

Latitudinal differences in the amplitude of the OAE-2 carbon isotopic excursion: $p\text{CO}_2$ and paleo productivity

E. C. van Bentum¹, G.-J. Reichart¹, A. Forster^{2,3}, and J. S. Sinninghe Damsté^{1,2}

¹Utrecht University, Institute of Earth Sciences, P.O. Box 80.021, 3508 TA Utrecht, The Netherlands

²NIOZ Royal Netherlands Institute for Sea Research, Department of Marine Organic Biogeochemistry, P.O. Box 59, 1790 AB Den Burg (Texel), The Netherlands

³Lausner Weg 16 a, 04207 Leipzig, Germany

Correspondence to: G.-J. Reichart (reichart@geo.uu.nl)

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Abstract. A complete, well-preserved record of the Cenomanian/Turonian (C/T) Oceanic Anoxic Event 2 (OAE-2) was recovered from Demerara Rise in the southern North Atlantic Ocean (ODP site 1260). Across this interval, we determined changes in the stable carbon isotopic composition of sulfur-bound phytane ($\delta^{13}\text{C}_{\text{phytane}}$), a biomarker for photosynthetic algae. The $\delta^{13}\text{C}_{\text{phytane}}$ record shows a positive excursion at the onset of the OAE-2 interval, with an unusually large amplitude ($\sim 7\text{‰}$) compared to existing C/T proto-North Atlantic $\delta^{13}\text{C}_{\text{phytane}}$ records (3–6‰). Overall, the amplitude of the excursion of $\delta^{13}\text{C}_{\text{phytane}}$ decreases with latitude. Using reconstructed sea surface temperature (SST) gradients for the proto-North Atlantic, we investigated environmental factors influencing the latitudinal $\delta^{13}\text{C}_{\text{phytane}}$ gradient. The observed gradient is best explained by high productivity at DSDP Site 367 and Tarfaya basin before OAE-2, which changed in overall high productivity throughout the proto-North Atlantic during OAE-2. During OAE-2, productivity at site 1260 and 603B was thus more comparable to the mid-latitude sites. Using these constraints as well as the SST and $\delta^{13}\text{C}_{\text{phytane}}$ -records from Site 1260, we subsequently reconstructed $p\text{CO}_2$ levels across the OAE-2 interval. Accordingly, $p\text{CO}_2$ decreased from ca. 1750 to 900 ppm during OAE-2, consistent with enhanced organic matter burial resulting in lowering $p\text{CO}_2$. Whereas the onset of OAE-2 coincided with increased $p\text{CO}_2$, in line with a volcanic trigger for this event, the observed cooling within OAE-2 probably resulted from CO_2 sequestration in black shales outcompeting CO_2 input into the atmosphere. Together these results show that the ice-free Cretaceous world was sensitive to changes in $p\text{CO}_2$ related to perturbations of the global carbon cycle.

1 Introduction

The Mid-Cretaceous is characterized by an overall warm climate (Huber et al., 2002), punctuated by several colder periods (e.g., Bornemann et al., 2008; Forster et al., 2007). This overall warm climate probably resulted from elevated atmospheric greenhouse gas concentrations, as atmospheric $p\text{CO}_2$ levels are estimated to have been 3–8 times higher than pre-industrial values (Schlanger et al., 1987; Wilson et al., 2002; Huber et al., 1999; Berner, 1992; Barclay et al., 2010; Berner and Kothavala, 2001). The most widely accepted explanations for these high atmospheric $p\text{CO}_2$ levels are increased rates of seafloor spreading and enhanced plate margin volcanism (e.g. Turgeon and Creaser, 2008; Kerr, 1998; Blättler et al., 2011; Jenkyns, 2010).

Superimposed on this period of high atmospheric $p\text{CO}_2$ levels, several short lived episodes of increased organic matter (OM) deposition, so-called ocean anoxic events (OAEs) (Schlanger and Jenkyns, 1976; Arthur et al., 1988; Jenkyns, 1980), occurred. Generally, in marine settings this enhanced OM burial during OAEs is thought to be the result of either enhanced bioproductivity or increased anoxia or a combination of these two factors (Kuypers et al., 2002b). One of the most pronounced and widespread OAEs is OAE-2, which occurred at the Cenomanian/Turonian boundary (C/T; 93.5 Ma, Gradstein et al., 2004) and which is also known as the Cenomanian Turonian Boundary Event (CTBE). A positive carbon isotopic excursion accompanying OAE-2 has been observed both in marine carbonates and in marine and terrestrial OM (Hasegawa, 1997). This excursion has been attributed to enhanced OM burial (Arthur et al., 1988; Scholle and Arthur, 1980), because organisms preferentially take up light carbon ^{12}C leaving the remaining carbon in the ocean–atmosphere reservoir enriched in ^{13}C .

Since phytoplankton fix dissolved inorganic carbon (DIC) during photosynthesis the export of phytoplanktonic biomass to deeper water and the subsequent burial act as a biological carbon pump. Due to the exchange of CO_2 between atmosphere and ocean, this biological carbon pump effectively removes CO_2 from the atmosphere. The strength of this biological pump, therefore, modulates greenhouse climate (Royer et al., 2007; Berner, 1992; Arthur et al., 1988). During OAE-2, the increased burial of OM likely resulted in a more efficient carbon pump, lowering $p\text{CO}_2$ levels. Recently a reconstruction based on the stomatal index of land plants demonstrated that during OAE-2, two intervals of enhanced OM burial and associated $p\text{CO}_2$ decreases occurred (Barclay et al., 2010). This decrease in $p\text{CO}_2$ within OAE-2 was initially demonstrated by the observed larger amplitude of the carbon isotopic excursion when measured on organics compared to carbonates, since the rate of isotopic fractionation during carbon fixation by phytoplankton decreases at lower $p\text{CO}_2$ values (Freeman and Hayes, 1992). A reduction in $p\text{CO}_2$ of about 300 ppm during the OAE-2 interval was calculated using the isotopic values of biomarkers for photosynthetic algae and cyanobacteria (Sinninghe Damsté et al., 2008). Such $p\text{CO}_2$ reconstructions based on isotopic fractionation rely on assumptions for paleoproductivity, temperature and equilibrium CO_2 exchange between ocean water and atmosphere, and, therefore, should be considered as estimates.

A short-lived cooling within OAE-2, called the Plenus Cold Event has been observed at several locations (Forster et al., 2007; Gale and Christensen, 1996; Voigt et al., 2004; Jarvis et al., 2011). The Plenus Cold Event is probably related to lower $p\text{CO}_2$ levels at that time (Sinninghe Damsté et al., 2010), which would be in line with the two stomata based intervals of lower $p\text{CO}_2$ coinciding with maxima in the carbon isotope excursion (Barclay et al., 2010). However, this carbon isotopic record used by Barclay et al. was measured on bulk organic matter, which might have been affected by compositional changes as well. Preferably reconstructed temperature and $p\text{CO}_2$ records should be based on the same sedimentary record.

Here we compare the observed change in the compound specific isotope record of sulfur-bound phytane ($\delta^{13}\text{C}_{\text{phytane}}$) at Demerara Rise with other published $\delta^{13}\text{C}_{\text{phytane}}$ records from the proto-North Atlantic along a latitudinal gradient. Observed differences in the amplitude of the $\delta^{13}\text{C}_{\text{phytane}}$ excursion during OAE-2 are subsequently discussed in terms of variations in productivity and $[\text{CO}_2(\text{aq})]$. The boundary conditions from this comparison are used to reconstruct atmospheric $p\text{CO}_2$ levels across the OAE-2 interval.

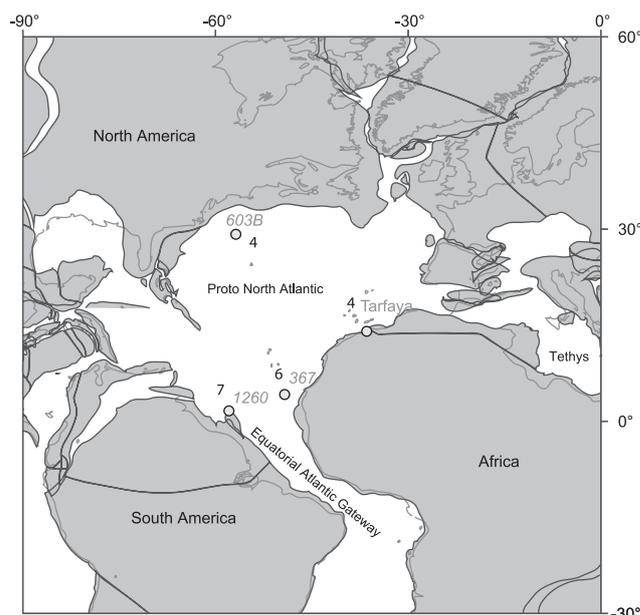


Fig. 1. Reconstruction of the proto-Atlantic Ocean during the Cenomanian/Turonian created with GEOMAR map generator; www.odsn.de/odsn/services/paleomap/paleomap.html. Circles indicate the paleo-location of the discussed records. For each site the amplitudes of the OAE-2 $\delta^{13}\text{C}_{\text{phytane}}$ excursion (in ‰) is indicated in black numbers (Site 1260, this study; Site 367, Kuypers et al., 2002b; Tarfaya, Tsikos et al., 2004; Site 603B, Sinninghe Damsté et al., 2008).

2 Setting and stratigraphy

During the Cenomanian-Turonian, Demerara Rise was situated in the tropical region of the proto-North Atlantic off the coast of Suriname (Fig. 1). As Demerara Rise was a submarine plateau at the time, the Cenomanian-Turonian sediments at ODP Site 1260 were most likely deposited at intermediate water depth, probably between 500–1500 m (Erbacher et al., 2004b; Saganuma and Ogg, 2006). The Cenomanian-Coniacian sediments of the studied sequence are mostly dark, laminated, carbonaceous, calcareous mud- to marlstones (black shales), interbedded with occasional thin calcareous layers and foraminiferal packstones (Erbacher et al., 2004a; Nederbragt et al., 2007). OM from Demerara Rise is thermally immature with organic carbon contents of up to 20% and mainly of marine origin (Erbacher et al., 2004a, b; Forster et al., 2004; Meyers et al., 2006). Since Demerara Rise experienced anoxic bottom water conditions during most of the Cenomanian – Coniacian (Erbacher et al., 2004b; Saganuma and Ogg, 2006; van Bentum et al., 2009) the OM is excellently preserved. Furthermore, in contrast to the previously drilled Demerara Rise Site 144 (DSDP), where only part of OAE-2 was recovered, the ODP Site 1260 cores span the entire OAE-2 interval (Erbacher et al., 2004a).

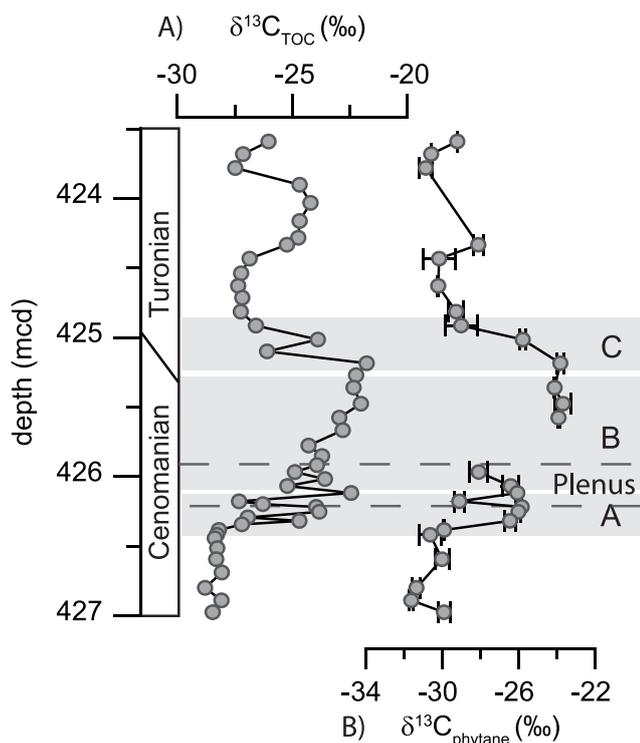


Fig. 2. Stable carbon isotope and biomarker data for OAE-2 at Demerara Rise, ODP Site 1260. **(A)** isotope values of organic carbon ($\delta^{13}\text{C}_{\text{TOC}}$) in ‰VPDB (Forster et al., 2007). **(B)** isotope values of S-bound phytane ($\delta^{13}\text{C}_{\text{phytane}}$) in ‰VPDB (this study). Grey shaded areas mark phases **(A)**, **(B)** and **(C)** of OAE-2 (see text for details). Scale in meters composite depth (mcd).

The exact stratigraphic position of OAE-2 was determined using the positive isotope excursion of organic carbon (Fig. 2a; Forster et al., 2007). This carbon isotope excursion accompanying OAE-2 can be divided into three phases (cf. Kuypers et al., 2002a; Forster et al., 2007; Tsikos et al., 2004). Phase A (426.41–426.21 mcd, Fig. 2) consists of the onset of the excursion, up to the first isotopic maximum. Phase B (426.21–425.27 mcd, Fig. 2) starts with a decline in values of the stable carbon isotopes of bulk organic carbon ($\delta^{13}\text{C}_{\text{TOC}}$), followed by a second increase and ends with an interval of steadily high $\delta^{13}\text{C}_{\text{TOC}}$ values. Finally, the gradual return to nearly pre-excursion values is part of phase C (425.27–424.85 mcd, Fig. 2). Phase A is equivalent to the “first build-up” phase of the proposed European reference section at Eastbourne (Paul et al., 1999). The decline and second increase in phase B corresponds to the “trough” and “second build-up” phase in Eastbourne, while the high values correspond to the “plateau” (Paul et al., 1999). Following earlier work (Kolonis et al., 2005; Kuypers et al., 2002b; Tsikos et al., 2004) phases A and B together are referred to as OAE-2, while phase C represents the recovery phase after the OAE-2 interval. Estimates for the duration

of OAE-2 range from 200 ky to 700 ky (Arthur and Premoli-Silva, 1982; Arthur et al., 1987; Sageman et al., 2006; Frija and Parente, 2008; Erbacher et al., 2005), however, the recent record of Voigt et al. (2008) suggests a duration of 430–445 kyr for OAE-2.

3 Materials and methods

Sediments used for this study were collected during Ocean Drilling Program (ODP) Leg 207 at Site 1260 (holes A and B) on Demerara Rise (Erbacher et al., 2004a). Biomarkers were analyzed in sediment samples previously used to determine total organic-carbon content (TOC), carbonate (CaCO_3) content, stable carbon isotopes of bulk organic carbon ($\delta^{13}\text{C}_{\text{TOC}}$, Fig. 2a) and the TEX_{86} sea surface temperature proxy (Forster et al., 2007). Sediment samples (3 to 5 g dry mass) were taken approximately every 10 cm above and below the OAE-2 black shales, while within the OAE-2 section, samples were taken every 2–5 cm. Sediments were freeze-dried, powdered and subsequently extracted with an Accelerated Solvent Extractor (Dionex) using a dichloromethane (DCM) – methanol mixture (9:1, v/v). Elemental sulfur was removed from the extracts using activated copper. The extracts were then separated into apolar and polar fractions using a column of activated alumina by elution with hexane/DCM (9:1, v/v) and DCM/methanol (1:1, v/v), respectively.

Raney Nickel desulfurization and subsequent hydrogenation (Sinninghe Damsté et al., 1993) were used to release sulfur-bound biomarkers from polar fractions. To ensure sufficient yield this process was only performed on samples that produced polar fractions weighing >5 mg. The desulfurized fraction was separated further into apolar and polar fractions. The apolar fraction obtained from the desulfurized polar fraction was separated into saturated aliphatic, unsaturated aliphatic and aromatic fractions by column chromatography using AgNO_3 -impregnated silica as the stationary phase and hexane, hexane/DCM (9:1, v/v) and hexane/DCM (1:1, v/v) as eluents.

All fractions were analyzed on a Hewlett-Packard (HP) gas chromatograph (GC) fitted with a flame ionization detector (FID) and a sulfur-selective flame photometric detector (FPD). Samples were injected on-column, on a CP-Sil 5CB fused silica column (50 m \times 0.32 mm i.d.) with helium as carrier gas set at constant pressure (100 KPa). The oven program started at 70 °C, was then heated by 20 °C min to 120 °C and finally by 4 °C/min to 320 °C and kept at this temperature for at least 15 min. To identify compounds, samples were measured on a GC-MS (Thermo Trace GC Ultra) with a mass range m/z 50–800 using a similar column and heating program as for the GC, however, with the carrier gas at constant flow.

Compound specific isotope ratios were measured using a GC isotope-ratio mass spectrometer (HP GC coupled to a

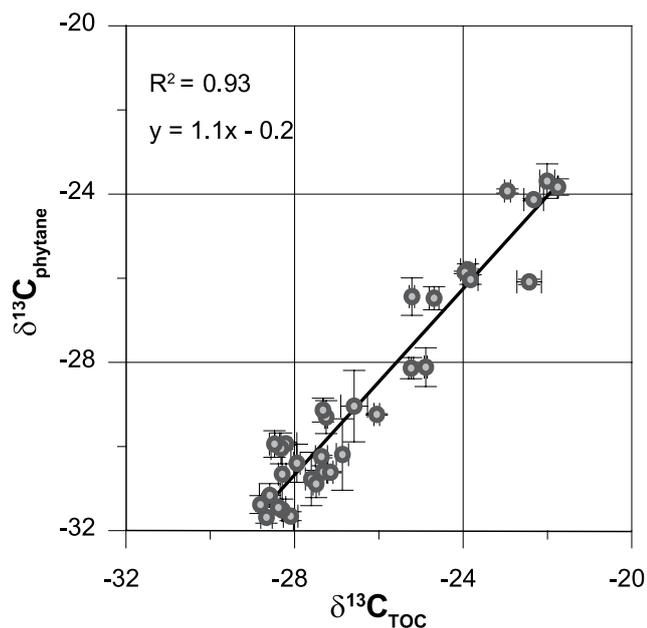


Fig. 3. Sulfur-bound $\delta^{13}\text{C}_{\text{phytane}}$ values plotted versus $\delta^{13}\text{C}_{\text{TOC}}$. Error bars are based on replicate analyses. Line indicates linear regression, with an r^2 of 0.93.

Thermo Delta-plus XL). For most GC-IRMs measurements a similar column and oven program were used as for the GC and GCMS measurements. Samples were all measured at least in duplicate and $\delta^{13}\text{C}$ values are reported in the standard delta notation against the VPDB standard. IRM performance was monitored with off line calibrated, co-injected, internal standards, standard mixtures (both in house and Schimmelmann standard mixtures B and C) and through the multiple analyses of samples. Accuracy and precision was around 0.3–0.6‰ for phytane based on multiple analyses of samples and standards.

4 Results and discussion

4.1 The OAE-2 carbon isotope excursion at Demerara Rise

The S-bound phytane carbon isotope ($\delta^{13}\text{C}_{\text{phytane}}$) record at Demerara Rise shows a clear 7‰ excursion across the OAE-2 interval (Fig. 2b). The $\delta^{13}\text{C}_{\text{phytane}}$ excursion follows the same trend as the bulk $\delta^{13}\text{C}_{\text{TOC}}$ record, except that $\delta^{13}\text{C}_{\text{TOC}}$ values are about 2‰ higher than the $\delta^{13}\text{C}_{\text{phytane}}$ values (Fig. 3a). Prior to the OAE-2 interval, $\delta^{13}\text{C}_{\text{phytane}}$ values equal approximately -31 ‰. At the onset of the OAE-2 interval, $\delta^{13}\text{C}_{\text{phytane}}$ values rapidly rise to -26 ‰, maintaining this value until 426.2 mcd (Fig. 2b). Here a sudden drop of more than 3‰ to -29 ‰ is observed, although limited to one data point. After this, values increase again to around -26 ‰ subsequently dropping to about -28 ‰. Due to the

low OM content, $\delta^{13}\text{C}_{\text{phytane}}$ could not be measured in the intercalated carbonate layer between 425.96 and 425.57 mcd. Above this carbonate layer $\delta^{13}\text{C}_{\text{phytane}}$ values remain constant, at values around -24 ‰ until 425 mcd. Above the OAE-2 interval, within the so-called phase C (cf. Kuypers et al., 2002a; Forster et al., 2007; Tsikos et al., 2004) $\delta^{13}\text{C}_{\text{phytane}}$ values gradually return to near pre-excursion values.

At Demerara Rise Site 1260, the bulk OM $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{TOC}}$) record shows a positive excursion of 6.6‰ (Forster et al., 2007) during the OAE-2 interval. The predominantly marine source of the OM and its low thermal maturity indicate that the rapid fluctuations observed in the $\delta^{13}\text{C}_{\text{TOC}}$ record during the onset phase of the OAE-2 interval (Fig. 2a) are most likely not caused by changes in OM preservation or thermal maturity but by fluctuating inputs of terrestrial OM or, more likely, changes in the composition of marine OM at this location. Carbohydrates and proteins are for instance typically enriched in ^{13}C relative to lipids. Such variability could overprint the $\delta^{13}\text{C}_{\text{TOC}}$ record (van Kaam-Peters et al., 1998; Sinninghe Damsté et al., 2002). Compound specific isotope records, however, are unaffected by changes in the composition of OM, and provide a more accurate representation of the true amplitude of the isotopic excursion during the OAE-2 interval (Fig. 2; Kuypers et al., 2002, 2004).

At Demerara Rise, most biomarkers were sequestered in the sediment in macromolecular aggregates through incorporation of inorganic sulfur species during early diagenesis (cf. Brassell et al., 1986; Sinninghe Damsté et al., 1989) as demonstrated by the high yield after desulfurization. To measure the carbon isotopic value of these biomarkers, they were released by Raney Nickel desulfurization. In this way, amongst other compounds S-bound phytane was recovered. Since S-bound phytane is derived from marine photosynthetic algae and cyanobacteria (Koopmans et al., 1999), its stable carbon isotopic composition ($\delta^{13}\text{C}_{\text{phytane}}$) represents the weighted average of $\delta^{13}\text{C}$ of marine primary producers and is not influenced by fluctuating inputs of terrestrial OM or changes in the composition of marine OM. Preservation of isotopically heavy carbohydrates through sulfuration will result in more positive $\delta^{13}\text{C}_{\text{TOC}}$ than $\delta^{13}\text{C}_{\text{phytane}}$ values (Sinninghe Damsté et al., 1998). The observed 2‰ offset between $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}_{\text{phytane}}$ (Fig. 3) can hence be explained by the isotopic heterogeneity of marine OM (Hayes, 1993; Schouten et al., 1998).

4.2 Latitudinal variations in the amplitude of the carbon isotope excursion

High atmospheric $p\text{CO}_2$ levels during the Cretaceous resulted in stronger fractionation between DIC and marine OM compared to today (Arthur et al., 1985a). Consequently, Cretaceous OM is overall depleted in $\delta^{13}\text{C}$ by 4–5‰ compared to present-day OM. Superimposed on this $\delta^{13}\text{C}$ offset a positive excursion is observed during OAE-2. The

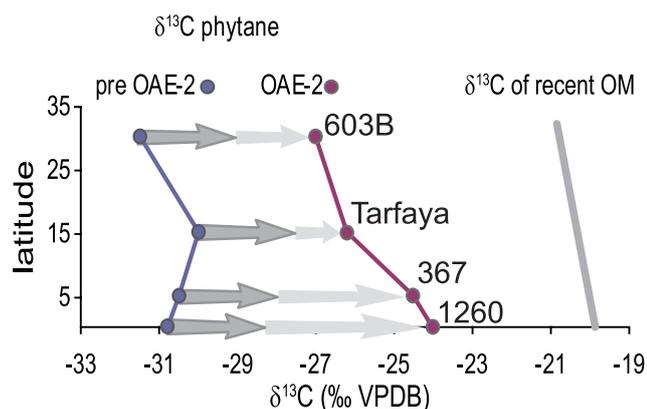


Fig. 4. Latitudinal gradient in $\delta^{13}C_{\text{phytane}}$ prior to OAE-2 and during OAE-2 (Site 1260, this study; Site 367, Kuypers et al., 2002b; Tarfaya, Tsikos et al., 2004; Site 603B, Sinninghe Damsté et al., 2008) compared to the gradient observed in the $\delta^{13}C$ of recent OM (from Rau et al., 1982). The dark grey arrows indicate the size of the $\delta^{13}C_{\text{phytane}}$ excursion that has been interpreted as the result of enhanced global OM burial, the light grey arrow represents the amount of the excursion that is due to local variations.

observed amplitude of the positive $\delta^{13}C_{\text{phytane}}$ excursion at Site 1260 is large in comparison to other known OAE-2 $\delta^{13}C_{\text{phytane}}$ records. Based on carbonate $\delta^{13}C$ records, approximately 2.5 ‰ of the OAE-2 excursion has been interpreted as the result of enhanced global OM burial, shifting the $\delta^{13}C$ of the global carbon reservoir towards more positive values (Kuypers et al., 2002b; Schlanger et al., 1987; Jenkyns et al., 1994; Arthur et al., 1984; Tsikos et al., 2004; Bowman and Bralower, 2005). The remainder of the 6.6 ‰ excursion at Demerara Rise must, therefore, be due to other processes. Possible causes include changes in $[CO_2(aq)]$, changes in the $\delta^{13}C$ of the local inorganic carbon pool, changes in inorganic carbon speciation, changes in temperature and changes in marine productivity, which influence phytoplankton growth rate and dimension (Hayes, 1993, 2001; Takahashi et al., 1991).

Carbon isotopic values of S-bound phytane from sites at four different latitudes (ODP Site 1260, this study; sites 367 and 603B, Kuypers et al., 2002b; S57 Core, Tarfaya Basin, Tsikos et al., 2004, see Fig. 1 for paleo-locations) show that the amplitude of the $\delta^{13}C_{\text{phytane}}$ OAE-2 excursion in the proto-North Atlantic decreases towards higher latitudes (Fig. 4). Prior to the OAE-2 interval, $\delta^{13}C_{\text{phytane}}$ values at the different sites are rather similar (Fig. 4), with slightly more positive values at Tarfaya and more negative values at Site 603B. During the OAE-2 excursion, all $\delta^{13}C_{\text{phytane}}$ values increased, but all to a different extent. Consequently, $\delta^{13}C_{\text{phytane}}$ decreases by about 3 ‰ from the equator to 30° N during OAE-2 (Fig. 4). With a global enrichment in the isotopic composition of the DIC reservoir of about 2.5 ‰ (indicated by the dark grey arrow in Fig. 4), the latitudinal offset between the different sites has to be explained by one of the

possible additional effects mentioned previously, influencing the carbon isotopic fractionation during algal photosynthesis.

Marine plankton in present-day oceans shows a similar, albeit more modest, decrease in $\delta^{13}C$ values with increasing latitude (Goericke and Fry, 1994; Rau et al., 1982, 1989) (Fig. 4). To compare present day $\delta^{13}C_{\text{TOC}}$ values with OAE-2 $\delta^{13}C_{\text{phytane}}$ values the trend has to be offset by 1.5 ‰ (4 ‰ more negative for the offset between total organic carbon and phytol, Schouten et al., 1998) and 2.5 ‰ towards more positive values due to the difference in the global DIC reservoir (Arthur et al., 1985b). The recent gradient in $\delta^{13}C_{\text{TOC}}$ values is thought to be primarily due to latitudinal changes in $[CO_2(aq)]$ (Goericke and Fry, 1994; Rau et al., 1982, 1989), which, in turn, is mainly controlled by the latitudinal decrease in sea surface temperatures (SST) and changes in marine primary productivity and OM remineralization. Isotopic fractionation associated with photosynthesis (ϵ_p) increases with increasing $[CO_2(aq)]$. Since CO_2 dissolves better in colder water, OM produced by phytoplankton photosynthesis in colder and thus CO_2 rich waters, is relatively ^{13}C -depleted (Rau et al., 1989, 1992).

4.3 Reconstruction of changes in $[CO_2(aq)]$ versus time and latitude within the proto-North Atlantic

Based on $\delta^{13}C_{\text{phytane}}$ records $[CO_2(aq)]$ can be calculated using reconstructed SSTs, estimates for $\delta^{13}C$ of DIC, and a factor related to primary productivity (b) (e.g., Sinninghe Damsté et al., 2008; Bice et al., 2006; Freeman and Hayes, 1992; Jasper et al., 1994). Following this approach, a theoretical gradient in $[CO_2(aq)]$ was here reconstructed by calculating $[CO_2(aq)]$ for four different locations in the northern proto-Atlantic (Table 1; Figs. 1, 4 and 5). Since the meridional SST gradient changed during OAE-2 (Sinninghe Damsté et al., 2010), we calculated $[CO_2(aq)]$ for three different time intervals with different temperature gradients: (1) prior to OAE-2 with no latitudinal temperature gradient (Fig. 5b: “pre-OAE-2” - green line), (2) during the Plenus Cold Event, within OAE-2 when there was a temperature gradient (Fig. 5b: “cooling” - light blue line) and, (3) during the maximum isotopic excursion within the OAE-2 interval when there was again no temperature gradient (Fig. 5b: “plateau” - dark blue line).

Assuming a general 4 ‰ offset ($\Delta\delta$) between phytol and biomass (Schouten et al., 1998), $\delta^{13}C_{\text{phytane}}$ values from the four different sites (Table 1) were used to estimate the isotopic composition of primary photosynthetic carbon (δ_p):

$$\delta_p = \delta_{\text{phytane}} + \Delta\delta \quad (1)$$

The isotopic composition of $CO_2(aq)$ in the photic zone (δ_d) can be calculated from the stable carbon isotopic composition of planktonic foraminifera. Since biogenic carbonates were poorly preserved in the OAE-2 sediments, the average isotopic value of foraminifera from just below the OAE-2 interval at ODP Site 1260 was used (data from Moriya

Table 1. Summary of data from the four discussed sites. Productivity estimates based on TOC contents and mass accumulation rates of organic carbon ($MAR_{C_{org}}$) in $g\ m^{-2}\ yr^{-1}$ (Forster et al., 2008; van Bentum et al., 2009) at the different sites. Photoc zone anoxia (PZA) based on the occurrence of isorenieratane or its derivatives (Site 1260, this study; Site 367, Kuypers et al., 2002b; Tarfaya, Tsikos et al., 2004; Site 603B, Sinninghe Damsté et al., 2008). Temperatures are SSTs in $^{\circ}C$ (based on: Forster et al., 2007; Sinninghe Damsté et al., 2010), isotope values of S-bound phytane ($\delta^{13}C_{phytane}$) in ‰ VPDB . (Site 1260, this study; Site 367, Kuypers et al., 2002b; Tarfaya, Tsikos et al., 2004; Site 603B, Sinninghe Damsté et al., 2008).

Site	Period	$MAR_{C_{org}}$	Productivity estimate	PZA	Temp	$\delta^{13}C_{phytane}$
603B	Pre OAE-2	0.3	Low/normal	No	39	-31.5
	Cooling	1.4	Higher	Strong	31	-29.0
	Plateau				43	-27.0
Tarfaya S57	Pre OAE-2	2	High	Occasional	39	-30.0
	Cooling	12	Even higher	More often	35	-27.5
	Plateau				43	-26.2
Senegal 367	Pre OAE-2	3	High	Occasional	39	-30.5
	Cooling	9	Even higher	More often	37	-26.5
	Plateau				43	-24.5
Demerara Rise 1260	Pre OAE-2	0.2	Normal/high	Occasional	39	-30.8
	Cooling	0.3	Normal/high	Strong	37	-26.2
	Plateau				43	-24.0

and Wilson, as in Sinninghe Damsté et al., 2008). The isotopic value of the foraminifera was corrected for calcite-carbonate enrichment according Eq. (2) (1 ‰ Romanek et al., 1992). The temperature dependent carbon isotopic fractionation ($\varepsilon_{b(a)}$) was corrected with respect to HCO_3^- according to Eq. (3) (Mook et al., 1974), with temperature (T, here equal to SST) given in K° .

$$\delta_d = \delta^{13}C_{plank.foram} - 1 + \varepsilon_{b(a)} \quad (2)$$

$$\varepsilon_{b(a)} = 24.12 - 9866/T \quad (3)$$

Based on the 2–2.5 ‰ global carbon isotope excursion in bulk carbonate (Hayes et al., 1989; Wilson et al., 2002; Tsikos et al., 2004; Jarvis et al., 2006) we assumed DIC to have been enriched by 2 ‰ during OAE-2. Although 2 ‰ is only an estimate, a different value for DIC would cause an overall shift of the reconstructions, rather than affecting differences between sites and through time. Calculating sensitivity of the equations to the input variables temperature, foraminiferal $\delta^{13}C$ and biomarker $\delta^{13}C$ demonstrated that foraminiferal $\delta^{13}C$ values overall do not appreciably impact calculated $[CO_2(aq)]$ values (Bice et al., 2006).

The photosynthetic fixation of carbon (ε_p) was subsequently determined using the following equation (Freeman and Hayes, 1992):

$$\varepsilon_p = 10^3 ((\delta_d + 1000) / (\delta_p + 1000) - 1) \quad (4)$$

ε_p was accordingly used to calculate $[CO_2(aq)]$ (Bidigare et al., 1997):

$$\varepsilon_p = \varepsilon_f - b/[CO_2(aq)] \quad (5)$$

With ε_f being the maximum isotopic fractionation associated with the photosynthetic fixation of carbon, which is 25 ‰ in the case of algae (Bidigare et al., 1997). Parameter b is related to productivity and depends on growth rate and cell dimensions (Bidigare et al., 1997; Popp et al., 1998).

From Eqs. (3) and (5) it is evident that $[CO_2(aq)]$ calculations (and subsequently pCO_2 calculations, see Eq. 6) are strongly affected by productivity (b) and SSTs (Fig. 6). Although at high (>3000 ppm) pCO_2 values ε_p has a limited sensitivity, the 6 ‰ range in ε_p used for our calculations (gray rectangle Fig. 6) results in a rather robust estimate of pCO_2 changes. Hence, we calculated three different scenarios that could potentially explain the observed latitudinal differences in the $\delta^{13}C_{phytane}$ records by changing b and SST.

4.3.1 The “constant” productivity scenario (I)

To assess the impact of productivity changes across the North Atlantic we first reconstructed the hypothetical $[CO_2(aq)]$ needed to explain the observed $\delta^{13}C$ values. For constraining SST values, a detailed reconstruction exists for sites 1260 and 367 based on TEX_{86} (Forster et al., 2007). However, no such temperature records exist for the other two sites. The latitudinal temperature gradients recently reconstructed by Sinninghe Damsté et al. (2010) show that prior to OAE-2 no appreciable latitudinal temperature gradient existed across the proto North Atlantic and thus, SSTs were likely similar for all four sites. During OAE-2 a cold interval, known as the Plenius Cold Event, occurred (Jefferies, 1962; Voigt et al., 2004; Gale and Christensen, 1996; Forster et al., 2007). At

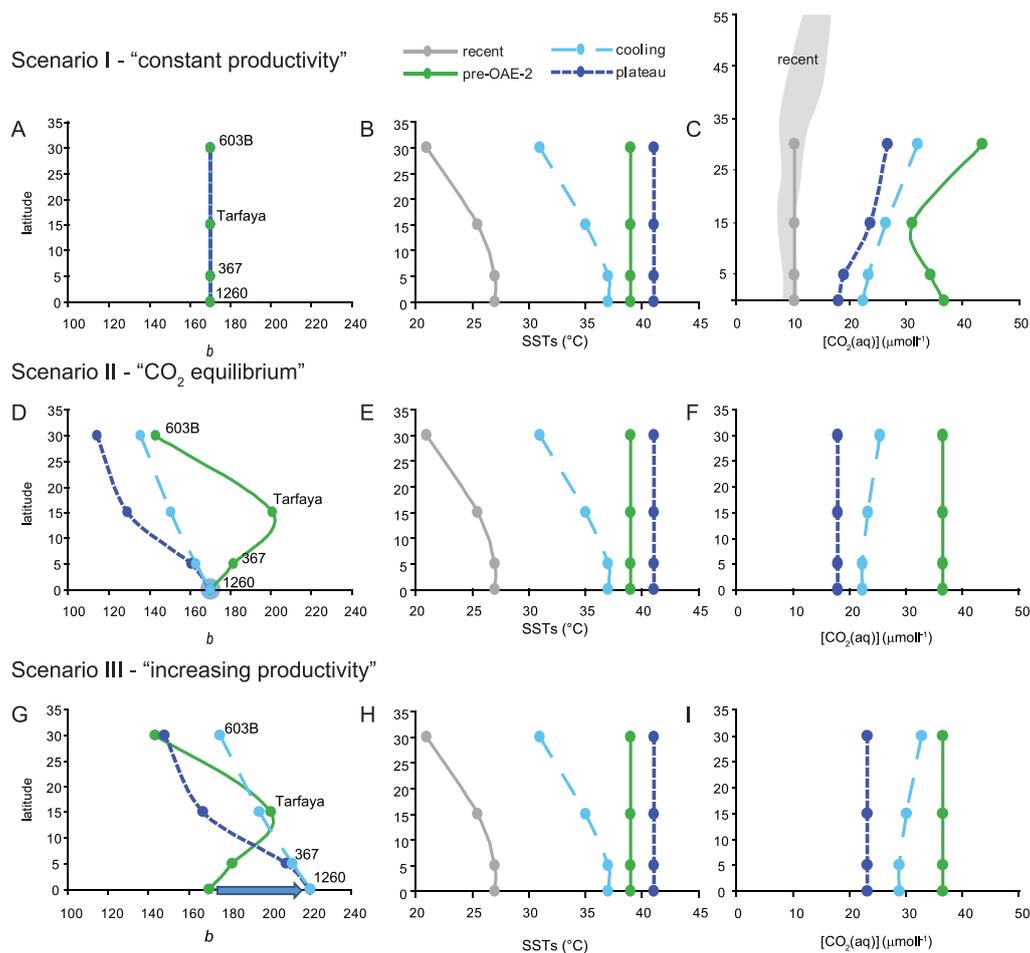


Fig. 5. Scenario (I) where $[\text{CO}_2(\text{aq})]$ is calculated using $b = 170$ (A) for all time slices. Sea surface temperatures are based on Sinninghe Damsté et al., 2010 (B). Values of $[\text{CO}_2(\text{aq})]$ in $\mu\text{mol l}^{-1}$ (C) (Gray area indicates recent values from Goericke and Fry, 1994). Scenario (II) where b is allowed to vary (D). Sea surface temperatures are based on Sinninghe Damsté et al., 2010 (E). Values of $[\text{CO}_2(\text{aq})]$ in $\mu\text{mol l}^{-1}$ (F). Scenario (III) where b is allowed to vary, with b increasing at the onset of OAE-2. (G). Sea surface temperatures are based on Sinninghe Damsté et al., 2010 (H). Values of $[\text{CO}_2(\text{aq})]$ in $\mu\text{mol l}^{-1}$ (I).

this time, temperatures were cooler in the north (Site 1276) than at the equator and a latitudinal temperature gradient was established (Sinninghe Damsté et al., 2010). During the later warmer episodes of OAE-2, the SSTs gradient was absent again in this part of the proto-North Atlantic. These temperature gradients can be used to estimate SSTs for the two other sites (Fig. 5b). Now that we have an SST estimate for all four sites we still need to restrain b .

In recent settings, b correlates positively with phosphate concentration. Since phosphate concentrations correlate with $\delta^{15}\text{N}$ values, $\delta^{15}\text{N}$ can be used to estimate b (Andersen et al., 1999). Using these correlations, b was previously estimated to have been 170 ‰ μM at Demerara Rise during the Albian-Santonian (Bice et al., 2006). This value is relatively high, but within the range of values observed today in the South Atlantic (80–250 ‰ μM) (Schulte et al., 2003 and references therein) and is in line with the reconstructed high productiv-

ity at Site 1260 (Hetzl et al., 2009). In this scenario (I), we applied this rather high b -value to all four sites (Fig. 5a).

Using this b value of 170 ‰ μM and the reconstructed temperature records $[\text{CO}_2(\text{aq})]$ was calculated (Fig. 5a–c). The latitudinal $[\text{CO}_2(\text{aq})]$ shows a strong increase towards higher latitudes during the OAE-2 interval, which is needed to explain the observed latitudinal $\delta^{13}\text{C}$ offset (both during the plateau and the cooling phase, blue lines) (Fig. 5c). Unlike the $[\text{CO}_2(\text{aq})]$ gradient observed today, the calculated $[\text{CO}_2(\text{aq})]$ before OAE-2 shows lowest values at 15 degrees north (Tarfaya Basin). Moreover, the low $[\text{CO}_2(\text{aq})]$ at Tarfaya prior to OAE-2 is in contrast to the inferred strong local upwelling conditions (Kolonic et al., 2005). Clearly latitudinal differences in sea surface productivity must have played a major role in shaping the $\delta^{13}\text{C}$ phytane gradients and it is not realistic to assume productivity was similar for all four sites.

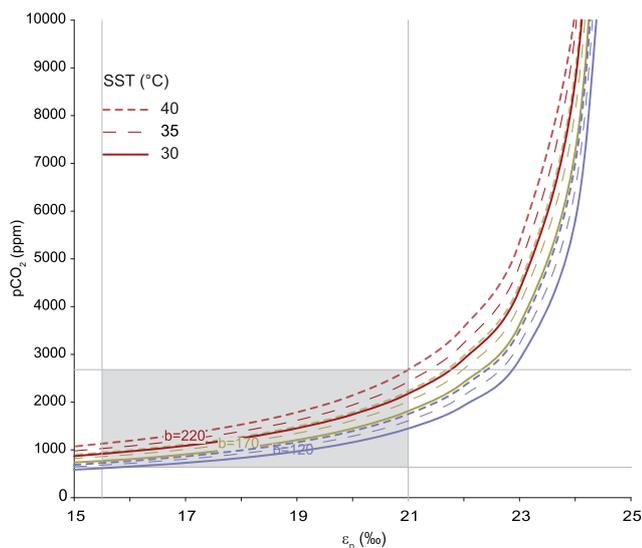


Fig. 6. The relationship between ε_p and $p\text{CO}_2$ (figure modified from: Pagani, 2002; Bijl et al., 2010). The SST ranges are based on the SSTs reconstructed with TEX₈₆ for the Cenomanian-Turonian. Values for b are based on values reconstructed for b at Demerara Rise (Bice et al., 2006) and on the values for b calculated in this paper. The grey area indicates the values for ε_p calculated across the OAE-2 interval.

4.3.2 The “CO₂ equilibrium” scenario (II)

The small differences in $[\text{CO}_2(\text{aq})]$ today across the latitudinal transect studied (see grey area in Fig. 5c), indicates that we may realistically assume atmospheric $p\text{CO}_2$ to be in equilibrium with the surface water. This was probably even more so during OAE-2, when surface waters were probably strongly stratified (van Bentum et al., 2009). When we assume atmospheric $p\text{CO}_2$ to be in equilibrium with the surface water we can recalculate $[\text{CO}_2(\text{aq})]$ and use these new $[\text{CO}_2(\text{aq})]$ values to calculate the hypothetical values for b that would explain the observed isotopic gradient. Using the solubility constant K_0 (Weiss, 1974), $p\text{CO}_2$ is related to $[\text{CO}_2(\text{aq})]$ as follows:

$$p\text{CO}_2 = [\text{CO}_2(\text{aq})]/K_0 \quad (6)$$

In this scenario (scenario II, Fig. 5d, e and f) we calculated b values for the other 3 sites, assuming that productivity at Demerara Rise remained more or less similar during all three time slices and applying the same SST gradients as in scenario I (Sinninghe Damsté et al., 2010). To explain the observed carbon isotopic trend, during the OAE-2 interval (see Fig. 4) productivity is here predicted to decrease with increasing latitude, while prior to the OAE-2 interval, b is higher at Tarfaya and Senegal Site 367 than at Demerara Rise and Site 603B. The high productivity at Tarfaya and Site 367 agrees well with previously inferred productivity values

since Tarfaya and Site 367 are thought to have experienced high productivity prior to the OAE-2 interval. (Site 1260, this study; Site 367, Kuypers et al., 2002b; Tarfaya, Tsikos et al., 2004; Site 603B, Sinninghe Damsté et al., 2008). It seems therefore that the offset in $\delta^{13}\text{C}_{\text{phytane}}$ prior to the OAE-2 interval at Tarfaya (Fig. 4) was mainly due to the higher productivity at that time when compared to the other sites.

4.3.3 The “increasing productivity” scenario (III)

Scenario II assumed that productivity remained constant at Demerara Rise across the OAE-2 interval. However, evidence from nannofossils (Hardas and Mutterlose, 2007) points to enhanced productivity during OAE-2. Changes in productivity at Demerara Rise would imply that productivity at the other sites must have changed as well in order to explain the $\delta^{13}\text{C}$ trends versus time and latitude as observed in Fig. 4.

In scenario III (Fig. 5g, h and i), we used the same SSTs as in scenarios I and II but assumed now that factor b at Demerara Rise increased from 170 to 220 at the onset of the OAE-2 (Fig. 5g). The latitudinal changes in $\delta^{13}\text{C}_{\text{phytane}}$ were subsequently used to calculate b at the other 3 sites. This would imply that b increased at most sites during OAE-2 (Fig. 5g). This scenario is in line with most existing reconstructions, as enhanced productivity is often seen as an important cause of the increased OM burial during OAE-2 (e.g. Kuypers et al., 2002b). Still, while productivity increased during OAE-2 over most of the proto-North Atlantic, this scenario suggests that productivity at Tarfaya remained similar or even decreased somewhat. In general TOC and the productivity pattern reconstructed using the ^{13}C values agree, the exception is Tarfaya, where TOC values increase over the C/T OAE interval (Tsikos et al., 2004). Still, TOC is not a direct proxy for productivity, since TOC is also effected by changes in preservation.

An important observation when comparing scenarios II and III is to what degree changes in productivity impact the reconstruction of $p\text{CO}_2$. Whereas scenario II, with productivity kept constant at Demerara Rise, suggests a decrease in $[\text{CO}_2(\text{aq})]$ between pre-OAE-2 and during the OAE-2 plateau phase of $20 \mu\text{mol l}^{-1}$ (Fig. 5f), this difference is only $15 \mu\text{mol l}^{-1}$ in scenario III (Fig. 5i), with b increasing from 170 to 220. This provides an uncertainty envelope for calculating downcore changes in $p\text{CO}_2$.

These reconstructions show that before OAE-2 productivity was probably higher at Site 367 and at Tarfaya than at Sites 1260 and 603B. During OAE-2 productivity increased in most of the proto-North Atlantic, resulting in more comparable productivity within the proto-North Atlantic.

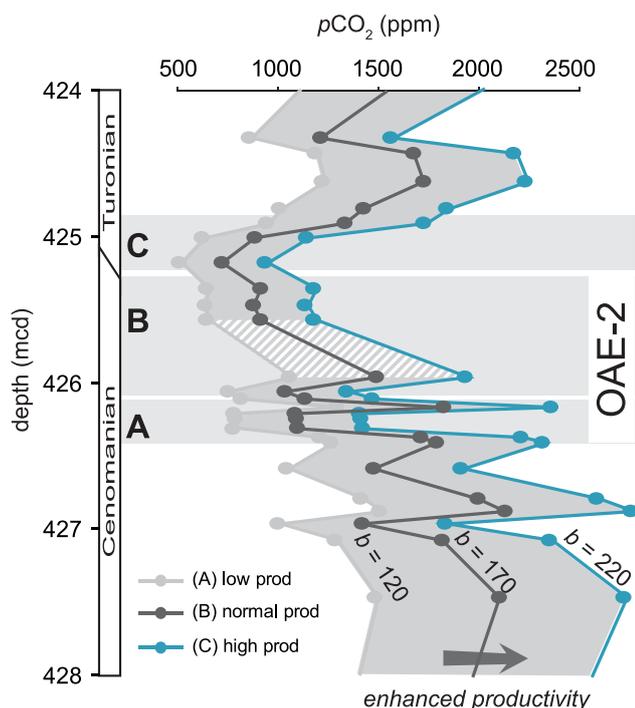


Fig. 7. Plots of $p\text{CO}_2$ levels across the OAE-2 interval at Demerara Rise Site 1260. Calculated with low ($b = 120$), normal ($b = 170$) and high ($b = 220$) productivity.

4.4 Changes in atmospheric $p\text{CO}_2$ -feedback mechanisms

Demerara Rise Site 1260 is an excellent location to reconstruct downcore $p\text{CO}_2$ as a detailed downcore SST record exists (Forster et al., 2007) and both the isotopic composition of $\text{CO}_2(\text{aq})$ in the photic zone and productivity values for b were reconstructed here (Bice et al., 2006). Inserting these values, and the $\delta^{13}\text{C}_{\text{phytane}}$ record into Eqs. (1) to (6), results in a $p\text{CO}_2$ reconstruction across the OAE-2 interval. For this reconstruction the value of the foraminiferal carbonate carbon was enriched in 0.25 ‰ increments in order to mimic the globally observed isotopic excursion more accurately. By calculating $p\text{CO}_2$ using three different values for b we generated an uncertainty envelope. Although the trends of the $p\text{CO}_2$ levels are similar for the different values of b , absolute values differ. The calculations show an initial increase in $p\text{CO}_2$ levels at the start of the OAE-2 interval and then a steady decline (Fig. 7), with two superimposed spikes of decreased $p\text{CO}_2$ concentrations. These results are similar to the $p\text{CO}_2$ reconstruction of Barclay et al. (2010), which shows two intervals of enhanced OM burial and associated $p\text{CO}_2$ decreases during OAE-2. At the onset of the OAE-2 period a temporal offset is observed between the atmospheric CO_2 increase and the subsequent rise in SSTs (Fig. 8). A similar, but reverse offset is evident for decreasing CO_2 concentrations and SSTs during the Plenus

Cold Event. Part of this offset may be due to a time-lag between the start of magmatic activity versus the onset of OAE-2 and the increased SSTs. Turgeon and Creaser (2008) postulated a time-lag of at least 9 up to 23 kyr. between the first evidence for magmatic activity and the onset of OAE-2 at ODP site 1260. Such large time-lags are not consistent with the results of OAE-2 ocean-climate modeling (Flögel et al., 2011) and are much longer than the time-lag observed in today's ocean-climate system. Probably, some part of the large temporal offset can be explained by the fact that we are comparing aquatic temperatures to atmospheric CO_2 concentrations in this study, while atmospheric temperatures are used in the ocean-climate model of Flögel et al. (2011). In our reconstruction, local SST records, which are prone to be affected by additional factors other than atmospheric CO_2 concentration, are compared with atmospheric global CO_2 signals. In addition, assumptions that are necessary for any kind of paleo-oceanic climate modeling are difficult to be constrained within the setting of the recent state of the earth's climate system (namely response times of the global ocean-climate system or "climate sensitivity"; see review by Zeebe, 2011). Additionally, currently available climate models may not be suited to resolve time-durations of just a few kyrs associated with abrupt climate changes in the past (Valdes, 2011). Nevertheless our data shows that there are clear indications that higher CO_2 levels were inducing higher SSTs (e.g. during volcanic outgassing) and that lower CO_2 levels (due to burial of OM) resulted in lower SSTs.

The tentative increase in atmospheric $p\text{CO}_2$ at the start of the OAE-2 interval (Fig. 8) corresponds with an increase in osmium and zinc concentrations (Turgeon and Creaser, 2008; van Bentum et al., 2009) in the Demerara Rise sediments. Turgeon and Creaser (2008) show that the two observed pulses in Os concentrations coincide with low Os isotope values. This, together with the similar Os pattern in two different sections, implies that the raised Os concentrations are probably due to enhanced volcanic activity. Increases in osmium and zinc concentrations are probably related to magmatic activity, and are therefore possible evidence for a pulse of magmatic activity at the start of OAE-2 (Turgeon and Creaser, 2008). Enhanced magmatic activity would result in an increase in CO_2 and since CO_2 is a greenhouse gas, this increase could be responsible for the raised SSTs at the start of the OAE-2 interval (Fig. 8). Using marine strontium isotope ratios Frija and Parente (2008) demonstrated that the increased temperatures at the onset of OAE-2 resulted in enhanced continental weathering. Although Frija and Parente explain part of the strong positive strontium isotopes shift with increased ocean stratification, a recent study using stable Ca isotopes and modeling (Blättler et al., 2011) demonstrated that a three-fold increase in weathering rates at the onset of OAE-2 would explain the total magnitude of the Sr isotope shift. The increased weathering would result in the enhanced drawdown of carbon (Walker et al., 1981), acting as a negative feedback (Fig. 9). At the same

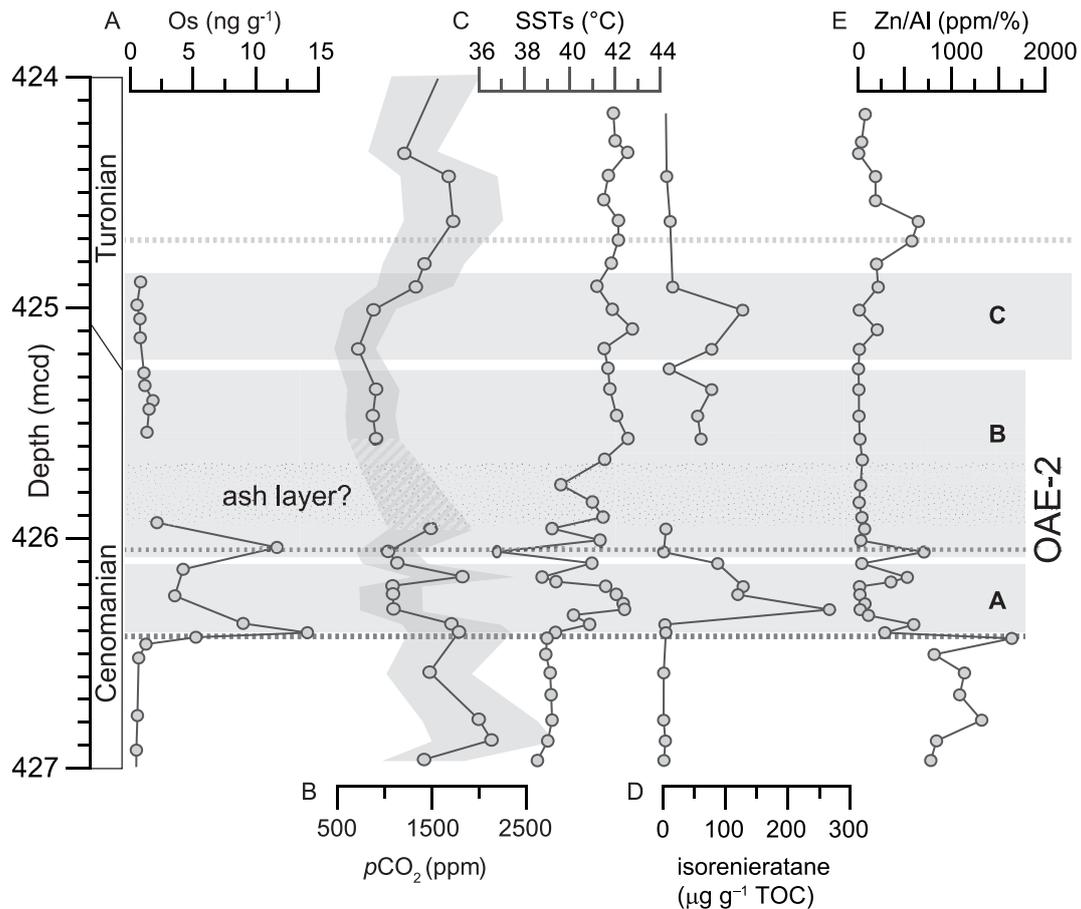


Fig. 8. (A) Osmium concentrations from Turgeon and Creaser (2008) (B) $p\text{CO}_2$ in ppm with the black line calculated using $b = 170$, the light grey area denotes the $p\text{CO}_2$ uncertainty calculated with b between 120 and 220 (C) Sea surface temperatures (SST) in $^{\circ}\text{C}$ as reconstructed by TEX_{86} (Forster et al., 2007; using the calibration of Kim et al., 2008) (D) S-bound isorenieratane concentrations in $\mu\text{g g}^{-1}$ TOC (van Bentum et al., 2009) (E) Zn/Al in (ppm %). Grey areas indicate the OAE-2 interval, stippled grey lines indicate possible magmatic pulses.

time enhanced weathering would increase nutrient input into the ocean, which probably resulted in a more efficient carbon pump. High S-bound isorenieratane concentrations (van Bentum et al., 2009) during this warmer period reveal that stratification was strong, which could be the result of the high SSTs. The increased stratification could also have decreased CO_2 outgassing from the deep ocean to the atmosphere (Toggweiler, 1999).

After a period of decreased $p\text{CO}_2$, still during the OAE-2 interval, the constant, warm temperatures became cooler and started to fluctuate (late phase A, Fig. 8c). This period of cooling is likely the equivalent of the Plenus cold event observed in NW Europe (Jefferies, 1962; Voigt et al., 2004; Gale and Christensen, 1996). This cooling has previously been attributed to a drop in atmospheric $p\text{CO}_2$ levels, which in turn was caused by enhanced carbon sequestration by OM burial (Hasegawa, 2003; Forster et al., 2007; Gale and Christensen, 1996). The cooling led to a stronger latitudinal temperature gradient in the proto-North Atlantic (Sinninghe Damsté et al., 2010) and as a result, the colder waters at

higher latitudes could have taken up more CO_2 . A drop in isorenieratane concentrations (van Bentum et al., 2009) (Fig. 8) and a possible benthic foraminifer repopulation event (Friedrich et al., 2006) reveal that stratification at Site 1260 did indeed decrease during this cooler interval.

At the start of phase B, another rise in osmium concentrations is followed by an increase in $p\text{CO}_2$. The higher atmospheric $p\text{CO}_2$ again could explain the subsequent temperature increase (lower part of phase B, Forster et al., 2007). It appears that the increase in volcanic activity counterbalances the episode of cooling during OAE-2 (see Turgeon and Creaser, 2008; van Bentum et al., 2009; Snow et al., 2005). Changes in nannofossil assemblages indicate higher productivity at Demerara Rise at this time (Hardas and Mutterlose, 2007). This increase in productivity could be related to enhanced continental weathering (e.g., Blättler et al., 2011) as a consequence of the second pulse of magmatic activity and the subsequent increase in $p\text{CO}_2$. Alternatively, enhanced ocean mixing due to cooling could have resulted in the recycling of nutrients from deeper water masses. A drop in

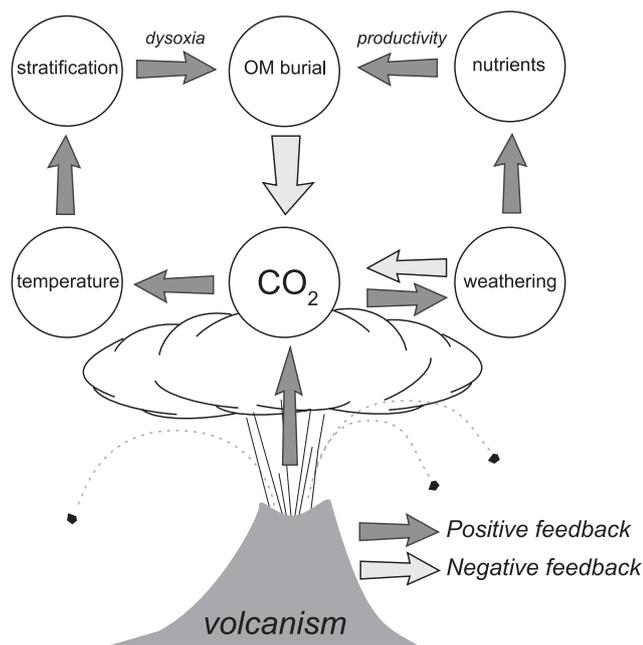


Fig. 9. Conceptual model of positive and negative feedback mechanisms of the Earth's oceans and climate system related to changes in atmospheric $p\text{CO}_2$ concentrations induced by volcanism and OM burial.

isorenieratane concentrations during phase B does reveal a decrease in stratification at this time (Fig. 8).

The carbonate rich layer found at 425 mcd has been interpreted as an ash layer (Hetzl et al., 2009). Therefore, it seems likely that an additional, second magmatic pulse occurred at this time, raising atmospheric $p\text{CO}_2$. During this warmer period, the latitudinal temperature gradient was minimized again and higher SSTs apparently intensified oceanic stratification, as both isorenieratane and chlorobactane concentrations increased again at the end of the OAE-2 period (upper part of phase B, van Bentum et al., 2009).

The reconstructed $p\text{CO}_2$ record increases after termination of the OAE-2 event. This increase is, however, not matched by increasing TEX_{86} -based SSTs. This could either be due to a local effect, increased upwelling after OAE-2 for example might have prevented SSTs at Demerara Rise from increasing. Another possible explanation for this observation could be due to the fact that temperature sensitivity to $p\text{CO}_2$ decreases at higher levels of $p\text{CO}_2$ (Fig. 6). In addition, Jarvis et al. (2011) observed that the elevated global sea level during the early Turonian could have decreased continental weathering rates, which would lead to a decrease in oceanic nutrient supplies and bioproductivity, resulting in an increase in $p\text{CO}_2$.

Climate during the Cretaceous seems to have responded quite rapidly to disequilibria in carbon cycling. Increased magmatic CO_2 outgassing resulted in an overall warmer climate, which enhanced oceanic stratification, ocean anoxia

and associated OM preservation (Fig. 9). At the same time, increased weathering due to high atmospheric $p\text{CO}_2$ resulted in enhanced nutrient input into the proto-North Atlantic, which in turn increased productivity. Furthermore, primary productivity might have removed carbon more efficiently from the atmosphere under high $p\text{CO}_2$ conditions, as suggested by mesocosm experiments showing that under higher $p\text{CO}_2$ levels more inorganic carbon was removed using less nutrients (Riebesell et al., 2007). The widespread enhanced OM burial during OAE-2 withdrew CO_2 from the atmosphere, cooling the Earth in the process (Bralower, 2008; Snow et al., 2005). At the same time, the increased ocean stratification could have decreased CO_2 outgassing from the deep ocean to the atmosphere (Toggweiler, 1999). This implies that OAEs acted as a global negative feedback mechanism in response to massive CO_2 inputs (e.g. Turgeon and Creaser, 2008; Barclay et al., 2010).

5 Conclusions

The observed positive isotope excursion of phytane ($\sim 7\%$) at Demerara Rise is unusually large compared to other C/T phytane records (3–6%) from locations in the proto-North Atlantic. Using reconstructed SST gradients we demonstrate that before OAE-2 productivity was probably higher at Site 367 and at Tarfaya than at Sites 1260 and 603B. During OAE-2 productivity increased in most of the proto-North Atlantic, resulting in more comparable productivity between the sites in the proto-North Atlantic.

Magmatic activity, atmospheric $p\text{CO}_2$ and temperature during OAE-2 are linked through both positive and negative feedback mechanisms. Enhanced magmatic episodes seem to have raised $p\text{CO}_2$, increasing global temperatures. Higher SSTs and stratification, together with enhanced nutrient input due to more intense weathering, resulted in a more efficient carbon pump as OM burial increased. Organic matter burial lowered $p\text{CO}_2$ again, cooling the greenhouse climate. When at the end of OAE-2 carbon burial rates were reduced, $p\text{CO}_2$ increased again. This implies that Cretaceous climate was sensitive to small changes in the (internal) feedbacks in the global carbon cycle.

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