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MINI-REVIEW

# Eutrophication, microbial-sulfate reduction and mass extinctions

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**ABSTRACT**

In post-Cambrian time, life on Earth experienced 5 major extinction events, likely instigated by adverse environmental conditions. Biodiversity loss among marine taxa, for at least 3 of these mass extinction events (Late Devonian, end-Permian and end-Triassic), has been connected with widespread oxygen-depleted and sulfide-bearing marine water. Furthermore, geochemical and sedimentary evidence suggest that these events correlate with rather abrupt climate warming and possibly increased terrestrial weathering. This suggests that biodiversity loss may be triggered by mechanisms intrinsic to the Earth system, notably, the biogeochemical sulfur and carbon cycle. This climate warming feedback produces large-scale eutrophication on the continental shelf, which, in turn, expands oxygen minimum zones by increased respiration, which can turn to a sulfidic state by increased microbial-sulfate reduction due to increased availability of organic matter. A plankton community turnover from a high-diversity eukaryote to high-biomass bacterial dominated food web is the catalyst proposed in this anoxia-extinction scenario and stands in stark contrast to the postulated productivity collapse suggested for the end-Cretaceous mass extinction. This cascade of events is relevant for the future ocean under predicted greenhouse driven climate change. The exacerbation of anoxic "dead" zones is already progressing in modern oceanic environments, and this is likely to increase due to climate induced continental weathering and resulting eutrophication of the oceans.

Macro-evolutionary analysis of the marine fossil record led to the insight that the evolution of life on Earth, for the last ±500-million-year interval, is marked by fluctuations in global marine faunal diversity.[1,2] Short-term time intervals with high extinction rates have been dubbed mass extinctions, of which 5—the so-called "Big Five"—stand out for their magnitude: the end-Ordovician, the Late Devonian, the end-Permian, the end-Triassic and the end-Cretaceous.[2-4] Adverse environmental conditions are generally assumed to be the cause of these biodiversity crises, with both extraterrestrial and terrestrial sources as proposed triggers.[5-9] The most famous mass extinction is undoubtedly the biotic crisis at the end of the Cretaceous, which marks the demise of the non-avian dinosaurs, and has been connected to a bolide impact,[6] although challenged by other working groups.[7] The resulting global impact winter, caused by the injection of dust and aerosol into the stratosphere reducing incoming solar radiation, has often been associated with a marine productivity collapse, in turn leading to the demise of organisms in higher trophic levels.[6,10] A reduced vertical water column carbon isotope gradient is recorded by carbonate fossils (or "Strangelove" ocean) and provides evidence in support of such primary productivity collapse.[11] Although some authors suggest that selective extinction among calcifying marine organisms, mediated by a transient ocean acidification event, is a more likely explanation for both the observed marine extinction and the distinct carbon isotope signal.[12]

In contrast, the other mass extinctions, among which the largest of them all—the end-Permian mass extinction—have, more often, been tied to Earth-bound processes. Although extraterrestrial causes have not been ruled out for these events, conclusive evidence, equal to the end-Cretaceous impact indices, is lacking.[13,14] Examples of proposed kill mechanisms inherent to the Earth system are the consequences of glaciations, sea level changes, global warming, large igneous provinces (LIPs) and ocean chemistry changes, possibly coupled with synergistic effects resulting from the interactions of the

listed mechanisms. One common ground for at least 3 of the "Big Five" extinctions (Late Devonian, end-Permian and end-Triassic) is the compelling evidence for synchronous (or in close temporal relation) widespread occurrence of oxygen deficient (anoxic) and hydrogen sulfide-enriched (euxinic) marine regions.[15-21] In addition, a possible fourth extinction event can be added to this list, based on tentative evidence for sulfidic and anoxic conditions during the end-Ordovician mass extinction.[22] In this brief review we want to extend on our conclusions regarding our recent publication in Proceedings of the National Academy of Sciences (PNAS) of the United States of America,[23] in which we postulate a prominent role for marine primary productivity, a side effect of greenhouse warming, creating harmful marine conditions during the end-Permian mass extinction. In addition, we compare the ocean chemical state and extinction dynamics of the latest Permian with conditions during some of the other Phanerozoic major extinction events as well as implications for the future ocean if further affected by warming.

## Metabolism and marine anoxia

A prominent mechanism inferred to induce the widespread generation of anoxic and euxinic water masses is water column stagnation[24] and reduced $O_2$ solubility with increasing seawater temperature.[19] Postulated events of large-scale water column stagnation have been regarded as an upscaled analog of the modern Black Sea in which the water column is stratified in a large and deep basin. This stratification was possibly initiated ~7500 years ago by an intrusion of saline water through the Bosporus Strait.[25,26] Besides physical processes, metabolic activity above and below the sediment-water interface plays a prominent role in determining seawater $O_2$ and $H_2S$ levels, as marine dissolved oxygen is efficiently depleted by remineralization of organic matter due to oxygen consumption during aerobic respiration.[27] Similarly $H_2S$ is the by-product of microbial-sulfate reduction (MSR), which uses sulfate as an electron acceptor (instead of oxygen) in conjunction with their metabolism. The control of these metabolic pathways on the ambient chemical environment can be viewed and mapped in modern open ocean environments, where oxygen minimum zones (OMZs) occur at intermediate water depths, e.g., at the coastal upwelling system zones of Namibia and Peru. OMZs develop when $O_2$ consumption by respiration (forced by organic matter availability) exceeds $O_2$ addition formed during photosynthesis, water column mixing and diffusion[25,28] and are often characterized with an episodic (often seasonal) nature of oxygen depletion (or hypoxia: 0.5–2 ml of $O_2$/liter).[29]

This type of marine anoxia is geographically more widespread than the "landlocked and stratified basin-type anoxia," as found in the Black Sea, cf. ref. 29. Moreover, microbial sulfate reduction may take place even when more favorable electron acceptors are available and therefore, this metabolic pathway is not limited to anoxic sediments but can occur in oxygen-rich sediments[30,31] or nitrate-rich seawater, such as OMZs.[32] These environments can turn sulfidic (for prolonged time intervals or as recurrent episodes) by increased MSR activity potentially under increased organic carbon loading of the sediment and water column as observed in the OMZ of Peru.[33] It does not solely depend on the local sedimentary environment as reported for the OMZ of Namibia, where it was invoked that perhaps methane eruptions release porewater $H_2S$, creating a local water column with an increased hydrogen sulfide pool.[34] In addition, it is suggested that organic carbon and the accompanying biochemical reactions of (an)aerobic respiration act as key drivers for the biogeochemical carbon and sulfur cycles and, as such, as Earth's thermostat.[25,35-37] Notably, eutrophication of the marine shelf is an expected climate feedback mechanism (acting on a sub-million year timescale), as elevated temperatures induce continental weathering and successive transport of excess nutrients to the ocean (Figure 1). This productivity feedback, which amplifies organic carbon production and subsequent burial, has been proposed to dampen the effect of $CO_2$ induced climate warming by sequestering excessive atmospheric carbon in the form of sedimentary organic matter.[38,39] This suggests that productivity-driven anoxia and euxinia are inevitable lethal feedbacks of greenhouse warming which can potentially act adversely on marine organisms through suffocation and sulfidic toxicity.[16,40] These killing agents can potentially be accompanied by other marine life impacting effects related to a sudden increase of atmospheric $CO_2$; notably ocean acidification and the effects of thermal stress on the organism.[41]

Earth Scientists have a suite of geochemical tools at their disposal to infer ancient ocean water column $O_2$ and $H_2S$ concentrations, including redox sensitive trace elements[28,42] and organic biomarkers. An example of the latter includes carotenoids isorenieratene and related diagenetic products (aryl isoprenoids) which are organic compounds produced by green sulfur bacteria (microbes which employ $H_2S$ for photosynthesis).[17,20-22] Application of these ocean-chemistry proxies enabled robust inferences on the spatial and temporal extent of ancient anoxic and sulfidic intervals (see ref. 43 for possible complications with certain redox sensitive trace elements). The multiple occurrences of sediment enriched in molybdenum and vanadium attests to the global significance of oxygen-depleted and sulfide-bearing water,
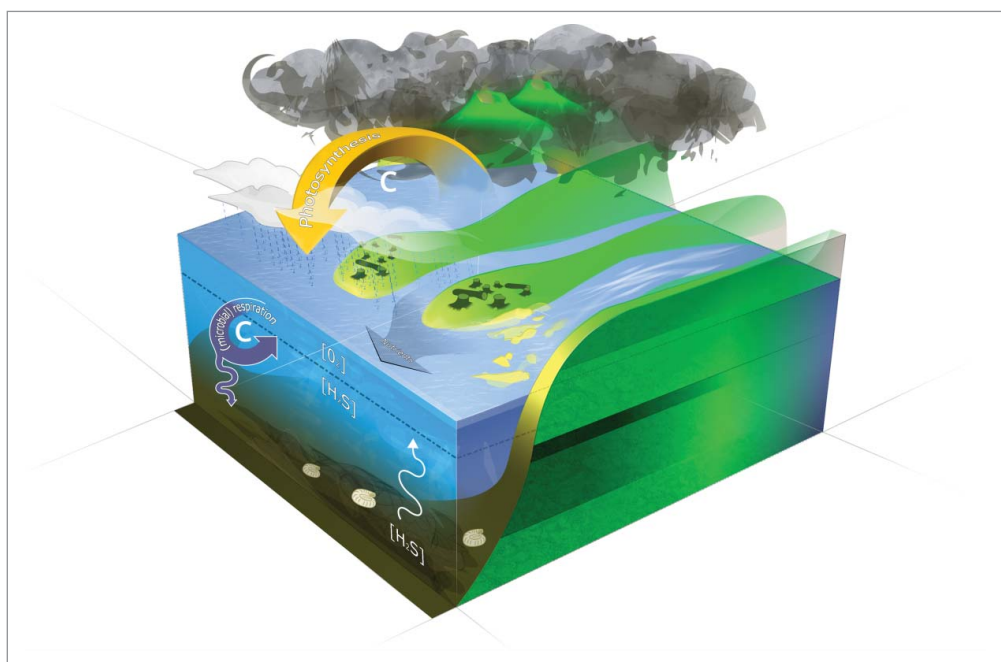
**Figure 1.** A conceptual model for the productivity feedback as envisioned for the latest Permian. In the sketched scenario $CO_2$-outgassing associated with emplacement of the Siberian Trap basalt is held responsible for climate warming and consequential increased continental weathering by an amplified hydrological cycle but also massive destruction of vegetation. Increased river discharge (here depicted as a braided river system) supplies the ocean with excess nutrients. Eutrophication of the ocean starts a vigorous carbon loop driven by microbial respiration within the water column where, among other metabolic pathways, microbial-sulfate reduction plays a pivotal role. Artwork by Mark Schobben.

during the Late Devonian,[17,44] end-Permian[45-47] and end-Triassic.[21,48] On the contrary, some deposits in the immediate aftermath of the EPME record a stark depletion of redox sensitive trace elements; the authors of this study relate this to a global depletion of these chemical components due to widespread euxinia.[49] Also, local $H_2S$ enrichment of the photic zone (the upper sunlit 100 meter of the water column) seems to have occurred during the Late Devonian,[17] end-Permian[20] and in the immediate aftermath of the end-Triassic mass extinction,[21] as indicated by the presence of green sulfur bacteria.

In some instances geochemical investigations resulted in the reconstruction of water column vertical redox profiles (at least for the latest Permian), leading to recognition that these anoxic intervals are (possibly) instigated by intensification of OMZs, likely, due to proliferation of marine carbon production.[45,49-52] This observation can be further supported by stratigraphic profiles of sedimentary phosphorus and barium, which arguably trace ancient nutrient content and organic carbon transport though the water column, respectively.[53,54] Finally, circumstantial evidence[55,56] and quantitative indices[57-59] suggest that these critical time intervals are connected with climate warming and enhanced continental weathering,[60,61] thereby acknowledging the possible existence

of the previously outlined productivity feedback (Figure 1). Controversy exists around the cause of greenhouse warming during these time intervals. However, the end-Permian and end-Triassic are time-equivalent with LIPs, which are associated with massive outgassing of carbon dioxide, serving as a possible driving force behind climate change.[9,62-64] Added together, these indices suggest that primary productivity might have induced a critical control on some of the anoxic and euxinic events that mark Earth history.

## Sedimentary sulfate

The aforementioned geochemical analyses are in many cases restricted to recording a local anoxic signal and do *not* yield insight in global secular changes of ocean redox chemistry (however see refs. 49, 65 for studies that elude to the global extent of anoxia). Fortunately the cell internal process associated with MSR metabolism—the conduit of marine hydrogen-sulfide—is known to induce a kinetic isotope fractionation on both sulfur and oxygen of sulfate.[66,67] In addition, sulfate is a conservative anion due to a long oceanic mixing/residence time and therefore, a global change in MSR (due to global increase or decrease in the extent of anoxic/euxinic waters or organic matter availability) produces a signal recorded in the

isotope composition of the global marine dissolved sulfate pool, which, in turn, can be recorded in the marine sedimentary rock record.[35,36,68-71]

Recently, we inferred that a stark increase of the areal extent of marine euxinic regions occurred coevally with the end-Permian mass extinction, based on a temporal record of sulfate-sulfur and sulfate-oxygen isotopes in limestone spanning the P-Tr boundary sections in Iran.[23] Mainly the oxygen isotope composition of sulfate is directly tied to MSR, as the cell internal biochemical reaction during metabolism results in the loss of the sulfate-oxygen and serves as a net-sink for the light oxygen isotope (see also ref. 72). On the other hand, the sulfur compound of sulfate leaves the Earth surface system through burial as sedimentary sulfides. Globally pervasive euxinia, but limited sedimentary sulfide burial (due to a reactive iron limitation), can thereby explain a positive sulfate-oxygen isotope trend and a concomitant negative trend in sulfate-sulfur isotopes. By coupling these results to a box-model we could show that an increased supply of organic carbon—possibly stimulated by flourishing plankton communities—could drive this scenario of intense MSR activity. The study sketches a greenhouse world in which marine life blooms but at the expense of many of the common Permian "higher" taxa (e.g., brachiopods and ammonites). The scenario contradicts extinction models of reduced primary productivity, e.g. ref. 73. More stringently this notion suggests that MSR can be a catalyst involved in the deterioration of the marine (chemical) environment. Critically one should note that *not* all instances of widespread anoxia and euxinia in Earth history are marked by increased extinction risk (among higher taxa), most notably the Mesozoic Ocean Anoxic Events (OAEs) are only associated with none- or somewhat-amplified extinction rates among higher taxa. However, this is also true for all previous proposed triggers, e.g., LIPs and asteroid impacts, which occur more frequently in the geological record than large extinction events.[7,62,74] A combination of factors, e.g., the locus of environmental stress and certain thresholds in ecosystem stability, should all be accounted for when trying to explain these critical events in the evolution of life. An end-Permian example of the former concept would be that marine anoxia impinged the shallow water coastal systems which happened to be the locus of Paleozoic marine biodiversity.[19] However, the latter concept can be formulated as the idea of a planetary state shift,[75,76] which suggests that the sum of destabilising disturbances (e.g., ocean anoxia, global warming and excess nutrients) can push the Earth system across a boundary (or "tipping point") causing a cascade accumulating in a mass extinction, cf. ref. 10. In addition, other synergistic effects of increased atmospheric $CO_2$, such as ocean acidification and the effects of thermal stress could have been equally important for the demise of marine taxa and have been proposed as drivers behind some of the extinction events, based on quantitative analysis of the marine fossil record (e.g. selective loss among higher marine taxa)[77-79] and geochemical proxy data.[80-82]

The previously sketched scenario for productivity-driven anoxia at the EPME might be a more common causal mechanism behind mass extinctions and challenges the concept of reduced primary productivity leading into these events, e.g., ref. 73 and corroborates with modeling studies that invoked increased productivity as a driver of marine anoxia, e.g., refs. 27 and 83. If the idea of eutrophication as an important driver for extinctions withstands the test of future studies, it would make the end-Cretaceous biodiversity crisis and related primary productivity crash, rather, an oddity among the other extinction events.

## Dynamic of mass extinctions

A productivity increase during these biodiversity crises might be linked to changes in the plankton community, as inferred for the Late Devonian,[17] end-Permian[84,85] and end-Triassic.[21] A much cited change in plankton composition is the domination of bacterial heterotrophs (e.g., sulfate reducing microbes) and autotrophs (e.g. cyanobacteria and green sulfur bacteria) over eukaryotes.[84] A dominance of hopane over sterane abundances in Late Devonian and Permian-Triassic sedimentary rocks, the diagenetic products of organic compounds produced by bacteria (hopanoids) and eukaryotes (sterols), respectively, lend robust support to this suggestion of a plankton turnover.[17,84] More specifically, 2-methylhopanes have been assigned a cyanobacterial origin,[86] and stratigraphic distribution patterns can, therefore, be apportioned with great confidence to an increased importance of cyanobacteria during the latest Permian.[87]

In terms of global marine biomass, rather than marine species richness, one may argue about the severeness of these mass extinctions where it seems that life flourishes. Interestingly, the modern marine microbial food web has been reported to respond to warming seawater by an amplification of bacterial production and respiration.[88] So we postulate the idea that the end-Permian mass extinction (linked with greenhouse warming) is a change between 2 equilibrium states, i.e. from a high-diversity eukaryotic to a high-biomass microbe dominated ocean. This also corroborates with a study by Bambach and co-authors[4], in which they state that the "Big Five" mass extinctions should rather be referred to as; "mass depletions of marine diversity." This interpretation does *not* make these events less significant as these processes

shaped the course of evolution by physiological selectivity, annihilating antecedent ecosystems and thereby paved the way for modern ecosystems.[2,4] The vast amount of organic carbon produced by marine heterotrophic microbes, among which sulfate reducing microbes belong, make them an important driver of the global carbon cycle.[88] As mentioned in our PNAS paper,[23] increased amounts of easily degradable bacterial organic matter could shunt carbon in a microbial food web with a high turnover rate and result in a decreased export of organic carbon to the seabed. Hypothetically this could lead to a more permanent state shift of the Earth system,[75,76] as it would inhibit the productivity feedback (Figure 1) argued to dampen greenhouse warming (see above). This would help explain the persisting heat during a long interval in the Early Triassic world,[89,90] but, on the other hand, permits reoccurring widespread marine anoxia and euxinia.[91] The impetus for this change between equilibrium states is being provided by climate change (warming) and the successive productivity feedback as well as plankton community turnover.

## Lessons for the future ocean

The acknowledgment of human-driven global change as a new geological epoch—the Anthropocene[75,76,92]—and a possible impending sixth mass extinction,[93] justifies a reflection on societal relevance of studying mass extinction events and ancient ocean chemistry. Ancient global eutrophication events could be important lessons for the future ocean, especially as the causes are interchangeable between the past extinction events and current biodiversity loss.[92,94] According to the current prognosis, future projected climate change will be forced by human-induced carbon release, as stated in the fifth report of the Inter-governmental Panel on Climate Change.[95] Also, human action has already adversely affected coastal systems as documented by Diaz and Rosenberg[29] who showed a spread of anoxic zone in shelf seas, such as the Baltic Sea, already underway since the early 20th century. The causes of this spread of so-called ocean anoxic "dead" zones have been related to the use of fertilizers in agriculture combined with insufficient care to prevent soil erosion on croplands. In addition, these authors noted that climate change (warming) will further exacerbate eutrophication by increasing the riverine influx of nutrients by continental weathering and increased river discharge. A certain amount of fertilization might be beneficial for fish stocks,[96] but conversely an unchecked and unbalanced addition can have grave and possibly not easily reversible consequences for marine ecosystems, e.g., mass mortality of benthic communities and

increased microbial growth. In light of the former notions, it is troublesome that some "climate engineers" propose to stimulate the natural weathering of silicate rock. Weathering of silicate rock is known to sequester atmospheric $CO_2$ by the chemical reaction associated with the breakdown of silicates. Stimulating this process of chemical weathering, i.e., by exposing a larger surface area of silicates, is proposed by climate engineers as a tool to mitigate anthropogenic induced greenhouse warming, e.g. ref. [97], but will likely also increase the flux of nutrients to marine coastal systems.

The ancient examples (e.g., end-Permian mass extinction) provide evidence of how intense greenhouse warming creates lethal feedback mechanisms (e.g. increased weathering and subsequent ocean fertilization) that then will lead to a reduction in biodiversity, alters ecosystems and influences evolutionary processes. These findings urge to limit the input of nutrients into the ocean as the widespread occurrence of marine anoxic "dead" zones could become a more permanent feature of the future Earth.

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