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

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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 ($\sim 7\%$) 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 (Forster et al., 2007; e.g., Bornemann et al.,

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2008). 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; Berner, 1992; Huber et al., 1999; Berner and Kothavala, 2001; Wilson et al., 2002; Barclay et al., 2010).
5 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. Kerr, 1998; Turgeon and Creaser, 2008; Jenkyns Hugh, 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 oceanic anoxic events (OAEs) (Schlanger and Jenkyns, 1976; Arthur et al., 1988), 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., 15 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. This excursion has been attributed to enhanced OM burial (Arthur et al., 1988), as organism preferentially take up light carbon ^{12}C leaving the remaining carbon enriched in ^{13}C .

20 Since phytoplankton fixes dissolved inorganic carbon (DIC) during photosynthesis the export of phytoplanktic 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 (Arthur et al., 1988; Berner, 1992; Royer et al., 2007). During OAE-2, the increased burial of 25 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

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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 5 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.

10 A short-lived cooling within OAE-2, called the Plenus event has been observed at several locations (Gale and Christensen, 1996; Voigt et al., 2004; Forster et al., 2007). 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., 15 2010). However, this carbon isotopic record 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 20 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 25 interval.

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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 sandy limestones (Erbacher et al., 2004a). 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 the OAE-2 was recovered, the ODP Site 1260 cores span the entire OAE-2 interval (Erbacher et al., 2004a).

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; Tsikos et al., 2004; Forster et al., 2007). Phase A (426.41–426.21 mcd, Fig. 2a and b) consists of the onset of the excursion, up to the first isotopic maximum. Phase B (426.21–425.27 mcd, Fig. 2a and b) 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. 2a and b). 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 correspond to the “through” and “second build-up” phase in Eastbourne, while the high

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values correspond to the “plateau” (Paul et al., 1999). Following earlier work (Kuypers et al., 2002b; Tsikos et al., 2004; Kolonic et al., 2005) 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; Voigt et al., 2008), 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 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

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reconstructed by calculating $[\text{CO}_2(\text{aq})]$ 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 $[\text{CO}_2(\text{aq})]$ 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), $\delta^{13}\text{C}_{\text{phytane}}$ 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 $\text{CO}_2(\text{aq})$ 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 and Wilson, as in Sinninghe Damsté et al., 2008). The isotopic value of the foraminifera was corrected for calcite-bicarbonate 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° .

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

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

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

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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 $\delta^{13}\text{C}$ and biomarker $\delta^{13}\text{C}$ demonstrated that foraminiferal $\delta^{13}\text{C}$ values overall do not appreciably impact calculated $[\text{CO}_2(\text{aq})]$ 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 $[\text{CO}_2(\text{aq})]$ (Bidigare et al., 1997):

$$\varepsilon_p = \varepsilon_f - b/[\text{CO}_2(\text{aq})] \quad (5)$$

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 $[\text{CO}_2(\text{aq})]$ calculations (and subsequently $p\text{CO}_2$ calculations, see Eq. 6) are strongly affected by productivity (b) and SSTs (Fig. 6). Although at high (> 3000 ppmv) $p\text{CO}_2$ 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 $p\text{CO}_2$ changes. Hence, we calculated three different scenarios that could potentially explain the observed latitudinal differences in the $\delta^{13}\text{C}_{\text{phytane}}$ 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 $[\text{CO}_2(\text{aq})]$ needed to explain the observed $\delta^{13}\text{C}$ 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

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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 Plenus Cold Event, occurred (Jefferies, 1962; Gale and Christensen, 1996; Voigt et al., 2004; Forster et al., 2007). At 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 productivity 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 [CO_2 (aq)] was calculated (Fig. 5a–c). The latitudinal [CO_2 (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 [CO_2 (aq)] gradient observed today, the calculated [CO_2 (aq)] before OAE-2 shows lowest values at 15 degrees north (Tarfaya Basin). Moreover, the low [CO_2 (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.

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4.3.2 The “ CO_2 equilibrium” scenario (II)

The small differences in [CO_2 (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 [CO_2 (aq)] and use these new [CO_2 (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 [CO_2 (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 nanofossils (Hardas and Mutterlose, 2007)

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points to enhanced productivity within 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.

An important observation 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.

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 exist (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

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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.

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. 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). 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 become cooler and start to fluctuate (late phase A, Fig. 8c). This period of cooling is likely the equivalent of the Plenius cold event observed in NW Europe (Jefferies, 1962; Gale and Christensen, 1996; Voigt et al., 2004). 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 (Gale and Christensen, 1996; Hasegawa, 2003; Forster et al., 2007). The cooling lead to a stronger latitudinal

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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 CO₂. 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). 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., Jenkyns, 2010) 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 isorenieratane concentrations during phase B does reveal a decrease in stratification at this time (Fig. 8).

The carbonate rich layer found directly above the period of high SSTs has been interpreted as an ash layer (Hetzl et al., 2009). It, therefore, 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 TEX₈₆-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).

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Climate during the Cretaceous seems to have rapidly responded to disequilibria in carbon cycling. Increased magmatic CO₂ 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 CO₂ from the atmosphere, cooling the Earth in the process (Snow et al., 2005; Bralower, 2008). At the same time, the increased stratification could have decreased CO₂ 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 CO₂ inputs (Barclay et al., 2010; Turgeon and Creaser, 2008).

5 Conclusions

The observed positive isotope excursion of phytane (~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 demonstrated 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

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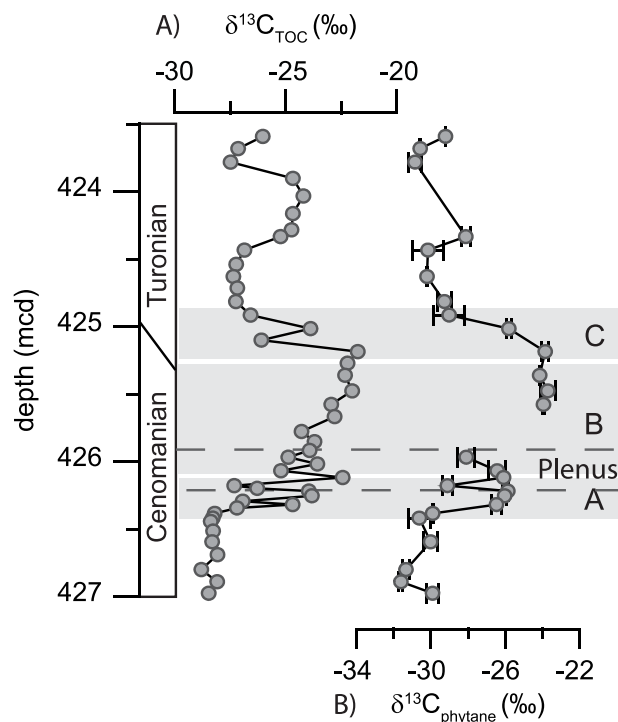


Fig. 2. Stable carbon isotope and biomarker data for OAE-2 at Demerara Rise, ODP Site 1260. **(A)** isotope values of organic carbon ($\delta^{13}\text{C}_{\text{TOC}}$) in ‰ VPDB (Forster et al., 2007). **(B)** isotope values of S-bound phytane ($\delta^{13}\text{C}_{\text{phytane}}$) in ‰ VPDB (this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

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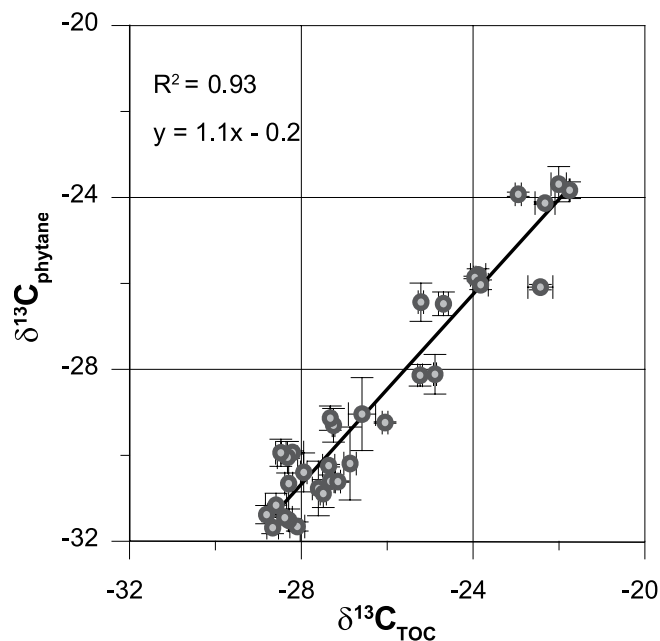


Fig. 3. Sulfur-bound $\delta^{13}\text{C}_{\text{phytane}}$ values plotted versus $\delta^{13}\text{C}_{\text{TOC}}$. Error bars are based on replicate analyses. Line indicates linear regression, with an r^2 of 0.93.

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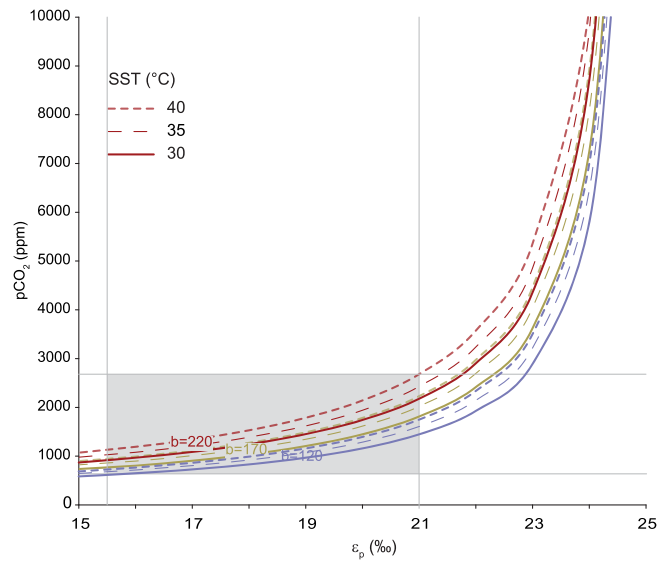


Fig. 6. The relationship between ϵ_p and $p\text{CO}_2$ (figure modified from: Pagani, 2002; Bijl et al., 2010). The SST ranges are based on the SSTs reconstructed with TEX_{86} for the Cenomanian-Turonian. Values for b are based on values reconstructed for b at Demerara Rise (Bice et al., 2006) and on the values for b calculated in this paper. The grey area indicates the values for ϵ_p calculated across the OAE-2 interval.

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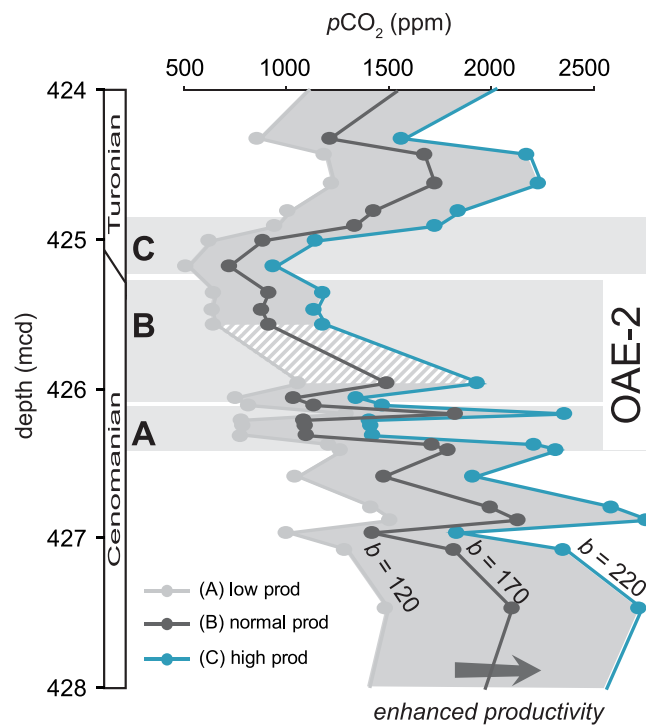


Fig. 7. Plots of $p\text{CO}_2$ levels across the OAE-2 interval at Demerara Rise Site 1260. Calculated with low ($b = 120$), normal ($b = 170$) and high ($b = 220$) productivity.

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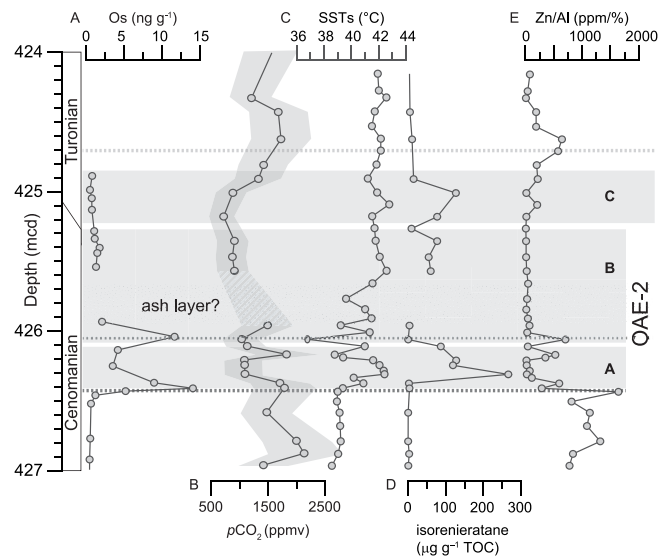


Fig. 8. (A) Osmium concentrations from Turgeon and Creaser (2008) (B) $p\text{CO}_2$ in ppm with the black line calculated using $b = 170$, the light grey area denotes the $p\text{CO}_2$ uncertainty calculated with b between 120 and 220 (C) Sea surface temperatures (SST) in $^{\circ}\text{C}$ as reconstructed by TEX86 (Forster et al., 2007; using the calibration of Kim et al., 2008) (D) S-bound isorenieratane concentrations in $\mu\text{g}/\text{TOC}$ (van Bentum et al., 2009) (E) Zn/Al in $(\text{ppm}\%^{-1})$. Grey areas indicate the OAE-2 interval, stippled grey lines indicate possible magmatic pulses.

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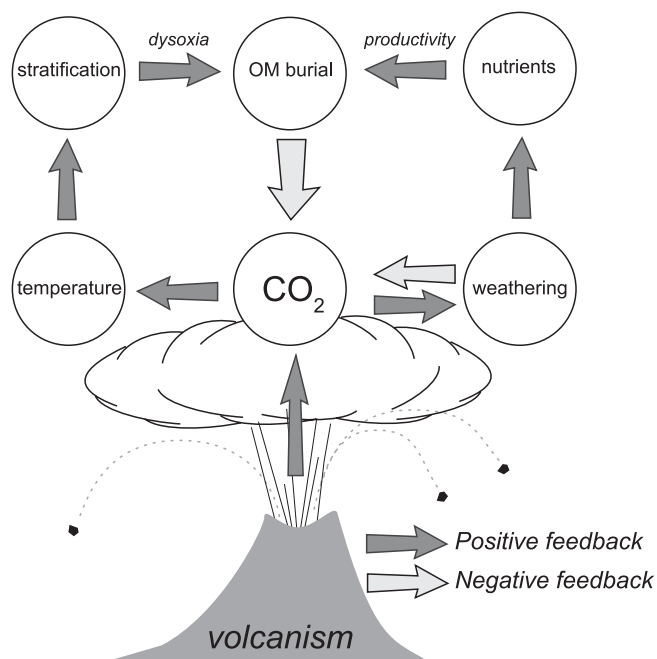


Fig. 9. Conceptual model of positive and negative feedback mechanisms of the Earth's oceans and climate system related to changes in atmospheric $p\text{CO}_2$ concentrations induced by volcanism and OM burial.

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