



## Biogeochemistry of the North Atlantic during oceanic anoxic event 2: role of changes in ocean circulation and phosphorus input

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**Abstract.** The geological record provides evidence for the periodic occurrence of water column anoxia and formation of organic-rich deposits in the North Atlantic Ocean during the mid-Cretaceous (hereafter called the proto-North Atlantic). Both changes in primary productivity and oceanic circulation likely played a role in the development of the low-oxygen conditions. Several studies suggest that an increased input of phosphorus from land initiated oceanic anoxic events (OAEs). Other proposed mechanisms invoke a vigorous upwelling system and an ocean circulation pattern that acted as a trap for nutrients from the Pacific Ocean.

Here, we use a detailed biogeochemical box model for the proto-North Atlantic to analyse under what conditions anoxia could have developed during OAE2 (94 Ma). The model explicitly describes the coupled water, carbon, oxygen and phosphorus cycles for the deep basin and continental shelves. In our simulations, we assume the vigorous water circulation from a recent regional ocean model study. Our model results for pre-OAE2 and OAE2 conditions are compared to sediment records of organic carbon and proxies for photic zone euxinia and bottom water redox conditions (e.g. isorenieratane, carbon/phosphorus ratios). Our results show that a strongly elevated input of phosphorus from rivers and the Pacific Ocean relative to pre-OAE2 conditions is a requirement for the widespread development of low oxygen in the proto-North Atlantic during OAE2. Moreover, anoxia in the proto-North Atlantic is shown to be greatly influenced by the oxygen concentration of Pacific bottom waters. In our model, primary productivity increased significantly upon the transition from pre-OAE2 to OAE2 conditions. Our model captures the regional trends in anoxia as deduced from observations, with euxinia spreading to the northern and eastern

shelves but with the most intense euxinia occurring along the southern coast. However, anoxia in the central deep basin is difficult to achieve in the model. This suggests that the ocean circulation used in the model may be too vigorous and/or that anoxia in the proto-North Atlantic was less widespread than previously thought.

### 1 Introduction

During the mid-Cretaceous, atmospheric CO<sub>2</sub>, sea surface temperatures (SSTs) and sea level were higher than at present (Freeman and Hayes, 1992; Barron et al., 1993; Herman and Spicer, 2010; Schouten et al., 2003). The geological record for this period bears evidence for several oxygen depletion events in oceanic waters (e.g. Schlanger and Jenkyns, 1976; Erbacher et al., 2004; Kuypers et al., 2004; Jenkyns, 2010). During these events, extensive black shales formed on the sea floor of the North Atlantic Basin (hereafter called the proto-North Atlantic). In some areas, biomarker abundances indicate photic zone euxinia, implying that the water column contained free sulfide from the sea floor to the base of the photic zone (Sinninghe Damsté and Köster, 1998; Kuypers et al., 2002; van Bentum et al., 2009; Hetzel et al., 2011). The most studied of these so-called oceanic anoxic events (OAEs) occurred at the Cenomanian–Turonian boundary, approximately 94 Myr before present, and is termed OAE2.

Our knowledge of OAE2 is mostly based on sediment records from the proto-North Atlantic (Jenkyns, 2010). OAE2 is characterized by a positive carbon isotope excursion detectable in both marine carbonates and organic carbon.

This excursion is related to increased burial of particulate organic carbon (POC), especially on the continental shelves along the northern, western and southern shores of the proto-North Atlantic, and in the deep waters in the south of the basin (e.g. Scholte and Arthur, 1980; Schlanger et al., 1987; Arthur et al., 1994; Sinninghe Damsté and Köster, 1998; Voigt, 2000; Bowman and Bralower, 2005). The high POC burial was likely the result of both increased primary productivity (Erbacher et al., 1996; Gale et al., 2000) and enhanced preservation of organic matter in the sediments under anoxic bottom waters (e.g. Arthur and Dean, 1988; Schlanger et al., 1987; Erbacher et al., 2005). Rates of organic matter burial were sufficiently high to lead to major atmospheric CO<sub>2</sub> drawdown, resulting in an associated short-lived cooling event (Plenus Cold Event; Gale and Christensen, 1996) during the early stage of OAE2 (Forster et al., 2007; Sinninghe Damsté et al., 2010).

Potential causes of a rise in primary productivity during OAE2 include an increased input of nutrients from land (Wagner et al., 2007; Monteiro et al., 2012), leaching of nutrients from flooded shelves (Erbacher et al., 2001; Föllmi, 1995, 1999; Handoh and Lenton, 2003) and the inflow of nutrient-rich Pacific waters (Trabucho Alexandre et al., 2010). During low-oxygen conditions, enhanced recycling of phosphorus (P) from organic matter relative to carbon could have helped to sustain the higher productivity and anoxia (Mort et al., 2007; Kraal et al., 2010b; Tsandev and Slomp, 2009; Jilbert et al., 2011). Increased upwelling of nutrient-rich waters may have been another important factor in sustaining high productivity (e.g. Parrish and Curtis, 1982; Sinninghe Damsté and Köster, 1998; Kuypers et al., 2002; Piper and Calvert, 2009). This contrasts with the traditional view that the Cretaceous ocean was more stratified than the modern ocean because of the reduced SST gradients with latitude (e.g. Schlanger and Jenkyns, 1976; Ryan and Cita, 1977; Arthur and Fischer, 1977). Recent results of several general circulation models suggest that the overturning during the mid-Cretaceous could indeed have been much more vigorous than previously thought ( $\sim 20$  instead of  $\sim 10$  Sv; 1 Sverdrup =  $10^6$  m<sup>3</sup> s<sup>-1</sup>) (e.g. Poulsen et al., 2001; Flögel et al., 2011; Topper et al., 2011). Because a vigorous circulation leads to a better ventilation of an ocean basin, bottom water anoxia in such a basin necessarily implies a high oxygen consumption. At present, it is still unclear under what conditions a vigorous circulation could have allowed the development of anoxia on the continental shelves and in the deep basin of the proto-North Atlantic.

In this study, we first describe the bathymetry and the circulation assumed for the proto-North Atlantic. We also compile and describe the published evidence for spatial trends in the occurrence of photic zone euxinia, P recycling and enhanced burial of POC in the basin prior to and during OAE2. We then present a new multi-box model of the water, carbon, phosphorus and oxygen cycles for the proto-North Atlantic. The water cycle in our model is based on the proto-North

Atlantic circulation as derived by Topper et al. (2011). With our box model, we assess under what conditions widespread anoxia could have developed in the proto-North Atlantic. In particular, we focus on the required P inputs, including the relative role of inputs of P from the Pacific Ocean and from rivers and the resulting rates of primary productivity and burial of POC. We also assess the role of a reduction in oxygen input from the Pacific Ocean and the strength of ocean circulation.

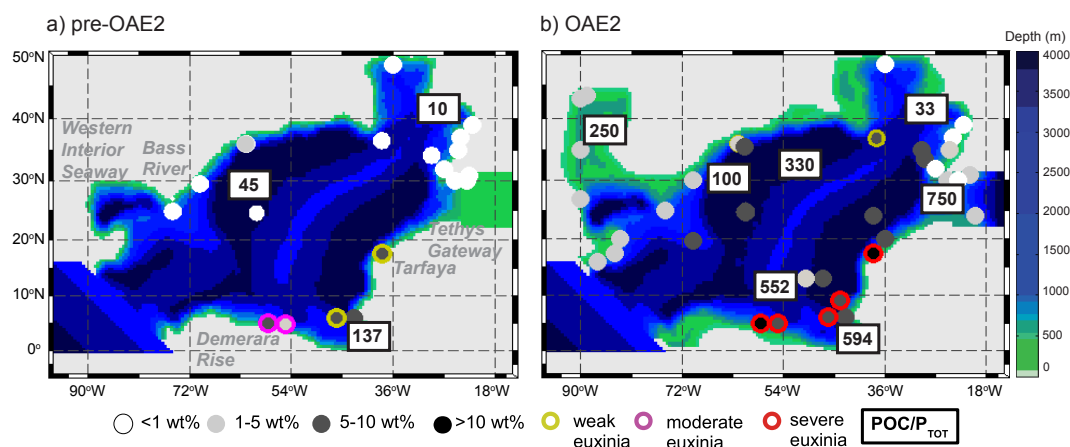
## 2 The proto-North Atlantic

### 2.1 Bathymetry and ocean circulation

Prior to and during OAE2, the proto-North Atlantic was a wide, semi-enclosed deep basin that was connected to the Pacific Ocean via the Central American Strait and to the Tethys Ocean via the Tethys gateway (Fig. 1). The bathymetry shown for both intervals (Fig. 1) has been reconstructed by Topper et al. (2011) based on earlier work by Müller et al. (2008) and Sewall et al. (2007). The total surface area of the proto-North Atlantic prior to OAE2 is  $\sim 2.2 \times 10^7$  km<sup>2</sup>. This represents only about 5% of the surface area of the global ocean in the mid-Cretaceous. In this reconstruction, the deep basin, which is up to 5 km deep, is enclosed by steep continental slopes in the north and south. A mid-oceanic ridge runs from the north-east to south-west in the deep basin. Continental shelves, in our model, account for  $\sim 13$ % of the total basin area, and their area doubled during the event due to sea level rise.

The zonal overturning during OAE2 (Fig. 2a) in the proto-North Atlantic circulation model of Topper et al. (2011) is  $\sim 20$  Sv, which is in agreement with other recent model simulations (Otto-Bliesner et al., 2002; Trabucho Alexandre et al., 2010). The meridional overturning during OAE2 in the model of Topper et al. (2011) is 15 Sv and thus is quite similar to that in the present-day Atlantic ( $\sim 18.7$  Sv; Cunningham et al., 2007). According to this model the upwelling regions were situated in the southern Atlantic to the west of the North African coast, in the northern part of the Western Interior Seaway and along the coast in the north and north-west (Fig. 2b).

Several features are not included in our bathymetry since their position and/or presence are/is not well defined. For example, in the Central American Strait, the Caribbean Plateau basalts and a shallower sill may have restricted the flow of Pacific water to the proto-North Atlantic. A narrowing of the strait could have decreased the water flux from the Pacific Ocean by as much as 16 Sv, while shallowing of the strait would have mainly affected the deep proto-North Atlantic circulation (Topper et al., 2011). Carbonate platforms in the western Tethys gateway could also have inhibited water exchange between the proto-North Atlantic and the Tethys Ocean. Restraining the Tethys gateway water exchange may



**Fig. 1.** Bathymetry of the proto-North Atlantic (a) prior to OAE2 and (b) during OAE2 as reconstructed by Topper et al. (2011). Dots indicate locations for which the sediment organic carbon contents are known, with the extent of grey to black shading of the dots being indicative of the average organic carbon content. Circles around the dots indicate where bottom waters were euxinic, with the colour scale from yellow to red being indicative of the severity and/or duration of euxinia. Average ratios of particulate organic carbon to total phosphorus ( $\text{POC}/\text{P}_{\text{TOT}}$ ) are indicated as numbers. The corresponding data and references are provided in Table S1 (Supplement). For (a), we consider the 200 kyr prior to OAE2.

have halved the strength of the zonal overturning (Topper et al., 2011). The opening of the connection between the North and the South Atlantic (e.g. Friedrich and Erbacher, 2006; Jones et al., 1995; Poulsen et al., 2003) could potentially have increased the overturning and the upwelling in the proto-North Atlantic (Topper et al., 2011).

In the model of Topper et al. (2011), the SSTs of the proto-North Atlantic in the mid-Cretaceous range from 20 to 28 °C (Supplement, Fig. S1). Proxy data for SST from oxygen isotopes and Mg/Ca ratios of planktonic foraminifera (Bice et al., 2006) and TEX<sub>86</sub> (Forster et al., 2007; Schouten et al., 2003; Sinninghe Damsté et al., 2010) indicate a significantly higher SST range from 29 to 35 °C for 0–50°N (e.g. Huber et al., 2002; Bice et al., 2003; Jenkyns et al., 2004), with a maximum SST of 42 °C at Demerara Rise (Bice et al., 2006). Oxygen isotopes from benthic foraminifera suggest that bottom water temperatures ranged from 14 to 18 °C (Voigt et al., 2004). Thus, surface and bottom waters were significantly warmer than modern North Atlantic waters. The generally observed discrepancy between temperatures in climate (e.g. Poulsen et al., 2001; Otto-Bliesner et al., 2002) and ocean models of the Cretaceous and those derived from proxy data indicates that models may not adequately capture all key aspects of the climate dynamics (Bice et al., 2006).

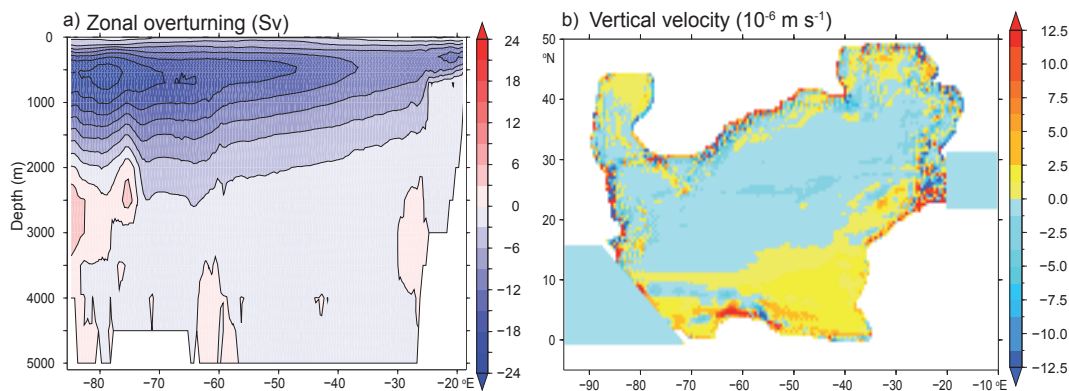
Salinity in the mid-Cretaceous as calculated with the various models is typically only 1 to 2 units higher than at present. Regional trends may, however, be quite different. For example, in the model of Topper et al. (2011), the warmest and most saline waters are located to the north of the oceanic ridge (25–35° N), whereas in the modern North Atlantic, the warmest and most saline waters are located near the Equator. In addition, the model suggests that the southern part of the

basin was well mixed, whereas the northern basin was more stratified (Fig. S1).

## 2.2 Biogeochemistry

Strong regional variations are observed in organic carbon contents in sediments deposited prior to and during OAE2 (Fig. 1). Prior to OAE2, sediment organic carbon contents greater than 5 wt% and black shale formation are observed in the southern part of the proto-North Atlantic. At one site in the northern Atlantic, organic-rich black shales alternate with green clay stones, indicating periodic bottom water anoxia (Kuypers et al., 2004). Sediments from other parts of the basin are relatively organic-lean, with concentrations below 1 wt%. During OAE2, the areas where organic-rich sediments were deposited expanded to include the northern and north-eastern coastal areas, and more continuous deposition is observed at deep basin sites. Although there is evidence for terrestrial organic material at some coastal sites (e.g. Tarfaya, the Western Interior Seaway and Hatteras Formation; Leine, 1986; Kolonic et al., 2005; Herbin et al., 1986; White and Arthur, 2006; Owens et al., 2012), most of the organic matter in the proto-North Atlantic is of marine origin.

The spatial trends in the biomarker isorenieratane, which is an indicator of photic zone euxinia, are in line with the organic carbon data (Sinninghe Damsté and Köster, 1998; Kuypers et al., 2002; van Bentum et al., 2009). Prior to OAE2, occasional photic zone euxinia occurred in the southern basin at several locations (e.g. Demerara Rise and Tarfaya). During OAE2, the euxinia intensified and spread to coastal regions in the north (Fig. 1b). However, low concentrations of isorenieratane in sediments suggest that euxinia in these northern areas was less common than in the southern



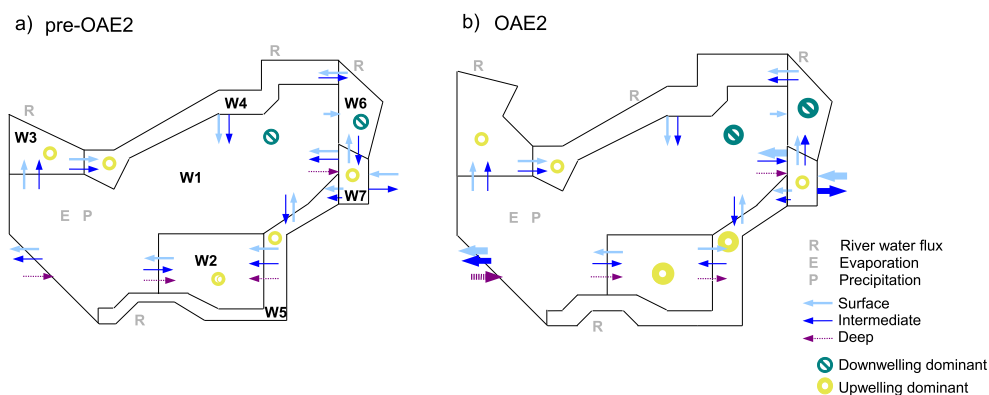
**Fig. 2.** (a) Zonal overturning for the proto-North Atlantic during OAE2 (21 Sv) as calculated by Topper et al. (2011). Contour lines are drawn every 3 Sv. Negative values are anticlockwise velocities. (b) Vertical velocities at a depth of 100 m during OAE2; the strongest upwelling region is located in the southern proto-North Atlantic, followed in decreasing order by the north-west, north-eastern and northern coast. Note that longitudes are shifted following Topper et al. (2011).

proto-North Atlantic (van Bentum et al., 2012). These results are in line with those of a recent study of iron (Fe) and molybdenum (Mo) geochemistry during OAE2 that emphasizes the heterogeneity of the depositional conditions in the proto-North Atlantic (Owens et al., 2012).

The dynamics of P in sediments strongly depend on the bottom water redox conditions. In sediments overlain by oxic bottom waters, P can be retained in bacterial cells in the form of polyphosphate (Schulz and Schulz, 2005) and can be bound to iron oxides (Slomp et al., 1996). Upon a redox change to anoxic conditions, most of this P will be released to the porewater. Release of P from organic matter relative to carbon is also enhanced (Ingall et al., 1993). Typically, only part of this released P is sequestered in authigenic P minerals. A major proportion of the P will escape to the overlying water, with the net result being increased regeneration of P from the sediment relative to carbon (e.g. Ingall et al., 1993; Jilbert et al., 2011). Sediment P speciation is not preserved during long-term burial over 94 Myr (Filippelli and Delaney, 1996; Kraal et al., 2010b). In addition, post-sampling alteration of P speciation due to exposure to oxygen is a major problem for many Cretaceous samples (Kraal et al., 2009). However, ratios of particulate organic carbon to total phosphorus ( $POC/P_{TOT}$ ) can be used as an indicator of bottom water redox conditions, with high ratios being indicative of more reducing conditions (Algeo and Ingall, 2007; Kraal et al., 2010a). Ratios of  $POC/P_{TOT}$  for pre-OAE2 and OAE2 sediments (Fig. 1) confirm the trends in organic carbon content and biomarker data. Prior to OAE2, ratios are highest in sediments of the southern proto-North Atlantic when compared to the other areas and increase in all regions during OAE2. The highest  $POC/P_{TOT}$  ratios are observed in euxinic settings. These trends have been previously interpreted to indicate a major role for P recycling in sustaining productivity during OAE2 (Mort et al., 2007; Tsandev and Slomp, 2009).

Because of the redox-dependent dynamics of P in sediments, burial fluxes of P are not a good measure of changes in inputs of P to the marine system. Besides riverine inputs, other inputs include the inflow of water from the Pacific Ocean and Tethys gateway and release of P from shelf erosion during flooding. A recent calcium isotope study suggests that continental weathering may have increased by a factor of 3 during OAE2 (Blättler et al., 2011), implying that P inputs from rivers likely also increased. Potential inputs from the Pacific Ocean are a function of the inflow and outflow of water at the Central American Strait and P concentration of the water. Sea level was rising at the onset of OAE2 and continued to rise for about 200 kyr more (Leckie et al., 2002). Bjerrum et al. (2006) estimated that the sea level rise could have led to a total release of up to 580 Tmol of dissolved P into the global ocean during the transgression.

All coastal areas where POC burial was high and the water column was at least occasionally euxinic are associated with upwelling conditions (Figs. 1 and 2b). This is in line with elevated marine productivity being responsible for increased burial of organic matter during OAE2, as suggested earlier based on organic geochemical proxies (e.g. Gale et al., 2000; Kuypers et al., 2002) and records of organic-walled dinoflagellate cysts (e.g. Pearce et al., 2009). Quantitative reconstructions of primary productivity for OAE2 rely on assumptions about the preservation of organic material in the sediment under low-oxygen conditions. Estimates of primary productivity for the southern proto-North Atlantic range from 5 to 20 mol C m<sup>-2</sup> yr<sup>-1</sup> (Sinninghe Damsté and Köster, 1998; Kuypers et al., 2002). These values are similar to those found in the open ocean in the modern Atlantic (10–15 mol C m<sup>-2</sup> yr<sup>-1</sup>; Campbell and Aarup, 1992; Marra et al., 1992; Lohrenz et al., 1992), but are low when compared to rates along the present-day north-west African coast (35–700 mol C m<sup>-2</sup> yr<sup>-1</sup>; Loyd, 1971; Lachkar and Gruber,



**Fig. 3.** Schematic showing the subdivision of the proto-North Atlantic into seven boxes (not to scale) for (a) pre-OAE2 and (b) OAE2 conditions. The symbols R, E and P indicate locations where river water fluxes, evaporation and precipitation are included in the model. Horizontal arrows indicate lateral flows of water. The regions dominated by upwelling and downwelling are also indicated. Enlarged symbols indicate a significant increase in the water flux during OAE2.

2012) and the typical range for other upwelling areas ( $16\text{--}300\text{ mol C m}^{-2}\text{ yr}^{-1}$ ; Millero, 1996; Fashman, 2003).

### 3 Model description

A multi-box model describing the coupled cycles of water, carbon, oxygen and phosphorus for the proto-North Atlantic was developed for pre-OAE2 and OAE2 conditions. Our model approach is similar to that used in other box model studies for the modern and ancient ocean (e.g. Rabouille et al., 2001; Slomp and Van Cappellen, 2007; Tsandev and Slomp, 2009). This approach involves the calculation of an initial steady state for the elemental cycles. This is followed by the parametrization of the biogeochemical processes using simple rate laws. The response of the model to perturbation is then assessed (e.g. changes in circulation, nutrient input). Here, we use the initial steady state for pre-OAE2 conditions, apply a perturbation in a model experiment and then assess the new steady state for OAE2 conditions. The water cycles for both time intervals are described below, as are the initial reservoir sizes and steady-state fluxes for the various elements for the pre-OAE2 proto-North Atlantic. The ordinary differential equations describing mass conservation are solved using R, a free software package (R Development Core team, 2006; Soetaert et al., 2010).

#### 3.1 Water cycle

The proto-North Atlantic is divided into seven boxes based on the location of upwelling and downwelling areas and the bathymetry during OAE2 (Fig. 3). We assume that the limit between the coastal and open ocean is 700 m following the pronounced change of slope in the bathymetry (dark green areas in Fig. 1). We divide the coastal ocean into five boxes (W3, W4, W5, W6 and W7) according to the upwelling/downwelling areas defined in the model of Top-

per et al. (2011). These five boxes are further divided vertically into a surface water (0 to 100 m) and shallow bottom water (100 to 700 m) box. Two open-ocean boxes (W1 and W2) are defined, according to their difference in upwelling/downwelling regime, and divided vertically into a surface (0 to 100 m), intermediate (100 to 700 m) and deep bottom water (700 to 5000 m) box. This division is used for both pre-OAE2 and OAE2 settings. This subdivision is chosen in order to capture the major ocean circulation patterns calculated by the model of Topper et al. (2011).

Reservoir sizes for the water cycle (Table S2) and vertical and horizontal water fluxes were calculated from the pre-OAE2 run and reference run for OAE2 of Topper et al. (2011). In a few cases, the exchange fluxes between the coastal and deep boxes could not be extracted from the circulation model and were calculated by assuming steady state. River fluxes are not included in the model of Topper et al. (2011) because they are not significant compared to exchange with the global ocean. Given the importance of rivers for biogeochemical processes, however, fluxes of river water to all coastal boxes were defined in our model (Fig. 3) based on modern river inputs (Gupta, 2007). We assume a slightly enhanced hydrological cycle for OAE2 (van Helmond et al., 2013) and therefore increased the water discharge into the north-western proto-North Atlantic when compared to pre-OAE2 conditions. The addition of river water fluxes required small adjustments of the water fluxes from the values of Topper et al. (2011) to maintain steady state (Table S2). Both water cycles capture the key characteristics of the upwelling regime and circulation (Fig. 3) of the ocean circulation model of Topper et al. (2011).

#### 3.2 Biogeochemical cycles

The model includes a simplified description of the carbon, phosphorus and oxygen cycles. Particulate organic carbon



**Table 1.** Mean sediment POC contents for each box, where observations have been recorded, and corresponding POC burial fluxes, rates of primary productivity and oxygen concentrations in bottom waters for pre-OAE2 conditions. The mean POC contents have been calculated from the observations shown in Fig. 1 and Table S1.

Box	Mean POC (wt%)	POC burial flux (mmol m <sup>-2</sup> yr <sup>-1</sup> )	Primary productivity (mol m <sup>-2</sup> yr <sup>-1</sup> )	Bottom [O <sub>2</sub> ] (μM)
Open ocean				
W1 (central)	~0.5	1	11	150
W2 (southern)	~5.7	9	88	127
Coastal ocean				
W3 (Western Interior)	n.a.	214	86	128
W4 (northern)	~0.5	202	81	116
W5 (southern)	4.7	485	130	30
W6 (north-eastern)	~0.1	22	9	157
W7 (Tethys gate.)	~0.5	168	67	140

n.a. = not available.

is the only carbon phase in the model. For dissolved oxygen, only changes in intermediate and deep waters are considered; that is, surface water concentrations are assumed to be in equilibrium with the atmosphere and are therefore not explicitly modelled. Phosphorus is present as particulate organic P (POP) and soluble reactive P (SRP).

Key processes in the model are primary production; remineralization; export of POC and POP; and burial of POC, POP, iron oxide-bound P (Fe-P) and authigenic carbonate fluorapatite (Ca-P) (Ruttenberg and Berner, 1993; Slomp and Van Cappellen, 2007). The exchange of solutes between boxes is coupled to the transport of water.

### 3.3 Initial conditions for pre-OAE2

Initial reservoir sizes of POC, SRP and oxygen in the water column for pre-OAE2 conditions are based on typical concentrations in the modern Atlantic Ocean (Sarmiento and Gruber, 2006) and mass balance constraints. This is a common approach when parametrizing biogeochemical ocean models for the past ocean (e.g. Van Cappellen and Ingall, 1994; Monteiro et al., 2012). Exchange of oxygen and SRP between boxes is calculated by multiplying the water fluxes by the concentration in the source reservoir.

Sediment organic carbon contents for pre-OAE2 conditions from our data compilation (Table S1) are used to qualitatively estimate the rates of burial of POC in each box (Table 1). Rates of POC burial were estimated from POC contents using typical rates of sediment accumulation for the deep sea and coastal zone (~2 g m<sup>-2</sup> yr<sup>-1</sup> for W1 and W2 and ~120 to 480 g m<sup>-2</sup> yr<sup>-1</sup> for the other boxes; Middelburg et al., 1997). Calculated rates of POC burial fall within the ranges typically observed in modern continental margin and deep-sea environments (Middelburg et al., 1997; Schulz and Zabel, 2006). Corresponding rates of primary productivity are calculated assuming a burial efficiency of 0.01 % in the open ocean and 0.3 % for coastal areas (Wollast, 2002),

except for the southern low-oxygenated coast, where we assume a burial efficiency of 0.4 %. In both the open and coastal ocean, 13 % of primary productivity is assumed to be exported from surface waters. In the open ocean, 3 % of the organic matter produced in the surface water reaches the bottom waters.

The degradation of organic matter determines the oxygen consumption in the intermediate and deep waters assuming a ratio between carbon and oxygen of 106 to 138. Surface water oxygen is assumed to be in equilibrium with the atmosphere and is not explicitly modelled. The dependency of the oxygen solubility on temperature and salinity is accounted for using the equation of Weiss (1970) as revised by Benson and Krause (1984) and temperatures and salinities from Topper et al. (2011) (Fig. S1). There is no inflow of intermediate or deep water from the Tethys gateway. However, there is an inflow of Pacific deep water, which is assumed to contain more oxygen and less SRP than modern Pacific deep water (Table 2) due to the assumed high rate of ocean circulation. Note that deep-water formation in the mid-Cretaceous took place in the North Pacific and Southern Ocean (Trabucho Alexandre et al., 2010). A high overturning is thus expected to lead to the entry of young (i.e. low in nutrient content and well oxygenated) waters into the proto-North Atlantic. Initial oxygen concentrations in the bottom water of each box calculated from the mass balance for oxygen (Table 1) are in line with observations for pre-OAE2 conditions. This indicates that our estimated values for primary productivity (and POC burial) are reasonable estimates at the given oceanic circulation.

Uptake and release of P due to primary productivity and remineralization, sinking of organic matter and the initial reservoir size of POP are calculated from the carbon cycle through the Redfield ratio (C : P ratio of 106 : 1). River inputs of SRP are calculated from the water flux and typical SRP concentrations for pre-anthropogenic rivers (Table 2). Modern values are used because little quantitative information

**Table 2.** Initial concentrations of SRP and oxygen ( $\mu\text{mol L}^{-1}$ ) in waters entering the proto-North Atlantic from the Pacific Ocean, the Tethys gateway and rivers. For comparison, concentrations in modern Pacific bottom waters and the range of SRP concentrations in pre-anthropogenic rivers are also given. SRP concentrations in rivers entering boxes W3 and W4 are within the range for the North American rivers. The SRP concentration for the riverine input in W5 is based on that of the Amazon. The low SRP input from the western river is based on climatic constraints for the mid-Cretaceous.

Ocean	Receptor	Source	[O <sub>2</sub> ]	[SRP]
Proto-North Atlantic				
	W1	Pacific bottom waters	200	1.3
	W7	Tethys gateway surface waters		0.1
	W3	North-western river		0.1
	W4	Northern river		0.6
	W5	Southern river		1.2
	W6	Western river		0.04
Modern				
		Pacific bottom waters	130 *	3 *
		Global pre-anthropogenic rivers		~0.02–9**

\* Sarmiento and Gruber, 2006; \*\* Harrison et al., 2005

about Cretaceous river flow and nutrient concentrations is available. The total river input to the proto-North Atlantic equals  $0.013 \text{ Tmol P yr}^{-1}$ , which is equivalent to 12 % of the global modern non-anthropogenic P input ( $0.11 \text{ Tmol yr}^{-1}$ ; Slomp, 2011). Under oxic conditions, the burial of authigenic Ca-P is assumed to be 50 % of the total P burial, whereas Fe-P and POP burial each account for 25 % (Ruttenberg, 1993). When oxygen is less than  $170 \mu\text{mol L}^{-1}$  (Table 1), burial of P is assumed to depend on the oxygen concentration in the bottom water. The biogeochemical conditions for OAE2 are obtained by implementing the OAE2 water cycle in the parametrized model for pre-OAE2 conditions. All reservoir sizes and fluxes are listed in Tables S3, S4 and S5.

### 3.4 Rate laws for biogeochemical processes

The process descriptions for carbon, oxygen and phosphorus cycling in the water column mostly rely on simple first-order rate expressions (Table S6) and are largely similar to those described in Slomp and Van Cappellen (2007). Here, we briefly describe the parametrization of the major processes included in the model.

Primary productivity (PP) in both the open and coastal ocean is assumed to be a function of the available soluble reactive phosphate (SRP), a first-order rate constant ( $k_{\text{PP}}$ ) and the Redfield ratio (C : P = 106 : 1):

$$\text{PP}_{\text{open/coast}} = k_{\text{PP}} \cdot \text{SRP} \cdot 106. \quad (1)$$

Degradation of organic matter under oxic conditions (CREL) is assumed to be a function of the available particulate organic carbon (POC) and a first-order rate constant ( $k_{\text{REL}}$ ):

$$\text{CREL}_{\text{open/coast}} = k_{\text{REL}} \cdot \text{POC}. \quad (2)$$

In intermediate waters that are low in oxygen, degradation of organic matter is assumed to slow down when oxygen concentrations ([O<sub>2</sub>]) are below  $1 \mu\text{mol L}^{-1}$  and to come to a halt when oxygen is exhausted:

$$\text{CREL}_{\text{inter}} = k_{\text{CREL}} \cdot \text{POC} \cdot [\text{O}_2] \text{ if } [\text{O}_2] \leq 1 \mu\text{mol L}^{-1}, \quad (3)$$

where  $k_{\text{CREL}}$  is the rate constant for remineralization of POC. This is based on observations of enhanced organic matter export in anoxic waters (Andersson et al., 2008; Middelburg and Levin, 2009).

Redox-dependent POC and P burial are implemented as described previously by Slomp and Van Cappellen (2007). Particulate organic P burial (POPBUR), in both the open and coastal ocean, depends on the export flux of POP (POPEXP) from surface waters:

$$\text{POPBUR}_{\text{open/coast}} = k_{\text{POPBUR}} \cdot \text{POPEXP} \cdot \left(0.6 + 0.4 \cdot \frac{[\text{O}_2]}{[\text{O}_2]_{\text{crit}}}\right), \quad (4)$$

where  $k_{\text{POPBUR}}$  is a rate constant for burial of exported POP and  $[\text{O}_2]_{\text{crit}}$  ( $=170 \mu\text{mol L}^{-1}$ ) is the oxygen concentration at which the burial efficiency starts to decrease. The numbers on the right-hand side of the equation are empirical and control the burial efficiency, where the coefficient of  $\frac{[\text{O}_2]}{[\text{O}_2]_{\text{crit}}}$  determines the percentage by which the burial flux is reduced under anoxic conditions.

The burial fluxes of POP and POC in low-oxygenated waters are coupled through a redox-sensitive burial ratio (C/P)<sub>burial</sub> (Van Cappellen and Ingall, 1994):

$$\text{(C/P)}_{\text{burial}} = \frac{\text{(C/P)}_{\text{oxic}} \cdot \text{(C/P)}_{\text{anoxic}}}{\frac{[\text{O}_2]}{[\text{O}_2]_{\text{crit}}} \cdot \text{(C/P)}_{\text{anoxic}} + \left(1 - \frac{[\text{O}_2]}{[\text{O}_2]_{\text{crit}}}\right) \cdot \text{(C/P)}_{\text{oxic}}}, \quad (5)$$

where (C/P)<sub>oxic</sub> and (C/P)<sub>anoxic</sub> are the end member values for POC burial under oxic and anoxic bottom waters, respectively. Here, we assume that (C/P)<sub>oxic</sub> is equal to the

**Table 3.** Summary of experiments starting from the standard run in OAE2 conditions, with the description and the total number of runs for each experiment.

Experiments	Description	No. of runs
Standard	Initial carbon, phosphorus and oxygen reservoirs with OAE2 water cycle	1
E1	Increased riverine P input	11
E2	Increased P supply from the Pacific bottom water	4
E3	Increased riverine P input and Pacific bottom water with an oxygen concentration of $130 \mu\text{mol L}^{-1}$	11 11
E4	Increased riverine P input and anoxic bottom water from the Pacific bottom water	8
E5	Increased riverine P input and reduced ocean circulation	45
E6	Weathering P supply of $0.03 \text{ Tmol yr}^{-1}$ (3 times pre-OAE2 value) erosive P input of $0.001 \text{ Tmol yr}^{-1}$ , SRP and oxygen concentrations in the Pacific bottom water of 2.9 and $130 \mu\text{mol L}^{-1}$	1
E7	As E6 but with decreased ocean circulation and oxygen concentration in Pacific bottom water	69

Redfield ratio of 106 in the open ocean and is higher in the coastal ocean at a value of 200. For  $(C/P)_{\text{anoxic}}$  we assume a value of 800 in the open ocean and 600 for the continental shelves based on a compilation of POC-to-POP burial ratios for various recent marine depositional environments (Slomp and Van Cappellen, 2007). The burial flux of POC (POCBUR) is then calculated as

$$\text{POCBUR} = \text{POPBUR} \cdot (C/P)_{\text{burial}}. \quad (6)$$

Consequently, the burial efficiency of POC from fully oxic to anoxic conditions can increase by up to a factor of  $\sim 7$  and  $\sim 3$  in the deep and coastal ocean, respectively. This is in accordance with earlier studies on enhanced preservation of POC under anoxic conditions (Hartnett et al., 1998; Reed et al., 2011).

The burial of Fe-P (FePBUR) is assumed to be linearly dependent on the oxygen concentrations, with no burial at all under anoxic conditions:

$$\text{FePBUR} = \text{FePBUR}_{\text{oxic}} \cdot \frac{[\text{O}_2]}{[\text{O}_2]_{\text{crit}}}, \quad (7)$$

where  $\text{FePBUR}_{\text{oxic}}$  is the initial burial rate in oxic conditions. Observations from recent and ancient sediments show that, under low-oxygen conditions, authigenic Ca-P formation can be limited or absent in the open and coastal ocean (Schenau and De Lange, 2000, 2001; Tamburini et al., 2002; Slomp et al., 2002, 2004; Mort et al., 2010; Kraal et al., 2010b). This is thought to occur because P escapes into the water column rather than precipitating as authigenic Ca-P when organic matter degradation occurs very close to the sediment–water interface and concentrations of iron oxides are low (e.g. Mort et al., 2010; Reed et al., 2011). The parametrization of the burial efficiency for authigenic Ca-P is similar to the parametrization in Eq. (4). Here, we assume that ocean anoxia may lead to a reduction of up to 50 % of authigenic

Ca-P formation (CaPBUR) in the open ocean and up to 82 % in the coastal areas:

$$\text{CaPBUR}_{\text{open}} = k_{\text{CaPBUR}_{\text{open}}} \cdot k_{\text{PREL}_{\text{deep}}} \cdot \left(0.5 + 0.5 \frac{[\text{O}_2]}{[\text{O}_2]_{\text{crit}}}\right), \quad (8)$$

$$\text{CaPBUR}_{\text{coast}} = k_{\text{CaPBUR}_{\text{coast}}} \cdot k_{\text{PREL}_{\text{coast}}} \cdot \left(0.18 + 0.82 \frac{[\text{O}_2]}{[\text{O}_2]_{\text{crit}}}\right), \quad (9)$$

where  $k_{\text{CaPBUR}}$  and  $k_{\text{PREL}}$  are the rate constants for authigenic Ca-P burial and remineralization of POP in bottom waters, respectively. Note that in our parametrization of Eqs. (4) and (9), the burial of POP and authigenic Ca-P is more sensitive to redox conditions than in the model of Slomp and Van Cappellen (2007). This modification allows POC to total P ratios that are in accordance with those observed in the geological record for the mid-Cretaceous (Mort et al., 2007; Algeo and Ingall, 2007; Kraal et al., 2010b).

### 3.5 Numerical experiments

For this study, we perform 7 sensitivity experiments for OAE2 conditions (E1, E2, E3, E4, E5, E6 and E7) that include from 1 to 69 runs each (Table 3). The aim of these experiments is to assess the response of dissolved oxygen in the proto-North Atlantic to changes in (1) inputs of P from rivers, (2) inputs of P and oxygen from the Pacific Ocean and (3) ocean circulation. All experiments start from the standard run, which is the new steady state that is obtained when the water cycle in the steady-state model for pre-OAE2 conditions is replaced by the water cycle for OAE2 (Table S2). The water cycle for OAE2 accounts for the rise in sea level and associated expanded continental shelves (Gale et al., 2002), increases in river flow and changes in ocean circulation. When implementing this new water cycle, the carbon, phosphorus and oxygen cycles require 10 kyr to reach a new equilibrium. The first two experiments evaluate changes in riverine P (E1)



and Pacific P (E2) supply alone. The P supply from all rivers is increased stepwise between runs following the function

$$P_{\text{river}} = 0.013n^{3.1314}, \quad (10)$$

where  $n$  is a number from 1 to 8. The concentration of P in Pacific bottom water is also incremented stepwise (E2), first by a factor of 3 to reach modern values ( $3 \mu\text{mol L}^{-1}$ , Sarmiento and Gruber, 2006) and then by an additional factor of 2.

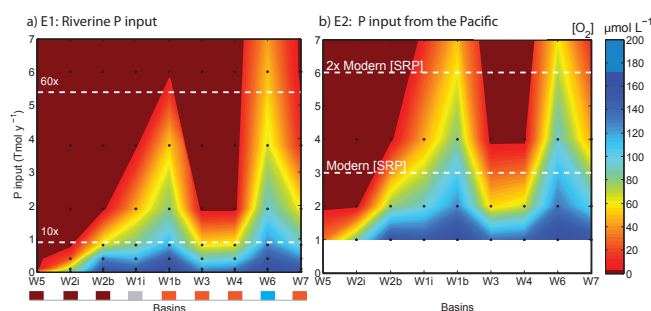
Because the oxygen concentrations in the Pacific Ocean are not well known, the third and fourth experiment assess the impact of differences in dissolved oxygen in Pacific bottom water entering the proto-North Atlantic. We use the modern oxygen concentration of Pacific bottom water of  $130 \mu\text{mol L}^{-1}$  (E3), instead of  $200 \mu\text{mol L}^{-1}$  (Table 2), and also assess the consequence of anoxic bottom waters in the Pacific Ocean (E4). In both experiments, the riverine P supply is increased as in E1. In addition, we test the sensitivity of the model to ocean circulation by decreasing the circulation in all boxes simultaneously to 90, 70, 50 and 30 % of the initial circulation, with first a constant riverine P input and then an increased P input following Eq. (10), giving a total of 45 runs (E5).

In two final experiments (E6 and E7), we assess under what conditions anoxia could have developed in the bottom waters of the central open ocean (W1) in the proto-North Atlantic. We assume a riverine input of P that is increased by a factor of 3 relative to pre-OAE2 conditions based on the increase in continental weathering as estimated from calcium isotopes by Blättler et al. (2011). We also assume an additional flux due to P erosion linked to sea level rise of  $0.001 \text{ Tmol yr}^{-1}$ . This is 16 % of the total erosion for the global ocean as estimated by Bjerrum et al. (2006) and is based on the length of the coastline of the proto-North Atlantic relative to the global coastline (Inman and Nordstrom, 1971). The SRP and oxygen concentrations in Pacific bottom water are set at 2.9 and  $130 \mu\text{mol L}^{-1}$ , respectively. While the circulation in the proto-North Atlantic and oxygen input from the Pacific Ocean are kept constant in experiment E6, in E7 we assess the sensitivity of our model to a reduction in both oxygen concentrations and ocean circulation in a total of 69 runs.

## 4 Results and discussion

### 4.1 Relation between phosphorus input and widespread anoxia

In the standard run for OAE2 conditions, primary productivity decreases in most regions because the same amount of SRP is available in a larger volume of water. For example, there is a reduction in primary production of  $\sim 30 \text{ mol m}^{-2} \text{ yr}^{-1}$  in the Western Interior Seaway (W3) and along the southern coast (W5), where the major shelf en-



**Fig. 4.** Oxygen concentrations versus riverine P input for (a) experiment E1 and (b) experiment E2. The basins of the model are W5 (southern coast), W2 (southern open ocean), W1 (central open ocean), W3 (Western Interior Seaway), W4 (northern coast), W6 (north-eastern coast) and W7 (Tethys gateway), and  $i$ ,  $b$  are the indexes for intermediate and bottom waters. The levels of P input are indicated relative to the standard run (dashed horizontal white lines, where, for example, 10× indicates a P input that is 10-fold higher than in the standard run). The colour bars below the  $x$  axis indicate the oxygen conditions for each basin as deduced from observations for OAE2 (Fig. 1b), where dark red denotes euxinic/anoxic; orange, low oxygen/anoxic; blue, low oxygen/oxic; and grey, uncertain. In (b), the P levels corresponding to the SRP concentration of the modern Pacific bottom water and its doubling are indicated (dashed horizontal white lines).

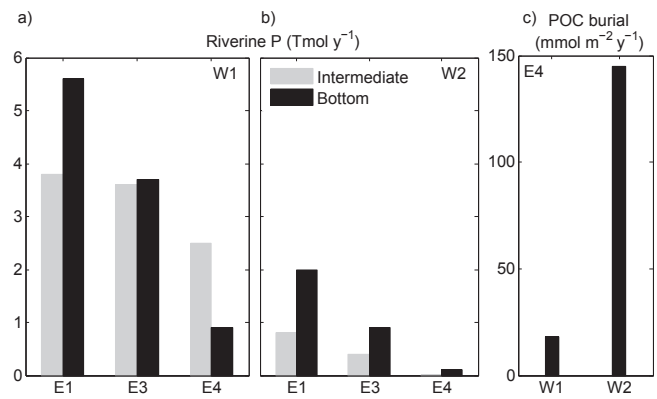
largement occurred. Due to the lower primary productivity and the enhanced ocean circulation, oxygen concentrations in most regions increase by about  $30 \mu\text{mol L}^{-1}$ . An additional P input of  $0.1 \text{ Tmol yr}^{-1}$  is required for the primary productivity to be similar to pre-OAE2 values. This P input rate is as large as the modern global riverine P input (Slomp, 2011). At this level of P input, anoxia only develops along the southern coast (W5) of the proto-North Atlantic (Fig. 4a). This is not in line with data on redox conditions for OAE2 since those suggest anoxia in the north-eastern and northern coastal areas and dysoxia or anoxia in the open ocean (Fig. 1b).

In experiment E1 (Fig. 4a), the P supply needed for the central open ocean (W1) to become anoxic is about 60 times higher than the initial riverine input of P. This P supply is much larger than what can be explained by weathering alone. Because of the larger volume of water involved, a relatively small change in the SRP concentration in Pacific bottom water has a much larger impact on SRP availability in the proto-North Atlantic than an equivalent change in river water SRP (Fig 4b). Note, however, that riverine P input enters surface waters and directly fuels primary production, whereas input from Pacific bottom water first needs to be upwelled in the southern proto-North Atlantic before it can be used by primary producers. Consequently, less total input of SRP is needed to achieve anoxia when the input comes from rivers (Fig 4). Assuming that the P supply comes from the Pacific Ocean only, SRP concentrations that are higher than modern Pacific P concentrations are required for anoxia to develop in northern waters (W3 and W4) and increase primary

productivity along the north-eastern coast (W6). Over the past 542 Myr, dissolved phosphate concentrations in sea water have remained relatively constant (Planavsky et al., 2010). Therefore, a concentration of SRP that is twice that of modern concentrations is unlikely. While increased input of SRP from the Pacific Ocean alone probably did not drive the basin to anoxia, we conclude that it may have contributed to its development.

In both experiments, the regional response of oxygen concentrations to increased P input is similar. The southern coast (W5) is most sensitive to low oxygen, followed by the intermediate and bottom waters of the southern open ocean (W2), the Western Interior Seaway (W3) and the northern coast (W4). The central open ocean (W1), the north-eastern coast (W6) and the Tethys gateway (W7) do not easily become anoxic. This regional response is also evident if we compare primary productivity and burial rates of POC and P in the various basins for E1, when, for example, assuming a riverine P input of  $0.4 \text{ Tmol yr}^{-1}$  (Table 4). This input is 4 times the modern global riverine P input and at these P levels, only the southern coast develops anoxia, with most of the proto-North Atlantic remaining well oxygenated. Rates of primary productivity and POC burial fluxes are within the typical range for modern-day environments (Table 4 and Sect. 2.2). While organic-rich sediments (e.g. black shales) can form in the box along the southern coast (W5) in this run, POC accumulation in sediments in the other basins only occurs where sufficient POC is buried, such as in the Western Interior Seaway (W3) and the northern (W4) and eastern coast (W7), in line with observations. Note that POC/ $P_{\text{TOT}}$  ratios in this run are lower than indicated by the compilation of data (Fig. 1 and Table 4), suggesting that we are not fully capturing the redox conditions as observed in the proto-North Atlantic during OAE2. However, more POC/ $P_{\text{TOT}}$  data would be required to better constrain the parametrization of the redox parameters in the proto-North Atlantic.

Besides inflow from the Pacific Ocean, other lateral flows of water and solutes are also important in controlling oxygen concentrations in the waters of the proto-North Atlantic. For example, the Western Interior Seaway (W3) is very sensitive to the bottom water oxygen concentrations in the southern open ocean (W2). Low-oxygenated waters from the southern open ocean can impact intermediate waters in the central open ocean (W1i). These low-oxygenated, but not necessarily anoxic, waters may then spread into the Western Interior Seaway. This is in line with previous work of White and Arthur (2006), suggesting that dysoxic to anoxic conditions in the seaway spread due to a flooding of preconditioned, low-oxygenated open-ocean waters. Here, we confirm that the oxygen deficit due to high productivity in a well-mixed Western Interior Seaway is difficult to sustain by riverine inputs alone (Fig. 4) and that an intermediate low-oxygenated layer in the central open ocean with an oxygen concentration as high as  $50 \mu\text{mol L}^{-1}$  greatly aids the formation of dysoxic/anoxic conditions in the seaway.



**Fig. 5.** Riverine P input required for anoxia in (a) the central open ocean (W1) and (b) the southern open ocean (W2) when the Pacific bottom water is well oxygenated (E1) and when oxygen is reduced to  $130 \mu\text{mol L}^{-1}$  (E3) and to  $0 \mu\text{mol L}^{-1}$  (E4). (c) POC burial in the open ocean when anoxic water enters the proto-North Atlantic from the Pacific Ocean (E4).

In experiment E3, where an oxygen concentration of  $130 \mu\text{mol L}^{-1}$  in the Pacific bottom water is assumed, the riverine P input required to reach anoxia in the bottom water of the central open ocean (W1b) is about 33 % less than in E1 (Fig. 5a). A similar but more pronounced trend is observed for the deep southern open ocean (W2b), where anoxia is reached with 45 % less riverine P input when compared to E1 (Fig. 5b). The central intermediate water (W1i), and consequently the Western Interior Seaway, and the other coastal areas are not significantly affected by the decreased oxygen in the Pacific bottom water (not shown), due to the high ocean ventilation above 700 m. The southern intermediate water (W2i), however, is more sensitive to this oxygen decrease because it is located in an upwelling area.

If the bottom water entering the proto-North Atlantic from the Pacific Ocean is fully anoxic (E4), the riverine P input needed to obtain anoxia in the central and southern deep waters decreases drastically. Here, the intermediate waters are also affected by the anoxic Pacific bottom waters, since surface ventilation cannot compensate for such oxygen draw-down. While the primary productivity in E4 is similar to that in E1 (not shown), POC burial is higher in the former experiment due to enhanced preservation of POC under low-oxygen conditions (Fig. 5c). These results highlight that the input of anoxic bottom water from the Pacific greatly reduces the riverine P input required to achieve anoxia in the central (W1) and southern (W2) open ocean. Observations to accurately constrain the oxygen concentration in the deep Pacific Ocean are limited. Based on results of an intermediate complexity Earth system model, Monteiro et al. (2012), however, concluded that the equatorial Pacific Ocean was most likely dysoxic/anoxic at the sea floor during OAE2. Results of a global multi-box model for the mid-Cretaceous Ocean by

**Table 4.** Primary productivity ( $\text{mol m}^{-2} \text{yr}^{-1}$ ), burial fluxes of POC, POP, Ca-P and Fe-P ( $\text{mmol m}^{-2} \text{yr}^{-1}$ ) and the molar ratios of POC/POP and POC/ $P_{\text{TOT}}$  in the different areas of the proto-North Atlantic during OAE2 conditions in experiment E1 when assuming a riverine input of  $0.4 \text{ Tmol yr}^{-1}$ . See corresponding oxygen levels in Fig. 4a.

Box	Primary productivity	POC burial flux	POP burial flux	Ca-P	Fe-P	POC/POP	POC/ $P_{\text{TOT}}$
W5	319	3777	6.29	3.78	0	600	379
W2	117	20	0.15	0.29	0.09	135	38
W1	18	3	0.03	0.05	0.01	118	33
W3	69	706	2.51	3.93	0.5	281	102
W4	55	412	1.54	2.77	1.17	267	75
W6	13	84	0.39	0.75	0.16	217	65
W7	84	368	1.55	2.75	1.09	238	68

Flögel et al. (2011) show similar oxygen conditions for the global bottom waters.

In the experiments E1 to E4, bottom water concentrations of SRP in every box increase with decreasing oxygen (not shown). This is due to the higher remineralization rate and the enhanced P recycling under low-oxygen conditions. However, in the open ocean (W1 and W2) most SRP remains below 700 m due to limited vertical transport. Above this depth, efficient transport of P to the surface does occur. At the same time, however, the efficient vertical transport leads to a high ventilation in the upper 700 m of the water column, and thus anoxic conditions in the intermediate central open ocean (W1i) are difficult to achieve.

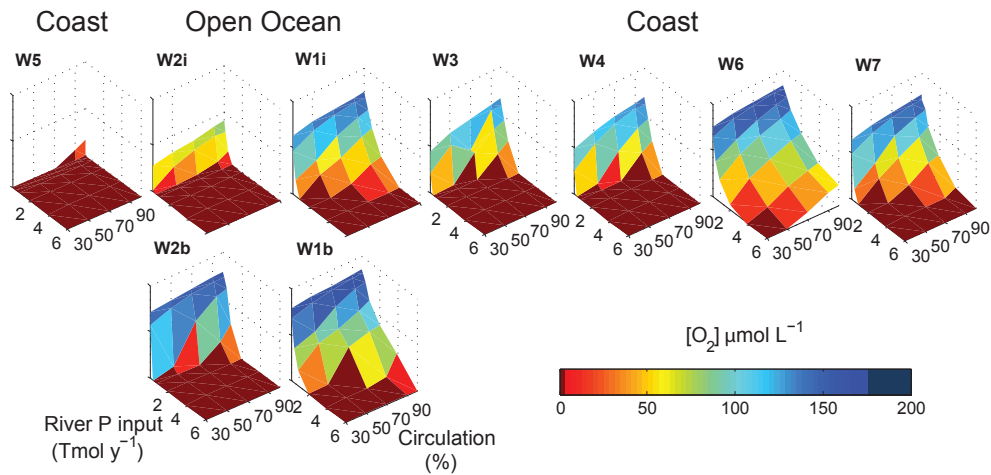
In summary, the results of the experiments show that an external P forcing is required to initiate OAE2. We observe a strong regional response of the oxygen decrease, with several coastal areas and the southern open ocean being highly sensitive to increased P input and associated primary productivity. These results also highlight that an input of anoxic Pacific deep water greatly reduces the riverine P input required to achieve anoxia in the proto-North Atlantic. However, whether the bottom waters in the Pacific Ocean were anoxic remains uncertain. From experiments E1 and E4, we conclude that, given the vigorous circulation of Topper et al. (2011), anoxia in the proto-North Atlantic, as deduced from observations (Fig. 1b), can only be reached when assuming a high external P input and inflow of low-oxygenated waters from the Pacific Ocean. Because mid-Cretaceous bottom water temperatures in the Pacific Ocean were higher than today, lower oxygen concentrations and higher rates of remineralization than in the modern Pacific Ocean are a possibility. This could have increased nutrient availability and reduced oxygen concentrations, activating enhanced P recycling. Even with this high input from the Pacific Ocean, it is difficult to obtain anoxia in the central open ocean (W1), suggesting that the ocean circulation assumed here may be too vigorous.

## 4.2 Reduced ocean circulation

The Atlantic meridional ocean circulation (Otterå and Drange, 2004) strongly depends on global continental runoff and solar irradiation. Both are not well known for the Cretaceous, which creates a major uncertainty in the calculated ocean circulation as obtained by general circulation models. The position of bathymetric features and the internal parametrization of vertical mixing creates additional uncertainty in the calculated flow in the proto-North Atlantic.

Since the circulation in the proto-North Atlantic is not well defined and the results of experiments E1 and E4 suggest it may be too vigorous, we assess the effect of a reduced circulation by decreasing all water fluxes simultaneously in steps of 20%. We also vary riverine P inputs stepwise following Eq. (10). The results show that oxygen concentrations in the proto-North Atlantic are generally not very sensitive to changes in ocean circulation alone (Fig. 6). This is because the reduced mixing not only decreases the rate of ventilation but also the upward transport of P. As a consequence, primary productivity remains too low for anoxia to develop and the positive feedback between low oxygen and increased P recycling is not initiated. An additional P supply is required in order to increase primary productivity.

Each basin responds differently to increased riverine P input, confirming again the strong regional sensitivity to oxygen depletion. The relation between decreased circulation and oxygen concentrations is non-linear when riverine P is added. This implies that P recycling increases with reduced ocean circulation, giving a positive feedback to anoxia. However, P recycling alone is not strong enough to significantly increase primary productivity. This contrasts with earlier studies of global P dynamics (e.g. Van Cappellen and Ingall, 1994; Tsandev and Slomp, 2009) that highlight that P recycling enhances primary productivity in a more stagnant ocean. This difference is related to the specifics of the circulation of the proto-North Atlantic used here, with strong ventilation of intermediate waters and exchange of water with other basins.



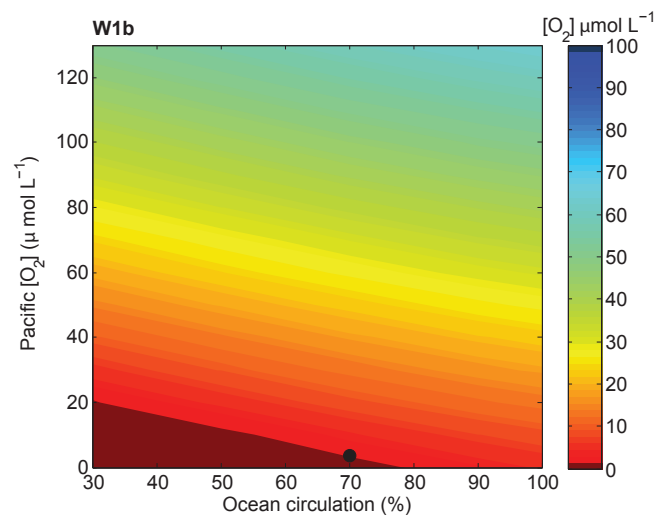
**Fig. 6.** Sensitivity of oxygen concentrations in the bottom water of each box to changes in river input of phosphorus and ocean circulation (E5). The ocean circulation is reduced from 100 to 30 %. For further details, see the text.

The results of experiment E5, where both circulation and P input are varied, show that ocean circulation plays an important role in controlling the oxygen distribution in the proto-North Atlantic and determines which regions can easily become anoxic when additional P is supplied (Fig. 6). With a decreased circulation, the riverine P input required to reach anoxia in all basins is reduced. The P supply needed to reach anoxia in the central open ocean (W1), however, is higher than what can be explained by riverine and Pacific P supply.

#### 4.3 Under what conditions could anoxia develop in the central open ocean?

When compared to the coastal areas, data on redox conditions for deep-basin sites in the central proto-North Atlantic (W1) are scarce (Fig. 1 and Table S1). However, redox proxy data, including POC/P<sub>TOT</sub> ratios and sediment trace metal contents, are available for three sites at water depths greater than 3000 m. These are all suggestive of dysoxic and anoxic conditions during deposition. The model results of Monteiro et al. (2012) also suggest that, with a meridional overturning of ~6–12 Sv, the entire deep proto-North Atlantic may have contained from 0 to 25 μmol L<sup>-1</sup> of dissolved oxygen. In our model, neither increased P supply nor a reduction in ocean circulation alone can drive the bottom waters of the central open ocean (W1) to anoxia. This suggests that multiple factors acted at the same time and that changes in the SRP and oxygen concentrations of bottom waters in the Pacific Ocean may have been important.

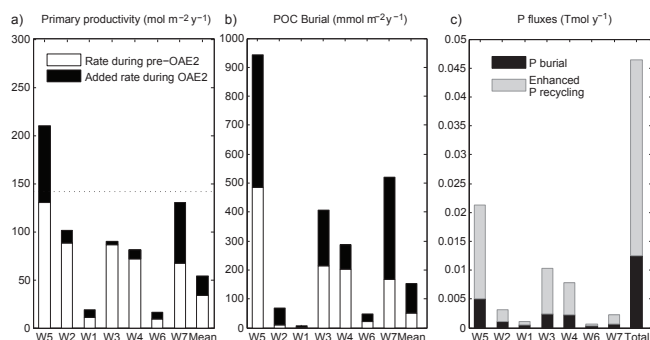
In experiment E6, such a combination of factors is assessed in an attempt to define a real scenario for OAE2. In this experiment, we assume a 3-fold increase in P input from rivers and increased erosive input of P, together amounting to 0.031 Tmol yr<sup>-1</sup>, and elevated SRP and lower oxygen concentrations in Pacific bottom waters (at 2.9 and 130 μmol L<sup>-1</sup>, respectively; Table 3 and Sect. 3.5). In this



**Fig. 7.** Sensitivity of oxygen concentrations in the bottom water of the central open ocean (W1) to ocean circulation and changes in oxygen concentrations in Pacific bottom water. The black dot indicates the run where most of the proto-North Atlantic is anoxic with an ocean circulation of 70 % (E7).

experiment, the southern open ocean and coast (W5 and W2) become anoxic, and oxygen concentrations in the Tethys gateway (W7), the Western Interior Seaway (W3) and the northern coast (W4) drop below 60 μmol L<sup>-1</sup> (not shown), in agreement with observations (Fig. 4a). However, oxygen concentrations in the bottom waters of the central open ocean (W1) remain above 60 μmol L<sup>-1</sup>.

How can anoxia in the central open ocean then be reached? As outlined earlier, there is a particularly large uncertainty in the ocean circulation and oxygen concentration of Pacific bottom waters during OAE2. In experiment E7 we therefore assess the sensitivity of oxygen in the bottom water of the



**Fig. 8.** Results for experiment E7 where ocean circulation is reduced to 70 % and the Pacific bottom water has an oxygen concentration of  $5 \mu\text{mol L}^{-1}$  (see black dot in Fig. 7) for (a) primary productivity, (b) POC burial, and (c) P burial and enhanced P recycling. As a reference, the primary productivity and POC burial prior to OAE2 are shown for each region. Mean refers to the area-weighted mean for the proto-North Atlantic. The dashed line in (a) represents the mean primary productivity in modern upwelling areas. The enhanced P recycling flux is calculated as the reduction in P burial due to increased anoxia following Eqs. (7), (9) and (8).

central open ocean (W1) to changes in both parameters using the other settings of E6. Our results indicate that, in our model setup, the bottom water in the central open ocean can only become anoxic when circulation is reduced to 80 % or less and oxygen concentrations in Pacific bottom waters are less than  $20 \mu\text{mol L}^{-1}$  (Fig. 7). The resulting primary productivity for all combinations of low oxygen in Pacific bottom waters and reduced ocean circulation is similar. As an example, we plot the rates of primary productivity and POC and P burial for a range where ocean circulation is reduced to 70 % and Pacific bottom waters are nearly anoxic (Fig. 8). In this run, anoxia is observed in the bottom waters of the central open ocean (W1b), the Tethys gateway (W7), the Western Interior Seaway (W3) and the northern coast (W4). With the given circulation, the intermediate waters of the central open ocean (W1i) remain well ventilated and thus do not develop anoxia. This is in line with the lower abundance of isorenieratane in OAE2 sediments of this part of the proto-North Atlantic (Kuypers et al., 2004; van Bentum et al., 2012). Low-oxygen conditions in bottom waters of the deep basin without a stagnant ocean circulation were also successfully reproduced using global models for mid-Cretaceous biogeochemistry by Flögel et al. (2011) and Monteiro et al. (2012). Note, however, that both models do not contain an explicit representation of the coastal zone. Also, both models do not capture the regional circulation pattern in the proto-North Atlantic in the same detail as in our model. Finally, a critical assumption in the model of Flögel et al. (2011) involves the increase in planktonic C : P ratios under high  $p\text{CO}_2$  based on mesocosm experiments.

Primary productivity increases by ca. 60 %, on average when compared to pre-OAE2 conditions. The greatest rel-

ative increase (Fig. 8a) is found along the Tethys gateway (W7), followed by the north-eastern coast (W6), the central open ocean (W1) and the southern coast (W5). Rates of POC burial also increase during OAE2 (Fig. 8b), with enhanced preservation of POC being important at all sites where bottom waters are anoxic (i.e. all basins except W6). The largest relative increase in POC burial is observed at deep basin sites in the central open ocean, which is in line with observations for OAE2 (Kuypers et al., 2004; Kraal et al., 2010b; van Bentum et al., 2012). The total burial of POC in the proto-North Atlantic calculated by our model is  $4 \text{ Tmol C yr}^{-1}$ , with most of the burial occurring in the coastal ocean (91 %). This highlights the role of burial of POC in coastal areas as the likely sink for  $\text{CO}_2$  during the cooling event in the early stage of OAE2.

Phosphorus is also mostly buried in coastal areas (Fig. 8c). Redox-dependent release of P occurs in all basins but is most pronounced in the most anoxic coastal areas. At the basin scale, redox-dependent P recycling supplies ca.  $0.03 \text{ Tmol P yr}^{-1}$ , which is equivalent to the riverine input of P. However, because of the circulation in the proto-North Atlantic, the recycled P in bottom waters does not easily reach surface waters in the open ocean. Enhanced P recycling is important in the coastal ocean, however, especially in the southern coastal area (W5).

## 5 Conclusions

Our data compilation highlights the strong regional variability in ocean biogeochemistry in the proto-North Atlantic during OAE2. While bottom waters in the southern coastal ocean were already largely anoxic and euxinic prior to OAE2, the euxinia intensified and spread to the southern open ocean and northern coastal areas during the event. However, bottom waters in the north-eastern coastal areas remained oxic. The scarce data for redox conditions in the central open ocean are indicative of dysoxic and anoxic bottom waters, but the duration and intensity are not well constrained.

Our multi-box model for the proto-North Atlantic captures the observed regional trends in redox conditions in coastal and open-ocean waters during OAE2. High inputs of phosphorus from rivers and the Pacific Ocean are needed to achieve widespread anoxia when assuming a vigorous ocean circulation. Low-oxygen conditions in Pacific bottom waters are an additional requirement. In our model, anoxia in the bottom waters of the central open ocean in the proto-North Atlantic can only be reached if ocean circulation is reduced. This implies that the ocean circulation was less vigorous than both the modern one and the circulation suggested in various recent model studies for the Cretaceous ocean. Alternatively, the bottom waters in the central open ocean may not have been generally anoxic. Additional geochemical analyses of sediments from the deep sea of the proto-North



Atlantic are required to further constrain the redox conditions in the basin. Future work should also concentrate on the development and application of 3-D biogeochemical models for the proto-North Atlantic that include sediment processes and coastal zone dynamics.

Our model results suggest that both enhanced primary productivity and preservation of organic carbon under anoxia contribute to the enhanced organic carbon burial in the proto-North Atlantic, with their relative role varying regionally. Our study also highlights the importance of the continental shelves for the burial of organic carbon and phosphorus during OAE2.

**Supplementary material related to this article is available online at <http://www.biogeosciences.net/11/977/2014/bg-11-977-2014-supplement.pdf>.**

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