

# Impact of the evolution of carbonate ballasts on marine biogeochemistry in the Mesozoic and associated changes in energy delivery to subsurface waters

YUICHIRO KASHIYAMA<sup>1,4</sup>, KAZUMI OZAKI<sup>2</sup> AND EIICHI TAJIKA<sup>3</sup>

<sup>1</sup>*Department of Chemistry, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan*

<sup>2</sup>*Department of Earth and Planetary Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-0033, Japan*

<sup>3</sup>*Graduate School of Frontier Science, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan*

<sup>4</sup>*(Current Address) Ritsumeikan Global Innovation Research Organization, 1-1-1 Noji-higashi, Kusatsu, Shiga 525-8577, Japan (e-mail: chiro@fc.ritsumei.ac.jp)*

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**Abstract.** We have examined the impact of the Mesozoic algal revolution using biogeochemical simulations to analyze the energy flux into the subsurface environment. In particular, the delivery scheme of energy to the subsurface was dramatically altered by the appearance of mineralized exoskeletons, both in algal groups (e.g., coccolithophores) and in zooplanktic taxa. These biominerals, acting as ballast, accentuated the delivery of organic matter to subsurface waters. Thus, the elevated organic carbon flux associated with evolutionary developments in Mesozoic taxa caused an intense but short-lived oceanic euxinia, without an associated mass extinction event, in sharp contrast to the relatively prolonged Paleozoic euxinia that were generally coincident with mass extinctions.

**Key words:** Anoxia, ballast hypothesis, biogeochemical models, euxinia, Mesozoic marine revolution

## Introduction

The Mesozoic marine revolution, which affected nektic and benthic macroorganisms and communities (e.g., Aberhan *et al.*, 2006; Harper *et al.*, 1998; Oji, 1996; Palmer, 1985; Roy, 1994; Tomita, 2011, this volume; Vermeij, 1977, 1987), was coincident with a drastic changes within the microbial ecosystem involving marine photosynthetic primary producers, which should have been a primary determinant of energy flows in marine ecosystems. Recent studies have concluded that the major algal clades flourishing in modern oceans appeared in the early Mesozoic fossil record, displacing major groups of green algae which were prominent in the Paleozoic (Falkowski *et al.*, 2004a, 2004b; Falkowski and Knoll, 2007; Katz *et al.*, 2007). Although the fossil record of non-skeletal Paleozoic algae is limited, existing data suggest that oceanic photosynthetic production was chiefly dominated by green algae, from which land plants originated and diversified in the latter half of the era; hence, land plants and green algae belong to the same clade. The “ecological resetting” of oceanic phototrophs apparently occurred in the early Mesozoic, because algae with mineralized tissues, es-

pecially dinoflagellates, coccolithophores, and diatoms, are abundant in the fossil record during and after the late Triassic (Falkowski *et al.*, 2004a). Algae belonging to these three important groups possess plastids evolutionarily derived from secondary red algae symbionts (hereafter, secondary red algae).

In the modern environment, the presence of effective ballasts formed among these secondary red algae is a strong determinant on the sinking velocity of particulate organic matter (POM) into the deep ocean (Armstrong *et al.*, 2002; Klaas and Archer, 2002; Honjo *et al.*, 2008). According to the latest understanding of the processes affecting the flux rate of organic carbons, ballasts contribute to the sinking of POM constituents, such as masses of microbes and their carcasses conglutinated with mucus secreted by various planktic organisms (e.g., Alldredge and Cohen, 1987; Kepkay, 1994) as well as the fecal pellets of macrozooplankton; ballasts contribute to the “rain” or “snow” of POM falling into deeper water masses. Ballasts can consist of any material with a relatively high density, including opal (*i.e.*, amorphous silica secreted by plankton such as radiolarians and diatoms), lithogenic minerals (*i.e.*, suspended clays and dust), and cal-

cium carbonate (Armstrong *et al.*, 2002; Klaas and Archer, 2002). Calcium carbonate is an especially dense and efficient ballast material (density,  $2.71 \text{ g cm}^{-3}$ ), effectively contributing to the export of organic carbon into the deep ocean; it is 30% more dense than opal ( $2.1 \text{ g cm}^{-3}$ ) and can increase the sinking velocity of POM by as much as 50%. Carbonate minerals constitute nearly 80% of the ballast particles involved in POM transport in modern oceans (Honjo *et al.*, 2008).

The marine sedimentary record from the Jurassic onwards contains abundant fossils of algae that produced a variety of mineralized tissues, of which the calcified dinoflagellates, coccolithophores, and diatoms are of particular importance (Falkowski *et al.*, 2004a). In the later Mesozoic, magnificent pelagic accumulations of micritic calcium carbonate, impressively represented by the chalks deposited in the Cretaceous western Tethys Sea, give the impression that pelagic primary production was greatly enhanced during this time. In contrast, the oceans lacked organisms that produced efficient carbonate ballasts prior to the Late Triassic. Acritarchs were highly productive in the Paleozoic, and they produced ballast-like materials (*e.g.*, Munnecke and Servais, 2008; Kaźmierczak and Kremer, 2009; Molyneux, 2009); however, they were localized on continental shelves and generally absent in pelagic realms. These facts imply that the efficiency of organic carbon export and hence the energy delivery to the deep ocean, expressed as a function of sinking rates, was very different in Proterozoic–Paleozoic oceans compared with Mesozoic–Cenozoic oceans.

To test this postulate, we focus on the development of anoxia/euxinia in the Mesozoic oceans and those in older ages because presence/absence of the ballast-forming organisms should have been a critical factor therein. Although global oceanic euxinic events have occurred repeatedly during the Phanerozoic, the nature and consequences of these events varied temporally. In particular, major euxinia in the Paleozoic, which seem to have developed and terminated gradually (*e.g.*, Isozaki, 1997; Rimmer *et al.*, 2004; Cao *et al.*, 2009; Gill *et al.*, 2011), have strikingly different characteristics from those in the later Mesozoic, referred to here as Cretaceous ocean anoxic events (Cretaceous OAEs; Schlanger and Jenkyns, 1976), which seem to have developed and terminated relatively quickly. Moreover, Paleozoic euxinia was coincident with major mass extinction events, such as the Late Devonian and the Late-Permian mass extinctions (*e.g.*, Isozaki, 1997; Algeo and Scheckler, 1998; Grice *et al.*, 2005; Cao *et al.*, 2009), whereas the Cretaceous OAEs were coincident not with mass extinctions, but with relatively minor turnovers involving limited numbers of taxa (*e.g.*, Kaiho, 1994; Erba, 2006).

In the present work, we added a term for the sinking velocity of particulate organic matter ( $V_{\text{POM}}$ ) to the biogeochemical model proposed by Ozaki *et al.* (2011), which is one of a number of recent models that have successfully identified the

principal determinants of oceanic anoxia and euxinia (also see Romaniello and Derry, 2010). Using our modified model, therefore, we examined the influence of presence/absence of carbonate ballast production on the development of euxinia by simulating reduced/increased sinking velocities of POM. Here, we did not consider siliceous diatoms tissues as components of pelagic ballast production because the rise of this group (*ca.* 90 Ma; Delwiche, 2007) postdated the last Mesozoic anoxia/euxinia event (OAE-2, 93.5 Ma; Kuroda *et al.*, 2005; Kuroda and Ohkouchi, 2006), although there is evidence of earlier occurrences of massive diatom production starting from 115 Ma (see Delwiche, 2007, and references therein). The results will demonstrate how the evolution of carbonate ballast-producing plankton was a key factor in the different dynamics of anoxia/euxinia between Paleozoic and Mesozoic oceans.

## Models

### The model developed by Ozaki *et al.* (2011)

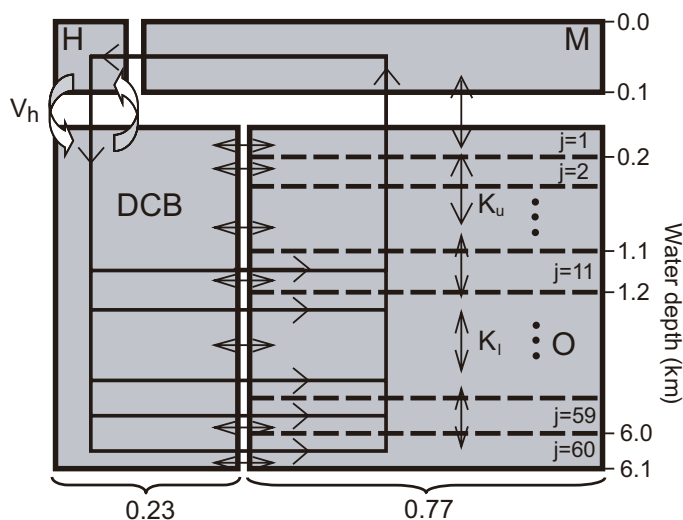
Here, we briefly summarize the essential characteristics of the model proposed by Ozaki *et al.* (2011). The model is a vertical one-dimensional description of biogeochemical processes occurring in the water column (see Figure 1a); it considers all important biogeochemical factors, such as biological pumps of organic matter and carbonate; dissolution, decomposition, sedimentation, and burial of biogenic particles; redox reactions in aerobic and anaerobic environments; flux rates promoted by ocean circulation (advection), vertical diffusion, and horizontal water exchange; and exchange of materials between external reservoirs and the ocean, such as phosphorus influxes from fluvial and atmospheric sources and release from sediments.

In the model, oceanic circulation and eddy diffusion are expressed in terms of three distinct boxes (see Figure 1a): the surface mixed layer (M); the high-latitude surface layer (H), which is a source of downwelling water; and the ocean interior (O), which includes the subsurface water column as well as deep-water circulation boxes (DCBs). The water column is divided into 61 layers, each 100 m thick, extending from the surface to the maximum ocean depth of 6100 m. The model also considers topographic effects that determine the breadth (lateral extent) of each layer, with breadth gradually decreasing from the surface with increasing depth.

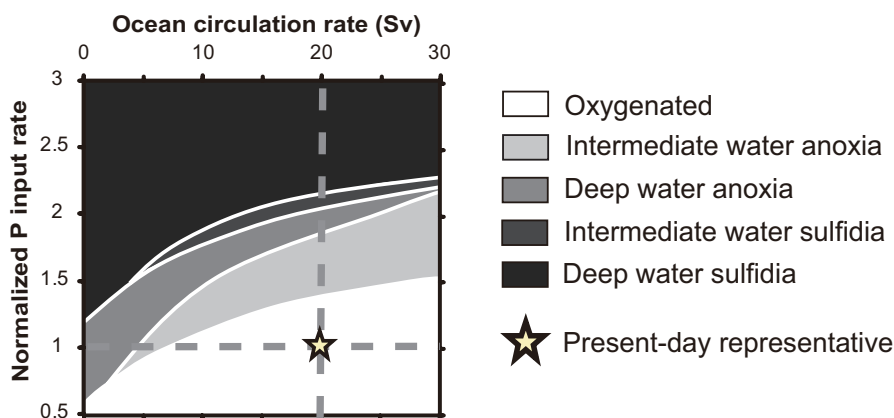
### Modification of Ozaki *et al.*'s model in the present work

We focus primarily on processes in the surface mixed layer, in which photosynthetic primary productivity is the principal energy source for the entire marine ecosystem, both in the water column, and on and within the sediment. In Ozaki *et al.*'s model, the flux of POM and carbonate particles is assumed to originate only in the surface layers (H and M; Figure 1a). The model calculates the flux rate of POMs

## (a) One-dimensional ocean model



## (b) Ocean redox conditions



**Figure 1.** **a.** Schematic illustration of the model ocean developed by Ozaki *et al.* (2011). M, H, and DCB denote the mixed surface layer, the high-latitude surface layer, and deep-water circulation boxes, respectively. H represents 5% of the ocean surface area. DCB represents 23% of the volume at each depth.  $K_u$ ,  $K_l$ , and  $V_h$  denote the high diffusion coefficient, low diffusion coefficient, and polar convection, respectively. **b.** Oceanic redox conditions based on different patterns in the vertical distributions of molecular oxygen and hydrogen sulfide concentrations, illustrating variations in response to modulating ocean circulation rates and riverine phosphorus input rates, normalized by values of present-day estimates. Figures modified after Ozaki *et al.* (2011).

as the rate of export production of organic matter and carbonate particles, assuming that the supply of phosphate to surface waters limits net primary productivity on geological time scales (*e.g.*, Broecker and Peng, 1982; Tyrrell, 1999). In other words, export productions of these constituents are assumed to be proportional to the flux of phosphorus from external sources, including the flux of recycled phosphorus from deeper waters. Flux constants are derived from studies on modern oceans (see the references in Ozaki *et al.*, 2011)

and are held constant throughout the model calculations.

Ozaki *et al.* (2011) predicted that the phosphorus flux into the surface mixed layer controls redox conditions within the water column (Figure 1b); thus, we can infer that processes involving net primary and export production in surface waters are instrumental factors controlling water column conditions. Because our research considers evolutionary changes in the composition of primary producers, it is critical to understand how and which evolutionary factors would potentially influ-

ence or modify the flux constants for primary and export production.

The above analyses of the biogeochemical model indicate that the quality and quantity of export production are affected by a variety of biological, ecological, and environmental factors in the surface mixed layer. Such factors may involve the control of photosynthetic and respiratory processes; alteration of the chemical properties of exported organic carbon or POM; and modification of the physical properties of produced POM, thereby affecting the rate of export and the “energy flux rate.”

Two categories of factors affect the export production of organic carbon: the quality (chemical properties) and quantity of organic matter to be exported; and the mechanisms of export, especially the influence of mineral ballasts associated with POM particles. Below, we describe evolutionary changes in these two categories of factors throughout the Phanerozoic, in particular comparing conditions in the Paleozoic and the later Mesozoic, and examine how these conditions potentially altered energy flux rates from the surface mixed layer to the subsurface water column.

## Results

We examined how redox conditions in the water column were affected by changes in the sinking velocity of POM, according to the biogeochemical model of Ozaki *et al.* (2011). The model simulations were run with sinking velocities ranging step-wise from 20 to 120 m day<sup>-1</sup> in increments of 5 m day<sup>-1</sup>; note that the sinking velocity was fixed at 100 m day<sup>-1</sup> in Ozaki *et al.*'s (2011) original model. The riverine influx of phosphorus (0.18 Tmol P year<sup>-1</sup>) and the oceanic circulation rate (20 Sv; 1 Sv = 10<sup>6</sup> m<sup>3</sup> s<sup>-1</sup>) were fixed to values estimated for the modern ocean. The results of the simulations are shown in Figure 2.

Figure 2a shows that anoxic conditions appear when the sinking velocity is <39 m day<sup>-1</sup>, which is 39% of the modern average. Anoxic conditions appear simultaneously in the middle of the water column (*i.e.*, the oxygen minimum zone) and in deep water. The entire water column, except for surface layers, becomes anoxic at sinking rates of <34 m day<sup>-1</sup>. Euxinic conditions appear in both the middle and the bottom of the water column at sinking rates of <26 m day<sup>-1</sup>, and expand to the entire subsurface water column at rates of ca. 21 m day<sup>-1</sup>. Figure 2b shows that reductions in the velocity of sinking POM are also coupled to increased concentrations of phosphorus throughout the water column.

## Discussion

The observed trends in the expansion of reduced water masses as a function of sinking rate are in contrast with the results obtained by Ozaki *et al.* (2011), who found that re-

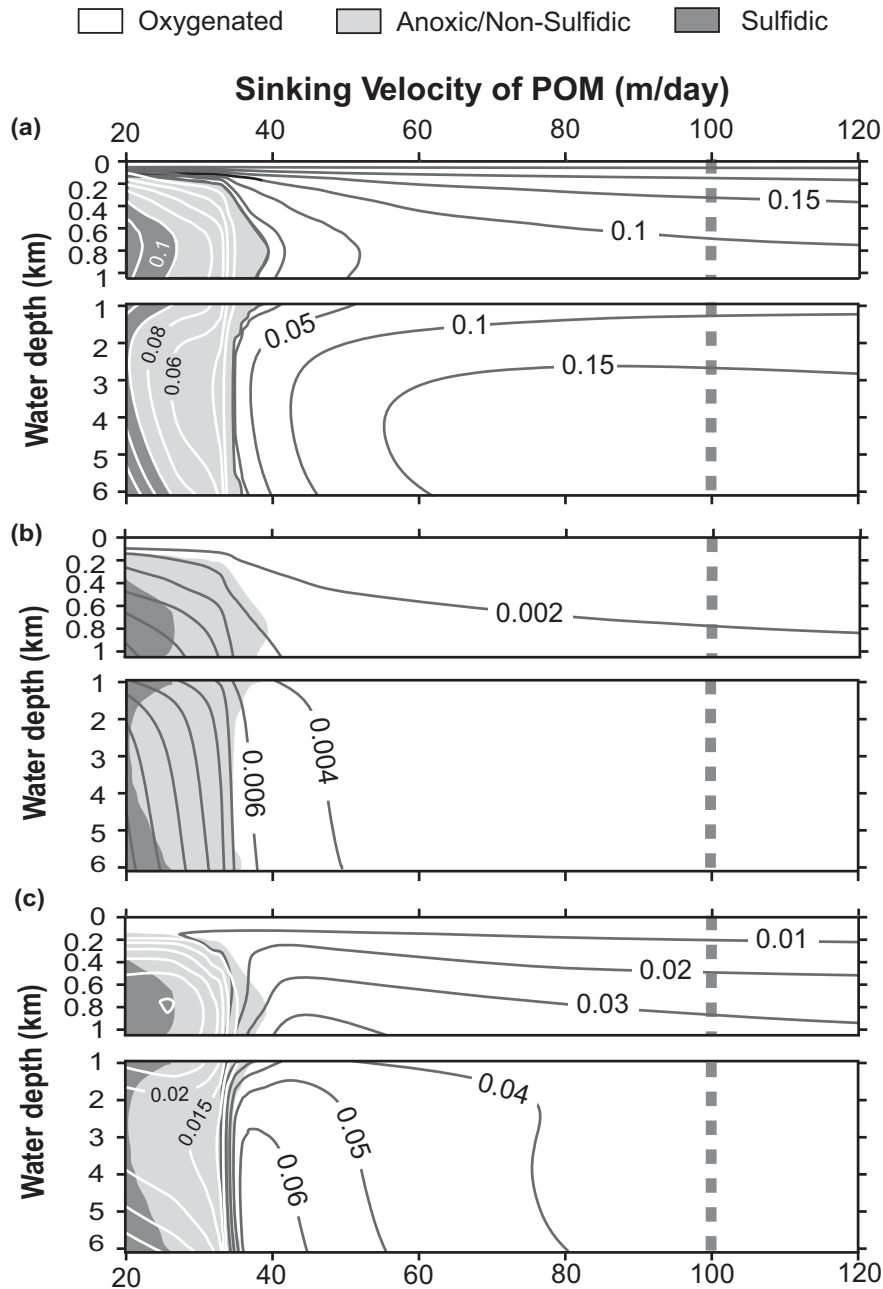
duced water masses generally expand outwards from intermediate depths in the water column, in response to changes in riverine phosphorus flux rates, oceanic circulation rates, and sea surface temperatures. The observed pattern in the present work is, however, entirely attributed to the sinking velocity of POM, the only parameter that we varied in the present simulations. Increased concentrations of phosphorus in response to reductions in the velocity of sinking POM (Figure 2b) most likely reflect enhanced remineralization of POM in the water column due to the extended residence times of organic particles. This in turn increases the phosphorus return flux rate back to the surface mixed layer, which enhances the rate of export production, resulting in a positive feedback loop that favors reducing conditions in the water column. Reduction of the water column naturally enhances consumption of nitrates (denitrification), as nitrates are electron acceptors for respiration; this results in the requirement for a supply of new nitrogen via nitrogen fixation pathways, presumably by cyanobacteria in the surface mixed layer which support photosynthetic production (Figure 2c; Ohkouchi *et al.*, 2006; Kashiyama *et al.*, 2008a, 2008b).

The results imply that reduced sinking velocity of POM was one of the key factors which led to the generation of ocean anoxia and euxinia in the past oceans, along with other conditions such as elevated riverine flux rates of phosphorus as Ozaki *et al.* (2011) and others (Van Cappellen and Ingall, 1994; Meyer and Kump, 2008) have previously suggested. We therefore infer that the presence or absence of mineralized ballast particles would have been a critical factor in the causation and consequences of the anoxia/euxinia.

*Evolutionary patterns of coccolithophores in the Mesozoic Era.*—The rise of coccolithophores (also referred to as “calcareous nannoplankton”) led to a revolution in marine biogeochemical cycles. In particular, the coccolithophores changed the dynamics of pelagic sedimentation by sequestering massive quantities of calcium carbonate in sediments; the productivity of coccolithophores fundamentally altered the marine carbonate system and the carbon cycle of the planet.

The oldest evidence for coccoliths is in the Late Triassic (ca. 220 Ma; Brown *et al.*, 2004; Onoue and Yoshida, 2010); however, they suffered a major mass extinction at this time, leaving only a single known species that was the ancestor to the first major coccolithophore radiation in the late Early Jurassic (Erba, 2006, and references therein). The Middle to Late Jurassic was marked by the appearance and dispersion of the cosmopolitan coccolithophore genus *Watznaueria*, which formed a major successful clade during the Mesozoic (Cobianchi *et al.*, 1992; Mattioli and Erba, 1999).

The Jurassic–Cretaceous boundary represents a major turnover event for coccolithophores; the evolution of new groups, including a major clade of heavily calcified nannocoids, flourished during the Early Cretaceous (Roth, 1987, 1989; Weissert and Erba, 2004); these radiations were pre-



**Figure 2.** Oceanic redox conditions represented by oxygen and hydrogen sulfide profiles, as functions of variations in the sinking velocity of POM. Contours indicate the concentrations of (a) molecular oxygen, (b) inorganic phosphorus, and (c) nitrate. Vertical dotted lines indicate present-day average values of the sinking velocity (100 m/day).

ceded by extinctions (Roth, 1987, 1989). The OAE-1 intervals around the Aptian–Albian boundary were a period of high turnover for coccolithophores; this was not a time of major extinctions but of accelerated origination and diversification following the anoxia/euxinia event (Roth, 1987; Leckie *et al.*, 2002; Erba, 2004, 2006). Similarly, the OAE-

2 interval at the Cenomanian–Turonian boundary was correlated with high turnover rates of coccolithophores, and was again characterized by rapid speciation immediately following anoxia/euxinia (Erba, 2004).

In sharp contrast, the extinction of coccolithophores across the Cretaceous–Paleogene boundary was incomparably in-

tense; 70%–90% of coccolithophore genera became extinct at this time (Brown *et al.*, 2004; Jiang *et al.*, 2010). Furthermore, the recovery of coccolithophore diversity was rather sluggish (Jiang *et al.*, 2010), requiring the entire Paleocene (ca. 10 Myr) to fully reestablish their diversity (Brown *et al.*, 2004). Such a post-event turnover pattern is strikingly different from that observed during the Mesozoic, where diversification started immediately after, during, or preceding the anoxia/euxinia event. This contrast suggests fundamental qualitative differences between Mesozoic turnover events and the Cretaceous–Paleogene mass extinction. In fact, the cause of the Cretaceous–Paleogene mass extinction is not generally linked to anoxia/euxinia (*cf.* Schulte *et al.*, 2010), whereas Mesozoic events are often coincident with anoxia/euxinia.

If the Mesozoic turnover events of coccolithophores are distinct from mass extinction events (in which deterioration is generally supposed, at least during critical intervals), it is likely that Mesozoic ocean anoxia/euxinia did not suppress the production of coccolithophores and other phytoplankton (Erba, 2004), but only affected their patterns of evolution by exposing the groups to different forcing factors, upon which natural selection could act. This idea is concordant with the observation by Kashiyama *et al.* (2010) that chlorophyll *c* derived from fossil porphyrins is rather abundant in the black shales deposited during OAEs; in other words, secondary red algae (including coccolithophores), the only chlorophyll *c* producers, were active components of primary production during OAEs. Thus, although carbonate fossils are absent within the OAE black shales, most likely because of the elevated carbonate compensation depth (CCD), it is plausible to assume that carbonate minerals produced by organisms such as coccoliths and nannoliths, as well as the calcified tissues of dinoflagellates and planktic foraminiferans, were possibly still being produced during times of anoxia/euxinia.

*Evolutionary patterns of planktic Foraminifera in the Mesozoic Era.*—Planktic foraminifera evolved from benthic relatives in the Early Jurassic (Hart *et al.*, 2003). However, the first major radiation leading to a globally significant planktic foraminiferan component did not occur until the Early Cretaceous (near the Aptian–Albian boundary; Hart *et al.*, 2002). The Cenomanian–Turonian boundary (*i.e.*, OAE-2) was marked by a major turnover event of planktic Foraminifera; nevertheless, no clear interval of apparent absence has been identified (Tewari *et al.*, 1996). One planktic foraminiferan genus, *Praeglobotruncana*, was unusually tolerant and appeared unaffected by events at the boundary (Tewari *et al.*, 1996). These observations suggest that planktic foraminifers were present in the euxinic oceans of OAE-2, potentially producing ballasts for POM export.

*Production of calcium carbonate minerals during OAEs.*—As observed above in the case of coccolithophores, patterns of speciation, diversification, turnover, and extinction of successful post-Mesozoic secondary red algae, although based

only on body fossil records, are often coincident with geological events related to global climate changes or catastrophic disturbances (Erba, 2006); this suggests that eukaryotic phytoplankton (but not necessarily pico-phytoplankton, which are not preserved in the fossil record) are highly susceptible to environmental perturbations. However, it is more significant to understand whether the production of these eukaryotic phytoplankton taxa was suppressed during a particular geological event; this is particularly relevant for the analysis of biogeochemical cycles during anoxia/euxinia. According to Klaas and Archer (2002), the presence or absence of biomineralized ballasts and the resulting impact on the descent of organic particles is an issue of particular importance.

It is possible that plankton-produced skeletons of calcium carbonate are affected by the pH and/or alkalinity of the ambient sea water. However, in the case of coccolithophores, sea water chemistry is not necessarily a forcing factor for the deposition of carbonate because the intracellular calcification mechanism (in the Golgi apparatus and/or the vesicles derived from it) is metabolically well controlled (Brown *et al.*, 2004). Furthermore, many lineages of primnesiophytes, which include all coccolith-forming groups (Cuvelier *et al.*, 2010), do not secrete carbonate tissues during the course of their life cycles. Coccolith- and nannolith-forming primnesiophytes (*i.e.*, coccolithophores) are thus thought to be a paraphyletic group, suggesting multiple, independent innovations of the calcification property (de Vargas *et al.*, 2007). Based on these observations, we infer that environmental factors influencing oceanic carbonate and cationic chemistry are not necessarily factors causing (mass) extinctions of coccolithophores.

On the other hand, studies based on both fossils and genomes suggest that the carbonate chemistry of past oceans has in fact affected the evolution of coccolithophores, broadly shaping their diversity patterns (Weissert and Erba, 2004; de Vargas *et al.*, 2007). For example, Erba (2006) pointed out significant correlations between the timing of originations and the prosperity of coccolithophores, and the shift from the Paleozoic–Triassic “aragonite” sea (presumably representing an interval with low Ca<sup>2+</sup>-to-Mg<sup>2+</sup> concentration ratios) to the Jurassic–Paleogene “calcite” sea. Erba inferred that the “aragonite” and “calcite” seas represent intervals with low and high Ca<sup>2+</sup>-to-Mg<sup>2+</sup> concentration ratios, respectively; the origin of the “calcite” sea was considered a result of elevated volcanic activity during the breakup of Pangaea.

Erba (2006) expected that the dominance of smaller and less calcified coccoliths in a geological interval reflected elevated levels of *p*CO<sub>2</sub>, arguing that the calcite skeletons of coccoliths and nannoliths could represent a source of carbon for photosynthesis (presumably after metabolic conversion of carbonate to bicarbonate, or CO<sub>2</sub>-aq); excess carbon dioxide in the environment could result in the loss of the metabolic advantage of coccolith/nannolith formation for their photo-

synthesis, or even inhibit their formation by lowering the pH. However, such evolutionary and physiological events should be coincident with either poorly preserved or unpreserved carbonate fossils due to the expected elevation of the carbonate compensation depth caused by an incidental rise of atmospheric  $p\text{CO}_2$ ; this is particularly relevant to Cretaceous OAEs, which were accompanied by large excursions of  $p\text{CO}_2$  due to widespread volcanism, which introduced large volumes of  $\text{CO}_2$  into the atmosphere (e.g., Kuroda *et al.*, 2007). It is difficult to interpret the connection between carbonate ballast production and the pH values of surface sea water (or atmospheric  $p\text{CO}_2$ ) based on geological evidence alone.

The relationship between photosynthetic efficiency and coccolith formation remains controversial (Erba, 2006; de Vargas *et al.*, 2007). As is the case for many other phytoplankton taxa, the availability of nutrients and trace metals should be as significant as primary productivity rates in the formation of carbonate ballasts (Falkowski *et al.*, 2004b; Erba, 2006). Thus, it is critical for the interpretations herein to understand the impacts of the pH of sea water on coccolith/nannolith formation (e.g., Engel *et al.*, 2005) and on biomineralization by planktic foraminifera (cf. Kuroyanagi *et al.*, 2009); experimental investigations of modern species play an important role in this regard.

In summary, carbonate ballast production during Cretaceous OAEs by coccolithophores and planktic foraminifera was unlikely to have been significantly suppressed, regardless of the magnitudes of environmental changes during these periods. This means that rates of export production, as well as the sinking velocities of exported organic carbon materials, were sufficiently fast to efficiently deliver organic carbon into deeper waters, although gradual dissolution of carbonate ballasts in the course of sinking could have been expected, due to an elevated CCD during OAEs. Thus, ballast production should contribute to a significant contrast between Paleozoic and Mesozoic euxinia, based on the absence or presence, respectively, of candidates for efficient carbonate ballasts.

*Influences of the absence and presence of carbonate ballasts on Paleozoic and Mesozoic euxinia: a synthesis.*—According to the present modeling results, we hypothesize that the presence of carbonate ballasts produced by coccolithophores and planktic foraminifera played a key role in the development of short-lived euxinia associated with Cretaceous OAEs. Regardless of the factors that trigger OAEs, a sudden increase in riverine phosphorus influx is the most likely direct cause of the initiation of euxinia during OAEs (Kashiyama *et al.*, 2008a); this might or might not correspond to the initiation of the deposition of black shale deposits (cf. Kuroda and Ohkouchi, 2007). Temporal suppressions or extinctions of coccolithophores and planktic foraminifera may cause a reduction in the production rate of carbonate ballasts. However, the primary production rate should spontaneously escalate in response to the elevated re-

generation of phosphorus from sediments in reducing conditions (e.g., Van Cappellen and Ingall, 1994), in addition to increased influx rates of riverine phosphorus.

After the initial disturbance to the oceanic environment, carbonate ballast production by coccolithophores and planktic foraminifera should adjust to the new environmental conditions, thereby initiating turnover within their lineages. With elevated carbonate ballast production coupled to elevated levels of primary production, a large flux of rapidly sinking organic matter will deliver high levels of carbon and phosphorus to the bottoms of basins, resulting in the deposition of extremely carbon-enriched (up to 30% C) black shales. The time lags between potential triggering events, the formation of euxinia, and the initiation of black shale deposition, within and between basins, is concordant with the sedimentary record, as reviewed by Kuroda and Ohkouchi (2006). Phosphorus, nitrogen, and sulfur are efficiently remineralized in sediments, leaving organic deposits with unusually high C/N ratios (cf. Ohkouchi *et al.*, 2003).

The very high C/P ratios observed in black shales are due to anoxic bottom water conditions (e.g., Ruttenger, 2003); the large flux of phosphorus sequestered in sediments is represented by the tremendous quantity of organic carbons sequestered in OAE black shales. Regarding the sequestration of phosphorus into sediments, a net return flux of phosphorus to the surface mixed layer would have gradually diminished and returned to normal, ultimately terminating the anoxic and euxinic conditions within several hundred thousand years (Kuroda *et al.*, 2005). Thus, the evolution of planktic organisms forming mineral ballasts is critically important for rapid terminations of OAE euxinia, without the prolonged environmental stresses that eventually cause mass extinction events.

In contrast, the Paleozoic global anoxic/euxinic events were prolonged and typically coincident with mass extinction events (Isozaki, 1997; Rimmer *et al.*, 2004; Cao *et al.*, 2009; Gill *et al.*, 2011). The Late Devonian mass extinction seems to have encompassed a series of multiple extinction events, which appear coincident with the deposition of organic-rich black shales (Algeo and Scheckler, 1998). The entire record of Late Devonian sedimentation represents the formation of organic-rich black shales (Rimmer *et al.*, 2004), implying prolonged global anoxia and/or euxinia. The most significant example of global anoxia/euxinia occurs at the Permian–Triassic boundary (Isozaki, 1997), coinciding with the Late-Permian mass extinction event, the largest mass extinction event in the Phanerozoic. The event itself was coincident with the climax of euxinia (Grice *et al.*, 2005; Cao *et al.*, 2009). Permian–Triassic anoxia was extremely long-lived, in which oxygen-depleted conditions in the deep sea extended up to ca. 12 Myr, whereas the core interval of the anoxia lasted ca. 3 Myr (Kakuwa, 2008). In contrast to the later Mesozoic OAEs, prolonged and gradually terminating anoxia/euxinia are expected characteristics of settings which

lack organisms producing effective mineral ballasts; in these settings, phosphorus was remineralized before reaching the bottom of the basin, where it was deposited and sequestered; thus, there is no mechanism to interrupt the high rate of phosphorus reflux from the subsurface layers to the surface mixed layer. Sequestration of phosphorus in reduced basins is hindered by the absence of sedimentation mechanisms associated with mineralized ballasts and the escalation of organic matter export from the surface to deep waters.

### Conclusions and Further Implications

In the present work, we have not considered triggering factors of anoxia/euxinia. The models of Ozaki *et al.* (2011), and the models developed in the present work, do not in fact require specification of external forcings for the initiation of anoxia/euxinia events. However, the models do require the identification of possible *extrinsic* factors that would increase phosphorus influx into the oceans and/or reduce oceanic circulation. It implies that a common mechanism could have operated at different times and in the context of different anoxia/euxinia, irrespective of their triggers. For example, increased phosphorus influx into the oceans could have been associated with the sediment “surge” due to elevated chemical weathering and continental erosion in the latest Permian to the earliest Triassic (Algeo and Twitchett, 2010). Similarly, increased continental weathering has been also claimed for the Cretaceous OAE intervals (Jenkyns, 2010).

To understand each anoxia/euxinia event, however, we stressed the importance of identification of possible *intrinsic* factors that must be treated in the model. Such factors would modify the rates of primary production of given nutrients (affecting the *f*-ratio), the qualities of exported organic matter affecting redox reaction kinetics (expressed by kinetic constants, as employed in the multi-G method; Ozaki *et al.*, 2011), the Redfield ratio, as well as sinking velocities and their relation to the densities and compositions of ballasting biominerals. Those intrinsic parameters that represent the various mechanisms could have evolved along with the evolution of the organisms, in particular the secondary red algae.

The possibility that post-Late Triassic secondary red algae had significant evolutionary impacts on the quality and quantity of export productivity during anoxia/euxinia can be examined for anoxic intervals of the later Mesozoic, in which the increased flux of labile organic carbons into the deep oceans, in both coastal and pelagic settings, could have led to the evolution of pelagic–benthic coupling (Kitazato and Kotake, 2008). Thus, the increased flux of energy into benthic and nektic communities, as well as the expansion of benthic habitats into pelagic realms, probably supported the Mesozoic marine revolution and escalated during this time (*e.g.*, Vermeij, 1987).

We are still largely ignorant of the evolutionary history of phytoplankton groups, as recent paradigm shifts in our understanding of marine phytoplankton are completely revising the textbook model of photosynthetic production. We cannot discuss all of the potential implications of these observations in the present work, simply because their quantitative significance for biogeochemical cycling, their contributions to the export flux of energy in particular, and their evolutionary histories have been virtually unexplored until now.

The Cenozoic era is the age of diatoms, which began to diversify in the pelagic ocean after the last global euxinic event (OAE-2); diatom diversification continued after the end-Cretaceous mass extinction event, and they finally took the place of coccolithophores in the Neogene. The impact of increased opal production by diatoms on biogeochemical cycles still needs to be examined in future studies. Coccolithophores are, however, still a major group in terms of contributing to pelagic primary production in the modern ocean, accounting for approximately 80% of the ballast materials involved in export production (Hofmann and Schellnhuber, 2009).

Our understanding of the Mesozoic biogeochemical revolution that underlies the Mesozoic marine revolution requires continued research. Obviously, other major OAEs in earlier Mesozoic time need to be examined with our model. In particular, the early Toarcian event (*e.g.*, Jenkyns, 2010, and references therein) is of particular interest since it lies between the Cretaceous and Paleozoic anoxia/euxinia and possibly reflects the rise of various secondary red algae as well as of planktic foraminiferans.

Advancements in this area would also contribute to an understanding of evolutionary and biogeochemical changes in the Cenozoic—how do physical environmental changes, the geochemistry of the oceans, and the evolutionary dynamics of marine organisms interact and contribute to the situation observed on Earth today? These questions can be extended even further: why are global anoxia/euxinia absent in the Cenozoic? How do modern diatom-dominated (or, more precisely, picoplankton-dominated) marine production systems respond to environmental disturbances (*e.g.*, sudden increases in phosphorus influx)? What are the consequences of such disturbances? And how do human activities, represented by high rates and volumes of CO<sub>2</sub> emission into the atmosphere, affect biogeochemical cycles? Recent work by Stramma *et al.* (2008) and Hofmann and Schellnhuber (2009) predicts an expansion of oxygen minimum zones, caused by reduced export productivity associated with an inhibition of carbonate ballast production due to oceanic acidification, a consequence of elevated levels of atmospheric pCO<sub>2</sub>. Will human activities initiate another anoxia/euxinia? If so, what will be the consequences?



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