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Productivity and sea-surface temperature changes recorded during the late Eocene-early Oligocene at DSDP Site 511 (South Atlantic)

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Abstract

This study investigates paleoenvironmental changes during the Eocene-Oligocene transition (EOT) at Deep Sea Drilling Project (DSDP) Site 511 (South Atlantic), as inferred from lipid biomarker (long-chain diols, alkenones) and calcareous nannofossil accumulation rates, as well as changes in sedimentation regime (i.e. relative contributions of total organic carbon-TOC-, calcium carbonate, and biogenic silica). Sea-surface temperatures (SSTs) reconstructed from the alkenone unsaturation index $U^{K'}_{37}$ indicate a progressive but significant cooling ($\sim 8^\circ\text{C}$) from 34.5 Ma to 33.6 Ma, consistent with estimates derived from other temperature proxies (TEX_{86} ; $\delta^{18}\text{O}$) at the same site and for the same time interval. This cooling is associated with a marked increase in primary productivity, as indicated by high accumulation rates of biogenic silica, TOC, alkenones, long-chain diols, and calcareous nannofossils. Together, these results are consistent with an enhancement of upwelling conditions favorable to the development of siliceous organisms at DSDP Site 511, possibly induced by the Oi-1 glaciation in Antarctica that occurred during this period.

Keywords: Paleotemperatures; SST; productivity; $U^{K'}_{37}$; upwelling conditions; Eocene-Oligocene; DSDP Site 511; calcareous nannofossils; lipid-biomarkers.

1. Introduction

The Eocene-Oligocene transition (EOT; ~ 34 Ma) marks the change from a “greenhouse” to an “icehouse” climate, which saw dramatic cooling and the formation of a large and permanent ice-sheet on East Antarctica (e.g., Zachos et al., 2001; Lear et al., 2008). Some drivers proposed for this abrupt cooling include a substantial decrease in atmospheric CO_2 (DeConto and Pollard, 2003; Pagani et al., 2005, 2011), perhaps coupled with an orbital configuration that reduced polar seasonality (Coxall et al., 2005). Alternatively, the thermal

isolation of Antarctica from mid-latitude warm currents as a consequence of the opening of the circumpolar passages (Tasmanian Gateway and Drake Passage) and the onset of the Antarctic Circumpolar Current (ACC) may instead have been a major protagonist (e.g., Kennett, 1977; Lawver and Gahagan, 2003; Persico and Villa, 2004; Lagabriele et al., 2009).

Associated with the EOT is a biotic turnover, both in the marine realm (e.g., Aubry, 1992; Dunkley Jones et al., 2008; Funakawa and Nishi, 2008; Villa et al., 2008; Wade and Pearson, 2008), and in terrestrial fauna and flora (e.g., Hooker et al., 2004; Jaramillo et al., 2006). The interval is also marked by a perturbation of the carbon cycle (Shackleton and Kennett, 1975; Zachos et al., 2001; Merico et al., 2008), linked to an increase of marine primary production (Diester-Haass and Zahn, 1996; Salamy and Zachos, 1999; Nilsen et al., 2003; Anderson and Delaney, 2005), a deepening of the Carbonate Compensation Depth (CCD) (Coxall et al., 2005; Rea and Lyle, 2005), and a sea-level fall (e.g., Pekar et al., 2002; Miller et al., 2008).

These changes are well documented both in oxygen ($\delta^{18}\text{O}$) and carbon ($\delta^{13}\text{C}$) isotope records from planktonic and benthic foraminifera (e.g. Kennett and Stott, 1990; Diester-Haass and Zahn, 1996; Zachos et al., 1996, 2001), and by shifts in foraminifera, radiolarian and calcareous nannofossil assemblages (e.g. Boersma and Premoli Silva, 1991; Aubry, 1992; Keller et al., 1992; Lazarus and Caulet, 1993; Villa et al., 2008). Alkenone-based proxies such as $\epsilon_{\text{p}37:2}$, the $\delta^{13}\text{C}$ fractionation occurring during algal photosynthesis, and U^{K}_{37} , the alkenone unsaturation index, have been used to reconstruct variations in partial pressure of CO_2 ($p\text{CO}_2$) and sea surface temperatures (SSTs) respectively during the late Eocene-early Oligocene (Pagani et al., 2005, 2011; Liu et al., 2009). While such paleoenvironmental changes during this time interval have been noted at a number of sites in the Southern Ocean, only a few studies have investigated signals from high-latitude sites in the Atlantic Ocean (e.g., Nilsen et al., 2003; Pagani et al., 2005, 2011; Liu et al., 2009). The study of these high-latitude sites is, however, important in better constraining oceanographic changes taking place over the EOT,

since subpolar waters also played a major role in global climate regulation at that time (e.g., Diester-Haass and Zahn, 1996; Lagabriele et al., 2009). In addition, such studies may help to better constrain the timing of the onset of Antarctic Circumpolar Current (ACC), a matter which is still subject to some debate (e.g., Barker and Thomas, 2004).

In this study, we used a multi-proxy approach, comparing accumulation rates in calcareous nannofossils, total organic matter, calcium carbonate/biogenic silica and lipid biomarkers (both alkenones and long-chain diols) with reconstructions of sea-surface temperature (SST) from the alkenone unsaturation index (U_{37}^K) at Deep Sea Drilling Project (DSDP) Site 511 (South Atlantic) during the Eocene-Oligocene (37.5-31.4 Ma). Through such approaches, we aimed to provide a comprehensive picture of the changes in temperature and trophic conditions occurring at DSDP Site 511, and to infer from these the oceanographic changes associated with to the onset of the ACC during the Eocene-Oligocene transition.

2. Oceanographic setting

DSDP Site 511 (51°00.28'S, 46°58.30'W), drilled during DSDP Leg 71 at 2589 m water depth, is on the back slope of a cuesta-type ridge in the basin province of the Falkland Plateau (southwest Atlantic Ocean) about 10 km south of Maurice Ewing Bank (Ludwig et al., 1983; Figure 1).

The Falkland Plateau extends eastwards off southernmost South America, and is bounded by the Falkland Escarpment to the north and by the Falkland Trough and North Scotia Ridge to the south (Figure 1). Today, DSDP Site 511 is situated north from the Polar Front and other frontal zones presented in Figure 1. The Sub-Antarctic Front (SAF), after crossing the North Scotia Ridge, hugs the continental shelf before merging with the boundary current of the Argentine Basin (Arhan et al., 2002; Allen et al., 2005). The Polar Front (PF) bifurcates into

two branches (one over the sill of the Falkland Plateau and one along the axis of the Falkland Trough) north of Shag Rocks Passage. The relative strengths of these branches may vary through time, and may result in extensions of the PF crossing the Maurice Ewing Bank (Arhan et al., 2002). In addition, the Falkland Plateau is influenced by the deep water components of the ACC, that flow northward through Shag Rocks Passage into the Falkland Trough and eastward toward the Georgia Basin (Arhan et al., 2002; Allen et al., 2005).

During the Paleogene, DSDP Site 511 was located at approximately 55°S, 42°W (Ludwig et al., 1983; Basov and Krasheninnikov, 1983; Syke et al., 1998). A total of 183 m of upper Eocene and lower Oligocene diatom ooze and nannofossil-diatomaceous oozes were deposited at a water depth of about 2500 m, containing well-preserved calcareous nannofossils and diatoms (Ludwig et al., 1983). It should be noted that DSDP Site 511 is characterized at 5 meters below the sea floor (mbsf) by a large unconformity between lower Oligocene and Pliocene sediments. This unconformity marks a major widespread erosional hiatus on the Falkland Plateau, interpreted as the result of an intensification of the ACC in response to cooler climatic conditions (Ciesielski and Weaver, 1983).

3. Material and methods

3.1. Sampling and age model

A total of 40 sediment samples were selected from Cores 2 to 20, between 10 and 180 meters below the sea floor (mbsf). The studied interval covers the Nannofossil Zones NP19-NP22 of Martini (1971) and spans the latest Eocene-early Oligocene (Ludwig et al., 1983; Wise, 1983).

The age model used in this study is based on the foraminiferal oxygen isotope data ($\delta^{18}\text{O}$) from Muza et al. (1983) and on calcareous nannofossil bioevents (first or last occurrences) determined by Liu et al. (2009), Schumacher and Lazarus (2004), and Wise (1983). Age control points are presented in Table 1 and have been recalibrated in the present study according to the latest geological timescale (Gradstein et al., 2012).

3.2. Sediment composition analyses

3.2.1. Total Organic Carbon

Sub-samples (ca. 100 mg of ground samples) were acidified with 2N HCl in pre-cleaned (combustion at 450°C) silver capsules until effervescence ceased, dried in an oven (50°C) and wrapped in tin foil before analyses. Duplicate Total Organic Carbon (TOC) analyses were performed with a Thermo FlashEA 1112 elemental analyser, using aspartic acid (36.09% of carbon) and nicotinamid (59.01% of carbon) as calibration standards. Repeat measurement of an in-house reference material (fine ground low carbon sediment) was made to ascertain accuracy. Reproducibility achieved for duplicate analyses was better than 10% (coefficient of variation).

3.2.2. Calcium carbonate (CaCO_3) and insoluble components

For each sample, approximately 300 mg of powdered bulk sediment was dissolved in 1N HCl and the amount of CO_2 released from the sample, which is proportional to the calcium carbonate (CaCO_3) content, was measured using a Dietrich-Frühling™ calcimeter.

The insoluble component of the sediment (i.e. matter not dissolved using HCl) was quantified by subtracting the TOC and the CaCO_3 contents from the bulk rock. Scanning Electron Microscope (SEM) observations (Plate 1) show that this is essentially composed of

biogenic silica and, to a minor extent, coccoliths and clays. Diatoms and, to a lesser extent, radiolarians are indeed dominant in all the studied samples (Ludwig et al., 1983; Gombos and Ciesielski, 1983).

3.3. Lipid biomarkers

Roughly 15 g of sample was ground, after which lipids were extracted by way of sonication in Dichloromethane (DCM; 5 x 50 mL). Following evaporation of the solvents, the total lipid extract was separated into four lipid fractions of increasing polarity by chromatography over a solid phase extraction (SPE) silica-NH₂ cartridge (0.5 g packing), with hexane (Hex), Hex/DCM (3:1 v/v), DCM/acetone (9:1 v/v) and Methanol (MeOH) as eluents, respectively. Alkenones, eluting in the second fraction, were identified and quantified by gas chromatography/mass spectrometry (GC/MS) and gas chromatography/flame ionization detector (GC/FID), respectively. Alkenone abundances were determined using hexatriacontane (*n*-C₃₆ alkane) as internal standard. Long-chain diols, eluting in the third fraction of the SPE chromatography, were silylated [pyridine/N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), 2:1 v/v] before GC/FID and GC/MS analyses. Diol abundances were determined by GC/MS from total ion current (TIC) chromatograms using 1,2-dipalmitoyl glycerol as an external standard.

GC/MS analyses were performed on a MD800 Voyager spectrometer interfaced to an HP6890 gas chromatograph, equipped with an on-column injector and a DB-5MS column (30 m x 0.25 mm x 0.25 µm). The oven temperature was programmed from 60°C (1 min) to 130°C at 20°C min⁻¹, and then to 310°C (20 min) at 4°C min⁻¹. Helium was used as the carrier gas at constant flow. GC/FID analyses were performed on an HP-6890 Series gas chromatograph configured with an on-column injector and an HP5 (30 m x 0.32 mm x 0.25

µm) capillary column. Helium was used as the carrier gas at constant flow and the oven temperature program was the same as for GC/MS analyses. The reproducibility achieved for duplicate analyses of all samples was better than 5% (coefficient of variation).

3.4. Calcareous nannofossil counts/analyses

Slides for quantitative counts of calcareous nannofossil were prepared following the Random Settling method of Beaufort (1991), as modified by Geisen et al. (1999). A small amount of dried sediment powder (5 mg) was mixed with water (with basic pH, over-saturated with respect to calcium carbonate) and the homogenised suspension was allowed to settle for 24 hours onto a cover slide. The slide was dried and mounted on a microscope slide with Rhodopass. Four hundred calcareous nannofossils (coccoliths and nannoliths) were counted in a variable number (between 15 and 30) of field of views using a polarizing optical ZEISS microscope (magnification 1000x). In order to test the reproducibility of our counts, each slide was counted twice and the repeatability achieved was better than 10 % (coefficient of variation).

Absolute abundance of nannofossils per gram of sediment was calculated using the formula:

$$X = (N \cdot V) / (M \cdot A \cdot H) \quad (1)$$

where X is the number of calcareous nannofossils per gram of sediment; N the number of nannofossils counted in each slide; V the volume of water used for the dilution in the settling device (cm³); M the weight of powder used for the suspension (g); A the surface considered for nannofossil counting (cm²); H the height of the water over the cover slide in the settling device (2.1 cm). Species-specific relative abundances (percentages) were also calculated from the total nannofossil content.

Taxonomic concepts adopted here followed the species classification suggested by Young and Bown (1997), Bown (1998) and Young et al. (2003) (see also Taxonomic remarks in Appendix). The preservation of calcareous nannofossils (degree of etching and overgrowth) was estimated by optical and scanning electron microscopy observations, using the recommendations of Roth (1984).

3.5. Mass accumulation rates

The calculation of accumulation rates permits to overcome the effects of a variable sedimentary dilution on sediment components and to effectively compare data from different intervals in a time-series. The formula introduced by Davies et al. (1995) was first used to calculate the mass accumulation rates (MAR):

$$\text{MAR} = T \cdot [\text{BD} - (\text{P} \cdot \text{W})] \quad (2)$$

where MAR is the mass accumulation rate ($\text{g}/\text{m}^2/\text{yr}$), T the sedimentation rate (m/Ma), BD the wet bulk density (g/cm^3), P the porosity (weight percent) (Ludwig et al., 1983) and W the seawater density ($1.025 \text{ g}/\text{cm}^3$).

Accumulation rates of CaCO_3 ($\text{g}/\text{m}^2/\text{yr}$), biomarkers ($\mu\text{g}/\text{m}^2/\text{yr}$) and coccoliths ($\text{specimens}/\text{m}^2/\text{yr}$) were then obtained by multiplying the MAR with CaCO_3 content (g/g sediment), biomarker concentrations ($\mu\text{g}/\text{g}$ sediment) and coccolith abundances ($\text{specimens}/\text{g}$ sediment).

3.6. Paleoenviromental proxies

Variations in sediment components (CaCO_3 , TOC), lipid-biomarkers (alkenones, long-chain diols), calcareous nannofossil accumulation rates and sea-surface temperatures (SSTs)

were used to characterize environmental changes occurring at DSDP Site 511 during the EOT.

Calcium carbonate and silica accumulation rates are currently used as proxies of calcareous (nannofossils, foraminifera) and siliceous (diatoms, radiolarian) production, respectively (e.g., Faul et al., 2003; Nilsen et al., 2003). The sedimentary abundance of alkenones has been widely used as an indicator of calcareous nannofossil primary productivity (e.g., Brassell, 1993; Villanueva et al., 1997; Grimalt et al., 2000; Ternois et al., 2001). The total long-chain diol abundances can also be considered as a proxy of phytoplanktonic productivity, with eustigmatophytes and diatoms both having been identified as potential producers of these biolipids (e.g., Versteegh et al., 1997; Sinninghe Damsté et al., 2003; Rampen et al., 2007).

Sea-surface temperatures (SSTs) were converted from the U_{37}^K index, which is the ratio between diunsaturated ($C_{37:2}$) and triunsaturated ($C_{37:3}$) alkenones ($U_{37}^K = [C_{37:2}] / [C_{37:2} + C_{37:3}]$; Prahl and Wakeham, 1987), using the global calibration of Conte et al. (2006). The error range for SST estimates is $\pm 1.5^\circ\text{C}$ (analytical error: 0.3°C ; calibration error: 1.2°C).

Simple linear regression analyses were used to highlight the relationships between variations in nannofossil, silica, calcium carbonate contents and in sea surface temperatures (SSTs). The normality of the data and residual distributions was checked using Shapiro-Wilk tests. All statistical analyses were performed using JMP version 8.0.1 (SAS institute) software and significance was accepted for $\alpha = 0.05$.

4. Results

4.1. Age model

According to our new age model, the Eocene-Oligocene transition (EOT) is located between 99.7 and 129.1 mbsf, as evidenced by a shift in $\delta^{18}\text{O}$ values (Muza et al., 1983). The accumulation rates calculated were not constant: 10.3 m/Ma between 148-178 mbsf, 65.3 m/Ma between 99-148 mbsf, and 38.8 m/Ma between 8-99 mbsf. The time interval studied (10-180 mbsf) is thus calculated as being between ~31.4 and ~37.5 Ma. This age-depth model slightly differs from that of Schumacher and Lazarus (2004), who did not integrate the available isotopic data, but it is very similar to the one presented by Liu et al. (2009).

4.2. Sea-surface temperatures

Alkenone unsaturation ratio could be determined in all the samples except one at 10 mbsf (31.4 Ma), due to very low alkenone concentrations. Calculated SSTs averaged 12°C during the time interval studied, showing a steady decrease from ca. 18°C between 37.5-34.5 Ma (late Eocene) to ca. 10°C between 34.5-33.6 Ma (around the Eocene-Oligocene transition). SST estimates remain relatively constant during the early Oligocene (Figure 2). SST values calculated from $\delta^{18}\text{O}$ planktonic foraminifera (Muza et al., 1983), U_{37}^K and tetraether index (TEX₈₆) measurements (Liu et al., 2009; Pagani et al., 2011) show very similar trends to that observed in the present study (Figure 2). Nevertheless, our dataset provides a more continuous paleotemperature record with respect to these previous studies at DSDP Site 511. While some discrepancies in absolute values are visible, they can easily be explained by (1) analytical and calibration errors of each proxy, (2) differences in habitat depth in the water column between foraminifera, coccolithophores and archaea, or (3) differences in core depths of the studied samples.

4.3. Sediment composition

272

273 The studied samples are characterized by relatively high total organic carbon (TOC)
274 contents for a deep-sea site (0.60 wt%; 0.15 g/m²/yr in average), and a low calcium carbonate
275 (CaCO₃) content (9 wt%; 1.9 g/m²/yr in average) (Figure 3).

276 Accumulation rates of CaCO₃, TOC and insoluble components (biogenic silica and clays)
277 show a similar overall trend throughout the time interval studied (Figure 3): accumulation
278 rates were low between 37.5 and 35 Ma (late Eocene), progressively increased around the
279 Eocene-Oligocene transition (35-33.6 Ma), and were steadily high during the early Oligocene
280 (33.6-31.5 Ma). The increases in accumulation rates of TOC (from 0.02 to 0.20 g/m²/yr) and
281 of insoluble components (from 3.8 to 26.5 g/m²/yr) are more pronounced than that of CaCO₃
282 (from 0.6 to 2.3 g/m²/yr). One single sample at 138.6 mbsf (34.21 Ma) has a very low CaCO₃
283 content (0.8 wt%; 0.2 g/m²/yr).

284

285 ***4.4. Phytoplanktonic lipids***

286

287 All studied samples show the presence of two C₃₇ and two C₃₈ alkenones identified
288 respectively as: heptatriacontatrien-2-one (MeC_{37:3}), heptatriacontadien-2-one (MeC_{37:2}),
289 octatriacontatrien-3-one (EtC_{38:3}) and octatriacontadien-3-one (EtC_{38:2}). A general decreasing
290 trend in alkenone content is observed during the late Eocene-early Oligocene, but three
291 periods of increased alkenone accumulation rates are observed at about 34.5-33.6 (up to 18.2
292 µg/m²/yr), 33-32.5 (up to 7.6 µg/m²/yr) and 31.8 Ma (up to 13.1 µg/m²/yr) (Figure 3).

293 Eight long-chain diols, presumably produced by diatoms (Rampen et al., 2007) and/or
294 from Eustigmatophyte microalgae (Volkman et al., 1999), are present in the studied samples.
295 These compounds were identified as: hexacosane-1,12-diol (1,12 C₂₆), hexacosane-1,13-diol
296 (1,13 C₂₆), hexacosane-1,14-diol (1,14 C₂₆), octacosane-1,12-diol (1,12 C₂₈), octacosane-1,13-

diol (1,13 C₂₈), octacosane-1,14-diol (1,14 C₂₈), triacontane-1,13-diol (1,13 C₃₀), triacontane-1,14-diol (1,14 C₃₀). Diols show much lower accumulation rates (mean 0.5 µg/m²/yr) than alkenones, with values close to the detection limit between 37.5 and 34.2 Ma, but their production progressively increased across the EOT (34.2-33.6 Ma; Figure 3). Peaks of maximum diol accumulation rates are observed during the early Oligocene at 32.9 Ma (1.4 µg/m²/yr) and at 31.8 Ma (5.4 µg/m²/yr). This overall distribution matches with that of TOC, although higher variations in diol accumulation rates are observed (Figure 3).

4.5. Calcareous nannofossil assemblages

Optical and scanning electron microscopy observations show that calcareous nannofossils are generally well preserved in all investigated samples, with very limited etching and overgrowth (Plate 1). Delicate coccoliths that are prone to dissolution, such as *Zygrhablithus* and *Pontosphaera*, are commonly observed with pristine structures. This indicates that coccolith assemblages are not strongly biased by selective dissolution in the water column or diagenetic effects, and is in accordance with previous studies that attested good preservation of calcareous nannofossils at DSDP Site 511 (Ludwig et al., 1983; Wise, 1983).

Nannofossil assemblages are dominated by the genus *Reticulofenestra*, which accounts for on average 75% of the total nannofossils. This genus is mainly represented by the species *R. dictyoda*, *R. minuta*, *R. clatrata* and *R. bisecta*. Other species belonging to this genus (*R. hillae*, *R. umbilica*, *R. daviesii*, *R. reticulata* and *R. stavensis*) are present in lower abundances. The remaining nannofossil taxa (*Blackites* spp., *Chiasmolithus* spp., *Clausicoccus* spp., *Coccolithus* spp., *Ericsonia* spp., *Helicosphaera* spp., *Isthmolithus recurvus*, *Pontosphaera* spp., *Umbilicosphaera* spp., *Zygrhablithus* spp.) account for 16% of the total nannofossil assemblage on average.

As the species-specific abundance trends match with total abundance, here only total abundance data converted into accumulation rates are discussed. Accumulation rates of total calcareous nannofossils and of the dominant genus *Reticulofenestra* show quite similar temporal variations (Figure 3). Nannofossil accumulation rates are relatively low ($4.4 \cdot 10^9$ nannofossils/m²/yr) during the late Eocene (37.5-34.2 Ma), but they progressively increase during the EOT (34.2-33.6 Ma) and stabilize at about $15.8 \cdot 10^9$ nannofossils/m²/yr during the early Oligocene (Figure 3). A significant and positive linear correlation ($R^2=0.62$; $p<0.0001$) is observed between the CaCO₃ measurements (g/m²/yr) and nannofossil accumulation rate estimates (specimens/m²/yr) (Figure 4), suggesting that calcareous nannofossils are the major carbonate producers at DSDP Site 511.

5. Discussion

5.1. Preservation of biogenic sedimentary components

Although the majority of organic matter produced in the surface oceans is remineralized before reaching the seafloor, the high sedimentation rate at DSDP Site 511 (38.8-65.3 m/Ma) likely induced a relatively rapid burial of organic matter, thus limiting its oxidation at the water/sediment interface. Since concentrations were converted into accumulation rates, also, potential effects of a variable dilution of organic matter over time can be excluded, and so changes in TOC concentrations likely reflect variations in primary productivity rather than changes in dilution by sedimentary input or in organic matter degradation. Despite the fact that alkenones and diols only represent a small fraction of TOC, the overall similar variations observed between TOC and lipid contents (Figure 3) suggest that changes in their

accumulation rates through time do not reflect an erratic degradation of these lipids relative to TOC.

As for organic matter, calcareous nannofossil abundances are also expressed in accumulation rates, avoiding a possible dilution effect on nannofossil abundance by a variable accumulation rate of siliceous organisms preserved in the same sediment. In addition, optical and scanning electron microscopy observations show that calcareous nannofossils are generally well preserved in all investigated samples (Plate 1). Sediments from DSDP Site 511 were deposited above the Carbonate Compensation Depth (CCD), which was at ~3500 m depth during the studied period (Basov and Krasheninnikov, 1983; Pälike et al., 2012). These observations suggest that the low nannofossil and CaCO_3 accumulation rates around the Eocene-Oligocene transition are not the result of enhanced dissolution during this period, but rather changes in production.

Notably, one sample (138.6 mbsf; 34.21 Ma) with very low CaCO_3 content (0.8 wt%) is devoid of calcareous nannofossils. This sample might correspond to the worldwide dissolution event recorded in different latitudes at ~34 Ma (Diester-Haass and Zachos, 2003; Coxall et al., 2005; Lear et al., 2008). This event, lasting 40-60 kyr, is thought to be linked to the climatic change occurring during the late Eocene-early Oligocene and has been interpreted as a temporary shoaling of the CCD (e.g., Coxall and Pearson, 2007). It cannot, however, be responsible for the low calcareous nannofossil content in other samples.

5.2. Sea-surface temperature changes

Based on continuous sampling spanning the late Eocene-early Oligocene, our data describe a regular decrease in SSTs from 18°C in the late Eocene to 10°C in the early Oligocene (Figure 2). This trend is in good agreement with previous studies that reported a cooling at

DSDP Site 511 for this time interval $\delta^{18}\text{O}$ in planktonic foraminifera indicates a cooling of ca. 10°C (Muza et al., 1983), associated with changes in foraminiferan or radiolarian assemblages: notably the disappearance of warm-water genera and an increase in the proportion of cool-water genera (Krasheninnikov and Basov, 1983; Weaver, 1983). A ~8°C cooling has also been previously reported by $U^{K'}_{37}$ and tetraether index (TEX_{86}) measurements in a more limited sample set than the one presently investigated (Liu et al., 2009) (Figure 2). Moreover, this significant cooling event has been seen in marine $\delta^{18}\text{O}$ records in several other oceanic sites, further supporting a global cooling event during the EOT (e.g., Zachos et al., 2001; Coxall et al., 2005; Liu et al., 2009).

The alkenone-based proxy $U^{K'}_{37}$ has been calibrated in extant coccolithophore cultures (*Emiliana huxleyi* and *Gephyrocapsa oceanica*) or contemporary core top sediments (e.g., Prahl et al., 1988; Conte et al., 1995; Müller et al., 1998; Riebesell et al., 2000), and appears to be species-dependent (e.g., Volkman et al., 1995; Conte et al., 1998). It may thus be necessary to identify ancient alkenone producers to ensure the applicability of this proxy in sediments predating the first occurrence of the contemporaneous alkenone producers (> 1.85 Ma). To identify ancient alkenone producers, it can be assumed that, under good conditions of preservation, the alkenone concentration is related to the number of coccoliths from alkenone-producing coccolithophore species in the same sediment. This approach has already been used to identify alkenone producers in sediments of late Quaternary (e.g. Müller et al., 1997; Weaver et al., 1999), Pliocene (e.g. Bolton et al., 2010; Beltran et al., 2011) and Oligocene-Miocene age (Plancq et al., 2012). Based on its continuous co-occurrence with these lipid biomarkers throughout the Cenozoic sediment record, the *Reticulofenestra* genus has been suggested as the most probable ancient producer of alkenones in pre-Quaternary sediments (e.g., Marlowe et al., 1990). At DSDP Site 511, the total alkenone content is neither correlated

with the abundances of *Reticulofenestra* genus ($R^2=0.0005$; $p>0.05$; Figure 4), nor with any individual *Reticulofenestra* species (see Table S1 in Supplementary data). Thus these data do not support *Reticulofenestra* as an important alkenone producer at DSDP Site 511 during the EOT.

Nonetheless, temperatures derived from the alkenone paleothermometer are consistent with those derived from other temperature proxies (TEX_{86} ; $\delta^{18}\text{O}$) all along the sediment section (Figure 2), suggesting that either the $\text{U}^{\text{K}'}_{37}$ index is less species-dependent than previously inferred, or that the ancient alkenone producers at DSDP Site 511 were phylogenetically closely related to modern producers. Some studies have already shown that changes in alkenone-producing species makeup did not involve significant changes in the $\text{U}^{\text{K}'}_{37}$ -temperature relationship (Müller et al., 1997, 1998; Villanueva et al., 2002). On the other hand, molecular (Fujiwara et al., 2001; Sáez et al., 2004) and micropaleontological data (Marlowe et al., 1990; Young, 1990, 1998; Young and Bown, 1997) revealed very close evolutionary relationships between *E. huxleyi* and *G. oceanica* and their Cenozoic ancestors, such as *Reticulofenestra* spp. Thus, although a few studies showed that the calibration of the $\text{U}^{\text{K}'}_{37}$ ratio is species-dependent (e.g., Conte et al., 1995, 1998), genetically-related factors are believed to have a small impact on the alkenone unsaturation of open-ocean producers. All these observations allow for confident application of the $\text{U}^{\text{K}'}_{37}$ in the Eocene-Oligocene sediments of DSDP Site 511, even if their producers are yet to be clearly identified.

5.3. Changes in primary productivity

Based on variations in sediment components (CaCO_3 , TOC), lipid-biomarkers (alkenones, long-chain diols) and nannofossil accumulation rates, three intervals of varying productivity can be distinguished (Figure 3):

(1) During the late Eocene (37.5-34.5 Ma), high SSTs are coupled with low biomarker and calcareous nannofossil accumulation rates, along with low TOC, CaCO₃ and biogenic silica contents (Figure 3). These observations attest for temperate sea-surface waters and overall oligotrophic conditions during this interval.

(2) Across the EOT (34.5-33.6 Ma), TOC, lipid-biomarker, biogenic silica and calcareous nannofossil accumulation rates indicate a gradual increase in phytoplanktonic productivity, which mirrors the progressive cooling through the EOT (Figure 3).

The highest alkenone accumulation rates are recorded during this period, but this strong alkenone production, intriguingly, does not correspond to the highest nannofossil accumulation rates (Figure 3). As aforementioned, this discrepancy is unlikely to be the result of an enhanced dissolution of calcareous nannofossils (see section 4.1). It may instead be explained by an increased production of alkenones per cell in response to decreasing temperature. Using pure cultures of *Emiliania huxleyi*, Sorrosa (2012) showed that a decrease in growth temperature from 20°C to 10°C induced an enhanced production of alkenone by a lower number of coccolithophorid cells. An alternative possibility is that non-calcifying haptophytes contributed to alkenone production at DSDP Site 511 during the EOT. Such producers are generally not considered as an important source of alkenone in the open ocean since they are believed to be restricted to coastal areas (Marlowe et al., 1990). Yet, some non-calcifying haptophytes are also known from oceanic waters, and their distribution and abundances in marine waters are virtually unknown and probably underestimated (Versteegh et al., 2001). Thus, the contribution of non-calcifying haptophytes to alkenone production at DSDP Site 511 cannot be excluded.

(3) During the early Oligocene (33.6-31.5 Ma), low SSTs, elevated TOC and biogenic silica content, and higher diol and nannofossil accumulation rates suggest cool sea-surface waters and steadily high trophic (eutrophic) conditions (Figure 3). During this interval, the

production of calcareous organisms (mainly nannofossils; Figure 4) seems to have been limited, as indicated by a restricted increase in CaCO₃ content and reduced alkenone accumulation rates (Figure 3). These observations suggest that siliceous organisms (such as diatoms) were the dominant producers at DSDP Site 511 during the early Oligocene.

5.4. Paleoceanographic changes at DSDP Site 511 during the EOT

This dataset shows a change in trophic conditions at DSDP Site 511 across the Eocene-Oligocene transition (34.5-33.6 Ma) that might have been more favorable to the development of diatoms. The significant and positive linear correlation between the TOC content and insoluble components (Figure 4), mainly composed of biogenic silica, further suggests that siliceous organisms (such as diatoms) mostly contributed to primary productivity. This change in trophic conditions is probably linked to the onset of an upwelling front, since diatoms represent a major constituent of phytoplanktonic assemblages in upwelling areas (e.g., Ziveri et al., 1995; Marañón et al., 1996; Schiebel et al., 2004). Gombos and Ciesielski (1983), using counting data, reported at DSDP Site 511 a decrease in abundance of diatom species such as *Pyxilla prolongata* and *Asterolampara vulgaris*, coupled with an increase in abundance of the diatom species *Melosira architecturalis*. Further study, however, would be needed to determine if these changes in diatom assemblages reflect the ecological changes evidenced in the present work during the EOT.

Upwelling conditions, resulting from increased cold water production and more vigorous oceanic circulation, have already been suggested at DSDP Site 511 during this time interval, based on carbon isotopic composition ($\delta^{13}\text{C}$) of benthic and planktonic foraminifera and changes in diatom assemblages (Muza et al., 1983; Weaver, 1983; Schumacher and Lazarus, 2004). In the present study, the significant linear correlation between alkenone-based sea-

471 surface temperatures and TOC content ($R^2=0.71$; $p<0.0001$; Figure 4) demonstrates that the
472 increase in primary productivity is coupled with a decrease in SSTs, which supports
473 upwelling conditions at DSDP Site 511. The Oi-1 glaciation in Antarctica occurring at ~ 34
474 Ma likely played a role in the expansion of subantarctic waters and of an upwelling front
475 towards DSDP Site 511 (Muza et al., 1983; Salamy and Zachos, 1999; Barker and Thomas,
476 2004). This glaciation is interpreted as resulting from the thermal isolation of the Antarctic
477 continent from mid-latitude warm currents, subsequent to the opening of the Drake Passage
478 and the establishment of the Antarctic Circumpolar Current (ACC) (Exon et al., 2001; Lawver
479 and Gahagan, 2003). This changed the ocean circulation, with the onset of deep-water
480 circulation from around the Antarctic continent (Shackleton and Kennett, 1975; Kennett and
481 Stott, 1990). Moreover, Salamy and Zachos (1999) hypothesized that high-latitude cooling
482 might have increased the intensity of atmospheric circulation, leading to surface divergence
483 and upwelling, and a migration of Antarctic water masses towards the equator. Previous
484 studies also inferred an enhancement of primary productivity during the Eocene-Oligocene in
485 South Atlantic, South Pacific and Southern Ocean, suggesting that this change in trophic
486 conditions, due to the strengthening of frontal system with upwelling, occurred at a more
487 global scale during this period (e.g., Nilsen et al., 2003; Persico and Villa, 2004; Schumacher
488 and Lazarus, 2004; Anderson and Delaney, 2005). Though the timing of the opening of the
489 Drake Passage is still debated, with estimates ranging from the Late Eocene to the Early
490 Miocene (e.g., Barker and Thomas, 2004; Lagabriele et al., 2009), changes in sea-surface
491 temperatures and in trophic conditions at DSDP Site 511 are evidence of the influence of
492 ACC since the Eocene-Oligocene transition. Besides, Lawver and Gahagan (2003) suggested
493 that the opening of Powell Basin between 34 and 30 Ma could have provided a pathway for
494 the ACC. Later during the Oligocene, the full opening of the Drake Passage may have
495 intensified the activity of ACC and deep-water circulation, as evidenced by the widespread

erosion of Oligocene-Miocene sediments in the Falkland Plateau (Ciesielski and Weaver, 1983).

6. Conclusion

The Oi-1 glaciation likely influenced distribution of Atlantic water masses, with the strengthening of frontal system with upwelling that migrated towards the equator, and can thus explain the increase in primary productivity and the steady and significant ($\sim 8^{\circ}\text{C}$) cooling recorded at DSDP Site 511 during the Eocene-Oligocene transition (EOT). This multi-proxy approach at a high-latitude site then helps to better constrain the timing of the onset of Antarctic Circumpolar Current (ACC), which was effective since the EOT.

Besides that, the comparison between calcareous nannofossil and alkenone contents in sediment samples from DSDP Site 511 does not allow an unequivocal identification of alkenone producers during the late Eocene-early Oligocene transition (EOT). However, sea-surface temperatures (SSTs) derived from the $U^{K'}_{37}$ ratio are consistent with temperatures derived from other proxies (TEX_{86} ; $\delta^{18}\text{O}$), suggesting that the calibration of the alkenone-based paleothermometer is either less species-dependent than previously supported or that ancient alkenone producers were phylogenetically closely related to modern producers. In specific cases, such as the present one, the identification of alkenone producers is thus not crucial to better constrain the reconstructions of paleo-SSTs based on alkenones.

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Appendix A: Taxonomic remarks

A1.Family Noelaerhabdaceae (Jerkovic, 1970 emend. Young and Bown, 1997)

This is the dominant family in the studied samples and includes the extant genera *Emiliana* and *Gephyrocapsa*. In the studied samples Noelaerhabdaceae are only represented by the genus *Reticulofenestra* (Hay, Mohler and Wade, 1966). They are elliptical to subcircular reticulofenestrids with an open central area and with no slits in the distal shield. The following species were observed in this study:

R. bisecta (Hay, Mohler and Wade, 1966; Roth, 1970): highly birefringent elliptical coccoliths (< 10 µm) with a closed central area in the distal shield.

R. clatrata (Muller, 1970): medium-sized coccolith with large margins and large central area filled by a sieve plate divided by a median suture.

R. daviesii (Haq, 1968; Haq, 1971): medium-sized coccoliths (5-8 µm) with plugs in central area.

R. dictyoda (Stradner in Stradner and Edwards, 1968): small to large (3-14 µm) elliptical coccoliths with a wide central area.

R. hillae (Bukry and Percival, 1971): large (> 12 µm) elliptical coccolith with a thick-wide collar around a small central opening which scales measuring less than one third of placolith length.

R. minuta (Roth, 1970): small elliptical coccoliths (< 3 µm) with a wide central area.

R. stavensis (Levin and Joerger, 1967; Varol, 1989): highly birefringent elliptical coccoliths (> 10 µm) with a closed central area in the distal shield.

R. umbilicus (Levin, 1965; Martini and Ritzkowski, 1968): very large (> 14 µm, as defined by Backman and Hermelin, 1986) elliptical coccoliths with a wide central area.

A2. Other coccoliths

Other coccoliths that do not belong to the Noelaerhabdaceae family are found in the studied samples. These are: *Blackites* spp. (Hay and Towe, 1962), *Chiasmolithus* spp. (Hay et al., 1966), *Clausicoccus* spp. (Prins, 1979), *Coccolithus formosus* (Kamptner, 1963; Wise, 1973), *Coccolithus pelagicus* (Wallich, 1877; Schiller, 1930), *Ericsonia* spp. (Black, 1964), *Heliscophaera* spp. (Kamptner, 1954), *Ismolithus recurvus* (Deflandre, 1954), *Pontosphaera* spp. (Lohmann, 1902), *Umbilicosphaera* spp. (Lohmann, 1902), *Zygrhablithus* spp. (Deflandre, 1959).

A3. Nannoliths

Nannoliths include forms without a distinct rim and for which the peculiar structure cannot be directly related to coccoliths. They are thus considered as *incertae sedis*. Nannoliths found in this study are *Discoaster* spp. (Tan, 1927) and *Sphenolithus* spp. (Grassé, 1952).

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Figure captions

Figure 1. Location of DSDP Site 511 in the South Atlantic Ocean. Bathymetric configuration (isobaths 1500 and 3000 m) and positions of the main oceanic fronts are shown. Abbreviations are: SAF = Subantarctic Front; PF = Polar Front; SACCF = Southern Antarctic Circumpolar Front; SB = Southern Boundary of the Antarctic Circumpolar Front; SRP = Shag Rocks Passage; MEB = Maurice Ewing Bank (adapted from Allen et al., 2005).

Figure 2. Paleo-sea surface temperatures (SSTs) derived from various temperature proxies at DSDP Site 511 during the late Eocene-early Oligocene. SSTs obtained in the present study (black line) are compared with those obtained by Liu et al. (2009) using the $U^{K'}_{37}$ (filled circles) and the TEX_{86} (empty circles) proxies, and with those of Muza et al. (1983) who used the stable oxygen isotope composition of planktonic foraminifera ($\delta^{18}O$; blue stars). Data from Liu et al. (2009) and Muza et al. (1983) are plotted according to the age model

determined in the present work. Sample depths (in meters below the sea floor; mbsf), ages, and Nannofossil Zones are also indicated.

Figure 3. Changes in sea-surface temperatures (SSTs) and primary productivity at DSDP Site 511 during the late Eocene-early Oligocene. Trend curves are 3-points moving average curves. **(a)** alkenone-based SSTs (°C), and accumulation rates of **(b)** Total Organic Carbon (TOC), **(c)** calcium carbonate (CaCO₃), **(d)** insoluble components (mainly silica), **(e)** alkenones, **(f)** long-chain diols, **(g)** total number of calcareous nannofossils, and **(h)** *Reticulofenestra* spp. Note that the horizontal scale is different for TOC with respect to CaCO₃ and the remaining component. Sample depths (in meters below the sea floor; mbsf), ages, and Nannofossil Zones are also indicated. Note that SST could not be determined in one single sample (10 mbsf; 31.4 Ma).

Figure 4. Correlations (linear regressions, significance threshold $\alpha = 0.05$) between **(a)** nannofossil and calcium carbonate (CaCO₃) accumulation rates, **(b)** alkenone and *Reticulofenestra* spp. accumulation rates, **(c)** TOC and silica proportions, and between **(d)** Total Organic Carbon (TOC) and sea surface temperatures (SSTs).

Table 1. Age model parameters at DSDP Site 511.

FO = first occurrence; LO = last occurrence. Datum levels identified by (1) Wise (1983), (2) Liu et al. (2009), and (3) Schumacher and Lazarus (2004). Ages are calibrated to the latest geological timescale (Gradstein et al., 2012).

Datum	Depth (mbsf)	Age (Ma)	References
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LO <i>R. umbilica/hillae</i>	8.5	31.35	1, 2
LO <i>Coccolithus formosus</i>	75	32.92	1
$\delta^{18}\text{O}$ (top excursion)	99.7	33.7	2
$\delta^{18}\text{O}$ (base excursion)	129.1	33.9	2
LO <i>Discoaster saipanensis</i>	148	34.44	1, 2, 3
FO <i>Chiasmolithus oamaruensis</i>	177.8	37.32	1

882

883 **Plate 1.** Scanning Electron Microscope (SEM) pictures showing that the studied samples are
884 dominated by diatoms and radiolarian (organisms producing a siliceous test) and that
885 coccoliths are generally well preserved. **(a-b)** Sample 511-5R4-63 (38.42 mbsf), **(c)** Sample
886 511-15R1-93 (129.43 mbsf), **(d-e)** Sample 511-17R1-68 (148.18 mbsf), **(f-h)** Sample 511-
887 20R1-66 (176.66 mbsf).

Figure 1 revised

Figure 2 revised

Figure 3 revised

Figure 4 revised

130 μm 1: *Coscinodiscus* sp.

8 μm 2: *Reticulofenestra* sp.

10 μm 3: *Pyxilla* sp.
4: *Reticulofenestra daviesii*

50 μm 5: *Coscinodiscus* sp.

80 μm 6: *Pyxilla* sp.
7: *Coscinodiscus* sp.?

70 μm 8: Undetermined diatom species

8 μm 9: *Reticulofenestra bisecta*

40 μm 10: *Reticulofenestra clatrata*
11: *Pyxilla* sp.

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