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The Global Marine Phosphorus Cycle: Response to Climate Change and Feedbacks on Ocean Biogeochemistry

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The Global Marine Phosphorus Cycle: Response to Climate Change and Feedbacks on Ocean Biogeochemistry

De mondiale fosfaatcyclus in de oceaan: de rol van klimaatverandering
en terugkoppelingen op de mariene biogeochemie

(met een samenvatting in het Nederlands)

PROEFSCHRIFT

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Promotor: prof. dr. P. Van Cappellen

Co-promotor: dr. ir. C. P. Slomp

It’s not easy being green.

- Kermit the Frog

посветено на Юлиян, дядо Васко, дядо Здравко и баба Фрида

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1

Introduction and thesis outline

1.1 General background

All life forms require phosphorus (P) in the form of phosphate – PO_4^{3-}. It is an essential component of living tissue, and is required for the formation of the nucleic acids RNA and DNA and to give structure to cellular membranes (phospholipids) (Jahnke, 1992). It also participates in cellular metabolism, through the energy carrying molecule adenosine triphosphate (ATP). Phosphate, in the form of hydroxyapatite, makes our bones and teeth strong. Life forms have depended on phosphorus for essential life processes and structures since they appeared on Earth (Nealson and Rye, 2004).

Yet, despite its critical role, phosphorus's biological availability in earth surface environments is rather limited. Only the eleventh most abundant element in the Earth's crust – at 0.09 wt% – it is liberated from rocks primarily by weathering processes (Föllmi, 1996) and then often transforms into recalcitrant, non-bioavailable form. (Ruttenberg, 2003; Benitez-Nelson, 2000; Filippelli, 2008). That is why every year, countries like China, Morocco and the United States mine millions of tones of phosphorus to turn into fertilizer that is then used to stimulate plant growth (Gilbert, 2009). It is also the reason why the abundance and bioavailability of phosphorus on land and in the oceans is of great interest to the Earth Sciences.

1.2 The marine phosphorus cycle

Rivers are the major source of phosphorus to the ocean (Figure 1.1), though most of that is in particulate, non-bio-available, form (Harrison et al., 2010; Beusen et al., 2005; Ruttenberg, 2003). Phosphorus is also transported through the atmosphere as dust, primarily as mineral aerosols (Mahowald et al., 2008). Atmospheric P inputs accounts for less than 10 % of the continental P supply to the oceans and much of it is inert (Graham and Duce, 1979, 1982). As a consequence, dust P is only important for ocean biogeochemistry in selected areas, such as oligotrophic open ocean regions far away from river inputs. Groundwater is a poorly documented vector of P into the oceans. While it sometimes plays a role at the local scale, it is unlikely to be important as a source of P at the global scale (Slomp and Van Cappellen, 2004; Slomp, in press).

Coastal waters receive and retain a significant proportion of the incoming P from land. They are a major filter of incoming nutrients due to their high productivity and short water column which allow for less decay prior to sedimentation (Ruttenberg, 1993, 2003; Benitez-Nelson, 2000). The capacity of

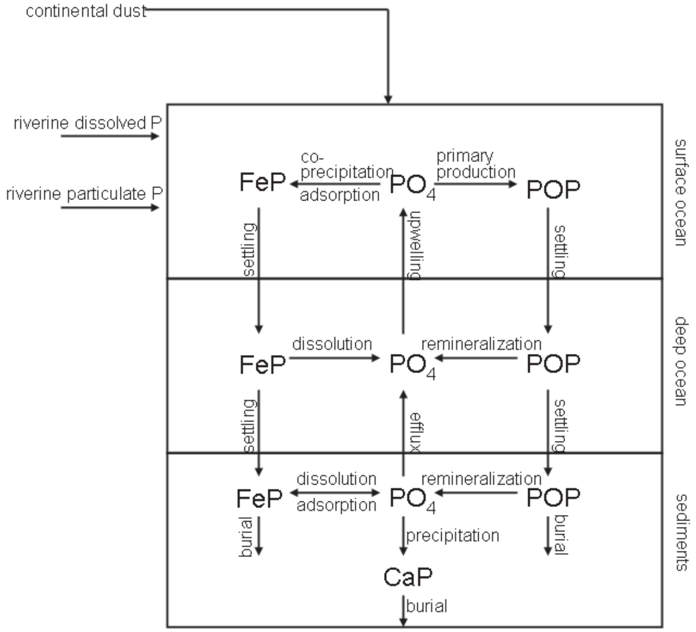

Figure 1.1 A representation of the processes affecting the partition of phosphorus in ocean waters and sediments. FeP – iron bound phosphorus; POP – particulate organic phosphorus; PO_4 –dissolved phosphorus; CaP – authigenic calcium associated P.

coastal environments to retain nutrients has been shown to be related to their water residence time, with more stagnant settings sequestering incoming nutrients from land more efficiently (Nixon, 1996). The bioavailable form of P in the water column is orthophosphate – PO_4^{3-}. During photosynthesis, this PO_4^{3-} may become incorporated into biota, in surface waters (Figure 1.1). The typical ratio of nutrients in the marine organic matter that is formed is C:N:P ≈ 106:16:1 and is known as the Redfield ratio (Redfield et al., 1963). Due to the large availability of dissolved inorganic carbon, marine phytoplankton tend to be nitrogen or phosphorus limited. Because certain marine organisms, such as cyanobacteria, are able to fix atmospheric N, phosphorus is assumed to be the growth limiting nutrient for marine phytoplankton for the global ocean over geological time scales (Holland, 1984; Smith, 1984; Tyrell, 1999),

Phosphorus is released from decomposing (remineralized) sinking biota (Figure 1.1), yielding typical P profiles in ocean waters (Figure 1.2). Some of the released P may be incorporated into, or sorbed onto, iron oxyhy-

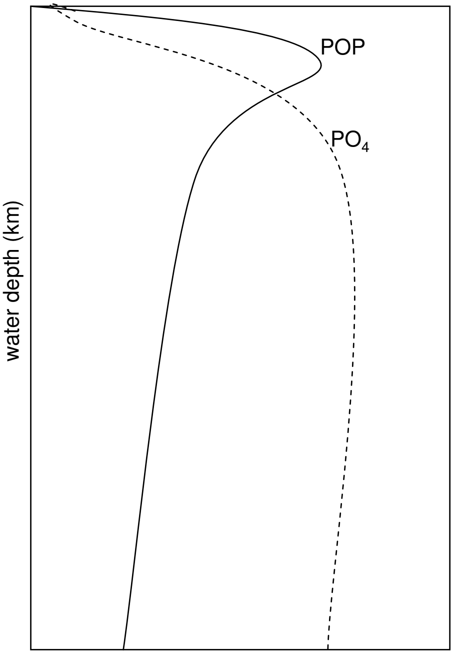

Figure 1.2 Typical distribution of dissolved and particulate organic phosphorus in ocean waters. POP – particulate organic phosphorus; PO_4 – dissolved phosphate.

droxides (FeP) – (Figure 1.1) – which are effective P scavengers (Benitez-Nelson, 2000) and a small fraction (<3%) of water column P is scavenged by hydrothermal plume particles (Froelich, 1982; Berner, 1973). The most important vector of P removal from sea water, however, is delivery to the seafloor of particulate organic matter (Delaney, 1998; Compton et al., 2000; Ruttenberg, 2003; Benitez-Nelson, 2000; Filippelli, 2008).

P is buried in sediments as organic phosphorus (POP), in-situ formed apatite (CaP) and iron oxide associated P (FeP) (Froelich, 1982; Ruttenberg, 2003; Filippelli, 2008 – Figure 1.1). No one sink is the total ocean major P removal process, though authigenic CaP formation phosphorus comprises a large fraction of buried P (Ruttenberg, 1993). Though not an important sink for the present ocean, the remains of fish (hard parts) have potentially played a role in P sequestration in sediments during periods of ocean anoxia (Schenau and de Lange, 2000, 2001; Slomp and Van Cappellen, 2007)

The speciation of P in the sediment is highly dependent on the depositional environment, as the relative importance of the controlling factors changes for different settings (Froelich et al. 1982). For example, sediments underlying well-oxygenated waters preserve iron-bound P and can form authigenic CaP (Ruttenberg and Berner, 1993; Slomp et al., 1996). Upwelling settings and organic matter rich sediments are hot-spots for authigenic P formation (Ruttenberg, 2003; Schenau et al., 2000). Fully anoxic basins, on the other hand, show evidence of enhanced phosphorus release from organic matter degradation under suboxic and anoxic conditions (Ingall et al., 1993; Slomp et al., 2002; Mort et al., 2010) as well as from iron oxides (Colman and Holland, 2000) with limited retention of the P in authigenic Ca-P (Ingall et al., 1993; Slomp et al., 2002; Mort et al., 2010).

Based on the processes illustrated in Figure 1.1 some hypothetical sample sedimentary profiles are given in Figure 1.3. Particulate organic phosphorus typically decreases with depth as organic matter is remineralized. Iron bound P also decreases as iron oxides dissolve below the redox boundary and phosphorus thus accumulates as pore water phosphate (PO_4) which can either diffuse back into the water column, or be incorporated into apatite (CaP) and buried.

1.3 Link to other biogeochemical cycles and climate change

The phosphorus and organic carbon cycles are linked through photosynthesis, which results in a connection between the phosphorus cycle and carbon dioxide in the atmosphere. The P and oxygen cycles, on the other hand are related through the redox dependence of P burial and through P-induced organic carbon burial in sediments (Lenton and Watson, 2000; Handoh and Lenton, 2003). Oxic environments enhance the burial of P in sediments while anoxic environments stimulate P recycling to the water column. Greater P availability in the water enhances photosynthesis at the

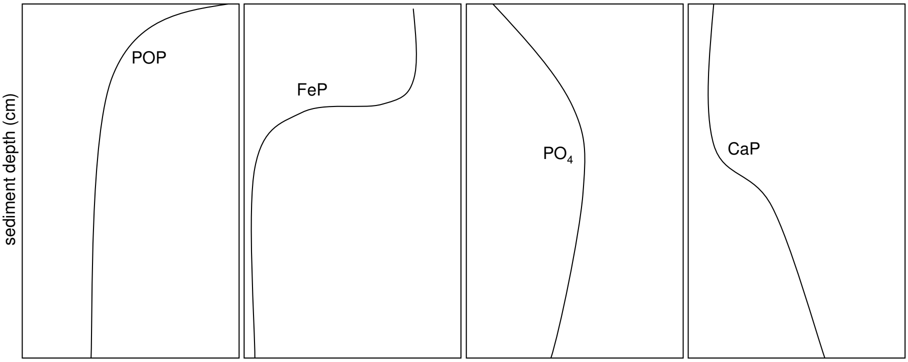

Figure 1.3 Typical depth distributions of phosphorus bearing species in ocean sediments. POP – particulate organic phosphorus; FeP – iron-bound phosphorus; PO_4 – porewater dissolved phosphate; CaP – authigenic calcium associated phosphorus (e.g. apatite).

sea surface and respiration at depth which impacts the oxygen content of the water column. As a consequence organic matter burial in sediments increases; the buildup of organic matter, in turn, enhances the accumulation of oxygen in the atmosphere and ocean. Phosphorus is thus intimately linked to the biogeochemical functioning of the ocean and to climate.

The residence time of P in the ocean, which was initially estimated at 50 to 100 kyrs (Broecker and Peng, 1982; Froelich et al., 1982; Jahnke, 1992) has been steadily revised downwards over the past decades to 25 kyrs (Ruttenberg, 1993), 10-17 krs (Ruttenberg, 2003) and 15 kyrs (Filippelli, 2002). This makes P a potential player in climate change on the time scales of thousands to hundreds of thousands of years. Changes in phosphorus cycling have been suggested to be important during climate change in Earth's history, particularly the recent glacial-interglacial transitions (Wallmann, 2003) and oceanic anoxic events (OAEs) (Mort et al., 2007); these same mechanisms may play an important role in the ocean's response to future climate change.

Glaciations, were cyclical periods in the earth's recent history when, due to changes in solar irradiation, the global temperature on Earth cooled. As a consequence, sea level in the oceans receded (Fairbanks, 1989; Lambeck and Chappell, 2001; Siddall et al., 2003) due to the formation of ice at the poles, dry arid conditions altered the hydrological and weathering cycles on the continents (Kump and Alley, 1994; Ganopolski, 1998) and ocean circulation changed due to changes in the temperature gradients of sea water. All of these, and other, environmental parameters had an impact on the cycling of P in the oceans and, as P is linked to the carbon cycle over these time scales, feedbacks onto the climate system were also possible.

Ocean anoxic events were episodes of oxygen depletion in the deep ocean, accompanied by accumulation of organic carbon rich sediments, on a wide scale (Schlanger and Jenkyns, 1976; Sarmiento et al., 1988; Erba, 2004). The phosphorus cycling in the ocean was likely altered during these periods. As mentioned earlier, the oxygen level in the water column is an important parameter for determining the speciation of P in marine sediments and the efficiency of phosphorus burial. The recycling of P from ocean sediments can then stimulate productivity in the ocean and oxygen demand in the water column, feeding back onto the ocean system.

1.4 A look to the future

The global phosphorus cycle is undergoing modifications form its pre-anthropogenic state. Mining of rock (phosphorite deposits) for use as fertilizer has increased in the second half of the twentieth century (Gilbert, 2009; Ruttenberg, 2001). Deforestation, increased agricultural activity, and waste disposal have resulted in increased P transport to the ocean, causing eutrophication in coastal waters, harmful algal blooms and low oxygen (hypoxic) conditions (Ruttenberg, 2003; Filippelli, 2002).

With the increased pressure mankind is putting on the Earth system, since the industrial revolution, the study of climate change has become an essential part of our striving to understand and mitigate the effects of civilization on Earth. Rising greenhouse gas levels, sea level rise, circulation slowdown and changes in the phosphorus delivery to the oceans are all projected in the context of future climate change. To better understand how the climate system behaves and how it responds to such stress, we often look to the past and the many climate settings the planet has undergone, such as glaciations and ocean anoxic events, to study its mechanisms and responses. One of the many intricate pieces of this complex interplay is the global phosphorus cycle, which is linked to essential biological behavior on land and in the oceans. Studying phosphorus in the context of climate change is therefore an essential part of the quest to understand the complex system that is Earth's climate.

1.5 Thesis outline

This thesis is concerned with examining the role and response of phosphorus in the ocean to climate change on time scales of thousands to millions of years. The focus lies largely on past climates, in particular glacial-interglacial transitions and ocean anoxic events. The work was carried out within the framework of a larger project on Global Nutrient Fluxes at the Land Ocean Interface (G-NUX). In **Chapter 2** of this thesis a box model of the global phosphorus, carbon and oxygen cycles in the ocean (Slomp and Van Cappellen, 2007) is used to study how the transition into glacial climate and subsequent deglaciation affected the cycling of P in the ocean and whether P could have, in turn, participated in shaping the changing climate, by affecting the productivity of the ocean.

In **Chapter 3**, the focus is on the marine oxygen cycle, specifically, whether changes in the supply and delivery of labile reactive P to the ocean during glaciations can explain oxygen depletion in the deep sea at glacial maxima and how that links to ocean productivity (i.e. is it necessary to invoke enhanced ocean productivity to explain increased oxygen demand in the deep sea).

Chapter 4 of this thesis tests the hypothesis that the enhanced recycling of phosphorus under low oxygen conditions, played a role in amplifying and sustaining oxygen depletion in the deep sea during oceanic anoxic events – that is that phosphorus was an essential player in climate change during those periods. This is done by adapting the box model of the marine P, organic carbon and oxygen cycles (Slomp and Van Cappellen, 2007) to a Cretaceous ocean and perturbing it with an enhanced continental supply of nutrients.

Finally, given the importance of reducing conditions on sedimentary P cycling, the sedimentary dynamics of phosphorus and associated elements (carbon, oxygen, nitrogen and sulfur) is examined along with their sensitivity to boundary conditions. In **Chapter 5**, a reactive transport model (RTM), with a mechanistic description of sedimentary transport and reaction processes (Reed et al., 2010) is used to test the effect of changing boundary conditions, such as oxygen concentration at the sediment water interface (SWI) and input of organic matter to the sediment, on the speciation and burial of phosphorus in generic deep sea sediments. The results are used to construct mechanistic redox dependent functions for P burial in ocean sediments and test whether this improved description of P burial alters the behavior of the box model used in Chapters 2 – 4.

2

Glacial-interglacial variations in marine phosphorus cycling: Implications for ocean productivity

with C. P. Slomp and P. Van Cappellen
published in 2008 in Global Biogeochemical Cycles, vol. 22, GB4004

Abstract

Using a box model of organic carbon (C) and phosphorus (P) cycling in the global ocean, we assess the effects of changes in the continental supply of reactive P, oceanic mixing, and sea level on the marine P cycle on glacial-interglacial timescales. Our model results suggest that mixing is a dominant forcing during early glaciation, causing retention of P in the deep ocean, thereby lowering primary production and associated organic C and P burial. Sea level fall is the dominant forcing during late glaciation, when reduced coastal trapping of reactive P enhances its transfer to the open ocean, restoring primary production and P burial. During post glacial periods changes in circulation and weathering dominate open ocean processes and oceanic primary production peaks. As primary production is reduced upon glaciation, changes in the marine P cycle are unlikely to drive enhanced primary production and CO_2 drawdown during glaciation.

2.1 Introduction

Cyclicity of 100 000 years in atmospheric CO_2 concentration is discernable as far back as 740 000 years ago (Petit et al., 1999; Siegenthaler et al., 2005). These changes in atmospheric pCO_2 are believed to be caused, to a large extent, by changes in the ocean/atmosphere exchange of CO_2, but there is not yet agreement on the underlying mechanisms. One suggested mechanism is a glacial increase in the strength of the biological pump as a result of increased nutrient availability (Broecker, 1982; Sigman and Boyle 2000; Peacock et al., 2006).

The debate over the role of the "nutrient-CO_2 connection" (Broecker, 1982) has recently been revived by the downward revision of the oceanic residence time of reactive phosphorus (P) (Latimer et al., 2006), with estimates now ranging from 8.8 to 38 ka (Wallmann, 2003; Ruttenberg, 1993, 2003) instead of the previously assumed 80 to 100 ka (Froelich et. al., 1982; Broecker, 1982). Thus, on time scales of glacial-interglacial cycles, the availability of P could exert a major control on global oceanic primary productivity (Filippelli, 2002; Holland, 1984; Tyrell 1999; Compton et. al., 2000). While physical and biological mechanisms for glacial-interglacial forcings on the carbon cycle itself are widely studied (Archer et al. 2000a; Heinze et al., 1999; Ridgwell, 2001; Archer et al., 2000b), the effects of these cycles on growth limiting nutrients have received less attention. A handful of modeling studies have estimated the consequences for the marine cycles of nitrogen (Christensen, 1994, Deutsch et al., 2004) and iron (Rigwell, 2003; Lefevre and Watson, 1999).

There is some debate over the key limiting nutrient exerting overall control on the organic carbon cycle. Sigman et al. (1999) propose nitrate utilization in the surface Antarctic was higher during the last ice age, using that to account for CO_2 drawdown. Latimer and Filippelli (2001) propose a micronutrient connection, suggesting that iron from hemipelagic sediments could have stimulated primary production during glacial periods. However, based on a simple theoretical study of nutrient co-limitation, Tyrrell (1999) concludes that while surface waters can be more depleted in nitrate than in phosphate in the steady state, it is the external input of phosphate which controls longer-term primary production in the global ocean, such as over glacial times.

Wallmann (2003) proposes that the response of the marine P cycle to fluctuations in sea level and terrigenous inputs results in a positive feed back loop, due to the redox dependence of P regeneration. An initial increase in primary production can cause enhanced respiratory oxygen consumption in the water column; low oxygen waters in turn lead to preferential regeneration of reactive P, culminating in a further enhancement of primary production. Below a threshold value in deep water oxygen concentration (100 μM), this feedback may allow even small increases in organic matter export to induce a rapid drop in the oxygen level. The corresponding P-driven spike in productivity could then drive the ocean to eutrophic conditions and cause it to become nitrogen (N) limited (Wallmann, 2003). However, on glacial – interglacial time scales, the deep ocean never reaches the critical level of oxygen depletion and thus remains P limited. The study of Wallmann (2003) focuses primarily on the transition from interglacial to glacial conditions and it does not consider the effect of circulation during glacial times. However, ocean circulation is likely a key factor in glacial-interglacial nutrient cycling and pCO_2 trends (Toggweiler, 1999; François et al., 1997; Sigman and Boyle, 2000; Broecker et al., 2004; Peacock et al., 2006; Willamowski and Zahn, 2000).

Using a 1 box model of the ocean, Van Cappellen and Ingall (1994) showed that a reduction in oceanic circulation (and mixing between deep and shallow waters) causes an initial drop in primary production, because the immediate supply of dissolved P to the surface waters is decreased. However, with time, as oxygen levels decrease, the deep water builds up phosphate and the upward transport of P is enhanced, boosting primary production. So the short term and long term effects of changes in circulation differ, and the effect of oceanic circulation on primary production is highly dependent on the time scale of the changes in circulation and on the oceanic residence time of the limiting nutrient. Slomp and Van Cappellen (2007) show that the response of the marine P cycle to oceanic circulation is further complicated when considering the continental margins separately, because of their differing biogeochemical dynamics from those of the open ocean (Slomp and Van Cappellen, 2007), and their high capacity for P storage (Ruttenberg, 1993; Howarth, 1995).

We note here, that circulation is not explicitly described in the box models described above. Rather, the effect of circulation is represented by the degree of mixing between deep waters and surface waters. Increased circulation thus is associated with enhanced exchange between surface and deep waters. It is this aspect of circulation only which is represented in box models and the model used for this study.

In the present study, we use a modified version of the 4-box model of Slomp and Van Cappellen (2007) and incorporate the changes in oceanic mixing in a generic full glacial-interglacial transition scenario. This allows us to examine the interaction effects of circulation with other forcings, in particular sea level change and variations in dust and river inputs of reactive P to the ocean. We simulate changes in speciation of sedimentary P burial, and examine the role of the oceanic residence time of phosphorus. By assuming that phosphorus controls primary production, we further determine the effects on the ocean organic C cycle and the possible link to climate. In particular, we test the hypothesis of a P driven boost in primary production during times of glaciation.

2.2 Glacial-interglacial climate change

In order to simulate changes in the marine P cycle and the associated organic carbon cycle, it is necessary to first properly identify and constrain the environmental/climate forcings which likely perturb these biogeochemical cycles during glaciations.

Besides the well-documented variations in temperature, four other global climate forcings could affect the global phosphorus cycle during glacial-interglacial transitions. These are sea level fluctuations, changes in riverine and aeolian reactive P supply to the open ocean, and changes in oceanic mixing, particularly the intensity of deep water upwelling. Here, we review the state of knowledge on the variability of these factors across glacial-interglacial transitions, and outline a climate change scenario for the last glacial-interglacial cycle.

2.2.1 Sea level

Sea level is perhaps the best constrained variable of glacial-interglacial cycles. As such, it is used as the time benchmark, as it inversely correlates to ice sheet volume and global temperature. According to paleoproxy records (Fairbanks, 1989; Lambeck and Chappell, 2001; Siddall et al., 2003), sea level dropped by up to 120 m at the last glacial maximum (LGM) – 20 000 years before present. As the continental shelf extends to approximately 250 m depth (average depth of 130m), a 120 m sea level drop is equated to a recession of the shoreline equivalent to a 50% loss of continental shelf from estimates made by Peltier (1994) and Wallman (2003). Transient, high frequency fluctuations in sea level, are not represented here. We simply follow the effects of the net change in coastal area during glaciation.

2.2.2 Riverine supply of reactive P

Föllmi et al. (1995) report that changes in chemical weathering (as the main long-term source of dissolved bioavailable phosphorus) were driven by changes in total continental weathering. By analyzing changes in exposed areas and changes in weathering processes, Kump and Alley (1994) concluded that the supply of reactive material from land at the LGM was not significantly different from the present. However, ice age temperatures are thought to have reduced precipitation and evaporation to about 10% - 15% below modern values (Kump and Alley, 1994; Ganopolski, 1998). It is this change in the hydrological cycle, and not the weathering regime on land, which leads to a similar decrease in riverine runoff and supply of organic carbon to the oceans (Ludwig et al., 1999; Ludwig and Probst, 1999; Hay and Southam, 1977). In this study, we employ a 10 % drop in the riverine supply of reactive P from the continents during glaciation. The onset of decline in chemical weathering during glaciation would have occurred after sea level and temperature had already begun to fall.

2.2.3 Dust

The general trend of eolian input to the oceans is a dust flux increase due to the cold, arid, windy climates of the glacial period and the increased area of exposed land (Delmonte et al., 2004; Broecker, 1997; Ann et al., 1991; Rea et al., 1994). Given that dust flux represents a small fraction of total P input to the coastal zone (<10% according to Lerman (1994) and Graham and Duce (1981)), the eolian input is mainly of importance for the surface waters of the open ocean (Benitez-Nelson, 2000; Graham and Duce, 1981). The reported increase in dust supply to the ocean ranges from 1.5 to 3 times greater during the LGM than interglacial values (Hesse, 1993; Ann et al., 1991; Anderson et al., 2006; Wallman, 2003). Suggestions of an order of magnitude greater dust supply to the open ocean at the LGM have also been put forward (Harrison et al., 2001; LeGrand et al., 1988; Kohfeld et al., 2001; Delmonte et al., 2004). The high estimates, however, are based on paleorecords of bulk dust deposition in ice cores, which do not necessarily reflect the trends in eolian reactive P supply.

The dust trend in our base-line model scenario is in line with flux estimates of Wallman (2003) and Anderson et al. (2006), namely a doubling of the dust flux of reactive P during glacial periods. According to dust records in ice cores, the aeolian flux increased primarily during the second half of the glacial period (Petit et al., 1999; Broecker and Henderson, 1998). Peacock et al. (2006) also propose that, if dust plays a role, it is only during the later phase (second half) of glaciation.

2.2.4 Mixing

Mixing, as the term is used here, refers to water exchange between water masses on the surface ocean and the deep sea, as well as upwelling on the coast; it is a measure of the connectivity between the water masses and their ability to exchange nutrients and oxygen. Note that oceanic mixing is a complex process which is heterogeneously distributed throughout the ocean, a feature which cannot be captured with a 4-box model. There has been quite

Table 2.1 List of studies comparing oceanic circulation during the last glacial to current (interglacial) oceanic circulation[a]

Area/Location	Method/Proxy	Circulation state relative to today [b]	Reference
Cariaco Basin	^{14}C + box model	-	Hughen et al. (2004)
North Atlantic	Modeling	-	Seidov et al. (1996)
General	modeling and ^{14}C	-	Meissner et al. (2003)
Florida Straights	$\delta^{18}O$ in benthic foraminifera	-	Lynch-Stieglitz et. al. (1999)
Southern ocean	$\delta^{15}N$, ^{230}Th-normalised opal fluxes, biogenic Ba rain rate, $^{231}Pa/^{230}Th$,authigenic U	-	François et al. (1997)
General	various (pertains to a different period)	-	Sigman et al. (2004)
Subarctic North Pacific	Biogenic Ba	-	Jaccard et al. (2005)
General	Box models	-	Toggweiler (1999)
General	Box model + CO_2 record	-	Peacock et al. (2006)
General	LGS (general circulation model)	-	Winguth et al. (2000)
General	$^{231}Pa/^{230}Th$ ratios + circulation biogeochemistry model	-	Marchal et al. (2000)
General	Summary of various studies	-/+	Corliss et al. (1986)
General	$^{14}C/C$, benthic and planktonic foraminifera	~	Broecker (1987)
General	Ocean general circulation model	~	Paul and Schafer-Neth (2003)
West Equatorial Pacific	$^{14}C/C$	~	
General	Modeling	~	Ganopolski (1998)
Atlantic	$^{231}Pa/^{230}Th$	~/+	Yu et al. (1996)
Northwest Pacific	$\delta^{13}C$ and $\delta^{18}O$ in cibicidoides	+	Keigwin (1998)
Equatorial Pacific	C37-39 alkenones	+	Lyle et al. (1992)
General	18 box model	+	Wunsch (2003)

[a] Locations and methodology are also given

[b] Symbols indicate: " ~ " = similar, " + " = increase, " – " = decrease

some debate concerning oceanic mixing during glacial times (Archer et al., 2000a; Peacock et al., 2006) as summarized in Table 2.1. Some of the disagreement stems from the methodologies used for estimating paleocirculation. Relying on paleoproxy tracer distributions (such as $\delta^{13}C$, $\delta^{18}O$ and CO_2 signatures) and inverse modeling, earlier reconstructions have been questioned recently by, for example, Rutberg and Peacock (2006), LeGrand and Wunsch (1995) and Bigg et al. (1998), who show sensitivity to boundary conditions and multistability of circulation model solutions.

Glacial mixing scenarios fall into three main categories (Table 2.1) based largely on overturning circulation: reduced intensities by up to 30 – 40% (Winguth et al., 2000; Meissner et al., 2003), similar intensity as today, and increased mixing rates. The dominant opinion, however, is one of a less ventilated glacial ocean (Sigman et al., 2004; Rahmstorf, 2002; Jaccard et al., 2005; François et al. 1997; Toggweiler, 1999). Recent work of Yu et al. (1996) and Wunsch (2003), corroborated by earlier propositions of Broecker (1987), suggest that if mixing had slowed down, it could not have been significantly slower than today. Marchal et al. (2000) expand on the findings of Yu et al. (1996) by determining a lower bound on glacial mixing; connectivity between water masses during glacial times could have been no more than 30% weaker than today's.

Whatever the debate over open ocean water exchange may be, the case for increased coastal upwelling is particularly strong due to the increased geostrophic circulation (particularly Eckman flow) caused by stronger Northern Hemisphere trade winds of the glacial period (Ganopolski et al., 1998, Wunsch, 2003; Jewell, 1994). Such a scenario is supported by regional coastal studies such as those of West et al. (2004), Romero et al. (2003) and Martinez et al. (1999). Therefore, the glacial ocean likely saw less water mixing between the surface and deep ocean but the coastal waters received a greater supply of upwelled deep water.

The timing of mixing changes implemented in our scenario is taken after Peacock et al. (2006), who propose that an early decrease in circulation, during the first 10 ka of glaciation, and a return to full mixing in the last 10 ka (deglaciation) of the glacial-interglacial cycle, agree best with recorded atmospheric CO_2 trends. Reduced circulation through most of the glacial is also in accordance with results of Hughen et al. (2004), and a similar timing of the circulation perturbation has been employed in carbon box modeling efforts (Köhler and Fischer, 2006).

2.2.5 Sea surface oxygen

An important effect of mixing is ventilation, the supply of oxygen to the deep ocean. As temperature decreases, oxygen solubility in the surface waters increases, and downwelled waters are enriched in oxygen, which may offset the effect of reduced downwelling on ventilation. For the purposes of representing a realistic ventilation rate, we include the oxygen solubility dependence on temperature (Pilson, 1998). We represent this effect by modulating the sea surface oxygen content using the sea surface temperature (SST) change during glaciation and deglaciation. The SST at the LGM is reported to be 1.5 – 7°C cooler than global average SST for preindustrial oceans (CLIMAP Project Members, 1981; McManus et al., 1999; Paul and Schafer-Neth, 2003), with most recent estimates converging on a 4°C cooling (Kageyama et al., 2006).

2.3 Model description

2.3.1 39 ka model

The 4-box model of Slomp and Van Cappellen (2007) explicitly represents the proximal and distal coastal zones, the surface open ocean and the deep ocean. Steady state water, organic carbon (C), oxygen (O) and phosphorus (P) cycles are parametrized to interglacial conditions (pre-industrial Holocene), imposing a 39 000 year (39 ka) oceanic residence time for P. The phosphorus cycle drives the organic carbon cycle, by assuming P limitation on marine primary production. This is a reasonable simplifying assumption given the spatial and temporal scales considered (Holland, 1984; Tyrell, 1999; Compton et al., 2000). The model calculations presented also assume a constant Redfield ratio of P fixation into organic matter (OM). It is important to note, however, that non-Redfield behavior may affect nutrient inventories, and therefore nutrient limitation itself (Sigman and Boyle, 2000; Falkowski, 1997).

The model accounts for the transformation of soluble reactive phosphorus (SRP) into particulate organic phosphorus (POP) and fish biomass, with separate parameterizations for the coastal zones and the open ocean. Three separate forms of buried phosphorus are considered; calcium-associated P (CaP), iron-bound P (FeP) and organic P (POP). The burial of both FeP and POP in deep sea sediments are dependent on deep water oxygenation. This is also the case for the burial of organic C (POC) and the burial ratio POC:POP (Slomp and Van Cappellen, 2007).

The only modification from the model of Slomp and Van Cappellen (2007) consists of an explicit representation of the eolian input of reactive P input to the ocean. To this end, the riverine reactive P flux is lowered slightly (11%), and the corresponding reactive phosphorus is introduced as a dust flux into the open ocean (Graham and Duce, 1981).

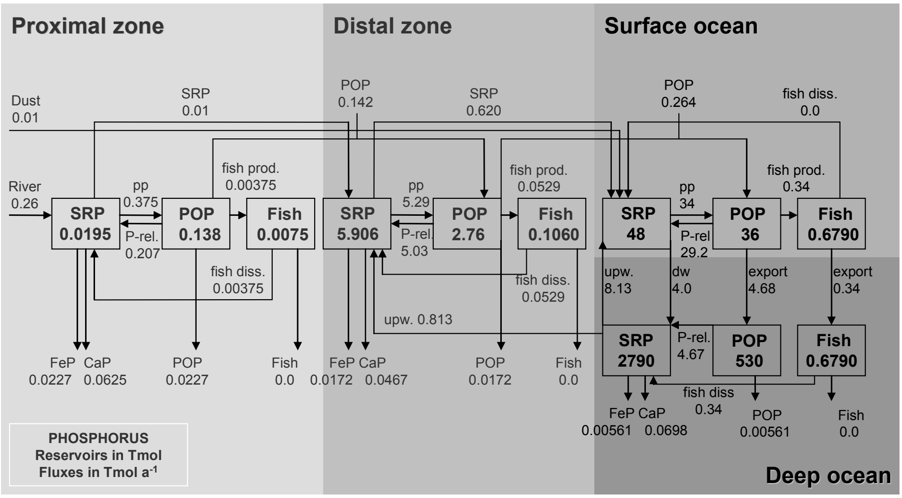

Figure 2.1 Pre-industrial steady state phosphorus cycle implemented in the model. The model incorporates 3 phosphorus species: soluble reactive phosphorus (SRP), particulate organic phosphorus (POP) and fish hard parts (fish). Four oceanic zones are represented: the proximal zone, directly influenced by river input, the distal zone (average water depth 130 m), the mixed layer of the surface ocean (average depth 150 m) and deep ocean water. The values given are for a 13 ka residence time. The corresponding reservoir and flux values for a 39 ka residence time of reactive P in the oceans are given in Slomp and Van Cappellen (2007).

Table 2.2 Comparison of reservoir masses and fluxes of the organic carbon cycle for a 39 ka P residence time model and a 13 ka residence time model[a]

	39 ka model	39 ka model[b]	13 ka model
		Reservoirs (Tmol)	
C1: POC proximal coastal zone	4.5	3.5	14.7
		Fluxes (Tmol/a)	
CF2: POC mineralisation in proximal zone	31.5	32.6	17.9
CF3: proximal sediment POC burial	3.6	3.6	6.8
CF4: POC export from proximal to distal zone	4.7	3.6	15
CF6: POC mineralization in distal zone	534	533	542
CF7: Distal sediment POC burial	2.7	2.7	5.2
CF10: POC mineralization in surface ocean	3131	3131	3132
CF11: POC export from surface to deep ocean	497	497	496
CF13: deep sea sediment POC burial	1.6	1.6	1.33

[a] Only modified reservoirs and fluxes are listed here; all other values are as specified by Slomp and Van Cappellen (2007). The 39 ka P residence time model is given by Slomp and Van Cappellen (2007), and the 13 ka residence time model is given by this work. POC = particulate organic carbon.

[b] Modified for dust flux

Export of POP and fish biomass to the deep ocean are calculated as the fraction of the primary production rate and, for POP, the input from the adjacent landward reservoir. We are aware that this description of export production does not take into account ballasting effects of settling material (e.g. De La Rocha and Passow, 2007; Boyd and Trull, 2007).

2.3.2 13 ka model

Recent studies have yielded considerably lower estimates of the residence time of reactive P in the oceans (Benitez-Nelson, 2000; Ruttenberg, 1993). We therefore also consider a version of the phosphorus cycle with a shorter residence time of 13 ka. The water cycle and oxygen cycle are kept the same as in the 39 ka model. The 13 ka phosphorus cycle is adjusted by tripling the input of riverine reactive P from the continents (maintaining atmospheric input the same), and adjusting the burial of phosphorus and organic carbon. Total organic carbon burial increases from 7.9 Tmol/a in the 39 ka residence time model (80% on the continental margins and 20% in the deep ocean) to 13.3 Tmol/a in the 13 ka residence time model (90% on the continental margins and 10% in the deep ocean) (Hedges and Keil, 1995).

In order to accommodate the increased burial of P within the constraints reported in the literature (particularly total C burial and C/P burial ratios in shelf and deep ocean sediments), the partitioning of buried reactive P phases is modified relative to the 39 ka residence time P cycle. In the 39 ka model P burial is characterized by CaP:FeP:POP = 50:25:25 everywhere in the ocean. In the 13 ka model, burial in the coastal zones is characterized by CaP:FeP:POP = 58:21:21 (Slomp et al., 1996) and that in the deep ocean by CaP:FeP:POP = 86:7:7 (Anderson et al., 2001). The latter ratios represent the extreme values for reported buried P speciation. This shift is accompanied by a shift in the total organic carbon to total reactive phosphorus burial ratio (Corg/Preac) in coastal sediments from 400 (39 ka model) to 300 (13 ka model). Some internal (unconstrained) fluxes are also adjusted to maintain mass balance. All other constraints are kept identical between the two versions of the P cycle. The steady state of the reduced residence time version of the P cycle is shown in Figure 2.1 and the resulting modifications to the organic carbon cycle (from the 39 ka model) are listed in Table 2.2.

Given the currently available estimates of organic matter (OM) burial rates and P partitioning in marine sediments, a 13 ka oceanic residence time is at the edge of the constraints imposed by budgets for the global oceanic P and organic C cycles. In particular, a residence time lower than 12 ka, and the corresponding higher burial of reactive P, would require a relative contribution of CaP in deep-sea sediments and a total POC burial exceeding the highest reported values so far (80-90% CaP, Anderson et. al., 2001; 13.3 Tmol POC/a, Hedges and Keil, 1995).

2.3.3 Model sensitivity to forcings

2.3.3.1 Response to sea level fluctuations

As the best constrained forcing parameter, sea level is treated separately and varied according to the prescribed scenario outlined in section 2.2.1. The model response to sea level fall and rise is shown in Figure 2.2. Results are given for the two oceanic residence times of reactive P (39 and 13 ka). For both residence times the model responds in the same qualitative way to the sea level forcing. The main difference is that the shorter residence time is more responsive to the forcing.

Upon sea level fall (glacial stage), the retention capacity of the coastal ocean for reactive P through burial decreases, due to the shrinking of the shelf. The

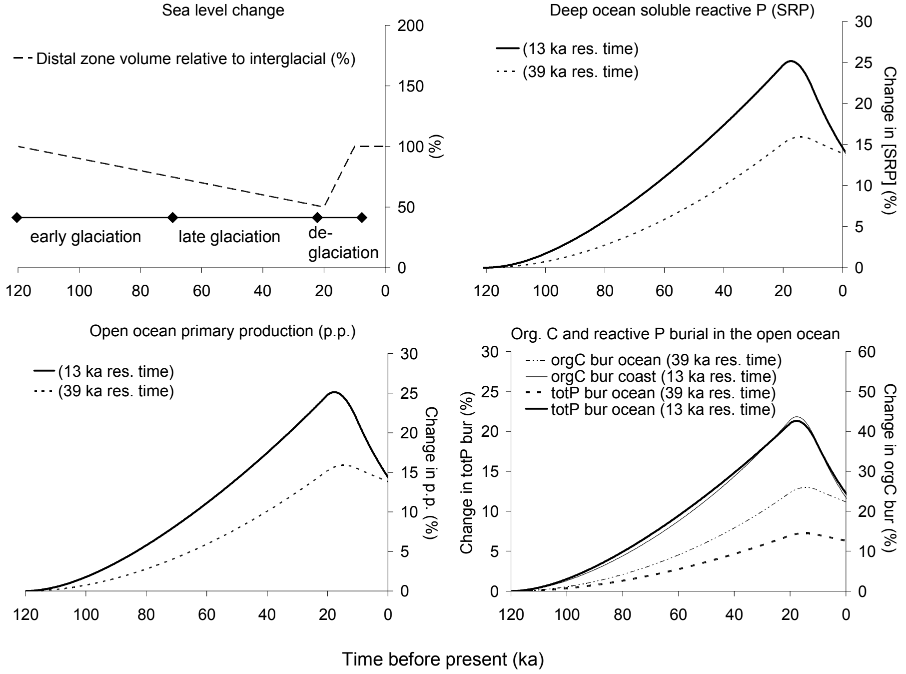

Figure 2.2 Model response to sea level change implemented as distal zone volume change: deep ocean soluble reactive phosphorus (SRP), oceanic primary production, organic carbon burial and reactive P burial. All responses are plotted as % change relative to interglacial values.

net effect is thus a transfer of reactive P to the open ocean. This stimulates open ocean primary production and export production and increases both the burial of organic carbon and reactive phosphorus in deep-sea sediments. Thus, increased open ocean productivity during glacial times does not require enhanced chemical weathering on the continents.

Upon sea level rise (interglacial stage), the re-flooding of the coast increases the retention capacity of the coast again, and higher amounts of reactive P and organic C get buried there. This reduces the export of P to the open ocean, lowers surface ocean productivity and organic matter export, thereby re-oxygenating the oceanic water column.

2.3.3.2 Sensitivity to mixing, weathering and dust

Because the changes in circulation, weathering and eolian input over a full glacial-interglacial cycle are more poorly constrained than sea level, we look at the system sensitivity to a wide range of these forcings. The transient effects of changes in mixing and reactive P input through rivers and dust, over a glacial-interglacial cycle, are summarized in Figure 2.3. As changes in the deep ocean reservoirs and burial rates closely follow primary production (as illustrated in Figure 2.2), only surface ocean production trends are shown. The sensitivity analysis is performed on the 13 ka residence time version of the model; as it is the more responsive of the two versions, it gives the upper bound of sensitivity.

A 30% reduction in oceanic mixing rates strength for most of the glacial period (110 000 – 20 000 years b.p.) raises coastal productivity by 8% and decreases open ocean productivity by 15%. As such, these effects are smaller than those accompanying sea level fall. In fact, for mixing to affect primary production to the same extent as sea level change, a 50 % reduction in vertical mixing would be necessary. Compared to oceanic upwelling, the effect of coastal upwelling is negligible (Figure 2.3).

Decreasing the reactive P input from rivers reduces primary production both in the coastal zone and in the open ocean. Our glacial scenario of a 10% reduction in riverine input reduces primary production by <10% in both marine compartments. As such, weathering has a more limited effect than sea level. However, if the supply of reactive P were to decrease by 50% it could reverse the sea level effect on open ocean productivity and more than double the sea level effect in the coastal zone. In such a case, total marine productivity would decrease. An accurate chemical weathering scenario is therefore paramount for a meaningful assessment of the biogeochemistry of the oceans during glacial-interglacial transitions.

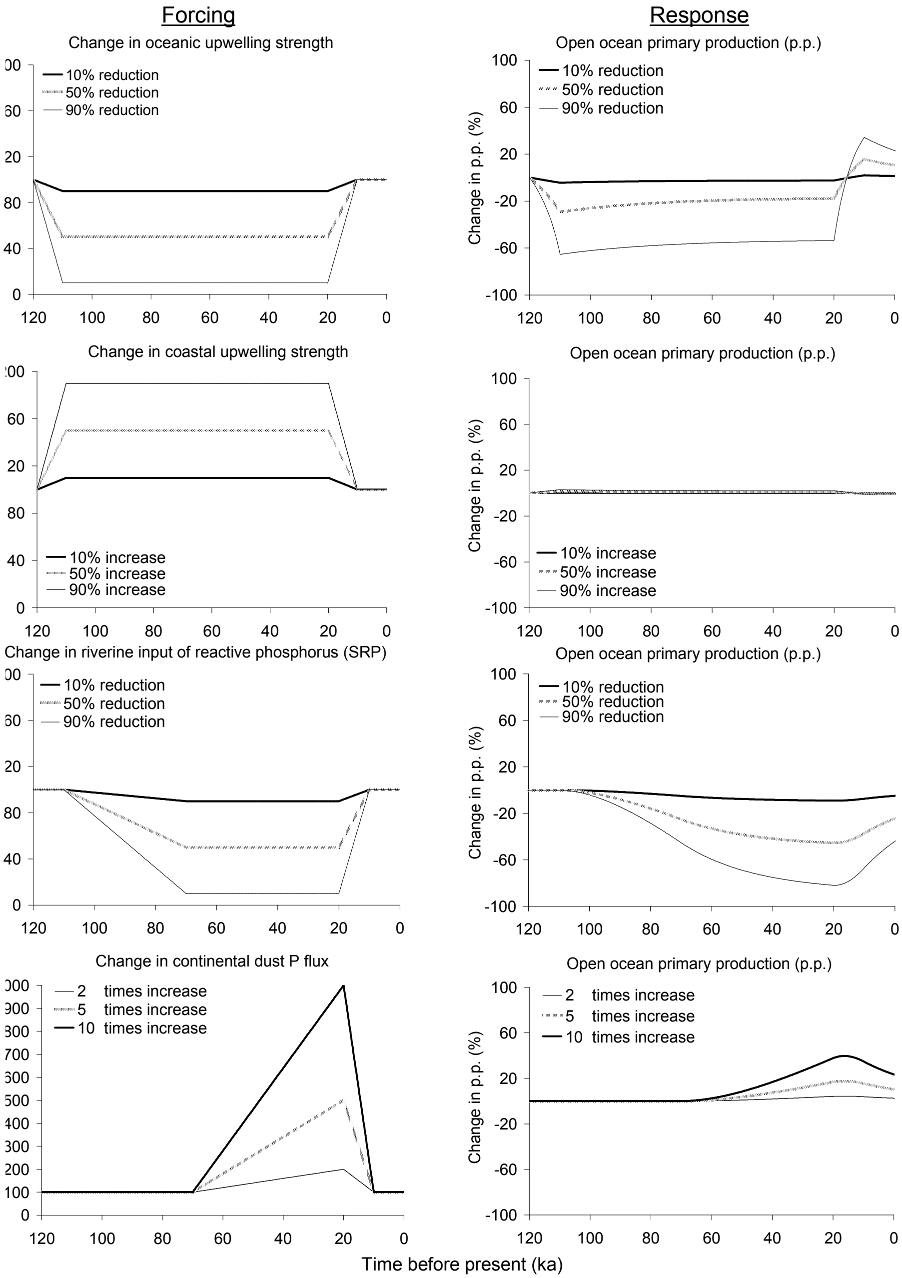

Figure 2.3 Sensitivity of primary production to changes in circulation (open ocean and coastal upwelling), nutrient loading from the continents and dust input. The results shown are for the 13 ka residence time version of the model; the 39 ka residence time version behaves in the same way but with a longer time lag. All values are given as % change relative to interglacial.

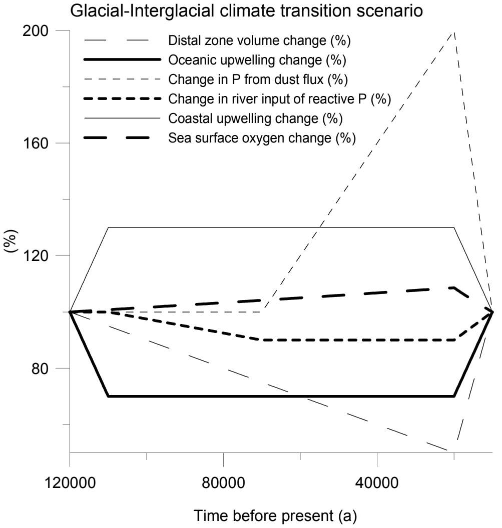

Figure 2.4 Glacial interglacial scenario implemented in box model. All parameters are plotted as % change relative to interglacial values. During 100 ka of glaciation the distal zone volume decreases to 50% of the starting value and returns linearly to the starting value during deglaciation. During the first 10 ka of glaciation coastal upwelling increases by 30% and oceanic upwelling decreases by 30%. During deglaciation they return to starting values. During the first 50 ka of glaciation continental input of reactive P decreases by 10% and returns to starting values during deglaciation. Dust supplied reactive P increases twofold during the last 50 ka of glaciation and returns to starting values upon deglaciation.

Increasing the reactive P input from dust to the surface ocean stimulates primary production, but the scale of this effect is very small for the specified glacial scenario. There would have to be an order of magnitude increase in the dust supplied to the surface of the ocean for the effect of dust to be comparable to those inferred for sea level, mixing and weathering. Doubling the reactive P input from dust boosts primary production only by 3-4%. Therefore, reactive P input via dust likely plays only a marginal role in the P cycle over glacial times.

Based on the sensitivity tests outlined above, sea level and oceanic mixing emerge as the critical climatic parameters. Weathering is also a potentially important forcing if varied significantly; however, coastal upwelling and dust have relatively negligible effects on the system relative to the other forcings.

2.3.4 Model implementation of glacial-interglacial scenario

The baseline glacial-interglacial scenario, based on the literature review outlined in section 2.2, accounts for the simultaneous variations in the major forcings on the marine P cycle: sea level, mixing, continental input of P and sea surface temperature (Figure 2.4). Sea level is implemented in the model by reducing the distal coastal zone volume linearly by 50% (see Figure 2.2) over 100 ka during glaciation and re-increasing it over 10 ka during deglaciation. The proximal coastal zone is assumed to move along the coast but its size remains the same. In the baseline scenario, the river input of reactive phosphorus is reduced linearly starting at 110 ka before present (BP) until 70 ka BP, when the weathering reaches 90% of the interglacial value and remains that way until deglaciation, when it increases linearly back to the interglacial value. The eolian reactive P input to the surface of the open ocean increases linearly, from 70 ka BP, until the LGM where the flux is double the interglacial value. The dust flux then returns linearly down to its initial value during deglaciation. We also implement the effect of a linear 4°C cooling during glaciation on O_2 solubility in surface waters according to Pilson (1998).

Circulation is represented in the model through an open ocean upwelling flux (vertical mixing in the ocean) and a coastal upwelling flux (oceanic deep water export to the coast). To change the upwelling rates, these fluxes are multiplied by a scaling factor. For the proposed baseline scenario, we impose a 30% decrease in oceanic upwelling during early glaciation (first 10 ka) and a return to full-strength mixing (over 10 ka) during deglaciation. Based on the work of Slomp and Van Cappellen (2007), the coastal upwelling term has only a negligible effect on the oceanic P reservoirs, and thus a strict constraint on coastal upwelling intensity is not necessary. We simply vary the coastal upwelling flux antisymetrically to the oceanic upwelling flux, i.e. coastal upwelling is increased by the same amount as oceanic upwelling is decreased.

2.3.5 Model spin-up

Given the time scales of glacial interglacial transitions (~100 ka for glaciations, ~10 ka for deglaciations), the marine P cycle could not have been at steady state during the repeated glacial-interglacial climate change characterizing the Quaternary, a concern raised previously by Wallmann (2003). Applying consecutive glacial-interglacial perturbations shows (Figure 2.5) that the system response during the first cycle is markedly different from subsequent responses. Under the applied periodic forcings, the system quickly shifts to an oscillatory mode exhibiting repetitive patterns (Figure 2.5). We therefore applied a spin up procedure, detailed below and illustrated in Figure 2.5, to allow the system to equilibrate with the imposed forcings.

Once the system is equilibrated with the cyclical forcings, the initial conditions of the model are offset so that the constraints on the interglacial marine P cycle (sections 2.3.1 & 2.3.2) are met for the equilibrated state of the system, rather than imposed as starting values. The constraints are assumed to be representative for the last interglacial (10 ka BP). This shift in initial conditions (starting values of reservoirs and fluxes) is applied until all reservoirs and fluxes specified in Figure 2.1 and Table 2.2 are satisfied for an equilibrated interglacial state (e.g. see Figure 2.5 for SRP and primary production examples).

The two residence time versions of the model show similar qualitative behavior but differ in the degree of departure between the initial and equilibrated state, as well as the equilibration time. The longer residence time model (39

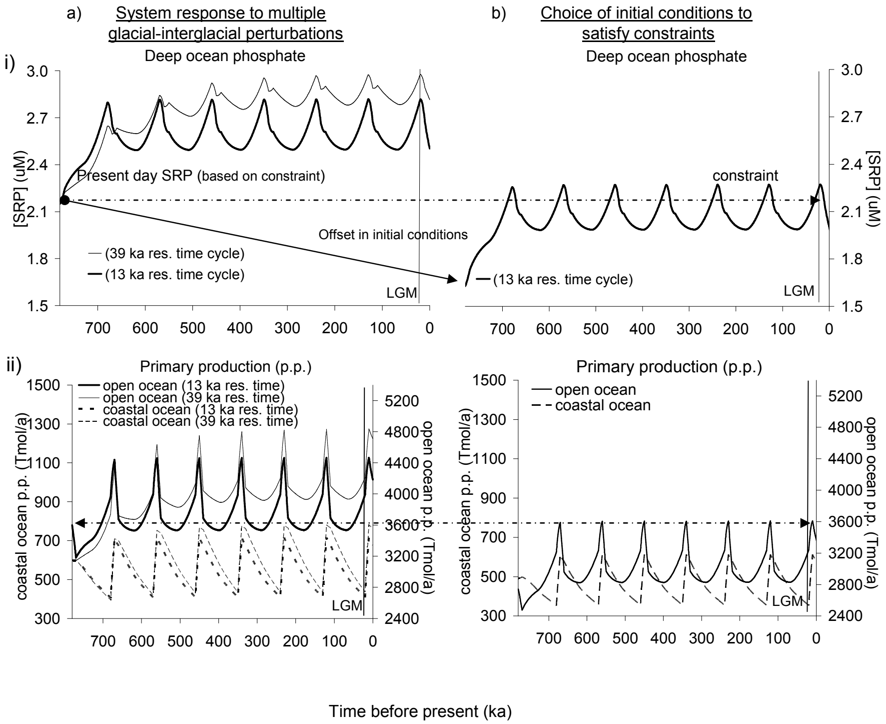

Figure 2.5 Model spin-up. Model response (soluble reactive P and primary production) to consecutive glacial interglacial perturbations. a) Based on an initial steady state, the system (both 13 ka and 39 ka version) is allowed to evolve under periodic perturbations. b) The initial conditions are adjusted so that model constraints are met at the last interglacial (10 ka BP). The spin up is applied to the 13 ka residence time version of the model only.

ka) moves further away from it's initial conditions and requires seven glacial-interglacial cycles to equilibrate with the forcings (equilibration is reached when the system returns to the same interglacial state at the end of a cycle), while the 13 ka residence time model only requires four glacial-interglacial cycles to equilibrate (Figure 2.5).

2.4 Results and discussion

The main objective of our simulations is to determine how primary production and burial of organic carbon and reactive phosphorus respond to the combined changes in the environmental forcings identified above.

2.4.1 Glacial-interglacial transition scenario

The results of the complete glacial-interglacial scenario, as detailed in section

2.3, are shown in Figures 2.6 & 2.7. The model outcomes, namely deep ocean SRP, primary production, organic C burial and reactive P burial, roughly follow the trends induced by sea level change (compare with Figure 2.2), with some notable differences. First, oceanic primary production and organic C and P burial decrease at the beginning of glaciation, before increasing again toward the LGM. Second, there is a temporal offset with respect to the LGM: primary

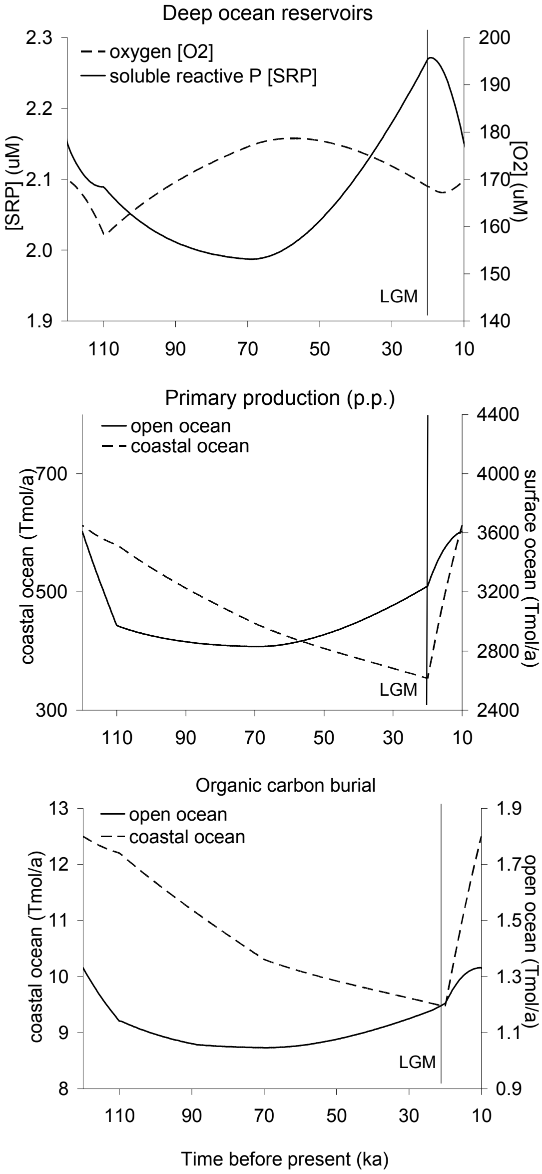

Figure 2.6 Model response to combined glacial scenario of sea level, circulation, weathering and dust flux changes: deep sea oxygen concentration [O_2] and soluble reactive P (SRP), primary production (p.p.) and organic carbon burial in the open ocean and coastal ocean (13 ka model after spin up).

production, organic carbon C and P burial all peak during the post glacial (interglacial) period. Thus, while sea level change emerges as a dominant forcing, it cannot alone describe the full glacial-interglacial scenario. Based on the sensitivity results, mixing and weathering act as important secondary forcings, counterbalancing and distorting the trends due to sea level.

During glaciation, soluble reactive phosphorus is gradually transferred to the open ocean; the deep ocean SRP inventory increases by 5 % relative to it's interglacial value at the LGM. Open ocean productivity initially drops, due to the slower mixing sequestering reactive P in the deep ocean, but, as the deep ocean P inventory increases, primary production increases again. It is noteworthy, however, that primary production during glacial time is predicted to be lower than during interglacial periods. Coastal production, decreases by 40% over the glacial period. Organic carbon burial follows the productivity trends with a 20% decrease in deep sea burial during glaciation and a concurrent 25% decrease in coastal areas.

During deglaciation the reactive P inventory of the deep ocean returns toward its starting value. However, due to enhanced vertical mixing, more reactive P is supplied to surface waters. As a result, oceanic production continues to increase until it peaks at 10 ka BP. This is due to enhanced weathering and mixing counteracting the effect of rising sea level.

Deep water oxygen initially decreases during glaciation (due to slow down in mixing) but increases in the middle and late glaciation. Waters are oxygenated then because the effect of reduced mixing is gradually overtaken by sea surface cooling bringing in more dissolved oxygen from surface waters. Deep water oxygen does not fall much during the glacial cycle. Although additional mechanisms can affect the deep-sea O_2 level, the estimated variations in deep sea oxygenation should have a negligible effect on the primary produc-

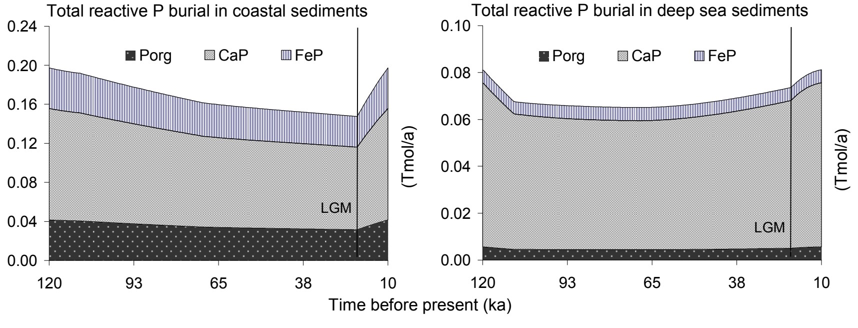

Figure 2.7 Model response to combined glacial scenario of sea level, circulation, weathering and dust flux changes continued. Reactive phosphorus burial: iron-bound phosphorus (FeP), calcium-associated authigenic phosphorus (CaP) and organic phosphorus (Porg).

tion linked to redox-dependent P regeneration.

In the deep ocean, iron-bound phosphorus burial is highest during the period when deep sea O_2 levels are highest. Thus, the iron-bound P fraction is low during glaciation and higher during interglacial periods. The burial of the other reactive P phases (CaP, POP), on the other hand, increases during interglacials (see Figure 2.7). Because FeP is a very small fraction of total reactive P, the net effect is one of a 10% decrease of reactive P preservation in deep sea sediments during the LGM. The role of coastal sediments in removing reactive P also decreases during glaciation. Burial of all P phases (CaP, FeP, POP) drops by approximately 13% in the coastal zone. Integrated over the coastal and open ocean, one glacial-interglacial perturbation has the effect of lowering total reactive P burial by 20%, thereby increasing the residence time of P in the ocean.

While the reactive P inventory of the ocean peaks during the LGM, primary production is lower throughout glacial times, it increases during post glacial periods, and is maximum at the end of interglacials. Similarly, the burial of P in the ocean does not increase during glaciation but decreases and then gradually returns to its interglacial value. These results therefore do not support our starting hypothesis of an enhancement in primary production due to changes in the marine P cycle during the glacial period. Therefore, the response of the marine P cycle to the imposed set of forcings does not, in itself, contribute to the drawdown of atmospheric CO_2 during glaciation.

2.5 Comparison to paleo-evidence

As far as reactive P and organic C behavior during glacial times is concerned, there is supporting evidence in the geological record for the predictions of the model. Model results show reactive P in deep ocean waters peaking during glacial maxima (0.13 μM higher than at interglacial). Elderfield and Rickby (2000) find the PO_4 inventory not significantly different in the sub-Antarctic regions but up by 0.6 μM in the Antarctic. Increase in the oceanic phosphate reservoir during glaciation has been proposed earlier and, while reports on the glacial deep water phosphate are sparse, estimates range up to 3.2 μM (Broecker, 1982) compared to our result of 2.3 μM at the LGM.

In a global study, Kohfeld et al. (2005) propose that throughout most of the world's oceans, primary production decreased at the beginning of glaciation (until stage 5a-d, ending approx. 80 ka BP) and subsequently increased. This is in line with our model results which show a dip in primary production until approx. 70 ka BP followed by an increase, returning to interglacial values (Figure 2.6). In contrast, Mix (1989) and Sarnthein et al. (1988) report a higher primary production (28- 80%) for the Atlantic at the LGM. However, in most current high production areas, new production at the LGM was higher, with peak production at approximately 15 ka BP (the interglacial period); in modern low production zones, glacial productivity did not vary systematically. Similar evidence was found by Pedersen (1983) in the eastern equatorial Pacific for a peak in surface ocean production at 15 - 14 ka BP. Filippelli et al. (2007) report higher primary production toward the end of glacials and the beginning of interglacials for sites in the Southern and equatorial Pacific oceans. Romero et al. (2006) also report continued surface water productivity enhancement after the LGM into the Holocene, off the coast of Chile.

Organic carbon burial in our model follows the trends of primary production. Organic carbon burial in the open ocean increases during the late glacial and peaks during the interglacial period. Broecker (1982) summarizes corroborating evidence which points to a peak in organic carbon burial after the glacial maximum. We also find that oceanic P burial is higher after the LGM than during glaciation. Tamburini (2001) reports a similar trend in the average standardized P mass accumulation rates (MAR) of 8 deep sea cores: there is an initial decrease in P burial until approx. 75 ka BP followed by a gradual increase back to starting values at approx. 10 ka BP. Although a quantitative comparison cannot be made, our model results also show a decrease in P burial until approx. 70 ka BP followed by an increase and return to interglacial values.

Overall, keeping in mind the heterogeneity of the ocean system, our model results tend to agree with the general glacial period constraints based on paleoceanographic evidence for the last glacial-interglacial cycle.

2.6 Conclusions and implications

The model results illustrate that the marine P cycle is sensitive to climate related variations accompanying glacial-interglacial cycles. The importance of individual forcings on the marine P cycle changes during the glacial-interglacial transition (Table 2.3). During early glaciation (120 ka BP – 70 ka BP), oceanic mixing has a dominant effect, due to the rapid change in overturning and the high sensitivity of the marine P cycles to that parameter. Primary production and associated burial of organic C and reactive P, all fall due to the slowdown in nutrient redistribution to the surface ocean. During late glaciation (70 ka BP – 20 ka BP), however, the cumulative effect of sea level fall on the coastal shelves becomes the prominent forcing. As the coastal filter shrinks, effective transport of nutrients to the open ocean helps restore primary production and burial fluxes. Deglaciation (20 ka BP – 10 ka BP), in turn, experiences the opposing effects of sea level rise and circulation (and weathering) increase. The net effect is one of enhanced primary production due to enhanced mixing and supply of nutrients, despite the increased ability of the coastal regions to re-

Table 2.3 Timeline of marine P cycle response to glacial interglacial transition.

Period	Time	Response	Dominant forcing(s)
Early glaciation	120 – 70 ka BP	Primary production, organic C and reactive P burial decrease	circulation slowdown
Late glaciation	70 – 20 ka BP	Reactive P is transported to the open ocean primary production, organic C and reactive P burial increase	sea level fall
Deglaciation	20 – 10 ka BP	More P retained in the coastal ocean Primary production, organic C and reactive P burial increase toward their maximum values	enhanced circulation and weathering

tain reactive P. Our results augment the conclusions of Wallmann (2003), who focused primarily on the role of sea level change, by showing that the trend in marine P cycling is not one of sea level change alone but other forcings have complementary effects on the system.

The assumed residence times of marine P (13 ka and 39 ka) do not qualitatively affect the P cycle's response to the imposed forcings, in particular the temporal change in primary production (Figure 2.5). There is a net enhancement of the deep ocean phosphate inventory during a glacial cycle. Despite the enhanced dissolved P inventory, however, primary production is lower during glaciation than during interglacial periods. Similarly, organic C and reactive P burial are lower during glacial times, increasing the residence time of P in the oceans.

These findings are significant for the debate over the role of the biological pump in CO_2 sequestration during glaciations. Our results show, that the biological pump may in fact have been weaker during glacial periods relative to interglacials. Thus, variations in the marine P cycle cannot be a contributing mechanism to the cyclical CO_2 drawdown trend, as production is lower at times when CO_2 drawdown should increase. In any event, given the magnitude of model-predicted fluctuations in the primary production, variation in the latter should be negligible compared to physical effects such as the sea surface temperature effect on CO_2 solubility or CO_2 sequestration due to circulation slowdown.

Our model does not capture the effects of wind regimes and temperature on circulation nor other spatially variable effects on mixing intensities and oceanic P cycling. Also, the results of the present model reflect the trend of the average (total ocean average) rather than the average of the trend. The realism of the results reported above could be further improved by subdividing the ocean in a larger number of boxes, for example, by including separate high latitude boxes, and by implementing a more dynamic modulation of the exchange of waters between the surface and the deep ocean. Also, a logical next step is the inclusion of a more elaborate description of the P cycle in a biogeochemical ocean general circulation model (GCM).

As yet, available GCMs do not include a separate representation of the continental margins. This makes box models such as ours indispensable tools to assess and untangle the combined affects of sealevel change and various climate forcings on the coupled P and C cycles. Our model allows us to show that sea level is likely not the only relevant forcing during glaciation and that during different periods of a glacial-interglacial cycle other climate variables (such as mixing and nutrient supply) gain importance. We also find counterintuitive results, such as a lowering of primary production during glacial times, contradicting the biological pump theory.

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3

Shelf erosion and submarine river canyons: implications for deep-sea oxygenation and ocean productivity during glaciation

with C. Rabouille, C. P. Slomp, and P. Van Cappellen
published in 2010 in Biogeosciences, vol. 7, p. 1973–1982

Abstract

The areal exposure of continental shelves during glacial sea level lowering enhanced the transfer of erodible reactive organic matter to the open ocean. Sea level fall also activated submarine canyons thereby allowing large rivers to deposit their particulate load, via gravity flows, directly in the deep sea. Here, we analyze the effects of shelf erosion and particulate matter re-routing to the open ocean during interglacial to glacial transitions, using a coupled model of the marine phosphorus, organic carbon and oxygen cycles. The results indicate that shelf erosion and submarine canyon formation may significantly lower deep-sea oxygen levels, by up to 25%, during sea level low stands, mainly due to the supply of new material from the shelves, and to a lesser extent due to particulate organic matter bypassing the coastal zone. Our simulations imply that deep-sea oxygen levels can drop significantly if eroded shelf material is deposited to the seafloor. Thus the glacial ocean's oxygen content could have been significantly lower than during interglacial stages. Primary production, organic carbon burial and dissolved phosphorus inventories are all affected by the erosion and rerouting mechanisms. However, re-routing of the continental and eroded shelf material to the deep sea has the effect of decoupling deep-sea oxygen demand from primary productivity in the open ocean. P burial is also not affected showing a disconnection between the biogeochemical cycles in the water column and the P burial record.

3.1 Introduction

The world ocean was a different environment during the glacial periods of the Pleistocene than it is today. The open oceans with colder surface water temperatures and different ocean ventilation were likely enriched in CO_2. There is also evidence from sediment proxies that oxygen levels of deep-sea waters were appreciably lower than today though not anoxic. For example, trends in authigenic uranium (U) and sedimentary molybdenum (Mo) concentrations point to decreased bottom-water oxygen throughout the Atlantic and in the Pacific, coinciding with glacial periods (François et al., 1997; Thomson et al., 1990; Bertine and Turekian, 1973; Mangini et al., 2001; Dean et al., 1997). In the sub-arctic Pacific, authigenic U concentrations were higher for sediments deposited during glacial maxima, while Mo concentrations were not significantly higher, suggesting bottom waters oxygenation was lower but did not reach full anoxia (Jaccard et al., 2009). Phosphorus speciation in the North Atlantic, particularly the decrease of authigenic and iron bound phases during Heinrich events 4 and 5, points to dysaerobic conditions in the North Atlantic as well (Tamburini et al., 2002). Similarly, mass balance and modeling studies (Boyle, 1988; Broecker, 1982; François et al., 1997; Peacock, 2006) have concluded that deep-sea oxygen must have been lower during glacial periods.

Low glacial oxygen concentrations in the deep sea have previously been attributed to changes in ocean circulation (Mangini et al., 2001; Schröder-Ritzrau, 2003), when the ventilation of the deep sea is reduced, or increased primary productivity in the surface ocean (Filippelli et al., 2007), which increases the rate at which organic matter sinks to the deep sea, causing greater oxygen demand in deeper waters. There is, however, quite some debate about the circulation and productivity of the ocean during glacial maxima. Reconstructions of circulation for the last glacial period range from slower to faster than present day (see Table 2.1 in chapter 2). Also many reports question whether productivity was higher during glacial time (Nameroff et al., 2004; François et al., 1997; Dean et al., 1997). Likely, primary production was higher in some parts of the ocean, but lower in others. In a glacial-interglacial transition scenario implemented in a box model for the carbon, oxygen and phosphorus cycles in the ocean, Tsandev et al. (2008) found global ocean productivity to decrease during glacial stages compared to interglacials. In addition, reduced circulation did not lead to appreciably lower deep-sea oxygen levels.

Here, we explore two additional mechanisms that may, in combination with the climatic forcings studied in Tsandev et al. (2008), help explain the observed variations in deep-sea oxygen levels and ocean primary production during glacialinterglacial cycles. In particular we consider two processes not generally included in biogeochemical models for the glacial ocean: the transfer of suspended particulate matter via submarine canyons (“the river canyon hypothesis”) and the erosion of recently deposited sediment from shelves exposed by sea level lowering (“the shelf nutrient hypothesis”).

3.1.1 The river canyon hypothesis

At present, most rivers discharge on their adjacent shelves due to the high sea level stand. During glacial times, however, with sea level dropping as much as 120 m below present levels at the last glacial maximum (LGM) (Fairbanks, 1989; Lambeck and Chappell, 2001; Siddall, 2003) many of the world’s large rivers were likely connected to submarine canyons (Fagherazzi et al., 2004; Damuth, 1977), with valley incisions extending as far as 200–760 km from the shelf edge (Possamentier, 2001; Rabouille et al., 2009). Under these settings, river suspended matter can be transported directly downslope via gravity driven bottom flows or turbidity currents to the abyssal plains (Khripounoff et al., 2003; Damuth, 1977; Pinet, 2006).

One notable modern day example of this type of land to ocean transport is the Congo river and its submarine canyon. It is the second largest river in the world (Milliman, 1991; Vangriesheim et al., 2009a) and it transfers particulate matter directly to the deep sea through its canyon and associated channel network (Rabouille et al., 2009; Babonneau et al., 2002). As sea level falls, as it does during glaciations, and large rivers form connections to their submarine canyons, upon shrinking of the continental shelf, an increasing fraction of the continental particulate load becomes routed directly to the deep ocean, rather than passing through the coastal shelf filter. The continental particulate material is then delivered by a mechanism similar to the Congo. If the fraction of continental material routed directly to the deep sea is significant, this can have a potentially large effect on the biogeochemical functioning of the ocean, during periods of sea level low stand.

3.1.2 The shelf nutrient hypothesis

While organic-rich sediments are deposited on continental shelves during interglacials – with the sediments consisting of material arriving from the continents and primary production on the shelf – these same sediments are exposed as sea level recedes during glaciation. Not only does this reduce the strength of the active margin sink, but it also leads to the erosion of shelf sediments and their subsequent delivery to the open ocean (Filippelli et al., 2007). In our previous modelling work (Tsandev et al., 2008) the effect of a shrinking shelf burial sink was considered, but that of shelf erosion on carbon and nutrient transfer to the open ocean was not.

Erosion of unconsolidated shelf sediment during glacial periods has long been recognised and is based on observations of glacial sediments (Broecker, 1982; Damuth, 1977; Hay, 1994; Pollock, 1997). This material was carried to the coastal ocean by rivers or runoff and exported offshore to deep-sea fans and abyssal plains by turbidity currents via submarine canyons, where the rivers were connected to their canyons. It is not clear whether the deposition of eroded material was episodic (Hay, 1994) or continuous, spread over thousands of years (Damuth, 1977). The timing and amount of sediment delivery to the deep sea depends on the rate of sea level change and other factors (van Heijst et al., 2001). In any case, the additional supply of large amounts of reactive marine organic-rich shelf sediments likely had an impact on the carbon and nutrient cycles of the open ocean and on deep-sea oxygen levels.

Another effect of sea level fall and shrinking of the coastal seas is that the proximal coast may disappear altogether. This allows particulate material arriving from rivers to flow directly into the open ocean, whereas this material would otherwise be trapped in proximal sediments. Hence the absence of a proximal coast has a twofold effect on the deep-sea nutrient supply: the exposed shelf becomes a source of nutrients and the continental particulate material flux can arrive to the open ocean. Thus the open ocean (and the deep sea, where canyons transport particulate matter downslope) is fertilized with new carbon and nutrients.

Here, we use an existing biogeochemical mass balance model to assess the impact of coastal discharge through submarine canyons and shelf erosion on the biogeochemistry of the glacial ocean, by incorporating these processes in the existing glacial-interglacial climate change scenario of Tsandev et al. (2008). The results imply that shelf erosion, in combination with particulate material rerouting via submarine canyons, has the potential to significantly impact the marine glacial oxygen and carbon cycles and that it may help explain deep-sea oxygen depletion during glacial periods.

3.2 Model description and implementation of new mechanisms

We start from a model of the coupled marine phosphorus, organic carbon and oxygen cycles (Slomp and Van Cappellen, 2007), as adapted for a 13 kyr residence time of phosphorus in the ocean by Tsandev et al. (2008). In the model, phosphorus is assumed to limit global ocean primary production, which is likely the case on glacial-interglacial time scales (Tyrell, 1999).

The model specifically accounts for the role of the coastal ocean as a filter for river inputs and redox dependent burial of phosphorus. It includes two coastal boxes (proximal and distal coastal zones) and a surface open ocean and deep ocean box (Figure 3.1). Particulate and dissolved material enters the ocean via the proximal zone. However, particulate material is assumed to mineralize (into dissolved nutrients) or get buried as proximal sediment. In the original formulation of the model by Slomp and Van Cappellen (2007) these processes that occur in the proximal zone are not explicitly modeled and only a dissolved nutrient (P) flux – flux (1) in Figure 3.1 – from the continents is implemented. Material from the proximal coastal ocean travels along the distal waters before entering the open ocean, with the exception of dust, which deposits directly to the surface of the open ocean. The effect of changing redox conditions on the burial of reactive P and preservation of organic carbon is implemented as well.

In this study, we use three different model settings for redox dependent burial of organic and authigenic phosphorus: (1) no redox dependent burial of organic or authigenic P; (2) Moderately redox dependent burial: 25% of the organic P and 50% of the authigenic P fractions is redox dependent (Slomp and Van Cappellen, 2007); (3) Highly redox dependent P burial: 75% of the organic P and 90% of the authigenic P fractions is redox dependent (Tsandev and Slomp, 2009). The actual strength of redox dependence of reactive P burial is not well known quantitatively, thus varying this parameter is important to assess its contribution to oxygen depletion in the deep sea. The other two re-

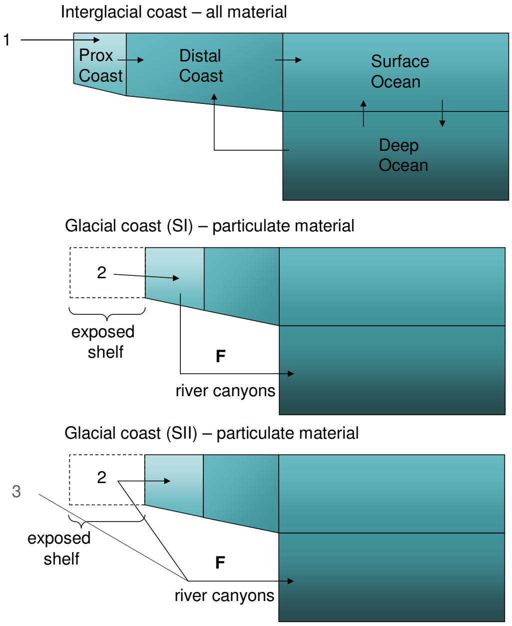

Figure 3.1 Path of material in the coastal and open ocean during glaciations. Transfer of dissolved material, such as dissolved riverine P (1), always remains the same. Particulate material can become rerouted directly to the deep sea by submarine canyons via turbidites or other gravity flows. In rerouting scenario SI a proximal zone remains to rework and trap material arriving from the continent. River canyons (fraction F) then shunt material from the proximal coast to the deep sea, bypassing the distal coast. In rerouting scenario SII, the entire coast is bypassed and major rivers (fraction F) discharge directly to the deep sea (3). Additionally surface sediment on exposed shelves can erode into the coastal ocean (2). This sediment represents labile marine organic matter deposited during previous interglacial stages. We assume it contains 2% organic carbon by weight and a C/P ratio of 300. Where river canyons form, this sediment is also shunted to the deep sea along with the continental particulate material.

active P phases (iron bound P and biogenic P) are not varied as the complete redox dependence of iron bound P burial is well established, and biogenic P is a minor component of the reactive P burial in marine sediments.

The above outlined model was subjected to a spin-up procedure by applying multiple glacial-interglacial cycles to the system, as outlined in (Tsandev et al., 2008), until it equilibrates with the periodically changing climate parameters. In each cycle, we assume a 100 kyr period of glaciation with a 30% decrease in ocean mixing, 10% decrease in river supply of P, 4°C lowering of sea surface temperatures and a shrinking of the continental shelves by 50%. During the 10 kyr of deglaciation that follows, all forcings are reversed (Tsandev et al., 2008).

The shelf nutrient loading and river canyon rerouting (illustrated in Figure 3.1) were then added to the other glacial forcings outlined above for a total of 6 environmental parameters perturbed during a glacial transition: ocean mixing, continental nutrient flux, surface water temperature, sea level, shelf erosion and river canyon rerouting comprise the new augmented glacial perturbation scenario. A shelf flux (2) is added to the displaced proximal zone, representing the organic material eroding from the exposed shelf. The formation of submarine canyons for major rivers is implemented by rerouting the proximal particulate organic material (POC and POP) to the deep-sea box for that fraction of the coast for which river canyons operate (F). This represents the transfer of the particulate load to the abyssal plains through turbidity currents in river canyons. Two different scenarios for this implementation are tested: when a proximal part of the shelf remains and separates the canyon head from the river outlet (SI) and when the river canyon intersects the entire continental shelf linking the particulate supply from exposed shelves (2) and from rivers (3) directly to the deep sea (SII). We represent these end member situations, though in reality the global coast-line may have been comprised of a combination of such settings. The 6 environmental variables outlined are therefore the only parameters imposed on the box model. All other variables are allowed to vary dynamically and are considered as part of the system's response.

Scenario I (SI) represents a bypass of the distal coastal ocean for rivers which form submarine canyons. Therefore a small shallow proximal zone still remains between continental particulate supply and the canyon head. Thus some filtering of incoming material still occurs in the near shore zone, namely the particulate material coming from the continents is processed and largely trapped in the proximal coast. Scenario II (SII) represents a bypass of the full shelf (proximal and distal zones) as is the case for the Congo. This means that the river and canyon head are connected thus completely bypassing the continental shelf. Particulate material from the continents now travels directly to the deep sea as does material eroded off the exposed shelves. The dissolved component (SRP), delivered by rivers to the sea, travels the same unaltered path as the water cycle and there is no difference between its behaviour under the standard glacial scenario and SI and SII. In other words, there is a decoupling between the fate of particulate and dissolved material arriving from the continents, whereby dissolved nutrients travel along the coastal zone, while particulate matter is able to avoid reworking on the coast and deposits in the deep sea. As the coastal zone acts as a strong filter for organic material and nutrients, this re-routing of POC and POP has the effect of supplying more reactive material to the deep, where it causes additional oxygen demand.

van Heijst and Postma (2001) postulate that there is a delay between shelf emergence and connection of incisions on the shelf (canyons) to the fluvial valley. We therefore induce a rerouting mechanism for particulate organic carbon and phosphorus via submarine river canyons, 50 000 years after the onset of glaciation, when sea level has receded significantly (25% shelf loss); we assume that at that point sea level was sufficiently low to trigger the connection of submarine canyons to their feeding rivers. Based on observations of the depositional dynamics of the Congo canyon (turbidites occurring every 2–3 years; Vangriesheim et al., 2009a), we can assume the deposition of canyon fan sediments to the deep ocean as being effectively quasi-continuous over glacial-interglacial timescales.

If bypass of the coastal zone occurred for particulate material travelling via the world's 20 major rivers (by water discharge) it would represent 45% of the riverine water flux to the coastal zone (Global NEWS database; see Beusen et al., 2005). We assess the potential effect of this rerouting mechanism by varying the extent of continental particulate matter rerouting in the context of a glacial-interglacial cycle for both scenarios.

The "shelf nutrient hypothesis" is implemented by adding a flux of particulate organic carbon to the ocean, representing new labile organic matter eroding from the aerially exposed shelves into the receded coastal ocean – flux (2) in Figure 3.1.

The amount of material delivered to the sea via erosion of exposed shelves is estimated from the work of Broecker (1982) and Hay and Southam (1977). Broecker (1982) estimates that 1.2×10^5 Tmol of carbon is transferred from aerially exposed shelves to the ocean. If we assume that this carbon is eroded over a period of 50 kyr, this is equivalent to a flux of 2.3 Tmol/yr. Hay and Southam (1977) estimate an erosional flux of 150×10^{14} g sediment/yr or 25 Tmol C/yr (at 2% C). For a 50 kyr deposition this equates to 12.5×10^5 Tmol C over a full glaciation.

Another way to estimate the erosional capacity of the shelves is to calculate their storage capacity during interglacials. The storage capacity of the shelves can be estimated from the amount of material depositing during the interglacial period both from continental supply (terrestrial org C) and in-situ production (marine org C). The estimates of the continental supply of total organic carbon (TOC) to the ocean range widely from 2.5 to 83 Tmol TOC/yr (Schlunz and Schneider, 2000 – see Table 1 for list of estimate sources). Assuming 50% is particulate (Smith and Hollibaugh, 1993; Rabouille et al., 2001) yields 1.8 – 41.5 Tmol POC/yr. We take an estimate of 25 Tmol/yr, which lies close to the POC load of rivers estimated by Ittekkot (1988). During sea level high stands this load is almost exclusively deposited on the continental shelves (Schlünz and Schneider, 2000; Berner, 1982, 1989; Hedges, 1992). The burial of organic C on the shelves arising from in-situ production (marine org C) is taken from the box model (6.3 Tmol C/yr – Slomp and Van Cappellen, 2007) and compares to the estimate of Rabouille et al. (2001) of 8 Tmol C/yr. Therefore the combined terrestrial and marine carbon storage of on the shelves during sea level highstands is 31.3 Tmol C/yr or a total of 3.1×10^5 Tmol C for 10 kyr of interglacial deposition. Table 3.1 summarizes the above data giving the possible range of particulate material load erodable during glacial sea level low stands.

The timing and manner in which shelf erosion occurs have an important effect on material delivery to the ocean. If erosion was continuous (Damuth, 1977) then material fluxes were likely smaller and were spread over a longer period of time. If it was episodic (Hay, 1994), deposition likely occurred over a short time period with large fluxes. We assume here that shelf erosion occurred over the later stage of glaciation and the LGM, when continental shelves were most exposed. We implement continuous moderate erosion – total particulate load delivered over the last 50 kyr of glaciation – which could represent slow uninterrupted erosion and deposition or very frequent and rapid depositional pulses such as seen in the Congo fan (Rabouille et al., 2009), on time scales much shorter than glacial transitions. We note however, there are other possible erosion scenarios, such as interspersed pulses of shelf sediment slumping to the sea at various points during glaciation. However, since we do not

Table 3.1: Estimates of flux of organic matter eroded from exposed shelves and supplied to the ocean during sea level low stand of glacial periods

	Low end estimate (Broecker, 1982)	**Carbon storage on shelves during interglacial**	**High end estimate (Hay and Southam, 1977)**
total sediment eroded from shelves (g)	1.5×10^{20}	1.88×10^{20}	7.5×10^{20}
org C (%)	1%	2%	2 %
C/P	300*	300*	300*
org C (g)	1.5×10^{18}	3.76×10^{18}	15×10^{18}
org C (Tmol)	1.2×10^{5}	3.13×10^{5}	12.5×10^{5}
org C(Tmol/yr) (based on 50 kyr flux)	2.3	6.3	25

* C/P ratio used in model

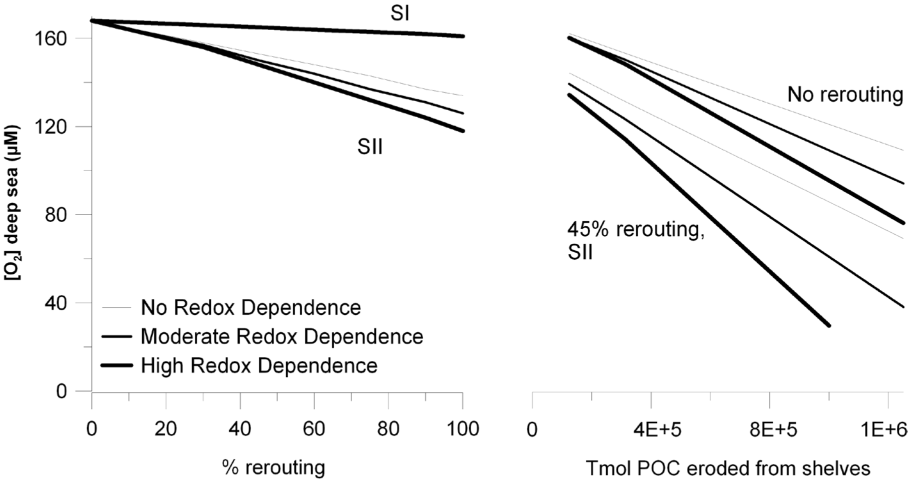

Figure 3.2 Effect of submarine river canyon formation (and rerouting of particulate material) and shelf erosion on deep-sea oxygen concentrations at the last glacial maximum (LGM). Left hand side plot: rerouting of particulate material past the coast via submarine river canyons. Light gray lines represent a system where organic and authigenic P burial are not redox dependent. Dark grey lines represent a moderate redox dependence (25% in organic P, 50% in authigenic P) as described in Slomp and Van Cappellen (2007). Black line represents high redox dependent burial of P (75% in organic P, 90% in authigenic P) as implemented in Tsandev and Slomp (2009) for anoxic settings. Both rerouting scenarios detailed in Figure 1 are plotted. Right hand side plot: a shelf erosion flux is applied as an event in the late glacial stage (50 kyrs) leading to the LGM. Results are shown both for shelf erosion without river canyon rerouting and with rerouting according to scenario SII. The results for SI lie within the plotted range.

have good constraints to define such a scenario we test the simplified version detailed above.

3.3 Results and discussion

The connection of river canyons to their rivers upon sea level low stand, thus rerouting the particulate load directly to the deep sea, has some effect on deep-sea oxygen levels (Figure 3.2). Rerouting scenario SI, where a proximal filter still exists, has only a minor effect – rerouting particulates past the distal coastal zone lowers deep-sea oxygen levels by a few μM at most, even if all of the continental rivers were connected to submarine canyons of this form. This is likely due to the fact that in our model the proximal zone is an efficient filter of incoming continental material. Most of the continental load of POC and POP is assumed to be buried or decomposed in the proximal coast (where oxygen demand is not calculated as it is assumed shallow enough to be equilibrated with the atmosphere). Therefore, river canyons which do not bypass the proximal zone play a minor role in fertilizing the deep sea as their input is filtered by a proximal coast which is very effective in processing and burying particulate material. Furthermore, the distal coastal zone is already significantly decreased during glacial times due to receding sea level; thus bypassing an already shrinking sink has a small effect on open ocean dynamics.

Rerouting scenario SII, on the other hand, where river canyons shunt the particulate load from rivers – flux (3) in Figure 3.1 – directly to the deep sea, is a much more efficient way to fertilize the deep ocean and increase its oxygen demand. Once the trapping ability of the proximal coast is bypassed, the particulate load of C and P arriving to the abyssal plains is significantly increased. The net effect is that, the absence of an active proximal zone filter allows the deep-sea nutrient supply to increase significantly and oxygen demand to increase as well, causing oxygen levels to drop by up to 50 µM.

The erosion of shelf sediment during sea level recession – flux (2) in Figure 3.1 – has a potentially significant effect on the oxygen demand in the deep sea. The range of shelf erosion estimates, detailed in Table 3.1, shows that such a flux can potentially cause severe oxygen depletion in deep-sea waters (Figure 3.2). Deep-sea oxygen levels can drop below 100µM during glaciations as opposed to 170µM during interglacials.

Given the relatively low oxygen concentrations attained when higher sediment loads are delivered to the ocean, we also examined the role of redox dependent burial of phosphorus. Redox dependent burial of reactive P can accentuate the effect of shelf erosion; when the redox sensitivity of P recycling from sediments is high, the recycled P fertilizes the surface ocean and creates greater respiratory demand from the settling POC. The difference between considering highly redox sensitive P burial and no redox sensitive P burial is negligible at low erosion fluxes but could result in ca. 40µM difference in deep-sea oxygen levels for high erosion fluxes. This is because in well oxygenated deep-sea environments (when carbon respiration demands are low) redox dependent P burial is not significant mostly because it is not observed. However, once oxygen levels drop (under higher carbon respiration demands), an accurate description of the redox dependence of reactive P burial becomes increasingly more important.

Combining the effects of shelf erosion and the rerouting of particulate material to the deep sea has even stronger effects (Figure 3.2). In the case of rerouting scenario SII, when the continental particulate load is augmented with material eroded from the exposed surrounding shelf, deep-sea oxygen levels can drop below 80 µM. Even if this synergy of shelf erosion and deep-sea deposition does not occur throughout the entire continental coastline, it could cause significantly depleted deep-sea oxygen zones in some areas where both mechanisms are at play. One example of this interplay could be the anomaly of 15–20µM of oxygen near the outlet of the Congo canyon at 4000m (Vangriesheim et al., 2009b).

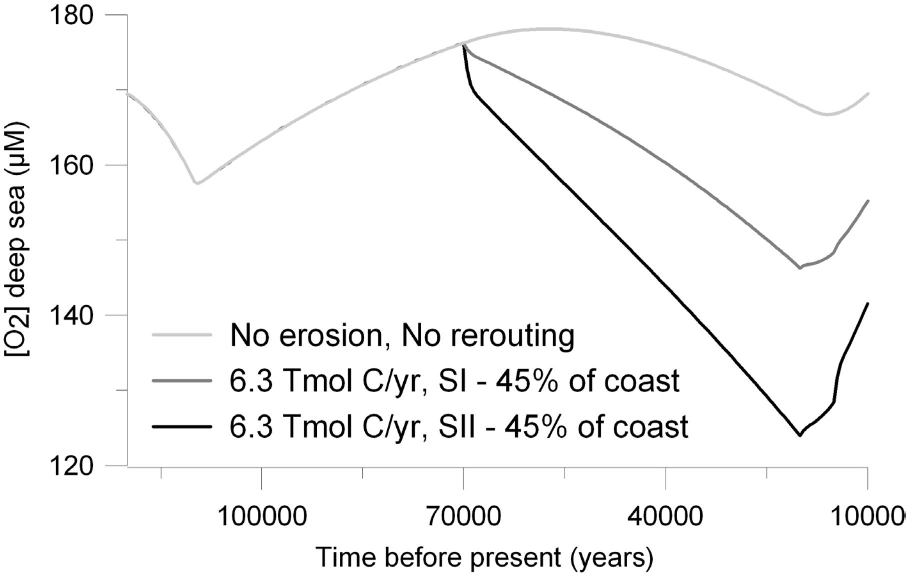

Figure 3.3 The evolution of deep sea oxygen concentrations during a glacial-interglacial cycle in the model. The light gray line represents a glacial interglacial climate change scenario as detailed in Tsandev et al. (2008) - Chapter 2 - without modifications. It corresponds to the oxygen profile of Figure 2.6 in Chapter 2. The dark gray line corresponds to the same glacial scenario with an additional flux of material eroded from exposed shelves (Table 3.1) and the formation of submarine canyons for major rivers (for 45% of the coast ocean) according to routing SI. The black line corresponds to the glacial scenario plus a flux of material eroded from exposed shelves and the formation of submarine canyons for major rivers (45% of coastal ocean) according to routing scenario SII. All runs assume a moderate redox dependence in P burial (Slomp and Van Cappellen, 2007).

When we examine the temporal variation in deep-sea oxygen throughout the glacial-interglacial transition (Figure 3.3) we see that the oxygen levels under a shelf erosion flux deviate from those of the glacial-interglacial scenario of Tsandev et al. (2008) (light gray line). Oxygen concentrations at the last glacial maximum (LGM) in the standard scenario are comparable to today's levels (167 μM – from Figure 3.3) while the oxygen levels when shelf erosion is present are noticeably lower (dark gray and black lines). If we use the organic matter sedimented on the shelves during an interglacial as the estimate of the amount of labile organic matter that could have eroded during glaciation (3.1×10^5 Tmol C – Table 3.1) and we deliver such a load to the sea during glaciation (6.3 Tmol C/yr over 50 000 yr), the deep ocean can reach oxygen levels near 125 μM. If more labile organic matter underlies the material deposited during the previous interglacial still further oxygen depletion is possible.

Given the impact of shelf erosion and submarine river canyons on deep-sea oxygen levels, we look at the corresponding effect on the other associated biogeochemical cycles in the context of glacial-interglacial climate change (Fig-

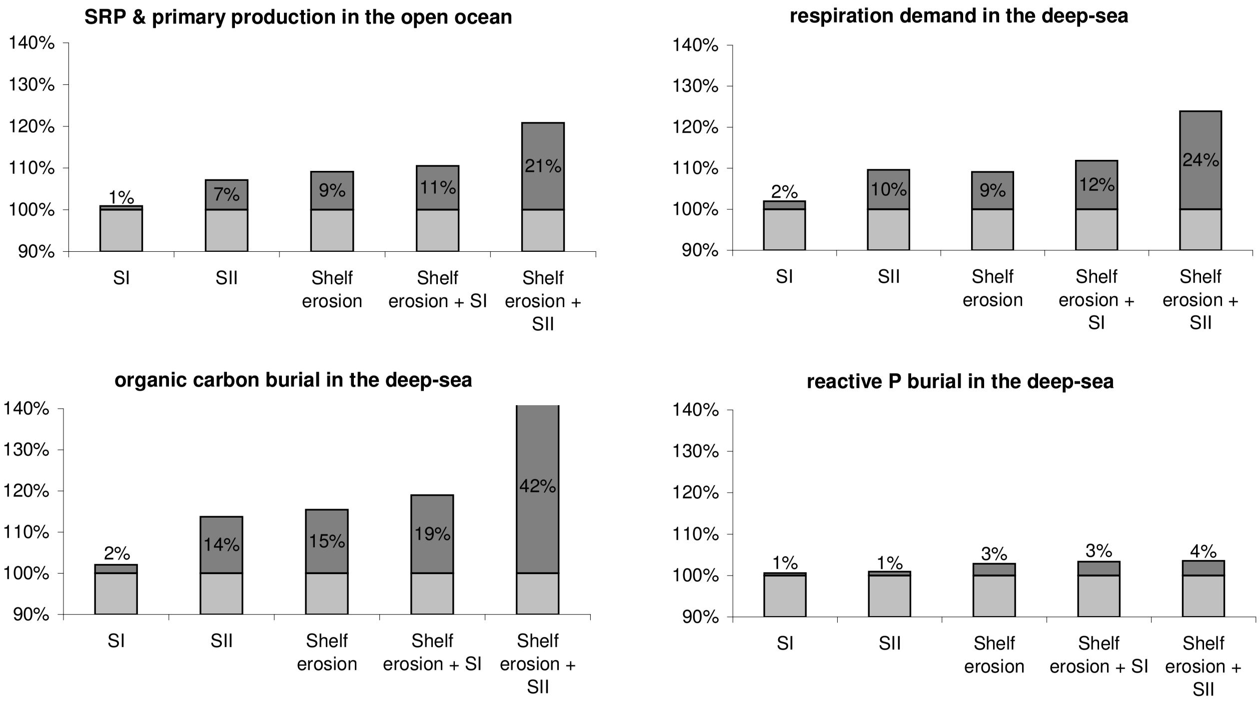

Figure 3.4 Effect of shelf erosion and rerouting of particulate material during glaciations on the biogeochemical cycling of the open ocean at the last glacial maximum (LGM). Light gray bars represent the values of biogeochemical variables (dissovled P reservoir (SRP), primary production, respirations demand, organic C and reactive P burial) at the LGM for the standard glacial-interglacial scenario used in Tsandev et al. (2008). Dark gray bars illustrate the change of value in these variables under different scenarios implemented in this paper. The 5 scenarios include the standard glacial scenario of Tsandev et al. (2008) plus formation of submarine canyons according to scenario SI and formation of submarine canyons according to SII, the erosion of 6.3 Tmol C/yr over 50 kyrs (shelf erosion), and a combination of the above. In all cases, moderate redox dependent burial of organic and authigenic P is assumed as per Slomp and Van Cappellen (2007).

ure 3.4). We examine the effect of augmenting the glacialinterglacial changes implemented in Tsandev et al. (2008) with both rerouting mechanisms by river canyons, shelf erosion, and their combined effects. Reservoir and flux values for the biogeochemical cycles of P and C at the last glacial maximum (LGM) are compared to the standard glacialinterglacial scenario implemented in Tsandev et al. (2008) (light gray bars). The net effect of all the mechanisms is some ocean fertilization. Dissolved reactive P (SRP) increases in the deep sea and correspondingly so does primary production. Rerouting scenario SI has a negligible effect while shelf erosion and rerouting scenario SII have a more pronounced effect. The combination of shelf erosion and river canyon rerouting has the greatest impact on the fertility of the open sea. However, as primary production is 11% lower during the LGM than during the interglacial period (result of chapter 2 – Figure 2.6), this fertilisation only brings the production in the ocean at the LGM close to interglacial levels but not much above them. Thus the net trend of a low production ocean during glacial times still remains despite greatly increased oxygen demand in the deep sea.

An interesting result is the respiration demand created in the open ocean. While the oxygen demand roughly follows the primary production trend it is actually higher for rerouting scenario SII than for shelf erosion. Also, while primary production remains relatively low (only 7% higher) under SII, oxygen demand increases (10% higher) and similarly when erosion and SII are combined. This implies that, in the case of routing scenario SII, the rerouting of material to the deep sea has the effect of decoupling deep-sea oxygen levels from the biogeochemical activity of the ocean, making low oxygen levels possible even for an ocean which is not fertilized enough to create a high oxygen demand from in-situ primary production.

The variable most affected by river canyons and the particulate load from the continents and shelves is organic carbon burial in the deep sea which increases twice as much as the dissolved phosphate reservoir. Therefore, most of the carbon arriving from the continent is buried in ocean sediments, which helps explain why ocean productivity can remain relatively low despite high loads of labile organic material. These model results are supported by observations of elevated organic matter burial in glacial sediments for various locations, including the Amazon fan (Goñi , 1997), the Gulf of Mexico (Newmann et al., 1973) and the continental margins of Africa and South America (Mollenhauer et al., 2004). Phosphorus burial on the other hand is nearly unaffected by the resulting ocean fertilization; even with large amounts of labile material supplied from the shelves, deep-sea P burial increases by no more than 4%. This is because, as oxygen levels fall, P is actively recycled to the water column. Therefore the fertilization of the ocean by labile organic material from land and coast goes unrecorded in the buried P record. Our finding that P burial records do not change significantly over glacial time scales is in accordance with observations for sediments from various ocean regions published by Tamburini and Föllmi (2009). In contrast, Filippelli et al. (2007) finds increased P burial at several high production sites in the Southern Ocean. Note, however, that our box model results refer to a total ocean average where productivity was not greater during glaciation and direct comparison to specific sites is difficult as local parameters often influence behaviour. Our finding that phosphorus burial cannot be readily used as a proxy for ocean productivity or organic matter flux to the seafloor is an important one; P burial is dependent on redox conditions in the sediment which can change the trend in burial irrespective of the activity of the overlying water column and decouple the P record from the productivity of the ocean.

3.4 Conclusion and implications

The effect of rerouting particulate material to the deep ocean via submarine river canyons promotes lower oxygen levels during sea level low stands. More importantly, it also decouples deep-sea oxygen content from the productivity of the surface ocean. That is, the open ocean does not need to be very active in terms of primary production to cause oxygen demand in the deep sea during glaciations. However, this effect is only felt strongly when the coast is completely bypassed by canyon incisions all the way into the river mouth and much less so if a proximal coastal filter remains between the rivers and their submarine canyons. Though this result may be surprising, giving the amount of reactive material that is being shunted to the open ocean, it is not as surprising in the context of a glacial scenario. Rerouting of the particulate matter delivered by major rivers, occurs in the late stage of glaciation when sea level is already low. Continental shelves (the distal zone) are already shrunk by 25% and another 25% is lost as the major rivers begin to form canyons and discharge particulate material to the deep. Thus, removing the distal zone for half of the continental supply has a reduced effect, as the already shrinking continental shelves play an increasingly smaller role towards the end of the glacial period. In the presence of a proximal shelf, there will always be significant trapping of material in the coastal ocean thus dampening the effect of submarine canyons.

If large amounts of organic matter were available on continental shelves and became eroded during sea level low stands, the glacial ocean's oxygen would be markedly different at the LGM. We do not know exactly what amounts of erodible labile shelf sediment are most likely, but within the range of values suggested in the literature we already see an impact on the ocean's oxygen levels during sea level low stands. The arrival of extra particulate organic matter from the erosion of exposed shelves, constitutes a supply of new labile material to the ocean. As sea level continuously recedes during glaciation, more and more shelves become exposed to erosion and, through that erosion, the coast becomes a source of carbon and nutrients to the ocean, rather than a filter (which is its role during interglacial stages). Depending on the amount of material being supplied and the manner in which it is delivered, this mechanism can have a potentially great impact on open ocean processes. If, late in the glacial period, the sediment deposited on shelves during interglacial sea level high-stands (3.1×10^5 Tmol C) becomes eroded and delivered to the ocean, the oxygen demand in the deep sea increases enough to draw deep-sea oxygen levels down to values near 125 μM.

Therefore, although we cannot say that there was enough shelf organic matter to drive complete oxygen depletion in the deep sea during glaciations, we can say that there was at least enough organic matter on the shelves to cause significant oxygen demand and do so without affecting the fertility of the open ocean to the same extent during glacial times.

A boost of organic matter to the ocean invariably creates a higher nutrient load in the open ocean and increases primary production and burial of carbon. Thus the ocean can become somewhat fertilized without invoking fertilization by micronutrients such as iron. And deep-sea oxygen levels can be lowered without invoking any further slowdown in circulation or drastic increases in primary production. Therefore, erosion processes on the continent and shelves can help explain low oxygen levels in the deep sea at the LGM in addition to previous proposals that circulation slowdown or iron fertilization caused the oxygen demand in the deep sea at glacial times.

For an ocean already depleted in oxygen, the redox dependent burial of calcium associated phases and organic phases of phosphorus becomes increasingly important as it is a positive feedback, fueling further oxygen depletion by recycling P from sea sediments. For moderately oxygenated deep-sea waters (>100μM [O_2]), the role of redox dependent P burial on oxygen depletion is small (Figure 3.2). As Figure 3.4 shows, the redox dependent nature of P burial can leave the reactive P reservoir in sediments quite insensitive to even major alterations of the marine biogeochemical cycles. It is therefore paramount that more investigations are done on the mechanisms by which P is recycled from sediments under changing redox conditions and a better quantitative relationship be established between oxygen in overlying waters and reactive P burial.

In summary, we show that the erosion of shelf sediments and formation of submarine canyons by large rivers have a potentially significant impact on ocean oxygen levels during glacial transitions. The continental shelves, which during interglacial stages act as sinks of carbon and phosphorus coming from land, can turn into sources of those elements and the shunting of labile material to the deep sea can decouple the deep ocean’s oxygen demand from the primary production of the overlying surface ocean. We also show that under declining redox conditions the P burial record is completely decoupled from the other biogechemical cycles as the redox dependent nature of P burial becomes increasingly important when bottom water oxygen levels drop near and below 100 µM.

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4

Modeling phosphorus cycling and carbon burial during Cretaceous Oceanic Anoxic Events

with C. P. Slomp

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Abstract

In the greenhouse world of the Cretaceous, there were episodes of oxygen depletion in the deep ocean associated with enhanced organic carbon burial in sediments (black shale formation). In this study, we use a box model of the oceanic phosphorus (P), organic carbon (orgC) and oxygen cycles to explore the hypothesis that variations in marine P availability control deep ocean oxygen depletion (anoxia) and the formation of black shales under Cretaceous ocean conditions. We find that, for the Cretaceous ocean, with large continental shelves, slow oceanic overturning and high sea surface temperatures, Oceanic Anoxic Events (OAEs) can be triggered by enhanced P supply from land, and that the system is particularly sensitive to oceanic mixing. In our baseline scenario, the deep sea becomes completely anoxic, while the shelves attain only partial anoxia. Sedimentary burial differs between the shelves and open ocean: while organic carbon burial is enhanced in both regions, deep sea reactive P burial decreases dramatically under anoxia, but not on the shelves, where oxygen depletion is not complete. Furthermore, our model results imply that OAEs can be sustained by P recycling from sediments under low-oxygen conditions. Ultimately, however, the feedbacks which result in the accumulation of atmospheric oxygen terminate the anoxic event. Atmospheric oxygen is modulated by land processes such as forest fires and oxidative weathering, which limit the rise of atmospheric O_2. Our model findings are corroborated by P burial data from the geological record for OAE2 (approximately 94 Myr BP). Through a sensitivity analysis we identify two necessary criteria for OAEs: low mixing of surface and deep waters (poor ocean ventilation) and enhanced sedimentary P recycling under low oxygen conditions. When these criteria are met, ocean anoxia is a robust result to a mild increase of continental supply of phosphorus, under a wide range of environmental conditions.

4.1 Introduction

Throughout the Early and Late Cretaceous, there are a number of documented periods of severe oxygen depletion in oceanic bottom waters, termed Oceanic Anoxic Events (OAEs). At least in the case of the Early Aptian (OAE1a) and the Cenomanian–Turonian boundary event (OAE2), oxygen depletion in oceanic bottom waters was widespread on a global scale (Schlanger and Jenkyns, 1976; de Gracianski et al., 1984; Schlanger et al., 1987; Sarmiento et al., 1988; Erba, 2004). These events are characterized by increased accumulation of organic carbon-rich sediments, and a positive excursion in the $\delta^{13}C$ record (Schlanger and Jenkyns, 1976; Scholle and Arthur, 1980; Schlanger et al., 1987; Arthur et al., 1988; Arthur and Sageman, 1994; Sinnighe Damsté and Köster, 1998). Understanding the mechanisms behind such events can provide insight into the functioning of global biogeochemical cycles in a warmer (greenhouse) world. Current climate change is driving the modern ocean toward conditions that exhibit similarities to the Cretaceous: sea level is currently rising (Gornitz, 1995; Hulme et al., 1999), ocean circulation is predicted to slow down (Bryden et al., 2005) and sea surface temperatures are increasing (Hulme et al.,1999). Furthermore, many studies predict the expansion of oxygen minimum zones (oxygen holes) and the formation of marine so called ‘dead zones’ where animal respiration is greatly limited (Oschlies et al., 2008; Schaffer et al., 2009; Hofmann and Schellnhuber, 2009; Brewer and Peltzer, 2009). Thus, a better understanding of Oceanic Anoxic Events may shed some light on the behaviour of our oceans in the future.

The Cretaceous was a time of extreme climatic conditions with intense volcanic activity on land and in the submarine realm (Larson, 1991; Erba, 2004). The warm humid climate contributed to an intensified hydrological cycle and enhanced export of weathered material from land to the oceans via rivers (Wagner et al., 2007). Thermohaline circulation is believed to have been slower than present day, due to the reduced thermal gradients between the tropics and the poles (Schlanger and Jenkyns, 1976; Ryan and Cita, 1977; Fischer and Arthur, 1977), and continental shelves are believed to have been as much as four times wider than today (Haq et al., 1987; Bjerrum et al., 2006), due to the almost complete absence of ice caps at high latitudes.

Along with the isotope excursions and organic carbon (orgC) accumulation characteristic of Cretaceous OAEs, these episodes are also associated with major changes in planktonic assemblages, which suggest high fertility and enhanced primary productivity (Erba, 2004). The sediments formed during these periods were also carbonate poor, which, combined with the concurrent increased organic carbon accumulation, suggest a severe perturbation of the marine C cycle (Erba, 2004).

Two mechanisms are commonly invoked to explain Oceanic Anoxic Events. These are decreased oxygen supply to the deep ocean due to slower oceanic circulation (Erbacher et al., 2001), and increased oxygen demand due to enhanced surfacewater productivity (Sarmiento et al., 1988; Handoh and Lenton, 2003). Volcanic activity (Erba, 2004; Kuroda et al., 2007) and methane emissions from marine hydrates are believed to indirectly increase the likelihood of ocean anoxia by causing a warming of the atmosphere and ocean (Wagner et al., 2007). Increased nutrient inputs, either through submarine volcanic events releasing micronutrients to the deep sea (Erba, 2004), nutrient leaching from flooded shelves (Erbacher et al., 2001) and/or increased continental supply of nutrients (Föllmi, 1995, 1999; Handoh and Lenton, 2003; Wagner et al., 2007) may have played a role in enhancing productivity.

Accumulating evidence from various core records and modeling studies suggest that changes in the oceanic phosphorus (P) cycle may have been of particular importance for the initiation and termination of periods of ocean anoxia and enhanced organic carbon (orgC) burial. For example, peaks in phosphorus accumulation in the sediment at the onset of the Oceanic Anoxic Event at the Cenomanian–Turonian boundary (93.55Ma, OAE2) have been interpreted to indicate that increased P availability triggered the enhanced productivity (Mort et al., 2007). Elevated organic C/total P burial ratios suggest that this initial boost in productivity may have been sustained by enhanced oceanic recycling of P relative to organic C under anoxia (Nederbragt et al., 2004; Mort et al., 2007; Kraal et al., in press). Previous modeling work of Wallmann (2003) has suggested that the deep sea becomes prone to eutrophication (via P release from sediments) and anoxia when deep-sea oxygen levels fall below a threshold.

The deep-sea burial record of P for OAE2 itself follows two distinct trends: while P burial is reduced in OAE sediments in most cores (e.g. Demerara Rise: Figure 4.1 and (Mort et al., 2007)), some cores record a peak during the event itself (e.g. Angola Basin: Fig. 4.1). Handoh and Lenton (2003) and Föllmi, (1995, 1999) also report peaks in P accumulation coinciding with Cretaceous OAEs. Based on model results, Handoh and Lenton (2003) suggest that a negative feedback involving a rise in atmospheric oxygen, due to high rates of organicmatter burial in the deep sea, may have terminated OAEs.

In this study, we use a box model of the marine carbon, oxygen and phosphorus cycles (Slomp and Van Cappellen, 2007) to assess whether enhanced delivery of P from the continents can trigger an OAE under Cretaceous ocean conditions, and what mechanisms can lead to its termination. We also investigate what conditions are necessary for the ocean to be predisposed to anoxia. In particular, we focus on the role of mixing intensity, sea surface temperature

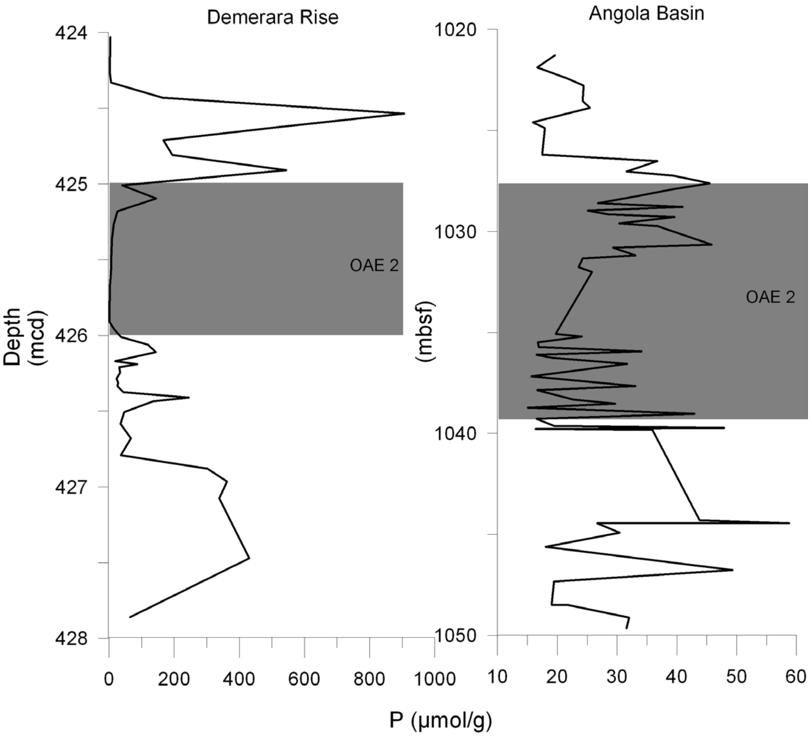

Figure 4.1 Adapted from Kraal et al. (in press.): phosphorus concentrations vs. depth for sites DSDP 530 (Angola basin) and ODP 1260 (Demerara rise). Grey bar indicates OAE 2.

(which affects oxygen solubility) and shelf size, and assess the prerequisites for the development of an anoxia-prone ocean.

4.2 Model description

We start from a model of the modern marine P cycle with a residence time of 39kyr. The choice of residence time of P is a midrange value of the various estimates ranging from 8.8 to 100 kyr (Froelich et al., 1982; Broecker, 1982; Ruttenberg, 1993; Wallmann, 2003; Ruttenberg, 2003), which should be adequately responsive to climate change forcings on the time scale of hundreds of thousands of years. The model also includes the relevant parts of the water, carbon (C) and oxygen (O_2) cycles, detailed previously in Slomp and Van Cappellen (2007) and Tsandev et al. (2008). In this model, ocean primary production is driven by the availability of soluble P in the photic zone, as this is believed to be the ultimate whole ocean limiting nutrient over geological time scales (Tyrrell, 1999). The model includes a separate representation of the continental shelves and the surface and open ocean, where the definition of the open ocean includes the continental slope. It also accounts for the redox dependent burial of organic C and the various forms of reactive P: organic P (orgP), P bound to iron oxides (FeP), authigenic calcium phosphate (authP) and biogenic P from fish debris (bioP). In the initial setting of the model, corresponding to preindustrial interglacial conditions, authP, orgP and FeP account for 50%, 25% and 25% of total reactive P burial, respectively (Ruttenberg, 1993) (Table 4.1).

The redox dependence of the burial of organic C (Hartnett et al., 1998; De Lange et al., 2008) and the various P phases is well documented (Ingall et al., 1993; Ingall and Jahnke, 1997; Slomp et al., 2004) but poorly quantified. It is implemented in the model as described in Slomp and Van Cappellen (2007). For clarity, we briefly repeat the basic assumptions pertaining to the redox-dependent burial of phosphorus.

Burial of FeP is assumed linearly dependent on the oxygen concentration in the deep ocean and vanishes completely under fully anoxic waters:

$$\mathrm{FeP_{burial}} = \mathrm{FeP_{burial;t=0}} \times \frac{[\mathrm{O2}]}{[\mathrm{O2}]_{t=0}} \tag{4.1}$$

Preferential regeneration of P from organic matter under anoxic conditions is included by assuming that burial of organic P may be reduced by up to 75% under full anoxia. The burial flux is also dependent on the export flux of organic P from the surface ocean:

$$\mathrm{orgP_{burial}} = k_{\mathrm{orgP}} \times \left(\text{export production}_{\mathrm{orgP}}\right) \times \left(0.25 + 0.75 \times \frac{[\mathrm{O_2}]}{[\mathrm{O_2}]_{t=0}}\right) \tag{4.2}$$

The burial flux of organic C is coupled to that of organic P through the organic C/organic P burial ratio, using the following equation adapted from Van Cappellen and Ingall (1994):

$$\left(\mathrm{orgC/orgP}\right)_{\mathrm{burial}} = \frac{\left(\mathrm{orgC/orgP}\right)_{\mathrm{ox}} \times \left(\mathrm{orgC/orgP}\right)_{\mathrm{anox}}}{\frac{[\mathrm{O2}]}{[\mathrm{O2}]_{t=0}}\left(\mathrm{orgC/orgP}\right)_{\mathrm{anox}} + \left(1 - \frac{[\mathrm{O2}]}{[\mathrm{O2}]_{t=0}}\right)\left(\mathrm{orgC/orgP}\right)_{\mathrm{ox}}} \tag{4.3}$$

where $(\mathrm{orgC/orgP})_{\mathrm{ox}}$=237 and $(\mathrm{orgC/orgP})_{\mathrm{anox}}$=4000 (Ingall et al., 1993) are the end member values for sedimenting organic matter buried under fully oxic and fully anoxic bottom waters, respectively.

Authigenic phosphorus formation can also be limited or absent in deep-sea sediments, under low oxygen conditions based on observations for several recent anoxic systems (Schenau and De Lange, 2000, 2001; Tamburini et al., 2002; Slomp et al., 2002, 2004) and OAE2 sediments (Mort et al., 2007; Kraal et al., in press). When there is active organic matter degradation close to the sediment water interface and concentrations of iron oxides are low, dissolved P escapes readily into the water column rather than forming authigenic minerals. Here, we assume that ocean anoxia may lead to a reduction of up to 90% of dissolved phosphate retention through authP formation:

$$\text{authP}_{\text{burial}} = k_{\text{auth}} \times \left(\text{respiration}_{\text{orgP}}\right) \times \left(0.1 + 0.9 \times \frac{[\text{O2}]}{[\text{O2}]_{t=0}}\right) \tag{4.4}$$

Biogenic phosphorus (fish debris), is the only phase of sedimentary phosphorus whose preservation is enhanced at low oxygen, according to the following relation:

$$\text{bioP}_{\text{burial}} = 0.5 \times f_{\text{bio}} \times \left(\text{export production}_{\text{bioP}}\right) \times \left(1 - \frac{[\text{O2}]}{[\text{O2}]_{t=0}}\right) \tag{4.5}$$

with f_{bioP}=0.021 (Slomp and Van Cappellen, 2007), which implies that only a small fraction of fish debris is preserved inmarine sediments. The factor 0.5 represents the redox-dependent portion of fish debris. It is implemented to moderate the effect of this phase of reactive P, since the significance of fish debris as a P sink is still under debate.

Note that the redox sensitivity of organic P (25%) and authigenic P (50%) burial previously used in this model was very conservative and primarily based on modern sediments (Slomp and Van Cappellen, 2007; Tsandev et al., 2008). Here we use a higher redox sensitivity, allowing sediment organic C/reactive P ratios which are more in accordance with those observed in the geological record for the Cretaceous (Mort et al., 2007; Algeo and Ingall, 2007). Thus we assume that 75% (instead of 25%) of organic P is recycled under full anoxia, while retention of dissolved phosphate through authP formation may be reduced by 90% (instead of 50%) under full anoxia. As there is still great uncertainty as to the sensitivity of P phases to changing redox conditions it is important to assess the model's behaviour over a range of redox sensitivities, to ensure some robustness in the system response. To assess the effect of changing the dependence of P burial on ocean redox conditions, later on in this study, we perform a sensitivity analysis over a range of redox sensitivities of reactive P.

In the coastal ocean (coast here refers to the distal zone of the box model), where oxygen content is not explicitly calculated, the degree of anoxia (DOA) function is based on primary productivity following Lenton and Watson (2000):

Table 4.1 Deep sea burial rates of organic Carbon (orgC) and various reactive P forms (see text) in the initial box model (Slomp and Van Cappellen, 2007) and in the present study after spin-up.

	DOA^{*}_{deep}	orgC	orgP	authP	FeP	bioP	totP
Tmol/yr							
initial	0	1.6	0.0068	0.0135	0.0068	0.0	0.027
			(25%)	(50%)	(25%)	(0%)	
After spin-up	0	0.0028	0.00057	0.0068	0.0	0.0153	0.0153
			(25%)	(50%)	(25%)	(0%)	

*The deep sea oxygen cycle is explicitly modeled but the result is presented as Degree Of Anoxia in the deep ocean: DOAdeep = 1-$[O_2]$deep/170μM

$$DOA_{coast} = 1 - 0.86 \times \frac{[O2]_{surf}}{[O2]_{surf,t=0}} \times \frac{\text{priamry production}_{t=0}}{\text{primary production}} \tag{4.6}$$

The burial of phosphorus phases is dependent on DOA in the coastal ocean and follows:

$$FeP_{burial} = k_{FeP,coast} \times [\text{dissolved P}]_{coast} \times (1 - DOA_{coast}) \tag{4.7}$$

$$orgP_{burial} = k_{orgP,coast} \times (\text{primary production}_{coast}) \times (1 - DOA_{coast}) \tag{4.8}$$

$$authP_{burial} = k_{authP,coast} \times (\text{respiration}_{coast}) \times (1 - DOA_{coast}) \tag{4.9}$$

$$bioP_{burial} = 0.5 \times (\text{fish production}_{coast}) \times (DOA_{coast}) \tag{4.10}$$

Termination of an OAE requires a mechanism for re-oxygenation of the ocean, which may be linked to changes in the atmospheric oxygen cycle as suggested by Handoh and Lenton (2003). These authors propose a possible sequence of events where high rates of organic matter burial in the deep sea result in oxygen release to the overlying water and atmosphere. This oxygen accumulates over time and ultimately saturates the surface ocean and re-oxygenates the deep waters. To allow testing of this negative feedback mechanism, an atmospheric oxygen cycle was added to the model following the description of Lenton andWatson (2000). Thus,we assume that the atmospheric O_2 reservoir is equilibrated with the surface ocean (Henry's law) and responds to the accumulation of organic C in the ocean (organic matter burial generates atmospheric oxygen). Accumulating atmospheric oxygen acts as a negative feedback to the primary production–anoxia–carbon burial loop. Additional terrestrial feedbacks are required for a realistic representation of atmospheric oxygen: i.e. high atmospheric oxygen is assumed to lead to increased fire frequency, which reduces vegetation biomass, continentalweathering and organic C burial on land and in the ocean. The sequence of feedbackswas taken from Table 5 of Lenton and Watson (2000), using their mathematical description of the relevant fluxes.

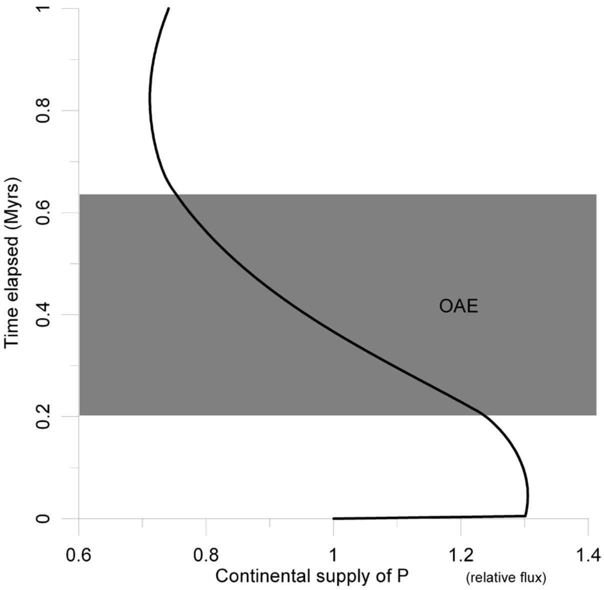

Figure 4.2 Trend in reactive P delivery to the coastal ocean from continental river discharge. The continental nutrient supply is modulated by the land feedbacks applied to atmospheric oxygen, as described in (Lenton and Watson, 2000). Relative flux is represented as the ratio of the weathering flux to the weathering flux at t_0 (initiation of the OAE). The dark bar identifies the period of anoxia in the deep ocean.

The model is originally calibrated for the modern pre-anthropogenic (interglacial) ocean, then spun up to mimic the Cretaceous ocean. Starting from an interglacial ocean as described in Slomp and Van Cappellen (2007), the shelf sizewas increased 3 fold, open oceanvertical mixingwas reduced by 50%, and sea surface temperaturewas increased by 6°C,which results in a corresponding reduced solubility of oxygen in surface waters. The model was allowed to equilibrate to the new conditions (for ca. 4 Myr). The spin-up process results in awarmer,more stagnant ocean with wide shelves and burial fluxes for the deep sea as listed in Table 4.1.We use this state as our initial condition for a pre-anoxic Cretaceous ocean. After spin-up, when the model is equilibrated with “Cretaceous-like” conditions, we apply a boost of nutrients (reactive P) delivered from the continents via rivers to the ocean (Figure 4.2).

We also test some modified versions of the model to assess the role of redox-dependent burial of reactive P and of the climatic forcings of the Cretaceous such as the mixing of ocean waters, size of continental shelves, sea surface temperature and strength of the weathering regime on land. The list of runs performed for this study is summarized in Table 4.2, along with the relevant modifications to the model setup.

Table 4.2 Model runs performed in this study and relevant parametrizations

Category	Starting Model	Parameter changes	Values relative to Tsandev et al. (2008)
General Cretaceous Setting (model spinup)	(Tsandev et al. , 2008) with coastal DOA (eqn. 6) and redox dependent P and C burial (eqns. 1-5, 7-10). Model augmented with atmospheric oxygen cycle and feedback to land and ocean processes as detailed in Lenton and Watson (2000) Table 5.	Ocean mixing flux (Vmix) Coastal volume (ShelfSize) Sea surface temp (SST) Spin up time (τ)	Vmix = 50% ShelfSize = 300% SST = + 6°C τ = 4 Myrs
General OAE Scenario	General Cretaceous Setting	After spinup, continental supply of P factor (w) increased	w = 130%
Redox sensitivity of P burial	General OAE Scenario	Eqn 2: $orgP_{burial} \propto \left(a + (1-a)\frac{[O_2]}{[O_2]_{t=0}} \right)$ Eqn 4: $authP_{burial} \propto \left(b + (1-b)\frac{[O_2]}{[O_2]_{t=0}} \right)$	a = 0 – 1.0 b = 0 – 1.0
Sensitivity to climate settings	General OAE scenario	Ocean mixing strength (vmix) Coastal volume (ShelfSize) Sea surface temperature (SST) Continental supply of P factor (w)	V_{mix} =20% –80% ShelfSize= 150%–400% SST=+2°C – +8°C w = 110% – 150%
Non-redox dependent P burial	General OAE scenario without redox dependent P burial (eqns. 1 – 5, 7 – 10) and without atmospheric feedback modulating continental supply of P (Lenton and Watson 2000, Table 5, eqn 23). Continental supply of P constant.	Continental supply of P (w)during spinup Continental supply of P factor (w) after spinup	w = 1.0 – 10.0 w = 1.1 – 3.0

4.3 Results and discussion

4.3.1. General OAE scenario

The trigger of anoxia for our Cretaceous scenario is an increase in the continental supply of reactive P to the ocean. As the supply of reactive P to the ocean increases so does primary productivity and carbon burial in the deep sea (Figure 4.3). The atmospheric O_2 also begins to build up. However, with increasing oxygen, vegetation biomass decreases (Lenton and Watson, 2000), and thus reduces the P weathering on land and the continental flux of weathered P to the ocean. Therefore the nutrient boost is short lived (Figure 4.2). Nevertheless, the ocean system goes into a mode of oxygen depletion and a full OAE develops from the short pulse of nutrients to the sea (Figure 4.3).

The deep sea undergoes oxygen depletion for a period of ca. 405,000 yr and organic C in deep sea sediments accumulates to 13 times pre-OAE values. Reactive P burial decreases, with peak burial occurring right before and after the OAE. Burial of all phases of P in the sediments decreases (authP, FeP, orgP) except for biogenic phosphorus, which is preserved under anoxia. However, since biogenic P is a small fraction of the total reactive P buried, it does not alter the overall trend of reduced total reactive P burial during OAEs. The coastal zone does not reach complete oxygen depletion and correspondingly the organic C and P burial do not follow the same anti-parallel pattern as observed for the open ocean. Organic C burial increases more moderately in the coastal than in the open ocean and reactive P burial follows a slow decreasing trend. After a period of anoxia, the enhanced organic C burial in the deep causes the accumulation of oxygen in the atmosphere. The rising atmospheric oxygen in turn increases sea surface oxygen levels and induces ventilation of the deep sea, thus terminating the anoxic event.

Comparing the general phosphorus trends for the deep sea in Figures 4.1 (geological record) and 4.3 (model results), we see that our model results capture the net trend in phosphorus burial during an OAE. That is, oceanic anoxic events are accompanied by a depletion of sedimentary phosphorus,

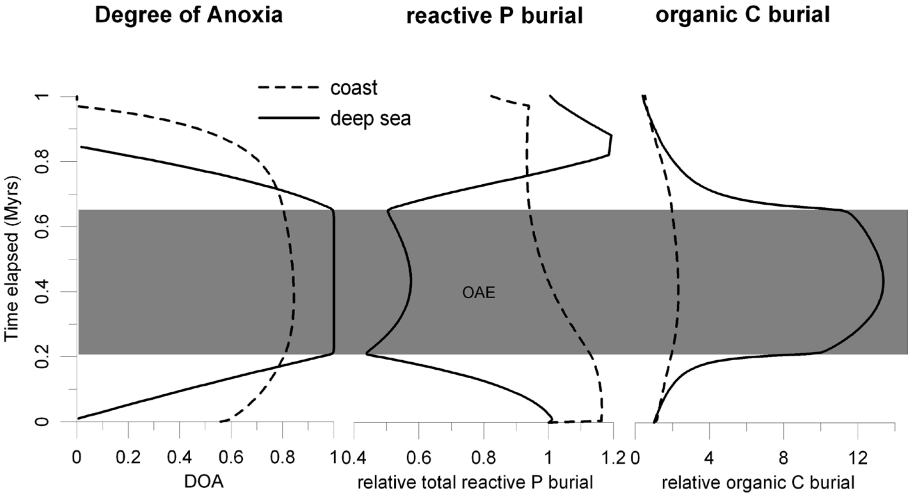

Figure 4.3 General scenario for OAE generation. Ocean conditions are 6 degree warming of sea surface temperature relative to interglacial, 50% reduction in oceanic mixing and 3 times increase in continental shelves relative to interglacial. At t_0 a 30% increase in continental P delivery is applied (see Figure 4.2 for the time evolution of the riverine P flux). Relative burial fluxes are presented as the ratio of burial flux to the burial at t_0.

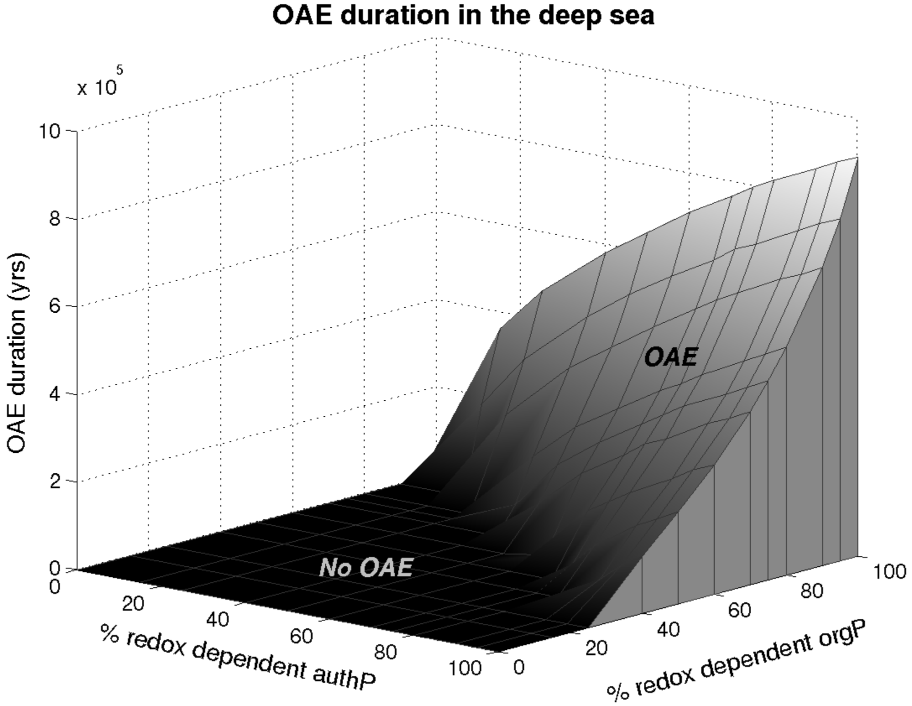

Figure 4.4 OAE duration under the general scenario, as a function of the redox dependent percentage of the two dominant P phases in the deep sea: organic and authigenic.

and, while there may be a small peak of P burial within the OAE itself, net P burial is lower during the anoxic event than it is before or after.

4.3.2. Redox-dependent P burial

Despite the agreement between the results in Figure 4.3 and the geological record discussed earlier, some questions emerge as to the robustness of the system's response under different conditions; especially given the many uncertainties about redox dependence of P burial and Cretaceous ocean conditions. We therefore performed a sensitivity analysis on the redox-dependent P recycling. More specifically, we varied the P recycling mechanism for the deep sea implemented in the model, by changing the percentage of reactive P which was recycled under dysoxic conditions (see Table 4.2). We varied the percentage of redox-dependent organic P and authigenic P burial from 0 to 100%. As the iron bound P fraction is known to be highly sensitive to redox conditions, and the fish debris is a small contributor to the total reactive P buried, we did not include them in the sensitivity analysis.

The occurrence of an OAE in the deep sea requires some minimum amount of P to be recycled from the sediments (Figure 4.4). When organic P and authigenic P have little or no redox dependence, oceanic anoxic events are not observed; and for only moderate redox dependencies in the two P phases, the OAEs are very short in duration. If either phase has a high redox dependence, an OAE does not occur, unless there is redox-dependent burial of the other phase as well, meaning that the critical amount of phosphorus recycled from sediments, and needed to sustain primary production, has to come from both P fractions. Also, when organic P burial is only moderately dependent on redox conditions, it is difficult to achieve deep-sea anoxia.

As the weathering flux fromthe continents does not remain high for long, a phosphorus source fromthe sediments is necessary to supply the dissolved P needed for sustained high primary production. However, even if the supply of phosphorus from the continents was maintained high throughout the event, by decoupling the atmospheric oxygen feedback on weathering (see Table 4.2), recycling of P from sediments in nevertheless still necessary to cause oxygen depletion in the deep sea, under reasonable continental weathering fluxes

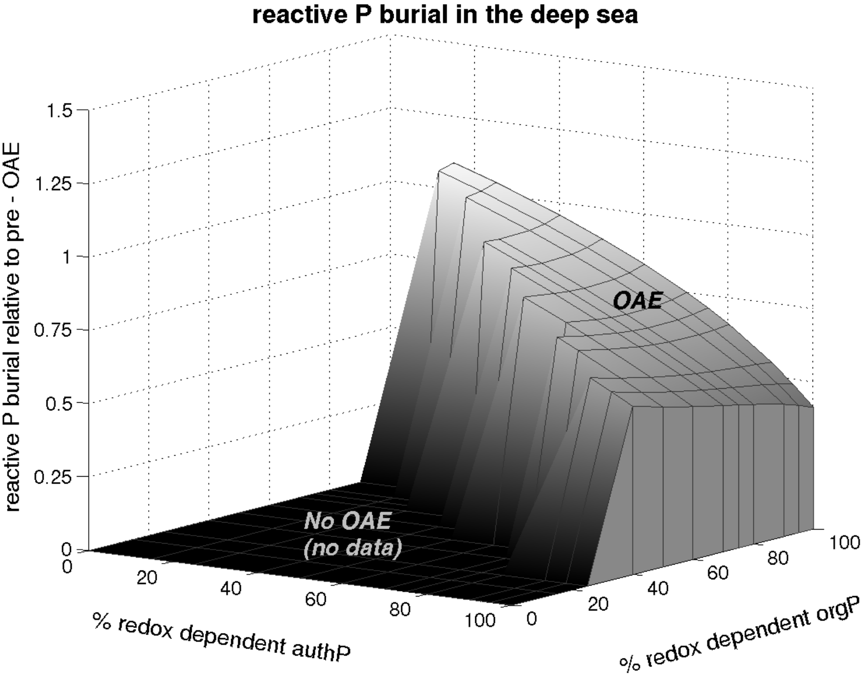

Figure 4.5 Relative total reactive P burial under the general scenario, as a function of the percentage redox dependent burial for the two dominant P phases in the deep sea: organic and authigenic. Relative P burial is presented as the ratio of peak P burial during the OAE to P burial at t_0.

(results not shown).

The duration of the anoxic event is also very sensitive to the redox dependence of P burial (Figure 4.4). We find, therefore, that a mechanism of recycling nutrients from deep sea sediments is essential for the model to generate an Oceanic Anoxic Event. The event can last up to 900,000 years, if there is a high proportion of redox-sensitive P phases. We can thus conclude that P recycling is an essential contributor to the mechanisms proliferating an OAE in the deep sea.

The change in total reactive P buried for different redox-sensitive fractions, shows a more muted response (Figure 4.5). Reactive P buried during the OAE varies within approximately a 60% range depending on how redox sensitive the different P phases are, meaning that even if 100% of a given P fraction is recycled, the resulting net amount of P buried decreases by only about 50%. This is due to intensified primary production fluxes and correspondingly intensified rain of organic matter to the sediment. Thus, when P is being lost from the sediment to the overlying water column, it induces higher primary production and is being sedimented again as organic P. This fluctuation of of total P burial for different redox sensitivities is significant, but not as dramatic as the response of OAE duration (Figure 4.4) to the same parameters, meaning that OAEs can occur and proliferate without a drastic change in the P burial record.

4.3.3 Effects of ocean conditions and external forcings (shelf size, mixing, temperature and weathering)

After having looked at redox-dependent recycling of P in the ocean and its contribution to ocean anoxia, we also examined the role of imposed forcings on deep-sea C and P burial fluxes and the occurrence and duration of OAEs. In these sensitivity analyses, we varied the shelf size, oceanic mixing, sea surface temperature and the magnitude of the initial weathering pulse (Table 4.2). This allowed us to assess whether oceanic anoxic events are a robust model result over a wide range of conditions or only a response to a limited range of environmental settings.

When the size of the continental shelves is increased, less organic carbon and reactive P are brought to and buried in the open ocean during the OAE (Figures 4.6a and 4.7). This is because the shelves act as a filter to nutrients coming from the continents; therefore by increasing that filter, less nutrients arrive to the open ocean and correspondingly less primary production and burial occur. This result is in accordance with previous work by Bjerrum et al. (2006) who find that increased shelf area promotes open ocean oxygenation.

It is interesting to note, however, how sensitive the duration of the OAE is to

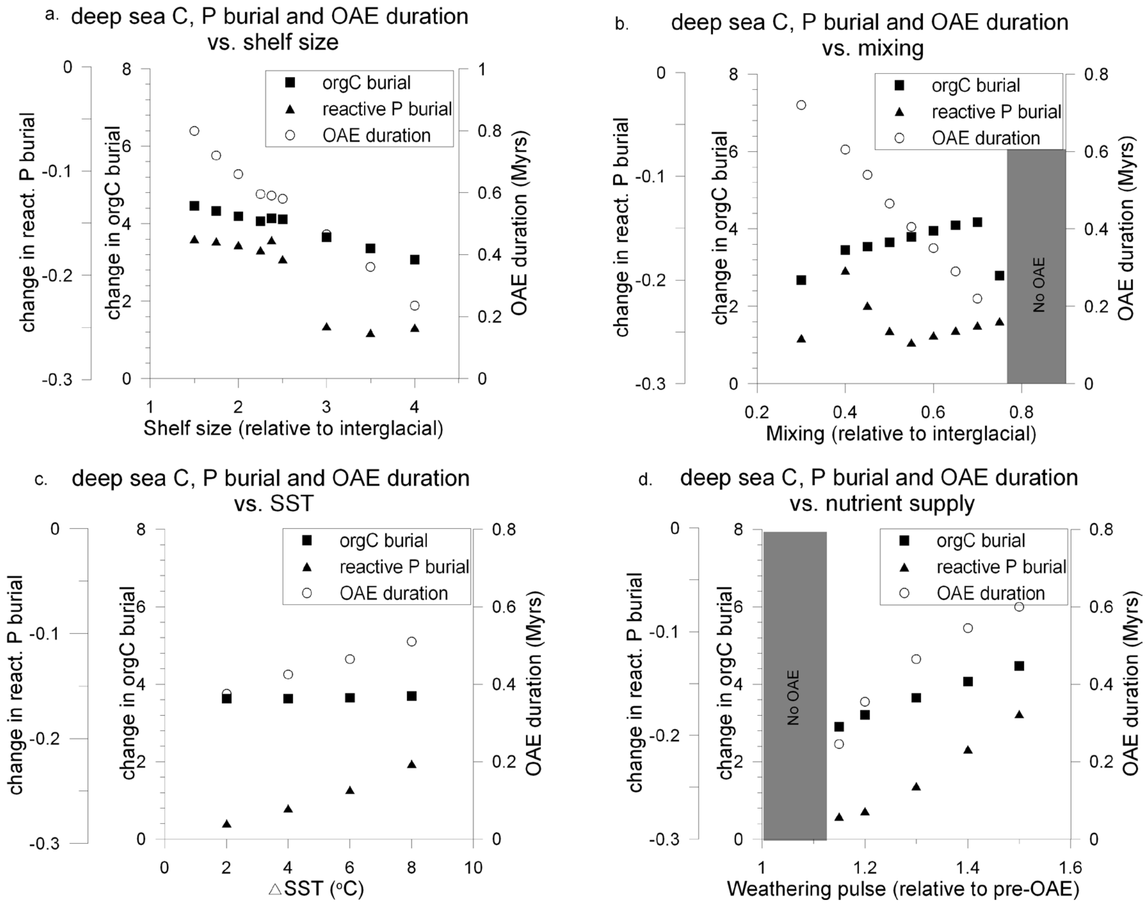

Figure 4.6 OAE duration and changes in organic C and reactive P burial during the OAE, as a function of oceanic conditions and external forcing. The change in burial is represented as the difference between peak OAE burial and the burial at t0. The differences are non-dimentionalised by scaling to the initial conditions for organic C and reactive P burial fluxes (1.6 Tmol org C/yr, 0.027 Tmol react P/yr (Slomp and Van Cappellen, 2007)). NOTE: the change in burial is presented here as a difference, rather than a ratio. This is because the burial fluxes at t_0 are not the same for different ocean conditions (shelf size, mixing and temperature) thus division by fluxes at t_0 would be misleading.

shelf size. Over a range of coastal volumes, from those similar to present day to shelves 4 times larger, the OAE lasts between 800 and 200kyr. Thus, larger ocean shelves not only make oxygen depletion in the deep sea more difficult, they make sustaining oxygen depletion difficult as well. Therefore, OAE duration shortens when ocean shelves expand. We did, however, observe Oceanic Anoxic Events over the full range of shelf sizes tested. Thus increasing the ocean coastal volume alone is not sufficient to eliminate the deep sea's susceptibility to oxygen depletion when other forcings are present. The changes in the deep sea carbon and P burial fluxes, as a result of changes in shelf size, are small in comparison to the fluctuation of the duration of the oceanic anoxic event. Deep-sea carbon burial, which is a function of open ocean productivity, is highest for small shelves. The amount of P buried in the deep sea during anoxia is also higher for small shelves (little filtering of nutrients in the coastal ocean). This is illustrated with the profile of P burial as shown as a function of time in Figure 4.7, where the total amount of P sequestered during the OAE is much greater for the smallest shelf size.

OAE duration is very sensitive to variations in the mixing intensity between deep and surface waters, while carbon and P burial during the OAE are less affected as seen in Figure 4.6b and the time trends in P burial in Figure 4.7. Slow mixing creates a disconnection between the surface and deep ocean, making the deep sea more prone to anoxia. Correspondingly, stronger mixing makes anoxia less likely because it requires large oxygen consumption to counterbalance the ventilation from surface waters. Therefore, as ocean mixing increases, oceanic anoxic events become shorter. It is noteworthy that, for high mixing intensities (similar to the present day ocean), an OAE does not occur. Ocean mixing has to be sufficiently low (≤75% of present day) to allow the ocean system to deplete deep sea oxygen.

Organic carbon burial in the deep sea is responsive to mixing. When water exchange is relatively high, while still allowing for deep-sea anoxia to occur, the conditions for carbon burial are optimal, with high export production from the surface ocean (high mixing fluxes) and deep-sea anoxia enhancing preservation. As the mixing intensity between surface and deep decreases, the transport of nutrients from the deep sea to the surface is hindered, primary production decreases, and carbon burial decreases slightly. The net result is high organic carbon accumulation in sediments overlain by relatively well mixed but anoxic waters. This result is in line with previous findings of Van Cappellen and Ingall (1994), who, however, did not take into account organic C preservation under anoxia. Mixing does not greatly affect the amount of P buried during an OAE (Figures 4.6 and 4.7). The non-linear behavior of P burial with mixing intensity, is due to the interplay of different mechanisms: decreased production, authigenic and organic P burial, but increased biogenic P burial under low mixing. However, the net result is only a small fluctuation in the reactive P burial due to opposing mechanisms.

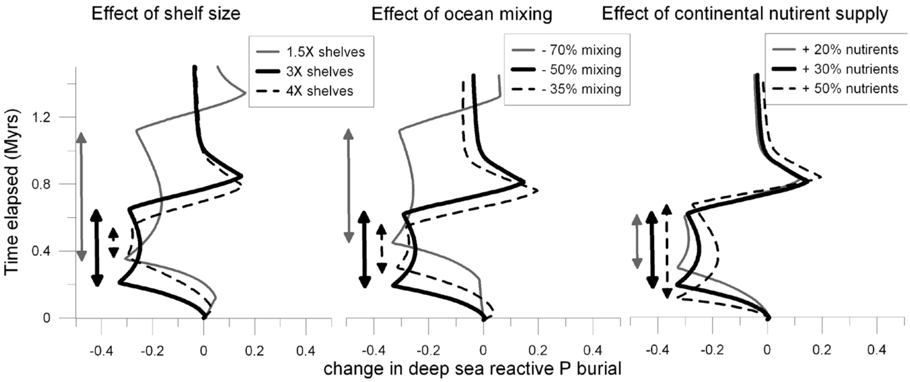

Figure 4.7 Change in P burial throughout an OAE for different oceanic conditions and continental nutrient supply. The change in burial is represented here as the difference between OAE burial and the burial at t0. The differences are non-dimentionalised by scaling to the initial conditions for organic C and reactive P burial fluxes (1.6 Tmol org C/yr, 0.027 Tmol react P/yr (Slomp and Van Cappellen, 2007)).

Modeled C and P burial are not very sensitive to variation in oxygen solubility, resulting from sea surface temperature changes. A moderate response was observed for OAE duration (Figure 4.6c), but not as large as found for the other forcing parameters. Thus, although oxygen solubility decreases strongly with sea-surface temperature, this does not result in an appreciable decrease in the capacity of the ocean to ventilate the deep sea.

Finally, we tested the effect of the strength of the triggering mechanism (nutrient delivery from the continents (Figures 4.6d and 4.7)). We observe that, a minimum nutrient supply has to be provided in order to generate an OAE, though that threshold is not very high. It is in fact the internal recycling of P from sediments, under dysoxic conditions, which amplifies the effect of the nutrient supply and sustains the high productivity and respiration for the duration of the anoxic event. Without this internal loop to recycle P from the sediments, the modulated external supply of nutrients would not be sufficient to induce high enough productivity to cause O_2 depletion in the deep sea.

Therefore, for the stagnant warm ocean of the Cretaceous, a moderate perturbation in nutrients delivered by rivers to the ocean, can result in a cascade effect causing complete oxygen depletion in the deep sea. Above that threshold, the response of the system is linear with respect to weathering strength; more nutrient supply leads to a more intense productivity-recycling loop and more phosphorus and organic C burial. The duration of the OAE also increases with increased weathering.

From this result it is possible to imagine a scenario where a different trigger (e.g. a slowdown in circulation) could also induce an anoxic event in the ocean, if it can bring initial oxygen levels low enough to initiate the positive feedback loop (Slomp and Van Cappellen, 2007).

Similarly, we can argue that if some external factor can bring about oxygen levels high enough to turn off the productivity–anoxia–nutrient recycling loop, the ocean can become ventilated. We tested this idea, by turning off the atmospheric negative feedback loop (the current mechanism for OAE termination) and increasing open ocean circulation instead. We found that increasing circulation can ventilate the ocean, but it would take a dramatic change in the circulation intensity. Once the ocean is anoxic, it would take overturning strengths 2.3 times greater than the present day to re-ventilate it (that is a 460% increase in Cretaceous circulation fluxes). So,while circulation change is a possible mechanism for ocean ventilation, a great change in the circulation regime would be required, making it an unlikely candidate for a mechanism to terminate anoxia.

We also tested the possibility of nutrient starvation in driving ocean re-oxygenation, in the absence of land and atmospheric oxygen feedbacks. In this scenario, we reduced the continental nutrient supply to see whether the ocean will run out of P and reventilate because of a reduced respiratory demand for oxygen in the deep sea.We found thatwe could not shift the ocean out of an OAE by cutting off the continental supply of phosphorus, over a period of 10 Myr. Given the nature of Cretaceous climate, a reduction in nutrient supply seems unlikely, even less so a large decrease in continental run-off; therefore we do not believe this to be a viable mechanism for ocean ventilation.

Thus,we conclude that negative feedbacks within the system, such as the land feedbacks onto the atmospheric oxygen cycle, are necessary to allow the ocean system to exit an anoxic state. Circulation changes and reduced nutrient delivery from land are unlikely to have forced the system out of anoxia in the Cretaceous.

4.4 Conclusion and implications

We find that our model can reproduce the general trend of P and organic carbon burial as observed in the geological record for OAE2. We also find that Oceanic Anoxic Events are a robust result of our model, provided some necessary criteria are met. Firstly, the global ocean has to be sufficiently stagnant (low mixing) to allow the system to achieve oxygen depletion in the deep sea. A well mixed ocean, even with high nutrient supply and high productivity cannot maintain oxygen depleted bottomwaters if those are overturned too frequently with ventilated surface waters.

With primary production being phosphorus limited, a boost of P supplied from the continents can trigger anoxia in a stagnant ocean. Furthermore, the increase in nutrient supply need not be high or long in duration, relative to the OAE (see Figure 4.2). However, some form of P recycling under dysoxic conditions is needed. It is in fact the internal recycling of P from sediments, under dysoxic conditions, which amplifies the effect of the nutrient supply and sustains the high productivity and respiration for the duration of the anoxic event. Without this internal loop to recycle P from the sediments, the external supply of nutrients would have to be increased by more than 70% to cause even a very short-lived O_2 depletion in the deep sea (results are not shown here). The sustaining mechanism of an OAE, in our model was not a climatic forcing but rather an internal feature of the deep-sea floor which propagates anoxia via the productivity–anoxia–phosphorus recycling positive feedback loop (Mort et al., 2007; Kraal et al., submitted for publication; Nederbragt et al., 2004). The degree of redox sensitivity of the burial of P phases is therefore an important factor in determining the occurrence and duration of OAEs.

Continental shelf sizes and sea surface temperatures are not critical for the occurrence of an Oceanic Anoxic Event. Anoxia was terminated in our model via a negative feedback of atmospheric oxygen accumulation with enhanced organic C burial, which causes elevated oxygen in surface waters and consequently ventilation of the deep ocean through mixing (Handoh and Lenton, 2003). Circulation was also tested as a termination mechanism, but atmospheric oxygen feedback is a much more likely termination mechanism.

These findings are relevant, given some of the tendencies of current climate change. Increasing greenhouse gases are leading to increased atmospheric and sea surface temperatures. Under these warmer conditions, ocean circulation is predicted to slow down (Manabe and Stouffer,1993; Stocker and Schmittner,1997; Quadfasel, 2005) while the hydrological and weathering regimes will likely be enhanced. Therefore, the findings of our modeling study suggest that the ocean of the future could become susceptible to developing bottom water anoxia.

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5

Phosphorus diagenesis in deep-sea sediments: sensitivity to water column conditions and global scale implications

with D. C. Reed and C. P. Slomp
in preparation for submission to Chemical Geology

Abstract

In this study, the impact of changes in bottom water oxygen and organic matter (OM) input on burial of phosphorus (P) in deep-sea sediments is examined using a reactive transport model. Results show that the burial of key reactive P phases, namely authigenic calcium associated P minerals (Ca-P), organic P (org P) and iron-bound P (Fe-P), responds non-linearly to both water column forcings. High organic matter (OM) flux with either very low or high oxygen favor the formation of authigenic Ca-P, while low oxygen and intermediate to high OM fluxes promote org P burial. Iron-bound P is only preserved in the sediment when oxygen levels are high and OM fluxes low. The conditions for maximum P recycling (or minimum P burial) are low bottom water oxygen concentrations and low OM fluxes to the sediment-water interface (hypoxic, oligotrophic deep-sea settings). The bivariate dependence of P burial on oxygen and OM flux was implemented in an existing box model of the global marine P, oxygen and organic carbon cycles, replacing simple empirical redox functions for P burial. The response of the original and new box model to decreased ocean mixing was then assessed. In the new model, org P instead of authigenic Ca-P is the dominant burial phase of P in deep-sea environments during periods of ocean anoxia. However, reduced ocean mixing leads to a similar response in total P burial and, as a consequence, to similar changes in deep-water anoxia and ocean productivity in both models.

5.1 Introduction

Phosphorus (P) is an essential component of marine life, acting as the growth limiting nutrient for primary production in the global ocean over long time scales (Holland 1978; Tyrell, 1999). Most of the reactive phosphorus arriving at the sediment water interface is primarily in the form of organic matter. Upon burial below the sediment water interface (SWI), part of this organic matter (OM) decomposes, releasing phosphate into the pore waters. This phosphate can bind to iron oxides or precipitate as an authigenic mineral (mostly carbonate fluoroapatite; CFA) or diffuse to the SWI and escape into the water column. As a consequence, the fate of P in the sediment depends on environmental conditions that allow iron oxides to exist, authigenic calcium phosphate minerals (Ca-P) to form and OM to be preserved. Key variables in this context are the oxygen concentration of the overlying waters and the amount of labile organic matter deposited on the sediment. Thus, for example, phosphorus bound to iron oxyhydroxides (henceforth called iron oxides) is readily lost to the pore waters in sediments overlain by anoxic bottom waters, because of reductive dissolution of the iron oxides that bind P (Mortimer, 1941; Ingall and Jahnke, 1994; Mort et al., 2010).

Field observations (Slomp et. al. 2002, 2004; Schenau and De Lange, 2001; Tamburini et al., 2002; Mort et al., 2007; Kraal et al., 2009) show that authigenic Ca-P formation is limited in low sedimentation rate environments overlain by dysoxic or anoxic water. When oxygen penetration into the sediment is shallow or non-existent, P is released from dissolving iron oxides and aerobic OM degradation close to the sediment water interface, where it can more readily escape to the water column. In oxic settings, by contrast, the presence of iron oxides helps in the redistribution of phosphate liberated by organic matter degradation, aiding the accumulation of large dissolved P concentrations which create optimal conditions for the precipitation of authigenic Ca-P (Slomp et al., 1996).

P incorporated in organic matter is preferentially released during organic matter degradation by anaerobic bacteria which have a limited ability to store P under anoxic conditions (Ingall and Jahnke, 1994). However, organic matter itself is known to be preserved under anoxic conditions (Ingall et al., 1993; Andersen, 1996; Hartnett et al., 1998; Moodley et al., 2005; De Lange et al., 2008) due to the limitation of anaerobic bacteria in oxidizing certain classes of organic compounds (Canfield, 1994) and due to the reduced speed of the other metabolic pathways degrading it, particularly sulfate reduction and methanogenesis. The preservation of organic P in sediments is therefore dependent on both the amount of P arriving as organic matter, the preferential release of the P and the degradation rate of the organic matter under reducing conditions. However, despite observations and qualitative understanding, quantitative insight in the processes that control P diagenesis in deep-sea sediments is still lacking. This holds particularly for the response of sedimentary P burial in deep-sea sediments to changes in water column oxygen and the incoming organic matter fluxes. Such knowledge is needed as global models of ocean biogeochemistry often have a simplistic description of sedimentary P dynamics (e.g. Wallmann, 2003; Handoh and Lenton, 2003; Slomp and Van Cappellen, 2007) and there is uncertainty over the role of redox-dependent P burial in deep-sea settings and its implications on the global scale (e.g. Tsandev et al., 2010).

Reactive transport models (RTMs) have long been a part of the study of early diagenesis in aquatic sediments, starting from the single component steady-state models as described by Berner (1980), followed by various steady-state and transient multi-component models that were developed in the mid-1990s (Boudreau, 1996; Soetaert et al., 1996; Van Cappellen and Wang, 1996). Applications of such models include case studies with detailed descriptions of the biogeochemical dynamics at a given site (e.g. Van Cappellen and Wang, 1996; Berg et al., 2003) and more generic simulations where the aim was to obtain representative profiles for a wide range of marine settings (Van Cappellen and Wang, 1995; Boudreau, 1996; Soetaert et al., 1996).

As yet, sedimentary P cycling is not often incorporated into such studies, with some exceptions such as the work of Van Cappellen and Berner (1988) and Slomp et al. (1996) who studied authigenic Ca-P precipitation in continental margin sediments and the factors influencing it. These studies highlighted the need for significant subsurface production of dissolved phosphate for authigenic Ca-P formation Recently, Reed et al. (2010) used a multi-component coupled benthic-pelagic RTM to describe the temporal dynamics in benthic P recycling and burial over a seasonal cycle at a location in the Baltic Sea. This work demonstrated that strong feedbacks occur between water column oxygen and sedimentary P dynamics in such a coastal setting.

In this paper we parameterize the benthic component of the RTM of Reed et al. (2010) for two generic deep-sea environments. The model includes a description of the sedimentary P cycle and accounts for the decomposition of org P, as well as the adsorption and coprecipitation of pore water phosphate to iron oxides and the precipitation of authigenic Ca-P for sufficiently high concentrations of pore water phosphate. Preferential release from organic matter under anoxic conditions (Ingall et al., 1993) is also included. Using parameters constrained in previous studies, we define two types of deep-sea environments: an oligotrophic, low sedimentation rate basin site and, a more active, mesotrophic deep-sea sediment. The oligotrophic setting represents many abyssal environments, where the organic matter flux to the sediments is low and consequently there is oxygen penetration into the sediment due to the low biological activity. The mesotrophic setting represents abyssal environments which receive higher organic matter loading and for which sedimentary oxygen is depleted within the first few centimeters (Emerson et al., 1985). We observe how these differences affect sedimentary phosphorus characteristics, such as the presence of iron oxides and iron-bound P, as well as the formation of authigenic Ca-P. We then subject the generic oligotrophic deep-sea setting to changing bottom water oxygen and organic matter flux and study how the deep-sea environment responds to changes in the oxygenation of the water column and the rain of organic matter. The response to these forcings is measured primarily in the behavior of phosphorus species in the sediment through the burial and efflux of phosphorus under changing conditions.

We link our RTM results to previous box modeling efforts of the global marine P cycle (Slomp and Van Cappellen, 2007), which looked at the effect of a slowdown in ocean mixing on the coupled cycles of oxygen, org C and P in the ocean. We use the RTM results to construct 2-dimensional redox functions for P burial under changing conditions at the sediment water interface (SWI), namely oxygen depletion in the water column and increased organic matter loading. By replacing the empirical redox relations of P burial initially used by Slomp and Van Cappellen (2007) with the mechanistically derived functions constructed from the reactive transport model, we examine how overall oceanic P, org C and oxygen behavior changes with a slowdown in ocean mixing. Do the mechanistically derived redox dependencies of P burial drastically change the marine P cycle's response to forcing and are the associated cycles of oxygen and organic carbon affected as well? Does introducing non-linear redox dependence in the burial of sedimentary P ultimately improve the description of the marine P cycle?

5.2 Model and experiment description

5.2.1 Reactive transport model (RTM)

The sediment component of the benthic-pelagic reactive transport model of Reed et al. (2010) was used in this study. The version of the model used here contains a reaction network of 21 chemical species and 21 reactions (Tables 5.1 - 5.3). The reactions were taken from Wang and Van Cappellen (1996), Boudreau et al. (1996) and Berg et al. (2003) augmented with sediment P diagenesis. The differences with the original sediment model of Reed et al. (2010) are that (1) boundary conditions at the sediment-water interface are prescribed instead of calculated (2) only one reactive pool of iron and manganese oxides is assumed to be present (3) reaction and transport parameters pertaining to deep sea settings are implemented. The discussion of reaction

Table 5.1: Chemical species included in the RTM (after Reed et al., 2010).

Species	Notation	Type
Organic carbon type[a] *i*	C_{org}^{i}	Solid
Organic phosphorus type *i*	P_{org}^{i}	Solid
Oxygen	O_2	Solute
Nitrate	NO_3^-	Solute
Manganese oxides	MnO_2	Solid
Iron oxides	$Fe(OH)_3$	Solid
Iron oxide bound phosphorus	$\chi Fe-P$	Solid
Sulfate	SO_4^{2-}	Solute
Manganese	Mn^{2+}	Solute
Iron	Fe^{2+}	Solute
Phosphate	H_3PO_4	Solute
Ammonia/Ammonium	$\sum NH_4^+$	Solute
Hydrogen sulfide	$\sum H_2S$	Solute
Methane	CH_4	Solute
Elemental Sulfur	S_0	Solid
Iron monosulfide	FeS	Solid
Pyrite	FeS_2	Solid
Authigenic phosphorus (apatite)	$P_{authigenic}$	Solid

a) there are 3 types of organic matter: very labile (α), moderately labile (β) and refractory (γ) of the form $(CH_2O)_a(NH_4^+)_b(H_3PO_4)_c$

and transport processes in this paper is limited to those processes that directly involve phosphorus.

Phosphorus in the model was subjected to the same transport processes as other constituents, namely molecular diffusion, bioturbation and burial. Organic matter follows a multi–G formulation (Berner, 1980) and was assumed to consist of 3 pools: very labile (α), moderately labile (β) and refractory (γ). The succession of oxidants used in the degradation of organic matter was described using a Monod scheme (Boudreau, 1997). Preservation of organic matter in anoxic sediments, was implemented with a slow sulfate reduction rate constant (Tables 5.3 and 5.4). Preferential regeneration of org P from organic matter is assumed to occur for sulfate reduction and methanogenesis. This was implemented by multiplying the organic matter decomposition rate with an acceleration factor (ε) for P release from OM:.

$$R_{Porg} = R_{Corg}\left(\varepsilon \cdot \frac{[P_{org}^{i}]}{[C_{org}^{i}]}\right) \tag{5.1}$$

Table 5.2: Chemical reactions included in the RTM (after Reed et al., 2010).

Primary redox reactions:

$$OM + aO_2 \longrightarrow aCO_2 + bNH_4^+ + cH_3PO_4 + aH_2O \tag{A1}$$

$$OM + \frac{4a}{5}NO_3^- + \frac{4a}{5}H^+ \longrightarrow aCO_2 + bNH_4^+ + cH_3PO_4 + \frac{2a}{5}N_2 + \frac{7a}{5}H_2O \tag{A2}$$

$$OM + 2aMnO_2 + 4aH^+ \longrightarrow aCO_2 + bNH_4^+ + cH_3PO_4 + 2aMn^{2+} + 3aH_2O \tag{A3}$$

$$OM + 4aFe(OH)_3 + 4a\chi Fe - P + 12aH^+ \longrightarrow aCO_2 + bNH_4^+ + (c + 4a\chi)H_3PO_4 + 4aFe^{2+} + 13aH_2O \tag{A4}$$

$$OM + \frac{a}{2}SO_4^{2-} + aH^+ \longrightarrow aCO_2 + bNH_4^+ + cH_3PO_4 + \frac{a}{2}H_2S + aH_2O \tag{A5}$$

$$OM \longrightarrow \frac{a}{2}CO_2 + bNH_4^+ + cH_3PO_4 + \frac{a}{2}CH_4 \tag{A6}$$

Other reactions:

$$O_2 + NH_4^+ + 2HCO_3^- \longrightarrow NO_3^- + 2CO_2 + 3H_2O \tag{A7}$$

$$O_2 + 2Mn^{2+} + 4HCO_3^- \longrightarrow 2MnO_2 + 4CO_2 + 2H_2O \tag{A8}$$

$$O_2 + 4Fe^{2+} + 8HCO_3^- + 2H_2O + 4\chi H_3PO_4 \longrightarrow 4Fe(OH)_3 + 4\chi Fe - P + 8CO_2{}^{*} \tag{A9}$$

$$2O_2 + FeS \longrightarrow SO_4^{2-} + Fe^{2+} \tag{A10}$$

$$7O_2 + 2FeS_2 + 2H_2O \longrightarrow 4SO_4^{2-} + 2Fe^{2+} + 4H^+ \tag{A11}$$

$$2O_2 + H_2S + 2HCO_3^- \longrightarrow SO_4^{2-} + 2CO_2 + 2H_2O \tag{A12}$$

$$2O_2 + CH_4 \longrightarrow CO_2 + 2H_2O \tag{A13}$$

$$MnO_2 + 2Fe^{2+} + 2\chi H_3PO_4 + 2H_2O + 2HCO_3^- \longrightarrow 2Fe(OH)_3 + 2\chi Fe - P + Mn^{2+} + 2CO_2 \tag{A14}$$

$$MnO_2 + H_2S + 2CO_2 \longrightarrow Mn^{2+} + S_0 + 2HCO_3^- \tag{A15}$$

$$2Fe(OH)_3 + 2\chi Fe - P \quad + H_2S + 4CO_2 \longrightarrow 2Fe^{2+} + 2\chi H_3PO_4 + S_0 + 4CHO_3^- + 2H_2O \tag{A16}$$

$$Fe^{2+} + H_2S \longrightarrow FeS + 2H^+ \tag{A17}$$

$$SO_4^{2-} + CH_4 + CO_2 \longrightarrow 2HCO_3^- + H_2S \tag{A18}$$

$$4S_0 + 4H_2O \longrightarrow 3H_2S + SO_4^{2-} + 2H^+ \tag{A19}$$

$$FeS + S_0 \longrightarrow FeS_2 \tag{A20}$$

$$H_3PO_4 \longrightarrow P_{authigenic} \tag{A21}$$

* χFe-P represents H_3PO_4 adsorbed onto iron oxides with the ratio χ

Precipitation and dissolution reactions for iron oxide and associated formation and release of sorbed or co-precipitated P are coupled by assuming a fixed ratio (χ) between solid phase phosphorus and iron (Table 5.3). The precipitation of authigenic Ca-P was implemented as a standard precipitation reaction, whereby authigenic Ca-P is assumed to precipitate if porewater phosphate concentrations reach a threshold (Van Cappellen and Berner, 1988; Slomp et al., 1996 – Table 5.3).

5.2.1.1 RTM parameterization

Though the local characteristics of marine sites are highly variable, a number of global studies have attempted to derive empirical predictive equations parameterizing diagenesis parameters (OM flux, OM decomposition and burial, bottom water oxygen, bioturbation, etc.) as a function of master variables such

Table 5.3: Reaction equations for the primary and secondary redox reactions in the RTM (after Reed et al., 2010).

$$R_{O2} = k_i C^{i}_{org}\left(\frac{[O_2]}{k_{O2}+[O_2]}\right) \tag{B1}$$

$$R_{NO3} = k_i C^{i}_{org}\left(\frac{[NO_3^-]}{k_{NO_3^-}+[NO_3^-]}\right)\left(\frac{k'_{O2}}{k'_{O2}+[O_2]}\right) \tag{B2}$$

$$R_{MnO2} = k_i C^{i}_{org}\left(\frac{[MnO_2]}{k_{MnO2}+[MnO_2]}\right)\left(\frac{k'_{NO_3^-}}{k'_{NO_3^-}+[NO_3^-]}\right)\left(\frac{k'_{O2}}{k'_{O2}+[O_2]}\right) \tag{B3}$$

$$R_{FeOH3} = k_i C^{i}_{org}\left(\frac{[Fe(OH)_3]}{k_{Fe(OH)_3}+[Fe(OH)_3]}\right)\left(\frac{k'_{MnO2}}{k'_{MnO2}+[MnO_2]}\right)\left(\frac{k'_{NO_3^-}}{k'_{NO_3^-}+[NO_3^-]}\right)\left(\frac{k'_{O2}}{k'_{O2}+[O_2]}\right) \tag{B4}$$

$$R_{SO4} = k_{sulf} C^{i}_{org}\left(\frac{[SO_4^{2-}]}{k_{SO_4^{2-}}+[SO_4^{2-}]}\right)\left(\frac{k'_{Fe(OH)_3}}{k'_{Fe(OH)_3}+[Fe(OH)_3]}\right)\left(\frac{k'_{MnO2}}{k'_{MnO2}+[MnO_2]}\right)\left(\frac{k'_{NO_3^-}}{k'_{NO_3^-}+[NO_3^-]}\right)\left(\frac{k'_{O2}}{k'_{O2}+[O_2]}\right) \tag{B5}$$

$$R_{CH4} = k_{meth} C^{i}_{org}\left(\frac{k'_{SO_4^{2-}}}{k'_{SO_4^{2-}}+[SO_4^{2-}]}\right)\left(\frac{k'_{Fe(OH)_3}}{k'_{Fe(OH)_3}+[Fe(OH)_3]}\right)\left(\frac{k'_{MnO2}}{k'_{MnO2}+[MnO_2]}\right)\left(\frac{k'_{NO_3^-}}{k'_{NO_3^-}+[NO_3^-]}\right)\left(\frac{k'_{O2}}{k'_{O2}+[O_2]}\right) \tag{B6}$$

$$R_1 = k_1[O_2][\textstyle\sum NH_4^+] \tag{B7}$$

$$R_2 = k_2[O_2][Mn^{2+}] \tag{B8}$$

$$R_3 = k_3[O_2][Fe^{2+}] \tag{B9}$$

$$R_4 = k_4[O_2][FeS] \tag{B10}$$

$$R_5 = k_5[O_2][FeS_2] \tag{B11}$$

$$R_6 = k_6[O_2][\textstyle\sum H_2S] \tag{B12}$$

$$R_7 = k_7[O_2][CH_4] \tag{B13}$$

$$R_8 = k_8[MnO_2][Fe^{2+}] \tag{B14}$$

$$R_9 = k_9[MnO_2][\textstyle\sum H_2S] \tag{B15}$$

$$R_{10} = k_{10}[Fe(OH)_3][\textstyle\sum H_2S] \tag{B16}$$

$$R_{11} = k_{11}[Fe^{2+}][\textstyle\sum H_2S] \tag{B17}$$

$$R_{12} = k_{12}[SO_4^{2-}][CH_4] \tag{B18}$$

$$R_{13} = k_{13}[S_0] \tag{B19}$$

$$R_{14} = k_{14}[FeS][S_0] \tag{B20}$$

$$R_{15} = \begin{cases} k_{15}\left([H_3PO_4]-C_{eq}\right), & [H_3PO_4] > C_{eq} \\ 0 & ,[H_3PO_4] \leq C_{eq} \end{cases} \tag{B21}$$

as water depth or sedimentation rate (Middelburg et al., 1997; Soetaert et al., 1996; Müller and Suess, 1979; Boudreau, 1994; Jourabchi et al. 2008; Tromp et al., 1995) in an attempt to capture overriding universal characteristics of diagenetic processes. Here we re-parameterized the model of Reed et al. (2010) using such general deep-sea parameters taken from previous studies of generic deep-sea sediments (Boudreau, 1994, 1996, 1997; Van Cappellen and Wang, 1995; Soetaert et al., 1996; Jourabchi et al., 2008; Van Cappellen and Berner, 1988). The changes relative to the parameterization of Reed et al. (2010) plus parameterization for the P variables and processes are detailed in Table 5.4.

The values of the sulfate reduction rate constant (k_{sulf}) and the accelaration factor for preferential regeneration of P from OM (ε) (Table 5.4) were fitted for this study. The sulfate reduction rate constant was chosen in order to allow modeled OM preservation efficiencies to lie within the typical range observed for anoxic sediments (Canfield, 1991). The preferential regeneration of P from organic matter was fitted to allow org C/org P ratios to vary between 200 and 500 over the range of conditions tested. This range is similar to that reported

Table 5.4: Model parameters differing from Reed et al. (2010) and parameters for P reactions. Bold values indicate difference between the oligotrophic and mesotrophic deep sea settings. BW: bottom water. SWI: sediment-water interface.

Parameter and unit	**Oligo-trophic deep-sea**	**Meso-trophic deep-sea**	**Reference***	**Comment**
Sedimentation rate υ (cm/yr)	**0.001**	**0.003**	(1), (2)	
OM flux to SWI (μmol/cm^2/yr)	**7.5**	**15.0**	See text	
Labile OM fraction α	0.9	0.9	(3)	
Bioturbation coefficient at SWI Db(0) (cm^2/yr)	**0.24**	**0.5**	(4)	≈15*(υ ^0.6)
Depth of bioturbation Xmix (cm)	**5**	**9.8**	(4), (5), (6)	
BW temperature Temp (^{o}C)	2	2	(1), (2)	
BW oxygen concentration $[O_2]_0$ (mM)	0.180	0.180	(1), (2)	
BW nitrate concentration $[NO_3^-]_0$ (mM)	0.03	0.03	(1), (2)	
BW manganese concentration $[Mn^{2+}]_0$ (mM)	0	0	(2)	
BW iron concentration $[Fe^{2+}]_0$ (mM)	0	0	(1), (2)	
BW sulfate concentration $[SO_4]_0$ (mM)	28	28	(1), (2)	
BW ammonium $[NH_4]_0$ (mM)	0	0	(1), (2)	
Manganese oxide flux to the SWI F_{MnO2} (μmol/cm^2/yr)	0.02	0.02	Fitted, data from (8), (9)	Adjusted F_{MnO2} to get $[MnO_2]$ 10 – 20 umol/g
Iron oxide flux to the sediment F_{FeOH} (μmol/cm^2/yr)	0.1	0.1	Fitted, data from (10), (11), (12)	Adjusted F_{FeOH} to get $[Fe(OH)_3]$ 80 – 150 umol/g
Decay constant for labile OM k_α (yr^{-1})	**0.150**	**0.335**	(3), (6)	$k_\alpha = 100*k_\beta$
Decay constant for moderately labile OM k_β (yr^{-1})	**0.0015**	**0.003**	(7)	$k_\beta \approx 2.2e\text{-}5(F^{2.1})$;
Molar ratios for OM a:b:c	200:21:1	200:21:1	(1)	C:N:P
Acceleration factor for P regeneration from OM ε (-)	200	200	Fitted, data from (13)	Adjusted to allow org C/ org P to vary between 200 and 500.
Sulfate reduction rate constant k_{sulf} (yr^{-1})	**1x10^{-4}**	**1x10^{-4}**	(14), (15), (16)	
Rate const. for R14 k_{14} (mM^{-1}yr^{-1})	10000	10000	(17)	
Rate const. for R7 k_7 (mM^{-1}yr^{-1})	10000	10000	(18)	
P/Fe ratio Fe-oxides χ (-)	0.01	0.01	Fitted, data from (8)	Adjusted to match field data for deep sea site
Threshold for authigenic Ca-P precip. Ceq (mM)	0.004	0.004	(19)	
Apatite precipitation rate constant k_v (mM^{-1}yr^{-1})	0.1	0.1	(20)	

*(1) Boudreau (1996); (2) Van Cappellen and Wang (1995); (3) Jourabchi et al. (2008); (4) Boudreau (1994); (5) Aller et al. (1980); (6) Soetaert et al. (1996); (7) Boudreau (1997); (8) Slomp et al. (2002); (9) Burdige, 1993); (10) Slomp et al. (2004); (11) Schenau et al. (2001); (12) Luff et al. (2000); (13) Slomp and Van Cappellen (2007); (14) Berner (1978); (15) Tromp et al. (1995); (16) Canfield (1991); (17) Berg et al. (2003); (18) Wang and Van Cappellen (1996); (19) Slomp et al. (1996); (20) Van Cappellen and Berner (1988).

for modern marine environments with different sedimentation rates (Slomp and Van Cappellen, 2007).

5.2.2 Numerical experiment

An oligotrophic and a mesotrophic deep-sea setting were defined (Table 5.4) to represent deep sea sediments with a low and moderate organic matter flux to the sediment water interface (SWI). The oligotrophic site, with a low sedimentation rate, shows oxygen penetration throughout the sediment, relatively low organic carbon content and lower biological activity - characteristics consistent with observed oligotrophic deep-sea settings (Martin and Bender, 1991; Smith et al., 1992; Sayles 1994; Hammond et al., 1996; Wenzhöfer et. al., 2001; Fischer et al., 2009). The mesotrophic deep-sea setting was defined to represent sites with a higher flux of organic matter to the sediment and corresponding faster oxygen consumption (eg. Emerson et al., 1985; Rutgers Van Der Loeff et al. 1990; Luff et al. 2000; Soetaert et al., 1996b). As a more active abyssal sediment, this type of site displays oxygen depletion in the top centimeters of the sedimentary column and slightly higher microbial and microfaunal activity. These simulated sediment examples are used as typical deep-sea settings for the study, with the main difference between them stemming from the flux of organic matter from the overlying water column, which results in different degrees of oxygen penetration into the sediment.

The reactive transport model was forced by changing two boundary conditions: the oxygen content at the SWI and the organic matter flux to the sediment surface. For a range of these conditions, steady-state solutions of the model were obtained and the P burial fluxes calculated at a depth of 50 cm in the sediment. These burial fluxes were used to assess the response of the sedimentary P cycle to the imposed forcings. Redox-dependent functions of P burial were constructed from the results and used in a box model of the marine P cycle as detailed below.

To create a relationship between the reactive transport model and the box model, we took the standard steady-state of the Slomp and Van Cappellen (2007) model and estimated the corresponding organic matter rain onto deep-sea sediments. We assumed that 10% of the organic carbon (org C) export to mid-water depth settles onto the SWI. This equates to a rain of 50 Tmol C/yr to the seafloor which translates into an areal flux of 15 µmol /cm^2/yr. This estimated organic carbon flux onto deep-sea sediments is relatively close to the value of 11 µmol/cm^2/yr calculated based on JGOFS US regional studies when assuming that 1% of surface primary production reaches the deep-sea floor (Berelson, 2001; Hedges and Keil, 1995).

Choosing a setting with an organic carbon flux to the SWI of 15 µmol/cm^2/yr corresponds to an environment which exhibits burial of all three forms of reactive P (Fe-P, authigenic Ca-P and org P). Given that this is also the organic carbon flux in the box model at steady-state, it allows us to link the reactive transport and box models. Since only a limited number of settings in our reactive transport model exhibit this type of burial of all three reactive P phases, we consider the oligotrophic setting with an organic C flux of 15 μmol/cm^2/yr and a bottom water oxygen concentration of 170 μM to be a good equivalent environment to the box model of Slomp and Van Cappellen (2007) at steady-state.

5.2.3 Box model

The box model of the global marine C, P and oxygen cycles of Slomp and Van Cappellen (2007) considers two types of continental margin environments as well as the surface and deep ocean. The oxygen cycle is only implemented explicitly in the deep sea. Burial of P in deep-sea sediments is considered to be redox-dependent. In the original version of the model, the burial of iron-bound phosphorus and organic phosphorus are modulated by empirical linear redox functions based on the oxygen concentration of deep ocean water. These functions imply that full anoxia reduces the organic P and Fe-bound P burial flux by up to 25% and 100%, respectively.

From the results of the reactive transport model, new redox-dependent functions of P burial were defined and implemented in the oceanic box model. We equate the burial fluxes of P and org C between the RTM for an organic C flux of 15 μmol/cm^2/yr and $[O_2]$ = 170 μM (the mesotrophic deep sea setting) and the box model of Slomp and Van Cappellen (2007). The burial fluxes for P and org C in this environment are set to 1 and all other burial fluxes, corresponding to environments with different organic carbon fluxes to the sediment and different bottom water oxygen concentrations, are scaled accordingly. The scaling factors are then made into lookup tables for each P phase and for org C. The P and organic carbon burial of the box model is then modulated by applying the scaling factors from the constructed lookup tables on the box model burial based on the deep-sea oxygen and org C rain into the deep-sea in each box model run. This approach allows the coupling of the burial of P and C in the box model to both the redox and organic matter flux dependent burial determined by the RTM, replacing the linear empirical redox functions previously used in Slomp and Van Cappellen (2007).

The modified box model's behavior was then compared with the behavior of the original model to test whether mechanistically derived redox dependence of P burial in deep-sea sediments altered the overall behavior of the oceanic P cycle (and associated O_2 and org C cycles). That is, we test whether implementing mechanistically derived redox dependence in the burial of sedimentary P changes and improves the description of the marine P cycle and whether this change affects associated cycles.

5.3 Results and discussion

5.3.1 Deep-sea environments

Sample profiles of key chemical constituents in the modeled deep-sea settings are given in Figure 5.1. For both settings, phosphorus retention is very low, with 90% or more of the incoming org P being recycled back into the water column. The major imposed difference between the oligotrophic and mesotrophic deep-sea sediments is the organic matter flux to the sediment and the rate at which that organic matter is degraded (Table 5.4). The net effect is a different oxygen penetration into the sediment for the two settings. For the oligotrophic setting, oxygen persists at depth in small concentrations, while for the mesotrophic deep sediment it is consumed within the top few centimeters. This difference has consequences for the sedimentary cycles of other species. Dissolved iron is present in the mesotrophic setting but not the oligotrophic one because iron oxides only dissolve in the former case. Subsequently, pore water phosphate concentrations increase in the mesotrophic setting causing the eventual precipitation of authigenic Ca-P. The oligotrophic setting, although it exhibits similar organic matter characteristics to the mesotrophic one, is more chemically inert in the sense that there is no oxide dissolution or authigenic Ca-P precipitation at depth. Comparing these two systems we see that a higher organic matter flux, causing more oxygen demand in the sediment, can bring about changes in the partitioning of sedimentary phosphorus phases, removing iron-bound P and forming authigenic Ca-P in its place.

5.3.2 Sensitivity to forcings

Starting from an oligotrophic deep-sea setting we change two boundary conditions, namely the flux of organic matter to the sediment water interface (SWI) and bottom water oxygen concentration. The first boundary condition represents trophic changes in the overlying water column, where high OM flux is typically associated with enhanced productivity. The second boundary condition – bottom water oxygen content – is meant to represent changes in redox conditions which could be due to different factors such as reduced water column mixing (stratification) or high oxygen demand due to enhanced productivity. The net burial of reactive P at steady-state was calculated under different combinations of boundary conditions and is shown in Figure 5.2. The total reactive P burial is highly variable over the range of conditions and behaves non-linearly when the redox state and OM flux are varied. Correspond-

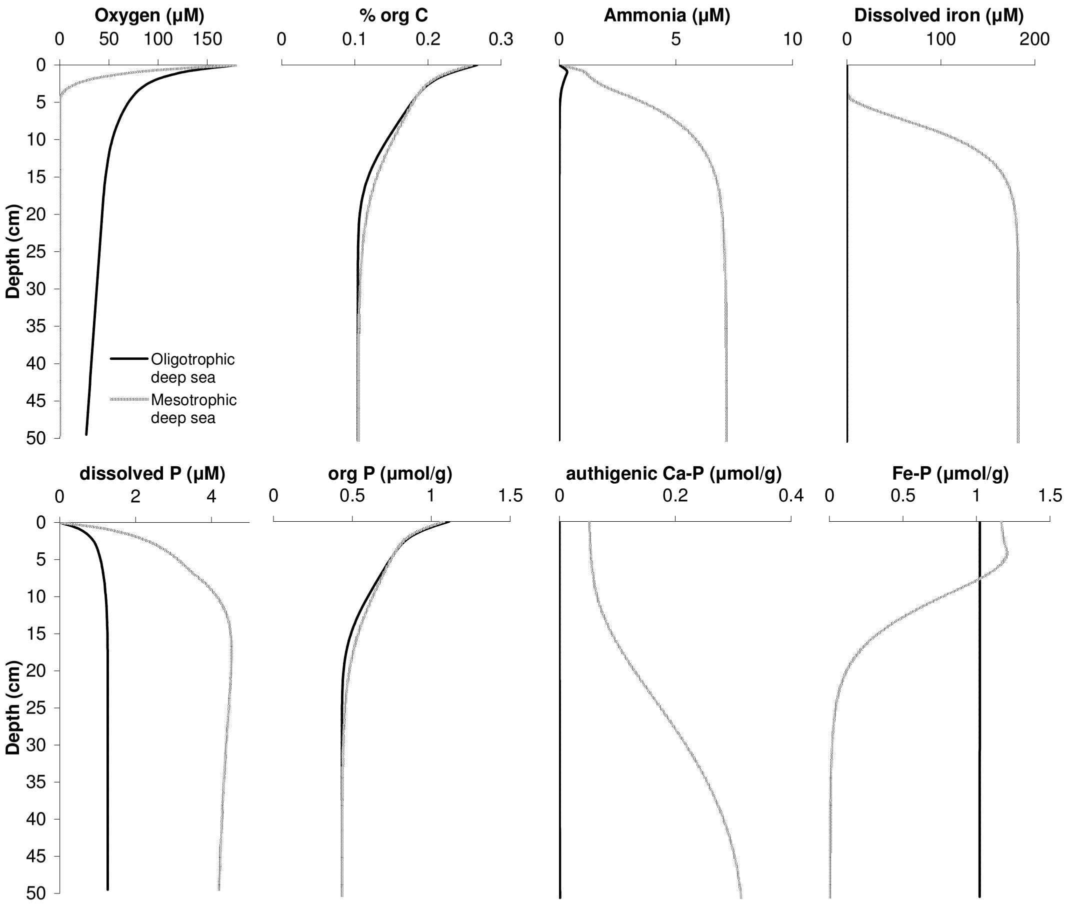

Figure 5.1 Sedimentary depth profiles corresponding to oligotrophic and mesotrophic deep sea settings as defined in this study. Unless otherwise specified, dissolved species are represented in µM while solid species are given in µmol/g.

ing organic carbon to total phosphorus burial ratios vary between 20 and 460 (data not shown). There are two sets of conditions optimal for P burial: in both cases the OM flux is high and the water column is either well oxygenated or fully anoxic. Phosphorus burial is at a minimum if the OM rain rate is low and oxygen concentrations are low.

When the total P burial is separated into its constituent phases (the three phases of solid reactive P) we see the contribution of each one to P sequestration in the sediment under different redox and trophic conditions. Iron-bound P is only present in well oxygenated settings with low to moderate organic matter flux. Low bottom water oxygen, or high oxygen demand due to high OM loading, are both detrimental to iron oxides and hence to iron-bound P. These results are in accordance with general observations of iron oxide behavior in marine sediments. They do not, however, account for the persistence of refractory iron oxide phases (e.g. Berg et al., 2003; Reed et al., 2010).

Organic phosphorus is buried in the sediment to a greater extent in moderate to high OM flux environments, as more material is supplied allowing more org P to be preserved in un-mineralized organic matter. Reducing the oxygen content favors the preservation of org P in the sediment; this is due to the preservation of organic matter under low oxygen conditions, which induces some preservation of the P associated with that organic matter. Thus, there are two competing mechanisms in low oxygen sediments, the preservation of organic matter and the preferential regeneration of P from organic matter. We see in Figure 5.3, that there is preservation of organic matter as oxygen is depleted and OM flux to the sediment increases. However, the efflux of P from the sediment (Figure 5.4) also increases with organic matter loading to the SWI - the more phosphorus brought to the sediment from the overlying water column, the higher the efflux back into the water column, so much of the incoming org P flux is recycled back into the water column. The net effect of these two mechanisms can be observed in the org P burial trend in Figure 5.2. Despite the preferential regeneration of P from organic matter, we see that the preservation of OM dominates the burial trend for org P in low oxygen environments; that is, although org P is preferentially regenerated from OM, more OM is being preserved causing a net accumulation of org P in the sediment.

Model results suggest that authigenic Ca-P formed mostly in settings with high OM fluxes and either high or low oxygen concentrations in the bottom water. Based on Figure 5.2, the precipitation of authigenic Ca-P is highly variable along the redox continuum, as well as with changing organic matter flux to the SWI. There appear to be two sets of conditions that form ideal settings for authigenic Ca-P precipitation, where authigenic Ca-P burial peaks, and other settings where it is absent. This is largely because the precipitation of authigenic Ca-P in the model is governed chiefly by the depth profile of pore water phosphate; if enough phosphate exists in the pore waters at a given depth to

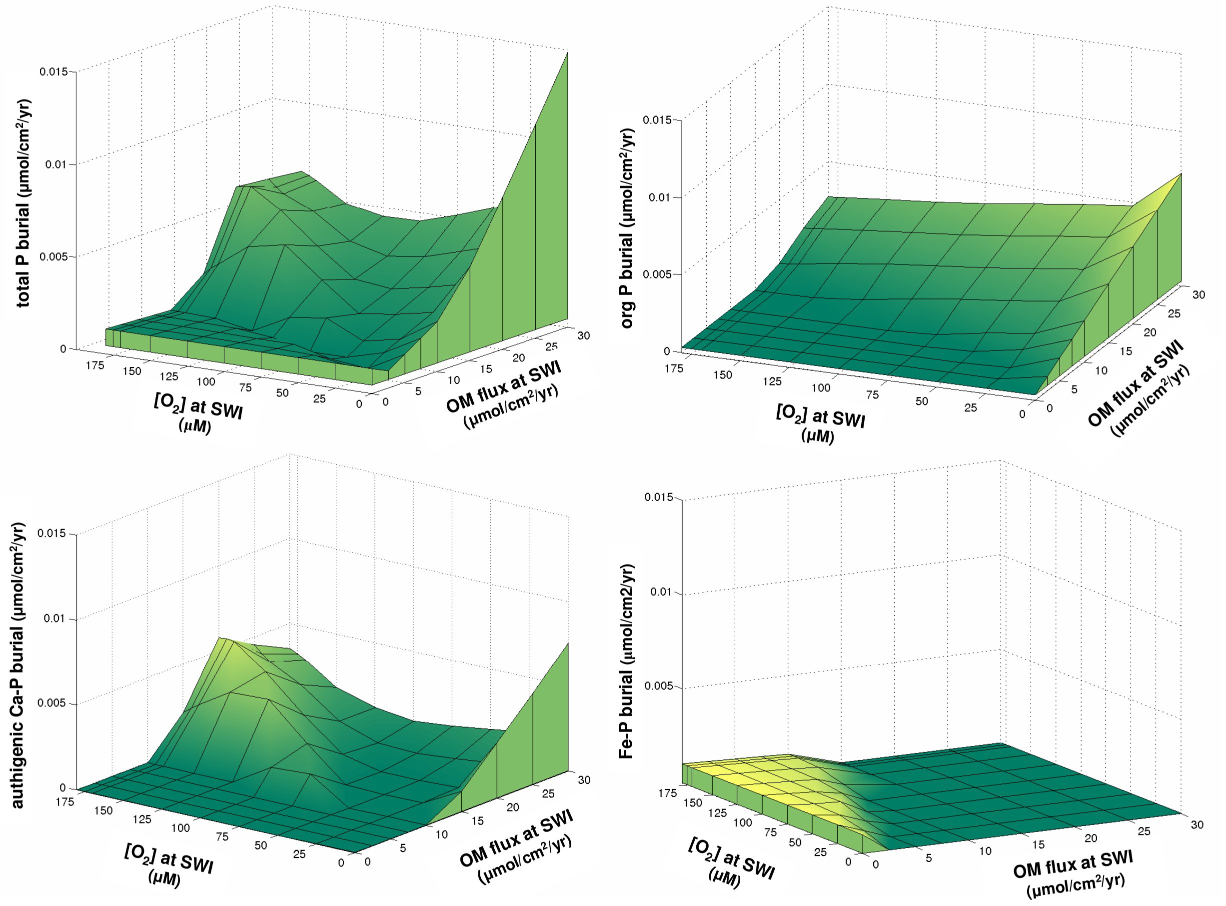

Figure 5.2 Phosphorus (P) burial fluxes (defined as P buried below 50 cm sediment depth) at steady-state as a function of organic matter (OM) flux and oxygen concentrations imposed on the sediment water interface (SWI). $[O_2]$ is given in µM, while OM and P burial fluxes are in µmol/cm²/yr.

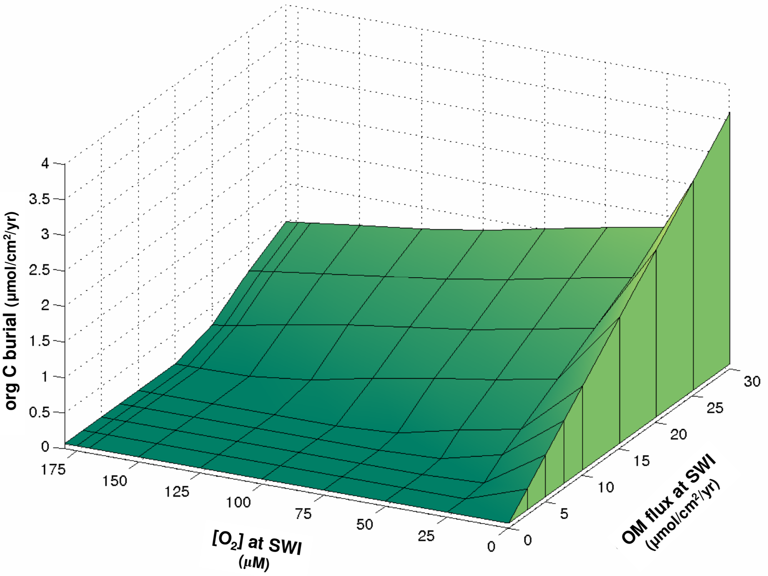

Figure 5.3 Organic carbon (org C) buried in sediments (below 50 cm depth) as a function of organic matter (OM) flux and oxygen concentrations imposed on the sediment water interface (SWI). [O_2] is given in µM, while OM and P burial fluxes are in µmol/cm²/yr.

surpass the saturation level for apatite precipitation, then it will form. For low OM fluxes and low oxygen concentrations, apatite does not form, whereas it does form for high organic matter fluxes and low oxygen concentrations. Note, however, that the possible effects of other factors that may control authigenic Ca-P formation under full anoxia, are not included in the model. For example, the formation of apatite may be hindered by the rise in porewater alkalinity that accompanies sulfate reduction (e.g. Jahnke et al., 1983; Jarvis et al., 1994; Tribovillard et al., 2009). In addition, fluoride availability may affect the conversion of amorphous calcium phosphate minerals to carbonate-fluorapatite (e.g. Schuffert et al., 1994). As a consequence, our RTM results may overestimate authigenic Ca-P formation at high OM fluxes under full anoxia.

Pore water phosphate concentrations are influenced by many of the model parameters: oxygen content, organic matter flux, iron oxide presence, OM reactivity, and so on. There is no one process which governs how much phosphate will be released to the pore waters at a given depth, but rather an interplay of reactions each influenced by different sedimentary parameters. At different depths in the sediment there are different sources and sinks of PO_4 (Figure 5.5), hence this profile is highly sensitive to parameters influencing several sedimentary reactions. Near the sediment water interface, the degradation of organic matter is a major source of phosphate. If iron oxides persist in the sediment, they can capture the phosphate released during OM degradation and help transport it further at depth. Upon their dissolution, iron oxides become a source of pore water phosphate, allowing phosphate concentrations to build up sufficiently high for precipitation of authigenic Ca-P. If this occurs, authigenic Ca-P formation becomes a sink of phosphate in the sediment, enhancing P burial. This role of Fe-oxides as an intermediate between org P and authigenic Ca-P has been demonstrated previously for continental margin settings (Heggie et al., 1990; Slomp et al., 1996). The implication of the work here is that there are a multitude of local effects at a given deep-sea site which would influence the likelihood of authigenic Ca-P precipitation, among those the depth of oxygen penetration in the sediment is critical, as it determines the depth of organic matter and iron oxide profiles. Oxygen penetration depth, on the other hand is determined by conditions such as the oxygen concentration in the overlying water column and the flux of labile OM to the SWI.

To help further understand the trends in P burial illustrated in Figure 5.2, sample profiles corresponding to selected boundary conditions are shown in Figure 5.6; low oxygen and high oxygen environments with low and high organic matter flux are shown. It is again notable from the profiles in Figure 5.6, that iron-bound P persists only when OM fluxes are low. On the other hand, phos-

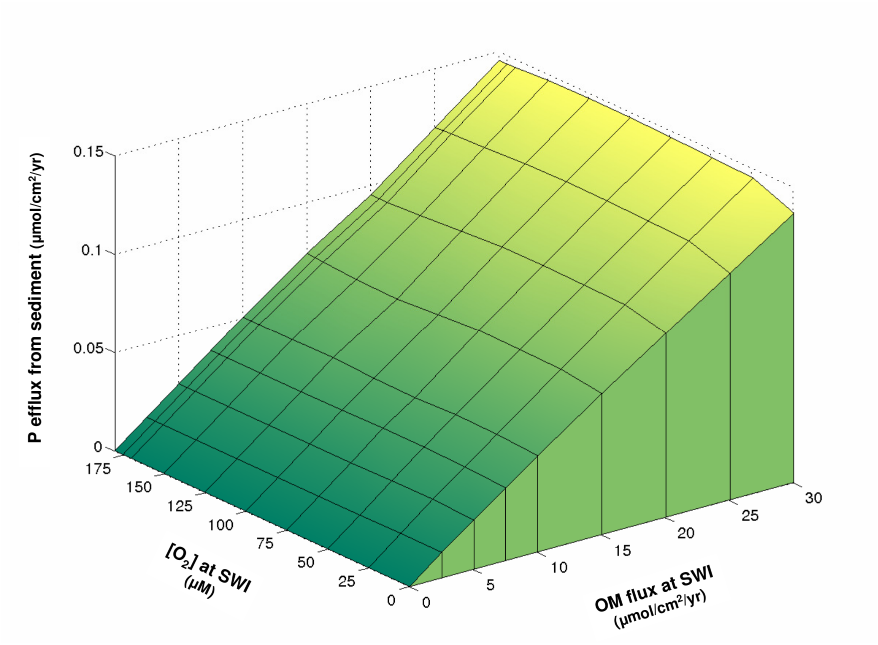

Figure 5.4 Phosphate efflux from the sediment as a function of organic matter (OM) flux and oxygen concentrations imposed on the sediment water interface (SWI). [O2] is given in µM, while OM and P fluxes are in µmol/cm^2/yr

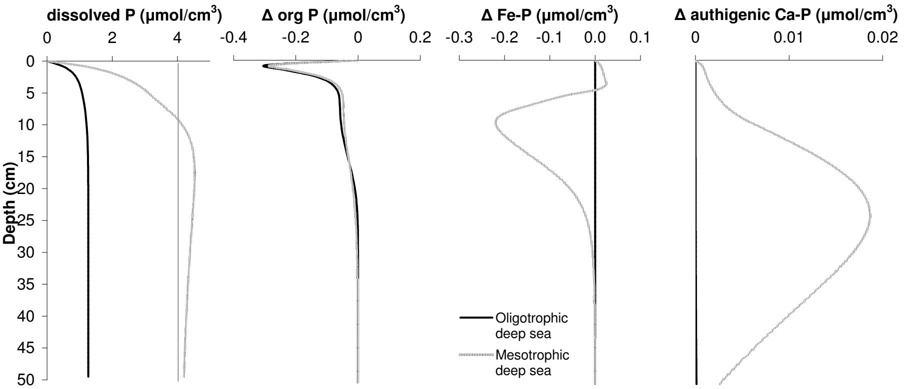

Figure 5.5 Pore water phosphate profile and changes in the concentration (accumulation/depletion) of P bearing species in the sediment. The sources and sinks of phosphate in the sediment are degrading organic matter, dissolving iron-bound P (Fe-P) and forming authigenic Ca-P. Dashed line represents mesotrophic setting, solid line oligotrophic setting. Vertical line in dissolved P graph represents threshold phosphate concentration for authigenic Ca-P precipitation.

phate is high enough to induce authigenic Ca-P precipitation only when OM fluxes are high. These processes are also governed by oxygen content and penetration into the sediment. High oxygen concentrations in the bottom water allow for some or full oxygen penetration into the sediment which helps preserve P in iron-bound forms and, at high OM fluxes, favors phosphate accumulation in the pore waters and the precipitation of authigenic Ca-P.

When full bottom water anoxia is imposed in Figure 5.2, and organic matter fluxes to the sediment are low, there is not much burial of P in the sediments. In fact there is a minimum in the total P burial for hypoxic settings (ca. 25 μM O_2) with low OM loading (ca. 5 μmol/cm^2/yr). Therefore the preservation of OM does not play a significant role as there is not enough organic matter supplied to compensate for the preferential regeneration of P. The burial trend of P changes significantly however, in high OM flux settings. Authigenic and org P are both buried to a greater extent under an anoxic water column and high OM fluxes; org P is retained due to the preservation of organic matter and authigenic Ca-P is formed due to the increased presence of phosphate in the sediment pore waters from iron oxide dissolution and organic matter mineralization (with P being preferentially released from the decaying organic matter). The organic carbon to organic phosphorus burial ratios in the RTM vary between 200 (for low OM flux, high [O_2]) and 450 (high OM flux, low [O_2]). Therefore, anoxic settings with a high organic matter flux sequester higher amounts of phosphorus, in both organic and authigenic form, even though there is preferential regeneration of P from the sediment, because the high loading simply does not allow for all the incoming phosphorus to be recycled back into the water column before being sequestered at depth.

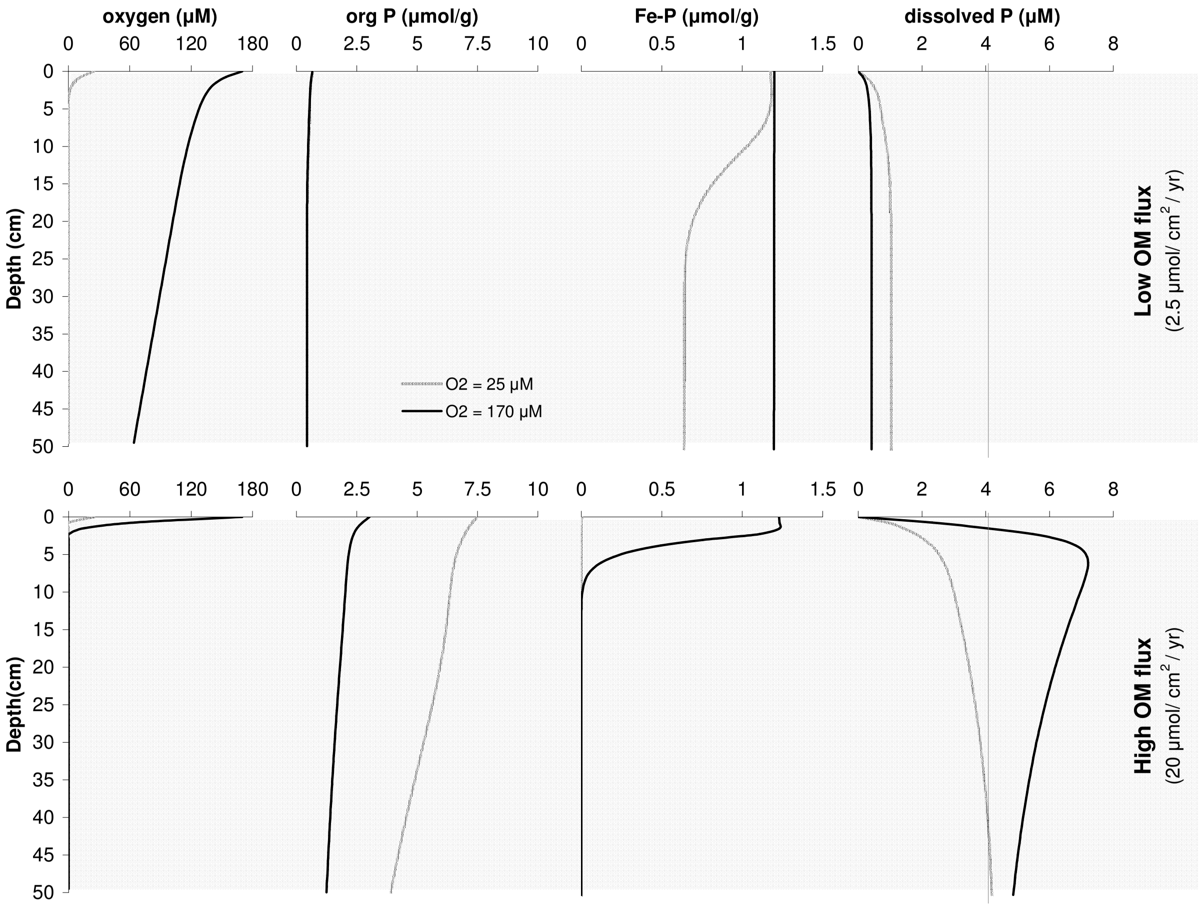

Figure 5.6 Depth profiles of dissolved oxygen (µM) and sedimentary P species corresponding to different organic matter flux and oxygen conditions at the sediment water interface (SWI). Vertical line in dissolved P graphs represents threshold phosphate concentration for authigenic Ca-P precipitation.

Our RTM results can help explain differences in dominant P burial forms observed in deep-sea environments in the sediment record. For example, the lack of authigenic Ca-P in Mediterranean sediments during sapropel formation (e.g. Slomp et al., 2002) can be attributed to the relatively low OM flux which creates conditions beneficial to maximum P recycling. Enrichments in total P in some Cretaceous black shales from the deep sea (e.g. Kraal et al., 2010) are likely due to more efficient P sequestration in a more mesotrophic, high OM setting. Similar comparison would be difficult in the present day ocean, as there are no studies of truly anoxic deep-sea settings to draw upon.

5.3.3 Link to the global marine P cycle

From the results of the reactive transport model, we see that phosphorus burial in deep-sea sediments does not depend linearly on the oxygen concentration of the overlying water column. This non-linear behavior can potentially affect P burial budgets in the deep sea as redox conditions in the water column change. Furthermore, for a given redox setting, there is a great dependence on the flux of organic matter to the sediment. Adding the dependence on the trophic activity of the overlying water column could potentially play an important role for phosphorus sequestration in deep-sea sediments and the marine P budget.

We therefore incorporate the results of Figure 5.2 into a box model of the marine P cycle of Slomp and Van Cappellen (2007). Instead of the empirical functions governing P burial detailed in Slomp and Van Cappellen (2007), we implement the oxygen and OM flux dependence derived from the RTM into the deep-sea box of the marine P cycle, as detailed in section 5.2.2, by building lookup tables from the plots in Figure 5.2 that modulate the P burial fluxes in the box model based on the prevailing redox and OM flux conditions calculated by the box model.

We then apply the same forcing, namely a slowdown in open ocean mixing, as was applied in Slomp and Van Cappellen (2007) and compare the P burial response and the effect on the other biogeochemical cycles.

It is clear that changing the redox functions for deep sea P burial dramatically changes the burial of each reactive P phase (Figure 5.7). For the original model formulation, authigenic Ca-P burial decreases as ocean mixing slows down. Under the new formulation authigenic Ca-P burial initially increases with a slowdown in circulation, as optimal conditions for authigenic Ca-P formation appear and then abruptly disappear, around a 50% mixing decrease, eliminating nearly all authigenic Ca-P formation in the deep sea. The overall trend in authigenic Ca-P burial remains the same with the enhanced redox dependence adapted from Figure 5.2 as with the original linear empirical func-

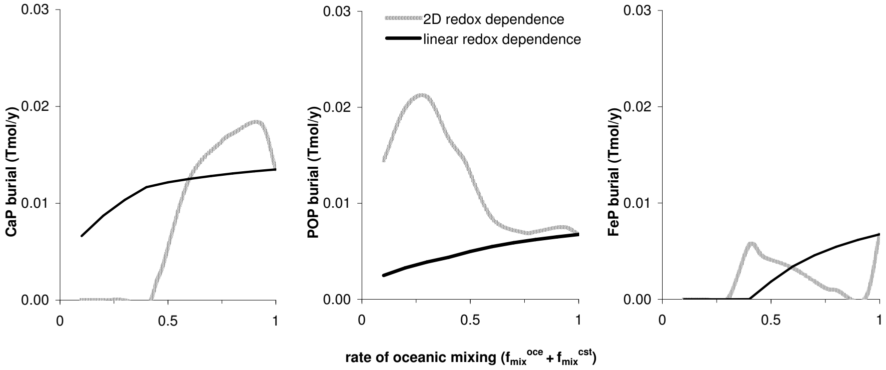

Figure 5.7 Box model P burial in response to reduced mixing in the open ocean (f_{mix}^{oce}) and coastal ocean (f_{mix}^{cst}) with an f_{mix} of 1 being the value for the modern ocean. Comparison between the linear redox-dependent P burial formulation used in Slomp and Van Cappellen (2007) – black line – and the 2 dimensional oxygen and OM loading dependent P derived from Figures 5.2 and 5.3 – grey line.

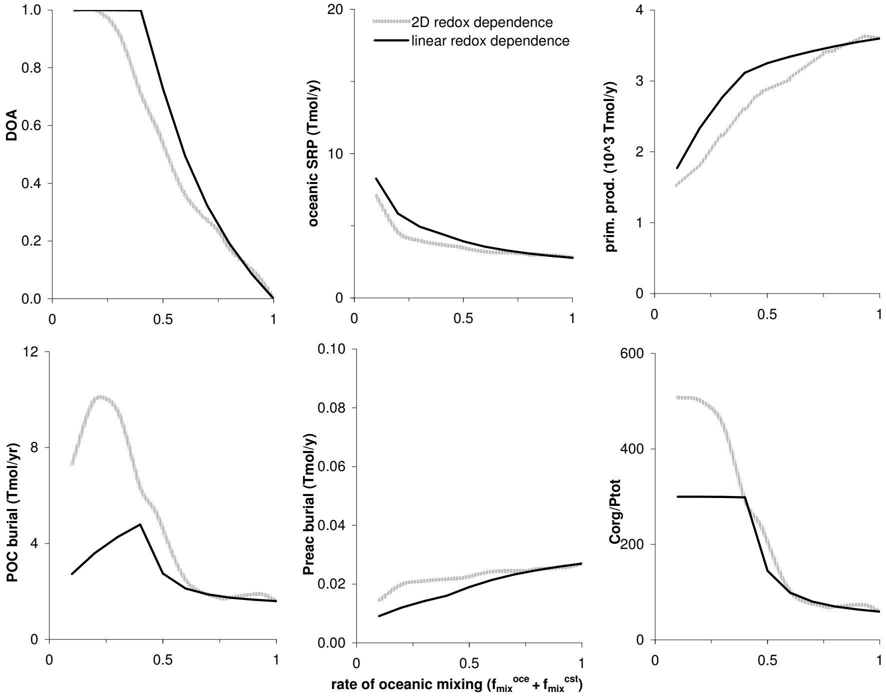

Figure 5.8 Box model response to reduced mixing in the open ocean (and coastal ocean). Comparison between results obtained with the linear redox-dependent P burial formulation used in Slomp and Van Cappellen (2007) – black line – and the 2 dimensional oxygen and OM loading dependent P derived from Figures 5.2 and 5.3 – grey line.

tions used in Slomp and Van Cappellen (2007).

According to the new redox and OM flux dependent burial, organic phosphorus initially accumulates as the ocean stagnates (Figure 5.7). This is because, as deep-sea oxygen concentrations decrease, organic matter builds up in sediments (Figure 5.3) and correspondingly so does organic phosphorus. Therefore, despite the preferential regeneration of P from organic matter for low oxygen conditions, there is enough build up of OM to sequester org P in the sediments, until oxygen depletion is strong enough to overcome this effect by releasing organic P from the sediment. This result is in contrast to the original model response of Slomp and Van Cappellen (2007) which predicts that org P is buried less efficiently as ocean circulation slows down.

Iron-bound P burial fluctuates significantly with circulation slowdown (Figure 5.7). This is because the burial of Fe-P is now dependent on 2 parameters – bottom water oxygen and OM rain onto the sediment – which work against each other. As circulation is decreased, oxygen in the deep sea is gradually depleted, enhancing Fe-P recycling to the water column. At the same time however, the OM flux to deep-sea sediments is reduced (results not shown) due to the circulation slowdown and corresponding drop in primary production (Figure 5.8). This has the effect of reducing oxygen demand in the sediments thus allowing iron-bound P to persist. Initially, as oxygen in the water column drops, iron oxides dissolve, but as the OM rain decreases they are allowed to build up again, until the degree of anoxia (DOA) is so high that oxides dissolve again.

Therefore, changing the burial dependence of phosphorus on oxygen and adding the effect of organic mater flux to the sediment has a pronounced effect on the burial efficiency of reactive P phases. Conditions are established where sedimentary phosphorus is preserved as specific phases: a better mixed ocean favours authigenic Ca-P formation, while a more stagnant ocean retains most of its phosphorus in organic form. Iron-bound P behaves very non-linearly and is a minor contributor to total buried P.

Despite the drastic changes in the burial of individual reactive P phases, the net P burial in deep-sea sediments remains essentially the same (Figure 5.8) due to the fact that the burial of the dominant phases (org P and authigenic Ca-P) occurs for different conditions along the redox continuum, leaving the cumulative burial trend unaltered. There is a net decrease in the P burial in sediments of the open ocean, albeit a slightly smaller decrease than previously predicted. The net effect on the associated oceanic cycles is therefore negligible. The degree of anoxia in the deep sea, the soluble reactive P inventory and primary production of the open ocean are essentially the same with changing ocean ventilation as in Slomp and Van Cappellen (2007); in both cases reduced mixing leads to a more anoxic and less productive ocean.

What is different between the results of the two formulations (Slomp and Van Cappellen (2007) and this study) is the amount of organic carbon buried – there is significantly more carbon preservation in deep-sea sediments as the redox conditions change when the 2D function (Figure 5.3) for carbon burial is implemented. Because the org C/tot P ratios also change (Figure 5.8), there is little net effect of this enhanced C burial on the total P burial – although we saw earlier this does have an impact on the organic P phase sequestered in the sediments. Since the overall P burial remains similar, so does P recycling to the water column. As a consequence, the primary productivity of the open ocean and redox conditions (DOA) also remain similar to the original formulation of Slomp and Van Cappellen (2007). Therefore, although there are some profound implications for the partitioning of P among its various solid phases, net sedimentary P burial is similar when non-linear and multi parameter dependence is considered instead of simple linear redox functions and there are no great effects on the marine cycles of oxygen and organic carbon.

5.4 Conclusions

Oxygen penetration into the sediment is critical to sedimentary P dynamics in the deep sea, as it diferentiates between regimes where iron oxides persist at depth and regimes where authigenic phosphorus precipitation occurs, thus determining the partitioning of P phases in the sedimentary P cycle. Oxygen penetration is most greatly influenced by two parameters, the oxygen in the overlying water column, representing oxygen supply, and the organic matter flux to the sediment, representing oxygen demand. The amount of P buried in deep-sea sediments responds to both these forcings non-linearly due to the interplay of multiple mechanisms. The conditions for minimum P burial (maximum recycling from sediments) are low oxygen concentrations and low organic matter flux (hypoxic, oligotrophic setting). As the organic matter loading increases, however, low oxygen settings turn to preservation environments for phosphorus.

Burial of organic P (org P) generally increases as OM flux to the sediment increases, because of the high loading of org P. For low OM fluxes, the redox conditions at the SWI do not have a major effect on P burial as organic matter preservation and preferential phosphorus regeneration from organic matter compete. As OM loading increases, however, its accumulation (preservation) dominates for hypoxic and anoxic environments and consequently org P is also preserved in the sediment.

Iron-bound and authigenic Ca-P appear to be mutually exclusive, that is settings favoring iron oxide burial do not allow for authigenic precipitation and vice versa. The main factor for this partitioning is the presence of oxygen deep in the sediment – if the sediment is oxic. Authigenic Ca-P formation depends on the presence of some iron oxide bound P at shallower sediment depths; these oxides trap the org P released during OM degradation before it can escape into the water column and make it available (upon dissolution) to the pore waters at greater depths thus making authigenic Ca-P formation possible. Therefore optimal conditions for authigenic Ca-P formation are environments where iron oxides are present at shallow depth but dissolve deeper down, releasing their associated P at greater depths – deep-sea settings which meet these criteria are settings with high oxygen concentrations in the water column combined with moderate to high organic matter fluxes. If organic matter loading is very high, however, iron oxides are not necessary to reach the required pore water concentrations of phosphate for authigenic Ca-P precipitation.

Non-linear and multi parameter dependent P burial has great implications for the marine sedimentary P cycle. Using 2-dimensional functions for P burial based on water column oxygen concentrations and organic matter changes the burial of different P phases in the box model of Slomp and Van Cappellen (2007). Interestingly, however, when all phosphorus phases are summed up, the net P burial remains largely unaltered; that is where organic and iron-bound phosphorus burial increases, authigenic Ca-P decreases. Therefore, the consequences of improving the redox-dependent P burial description for other associated ocean parameters such as water column oxygenation and primary production in the open ocean are actually small. As long as the net recycling of P from sediments remains the same, the partitioning is not important as the total amount of nutrient supplied to the water column from the sediment is the same and hence the fertility of the open ocean is unaffected. Therefore, while the specifics of sedimentary P burial are different with an improved redox-dependent P burial description, the overall marine P cycle and the associated oxygen and organic carbon cycles are not greatly affected.

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Summary / Samenvatting

Phosphorus (P) is an essential element for life on Earth. Through its role as a limiting nutrient for photosynthesis, its availability plays a critical role in the biogeochemical functioning of the oceans. Changes in the marine P cycle may, for example, lead to changes in oceanic primary production, organic carbon burial and atmospheric carbon dioxide. As a consequence, the global cycles of phosphorus and carbon are closely intertwined making phosphorus a potential player in long-term climate change.

The work included in this thesis focuses on the marine phosphorus cycle and its response to changing environmental conditions such as changes in ocean circulation, changes in continental weathering, sea level change and sea water cooling using an existing box model of the global marine phosphorus, organic carbon and oxygen cycles in which the coastal and open ocean are explicitly represented.

Chapter 2 focuses on glacial-interglacial transitions, specifically the last glacial-interglacial cycle (120 -10 kyrs BP). Using the box model, a climate change scenario for glaciations is defined and implemented. The effects of continental supply of reactive P, oceanic mixing, and sea level on the marine P cycle are examined on glacial-interglacial timescales. Results show that mixing is a dominant forcing during early glaciation and leads to an initial lowering of oceanic primary production. During late glaciation, sea level fall is the dominant forcing enhancing nutrient supply to the open ocean. Post glacial periods are times of peak productivity due to the effective upward mixing of phosphate from the deep sea. Furthermore, primary production is generally lower during glaciations relative to post glacial periods, suggesting that the biological pump hypothesis for CO_2 drawdown is unsupported if phosphorus limitation of the ocean is assumed.

In Chapter 3, the oxygen dynamics in the deep sea during the last glacial are examined. Shelf erosion during sea level low stands (“shelf nutrient hypothesis”) and particulate matter re-routing to the open ocean via submarine river canyons (“river canyon hypothesis”) are implemented in the box model as part of the glacial-interglacial transition scenario. The results indicate that shelf erosion and submarine canyon formation may significantly lower deep-sea oxygen levels, by up to 25%, during sea level low stands, mainly due to the supply of new material from the shelves and particulate organic matter bypassing the coastal zone. Primary production, organic carbon burial and dissolved phosphorus in the deep sea are affected by the erosion and rerouting mechanisms; however deep-sea oxygen demand is decoupled from primary productivity in the open ocean. P burial is not affected showing a disconnect between biogeochemical cycling in the water column and the P burial record.

In Chapter 4 marine P dynamics for another climate period are investigated, namely oceanic anoxic events of the early- and late- Cretaceous. The box model is modified and spun-up for Cretaceous ocean conditions and the hypothesis that P availability controls oxygen depletion and carbon accumulation is explored. The findings show that Oceanic Anoxic Events (OAEs) can be triggered by enhanced P supply from land, for an ocean with wide continental shelves, slow circulation and high sea surface temperatures. The system is most sensitive to oceanic mixing. The deep sea can become completely anoxic, while the shelves are only partially oxygen depleted. Reactive P burial in the deep sea decreases dramatically under anoxia, but on the shelves, where oxygen depletion is not complete, it does not. Model results also imply OAEs can be sustained by P recycling from sediments due to low oxygen in the water column. Ultimately land feedbacks, which result in the accumulation of atmospheric oxygen may terminate the anoxic event. These results are corroborated by P burial data from the geological record for OAE2 (approximately 94 Myrs before present). Through a sensitivity analysis, two necessary criteria for OAEs are identified: low mixing of surface and deep waters (poor ocean ventilation) and enhanced sedimentary P recycling under low oxygen conditions. When these criteria are met, ocean anoxia is a robust result to an increase of continental weathering.

Finally, Chapter 5 investigates phosphorus burial in deep-sea sediments, as a function of bottom water oxygen and organic matter flux to the sediment water interface, using a mechanistic reactive transport model for sediment diagenesis. Generic settings are defined for an oligotrophic and a mesotrophic deep-sea environment. The oligotrophic setting is then perturbed with changing boundary conditions of oxygen concentration and organic matter flux at the sediment water interface. Total reactive P burial responds non-linearly when these boundary conditions are varied. The different phases of reactive P are optimally buried under different sets of conditions with high organic matter flux and high or low oxygen favoring the formation of authigenic P, while hypoxic conditions and large organic matter fluxes allow for high organic P burial. Iron-bound P is preserved only when oxygen levels are high and OM fluxes low. Hypoxic, oligotrophic conditions are thus identified as optimum for P recycling from the sediment. The mechanistically derived redox P burial is implemented in the box model of the marine P, oxygen and organic carbon cycles and the response of this modified version of the box model to reduced mixing is assessed. Results show that, when compared to the original version of the box model, deep-sea burial of the various reactive P phases is different. However, because the total reactive P burial remains very similar, replacing the original empirical functions of redox dependent P burial by mechanistically derived functions does not significantly alter box model predictions of biogeochemical cycling in the ocean.

Fosfor (P) is een essentieel element voor het leven op Aarde en komt in natuurlijke milieus vooral voor in de vorm van fosfaat. Vanwege de rol van fosfor als een limiterend nutriënt voor fotosynthese speelt fosfaat een belangrijke rol in het biogeochemisch functioneren van de oceanen. Veranderingen in de mariene fosforcyclus kunnen bijvoorbeeld leiden tot veranderingen in de primaire productie en begraving van organische koolstof in de oceanen en in de hoeveelheid atmosferische koolstofdioxide. Als gevolg hiervan zijn de mondiale cycli van fosfor en koolstof sterk verweven. Dit maakt de fosfaat beschikbaarheid in oceaan water tot een potentieel belangrijke factor bij klimaatverandering, vooral op de lange termijn.

Het werk in dit proefschrift richt zich op de mariene fosforcyclus en de effecten van veranderende omstandigheden zoals veranderingen in oceaancirculatie, veranderingen in verwering op het land, zeespiegelfluctuaties en het afkoelen van zeewater op die P cyclus. Hiervoor wordt een bestaand boxmodel van de mondiale cycli van fosfor, organische koolstof en zuurstof gebruikt, waarin de kustzone en open oceaan expliciet zijn vertegenwoordigd.

In Hoofdstuk 2 worden overgangen van glaciale naar interglaciale periodes bestudeerd in het bijzonder de laatste glaciaal-interglaciaal cyclus (120 duizend – 10 duizend jaar geleden). Met behulp van het boxmodel werd een scenario van klimaatverandering gedefinieerd en geïmplementeerd. De effecten van de continentale toevoer van reactief (dwz biologisch beschikbaar) fosfaat, het mengen van oceaanwater en de zeespiegelstand werden onderzocht op een tijdschaal van 100 duizenden jaren. De resultaten laten zien dat menging van het oceaanwater een dominante rol speelt tijdens de vroege glaciatie en leidt tot een initiële afname van de primaire productie in de oceaan. Laat in de glaciatie is zeespiegeldaling de belangrijkste factor, waardoor de nutriëntentoevoer naar de open oceaan wordt vergroot. Na de glaciale periodes bereikt de productiviteit piekwaarden doordat fosfaat door menging effectief vanuit de diepzee naar de oppervlakte wordt getransporteerd. Bovendien is de productiviteit over het algemeen lager tijdens glaciaties ten opzichte van periodes na glaciaties, wat suggereert dat de biologische pomp-hypothese aangaande opname van CO2 door oceanen niet wordt ondersteund wanneer men aanneemt dat fosfaat limiterend is voor fotosynthese in de oceanen.

In Hoofdstuk 3 wordt de dynamiek van zuurstof in de diepzee tijdens het laatste glaciaal onderzocht. Erosie van sediment van het continentale plat tijdens lage zeespiegelstanden (“shelf nutriënt hypothese”) en direct transport van materiaal naar de open oceaan via onderzeese riviervalleien (“riviervalleihypothese”) zijn in het boxmodel geïmplementeerd als deel van het glaciaal-interglaciaal scenario van Hoofdstuk 2. De resultaten geven aan dat erosie en de vorming van onderzeese valleien de zuurstofconcentraties in de diepzee tijdens lage zeespiegelstanden significant kunnen verlagen , tot 25 %. Dit wordt vooral veroorzaakt door de toevoer van nieuw materiaal van het continentaal plat en materiaal dat de kustzone omzeilt. De primaire productie, begraving van organische koolstof en beschikbaarheid van opgelost fosfaat in de diepzee worden beïnvloed door de erosie- en transportmechanismen; het zuurstofverbruik in de diepzee is echter ontkoppeld van de primaire productiviteit in het oppervlakte water van de open oceaan. De begraving van fosfaat wordt niet beïnvloed, wat aantoont dat deze begraving in deze situatie niet direct gekoppeld is aan de biogeochemische cyclus in de waterkolom.

In Hoofdstuk 4 wordt de mariene P dynamiek voor een andere klimaatperiode onderzocht, namelijk voor perioden van zuurstofloosheid in de oceaan ("oceanic anoxic events" of "OAEs") in het vroege en late Krijt. Het boxmodel is aangepast aan de condities in de oceaan van het Krijt en de hypothese dat de beschikbaarheid van fosfaat de zuurstofloosheid en koolstofbegraving tijdens deze OAEs veroorzaakt wordt verkend. De resultaten laten zien dat OAEs kunnen worden veroorzaakt door een vergrote toevoer van fosfaat van het land in het geval van een oceaan met een groot continentaal plat, langzame circulatie en hoge temperaturen aan het zeewateroppervlak. Het systeem is het meest gevoelig voor oceaanmenging. De diepzee kan compleet zuurstofloos worden, terwijl het continentaal plat slechts ten dele lage zuurstofconcentraties ondervindt. De begraving van reactief fosfaat neemt dramatisch af onder zuurstofloosheid in de diepzee, maar niet in kustzeeën, waar het water niet geheel zuurstofloos wordt. De modelresultaten geven ook aan dat OAEs kunnen worden gevoed door het weer vrijkomen ("recyclen") van fosfaat uit sedimenten door de lage zuurstofconcentraties in de waterkolom. Uiteindelijk kunnen feedbacks vanaf het land, die resulteren in de accumulatie van atmosferische zuurstof, de periode van zuurstofloosheid beëindigen. Deze resultaten worden ondersteund door gegevens voor de fosfaatbegraving uit boorkernen voor OAE 2 (ongeveer 94 miljoen jaar geleden). Met behulp van een gevoeligheidsanalyse zijn twee benodigde criteria voor OAEs geïdentificeerd: langzame menging van oppervlaktewater en diep water (slechte oceaancirculatie) en een toename van het "recyclen" van fosfaat uit het sediment bij lage zuurstofconcentraties.

Ten slotte wordt in Hoofdstuk 5 fosfaatbegraving in de diepzee onderzocht als functie van het zuurstofgehalte in het bodemwater en de flux van organisch materiaal die de zeebodem bereikt. Dit wordt gedaan met behulp van een mechanistisch reactief-transport model voor sedimentdiagenese. Generieke diepzee-omstandigheden werden gedefinieerd voor een oligotroof en mesotroof diepzeemilieu. Het mesotrofe milieu werd vervolgens verstoord door de randvoorwaarden voor zuurstofconcentratie en de flux van organisch materiaal naar het water-sediment raakvlak te veranderen. De begraving van totaal reactief fosfaat reageert niet-lineair wanneer deze randvoorwaarden worden gevarieerd. De verschillende fasen van reactief fosfaat in het sediment worden optimaal begraven onder verschillende combinaties van omstandigheden, waarbij een hoge flux van organisch materiaal en hoge of lage zuurstofconcentratie de vorming van calciumfosfaat mineralen bevordert. Tegelijkertijd zorgen lage zuurstofconcentraties en hoge fluxen van organisch materiaal voor een sterke begraving van organisch fosfaat. Fosfaat gebonden aan ijzer wordt alleen gepreserveerd wanneer zuurstofconcentraties hoog zijn en fluxen van organisch materiaal laag. Oligotrofe condities met weinig zuurstof in het bodemwater zijn dus optimaal voor het “recyclen” van fosfaat uit het sediment. De zuurstofafhankelijke begraving van fosfaat als functie van de zuurstofbeschikbaarheid en organisch materiaal flux werd vervolgens geïmplementeerd in het boxmodel van de mariene cycli van fosfor, zuurstof en koolstof. Vervolgens werd de respons van de aangepaste versie van het boxmodel op verminderde menging van de oceaan onderzocht. De resultaten laten zien dat, vergeleken met het originele boxmodel, de begraving in de diepzee van de verschillende reactieve fosfaatfasen was veranderd. Echter, doordat de totale begraving van reactief P nagenoeg gelijk bleef, maakte het voor de biogeochemische processen in de water kolom niet uit of de meer empirische of mechanistische beschrijving van zuurstofafhankelijk P begraving was gebruikt: de respons van de biogeochemische cycli in de oceaan op een verminderde menging van de oceaan was in beide modellen hetzelfde.

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