Earth and Planetary Science Letters 304 (2011) 270–279

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Conditions required for oceanic anoxia/euxinia: Constraints from a one-dimensional ocean biogeochemical cycle model

Kazumi Ozaki *, Shigeo Tajima [1], Eiichi Tajika [2]

Department of Earth and Planetary Science, School of Science, University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

ARTICLE INFO

Article history:
Received 28 July 2010
Received in revised form 7 January 2011
Accepted 6 February 2011
Available online 3 March 2011

Editor: P. DeMenocal

Keywords:
anoxia
euxinia
oceanic anoxic events
biogeochemical cycles
phosphorus cycle

ABSTRACT

Widespread black shale depositional intervals termed oceanic anoxic events (OAEs) occurred repeatedly during the Phanerozoic Eon. Here we developed a new vertical one-dimensional ocean biogeochemical cycle model that involves several chemical reactions in an oxic–anoxic–sulfidic water column. To explore the theoretical constraints for global oceanic anoxia/euxinia quantitatively and systematically, we conducted sensitivity analyses of the proposed causal mechanisms, including elevated rates of riverine phosphorus (P) input, ocean stagnation, and lowered oxygen solubility due to climate warming. We gave special attention to the vertical chemical structure of the ocean and also to the characteristic behaviors of the marine P cycle under anoxic conditions, because the relationship between the depth of anoxia and the benthic phosphorus flux could be important for the occurrence of oceanic anoxia/euxinia. Steady-state simulations indicated that (1) a decrease in ocean stagnation or oxygen solubility is not enough by itself to achieve widespread anoxia with the present reactive P river input rate, and (2) shallow water anoxia followed by massive P liberation from surface sediments can lead to widespread eutrophication and anoxia/euxinia. We conclude that elevated riverine flux of reactive P is the most important factor for triggering global anoxic events via a positive feedback loop among ocean anoxia, phosphorus regeneration, and surface biological productivity.

1. Introduction

The formation of organic-rich, laminated sediments termed black shale occurred sporadically during the Phanerozoic. Since they are usually interpreted as a product of anoxic/euxinic bottom water conditions, such depositional events are called oceanic anoxic events (OAEs) (e.g., Schlanger and Jenkyns, 1976). Over the past three decades, many studies have investigated the connections among enhanced organic carbon (C_{org}) burial, ocean anoxia, biological extinction, and climate change (e.g., Arthur and Sageman, 1994; Jenkyns, 2010 and references therein). Accumulation of black shale accompanied by anomalous carbon isotopic excursions must indicate rapid and drastic disturbances in carbon cycling in the atmosphere–ocean system.

The proposed mechanisms for widespread, prolonged ($<10^6$ yr) oxygen depletion events are divided into two principal types: (1) enhanced biological productivity in the surface ocean, resulting in the consumption of large amounts of dissolved oxygen in intermediate to deep water (e.g., Hochuli et al., 1999; Kuypers et al., 2002; Schlanger and Jenkyns, 1976) and (2) ocean stagnation, which prevents oxygen from reaching deep water (e.g., Bralower and Thierstein, 1984; Erbacher et al., 2001; Hotinski et al., 2001). Considering the frequent occurrence of OAEs in the greenhouse world, a decrease in oxygen solubility into seawater owing to warm climate conditions would be an additional factor affecting the conditions required for global oxygen depletion in the ocean (e.g., Hotinski et al., 2001; Meyer and Kump, 2008). Furthermore, Bjerrum et al. (2006) obtained results suggesting that a larger shelf area acts as a buffer against oceanic eutrophication, resulting in lower productivity and an oxygenated ocean. They argued that a high sea-level stand reduces the organic carbon burial rate, suggesting a positive feedback loop between global warming and sea-level rise.

Studies of the early diagenetic processes at the sediment–water interface have revealed that the sediment retention potential for phosphorus tends to be depressed under anoxic bottom water conditions (e.g., Ingall and Jahnke, 1994; Ingall et al., 1993; Van Cappellen and Ingall, 1994). Observations of modern anoxic marine sediments revealed that the molar ratio of buried C_{org} to $P_{reactive}$ is almost 200 under fully anoxic–sulfidic conditions, whereas it is almost 60 or less in fully oxic settings (Algeo and Ingall, 2007), where $P_{reactive}$ represents the total bio-available phosphorus, including the organic (P_{org}), iron-bonded (P_{Fe}), and authigenic (P_{auth}) phases, i.e., $P_{reactive} \equiv P_{org} + P_{Fe} + P_{auth}$ (Anderson et al., 2001). Several recent

---

* Corresponding author. Tel.: +81 3 5841 4250.
E-mail address: ozaki@eps.s.u-tokyo.ac.jp (K. Ozaki).

[1] Present address: Microdevice Operations Division, Imaging IF Business Unit, Seiko Epson Corporation, Fujimi Plant 281 Fujimi, Fujimi-machi, Suwa-gun, Nagano-ken, 399-0293, Japan.

[2] Present address: Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa-shi, Chiba-ken, 277–8561, Japan.

0012-821X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2011.02.011

studies have reported decreases in the total phosphorus accumulation rate and increases in the C_{org}/P_{total} ratio during OAEs (Kraal et al., 2010; Mort et al., 2007, 2008; Murphy et al., 2000; Nederbragt et al., 2004). The intrinsic positive feedback loop among oxygen depletion, phosphorus regeneration, and surface biological productivity could promote and sustain anoxia during OAEs. Because of this feedback process, it is possible for the stagnant ocean to have a highly productive anoxic environment (Ingall and Jahnke, 1994; Van Cappellen and Ingall, 1994). The surface biological productivity is limited by the supply of P via upwelling of nutrient-rich intermediate waters to the surface ocean. However, on timescales longer than the residence time of P in the ocean ($>10^4$ years), the surface productivity is limited by the P inventory in the intermediate ocean, which is limited not only by the riverine P supply from continents to the ocean but also by the recycling of phosphorus in the ocean. Hence, this feedback process could be critical. This process may also increase the atmospheric oxygen levels (pO_2) through the accumulation of large amounts of organic carbon during OAEs, ultimately resulting in ocean oxygenation (Handoh and Lenton, 2003; Mort et al., 2007, 2008; Tsandev and Slomp, 2009; Van Cappellen and Ingall, 1996).

Although these suggestions for linkages among biogeochemical processes during OAEs are intriguing, few studies have quantitatively and systematically examined the effects of these causal mechanisms on widespread oceanic anoxia (Bjerrum et al., 2006; Hotinski et al., 2000; Meyer et al., 2008; Sarmiento et al., 1988; Shaffer, 1989; Tsandev and Slomp, 2009). In this article, we investigate the conditions for the occurrence of oceanic anoxia/euxinia by using a new ocean biogeochemical cycle model to reconstruct the marine biochemical cycling of carbon, alkalinity, nitrogen, oxygen, phosphorus, and sulfur. Because dissolved inorganic matter in the ocean shows remarkable vertical structure features, we develop a one-dimensional vertical ocean biogeochemical model. We evaluate the contributions of the causal mechanisms and describe a scenario for the occurrence of OAEs based on the behaviors of redox-dependent marine biogeochemical cycles.

2. Model description

2.1. Model ocean configuration and basic equation

We developed a vertical one-dimensional ocean biogeochemical model that includes ocean circulation (advection); vertical diffusion; horizontal water exchange; biological pumps of organic matter and carbonate; dissolution, decomposition, sedimentation, and burial of biogenic particles; and several redox reactions in aerobic and anaerobic environments. We also considered the input of material from external reservoirs to the ocean (as the sum of riverine input and deposition from the atmosphere) and carbon isotope fractionation. We considered the total dissolved inorganic carbon (DIC), $\delta^{13}C$ of DIC, total alkalinity (Alk), oxygen (O_2), phosphate (PO_4), nitrate (NO_3), ammonium (NH_4), sulfate (SO_4), and hydrogen sulfide (H_2S) as dissolved chemical components of seawater.

The model ocean consists of a surface mixed layer (M), a high-latitude surface layer (H), a deepwater circulation box (DCB), and multiple layers of ocean interior (O; see Fig. 1a). Below the surface layers (M and H), we used an averaged modern ocean topography (Millero, 2006) and assumed a deepest ocean depth of 6100 m, the area of which is less than 5% of the entire sea surface area (Fig. 1b). The ocean interior is divided into 60 depth levels with a 100-m vertical grid spacing; the layers are labeled with j ($j = 1 \ldots 60$) from surface to bottom (Fig. 1a). This treatment allows us to calculate the amount of buried biogenic particles in seafloor sediments at each depth. We assumed downwelling of the surface waters at H to the DCB and flows into the intermediate to deep oceanic layers, which, in turn, provide upwelling water to M.

The concentration of dissolved component X in the aphotic zone changes with time, as follows:

$$\frac{\partial[X]}{\partial t} = -A(z)w(z)\frac{\partial[X]}{\partial z} + \frac{\partial}{\partial z}\left(A(z)K(z)\frac{\partial[X]}{\partial z}\right) + \mathcal{B} + \mathcal{R} + \mathcal{D}. \tag{1}$$

$[X]$ represents the concentration of dissolved component X, and z represents the water depth (increasing upward). The first and second terms on the right-hand side express the advection and diffusion components, respectively. The factors $K(z)$, $A(z)$, and $w(z)$ are the vertical diffusion coefficient, areal fraction of the water layer at depth z to the sea surface area of $3.62 \times 10^{14}\ m^2$, and upwelling rate. The factors $\mathcal{B}$, $\mathcal{R}$, and $\mathcal{D}$ represent internal sources and sinks resulting from biological processes, chemical processes (formulated in the following subsections), and the lateral inflow of downwelling water, respectively. In this model, DCB water is assumed to flow into each ocean layer ($z < -1100$ m) in proportion to the volume of the layer. The oxygen concentration in the surface water is restored to a saturated concentration calculated by using the oxygen solubility in seawater at a given temperature (288 K for M, 275 K for H) and salinity (35 psu for M and 34 psu for H) and an atmospheric oxygen concentration of 0.21 atm (Garcia and Gordon, 1992). The upwelling rate is assumed to depend on the water depth owing to the seafloor topography and the route of deepwater lateral inflow. To include the highly convective

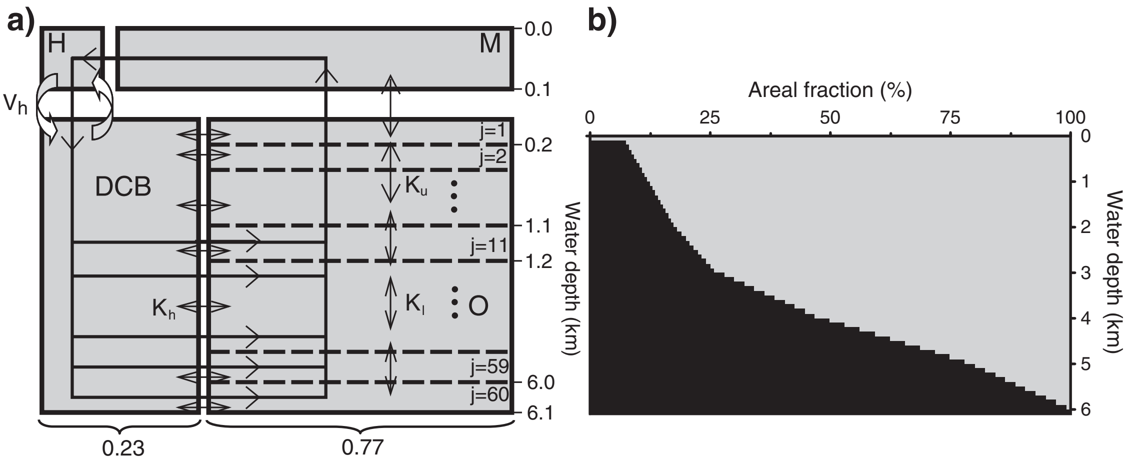

Fig. 1. (a) Schematic illustration of the model ocean used in this study. "M," "H," and "DCB" denote the mixed surface layer, high-latitude surface layer, and deepwater circulation box, respectively. An ocean area of 5% is assumed for the high-latitude surface box. The area of the DCB is held at 23%. K_u, K_l, K_h, and V_h are the high vertical diffusion coefficient, low vertical diffusion coefficient, horizontal diffusion coefficient, and polar convection, respectively. (b) Seafloor topography assumed in this study.