

論文の内容の要旨

論文題目 : A Theoretical Study on Oceanic Redox State and
Biogeochemical Dynamics

(海洋の酸化還元状態と生物地球化学循環に関する理論的研究)

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Atmosphere-ocean system has basically been kept in fully-oxygenated condition over the Phanerozoic Eon (542 million years ago to present). Considering the short residence time (roughly two or three million years) of molecular oxygen in the atmosphere-ocean system, one can expect that large fluctuations of Earth's redox state could have occurred during the Phanerozoic. However, geological evidence suggests a rather stable atmosphere-ocean oxygen concentration, at least, since Devonian, indicating that the input and output of molecular oxygen have been balanced in timescale longer than millions of years. Therefore, many scientific efforts have been made so far to elucidate the dynamics and stability of Earth's redox state.

Phosphorus is an essential element for all life and it is an “ultimate” bio-limiting nutrient which limits primary productivity on geological timescales. Considering an important role of phosphorus cycle on biological productivity (i.e., production of oxygen), we can expect that a critical aspect of regulation mechanism of the Earth's redox state probably lies in the dynamics of carbon and nutrient cycling in the Earth system.

Recent studies of marine sediments underlying anoxic bottom waters have revealed that the phosphorus retention potential is depressed under the reducing bottom water conditions. This finding is probably significant for considering the dynamics and

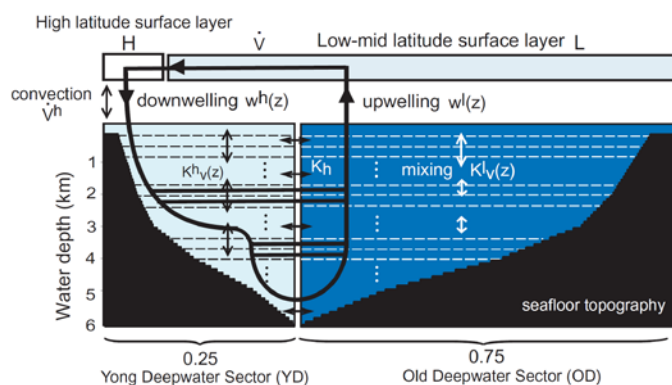


Fig. 1. Schematic illustration of the model ocean developed in this study. “L” and “H” denote the low-mid latitude mixed surface layer and high-latitude surface layer, respectively. $K^l_v(z)$ and $K^h_v(z)$ are the vertical eddy diffusion coefficient at old deepwater sector (OD) and young deepwater sector (YD). K_h and V_h are the horizontal diffusion coefficient, and polar convection, respectively. Seafloor topography assumed in this study is also depicted as building black blocks.

stabilization of oxygen concentration in the atmosphere-ocean system on different timescales. The previous efforts to elucidate the regulation mechanism of Earth's surface redox state and its variations rely on a simple dynamics of geochemical cycles of oxygen, carbon, sulfur, and phosphorus with low-resolution box models in which atmosphere-ocean system is expressed by a few boxes. In such models, one assumes reasonable (but a priori) relationships relating to internal biogeochemical cycles in the system. Marine biogeochemical cycles and chemical distributions, however, show strong vertical and horizontal heterogeneities. Thus, response of marine biogeochemical cycling to the change of environmental conditions would be intimately interrelated to each other. Consequently, the comprehensive understanding for relationship between causal mechanisms and marine biogeochemical dynamics remains unclear. To understand overall view of ocean redox state and its causal mechanisms, the development of a new numerical model, which involves comprehensive biogeochemical cycling in the ocean interior with robust circulation scheme, is highly required.

In this thesis, we developed a new model for the C-H-O-N-S-P coupled geochemical cycles based on recent experimental data and field observations, and quantitatively evaluated the dynamics and stability of the atmospheric and oceanic redox state. The critical aspect of this study is development of a comprehensive biogeochemical cycle model to explore the controls on Earth's marine redox conditions. Objective of this study is (1) to reveal the controlling factors of the atmosphere-ocean redox state, (2) to elucidate the conditions for occurrence of global oceanic anoxia/euxinia under a variety of settings, and (3) to obtain an insight into relationship between oceanic redox state and climate.

Structure of the model is schematically shown in Figure 1. In the model, ocean circulation and mixing are characterized by five physical parameters: (1) a water transport via thermohaline circulation, \dot{V} , associated with high latitude sinking and low-mid latitude upwelling of seawater, (2) constant horizontal diffusion between the regions, K_h , (3) strongly depth-dependent vertical diffusion in the high latitude region, $K_v^h(z)$, (4) high latitude convection, \dot{V}^h , and, (5) depth-dependent vertical diffusion in the low-mid latitude region, $K_v^l(z)$. These physical parameters are estimated based on the observed tracer distributions. This ocean model is specialized to describe comprehensive marine biogeochemical cycles of C, H, O, N, S, and P. We considered phosphate (PO_4^{3-}), nitrate (NO_3^-), dissolved oxygen (O_2), sulfate (SO_4^{2-}), ammonium (NH_4^+), total sulfide ($\Sigma \text{H}_2\text{S}$), dissolved inorganic carbon (DIC) with three isotopes (^{12}C , ^{13}C , ^{14}C), and alkalinity (ALK). The model includes several biochemical processes, such as biological productivity in euphotic layer, biological pump, remineralization in water column, and deposition and burial in marine sediments. In addition to redox reactions under oxic environment, decomposition of organic matters by nitrate and sulfate, oxidation processes of ammonium and hydrogen sulfide, and redox-dependent burial efficiency of phosphorus in marine sediments were also included.

We systematically examined the effects of five factors which should control the oceanic redox state on wide range of timescales, that is, (1) ocean circulation rate, (2) riverine reactive phosphorus input rate, (3) sea surface temperature (SST), (4) atmospheric oxygen concentration ($p\text{O}_2$), and (5) area of continental shelves. Based on the obtained results, we found that the marine environment is greatly affected by redox-dependent phosphorus regeneration in marine sediments. In other words, the ocean anoxia/euxinia is much easier to realize when we consider the preferential regeneration of phosphorus relative to carbon in marine sediments underlying anoxic bottom water condition. We also found that a decrease in oxygen solubility of seawater due to global warming (so a rise of SST) coupled with slower ocean circulation causes anoxia/euxinia, while ocean stagnation or a rise of SST alone is not enough to achieve global euxinia. Shallow water anoxia, which is easily caused by enhanced riverine P supply, would be a critical mechanism for developing anoxia/euxinia by promoting massive phosphorus liberation from sediments. Our results support the scenario that massive volcanic activity followed by rapid global warming would accelerate chemical weathering on land and nutrient loading to the ocean, probably triggering ocean eutrophication and global anoxia/euxinia. Obtained results also indicate that the requisite of riverine P input rate for global anoxia/euxinia strongly depends on $p\text{O}_2$ and shelf size (Figure 2).

Oceanic redox conditions

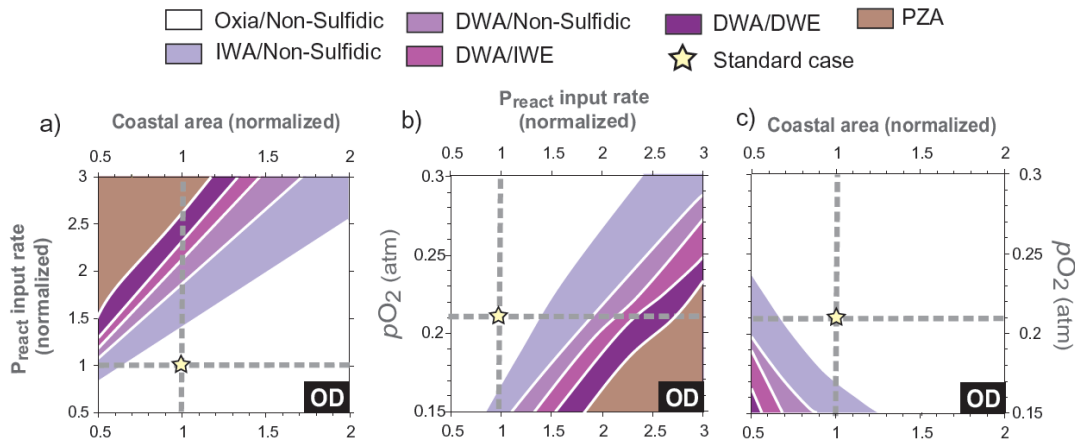


Fig. 2. Oceanic redox state with respect to riverine P input rate from continent to ocean, area of coastal shelves, and atmospheric oxygen concentration (pO_2). The enhanced P input is a critical factor for generation of global anoxia/euxinia. The threshold strongly depends on the coastal area and pO_2 . Greenhouse climate condition should enhance the nutrient delivery to the ocean. However, vast coastal area or high pO_2 would act as a buffer of oceanic de-oxygenation, implying a close relation between warm climate and fully-oxygenated ocean condition. Abbreviations: IWA=intermediate water anoxia. DWA=deepwater anoxia. IWE=intermediate water euxinia. DWE=deepwater euxinia. PZA=photic zone anoxia.

This conclusion provides further insight into the ocean redox state throughout the Phanerozoic. For instance, in the mid-Cretaceous, which is known as a prominent “greenhouse world”, the concentration of atmospheric carbon dioxide is estimated to be more than 1000 ppmv, and the reconstructed SST sometimes shows an extreme temperature ($> 35\text{ }^\circ\text{C}$). Under such a warm climatic condition, enhanced chemical weathering on land must have accelerated the delivery of phosphorus to the ocean, promoting de-oxygenation of the ocean via increased biological productivity. However, geological record indicates that the ocean environments had basically been kept in oxic except for some short time intervals called “Ocean Anoxic Events” (each interval is less than 10^6 yr). This paradoxical feature can be explained if one assumed a higher pO_2 level or vigorous ocean circulation at that time. There is however no supporting evidence for such conditions prevailed in the mid-Cretaceous. We found a possible solution for this paradox, i.e., if the widespread coastal area effectively traps nutrients delivered from continents, fully oxygenated ocean condition can be consistent with the greenhouse climate condition. This result also indicates that the tectonic evolution, such as variations of seafloor spreading rate and shelf area, and ocean redox state may have been intimately related with each other much more than previously thought.