspects determining its evolution, particularly those concerning the interaction with climatic forcing, are poorly understood. One difficulty of getting insight into this question is the scarcity of continuous marine productivity records that can be used for orbital frequency analysis.

Organic carbon models [Müller and Suess, 1979; Berger and Herguera, 1992; Sarnthein et al., 1992; 1981; Mix, 1989] and studies on foraminiferal populations [Mix 1989; Herguera and Berger, 1991; Thomas et al., 1995] have been used to estimate paleoproductivity changes in glacial and interglacial periods. These proxies have provided interesting results. However, their usefulness is constrained by problems such as interferences from terrigenous sources (organic matter [Villanueva et al., 1997a]) or complex food webs (foraminifera).

Paper number 98PA02318. 0883-8305/98/98PA-02318\$12.00 In the present paper we use two direct algal biomarkers for productivity measurements, heptatriaconta-8,15,22-trien-2-one  $(C_{373})$  and heptatriaconta-15,22-dien-2-one  $(C_{372})$ . These compounds are the major homologues of a complex distribution of  $C_{37}$ - $C_{39}$  diunsaturated and triunsaturated methyl and ethyl ketones that are uniquely synthesized by some Haptophyta [Volkman et al., 1980a; Marlowe et al., 1984]. In the Holocene the predominant synthesizing species is Emiliania huxleyi [Conte and Eglinton, 1993; Marlowe et al., 1990], constituting ~8% of the total organic carbon (TOC) in living cells [Prahl et al., 1988]. The sedimentary fluxes of these alkenones can be used to measure the changes in organic matter remains from some species of Haptophyceae algae accumulated in the underlying sediments. The export productivity due to this class of algae can therefore be determined from these fluxes.

The high-resolution study of these compounds in a core situated in the subtropical gyre of the North Atlantic (SU90/08, Figure 1) has allowed the elucidation of the influence of orbital cyclicities in the productivity changes of this area along the last two glacialinterglacial periods. The results obtained parallel other independent measurements such as the ice core accumulation rate of nonsea-salt sulphate (nss-SO<sub>4</sub><sup>2-</sup>) in the Vostok ice core (Antarctica [Legrand et al., 1988]).

#### 2. Materials and Methods

#### 2.1. Stratigraphy

Core SU90/08 was retrieved in the central North Atlantic (43°30'N 30°24'W). Reference ages between 0 and 64 kyr were determined using 10 accelerator mass spectrometry (AMS)  $^{14}$ C date measurements, ash layer 2 level (55 kyr [*Ruddiman and Glover*, 1972]) and the transition age between isotopic stages 4/3. The AMS  $^{14}$ C dates were determined on monospecific samples of *Neogloboquadrina pachyderma (sp.) and Globigerina bulloides* and were corrected for the ocean reservoir effect of 400 years [Bard, 1988]. Chronostratigraphic control of deeper levels was

<sup>&</sup>lt;sup>1</sup>Also at Department of Earth Sciences, Université Paris-Sud Orsay, 91405 Orsay, France.

Copyright 1998 by the American Geophysical Union.



Figure 1. Map showing the location of the cores indicated in this study.

determined by correlation of the benthic  $\delta^{18}$ O record of *Cibicides* wuellestorfi with the SPECMAP normalized isotope curve [Martinson et al. 1987]. The complete age-model construction is reported elsewhere [*Cortijo et al.*, 1997; Vidal et al, 1997]. Ages are expressed in radiocarbon dates. This core has not turbiditic episodes and exhibits regular sedimentation rates. A detailed stratigraphic description is given by *Grousset et al.* [1993].

#### 2.2. Core Sampling and Analysis

Alkenone analysis was performed every 2 cm in the top 7 m (average resolution 440 years) increasing to 1 cm at all profile discontinuities. Between 7 and 12 m the sampling rate was 10 cm (average resolution 2000 kyr). In all cases the samples were collected in sections of 0.5 cm ( $\sim$  55 years).

A detailed description of the analytical methods is given by *Villanueva and Grimalt* [1997] and *Villanueva et al.* [1997b]. Sediment samples were freeze-dried and manually grounded for homogeneization. Then they were extracted in an ultrasonic bath with dichloromethane. The evaporated extracts were digested in 6% methanolic potassium hydroxide, and nonacidic compounds were recovered by extraction with *n*-hexane. The acidic fractions

were recovered by acidification with 6N hydrochloric acid and reextraction with *n*-hexane. These extracts were derivatized overnight with 10% methanolic boron trifluoride and were used to calculate the concentrations of *n*-octadec-9-enoic acid (C<sub>18 1</sub>) and *n*octadecanoic acid (C<sub>18 0</sub>) which can be used to compile a fatty acid preservation index (FAPI: C<sub>18 1</sub>/(C<sub>18 0</sub> + C<sub>18 1</sub>))

Prior to instrumental analysis all extracts were derivatized with bis-trimethylsilyl-trifluoroacetamide (BSTFA) at room temperature. These extracts were analyzed by gas chromatography (GC) in a Varian Model 3400 equipped with a septum programmable injector (SPI), a flame ionization detector, and a CPSIL-5 CB (Chrompack, Middleburg, Netherlands) capillary column (length 50 m, i.d. 0.32 mm) coated with 100% dimethylsyloxane (film thickness 0.25  $\mu$ m). Selected samples were also analyzed by GC coupled to mass spectrometry (GC-MS) using a Fisons MD-800 instrument. Spectra were obtained in the electron impact mode (70 eV) through scanning from mass 50 to 550 every second.

#### 2.3. Figures of Merit

The quantitative determinations of  $C_{37}$  alkenones and *n*-alkanes were performed in triplicate. All calculations were performed us-

ing the mean values. Absolute concentration errors of these lipids were below 10%.  $U_{37}^k$  and FAPI errors were below 0.015 and 0.01, respectively.

#### 2.4. Time Series Analysis

Time series were studied with the Analyseries program [*Paillard et al.*, 1996] using Fourier transforms and the Blackman-Tuckey method. Correlation studies with core RC2407 data were performed using the data provided by A. McIntyre. Prior to calculation minor corrections of age scale were performed by cross comparison of the  $\delta^{18}$ O *G. bulloides* record with that of SU90/08 (Figure 2).

#### 3. Results

The total C<sub>37</sub> alkenone fluxes downcore SU90/08 range between 9.5 and 0.2 µg cm<sup>-2</sup> kyr<sup>-1</sup> (Figure 2), but they decrease further in the Holocene section and during the episodes of massive inputs of ice rafted detritus, the so-called Heinrich events [Heinrich, 1988]: H1, H2, H4, and H5 [Grousset et al., 1993]. These sedimentary fluxes are intermediate between other values found in oxic sedimentary environments from diverse open ocean sites. Thus C<sub>37</sub> alkenone fluxes of 0.25 and 0.33  $\mu$ g cm<sup>-2</sup> kyr<sup>-1</sup> are found in the northeast and central equatorial Pacific Ocean, respectively [Prahl et al., 1989, 1993], and high productivity zones such as the Maldives Islands area exhibit C<sub>37</sub> alkenone sedimentation rates between 1 and 20 µg cm<sup>-2</sup> kyr<sup>-1</sup> [Rostek et al., 1994]. These values are significantly lower than those found in marine basins where anoxic or dysoxic depositional conditions predominate. In these cases the C<sub>37</sub> alkenone sedimentation fluxes range between 200 and 1200 µg cm<sup>-2</sup> kyr<sup>-1</sup> [Sun and Wakeham, 1994; McCaffrey et al., 1990; Summerhayes et al., 1995].

The low concentrations of  $C_{37}$  alkenones near the Heinrich events are in agreement with other observations in the North Atlantic showing low abundances of phytodetritus foraminifera and low benthic accumulation rates [*Thomas et al.*, 1995]. These events are therefore characterized by low productivity. Neither the alkenone nor the foraminifera results support an iceberg-related physical mechanism for productivity increase in the past oceans [*Sancetta*, 1992].

The most distinct feature of the  $C_{37}$  alkenone record in SU90/08 is the predominance of a cyclic pattern. Blackman-Tuckey spectral analysis with a bandwidth of 0.018 kyr<sup>-1</sup> shows a large peak (35% of the total alkenone variance over the width of the peak) at the precessional component of the Milankovitch orbital forcing (0.043 = 1/23 kyr<sup>-1</sup>). The mean coherency is 0.92 over this peak (for comparison, 0.52 corresponds to the 80% significance level; Figure 3). This  $C_{37}$  alkenone signal is in opposition of phase with summer insolation at 43°N (phase angle  $\Phi = -149^{\circ} \pm 10^{\circ}$  and coherence  $\kappa = 0.89$ ; Table 1). No response to the other orbital cycles (1/100 and 1/40 kyr<sup>-1</sup>) is observed. The 280 kyr time span covered by this SU90/08 is sufficient to show prominent frequency in the case that these existed.

All the other climatic records in core SU90/08 show significant intensities at the 1/100 and 1/40 kyr<sup>-1</sup> bands (Figure 3). The single 1/23 kyr<sup>-1</sup> frequency signal of the C<sub>37</sub> alkenones stands out among the other proxies. Even the ratio between diunsaturated and triunsaturated alkenones (U<sup>k</sup><sub>37</sub>; Figure 2) that records sea surface temperatures (SST *Brassell et al.*, 1986a,b; *Prahl and Wakeham*, 1987] exhibits a spectral pattern coincident with the  $\delta^{18}$ O curves (Figure 3). The frequencies at 1/100 and 1/40 kyr<sup>-1</sup> reflect the influence of the ice sheet evolution and constitute a major compo-

nent of the North Atlantic variability, including the latitudes where core SU90/08 is situated [*Imbrie et al.*, 1992].

#### 4. Discussion

Only a small fraction of the  $C_{37}$  alkenones produced in the euphotic zone by algal synthesis is preserved in the underlying sediment. This process is general for the organic carbon arriving to the bottom sediments after water column transport in association with settling particles [Manighetti and McCave, 1995]. However, the  $C_{37}$  alkenones range among the lipids more refractory to biodegradation [Volkman et al., 1983; Kennedy and Brassell, 1992; Sun and Wakeham, 1994]. This context prompts the evaluation of the factors determining the distinct precessional signal of the  $C_{37}$  alkenones in SU90/08, paying particular attention to the influence of preservation changes in the development of this cyclic pattern.

#### 4.1. Preservation Effects

Comparison of the  $C_{37}$  alkenone flux and sedimentation rate provides a first evaluation of possible correspondences between depositional and diagenetic effects. As shown in Figure 4, the downcore trend of both variables is rather independent. In some episodes, higher sedimentation is reflected in higher alkenone flux. However, higher sedimentation rates are never reflected in decreases of  $C_{37}$  alkenone flux, evidencing that the  $C_{37}$  alkenone raises cannot be attributed to fictitious effects derived from depositional depletion.

The influence of oxidation and other degradation processes in the precessional record may be addressed by examination of the sedimentary composition of lipid molecules that are more labile to preservation effects than the C<sub>37</sub> alkenones. Fatty acids are more sensitive to degradation [Volkman et al., 1983; Kennedy and Brassell, 1992; Sun and Wakeham, 1994], and the unsaturated fatty acids are degraded faster than the saturated homologues [Sun and Wakeham, 1994]. This is the case of n-octadec-9-enoic acid which is eliminated from the sedimentary environment faster than its saturated homologue n-octadecanoic acid [Grimalt et al., 1992]. According to these differences these acids have been used to calculate a fatty acid preservation index as defined in section 2. Higher abundances of C<sub>181</sub> (higher FAPI values) must correspond to less degradation and vice versa. This ratio essentially reflects the changes in algal organic matter since C<sub>18</sub> acids are of algal origin [Parker, 1969; Boon et al., 1978; Volkman et al., 1980b].

The analysis of the fatty acid composition in selected sections of core SU90/08 having maximal and minimal C<sub>37</sub> ketone content shows that the FAPI values range between 0.09 and 0.23 (Figure 2). These values are consistent with the composition of sinking particles in the northeastern Pacific Ocean [Grimalt et al., Seasonal trends in ascending and descending fluxes of particulate lipids in the abyssal water column of the northerastern Pacific Ocean, submitted to Deep-Sea Research I, 1998]. Sediment traps deployed over 1 year and seasonal collection of the sinking material showed that the average FAPI at 1235 and 3785 m depth are 0.77 and 0.43, respectively. The values recorded in SU90/08 probably reflect the combined effects of water column and postdepositional degradation. However, the most interesting aspect of the FAPI values in core SU90/08 is the lack of correlation with C<sub>37</sub> alkenone fluxes (or concentrations) which is consistent with the lack of influence of depositional conditions in the precessional pattern recorded by these Haptophytae compounds.

Another aspect to be considered, in addition to the examination of the fatty acid composition, is the fact that postdepositional degradation usually affects all lipid compounds tending to uniformize



Figure 2. Downcore profiles of the  $\delta^{18}$ O record of *Globigerina bulloides*, U<sup>k</sup><sub>37</sub> index, C<sub>23</sub>-C<sub>33</sub> odd carbon numbered*n*-alkane flux, June 15 insolation at 43°N [*Berger*, 1978], and C<sub>37</sub> alkenone flux in SU90/08 core (43°30'N, 30°24'W). FAPI is the fatty acid preservation index (*n*-octadec-9-enoic acid / (*n*-octadec-9-enoic acid + *n*-octadecanoic acid)).



Figure 3. Variance spectra of the core profiles shown in Figure 2 (expressed as the logarithm of spectral power density versus frequency in cycles kyr<sup>-1</sup>, using the Blackman-Tuckey method and where lags = 30 [Jenkins and Watts, 1986]) compared with the spectrum of boreal summer insolation at 43°N. Bandwith (BW) and 80% confidence interval (CI) are indicated with a line segment. The three main orbital periods of eccentricity (100 kyr), obliquity (41 kyr), and precession (23 kyr) are marked with a vertical line. The coherency spectra between core profiles and insolation are shown at the bottom of each profile. The horizontal lines indicate the level of nonzero coherence at the 80% confidence interval.

the differences in source input variability [Grimalt et al., 1992; Haddad et al., 1992; Sun and Wakeham, 1994]. Information on specific inputs is contained in the deviations of individual molecules from the general trend [Grimalt et al., 1992; Haddad et al.,

1992; *Brassell*, 1993]. In core SU90/08 the dominant  $1/23 \text{ kyr}^{-1}$  cyclicity of the C<sub>37</sub> alkenones is specifically different from the downcore concentration trend of many other lipids, i.e., the C<sub>25</sub>-C<sub>33</sub> odd carbon numbered *n*-alkanes (Figures 2 and 3). This spe-

Table 1. Correlation and Phase Angle of Summer Insolation (June 21) at 43°N With the Variables Studied in SU90/08, Sea Surface Temperature (SST) in Core V30-97, and *Florisphaera profunda* Abundance in Core RC2407

Period,	Sedimentation Rate	δ <sup>18</sup> O 1 Globigerina bulloides	۲ ا <sup>k</sup>	C <sub>23</sub> -C <sub>33</sub> n-Alkanes	C <sub>37</sub> Alkenones	SST V3040	Florisphaera profunda Abundance
23	0.66	0.82	0.78	0.18	0.89	0.87	0.85
41	0.48	-71±11° 0.65	86±15° 0.76	0.43	-149±10° 0.43	20±11° 0.37	77±13° 0.27
100	0.39	-111±24° 0.41	58±18° 0.48	0.30	0.10	0.33	0.39

cific signal is different from the concentration record of the other lipid molecules which makes unlikely that it responds to preservation effects.

Finally, sedimentary bulk organic matter studies in the equatorial Atlantic upwelling zone, where the productivity signal and other climatic proxies are modulated to precession have shown that postdepositional preservation is not related to precession but to the 1/100 and 1/41 kyr<sup>-1</sup> cycles [*Verardo and McIntyre*, 1994]. This reflects that organic matter oxidation rates are influenced by the dynamics of the bottom waters, namely, the rates of production



Figure 4. Comparison of the  $C_{37}$  alkenone record in SU90/08 with the precession and the eccentricity cycles. The shaded bands outline the low productivity (low  $C_{37}$  alkenone flux) of the interglacial stages (maximum eccentricity) irrespectively of precession. The SU90/08 sedimentation rate is also included for comparison.

of North Atlantic Deep Water (NADW), which is modulated to the ice sheet response to insolation [Imbrie et al., 1992, 1993]. Conversely, water productivity is determined by surface water phenomena, such as nutriocline changes. These changes respond to direct insolation effects driven by precession in the equatorial zone.

All these aspects indicate that the dominant precessional alkenone signal in SU90/08 does not reflect changes in preservation. This alkenone record points to a direct link between Haptophyte productivity in the central North Atlantic gyre and the precessional pattern.

#### 4.2. Precessionally Driven Proxies at High Latitudes

The  $U_{37}^{k}$  index in SU90/08 (Figures 2-3) shows that SST at 43°N essentially follows the  $\delta^{18}$ O curve, exhibiting significant intensities at the 1/41 and 1/100 kyr<sup>-1</sup> bands. Examination of modern analogue foraminiferal SST transfer functions reveals the same trend [Vautravers, 1996]. These variables also have a significant maximum at the 1/23 kyr<sup>-1</sup> band, although at a lower intensity than the other Milankovitch periods. As shown in Table 1, correlation with summer insolation at 43°N reveals significant coherences of  $U_{37}^{k}$  and  $\delta^{18}O$  at 1/23 ( $\kappa = 0.78$  and 0.82, respectively) and 1/41 kyr<sup>-1</sup> ( $\kappa = 0.76$  and 0.65, respectively). These two variables also exhibit significant cross correlation and counterphasing at 1/23, 1/41, and 1/100 kyr<sup>-1</sup> ( $\kappa = 0.9, 0.9$ , and 0.92, respectively; Table 2). The overall spectral pattern is consistent with the latitudinal position of core SU90/08 since oceanic processes in high and intermediate latitudes are preferentially driven by the 1/41 and 1/100 kyr<sup>-1</sup> bands following the ice sheet response to insolation forcing [Imbrie et al., 1989, 1992, 1993].

The C<sub>37</sub> alkenones are only correlated with U<sup>k</sup><sub>37</sub> and  $\delta^{18}$ O at 1/23 kyr<sup>-1</sup> ( $\kappa = 0.78$  and 0.94, respectively; Table 2). Likewise, these alkenones are only correlated with summer insolation at 1/23 kyr<sup>-1</sup>, exhibiting high coherence ( $\kappa = 0.89$ ) and counterphasing ( $\phi = -149^{\circ} \pm 10^{\circ}$ ; Table 1). Oceanic processes dominated by 1/23 kyr<sup>-1</sup> are scarce and mostly located at low latitudes, such as the equa-

**Table 2.** Cross Correlation of the Variables Determined in Core SU90/08 and Correlation of  $C_{37}$  Alkenones With *F. profunda* Abundance in Core RC2407

Sedime	entation	δ¹³O	_	C <sub>23</sub> -C <sub>33</sub>	F. profunda		
	Rate G	. bulloides	U <sup>k</sup> 37	n-Alkanes	Abundance		
		23 kyr Pe	eriod				
$\delta^{18}O$ G. bulloides	0.3						
U <sup>k</sup> 37	0.38	0.9					
		-163±13°					
C23-C33 n-alkanes	0.46	0.5	0.6				
C <sub>37</sub> alkenones	0.5	0.94	0.78	0.37	0.82		
		77±13°	-123±20°	•	-133±16°		
41 kyr Period							
$\delta^{18}O$ G. bulloides	0.45						
U <sup>k</sup> 37	0.51	0.9					
		-167±12°					
C23-C33 n-alkanes	0.85	0.68	0.79				
	17±14°		176±16°				
C <sub>37</sub> alkenones	0.27	0.33	0.3	0.23	0.38		
100 kyr Period							
$\delta^{18}O$ G. bulloides	0.28						
U <sup>k</sup> 37	0.43	0.92					
		-162±11°					
C23-C33 n-alkanes	0.39	0.62	0.6				
C <sub>37</sub> alkenones	0.47	0 62	0.63	0.2	0.72		
					165±17°		

torial Atlantic Ocean where the activity of the Hadley cells controls the divergence intensity [Imbrie et al., 1989].

Thus minimal SST in the equatorial Atlantic Ocean is essentially dominated by precession. This is illustrated by compilation of the SST record in core V3040 (0°12'S 23°9.0'W [*McIntyre et al.*, 1989]) that exhibits high coherence ( $\kappa = 0.87$ ) and phasing ( $\phi = 20^{\circ} \pm 11^{\circ}$ ) with summer insolation at 1/23 kyr<sup>-1</sup> (Table 1). No coherence between this SST profile and insolation is observed at the other Milankovitch frequencies.

Since the  $C_{37}$  alkenone flux is related to productivity, further insight into the climatic information of this variable may be obtained by comparison with other productivity proxies. Minimal nutriocline stability in the equatorial Atlantic Ocean, estimated from the relative abundances of *Florisphaera profunda*, provides a good sedimentary record of past productivity at low latitudes [*Molfino and McIntyre*, 1990; *McIntyre and Molfino*, 1996]. The percent of *F. profunda* relative to the other coccolith species is modulated to precession being lowest (highest productivity) at boreal summer aphelion [*Molfino and McIntyre*, 1990]. Accordingly, spectral analysis of the percent of *F. profunda* in core RC2407 (1°20.5'S 11°53.3'W [*Molfino and McIntyre*, 1990]) shows that this percentage is only correlated with insolation at 1/23 kyr<sup>-1</sup> (coherence  $\kappa = 0.84$ ; Table 1).

*F. profunda* abundance in the equatorial Atlantic is also correlated with the C<sub>37</sub> alkenones at 43°N. As shown in Table 2, these two variables exhibit a coherence coefficient of  $\kappa = 0.82$  at 1/23 kyr<sup>-1</sup> and are nearly counterphased ( $\phi = -133^{\circ} \pm 16^{\circ}$ ) which is consistent with the fact that they measure opposite effects (*F. profunda* maxima correspond to productivity minima). No correlation between the two signals is observed at 1/41 kyr<sup>-1</sup>.

Changes in F. profunda abundance are related with trade wind intensities. Maximal trade winds involve minimal nutriocline depth and maximal productivity (minimal F. profunda abundance). Trade winds are higher when perihelion is aligned with boreal winter [Sarnthein et al., 1981]. These winds are counterphased with the north equatorial monsoons which are also precessionally driven [Pokras and Mix, 1987; Short and Mengel, 1986].

The activity of both trade winds and African monsoons is controlled by the activity of the Hadley cells which account for the wind circulation patterns at low latitudes. Core SU90/08 is too far north to be directly linked to equatorial divergence. Thus the  $C_{37}$ alkenone pattern in this core requires a specific mechanism determining the observed productivity changes.

#### 4.3. Ekman Effects and Precession

Productivity in open oceanic waters is related to the vertical transport of nutrients to the photic zone which depends on the wind regime and nutriocline depth. In the Holocene the nutriocline is shallow in the upwelling equatorial zone, where the Ekman effect of the northern and southern hemisphere trade winds results in divergence and pumping of deep waters to the surface. In contrast, the nutriocline is deepened in the North Atlantic subtropical gyre (10°-55°N), where the combined Ekman components of the trade winds and the westerlies give rise to water convergence. In these downwelling conditions, productivity is low irrespective of wind capacity or water column mixing.

This situation of low productivity is reflected in the alkenone record of core SU90/08. In the Holocene the concentrations of these compounds are very low (Figure 2). In fact, the SU90/08 results indicate that this situation of nutriocline downwelling also occurred in the previous two interglacials (stages 5e and 7; Figures 2 and 5).

In contrast, the precessional alkenone pattern of core SU90/08 points to different nutriocline conditions in the glacial times. In this period the subpolar-subtropical front was displaced southward [*Climate: Long-Range Investigation, Mapping, and Prediction,* 1984; *Keffer et al.*, 1988; *Manabe and Broccoli*, 1985] which involved considerable nutriocline shallowing at latitudes such as 40° [*Gordon,* 1986], affording nutrient transport to the photic zone by wind mixing. Thus the westerlies could determine water productivity, similarly to the trade wind forcing of nutriocline depth in the equatorial Atlantic [*Molina-Cruz,* 1977; *Sarnthein et al.,* 1981; *Pedersen,* 1983]. In this respect a precessional forcing of the percent of *F. profunda* has been observed in the equatorial Indian Ocean where productivity is driven by the wind intensity of westerlies, which is related to the Soutern Oscillation [*Beaufort et al.,* 1997].

In the North Atlantic (45°-60°N), recent studies on clay minerals have shown a dominant 1/23 kyr<sup>-1</sup> variance peak in the areas situated south of 52°N [*Bout-Roumazeilles et al.*, 1997]. This precessional pattern can also reflect the dominance of the westerlies in the atmospheric transport of terrigenous material to these latitudes. A predominant precessional modulation of the westerlies in the North Atlantic is also consistent with the observed precessional dominance of the insolation spectra at 40°30'N (Figure 2).

Further evidence of the precessional forcing of the westerlies is provided by studies of continental records. Thus the ammonium concentrations from Greenland Ice Sheet Project 2 (GISP2) ice cores exhibit a strong precessional cycle, indicating the influence of wind-transported terrigenous emissions to Greenland [*Meeker et al.*, 1997]. Furthermore, the magnetic susceptibility records of the loess plateau in central China show that East Asian monsoons were also precessionally driven [*An et al.*, 1991]. A teleconnexion between the North Atlantic westerlies and the East Asian winter monsoon has been observed [*Porter and Zhisheng*, 1995]. This teleconnexion effect and the precessional forcing of the East Asian monsoon are also consistent with a precessional dominance of the westerlies and Ferrel cell dynamics.

Evidence of the coupling of the changes in the dynamics of the Hadley and Ferrel cells can be obtained by examination of the results in Tables 1 and 2. The 1/23 kyr<sup>-1</sup> cross-spectral analysis of summer insolation and the productivity proxies driven by westerlies and trade winds (C<sub>37</sub> alkenones and % *F. profunda* respectively) reveal high coherency ( $\kappa = 0.89$  and 0.85, respectively) and phase angles of  $\phi = -149^{\circ} \pm 10^{\circ}$  and 77°  $\pm 13^{\circ}$ , respectively. These two productivity proxies also exhibit high coherency at 1/23 kyr<sup>-1</sup> ( $\kappa = 0.82$ ) and a phase angle of  $\phi = -133^{\circ} \pm 16^{\circ}$ . When the three angles are combined, a sum of 359° is observed, in almost full coincidence with the expected 360° value.

On the other hand the phase angle between  $C_{37}$  alkenones and summer insolation at 1/23 kyr<sup>-1</sup>,  $\phi = -149$ , corresponds to a phase of -31° when the winter insolation signal is considered. This angle involves a lag of ~2 kyr between insolation and the westerly driven  $C_{37}$  alkenones or about 1 month in the annual cycle. This lag is similar to that reported by *Short and Mengel* [1986] for the monsoon dynamics and can be explained by the delays in thermal response to astronomical forcing by the low heat capacity of the large land masses in the northern hemisphere.

In short the combined effect of the southward displacement of the subpolar-subtropical front and precessional forcing of the westerlies is consistent with the observed precessional change of  $C_{37}$  alkenones in SU90/08. During the glacials, when water convergence by Ekman pumping is displaced south of the 40°N band, the stability of the nutriocline depth and therefore productivity may depend on the intensities of the westerlies. A precessional forcing of these winds should be reflected in a precessionally driven signal of productivity markers such as the  $C_{37}$  alkenones. The phasing of the alkenone record with maximum boreal winter insolation is consistent with more active wind mixing by the westerlies and higher input of nutrients to the surface. In this respect this period is also characterized by lowest thermocline stability due to minimal boreal summer insolation. In contrast, in the interglacials the northward displacement of the subpolar-subtropical front involves strong water convergence and nutriocline deepening that interrupts the wind-driven productivity mechanism.

#### 4.4. Other Precessionally Driven Algal Productivity Markers

One important aspect of these observed cyclicities is their significance in terms of global marine productivity. In principle the above described C37 alkenones are specific markers of a rather limited group of Haptophyte encompassing the coccolithophorid producers E. huxleyi and Gephyrocapsa spp. Other haptophytes such as Crysotila sp. and Isochrysis sp. also produce C<sub>37</sub> alkenones, but they occur in coastal waters and are unlikely sources of these compounds in the open ocean. Coccolithophorid species only constitute a portion of the total haptophytes [Thomsen et al., 1994]. Irrespective of Haptophyte significance [Chavez et al., 1990], other algal species such as diatoms also account for a substantial fraction of primary production [Goldman, 1993; Claustre, 1994]. Contributions to global productivity derived from the growth of different algal groups could reflect different limitation effects by different macronutrients or micronutrients [Sunda and Huntsman, 1992; 1995; Brand et al., 1983].

However, the wind-driven mixing mechanism outlined in the present study is unspecific. Higher water column mixing by increased westerlies strength will probably incorporate a wide range of micronutrients and macronutrients to the photic zone. Furthermore, nutrient increase currently gives rise to successive blooming of different algal groups, for example, diatoms followed by *E. huxleyi* [*Green and Leadbeater*, 1994]. Thus, despite the specific character of the  $C_{37}$  alkenones, the observed precessional cyclicity probably reflects general marine productivity in the open ocean area represented by core SU90/08.

As described above, this precessional pattern observed at intermediate latitudes is coherent with the precessional productivity regime in the equatorial Atlantic and Indian Oceans [*McIntyre and Molfino*, 1996; *Molfino and McIntyre*, 1990; *Beaufort et al.*, 1997]. Likewise, the Dole effect, which depends on the activity of marine and terrestrial biosphere [*Bender et al.*, 1994] also shows a strong precessional forcing.

On the other hand the precessional driving of marine productivity is also recorded by other global parameters such as nss  $SO_4^{2^-}$ accumulation rate in the Vostok (Antarctica) ice core. This compound also exhibits a spectrum containing an almost single precessional band [*Legrand et al.*, 1988] and, like the  $C_{37}$  alkenones, very low nss  $SO_4^{2^-}$  in the interglacial stages. Marine nss- $SO_4^{2^-}$  essentially originates from dimethylsulphide, a compound that is emitted as a consequence of the decomposition of oceanic phytoplankton [*Savoie and Prospero*, 1989], particularly, haptophyte algae (both  $C_{37}$  alkenone synthesizers and nonsynthesizers) and dinoflagellates [*Liss et al.*, 1993, 1994]. The interdependence between dimethylsulphide emission and the availability of iron in surface waters has been observed [*Turner et al.*, 1996]. Thus the Antarctica nss  $SO_4^{2^-}$  profile is indirectly linked to marine biota paleoproductivity [*Prospero et al.*, 1991].

The close similarity of these two records obtained from such different locations and geologic materials is remarkable. In any case the elucidation of the biological, geochemical, or paleoclimatic links between them is beyond the scope of the present study. Thus *Phaeocystis*, a non- $C_{37}$  alkenone synthesizer Haptophyceae, is abundantly found in marine waters and produces large amounts of dimethylsulphide [*Liss et al.*, 1994]. In any case their common age-dependent trend is consistent with a generalized precessional forcing of productivity in the ocean

#### 5. Conclusions

Ice sheet responses to insolation forcing cannot account for the precessional productivity changes observed in this study since they are preferentially driven by the 1/41 and 1/100 kyr<sup>-1</sup> bands [*McIntyre et al.*, 1989]. The C<sub>37</sub> alkenone fluxes observed in core SU90/08 suggest that export production associated to some Haptophyta algae, and by extension, marine productivity, were modulated to precession in the glacial stages of at least the last two glacial cycles. This modulation was probably mediated by the influence of insolation in the dynamics of the Hadley and Ferrel cells. In the interglacial stages, productivity decreased because of the formation of a thick thermocline that limited the transport of nutri-

#### References

- An, Z., G.J. Kukla, S.C. Porter, and J. Xiao, Magnetic susceptibility evidence of monsoon variation on the Loess Plateau of central China during the last 130,000 years, *Quat. Res.*, 36, 29-36, 1991.
- Bard, E., Correction of accelerator mass spectrometry <sup>14</sup>C ages measured in planktonic foraminifera: Paleoceanographic implications, *Paleoceanography*, 3, 635-645, 1988.
- Barnola, J.M., D. Raynaud, Y.S. Korotkevich, and G Lorius, Vostok ice core provides 160,000-year record of atmospheric CO<sub>2</sub>, *Nature*, 329, 408-414, 1987.
- Beaufort, L., Y. Lancelot, P. Camberlin, O. Cayre, E. Vincent, F. Bassinot, and L. Labeyrie, Insolation cycles as a major control of equatorial Indian Ocean primary production, *Science*, 278, 1451-1454, 1997.
- Bender, M., T. Sowers, and L. Labeyrie, The Dole effect and its variation during the last 130,000 years as measured in the Vostok ice core, *Global Biogeochem. Cycles*, 8, 363-376, 1994.
- Berger, A.L., Long-term variations of daily insolation and Quaternary climatic changes, J. Atmos. Sci., 35, 2362-2367, 1978.
- Berger, W.H., and J.C. Herguera, Reading the sedimentary record of the oceans' productivity, in *Primary Productivity and Biogeochemical Cycles in the Sea*, edited by P.G. Falkowski and A.D. Woodhead, Plenum, New York, 1992.
- Berger, W.H., V.S. Smetacek, and G. Wefer, Ocean productivity and paleoproductivity: An overview, in *Productivity of the Ocean: Present and Past*, edited by W.H. Berger, V.S. Smetacek, and G. Wefer, pp. 1-34, Wiley, New York, 1989.
- Boon, J.J., J.W. de Leewuw, and A.L. Burlingame, Organic geochemistry of Walvis Bay diatomaceous ooze, III, Structure analysis of the monoenoic and polycyclic fatty acids, *Geochim. Cosmochim. Acta*, 42, 631-644, 1978.
- Bout-Roumazeilles, V., P. Debrabant, L. Labeyrie, H. Chamley, and E. Cortijo, Latitudinal

ents to euphotic zones irrespective of wind-driven water column mixing.

In short the results presented in this study are in agreement with previous reports indicating that marine productivity was higher in the glacial periods. However, they show that at least in the area represented by core SU90/08 of the North Atlantic, productivity during these periods was not constant but modulated to precession.

Acknowledgments. This study is part of the ENVIRONMENT Program EV5V-CT92-00117 (EEC) and the Programme National d'Études de la Dynamique du Climat (Institut National des Sciences de l'Univers, France). Core SU90/08 was acquired within the IFREMER/INSU program Paleocinat and studied with support from the Commissariat à l'Energie Atomique, the Centre National de la Recherche Scientifique, and the Ministère de l'Enseignement Superieur et de la Recherche (France). One of us (J.V.) thanks a Ph.D. grant from the Spanish Ministry of Education. Data on core RC2407 (*F. profunda* abundance,  $\delta^{18}$ O *G. bulloides*, and age scale) were kindly provided by A. McIntyre. We also thank J. Maxwell (Environmental and Analytical Unit, School of Chemistry, University of Bristol) for alkenone standards. We are also thankful to B. Popp for useful comments.

control of astronomical forcing parameters on the high-resolution clay mineral distribution in the 45°-60°N range in the North Atlantic Ocean during the past 300,000 years, *Paleoceanography*, 12, 671-686, 1997.

- Boyle, E.A., Paired cadmium and carbon isotope data in benthic foraminifera: Implications for changes in oceanic phosphorous, oceanic circulation, and atmospheric carbon dioxide, *Geochim. Cosmochim. Acta*, 50, 265-276, 1986.
- Brand, L.E., W.G. Sunda, and R.R.L. Guillard, Limitation of marine phytoplankton reproductive rates by zinc, manganese, and iron, *Limnol. Oceanogr.*, 28, 1182-1198, 1983.
- Brassell, S.C., Applications of biomarkers for delineating marine paleoclimatic fluctuations during the Pleistocene, in Organic Geochemistry: Principles and Applications, edited by M.H. Engel and S.A. Macko, pp. 699-753, Plenum, New York, 1993.
- Brassell, S.C., R.G. Brereton, G. Eglinton, J.O. Grimalt, G. Liebezeit, I.T. Marlowe, U. Pflaumann, and M. Sarnthein, Palaeoclimatic signals recognized by chemometric treatment of molecular stratigraphic data, Org. Geochem., 10, 649-660, 1986a.
- Brassell, S.C., G. Eglinton, I.T. Marlowe, U. Pflaumann, and M. Sarnthein, Molecular stratigraphy: A new tool for climatic assessment, *Nature*, 320, 129-133, 1986b.
- Broecker, W.S., Ocean chemistry during the glacial time, *Geochim. Cosmochim. Acta*, 46, 1689-1705, 1982.
- Chavez, F.P., K.A. Buck, and R.T. Barber, Phytoplankton taxa in relation to primary production in the equatorial Pacific, *Deep* Sea Res., Part A, 11, 1733-1752, 1990.
- Claustre, H., The trophic status of various oceanic provinces as revealed by phytoplankton pigment signatures, *Limnol. Oceanogr.*, 39, 1206-1210, 1994.
- Climate: Long-Range Investigation, Mapping, and Prediction (CLIMAP), The last interglacial ocean, Quat. Res., 21, 123-224, 1984.
- Conte, M.H., and G. Eglinton, Alkenone and

alkenoate distributions within the euphotic zone of the eastern North Atlantic: Correlation with production temperature, *Deep Sea Res.*, *Part I*, 40, 1935-1961, 1993.

- Cortijo, E., L. Labeyrie, L. Vidal, M. Vautravers, M. Chapman, J.C. Duplessy, M. Elliot, M. Arnold, J.L. Turon, and G. Auffret, Changes in sea surface hydrology associated with Heinrich event 4 in the North Atlantic Ocean between 40° and 60°N, *Earth Planet. Sci. Lett.*, 146, 29-45, 1997.
- Goldman, J.C., Potential role of large oceanic diatoms in new primary production, *Deep Sea Res.*, *Part I*, 40, 159-168, 1993.
- Gordon, A.L., Interocean exchange of thermocline water, J. Geophys. Res., 91, 5037-5046, 1986.
- Green, J.C., and B.S.C. Leadbeater (Eds.), The Haptophyte Algae, Syst. Assoc. Spec. Vol., vol. 51, Claredon, Oxford, England, U.K., 1994.
- Grimalt, J.O., R. de Wit, P. Teixidor, and J. Albaiges, Lipid biogeochemistry of *Phormidium* and *Microcoleus* mats, Org. Geochem., 26, 509-530, 1992.
- Grousset, F.E., L. Labeyrie, J.A. Sinko, M. Cremer, G. Bond, J. Duprat, E. Cortijo, and S. Huon, Patterns of ice-rafted detritus in the glacial North Atlantic (40°-55°N), *Paleoceanography*, 8, 175-192, 1993.
- Haddad, R.I., C.S. Martens, and J.W. Farrington, Quantifying early diagenesis of fatty acids in a rapidly accumulating coastal marine sediment, Org. Geochem., 19, 205-216, 1992.
- Heinrich, H., Origin and consequences of icerafting in the northeast Atlantic Ocean, during the past 130,000 yrs, *Quat. Res.*, 29, 143-152, 1988.
- Herguera, J.C., and W.H. Berger, Paleoproductivity from benthic foraminifera abundance: Glacial to postglacial change in the westequatorial Pacific, *Geology*, 19, 1173-1176, 1991.
- Imbrie, J., A. McIntyre, and A. Mix, Oceanic response to orbital forcing in the late Qua-

ternary: Observational and experimental strategies, in *Climate and Geosciences, NATO ASI Ser.*, vol. 51, edited by W.H. Berger et al., pp. 121-164, Kluwer Acad., Norwell, Mass., 1989.

- Imbrie, J., et al., On the structure and origin of major glaciation cycles, 1, Linear responses to Milankovitch forcing, *Paleoceanography*, 7, 701-738, 1992.
- Imbrie, J., et al., On the structure and origin of major glaciation cycles, 2, The 100,000-year cycle, *Paleoceanography*, 8, 699-735, 1993.
- Jenkins, G.M., and D.G. Watts, Spectral Analysis and Its Applications, Holden Day, San Francisco, Calif., 1986.
- Keffer, T., D.G. Martinson, and B.H. Corliss, The position of the Gulf Stream during Quaternary glaciations, *Science*, 241, 440-442, 1988.
- Kennedy, J.A., and S.C. Brassell, Molecular stratigraphy of the Santa Barbara Basin: Comparison with historical records of annual climate change, Org. Geochem., 19, 235-244, 1992.
- Legrand, M.R., R.J. Delmas, and R.J. Charlson, Climate forcing implications from Vostok ice-core sulphate data, *Nature*, 334, 418-420, 1988.
- Liss, P.S., G. Malin, and S.M. Turner, Production of DMS by marine phytoplankton, in *Dimethylsulphide: Oceans, Atmosphere and Climate*, edited by G. Restelli and G. Angeletti, pp. 1-14, Kluwer Acad., Norwell, Mass., 1993.
- Liss, P.S., G. Malin, S.M. Turner, and P.M. Holligan, Dimethyl sulphide and *Phaeocys*tis: A review, J. Mar. Syst., 5, 41-53, 1994.
- Manabe, S., and A.J. Broccoli, The influence of continental ice sheets on the climate of an ice age, J. Geophys. Res., 90, 2167-2190, 1985.
- Manighetti, B., and I.N. McCave, Depositional fluxes, palaeoproductivity, and ice rafting in the NE Atlantic over the past 30 ka, *Paleoceanography*, 10, 579-592, 1995.
- Marlowe, I.T., J.C. Green, A.C. Neal, S.C. Brassell, G. Eglinton, and P.A. Course, Long chain (n-C<sub>37</sub>-C<sub>39</sub>) alkenones in the Prymnesiophyceae: Distribution of alkenones and other lipids and their taxonomic significance, *Br. Phycol. Bull.*, 19, 203-216, 1984.
- Marlowe, I.T., S.C. Brassell, G. Eglinton, and J.C. Green, Long-chain alkenones and alkyl alkenoates and fossil coccolith record of marine sediments, *Chem. Geol.*, 88, 349-375, 1990.
- Martinson, D.G., N.G. Pisias, J.D. Hays, J. Imbrie, T.C. Moore, and N.J. Shackleton, Age dating and the orbital theory of ice-ages: Development of high resolution 0 to 300,000year chronostratigraphy, *Quat. Res.*, 27, 1-29, 1987.
- McCaffrey, M.A., J.W. Farrington, and D.J. Repeta, The organic geochemistry of Peru margin surface sediments, I, A comparison of the C<sub>37</sub> alkenone and historical El Niño records, *Geochim. Cosmochim. Acta*, 54, 1671-1682, 1990.
- McIntyre, A., and B. Molfino, Forcing of Atlantic equatorial and subpolar millennial cycles by precession, *Science*, 274, 1867-1870, 1996.

- McIntyre, A., W.F. Ruddiman, K. Karlin, and A.C. Mix, Surface water response of the equatorial Atlantic Ocean to orbital forcing, *Paleoceanography*, 4, 19-55, 1989.
- Meeker, L.D., P.A. Mayewski, M.S. Twickler, S.I. Witlow, and D. Meese, A 110,000-year history of change in continental biogenic emissions and related atmospheric circulation inferred from the Greenland Ice Sheet Project Ice Core, J. Geophys. Res., 102, 26,489-26,504, 1997.
- Mix, A.C., Influence of productivity variations on long-term atmospheric CO<sub>2</sub>, *Nature*, 337, 541-543, 1989.
- Molfino, B., and A. McIntyre, Precessional forcing of nutricline dynamics in the equatorial Atlantic, *Science*, 249, 766-769, 1990.
- Molina-Cruz, A., The relation of the southern trade winds to upwelling processes during the last 75,000 years, *Quat. Res.*, 8, 324-338, 1977.
- Müller, P.J., and E. Suess, Productivity, sedimentation rate, and sedimentary organic matter in the oceans, I, Organic carbon preservation, *Deep Sea Res.*, Part A, 26, 1374-1362, 1979.
- Neftel, A., H. Oeschger, J. Schwander, B. Stauffer, and R. Zumbrunn, Ice core sample measurements give atmospheric CO<sub>2</sub> content during the past 40,000 years, *Nature*, 295, 220-223, 1982.
- Paillard, D., L. Labeyrie, and P. Yiou, Analyseries 1.0: A Macintosh software for the analysis of geographical time series, *Eos Trans. AGU*, 7, 379, 1996.
- Parker, P.L., Fatty acids and alcohols, in Organic Geochemistry, edited by G. Eglinton and M.T. Murphy, pp. 150-200, Springer-Verlag, New York, 1969.
- Pedersen, T.F., Increased productivity in the eastern equatorial Pacific during the last glacial maximum (19,000 to 14,000 yr B.P.), *Geology*, 11, 16-19, 1983.
- Pokras, P., and A.C. Mix, Earth's precession cycle and Quaternary climatic change in tropical Africa, *Nature*, 326, 486-487, 1987.
- Porter, S.C, and A. Zhisheng, Correlation between climate events in the North Atlantic and China during the last glaciation, *Nature*, 375, 305-308, 1995.
- Prahl, F.G., and S.G. Wakeham, Calibration of unsaturation patterns in long-chain ketone compositions for paleotemperature assessment, *Nature*, 330, 367-369, 1987.
- Prahl, F.G., L.A. Muchlhausen, and D.L. Zahnle, Further evaluation of long-chain alkenones as indicators of paleoceanographic conditions, *Geochim. Cosmochim. Acta*, 52, 2303-2310, 1988.
- Prahl, F.G., L.A. Muehlhausen, and M. Lyle, An organic geochemical assessment of oceanographic conditions at MANOP site C over the past 26,000 years, *Paleoceanography*, 4, 495-510, 1989.
- Prahl, F.G., R.B. Collier, J. Dymond, M. Lyle, and M.A. Sparrow, A biomarker perspective on prymnesiophyte productivity in the northeast Pacific Ocean, *Deep Sea Res.*, *Part I*, 40, 2061-2076, 1993.
- Prospero, J.M., D.L. Savoie, E.S. Saltzman, and R. Larsen, Impact of oceanic sources of biogenic sulphur on sulphate aerosol concentra-

tions at Mawson, Antarctica, Nature, 350, 221-223, 1991.

- Rostek, F., G. Ruhland, F.C. Bassinot, L. Beaufort, P.J. Müller, and E. Bard, Fluctuations of the Indian monsoon regime during the last 170,000 years: Evidence from sea surface temperature, salinity and organic carbon records, in *Global Precipitations and Climate Change*, edited by M. Desbois and F. Désalmand, pp. 27-51, Springer-Verlag, New York, 1994.
- Ruddiman, W.F., and G. Glover, Vertical mixing of ice-rafted volcanic ash in North Atlantic sediments, Geol. Soc. Am. Bull., 83, 2817-2836, 1972.
- Sancetta, C., Primary production in the glacial North Atlantic and North Pacific Oceans, *Nature*, 360, 249-251, 1992.
- Sarnthein, M., G. Tetzlaff, K. Koopmann, W. Wolten, and U. Pflaumann, Glacial and interglacial wind regimes over the eastern subtropical Atlantic and northwest Africa, *Nature*, 293, 193-196, 1981.
- Sarnthein, M., K. Winn, and R. Zahn, Paleoproductivity of oceanic upwelling and the effect on atmospheric CO<sub>2</sub> and climatic change during deglaciation times, in *Abrupt Climatic Change*, edited by W.H. Berger and L.D. Labeyrie, pp. 311-337, D. Reidel, Norwell, Mass., 1987.
- Sarnthein, M., U. Pflaumann, R. Ross, R. Tiedemann, and K. Winn, Transfer functions to reconstruct ocean paleoproductivity, in Upwelling Systems: Evolution Since the Early Miocene, edited by C.P. Summerhayes, W.L. Prell, and K.C. Emeis, Geol. Soc. Spec. Publ., 64, 411-427, 1992.
- Savoie, D.L., and J.M. Prospero, Comparison of oceanic and continental sources of non-seasalt sulphate over the Pacific Ocean, *Nature*, 339, 685-687, 1989.
- Shackleton, N.J., M.A. Hall, J. Line, and C. Shuxi, Carbon isotope data in core V19-30 confirm reduced carbon dioxide concentration in the ice age atmosphere, *Nature*, 306, 319-322, 1983.
- Short, D A., and J.G. Mengel, Tropical climate phase lags and Earth's precession cycle, Nature, 323, 48-50, 1986.
- Summerhayes, C.P., D. Kroon, A. Rosell-Melé, R.W. Jordan, H.-J. Schrader, R. Hearn, J. Vıllanueva, J.O. Grimalt, and G. Eglinton, Variability in the Benguela Current upwelling system over the past 70,000 years, *Prog. Oceanogr.*, 35, 207-251, 1995.
- Sun, M.-Y, and S.G. Wakeham, Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea Basin, *Geochim. Cosmochim. Acta*, 58, 3395-3406, 1994.
- Sunda, W.G., and S.A. Huntsman, Feedback interactions between zinc and phytoplankton in seawater, *Limnol. Oceanogr.*, 37, 25-40, 1992.
- Sunda, W.G., and S.A. Huntsman, Cobalt and zinc interreplacement in marine phytoplankton: Biological and geochemical implications, *Limnol. Oceanogr.*, 37, 1404-1417, 1995.
- Thomas, E., L. Booth, M. Maslin, and N.J. Shackleton, Northeastern Atlantic benthic foraminifera during the last 45,000 years:

Changes in productivity seen from the bottom up, *Paleoceanography*, 10, 545-562, 1995.

- Thomsen, H A., K.R. Buck, and F.P. Chavez, Haptophytes as components of marine phytoplankton, in *The Haptophyte Algae*, Syst. Assoc. Spec. Vol., vol. 51, edited by J.C. Green and B.S.C. Leadbeater, pp. 187-208, Claredon Press, Oxford, England, U.K., 1994.
- Turner, S.M., P.D. Nightingale, L.J. Spokes, M.I. Liddicoat, and P.S. Liss, Increased dimethyl sulphide concentrations in sea water from in situ iron enrichment, *Nature*, 383, 513-517, 1996.
- Vautravers, M.M., Sédimentation et dissolution des carbonates biogéniques aux moyennes latitudes Nord et Sud. Approche quantitative et relations avec les paléocirculations océaniques des derniers 150,000 ans, Ph.D. dissertation, 288 p., University of Bordeaux, France, 1996.
- Verardo, D.J., and A. McIntyre, Production and destruction: Control of biogenous sedimentation in the tropical Atlantic 0-300,000 years B.P., *Paleoceanography*, 9, 63-86, 1994.
- Vidal, L., L. Labeyrie, E. Cortijo, M. Arnold, J.C. Duplessy, E. Michel, S. Becqué, and

T.C.E. van Weering, Evidence for changes in the North Atlantic Deep Water linked to meltwater surges during the Heinrich events, *Earth Planet. Sci. Lett.*, 146, 13-27, 1997.

- Villanueva, J., and J.O. Grimalt, Gas chromatographic tuning of the U<sup>3</sup><sub>37</sub> paleothermometer, Anal. Chem., 69, 3329-3332, 1997.
- Villanueva, J., J.O. Grimalt, E. Cortijo, L. Vidal, and L. Labeyrie, A biomarker approach to the organic matter deposited in the North Atlantic during the last climatic cycle, *Geochim. Cosmochim. Acta*, 61, 4633-4646, 1997a.
- Villanueva, J., C. Pelejero, and J.O. Grimalt, Clean-up procedures for the unbiased estimation of C<sub>37</sub> alkenone sea surface temperatures and terrigenous *n*-alkane inputs in paleoceanography, *J. Chromatogr. A757*, 145-151, 1997b.
- Volkman, J.K., G. Eglinton, E.D.S. Corner, and J.R. Sargent, Novel unsaturated straightchain C<sub>37</sub>-C<sub>39</sub> methyl and ethyl ketones in marine sediments and a coccolithophore *Emiliania huxleyi*, in *Advances in Organic Geochemistry 1979*, edited by A.G. Douglas and J.R. Maxwell, pp. 219-227, Pergamon, Tarrytown, N.Y., 1980a.
- Volkman, J.K., R.B. Johns, F.T. Gillan, G.J. Perry, and H.J. Bavor Jr., Microbial lipids of

an intertidal sediment, I, Fatty acids and hydrocarbons, *Geochim. Cosmochim. Acta, 44*, 1133-1143, 1980b.

Volkman, J.K., J.W. Farrington, R.B. Gagosian, and S.G. Wakeham, Lipid composition of coastal marine sediments from the Peru upwelling region, in *Advances in Organic Geochemistry 1981*, edited by M. Bjoroy et al., pp. 228-240, John Wiley, New York, 1983.

E. Cortijo, L. Labeyrie and L. Vidal, Centre des Faibles Radioactivités, Laboratoire Mixte CNRS-CEA, F-91190 Gif-sur-Yvette, France. (e-mail: Elsa.Cortijo@lsce.cnrs-gif.fr; Laurent.Labeyrie@cfr.cnrs-gif.fr)

J.O. Grimalt and J. Villanueva, Department of Environmental Chemistry (CID-CSIC), Jordi Girona, 18, 08034-Barcelona, Catalonia, Spain. (e-mail: jgoqam@cid.csic.es; j.villanueva@ geocean.u-bordeaux.fr)

J.-L. Turon, Laboratoire de Géologie et Océanographie, Université de Bordeaux I, 33405 Talence, France. (e-mail: turon@geocean.u-bordeaux fr)

(Received March 11, 1997; revised July 9, 1998; accepted July 10, 1998.)