

## Enhanced productivity led to increased organic carbon burial in the euxinic North Atlantic basin during the late Cenomanian oceanic anoxic event

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[1] Three Cenomanian/Turonian (C/T, ~93.5 Ma) black shale sections along a northeast-southwest transect in the southern part of the proto-North Atlantic Ocean were correlated by stable carbon isotope stratigraphy using the characteristic excursion in  $\delta^{13}\text{C}$  values of both bulk organic matter (OM) and molecular fossils of algal chlorophyll and steroids. All three sites show an increase in marine organic carbon (OC) accumulation rates during the C/T Oceanic Anoxic Event (OAE). The occurrence of molecular fossils of anoxygenic photosynthetic green sulfur bacteria, lack of bioturbation, and high abundance of redox sensitive trace metals indicate sulfidic conditions, periodically reaching up into the photic zone before as well as during the C/T OAE. During the C/T OAE, there was a significant rise of the chemocline as indicated by the increase in concentrations of molecular fossils of green sulfur bacteria and Mo/Al ratios. The presence of molecular fossils of the green strain of green sulfur bacteria indicates that euxinic conditions periodically even occurred at very shallow water depths of 15 m or less during the C/T OAE. However, bottom water conditions did not dramatically change as indicated by more or less constant V/Al and Zn/Al ratios at site 367. This suggests that the increase in OC burial rates resulted from enhanced primary productivity rather than increased anoxia, which is supported by stable carbon isotopic evidence and a large increase in Ba/Al ratios during the C/T OAE. The occurrence of the productivity event during a period of globally enhanced organic carbon burial rates (i.e., the C/T OAE) points to a common cause possibly related to the formation of a deep water connection between North and South Atlantic basins. **INDEX TERMS:** 4267 Oceanography: General: Paleooceanography; 4806 Oceanography: Biological and Chemical: Carbon cycling; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4840 Oceanography: Biological and Chemical: Microbiology; **KEYWORDS:** biomarkers, trace metals, green sulfur bacteria, compound-specific carbon isotopes, photic zone anoxia

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### 1. Introduction

[2] The interval spanning the Barremian to Turonian (~125–88 Ma) is known as the mid-Cretaceous “greenhouse” world [Barron, 1983]. Both marine and terrestrial

proxies indicate that the mid-Cretaceous climate was significantly warmer with a smaller equator-to-pole temperature gradient than the modern climate. It has been suggested that this resulted from an anomalous amount of oceanic volcanism, leading to 3 to 12 times higher atmospheric levels of carbon dioxide during the Cretaceous than at present [Berner, 1992]. The transition from the Cenomanian to the Turonian (C/T) marks a major turning point, with globally dispersed oxygen isotope data indicating that the mid-Cretaceous warming trend ceased at the C/T boundary and was followed by a deterioration at least until the Maastrichtian [Jenkyns *et al.*, 1994]. This long-term cooling was preceded by the global deposition of sediments rich (>1%) in organic carbon (OC) and devoid of or strongly impoverished in benthic faunas (black shales) [Schlanger

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and Jenkyns, 1976]. An increase in  $^{13}\text{C}/^{12}\text{C}$  ratios for marine carbonates and organic matter at the C/T boundary provides evidence for an increase in the global OC burial rate. This positive excursion in  $\delta^{13}\text{C}$  values likely resulted from preferential removal of  $^{12}\text{C}$  by the enhanced burial of  $^{13}\text{C}$  depleted OC as a response to the so-called “C/T oceanic anoxic event (OAE)” [Arthur *et al.*, 1988]. Originally, the term OAE was introduced to describe the episodic expansion and intensification of the oxygen minimum zone (OMZ), which was proposed to explain the seemingly global distribution of OC-rich sediments in pelagic sequences of Aptian-Albian and C/T age [Schlagner and Jenkyns, 1976]. The term OAE has been used by later workers more generally [Arthur *et al.*, 1987] “as a way of referring to time-bounded envelopes of particularly, perhaps more globally, widespread deposition of OC-rich sediments (black shales) in marine environments.” In accordance with this, the term C/T OAE (i.e., OAE2) will be used in this study for the 300–500 kyr period of latest Cenomanian to earliest Turonian age, during which OM burial rates were enhanced. This enhanced OM burial rate led to a significant drop in atmospheric carbon dioxide concentration [Freeman and Hayes, 1992; Arthur *et al.*, 1988; Kuypers *et al.*, 1999] and thereby could have triggered the early Turonian deterioration of the greenhouse climate.

[3] Two fundamentally different models have been used to explain the enhanced OM burial rate during the C/T OAE. The preservational model is based on decreased OM remineralization resulting from a decreased oxygen flux. In the mid-Cretaceous oceans anoxic water column conditions may have developed more readily than in the modern world’s oceans as minimal equator-to-pole thermal gradients and high sea surface temperatures should have resulted in a decreased formation of oxygenated bottom waters [Barron, 1983]. This could have resulted in basin-wide oxygen deficiency with the most intense dysoxia/anoxia occurring in the deepest parts of tectonically isolated basins such as the Cretaceous North and South Atlantic [Zimmerman *et al.*, 1987; de Graciansky *et al.*, 1984]. The reoccurrence of thinly laminated OM-rich sediments devoid of traces of benthic activity indicates that middle Cretaceous bottom waters were indeed periodically anoxic [Summerhayes, 1987; Bralower and Thierstein, 1987]. Sedimentary derivatives (molecular fossils) of a pigment indicative of anoxygenic photosynthetic bacteria recovered from abyssal and shelf sites indicate that anoxic conditions extended even into the photic zone of the southern proto-North Atlantic during the C/T OAE [Sinninghe Damsté and Köster, 1998].

[4] The productivity model is based on a greatly increased primary productivity that overwhelmed the oxic OM remineralization potential of the water column. Primary productivity (PP) in the modern marine environment is largely controlled by the input of biolimiting nutrients from deeper water into the surface waters. An enhanced supply of biolimiting nutrients could have led to increased PP and thus to an expansion and intensification of the OMZs during the C/T OAE [Schlanger and Jenkyns, 1976]. The deposition of OM-rich sediments would have largely been confined to places where the OMZ impinged on the continental

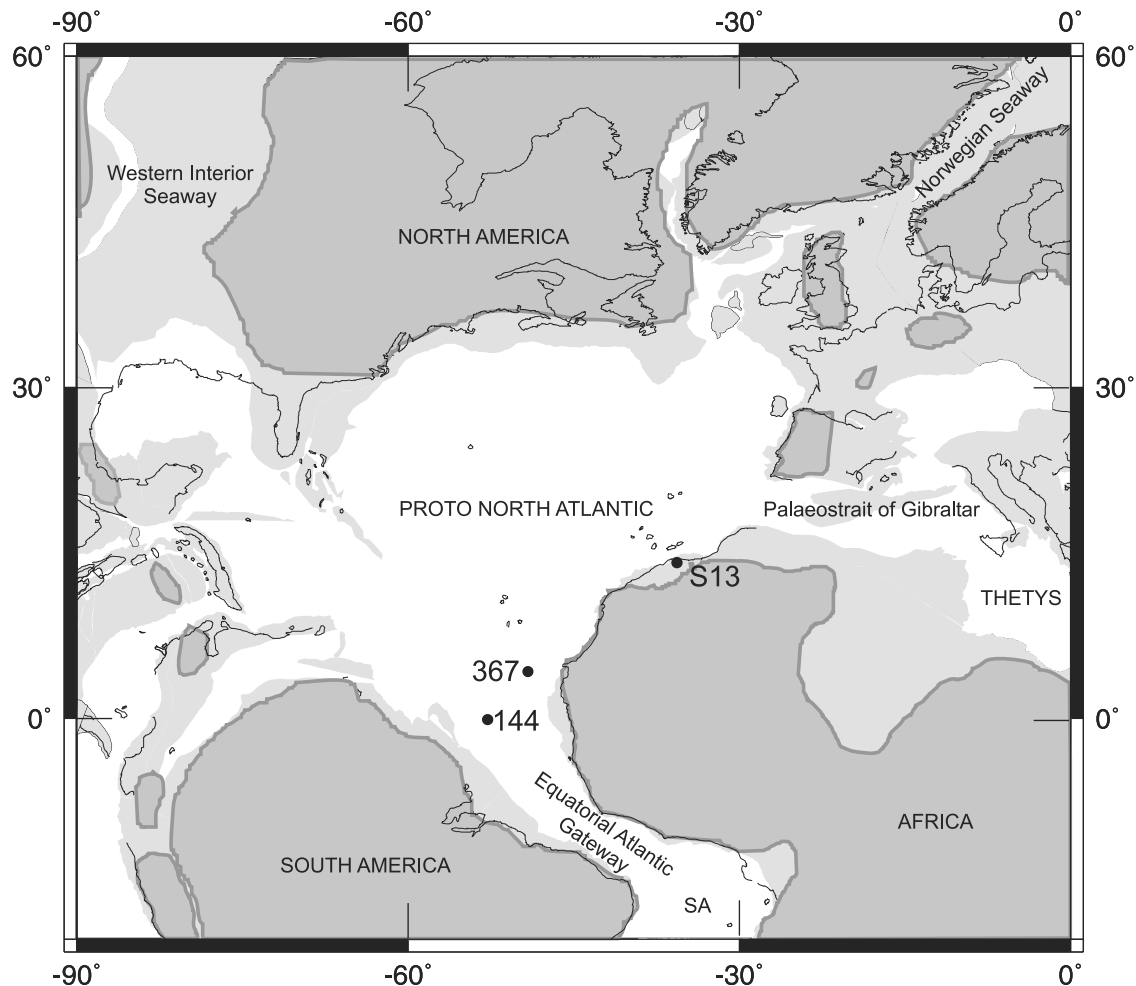
margin or other elevated portions of the seafloor, as the deepest places of the basin may have remained oxic. This model has especially been used to explain the OM-rich deposits in the Cretaceous Pacific Ocean [e.g., Schlanger and Jenkyns, 1976].

[5] In the proto-North Atlantic Ocean, black shales that can be over 80 m thick [Kuhnt *et al.*, 1990] and that can contain >40% OC [Herbin *et al.*, 1986] were deposited basin-wide during the C/T OAE, indicating that this was one of the main sites of carbon burial. This study focuses on the environmental conditions that led to the deposition of the especially well-developed C/T OAE black shales from the southern part of the proto-North Atlantic Ocean [de Graciansky *et al.*, 1984; Kuhnt *et al.*, 1990]. The C/T sections of three sites along a northeast-southwest transect from Morocco to French Guyana (Figure 1) were correlated by stable carbon isotope stratigraphy using the characteristic  $^{13}\text{C}$  excursion in both bulk OM and molecular fossils of algal chlorophyll and steroids. Carbon isotope stratigraphy was also used to calculate the increase in carbon accumulation rates at these sites of different palaeobathymetric setting during the C/T OAE. To test whether enhanced OM preservation resulting from reduced oxygen supply or enhanced productivity caused this increase in carbon burial we reconstructed (1) chemocline variations using redox sensitive trace metals and molecular fossils from pigments exclusively produced by bacteria that require both light and free hydrogen sulfide and (2) variations in primary productivity using Ba/Al ratios and  $^{13}\text{C}/^{12}\text{C}$  ratios for molecular fossils of algal chlorophyll and steroids. In addition, we discuss the oceanographic consequences of our findings.

## 2. Material and Methods

[6] The samples come from Shell exploration well S13 of the Tarfaya area (Morocco) and Deep Sea Drilling Project (DSDP) holes 144 off the coast of French Guyana (leg 14) and 367 off the coast of Senegal (leg 41). Sediment slices (3–5 cm) were taken from the cores, from which subsamples were subsequently freeze-dried and powdered in an agate mortar.

[7] Total organic carbon (TOC) contents were determined using a CN analyzer. The  $\delta^{13}\text{C}$  values ( $\pm 0.1\%$  versus Vienna Peedee belemnite (VPDB)) were measured on bulk sediments after removal of the inorganic carbonates with diluted HCl, using automated online combustion followed by conventional isotope ratio-mass spectrometry. For analyses of the soluble OM, powdered samples were Soxhlet extracted for ~24 hours to obtain the total extract, which was separated into an apolar and a polar fraction using column chromatography. Hydrocarbons were released from the polar fraction by Raney Nickel desulfurisation and subsequent hydrogenation [Sinninghe Damsté *et al.*, 1993]. Samples were analyzed by gas chromatography-mass spectrometry (GC-MS) for compound identification. Compound-specific  $\delta^{13}\text{C}$  analyses were performed using a GC-isotope-ratio-monitoring MS. The  $\delta^{13}\text{C}$  values for individual compounds are the means of duplicate runs ( $\sigma = \pm 0.3$  to 0.6) expressed versus VPDB. Pyrolysis (Py)-GC was



**Figure 1.** Palaeogeographical map of mid-Cretaceous (~94 Ma) North Atlantic showing the position of the three studied cores. Light shaded regions represent continental plates (from GEOMAR map generator; [www.odsn.de/odsn/services/paleomap/paleomap.html](http://www.odsn.de/odsn/services/paleomap/paleomap.html)). Dark shaded regions represent land [Scotese and Golonka, 1992].

conducted on a GC equipped with a FID and a cryogenic unit. Samples were pressed onto flattened ferromagnetic wires (Curie temperature of 610°C), which were subsequently inductively heated for 10 s. The desorbed fragments were flushed into the capillary column using helium.

[8] For major, minor, and trace element analyses, samples (~125 mg) were digested in 5 mL HF (40%) and 5 mL of a HClO<sub>4</sub>/HNO<sub>3</sub> mixture at 90°C. After drying by evaporation at 190°C, the residue was dissolved in 25 mL 1 M HCl. The resulting solutions were analyzed with a Perkin Elmer Optima 3000 inductively coupled plasma–atomic emission spectrometer (ICP-AES). The results were checked with international and house standards, and relative standard deviations in duplicate measurements are below 4%.

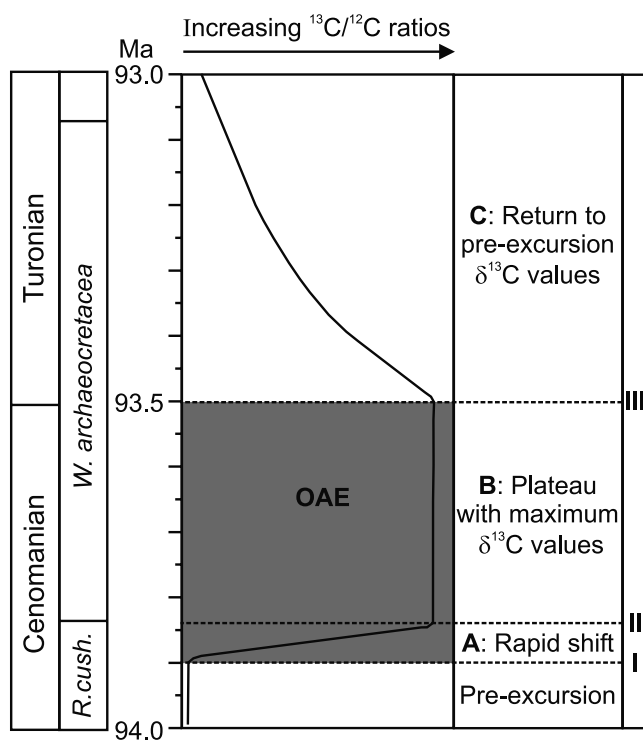
### 3. Results and Discussion

#### 3.1. Stratigraphy and Palaeosetting

[9] Our study concentrates on the C/T interval roughly between 95 and 93 Myr before present [Gradstein *et al.*, 1995], which spans two planktic foraminiferal zones of

global significance: the late Cenomanian *Rotalipora cushmani* zone and the latest Cenomanian to early Turonian *Whiteinella archaeocretacea* zone (Figure 2). This interval is particularly well developed in the Tarfaya basin (well S13; Morocco), where it reaches a thickness of ~150 m (Figure 3). The C/T sequence at site S13 consists of OM-rich biogenic carbonates that were deposited in an open shelf sea with a paleo-water depth at the depocenter (well S13) of 200–300 m [Kuhnt *et al.*, 1990]. Sedimentation rates were as high as 12 cm/kyr for the *W. archaeocretacea* zone [Kuhnt *et al.*, 1997] that contains the major part of the C/T OAE.

[10] The black shales that comprise the late Cenomanian sequence at Deep Sea Drilling Program (DSDP) Site 367 (off the coast of northwest Africa) consist of a mixture of terrigenous silicates and clay minerals, high amounts of organic carbon (total organic carbon (TOC) contents up to 50 wt %), and minor amounts of biogenic carbonate [Herbin *et al.*, 1986]. These sediments were deposited at a water depth of 3700 m. The deposition of such extremely OM-rich sediments at this abyssal site is hard to explain by the expanding OMZ model proposed by Schlanger and Jenkyns



**Figure 2.** Idealized representation of C/T stable carbon isotope excursion showing the bio- and chronostratigraphic position of the three main phases (modified after [Gale et al., 1993]). Dashed lines with Roman numerals show the position of the boundaries between the different phases (preexcursion, A, B, and C) of the isotope excursion.

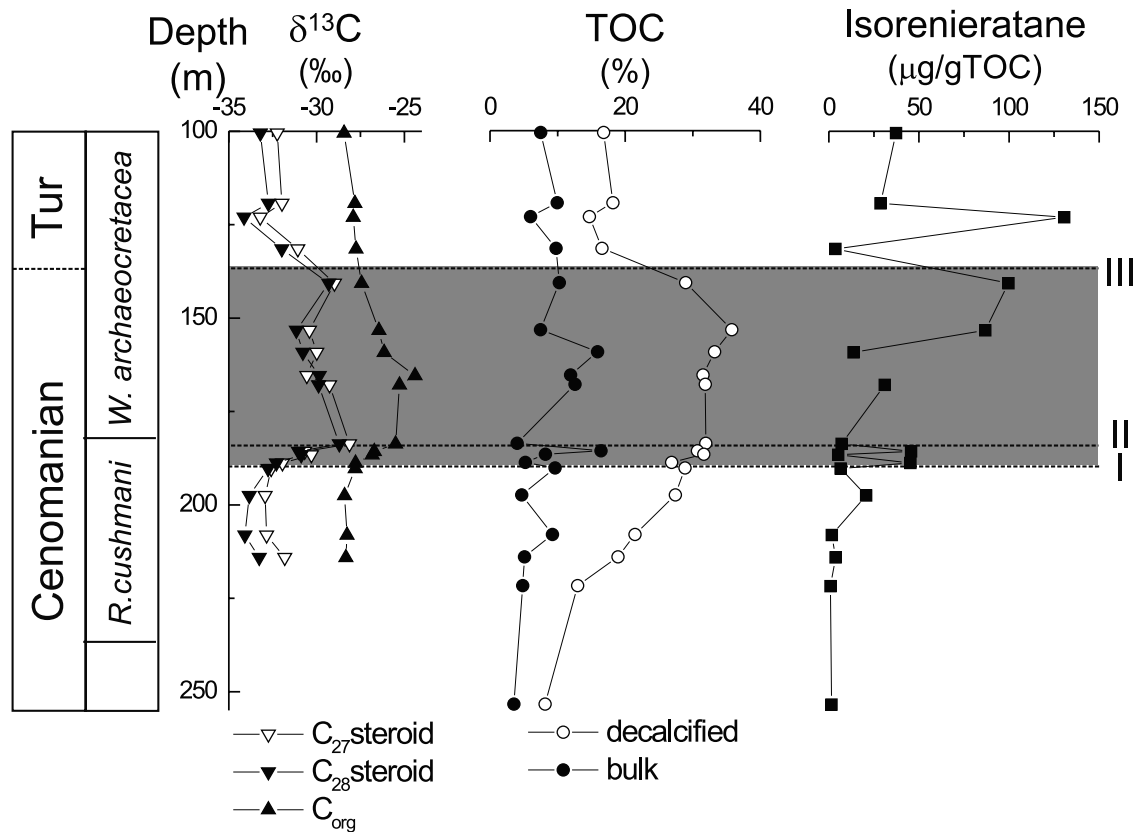
[1976]. Therefore it has been suggested that the deeper bottom waters (>3000 m) of the proto-North Atlantic were predominately oxic and that a large part of the OC-enrichment of mid-Cretaceous black shales at site 367 resulted from redeposition of sediments deposited where the OMZ impinged on the seafloor [Arthur et al., 1984]. Indeed, thin turbidites consisting of quartz silt or clayey foraminifer sand do occur but apparently represent only a minor component of the late Cenomanian section [see also *Shipboard Scientific Party*, 1977]. To the best of our knowledge, no direct evidence has so far been provided for a turbiditic origin of the OM-rich black shales itself [see Arthur et al., 1984, and references therein], and thus we believe that the deeper bottom waters were predominately anoxic during their deposition (see below).

[11] At site 144, the southwestern end of the transect, Cenomanian deposits consist of dark laminated carbonaceous cemented limestones and zeolitic calcareous clay [Hayes et al., 1972]. These hemipelagic sediments were deposited on an ancestral Mid-Atlantic Ridge at a water depth of ~1300 m [Berger and von Rad, 1972].

[12] In sharp contrast to the Tarfaya basin section [Kuhnt et al., 1990], biostratigraphically significant species are largely absent from the middle Cretaceous sediments from sites 144 and 367. Carbon isotope stratigraphy was used instead to constrain the C/T OAE interval and to correlate these abyssal sites with the Moroccan shelf site. The sharp

increase in  $^{13}\text{C}/^{12}\text{C}$  ratios that is observed worldwide for marine carbonates and OM at the C/T boundary [Scholle and Arthur, 1980; Arthur et al., 1988] has been shown to be a powerful tool in high resolution correlation [e.g., Gale et al., 1993; Hasegawa, 1997]. Although this positive excursion in  $\delta^{13}\text{C}$  values consists of several spikes and nudges [Gale et al., 1993], three main phases can be recognized (A to C; schematically depicted in Figure 2). Phase A is a rapid increase in  $^{13}\text{C}/^{12}\text{C}$  ratios (i.e., rapid shift) that occurred during the latest part of the *Rotalipora cushmani* zone [Gale et al., 1993; Kuhnt et al., 1990]. This is followed by a plateau with maximum  $\delta^{13}\text{C}$  values (phase B) mainly during the early part of the *Whiteinella archaeocretacea* zone. Finally, there is a gradual return to preexcursion  $\delta^{13}\text{C}$  values (phase C) during the early Turonian. The three boundaries (I to III) between the different phases of the isotope excursion and the preexcursion conditions are of particular stratigraphic significance. The positive excursion in  $\delta^{13}\text{C}$  values reflects a change in the global atmospheric-oceanic pool of inorganic carbon resulting from a global increase in the burial rate of  $^{13}\text{C}$ -depleted OC [Arthur et al., 1988]. By definition the C/T OAE is the main phase of enhanced carbon burial rates and therefore should be coeval with the interval between boundaries I and III (phases A and B, indicated as a shaded area in Figure 2).

[13] The use of molecular fossils that are specific for primary producers instead of bulk OM for stable carbon isotope stratigraphy greatly reduces the effect of heterotrophy, preservation, and diagenetic alteration on the carbon isotopic signature of OC [Hayes et al., 1989; Freeman and Hayes, 1992; Sinninghe Damsté et al., 1998]. At site S13 of the Tarfaya basin the stable carbon isotopic compositions of two steranes (5 $\alpha$ -cholestane, 24-methyl-5 $\alpha$ -cholestane) were used to define the C/T OAE (Figure 3). These steranes derive from  $\text{C}_{27}$  and  $\text{C}_{28}$  sterols, predominantly biosynthesised by marine algae [Volkman, 1986]. Their  $\delta^{13}\text{C}$  values record changes in the stable carbon isotopic composition of algae (Figure 3). Therefore the interval from the base of the stable carbon isotopic excursion (I) until the onset of declining  $\delta^{13}\text{C}$  values (III) for these steranes (indicated as a shaded area in Figure 3) should correlate to the C/T OAE. Milankovitch-derived sedimentation rates (12 cm/kyr) previously reported for the *Whiteinella archaeocretacea* zone of site S13 [Kuhnt et al., 1997] were used to calculate a duration of ~400 kyr for the C/T OAE. By analogy, phase A of the isotope excursion (Figure 2) was estimated to be ~60 kyr [Kuypers et al., 1999]. Although the sample resolution introduces a significant margin of error, the ~400 kyr for the C/T OAE is in good agreement with data from western Europe [Gale, 1995], indicating ~350 kyr (17 precession cycles) for the same interval. In addition, a duration of ~400 kyr has recently been reported for the Tunesian Bahloul formation [Caron et al., 1999], which approximately coincides with phases A and B of the C/T isotope excursion [Nederbragt et al., 1998]. In sharp contrast, the  $\delta^{13}\text{C}$  profile for bulk OC at site S13 (Figure 3) suggests a significantly shorter duration (~250 kyr) for the C/T OAE. This illustrates the benefits of using molecular fossils specific for primary producers instead of bulk OM for stable carbon isotope stratigraphy.



**Figure 3.** Stratigraphy [Kuhnt *et al.*, 1997], bulk organic carbon, and biomarker data of site S13 (Tarfaya basin). Carbon isotope values (in per mil versus VPDB) of bulk organic carbon ( $C_{org}$ ) and free steranes ( $C_{27}$  sterane ( $5\alpha$ -cholestane) and  $C_{28}$  sterane ( $5\alpha$ -24-methyl-cholestane)) derived from marine algae, TOC content of the bulk sediment and of the residue obtained after decalcification, and concentration profile of molecular fossil (S-bound isorenieratane) of a pigment of the brown strain of green sulfur bacteria. The dashed lines with Roman numerals show the approximate position of the boundaries between the different phases of the isotope excursion (see also Figure 2).

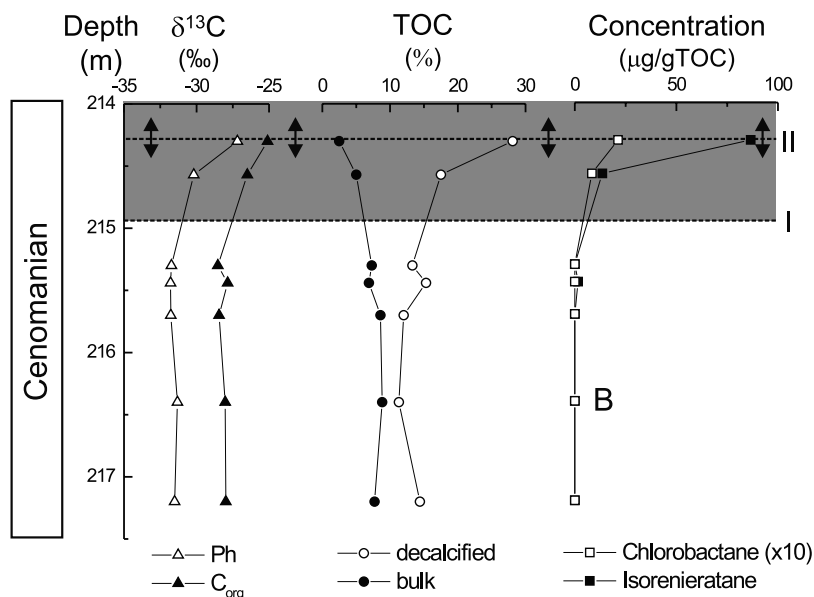
[14] At sites 144 and 367, sulfur (S)-bound phytane (Figures 4 and 5), which mainly derives from the phytol moiety of phytoplanktonic chlorophyll [Kohnen *et al.*, 1992], was used instead of the more specific algal steranes for carbon isotope stratigraphy because of the low abundance of the latter at these sites. The  $\delta^{13}C$  profiles for S-bound phytane (i.e., Ph) at sites 144 and 367 both show the rapid shift in  $^{13}C/^{12}C$  ratios that marks phase A (Figures 4 and 5). The offset of  $\sim 3\text{‰}$  between  $\delta^{13}C$  profiles for bulk OC and the molecular fossils of chlorophyll is well within the range reported for extant algae [Schouten *et al.*, 1998]. Assuming that the excursions in  $\delta^{13}C$  values at all sites are synchronous [Gale *et al.*, 1993], data from site S13 were used to calculate an average sedimentation rate for phase A of site 367 ( $\sim 3.5$  cm/kyr). Coring gaps obscuring the later part of phase A and the whole of phase B do not allow the calculation of sedimentation rates at site 144. Similarly, a coring gap obscuring the later part of phase B at site 367 does not allow an average sedimentation rate to be calculated for the whole C/T OAE.

[15] The shaded areas in Figures 4 and 5 most likely represent only a part of the total C/TOAE interval present at sites 144 and 367. However, the beginning of the rapid shift

in  $^{13}C/^{12}C$  ratios (earlier part of phase A) was recovered at all three sites (Figures 3, 4 and 5), allowing a direct comparison of the changes in OC accumulation rates that occurred during the onset of the C/T OAE.

### 3.2. Organic Carbon Accumulation Rates and Organic Matter Sources

[16] The C/T sediments of site S13 contain high amounts of OC with maximum total organic carbon (TOC) values of  $\sim 16\%$  (Figure 3). During the C/T OAE the average TOC content is significantly higher ( $\sim 10\%$ ) than before ( $\sim 5\%$ ) or after ( $\sim 8\%$ ) (Figure 3). Superimposed on these long-term trends are high-amplitude, short-term variations in TOC content throughout the investigated section. Previously reported cyclic variation in TOC content for C/T sediments from the Tarfaya basin [Kuhnt *et al.*, 1990] was attributed to fluctuations in the productivity of calcifying organisms and thus carbonate flux [Kuhnt *et al.*, 1997]. The TOC contents for the residues obtained after decalcification ( $=TOC_{decalcified}$ ) were determined in order to obtain a TOC record that is independent of these cyclic variations in carbonate flux and which thereby better reflects relative changes in OC accumulation rate during the C/T OAE. The  $TOC_{decalcified}$  record

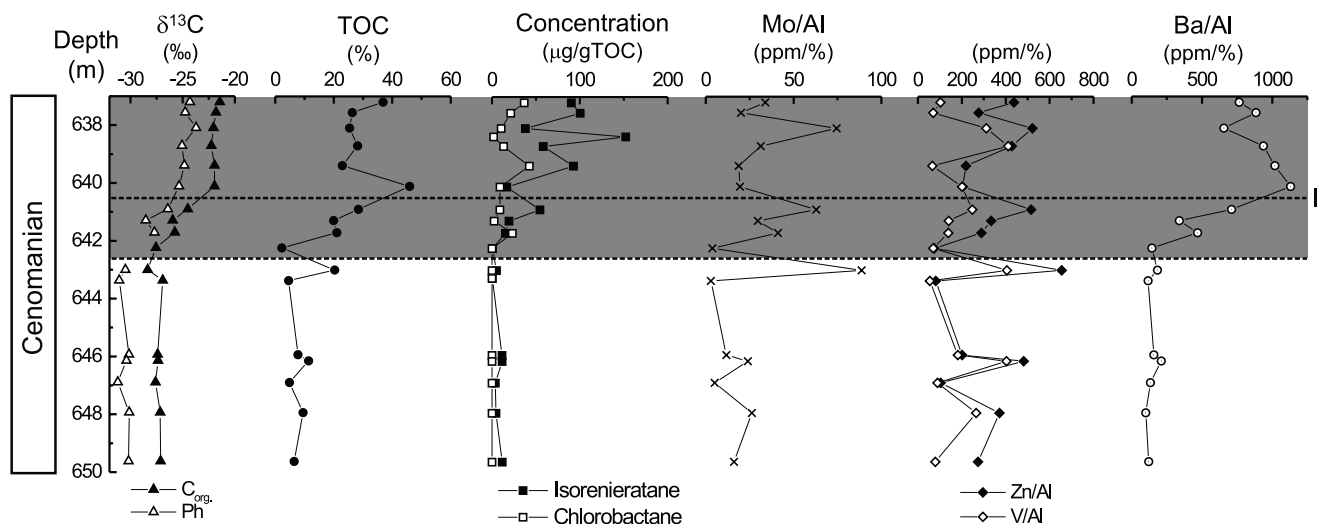


**Figure 4.** Stratigraphy, bulk organic carbon and biomarker data of site 144. Carbon isotope values (in per mil versus VPDB) of  $C_{org}$ , S-bound phytane (Ph) derived from phytoplanktonic chlorophyll, TOC content of the bulk sediment and of the residue obtained after decalcification, and concentration profile of molecular fossil (S-bound isorenieratane) of a pigment of the brown strain of green sulfur bacteria. The dashed lines with Roman numerals show the approximate position of the boundaries between the different phases of the isotope excursion (see also Figure 2), and B indicates the sample containing benthic foraminifera.

shows an increase followed by a decrease, with maximum values within the C/T OAE interval (Figure 3).

[17] At site 144 the TOC content for the bulk sediment shows a decrease during the C/T OAE (Figure 4), which

cooccurs with an increase in carbonate content reflected by a change from carbonaceous marl to carbonaceous limestone. The negative correlation between TOC and carbonate content may suggest depositional dilution of OC by an increased



**Figure 5.** Stratigraphy, bulk organic carbon, biomarker, and trace metal data of site 367. Carbon isotope values (in per mil versus VPDB) of  $C_{org}$ , S-bound phytane (Ph) derived from phytoplanktonic chlorophyll, TOC content of the bulk sediment, concentration profiles of the molecular fossils S-bound isorenieratane and S-bound chlorobactene of green sulfur bacteria derived from members of the brown and green strain, respectively, redox sensitive trace metals (Mo, Zn and V) normalized to Al, and the productivity proxy Ba/Al. The dashed lines with Roman numerals show the approximate position of the boundaries between the different phases of the isotope excursion (see also Figure 2).

carbonate flux [Ricken, 1993]. The TOC<sub>decalcified</sub> record (Figure 4) shows an increase during the C/T OAE for this site.

[18] Extremely high OC contents (maximum TOC = 46%) exceeding the range for most if not all Holocene open ocean sediments below ~2000 m characterize the Cenomanian sediments of site 367 (Figure 5). Depositional dilution of OC by carbonate is insignificant for these sediments due to deposition below the carbonate compensation depth (CCD). During the C/T OAE the average TOC content is significantly higher (~25%) than before (~9%) (Figure 5), suggesting that if sedimentation rates were constant OC accumulation rates increased significantly.

[19] Assuming constant sedimentation rates, the average OC accumulation rates before and during the C/T OAE were determined for sites S13 and 367 using the TOC contents of the bulk (i.e., nondecalcified) sediments. Prior to the C/T OAE, OC mass accumulation rates (OC MAR) for site S13 ( $9 \text{ gC m}^{-2} \text{ yr}^{-1}$ ) and site 367 ( $3 \text{ gC m}^{-2} \text{ yr}^{-1}$ ) are comparable to data for Holocene sites (Table 1) characterized by suboxic to anoxic bottom waters, high primary productivity (PP) ( $140\text{--}280 \text{ gC m}^{-2} \text{ yr}^{-1}$ ), and high bulk sediment mass accumulation rates ( $125\text{--}150 \text{ g m}^{-2} \text{ yr}^{-1}$ ). Only the OC MAR for the extremely productive (PP ~  $400\text{--}500 \text{ gC m}^{-2} \text{ yr}^{-1}$ ) Peruvian shelf is significantly higher. These values are also of the same order of magnitude as reported for Mediterranean Pliocene sapropels (i.e.,  $0.4\text{--}6.7 \text{ gC m}^{-2} \text{ yr}^{-1}$  [Nijenhuis and de Lange, 2000]), which are considered younger analogues of black shales [e.g., Thomson et al., 1995].

[20] During the C/T OAE, OC accumulation rates at sites 367 and S13 ( $9$  and  $26 \text{ gC m}^{-2} \text{ yr}^{-1}$ , respectively) were ~3 times greater than prior to the OAE. These values exceed those determined for most modern marine settings (Table 1) and are comparable to sites characterized by both high productivity and a high preservation potential (e.g., the Peruvian shelf). The OC accumulation rates are comparable to those determined for the OC rich interval of the *W. archaeocretacea* zone (~C/T OAE) of site CM10 off the coast of Senegal but significantly higher than values determined for the same interval of European (e.g., Gubbio) and northern North Atlantic (ODP Site 641A) sites (Table 1) [Kuhnt et al., 1990], confirming that the southern proto-North Atlantic was one of the main locations of OC burial during the C/T OAE.

[21] Microscopic screening of the decalcified and sieved ( $>10 \mu\text{m}$ ) samples reveals that the OM from both shelf (well S13) and deep sea sites (sites 144 and 367) is almost exclusively amorphous with rare vascular plant remains and pollen. High Rock Eval hydrogen indices (HI) [Herbin et al., 1986; Kuhnt et al., 1990] and the low abundance of lignin pyrolysis products generated from the kerogen indicate a marine origin for the thermally immature OM before, during and after the C/T OAE. This is supported by the low abundance (site 367) or even absence (sites S13 and 144) of molecular fossils of unambiguous terrestrial origin (e.g., leaf wax lipids and oleananes) in the extractable OM. Hence the increase in OC accumulation rates observed at all three sites resulted from enhanced marine OM burial during the C/T OAE. At site S13 and site 367 this increase in OC accumulation

rates could have been as large as  $17$  and  $6 \text{ gC m}^{-2} \text{ yr}^{-1}$ , respectively. The question that remains is, did this increase in the marine OC accumulation rates mainly result from increased preservation under anoxic conditions or from increased primary productivity?

### 3.3. Water Column Redox Proxies

#### 3.3.1. Molecular Fossils of Anoxygenic Photosynthetic Bacteria

[22] Anoxic conditions periodically reached up into the photic zone as indicated by the abundance of molecular fossils (i.e., S-bound isorenieratane showing the typical  $10\text{--}15\%$   $^{13}\text{C}$  enrichment relative to algal lipids [e.g., Sinninghe Damsté et al., 1993]) indicative of anoxygenic photosynthetic bacteria at sites S13, 144, and 367 (Figures 3, 4, and 5). This is in good agreement with earlier findings of Sinninghe Damsté and Köster [1998]. S-bound isorenieratane is formed in anoxic sediments upon sulfuration of the polyunsaturated pigment isorenieratene in the presence of reduced inorganic S species [Sinninghe Damsté et al., 1993]. Carotenoids such as isorenieratene are generally labile compounds [Sinninghe Damsté and Koopmans, 1997] that do not survive transport over long distances, clearly indicating a local marine rather than allochthonous source for S-bound isorenieratane. The pigment isorenieratene is exclusively produced by the brown strain of green sulfur bacteria [Imhoff, 1995], which require sunlight penetrating the euxinic part (e.g., containing reduced inorganic sulfur species) of an aquatic environment [van Gernerden and Mas, 1995]. Currently, these phototrophic bacteria are restricted to a few isolated euxinic basins in the marine realm such as the Black Sea. In such environments they thrive near the hydrogen sulfide/oxygen interface (i.e., chemocline) at depths of up to  $150 \text{ m}$ , where light levels are  $<1\%$  of surface irradiance [van Gernerden and Mas, 1995].

[23] Molecular fossils of isorenieratene were also found in sediments predating the isotope excursion albeit in much lower concentrations, indicating that sulfide-containing water periodically penetrated the photic zone before the actual onset of the C/T OAE (Figures 3, 4, and 5). While S-bound isorenieratane is present throughout the interval preceding the C/T OAE at site S13 and site 367, it was only found in one sample of the same interval at site 144 (Figure 4). This indicates that sulfide-containing water penetrated the photic zone more frequently at the southeastern side than at the southwestern side of the proto-North Atlantic Ocean, possibly reflecting a shallower average position of the chemocline (i.e., nearer to the photic zone). High-amplitude short-term fluctuations in S-bound isorenieratane concentrations occur during the C/T OAE at both site S13 and site 367, although the amplitude is more pronounced at the former site (Figures 3 and 5). The more pronounced fluctuations at site S13 could represent a sampling artifact as sample sizes are similar (~ $5 \text{ cm}$ ), but sedimentation rates are significantly lower at site 367. As a result, S-bound isorenieratane concentrations at site S13 (Figure 3) represent an average over a much shorter time-scale (~ $400$  years) than at site 367 (Figure 5) (~ $1400$  years), possibly leading to a less “smoothed” S-bound

**Table 1.** Age, Water Depth, Total Organic Carbon Content (TOC), Bulk Sediment (Bulk), and Organic Carbon (OC) Mass Accumulation Rates (MAR), Average Concentrations of Redox Sensitive Trace Metals (Mo, Ni, V, and Zn), Average Concentration of Ba, Export Productivity (EP), and Primary Productivity of Site S13, Site 367, and a Selection of Holocene Tertiary and mid-Cretaceous Sites<sup>a</sup>

Site	Age, Myr	Water Depth, m	Average TOC, wt	Bulk MAR, g m <sup>-2</sup> yr <sup>-1</sup>	OC MAR, g m <sup>-2</sup> yr <sup>-1</sup>	Average Mo, ppm	Average Ni, ppm	Average V, ppm	Average Zn, ppm	Average Ba, ppm	EP, g m <sup>-2</sup> yr <sup>-1</sup>	PP, g m <sup>-2</sup> yr <sup>-1</sup>
Tarfaya S13	~94 (before OAE)	300	5	254	9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tarfaya S13	~94 (during OAE)	300	10	254	26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DSDP site 367	~94 (before OAE)	3700	8.5	40	3	125	205	1728	1193	875	13	71
DSDP site 367	~94 (during OAE)	3700	24.6	40	9	92	380	912	513	2052	80	179
Senegal CM10	~94 (during OAE)	300	7	476	33	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Italy Gubbio	~94 (during OAE)	1500	12	0.7	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ODP site 641A	~94 (during OAE)	3500	10	0.7	0.1	1950	464	968	6866	1219	n.d.	n.d.
ODP site 969	2.943 (sapropel)	2201	17.7	40	7.1	407	299	1937	123	1316	16	n.d.
<i>Cretaceous and Tertiary Sites</i>												
<i>Holocene Sites</i>												
Arabian Sea	0-0.004	~2000	1	86	0.8	n.d.	n.d.	n.d.	n.d.	n.d.	~70	140-280
Central Pacific	0-0.01	5000-5700	0.3	1.5	0.004	n.d.	210	117	165	n.d.	n.d.	50
North Atlantic	0-0.01	2000-3000	0.01-1	1.7-86	0.02-1.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	75-230
Arabian Sea	<b>0-0.004</b>	<b>495</b>	<b>4</b>	<b>245</b>	<b>10</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>~70</b>	<b>140-280</b>
Arabian Sea	<b>0-0.004</b>	<b>~1000</b>	<b>5.5</b>	<b>124</b>	<b>6.1</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>~70</b>	<b>140-280</b>
Black Sea	<b>0-0.003</b>	<b>~2100</b>	<b>5.8</b>	<b>83</b>	<b>4.8</b>	<b>29</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>150-240</b>
Black Sea	<b>0-0.003</b>	<b>400-750</b>	<b>1.8</b>	<b>165</b>	<b>3.1</b>	<b>n.d.</b>	<b>75</b>	<b>106</b>	<b>81</b>	<b>n.d.</b>	<b>n.d.</b>	<b>150-240</b>
Carriaco Trench	<b>0-0.007</b>	<b>892</b>	<b>5.5</b>	<b>180</b>	<b>9.9</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>170</b>
Peru Shelf	<b>0-0.001</b>	<b>150-400</b>	<b>16.9</b>	<b>248</b>	<b>39</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>n.d.</b>	<b>400-500</b>

<sup>a</sup> For Holocene sites, see *van der Weijden et al.* [1999], *Arthur et al.* [1994], *Brunswick and Thurow* [1986], and *Bralower and Thierstein* [1987]. For Tertiary sites, see *Passier et al.* [1999]. For mid-Cretaceous sites, see *Kuhnt et al.* [1990] and *Thurow et al.* [1988]. Bold text indicates Holocene sites with oxygen-deficient bottom waters.



isorenieratane record at the former site. Fluctuations in S-bound isorenieratane concentrations could have resulted from changes in anoxygenic productivity. In accordance with the latter, fluctuations in the abundances of isorenieratane and its molecular fossils extracted from Holocene Black Sea sediments were attributed to changes in anoxygenic productivity related to fluctuations in the position of the chemocline [Repeta, 1993; Sinninghe Damsté et al., 1993]. The abundance of phototrophic sulfur bacteria in modern settings not only increases and decreases as euxinic conditions rise into or drop below the photic zone, respectively, but also shows a strong positive correlation with light intensity [van Gemerden and Mas, 1995]. Therefore the short-term variations and pronounced long-term increases in S-bound isorenieratane concentrations during the C/T OAE could be produced by either the chemocline penetrating the photic zone at a similar depth but over considerably longer timescales or by relatively short excursions to much shallower depths.

[24] The occurrence of molecular fossils of the pigment chlorobactene (i.e., S-bound chlorobactane) in the OAE sediments of sites 144 and 367 (Figures 4 and 5) and their absence prior to the OAE interval indicates a rise of the chemocline to shallower depths during the C/T OAE. Chlorobactene is exclusively produced by the green-colored strain of green sulfur bacteria [Imhoff, 1995], which thrives at a shallower depth (<15 m) than the brown strain since it requires a higher light intensity [van Gemerden and Mas, 1995]. Assuming a similar light dependence for these phototrophic sulfur bacteria during the mid-Cretaceous, the occurrence of S-bound chlorobactane indicates that the upper 15 m of the photic zone of the southern proto-North Atlantic periodically contained sulfide during the C/T OAE.

### 3.3.2. Trace Metals

[25] Further information on water column redox conditions can be gained from elements (e.g., Mo, Ni and Zn) that precipitate as sulfides under euxinic conditions and certain elements (e.g., Mo and V) that are immobilised under reducing conditions. Sediments underlying a euxinic water column are often characterized by a strong enrichment of these trace metals [e.g., Arthur et al., 1990; Calvert and Pedersen, 1993]. In accordance with this, very high trace metal concentrations were previously reported for mid Cretaceous black shales of site 367 [Brumsack and Thurow, 1986] and were attributed to enhanced trace metal scavenging in a euxinic water column. The average trace metal concentrations reported here for C/T sediments (Table 1) are in good agreement with the data from Brumsack and Thurow [1986].

[26] To evaluate the variations in redox conditions, the abundances of Mo, V, and Zn have been normalised to aluminium (Al) (Figure 5). The Mo/Al, V/Al, and Zn/Al profiles show strong fluctuations that could result from changes in detrital (i.e., clay minerals) sedimentation rate, the scavenging capacity of sediment and water column, and/or the trace metal abundance in the seawater. Enhanced Mo/Al ratios during the C/T OAE could have resulted from enhanced scavenging related to shoaling of the chemocline. Relatively high Zn/Al and V/Al values

occur both before and during the OAE. The lack of a clear increase in V/Al and Zn/Al ratios during the C/T OAE indicates that bottom water redox conditions did not change dramatically.

### 3.3.3. Synthesis of Redox Proxies

[27] The occurrence of molecular fossils of pigments from green sulfur bacteria at sites S13, 144, and 367 indicates that the photic (<150 m) zone of the southern proto-North Atlantic Ocean periodically contained sulfide already before the C/T OAE. The deposition of predominately laminated sediments devoid of or strongly impoverished in benthic faunas at sites S13 and 144 [Berger and von Rad, 1972; Kuhnt et al., 1990] suggests that these anoxic conditions periodically extended to at least 1300 m water depth. Arthur et al. [1984] suggested that the deeper bottom waters (>3000 m) of the proto-North Atlantic were predominately oxic. This is contradicted by other workers who have described the 367 black shales from this interval as laminated and deposited under dysoxic/anoxic conditions [e.g., Bralower and Thierstein, 1987; Sinninghe Damsté and Köster, 1998]. In any case, the abundance of elements that precipitate as sulfides under euxinic conditions or that are immobilized under reducing conditions throughout the investigated interval of site 367 strongly suggests that the deeper bottom waters were anoxic for extended times [see also Brumsack and Thurow, 1986; Arthur et al., 1990]. Consistent with this, very high TOC contents (up to 50%), and hydrogen indices (550–850 mg hydrocarbons/g TOC [Herbin et al., 1986]), the abundance of sulfur-bound compounds as well as the high preservation factors for OC are indicative of anoxic conditions during deposition of the sediments [see also Herbin et al., 1986; Sinninghe Damsté and Köster, 1998].

[28] During the C/T OAE, there was a significant rise of the chemocline as indicated by the increased concentrations of molecular fossils of green sulfur bacteria. Molecular fossils of the green strain of green sulfur bacteria (DSDP Site 144 and 367) indicate that euxinic conditions periodically even occurred above 15 m during the C/T OAE.

[29] Decreased degradation of OM resulting from anoxic bottom water conditions would have contributed to a high OC preservation in the southern proto-North Atlantic both prior to and during the C/T OAE. Thus shoaling of the chemocline during the C/T OAE probably did not enhance OM preservation significantly since it apparently only marginally affected the exposure to oxygen. This suggests that the observed increase in OC burial rates during the C/T OAE did not result from increased preservation.

## 3.4. Productivity Proxies

### 3.4.1. Sedimentary Barium

[30] Sedimentary Ba is generally considered as an indicator for paleoproductivity since it originates from barite formed in decaying phytoplanktonic OM [Dymond et al., 1992; Francois et al., 1995]. Such barite formation has been shown to occur in the well-oxygenated open ocean [Dymond et al., 1992; Francois et al., 1995] as well as in the suboxic to anoxic waters of OMZs and euxinic basins [Falkner et al., 1993; Dean et al., 1997]. Prior to the C/T OAE the average Ba concentration at site 367 is comparable

to data reported for C/T sediments and some Pliocene sapropels (Table 1). The fivefold increase in Ba/Al ratios indicates enhanced export productivity during the C/T OAE (Figure 5).

[31] Assuming that the mechanism for Ba enrichment in decaying OM during the Cretaceous was similar to that proposed for more recent settings [Bishop, 1988], we estimated productivity before and during the C/T OAE from Ba accumulation rates. Since under suboxic to anoxic diagenetic conditions Ba preservation may be reduced [Dymond *et al.*, 1992; Falkner *et al.*, 1993; Francois *et al.*, 1995; McManus *et al.*, 1998], the productivity values obtained here could represent underestimates of the absolute values. The amount of OC (in  $\text{gC m}^{-2} \text{yr}^{-1}$ ) that is transported out of the photic zone (the export productivity, EP) was calculated, using equations proposed by Francois *et al.* [1995] and Dymond *et al.* [1992]. For a thorough discussion of this method, see Nijenhuis and de Lange [2000]. The concentration of biogenic Ba was calculated using the Al content of the individual samples and assuming a detrital Ba/Al ratio of  $6.1 \times 10^{-3}$  [Dehairs *et al.*, 2000]. Export productivity was calculated assuming a constant sedimentation rate of 3.5 cm/kyr throughout the interval and using an average dry bulk density of  $1.14 \text{ g cm}^{-2} \text{kyr}^{-1}$  [Hayes *et al.*, 1972]. The calculated EP prior to the C/T OAE is comparable to data for the Pliocene sapropels but considerably lower than for modern high-productivity sites like the Arabian Sea (Table 1). During the C/T OAE the average EP value is 5-times higher than prior to the OAE and comparable to the Arabian Sea value.

[32] In the modern ocean, nitrate and phosphate formed upon remineralisation of particulate OM (POM) below the photic zone play a key role in sustaining primary productivity (= new production). Assuming this was also the case in the Cretaceous and the amount of nitrogen and phosphorus entering the photic zone was equal to the amount of nitrogen and phosphorus transported out (EP~new production), PP was calculated from the EP values for site 367 using the equation of Eppley and Peterson [1979]:

$$\text{total production} = (\text{new production} / 0.0025)^{1/2}.$$

The calculated average PP (Table 1) of  $70 \text{ gC m}^{-2} \text{yr}^{-1}$  before the C/T OAE is comparable to the low PP sites of the modern North Atlantic and central Pacific (Table 1). However, a significantly higher average PP of  $180 \text{ gC m}^{-2} \text{yr}^{-1}$  is calculated during the OAE, which is comparable to the high PP of the modern Arabian Sea and Black Sea. The calculated nearly threefold increase in PP ( $\sim 100 \text{ gC m}^{-2} \text{yr}^{-1}$ ) is large enough to explain the observed increase in OC accumulation rate at site 367 during the C/T OAE. As a consequence, preservation factors (PF = OC accumulation rate divided by the PP) for OC before and during the C/T OAE are identical (both  $\sim 5\%$ ). This PF is comparable to what was previously suggested [Bralower and Thierstein, 1987] for mid-Cretaceous black shales, and the maximum PF reported for the euxinic Holocene Black Sea [Arthur *et al.*, 1994] and is consistent with anoxic water column conditions during as well as before the C/T OAE.

### 3.4.2. Stable Carbon Isotopes

[33] The degree of photosynthetic carbon fractionation ( $\epsilon_p$ ) for marine phytoplankton shows a strong negative correlation with both growth rate and cell size [e.g., Laws *et al.*, 1995; Popp *et al.*, 1998]; therefore an increase in PP should be reflected in  $\delta^{13}\text{C}$  values of phytoplankton-derived organic matter. However,  $\epsilon_p$  values for marine phytoplankton also shows a pronounced dependence on  $\text{CO}_2$  concentration [Rau *et al.*, 1989]. Therefore the drop in atmospheric  $\text{CO}_2$  concentrations resulting from enhanced OC burial rate during the C/T OAE [Arthur *et al.*, 1988; Freeman and Hayes, 1992; Kuypers *et al.*, 1999] should likewise be reflected in the stable carbon isotopic composition of phytoplanktonic OC.

[34] To assess whether there is any carbon isotopic evidence for enhanced PP in the southern proto-North Atlantic during the C/T OAE, changes in  $\epsilon_p$  values for phytoplankton were determined. The  $\delta^{13}\text{C}$  values for inorganic carbon, which are needed to calculate  $\epsilon_p$ , could not directly be determined due to diagenetic alteration (S13 and site 144) or absence of carbonate carbon (site 367). Since enhanced OC burial during the C/T OAE should have affected the stable carbon isotopic composition of inorganic carbon globally in a similar way, data from other sites with better preserved carbonate records are used instead. Such globally dispersed sites indicate that the positive excursion in marine carbonate  $\delta^{13}\text{C}$  values was  $\sim 2.5\%$  [e.g., Arthur *et al.*, 1988; Jenkyns *et al.*, 1994]. However, shoaling of the chemocline discussed previously could have introduced  $^{13}\text{C}$  depleted recycled inorganic carbon into the photic zone causing smaller increases in  $\delta^{13}\text{C}$  values for inorganic carbon in the southern proto-North Atlantic. Therefore the estimated shift of 2.5‰ for inorganic carbon is likely a maximum value, and estimated shifts in  $\epsilon_p$  are interpreted as minimum values. Assuming a 2.5‰ excursion for inorganic carbon, the 6‰ increase in the  $\delta^{13}\text{C}$  values for S-bound phytane at site 367 (Figure 5) records a 3.5‰ decrease in  $\epsilon_p$  values. A slightly smaller decrease in  $\epsilon_p$  values is suggested by the 5‰ increase in  $\delta^{13}\text{C}$  values observed for steranes at site S13 (Figure 3). Coring gaps probably obscure the later part of phase A of the carbon isotope excursion at site 144. The 2‰ decrease in  $\epsilon_p$  values that was calculated from the 4.5‰ increase in  $\delta^{13}\text{C}$  values for S-bound phytane at site 144 (Figure 5) could therefore be larger. A significantly smaller decrease in  $\epsilon_p$  ( $<2\%$ ) is indicated by the 4–4.5‰ increase in  $\delta^{13}\text{C}$  values for S-bound phytane at site 603B (Kuypers *et al.*, unpublished results, 2001). For the Cretaceous Western Interior Seaway (North America) geoporphyry fractions were used to calculate a 1.5‰ decrease in  $\epsilon_p$  values during the C/T OAE [Hayes *et al.*, 1989] and subsequently interpreted as a  $\sim 20\%$  reduction in atmospheric  $\text{CO}_2$  concentration [Freeman and Hayes, 1992]. The shift in  $\epsilon_p$  values has only been directly measured for the Cretaceous Western Interior Seaway; nonetheless, the shift in  $\delta^{13}\text{C}$  values for the geoporphyry fractions is smaller than for any other OC record, be it bulk or molecular fossils of phytoplanktonic origin. This prompted us [Kuypers *et al.*, 1999] to suggest that the drop in  $\text{CO}_2$  concentrations could have been larger than the 20% suggested by Freeman and Hayes [1992]. However, sites 367 and S13 both exhibit

shifts in  $\delta^{13}\text{C}$  values larger than reported for any other site indicating significantly larger  $\epsilon_p$  shifts, and these are likely minimum estimates. Thus, although we can not determine the absolute effect of either decreased  $\text{CO}_2$  concentrations or enhanced algal growth rate/average cell size on the OC isotope records, it seems likely that an increase in PP accounts for the larger shift in  $\delta^{13}\text{C}$  values for molecular fossils of phytoplanktic origin at sites 367 and S13. This is entirely consistent with the increase in Ba/Al ratios for site 367 and the fact that these two sites experienced a dramatic increase in OC MAR while bottom water redox conditions did not change.

#### 4. Palaeoceanographic Implications

[35] The combined redox proxies indicate that the southern part of the proto-North Atlantic Ocean was already periodically euxinic from the bottom to at least the base of the photic (<150 m) zone before the C/T OAE. This is in good agreement with the results obtained from model simulations for the Albian and early Cenomanian proto-North Atlantic Ocean circulation [Poulsen, 1999] and probably resulted from a combination of overall sluggish circulation (possibly halothermal instead of thermohaline) and the tectonically isolated nature of the proto-North Atlantic (Figure 1). Sedimentological and geochemical data from the proto-North Atlantic indicate that anoxic conditions persisted in the southern and southeastern part, while the northern and northeastern part was oxic during most of the Albian to late Cenomanian [de Graciansky et al., 1984]. Conditions in the northwestern part were more versatile with alternating oxic and anoxic periods. The coexistence of oxic and anoxic conditions in the proto-North Atlantic could have resulted from a barrier restricting deep water exchange between the southeastern and northwestern part of the basin [de Graciansky et al., 1984]. Enhanced PP as a result of wind driven upwelling in the equatorial region [Handoh et al., 1999] could have further diminished the oxygen content of the southern part of the proto-North Atlantic Ocean.

[36] During the C/T OAE, there was a significant shoaling of the chemocline as indicated by the large increase in the concentrations of molecular fossils of green sulfur bacteria. The occurrence of molecular fossils of pigments specific for the green strain of green sulfur bacteria even indicates that the upper part of the photic zone (<15 m) periodically contained sulfide during the C/T OAE. However, the increase (up to  $17 \text{ gC m}^{-2} \text{ yr}^{-1}$ ) in OC accumulation rates at shallow ( $\sim 300 \text{ m}$ ; site S13), intermittent ( $\sim 1300 \text{ m}$ ; site 144), and deep ( $3700 \text{ m}$ ; site 367) water settings probably cannot be attributed to enhanced preservation as our trace metal data suggest there was no major change in bottom water redox conditions.

[37] There is evidence (e.g., enhanced Ba accumulation rates, significantly larger shifts in  $\delta^{13}\text{C}$  values for OC of phytoplanktic origin than in any other Cretaceous marine realm) for enhanced PP during the C/T OAE in the southern proto-North Atlantic. The increase in PP ( $\sim 100 \text{ gC m}^{-2} \text{ yr}^{-1}$ ) is large enough to explain the observed increase in OC accumulation rate at site 367 during the C/T OAE. In the modern ocean enhanced PP is closely linked with intensi-

fied upwelling of intermediate waters into the photic zone. In accordance with this it has been suggested that fertilization of the surface waters by upwelling stimulated primary productivity leading to the widespread deposition of OC-rich sediments during the C/T OAE [e.g., Arthur et al., 1987; Parrish, 1995]. Enhanced upwelling on a global scale has been attributed to either the initiation of a deep connection between the proto-North and South Atlantic basins [Tucholke and Vogt, 1979; Summerhayes, 1987] or the increased formation of warm, saline deep water as a result of a world wide transgression [Arthur et al., 1987].

[38] As alternatives to enhanced upwelling, enhanced volcanism [Sinton and Duncan, 1997] and leaching of flooded coastal lowlands [Erbacher et al., 1996] have been suggested as sources for biolimiting nutrients during the C/T OAE. Introduction of hydrothermal Fe to the surface waters could have produced large-scale plankton blooms, but only in basins where Fe was biolimiting. This was probably not the case for the small Atlantic basins where sufficient Fe could be supplied by riverine or aeolian input from the surrounding land [Sinton and Duncan, 1997]. Leaching of nutrients from flooded coastal areas could have enhanced PP in the southern proto-North Atlantic. Oxygen utilization resulting from mineralization of enhanced OM input could even have facilitated shoaling of the chemocline. However, it is hard to imagine how enhanced PP on its own could lead to euxinic conditions in the generally well mixed upper 15 m of the water column. Thus we conclude that the cooccurrence of enhanced PP and shoaling of the chemocline in the southern part of the proto-North Atlantic was caused by enhanced upwelling providing new nutrients and sulfide-containing water to the photic zone. The enhanced production of warm, saline deep water could have led to enhanced upwelling and thereby explain the observed changes in the southern proto-North Atlantic during the C/T OAE. It is generally assumed that the rate of production of warm, saline deep water was proportional to the area of shelf flooding and that maximum flooding occurred during the C/T OAE [Arthur et al., 1987]. However, according to Haq et al. [1987] the maximum sea level high stand occurred during the early/middle Turonian rather than late Cenomanian, which would argue against a world wide transgression being the ultimate driving force for the C/T OAE.

[39] Alternatively, influx of dense saline water from a different ocean basin could have caused the inferred upwelling. Evidence for the establishment of a deep water connection between the proto-North and South Atlantic basins through the Equatorial Atlantic Gateway may come from the widespread hiatus in the open ocean sediment record of the South Atlantic, which was attributed to an erosional event near the C/T transition [Zimmerman et al., 1987]. A similar unconformity has been recognized through much of the North Atlantic and western Tethyan Seaway [de Graciansky et al., 1984]. In addition, the sedimentary record of the Equatorial Atlantic Gateway has provided evidence for erosive deep water currents, and this has been attributed to the formation of a deep connection between proto-North and South Atlantic basins during the late Cenomanian [Wagner and Pletsch, 1999]. There is also evidence from

Nd isotopes for invigorated exchange of water between the Atlantic basins and the Pacific at approximately the same time [Stille *et al.*, 1996]. The influx into the proto-North Atlantic of large amounts of highly saline, old, oxygen deficient water from the South Atlantic would have displaced deep water toward the surface [Tucholke and Vogt, 1979; Summerhayes, 1987]. As a more or less stagnant anoxic basin possibly with a partly estuarine-like circulation [Arthur *et al.*, 1987; Thierstein and Berger, 1979], the proto-North Atlantic could have acted as a nutrient trap [Summerhayes, 1987] comparable to the Holocene Black Sea and Cariaco Trench that contain high levels of dissolved nutrients such as ammonium and phosphorus [Sarmiento *et al.*, 1988; Fry *et al.*, 1991]. Thus water brought to the surface as a consequence of the influx of South Atlantic

dense water was likely extremely nutrient-rich, such that upwelling could have globally enhanced PP and caused OC burial to increase; this would have persisted until nutrients from the proto-North Atlantic and the South Atlantic were depleted. Eventually, oxygenated deep water from the eastern Southern Ocean could have entered the proto-North Atlantic during the Turonian [Poulsen, 1999] ending the deposition of OC rich sediments.

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