Biogeochemical effects of atmospheric oxygen concentration, phosphorus weathering, and sea-level stand on oceanic redox chemistry: Implications for greenhouse climates

Kazumi Ozaki, Eiichi Tajika

1. Introduction

The atmosphere–ocean system has remained in a fully oxygenated condition since at least the Devonian (e.g., Dahl et al., 2010; Strauss, 2006) with the exception of oceanic anoxic events (OAEs) (e.g., Jenkyns, 2010; Leckie et al., 2002). The oceanic oxygen inventory and distribution are controlled both by physical and biogeochemical processes. Therefore, previous studies conducted to elucidate the conditions and causal mechanism(s) of OAEs have mainly focused on two distinct mechanisms, namely, stagnation of ocean circulation and/or enhanced biological productivity in surface water (Handoh and Lenton, 2003; Hotinski et al., 2000, 2001; Meyer et al., 2008; Monteiro et al., 2012; Nederbragt et al., 2004; Ozaki et al., 2011; Sarmiento et al., 1988; Shaffer, 1989, 1996; Slomp and Van Cappellen, 2007; Southam et al., 1982, 1987; Tsandev and Slomp, 2009; Van Cappellen and Ingall, 1996; Winguth and Winguth, 2012). Ozaki et al. (2011) conducted systematic sensitivity experiments with respect to the intensity of the thermohaline circulation and riverine reactive phosphorus \( P_{\text{react}} \) input rate with HILDA-type (Joos et al., 1991; Shaffer and Sarmiento, 1995; Siegenthaler and Joos, 1992) biogeochemical ocean modeling. Together with an experiment concerning sea surface temperature (SST), they found the following results: (1) ocean stagnation causes deepwater anoxia, but widespread sulfidic \( (i.e., H_2S\text{-rich}) \) waters do not form by themselves; (2) a large SST increase \( (> 10 \text{ K}) \) is required for the appearance of ocean anoxia, but euxinia cannot be caused even when the deviation of the SST from the reference value is greater than +15 K; and (3) riverine \( P_{\text{react}} \) input rate \( (R_\text{P}) \) of \( > 1.4 \times R_\text{F}^* \) (asterisk represents the reference value; Table 1) causes ocean anoxia via expansion of the oxygen minimum zone (OMZ), and a value of \( 2.2 \times R_\text{F}^* \) results in global euxinia via enhancement of phosphorus \( (P) \) liberation from the sediment–water interface at the continental slope and shelves. An increase in \( R_\text{F} \) causes shelf anoxia, giving rise to
massive P liberation from sediments to bottom waters and, therefore, to global-scale anoxia (Ozaki et al., 2011; Tsandev and Slomp, 2009).

According to geologic evidence, OAEs tend to occur in warm climatic conditions and no OAE has been identified during "icehouse" climatic conditions, such as during the late Paleozoic and Cenozoic (Frakes et al., 1992; Jenkyns, 2010). However, the spatio-temporal extent of ocean anoxia is restricted, even during "greenhouse" climatic conditions. For Cretaceous OAEs, it is noteworthy that global-scale anoxia is not a persistent phenomenon and it generally lasts for less than a million years (e.g., Leckie et al., 2002; Sageman et al., 2006; Voigt et al., 2008). Hence, one can expect that a warm climate would be one of the necessary conditions for the occurrence of OAEs, although it would not be sufficient alone to cause them, implying the existence of additional causal factor(s). Recently, several studies have suggested that there is an intimate connection between Cretaceous ocean anoxia and the activities of large igneous provinces (LIPs) (Adams et al., 2010; Kuroda et al., 2007; Snow et al., 2005; Tejada et al., 2009; Turgeon and Creaser, 2008). Massive injections of greenhouse gases associated with the activity of LIPs might have caused a rapid warming of the climate (e.g., Ando et al., 2008; Forster et al., 2007), enhancement of chemical weathering on land (Blättler et al., 2011; Frijia and Parente, 2008; Tejada et al., 2009), and oceanic eutrophication/de-oxygenation (e.g., Kuypers et al., 2002; Mort et al., 2007a). However, the critical value of \( R_p \) and \( R_p^{\text{crit}} \), as well as the required environmental perturbation of LIPs for the initiation of an OAE would be affected by other environmental factors, such as the background atmospheric oxygen concentration level. Without a quantitative estimate, because the phosphorus retention potential of marine sediment is depressed under the reducing conditions in the bottom water, giving rise to high phosphate availability in the anoxic ocean environment (e.g., Colman and Holland, 2000; Ingall and Jahnke, 1994; Van Cappellen and Ingall, 1996).

Sea level and coastal shelf area have varied considerably during the Phanerozoic (e.g., Miller et al., 2005; Müller et al., 2008; Ronov, 1994; Walker et al., 2002). High sea-level conditions are, in general, accompanied by greenhouse climatic conditions (e.g., early-middle Paleozoic and mid-Cretaceous). A shallow shelf is a primary locus for the deposition of biogenic materials because of a high rain flux of materials and high sediment accumulation rate (Berner, 1982; Dunne et al., 2007; Hedges and Keil, 1995). It can, therefore, be expected that a change in shelf area would have a critical role in the oceanic redox via changes in marine biogeochemical dynamics. Bjerrum et al. (2006) investigated the effect of sea-level change on oceanic biogeochemistry with a three-box ocean model coupled with an early diagenetic model of C, N, and P in seafloor sediments (Wallmann, 2003). The results indicated that a large expansion in shelf area would reduce the oxygen demand in the ocean, resulting in oxygenation of the open ocean. However, the overall effects of shelf size and other controlling factors (e.g., \( p_{O_2} \) and \( R_p \)) on the oceanic redox state have not been considered.

In this study, we set a three-step approach. First of all, we assess the long-term biogeochemical effect of \( p_{O_2} \) and \( A_{E_2} \) on the oceanic redox condition. This makes clear how each factor affects the oceanic redox state as a result of changes in marine biogeochemical cycles. Next, we focus on how \( R_p^{\text{crit}} \) for the generation of oceanic anoxia/euxinia is affected by \( p_{O_2} \) and \( A_{E_2} \) in order to gain insight into the long-term evolution of the marine redox state. Finally, the implications of this for the oceanic redox state under greenhouse climatic condition and causal mechanism of OAEs is discussed.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Reference value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocean circulation rate ( \nu )</td>
<td>( 10^8 \text{ m}^2/\text{yr} )</td>
<td>20</td>
</tr>
<tr>
<td>Riverine ( p_{\text{react}} ) input rate ( R_p )</td>
<td>( \text{T mol P/yr} )</td>
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</tr>
<tr>
<td>Atmospheric ( p_{O_2} )</td>
<td>( \text{atm} )</td>
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</tr>
<tr>
<td>Shelf area ( A_{E_2} )</td>
<td>( 10^4 \text{ m}^2 )</td>
<td>0.271</td>
</tr>
<tr>
<td>Sea surface temperature at ( L )</td>
<td>( \text{SST} )</td>
<td>288.15</td>
</tr>
<tr>
<td>Sea surface temperature at ( H )</td>
<td>( \text{SST}^{\text{b}} )</td>
<td>273.15</td>
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2. Methods

2.1. Model description

In order to shed light on the controlling factors of the long-term oceanic redox condition and the mechanism(s) behind the initiation of OAEs, we use a numerical model of the marine biogeochemical cycle. We employ an oceanic advection–diffusion–reaction biogeochemical cycle model (named CANOPS) to explore the impact of three causal factors (atmospheric \( p_{O_2} \); shelf area, \( A_{E_2} \); and riverine \( p_{\text{react}} \) input rate, \( R_p \)) on the oceanic redox state. CANOPS is an improved version of the transport-reaction model developed by Ozaki et al. (2011), which includes both physical and biogeochemical processes. The basic structure of CANOPS is illustrated in Fig. 1a. Below the surface water layers (L and H), the ocean interior comprises two regions: the high-mid latitude region ("young" deepwater region; YD) and low-mid latitude region ("old" deepwater region; OD). Each region is divided into 60 depth levels with a 100–m vertical grid spacing. The layers are labeled \( j=1, \ldots, 60 \) from the surface downwards. The total dissolved inorganic carbon (DIC), total alkalinity (ALK), oxygen \( (O_2) \), phosphate \( (P_{O_4}^{\text{a}}) \), nitrate \( (N_0^{\text{a}}) \), ammonium \( (N_4^{\text{H}}) \), sulfate \( (S_{O_4}^{2}) \), and total sulfide \( (\Sigma H_2S) \) are considered as dissolved chemical components of seawater. A further description of this model is presented in the Supplementary material.

2.2. Experimental setup

2.2.1. Atmospheric oxygen level

While several attempts have been made over the past three decades to reconstruct the variations in \( p_{O_2} \) during the Phanerozoic eon, the results vary widely (Bergman et al., 2004; Berner,
2. Shelf area

In order to represent the change in $A_{\text{org}}$ in the model, we change the areas of the surface and $j=1$ layers, as shown in Fig. 1b. $A_{\text{org}}$ is about $2.7 \times 10^{14} \text{ m}^2$, occupying 7.5% of whole ocean area today. The burial efficiency of $C_{\text{org}}$ on shelves is generally high (approximately 40–80%; Betts and Holland, 1991; Henrichs and Reeburgh, 1987). Hence, as the shelf area increases, the ratio of the $C_{\text{org}}$ burial flux to export flux for the whole ocean increases (1.37% and 2.3% for shelf areas of 100% and 200% of the present value, respectively).

Variations in sea level and shelf area during the Phanerozoic have been studied geologically and geomorphologically. According to comprehensive studies conducted by Alexander Ronov and his colleagues, the shelf area was tectonically controlled and exhibited two maximums during the Paleozoic and Cretaceous (e.g., Ronov, 1968, 1994). More recent estimates, which show that the shelf area at low-mid latitudes was 2–3 times larger during the Paleozoic and Cretaceous than at present, do not change this conclusion (Walker et al., 2002).

2.3. Redox index and edge of anoxia/euxinia

We categorize the oceanic redox state into six types based on the distributions of dissolved oxygen (OXA=oxic ocean, IWA=intermediate water anoxia, and DWA=deep water anoxia) and hydrogen sulfide (non-sulfidic, IWE=intermediate water euxinia, and DWE=deep water euxinia) in the ocean interior (Ozaki et al., 2011). This categorization provides information on the redox state of the ocean and may allow us to consider the causal mechanisms. It does not, however, provide any quantitative information on the spatial extent of anoxia/euxinia. In order to represent the spatial extent of reducing environments in the ocean, we introduce the “redox index” (RI), which is defined as follows:

$$\text{RI} = \frac{\int A_{\text{IWE}} dV}{\int A_{\text{OXA}} dV}$$

where $A_{\text{IWE}}$ and $A_{\text{OXA}}$ are the oceanic volume of the OD and YD regions, and $V$ is an index at each water depth, defined as follows:

$$i = \begin{cases} 0.0 & \text{for oxic water (O}_{\text{IWE}} \leq 0.001 \text{ mol/m}^3) \\ 0.5 & \text{for anoxic, non-sulfidic water (O}_{\text{IWE}} < 0.001 \text{ mol/m}^3 \text{ and } [\Sigma S_{\text{IWE}}] < 0.1 \text{ mol/m}^3) \\ 1.0 & \text{for euxinia (} [\Sigma S_{\text{IWE}}] > 0.1 \text{ mol/m}^3) \end{cases}$$

We also define a globally averaged redox index as follows:

$$\text{RI} = \frac{\int A_{\text{IWE}} dV + \int A_{\text{DWE}} dV}{\int A_{\text{IWE}} dV + \int A_{\text{DWE}} dV}$$
3. Results

3.1. Effect of atmospheric $pO_2$

The response of the oceanic biogeochemistry to changes in $pO_2$ is illustrated in Fig. 2. In these calculations, we assumed reference values for the other controlling factors (Table 1). As expected, O$_2$ concentrations decrease with decreased $pO_2$ and vice versa (Fig. 2c). In the OD region, anoxia (defined as $[O_2] < 0.001$ mol/m$^3$) appears when $pO_2$ is below 0.175 atm. The DWA appears at $pO_2 < 0.145$ atm, and a transition to pervasive euxinia (defined as the concentration of total sulfide $[\Sigma H_2S] > 0.1$ mol/m$^3$) occurs around $pO_2$ values below 0.125 atm. EoA and EoE appear for $pO_2 = 0.145 - 0.175$ atm and $pO_2 = 0.115 - 0.125$ atm, respectively (Fig. 2a). In the YD region, anoxia and euxinia appear when $pO_2$ is below 0.135 atm and 0.100 atm, respectively. The formation of deepwaters in high-latitude regions supplies “fresh” (i.e., cold, oxygen-rich) waters to YD regions, thus preventing the generation of oceanic anoxia relative to the OD region.

It is noteworthy that the decline of the oceanic oxygen concentrations results not only from the direct effect of atmospheric $pO_2$ on the oxygen concentration in the surface water, but also from the behavior of marine P cycling. The decrease in surface O$_2$ promotes de-oxygenation in the surface ocean, yielding an expansion of the OMZ (Fig. 2c). Preferential regeneration of phosphorus from organic matter in the seafloor sediment in the OMZ (Van Cappellen and Ingall, 1996), represented as an increase in $C_{org}/P_{preact}$ value of buried sediment in Fig. 2b, enhances phosphate concentration in the ocean (Fig. 2d), leading to an increase in surface productivity (Fig. 2b). This biogeochemical behavior (anoxia-productivity feedback; e.g., Algeo and Ingall, 2007) gives rise to further expansion of the OMZ. In particular, biological production is markedly enhanced at the EoE. This corresponds to a pronounced increase in the $C_{org}/P_{preact}$ ratio. Under such circumstances, anoxic waters reach the shelf region. This leads to a massive P release from shelf sediments to bottom waters, dragging the ocean into a pervasive euxinic condition. Further increases in $C_{org}$ export production and the $C_{org}/P_{preact}$ ratio of buried sediments at $pO_2 < 0.115$ atm mainly reflect the expansion of anoxia in the YD region. At a $pO_2$ of 0.05 atm, the oceanic interior is widely deoxygenated, and the $C_{org}/P_{preact}$ ratio approaches its maximum value of ~200 (Fig. 2b). In that case, the global export production of $C_{org}$ increases to more than three times the reference value owing to the efficient recycling of P in the ocean interior. It is noteworthy that this ~200 upper limit to the $C_{org}/P_{preact}$ ratio is deduced from observations of modern permanently anoxic environments, such as the Black Sea, the inner basin of Effingham Inlet, and the Framvaren Fjord (e.g., Algeo and Ingall, 2007). In contrast, evidence for decreases in phosphorus accumulation and increases in the $C_{org}/P_{preact}$ ratio up to 1500 during Cretaceous OAE2 has been reported (Kraal et al., 2010; Mort et al., 2007a; Nederbragt et al., 2004). Therefore, the intensity of anoxia-productivity feedback assumed in this study can be regarded as an underestimation.

In the oxygen-depleted oceans, enhanced denitrification tends to reduce marine fixed nitrogen (nitrate and ammonium). Nitrogen depletion is assumed to be compensated by fixation of nitrogen from the atmosphere in this model (Supplementary material). Therefore, nitrogen fixation required for maintaining the biological productivity should be enhanced. For instance, nitrogen fixation rate required to the nitrogen balance would be ~2580 Tg N/yr when $pO_2 = 0.1$ atm (not shown). This value is ~22 times the reference (preindustrial) value of 118 Tg N/yr. If the activity of nitrogen fixation is limited for some reasons (e.g., exhaustion of trace metals, such as Mo), marine biological productivity cannot be increased because of the limiting of nitrogen.

3.2. Effect of shelf size

The effects of $A_{ws}$ on the distributions of dissolved oxygen and phosphate in the ocean are shown in Fig. 3c and d, respectively. As the shelf area decreases, the ability of shallow sediments to retain P is diminished. This leads to increased dissolved P concentrations (Fig. 3d) and increased rates of primary production (Fig. 3b). In the OD region, anoxia appears at intermediate depths (at ~1000 m) when $A_{ws}$ is less than approximately 70% of the
Anoxia doubling nutrients, which include phosphorus, resulting in the ocean being of OD region. However, euxinia does not occur in this experiment. Previous results obtained by Bjerrum et al. (2006), suggesting the relative to the reference state (Fig. 3b). This behavior supports our model demonstrates that ocean tended to be against oceanic eutrophication and generation of anoxia. According to geographical studies (Ronov, 1994; Walker et al., 2002), shelf areas in low-mid latitude region were over 200% of present value during ‘greenhouse’ climatic periods, such as the mid-Cretaceous. Our model demonstrates that ocean tended to be more oligotrophic and well oxygenated in those periods than at present if other parameters are assumed to be the same. Therefore, changes in sea level stands and shelf area throughout geological history could have a quantitative importance for discussions of the paleo-oceanic redox state.

### 3.3. Oceanic redox conditions with respect to pO₂, A°C, and Rᵦ

Next, we systematically examine steady-state oceanic redox conditions for three parameters (pO₂, A°C, and Rᵦ). Fig. 4a represents the oceanic redox conditions in a steady state with respect to Rᵦ/Rᵦ* and A°C/A°C* in the OD region. The reference condition is represented as an asterisk in this figure. The enhanced phosphorus input is clearly crucial for the generation of anoxia/euxinia in the ocean. However, it is noteworthy that the Rᵦ/Rᵦ* for the initiation of

![Fig. 3. Effect of shelf area on ocean biogeochemistry. (a) Redox indexes. ‘Edge of Anoxia’ for the OD region is represented by light shading. (b) Export production of organic carbon (in 10⁵ mol C/yr). (c) Oxygen distribution for the OD region (in mol/m³). (d) Phosphate distribution for the OD region (in mmol/m³). In (c) and (d), anoxia is represented by light shading.]

![Fig. 4. Steady-state ocean redox state for the OD region; diagrams for (a) riverine Preact input rate from continent to ocean (Rᵦ/Rᵦ*) and shelf area (A°C/A°C*), (b) Rᵦ/Rᵦ* and atmospheric pO₂, and (c) pO₂ and A°C/A°C*, where the asterisk represents the reference condition (Table 1). Oceanic redox conditions based on oxygen and hydrogen sulfide profiles. Oxic, IWA, and DWA denote fully oxic conditions, intermediate water anoxia, and deepwater anoxia, respectively, and non-sulfidic, IWE, and DWE denote non-sulfidic conditions, intermediate water euxinia, and deepwater euxinia, respectively (Ozaki et al., 2011). In (a) and (b), the parameter region where bistable solutions (DWA/DWE or DWA/IWE) exist is colored by black shading.]

reference value (Fig. 3a and c). When A°C=0.5 × A°C*, anoxia appears at water depths of ~400–4000 m, occupying ~39% of the volume of OD region. However, euxinia does not occur in this experiment. By contrast, the vast shelf area should trap large amounts of nutrients, which include phosphorus, resulting in the ocean being in a more oligotrophic and oxygenated condition. For instance, doubling A°C gives rise to a ~45% decline in Corg export production relative to the reference state (Fig. 3b). This behavior supports previous results obtained by Bjerrum et al. (2006), suggesting the possibility that the vast shelf area may act as an efficient buffer against oceanic eutrophication and generation of anoxia.

According to geographical studies (Ronov, 1994; Walker et al., 2002), shelf areas in low-mid latitude region were over 200% of present value during ‘greenhouse’ climatic periods, such as the mid-Cretaceous. Our model demonstrates that ocean tended to be more oligotrophic and well oxygenated in those periods than at present if other parameters are assumed to be the same. Therefore, changes in sea level stands and shelf area throughout geological history could have a quantitative importance for discussions of the paleo-oceanic redox state.
anoxia/euxinia depends strongly on Ac. For instance, $R_o > 2.8 \times R_o^*$ is required when $A_{c1} = 1.5 \times A_{c2}^*$ for the generation of euxinia, although the threshold is approximately $2.0 \times R_o^*$ under the present value of $A_{c1}$. Fig. 4a indicates that vast shelf area would act as an efficient buffer of oceanic eutrophication and anoxia/euxinia.

Fig. 4b shows oceanic redox conditions with respect to $R_o/R_o^*$ and $pO_2$ in the OD region, assuming the present value of $A_{c2}$. This diagram indicates that $R_o^*$ increases with $pO_2$; while the value of $R_o^*$ necessary to initiate anoxia and euxinia is $1.4 \times R_o^*$ and $2.0 \times R_o^*$ at a $pO_2$ of 0.21 atm; these numbers are only $0.8 \times R_o^*$ and $1.35 \times R_o^*$ at $pO_2=0.015$ atm. On the other hand, $R_o > 2.5 \times R_o^*$ is required for anoxia to appear under $pO_2=0.30$ atm. This quasi-linear relationship can be explained by a simple balance of oxygen supply (via $pO_2$) and demand (via $R_o$). Considering a $pO_2$ range of $0.15-0.35$ atm estimated from mass balance models (e.g., Berner, 2009) during the Phanerozoic, changes in $pO_2$ play a fundamental role in discussions of not only the long-term evolution of paleoredox but also of the conditions necessary for the occurrence of OAEs.

In Fig. 4a and b, we found bistable solutions for the oceanic redox condition (colored by black shading). For instance, under the conditions of $R_o=2 \times R_o^*$, $A_{c1}=A_{c2}^*$, and $pO_2=pO_2^*$, there are two stable redox structures, DWA/IWE and DWA/DWE, depending on the initial condition. This bifurcation originates from the strong non-linearity of the redox-dependent marine P cycling. In particular, once shelf anoxia (anoxia at $j=1$ layer) is achieved, an enhanced recycling of $P$ sustains the DWA/DWE condition. For instance, Fig. 4a indicates that vast shelf area would act as a shuttle to the abyssal ocean. Because of this process, which is known as the ‘ballast effect’ or ‘ballast hypothesis’ (Armstrong et al., 2002; Ittekkot, 1993; Klaas and Archer, 2002), the delivery of

4. Discussion

4.1. Implications for the relationship between $pO_2$ and marine redox chemistry

The long-term oceanic redox history has previously been discussed based on the evolution of the atmospheric oxygenation state. Our sensitivity experiment with respect to the atmospheric $pO_2$ level (Fig. 2) provides some insights into the oceanic redox evolution through the Earth’s history. Fig. 2c indicates that global anoxia (DWA) in the low- to mid-latitude region appeared at $pO_2 < 0.145$ atm. This $pO_2$ value is larger than the previously estimated value of $0.1$ atm based on a three-box model (Canfield, 1998; Lasaga and Ohimoto, 2002). This is largely because our model includes the process of redox-dependent phosphorus liberation at the sediment–water interface (Colman and Holland, 2000; Ingall and Jahnke, 1994). Therefore, once anoxia appears in the water column, preferential regeneration of $P$ relative to $C$ enhances oceanic surface productivity (Fig. 2b), resulting in more reducing conditions. Without this mechanism, global anoxia occurs at $pO_2 < 0.09$ atm (Fig. 5), which is consistent with previous estimates (Canfield, 1998). Therefore, redox-dependent $P$ cycling exerts a crucial role in the conditions for a generation of anoxia/euxinia.

The obtained threshold of $pO_2$ between pervasive anoxia and euxinia is $pO_2 \sim 60\%$ PAL, and a fully oxic condition is not achieved until $pO_2$ is above $0.175$ atm (Fig. 2). Recent combustion experiments (Belcher et al., 2010) shows that fire activity would be greatly suppressed when $pO_2 < -0.18$ atm. On the other hand, there is a continuous record of charcoal since the Devonian (e.g., Algeo and Ingall, 2007; Glasspool and Scott, 2010). Therefore, it seems likely that atmospheric $pO_2$ has been $> -0.18$ atm since the Devonian. This value is roughly equal to the critical value for initiation of OAEs estimated from our study (Fig. 2). Recently, Dahl et al. (2010) presented the molybdenum isotopic value in sedimentary rocks and found a global oceanic oxygenation around the Silurian–Devonian period. If an increase in $^{98}Mo$ up to 2.0% can be regarded as a global oceanic oxygenation, such an oxygenation event would reflect the condition of $pO_2 > 0.175$ atm. Here, we must note that the $pO_2$ threshold is also a function of several environmental factors, such as $R_o$ and $A_{c1}$ (Fig. 4b and c). If $R_o$ is lower than that at present, the required $pO_2$ for oxygenation of the whole ocean also decreases and vice versa. If $R_o$ is 50% of the present value, then the threshold between oxic and anoxic oceans decreases to 0.105 atm, as shown in Fig. 4b.

The sensitivity experiment of $pO_2$ also provides insight into the Precambrian ocean redox state. The Proterozoic ocean was probably under anoxic (ferruginous/sulfidic) conditions, based on geological and geochemical data, such as sulfur isotopic composition (e.g., Canfield, 1998), iron speciation data (Canfield et al., 2008; Li et al., 2010; Planavsky et al., 2011; Poulton et al., 2010; Shen et al., 2002, 2003), and Mo concentrations (Scott et al., 2008). The reducing oceanic conditions are considered to be associated with low atmospheric $pO_2$ levels, but the actual value of atmospheric $pO_2$ during the Proterozoic are not well defined. Our model demonstrates that pervasive euxinia will occur at $pO_2 < 0.125$ atm (Fig. 2c). This transition of oceanic redox reflects the occurrence of shelf anoxia; anoxia at continental shelves effectively promotes a massive liberation of $P$ from sediments to bottom waters, leading to marine eutrophication and generation of euxinia. Without considering the anoxia-productivity feedback (A–P feedback), pervasive euxinia cannot be achieved even when $pO_2=0.05$ atm (Fig. 5). This is because the quantity of organic matter available for sulfate reduction is not enough to accumulate $H_2S$ in high concentrations.

We note that, in the past, the intensity of the biological pump was very different to that of the present ocean. In fact, the present biological pump is efficient, owing to large quantities of fecal pellets derived from zooplankton and high–density biominerals, such as opal (2.1 g/cm$^3$) and carbonate (2.71 g/cm$^3$), and sinking particulate organic matter (POM), and these biogenic materials act as a ‘shuttle’ to the abyssal ocean. Because of this process, which is known as the ‘ballast effect’ or ‘ballast hypothesis’ (Armstrong et al., 2002; Ittekkot, 1993; Klaas and Archer, 2002), the delivery of
biogenic materials to deepwater may not have been efficient before diversification of coccolithophores, foraminifera, and/or diatoms. If the intensity of the biological pump is weaker than at present because of a lower sinking velocity and/or higher degradability, the oxygen demand in the surface-intermediate waters would have been larger than at present (Kashiyama et al., 2011; Logan et al., 1995), giving rise to a threshold between oxic and anoxic oceans with a value greater than 0.145 atm. This idea provides further speculation for the discussion on marine redox chemistry in the aftermath of mass extinction (e.g., Permian–Triassic boundary ~ 251 Ma); efficient recycling of POM in a shallow part of the ocean promotes shelf anoxia, resulting in further eutrophication and anoxia by stimulating A–P feedback.

In summary, the relationship between the atmospheric pO2 and oceanic redox state is affected significantly by several factors, including $R_p$, $A_c$, ballast effect, among others. Hence, we must carefully consider these settings to quantitatively constrain the redox evolution of atmosphere–ocean system.

4.2. Oceanic redox states under Cretaceous greenhouse climatic condition

Figs. 3 and 4a demonstrate that vast shelf area may act as an efficient buffer against oceanic eutrophication and generation of anoxia/euxinia. This biogeochemical behavior will be important for discussions of the oceanic redox condition in ancient “greenhouse” climates. For instance, in the mid-Cretaceous, which is known as a prominent “greenhouse world”, the concentration of atmospheric carbon dioxide is estimated to have been ~1000 ppmv (Hong and Lee, 2012; Park and Royer, 2011; Royer et al., 2012), and the reconstructed seawater temperature shows higher values than those at present (e.g., Friedrich et al., 2012; Puč et al., 2003). During the Cretaceous it is likely that CO2 degassing rate from solid earth into the atmosphere–ocean system was probably higher than at present (e.g., Larson, 1991). Under warm and wet climatic conditions, an enhanced hydrological cycle could accelerate chemical weathering on land, leading to an enhanced delivery of nutrients to the ocean. If it is the case then ocean would tend to be de-oxygenated owing to the combined effect of enhanced nutrient input and a decrease in $O_2$ solubility in surface waters (Ozaki et al., 2011).

On the other hand, according to paleogeographic reconstructions, the mid-Cretaceous was accompanied by high sea-level conditions and vast shelf area of ~177–220% of that at present (Bjerrum et al., 2006; Ronov, 1994; Walker et al., 2002). If other factors are kept constant, export productivity decreases by ~40–52% relative to present value and the oxygen inventory of the ocean increases (Fig. 3). Therefore, because the vast shelf area acts as a major sink of nutrients delivered from the continent, oxic environments may have occurred in such a greenhouse world (Figs. 3 and 4a).

To assess the oceanic redox state underlying the greenhouse climatic condition and to highlight the biogeochemical effect of shelf area under such conditions, we conducted a systematic sensitivity experiment with respect to $pO_2$ and $A_c$ under the Cretaceous conditions (Fig. 6a). In this calculation $R_p$ is estimated using a simple weathering scheme which includes several controlling factors on the chemical weathering rate (see Appendix A). As a result, we estimate $R_p$ to be $1.38 \times R_p^*$ for the Cretaceous. Based on temperature reconstructions from $\delta^{18}O$ values of carbonate (e.g., Royer et al., 2004), we assume that the SST increases by 4 K for L. Considering a small thermal equator-to-pole gradient (e.g., Bice and Norris, 2002) and high deepwater temperature (e.g., Friedrich et al., 2012), we assume an increase in SST of +10 K for H. Considering the low physical erosion rate during the Cretaceous (Berner and Kothavala, 2001), we also assumed a low sedimentation rate relative to the present value.

Fig. 6a demonstrates that the Cretaceous oceanic redox was significantly affected by $A_c$. The ocean would have been in pervasive anoxia/euxinia (DWA/DWE) when $pO_2 = pO_2^*$ and $A_c = A_c^*$. This is the result of the combined effect of an enhanced $R_p$, and decreased oxygen solubility. When $A_c = A_c^*$, the ocean cannot be oxygenated unless $pO_2 > 0.31$ atm. On the other hand, given the geological constraints of the shelf area during the Cretaceous (~200% of present; Ronov, 1994; Walker et al., 2002), the ocean will be oxygenated when $pO_2 > 0.21$ atm. The vast shelf area plays a crucial role in the Cretaceous oceanic redox state.

In general, vast $A_c$ (and high sea-level stand) conditions reflect an increased oceanic crust production rate (e.g., Müller et al., 2008). An active tectonic forcing such as enhanced CO2 degassing gives rise to warm climatic condition via accumulation of CO2 in the atmosphere on the timescales of $> 10^5$ yr. Under warm climatic conditions, chemical weathering on land would be enhanced, leading to an increase in nutrient discharge to the ocean. However, oceanic eutrophication could be buffered by the vast shelf area (Figs. 3 and 6a). Therefore, our results highlight the intimate connection between the tectonic conditions, sea-level stand, climate, and long-term oceanic redox state: increased CO2 degassing results in an enhanced nutrient loading from continents via climatic warming. On the other hand, expanded shelves efficiently buffer the oceanic eutrophication.

**Fig. 6.** Oceanic redox condition with respect to (a) atmospheric $pO_2$ and $A_{cs}/A_{cs}^*$ ($R_p = 1.38 \times R_p^*$), and (b) $R_p/R_p^*$ and $pO_2$ ($A_{cs} = 2.12 \times A_{cs}^*$) for the OD region under the Cretaceous condition. Abbreviations have the same meanings as in Fig. 4. The parameter region where bistable solutions (DWA/DWE or DWA/IWE or DWA/non-sulfidic) exist is colored by black shading.
Variations in the CO₂ degassing rate throughout Earth's history have played a key role in regulating the oceanic redox state.

4.3. Implications for the initiation of OAEs

Finally, we consider the causal mechanisms of Cretaceous OAEs. Previous studies have suggested that there is an intimate connection between the two most widespread Cretaceous OAEs (i.e., OAE 1a and OAE 2) and the activities of LIPs (e.g., Adams et al., 2010; Kuroda et al., 2007; Snow et al., 2005; Tejada et al., 2009; Turgeon and Creaser, 2008). Massive injections of greenhouse gases associated with the activity of LIPs may have caused a rapid climate warming and enhancement of chemical weathering on land. An enhanced nutrient loading to oceans would cause oceanic eutrophication and de-oxygenation. In fact, increases in phosphorus accumulation rate around the initial stage of OAEs have been reported for several geological sections (Bomou et al., 2013; Gertsch et al., 2010; Hetzel et al., 2011; Kraal et al., 2010; Mort et al., 2007a, 2007b, 2008; Nederbragt et al., 2004; Pearce et al., 2009; Scopelliti et al., 2010; Westermann et al., 2010), implying enhanced biological activity and/or enhanced phosphorus input from land. Isotopic variations of strontium, osmium and calcium also indicate the enhancement of continental weathering accompanied by OAEs (Blättler et al., 2011; Frijia and Parente, 2008; Tejada et al., 2009). Considering the high weatherability of basalt (Dessert et al., 2001), the emplacement of LIPs followed by chemical weathering could promote phosphorus input to the oceans. To assess \( R_p^{\text{eu}^{\text{r}}} \) with respect to OAEs under Cretaceous conditions, we conducted sensitivity experiment on the oceanic redox state in terms of \( R_p^{\text{eu}^{\text{r}}} R^*_p \) and \( P_{O_2} \) (Fig. 6b). In this calculation, we assumed \( A_{p,p} = 2.12 \times A^*_p \) based on Walker et al. (2002).

Geologic records of the late Cenomanian show that ocean anoxia was already established in the proto-north Atlantic region before OAE2 (e.g., Adams et al., 2010). Therefore, the pre-Cretaceous ocean was likely located near (or in) the EoA. We can estimate such conditions at \( p_{O_2} = -0.20\text{--}0.22\text{ atm} \) (supposing \( R_p = 1.38 \times R_p^* \)). In such a case, a slight increase in \( R_p \) could cause widespread OAE. In contrast, if the Cretaceous \( p_{O_2} \) was high (\( > 0.28\text{ atm} \)) (Bergman et al., 2004; Glasspool and Scott, 2010), then \( R_p^{\text{eu}^{\text{r}}} \) would be much higher (\( > 2.5 \times R_p^* \)), thus requiring a large climatic perturbation to cause an OAE. If a transient threefold increase in the continental weathering, as inferred from the calcium isotopic variation (Blättler et al., 2011), was the case, then widespread anoxia could have been triggered even if \( p_{O_2} = 0.30\text{ atm} \). However, it is difficult to cause widespread euxinia, conflicting with the geological evidence (Monteiro et al., 2012). To cause pervasive euxinia by a threefold increase in \( R_p \), Cretaceous atmospheric \( p_{O_2} \) should be lower than \( \sim 0.28\text{ atm} \). Further investigations with a three-dimensional ocean model would make a logical next step towards assessing the relationship between paleoredox distribution, size of shelf area, and atmospheric \( p_{O_2} \) level, considering that paleogeography exerts an effect on the spatial distribution of anoxia/euxinia during the late Cretaceous (e.g., Meyer and Kump, 2008; Monteiro et al., 2012; Trabuco-Alexandre et al., 2010).

On the other hand, Handoh and Lenton (2003) claim that an increase in weathering forcing could drag the atmosphere–ocean system into a self-oscillating system, in which \( p_{O_2} \) has changes on the timescales of several millions of years. If so, high \( p_{O_2} \) conditions would be expected in the aftermath of an OAE and the pre-OAE \( p_{O_2} \) would be relatively low. Therefore, high \( p_{O_2} \) estimates (Bergman et al., 2004; Glasspool and Scott, 2010) and a series of OAEs during the Cretaceous may not be mutually inconsistent.

Although further investigation is required to test the linkages between the activities of LIPs, OAEs, and C–P–O biogeochemical dynamics, Fig. 6b demonstrates that an increase in \( R_p \) which is promoted by a climatic warming caused by the activities of LIPs could have caused Cretaceous OAEs.

5. Conclusions

We conducted a systematic sensitivity experiment with respect to the biogeochemical effects of the atmospheric \( p_{O_2} \) level, shelf area \( A_{p,p,} \) and riverine \( P_{\text{React}} \) input rate \( R_p \) on the oceanic redox condition. Pervasive anoxia and euxinia will occur at \( p_{O_2} < 0.145\text{ atm} \) and \( p_{O_2} < 0.125\text{ atm} \) at the present values of \( A_{p,p,} \) and \( R_p \). These critical values are higher than the previous estimate of \( \sim 50\% \) PAL, and reflect the preferential regeneration of \( P \) under anoxic waters. The sensitivity experiment for \( A_{p,p,} \) showed that changes in \( A_{p,p,} \) significantly affect marine redox by changing marine nutrient cycling. In particular, vast shelf areas result in oligotrophic and well-oxygenated conditions. We conclude that \( p_{O_2} \) and \( A_{p,p,} \) play a fundamental role in long-term oceanic redox.

We also assessed the oceanic redox state under Cretaceous "greenhouse" climatic conditions, highlighting the important role of \( A_{p,p,} \) on the marine redox state during the Cretaceous. If the vast \( A_{p,p,} \) (\( \sim 200\% \) of present) reconstructed from geomorphological studies (Ronov, 1994; Walker et al., 2002) is the case, an oxygenated oceanic condition would be achieved if \( p_{O_2} > \sim 0.21\text{ atm} \). Without considering this effect, the ocean becomes deoxygenated unless \( p_{O_2} > \sim 0.31\text{ atm} \). In other words, our results confirm that variations in sea-level stands (i.e., shelf size) are very likely to be a key controlling factor of the oceanic redox state on timescales longer than \( 10^6\text{ yr} \). It is suggested that tectonic evolution, such as variations in the seafloor spreading rate and shelf area, and oceanic redox are much more intimately related with each other than previously thought.

We also found that an increase in \( R_p \) is an important mechanism for Cretaceous OAEs. However, the required perturbation is significantly affected by \( p_{O_2} \). Further investigation is needed to elucidate the connection between the activities of LIPs and OAEs as well as to better understand the biogeochemical dynamics during OAEs.

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Appendix A. Formulation of the relationship between weathering rate and \( R_p \)

We discuss the relationship between the warm climatic conditions and ocean redox state in Section 4.2. To do this, we assumed several relationships between the climatic conditions and the weathering rate on land.

Phosphorus availability in the ocean is limited by the supply of \( P \) via chemical weathering of continents (apatite mineral is considered to be the primary phosphorus source; e.g., Föllmi, 1996; Guidry and Mackenzie, 2000). Since apatite is both in silicate and carbonate rocks, the discharge of \( P_{\text{react}} \) may be written as the sum of the two input rate coming from the weathering of silicate \( R_p^{\text{sil}} \) and carbonate rocks \( R_p^{\text{car}} \). Phosphorus is also derived from the oxidative weathering of old organic matter in sedimentary rock (i.e., kerogen). Hence, the total riverine \( P_{\text{react}} \) input rate \( R_p \)
may be written as

\[ R_V = R^\text{vol} + R^\text{carb} + R^\text{org} \]  

(A.1)

The contribution of each source is given by

\[ R^\text{vol} = \alpha_\text{vol} W_\text{vol} \]  

(A.2)

\[ R^\text{carb} = \frac{W_\text{carb}}{CP_{\text{carb}}} \]  

(A.3)

\[ R^\text{org} = \frac{W_\text{org}}{CP_{\text{org}}} \]  

(A.4)

where \( W_\text{vol} \), \( W_\text{carb} \), and \( W_\text{org} \) are weathering fluxes of silicate, carbonate, and organic matters, respectively. \( CP_{\text{carb}} \) and \( CP_{\text{org}} \) are molar ratios of carbon to phosphorus content in carbonate rock (=1000) and organic matter (=250), respectively. The factor \( \alpha_\text{vol} \) is an adjustment parameter, which is determined such that \( R_V=0.18 \text{ T mol/yr} \) for reference condition. Although the factors controlling chemical weathering are complex, the rate of chemical weathering is usually considered to be temperature dependent (Berner, 2004; Dessert et al., 2001). Here we adopt a simple but well-calibrated formula from the GEOCARB model (e.g., Berner, 2004, 2006a, 2006b). Carbonate and silicate weathering is affected by soil biological activity due to land plants and bacteria, as well as many other factors. The complete weathering formula is given by

\[ W_\text{carb} = f_{\text{bio}} f_{\text{vol}} f_{\text{f}} f_{\text{AD}} f_{\text{LA}} f_{\text{A}} W_\text{carb}^\text{a} \]  

(A.5)

\[ W_\text{vol} = f_{\text{vol}} f_{\text{bio}} f_{\text{f}} f_{\text{AD}} f_{\text{LA}} f_{\text{A}} W_\text{vol}^\text{a} \]  

(A.6)

\[ f_{\text{AD}} = f_A f_{\text{A}} f_{\text{f}} f_{\text{t}} \]  

(A.7)

\[ f_{\text{LA}} = f_{\text{f}} f_{\text{A}} f_{\text{t}} \]  

(A.8)

\[ f_{\text{bio}} = \left(1 + f_{\text{sil}} \Delta T \right)^{0.065} \exp(f_{\text{zz}} \Delta T) \]  

(A.9)

\[ f_{\text{vol}} = \left(1 + f_{\text{vol}} \Delta T \right)^{0.065} \exp(f_{\text{zz}} \Delta T) \]  

(A.10)

\[ f_{\text{A}} = \left(1 + f_{\text{A}} \Delta T \right)^{0.065} \]  

(A.11)

where \( t \) is the time in Myr, \( R_{\text{C/O}} = p_{\text{CO}_2}/p_{\text{CO}_4}^*, p_{\text{CO}_4}^* = 280 \text{ ppm} \), an asterisk indicates the reference value, and \( \Delta T \) is the deviation of the temperature from its reference value of 288.15 K. The meanings of factors are according to GEOCARB model (e.g., Berner, 2004, 2006b). For the Cretaceous conditions, we assumed atmospheric \( p_{\text{CO}_4} \) levels of 1000 ppm, which is in agreement with a recent reconstruction based on proxies (Hong and Lee, 2012; Park and Roeyer, 2011; Roeyer et al., 2012). All parameter values assumed in the calculation are listed in Table A1.

We also assumed that the continental weathering of kerogen is affected by temperature and runoff.

\[ W_{\text{org}} = f_{\text{bio}} f_{\text{vol}} f_{\text{f}} f_{\text{AD}} f_{\text{LA}} f_{\text{A}} W_{\text{org}}^* \]  

(A.12)

where \( W_{\text{org}}^* \) is the present weathering rate of organic matter.

The sedimentation rate (SR) at the seafloor is mainly affected by the input rate of terrigenous materials. We assumed a lowered SR to reflect the low physical erosion rate during the Cretaceous (Berner, 2006c; Berner and Kothavala, 2001):

\[ \text{SR}(t, z) = 0.465R^*z \]  

(A.13)

where \( z \) is the water depth in meters.

Appendix B. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.epsl.2013.04.029.

References


