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12.491 Biogeochemistry of Sulfiur
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Identifying the Existence and Extent of the Sulfidic Ocean at the PTB

The mass extinction that occurred at the Permian-Triassic boundary was a profoundly significant event in earth's history. The changes that were wrought upon the biota changed the world's ecosystems completely and permanently. However, the precise mechanism by which the extinction took place is still debated. Many lines of evidence suggest that this event was the result of an anoxic ocean, specifically one that had high concentrations of hydrogen sulfide in the water column, known as euxinia. But the identification of the presence of a sulfidic water column can also be supported by models that explain how such an ocean would come to be, and how the release of the toxic hydrogen sulfide gas could occur, suggesting a greater potential to act as the critical factor in the mass extinction. Below I discuss evidence for the presence of a sulfidic ocean, as well as examine the models that have been proposed for its existence. I will briefly analyze these different methods and models to examine where they support each other. The presence of a euxinic ocean at the Permian-Triassic boundary has the potential to explain many of the observations in the mass extinction, so it is important to critically assess and address the information that is put forth.

Although they were not the first group to use the size and size distribution of framboidal pyrites as a proxy for the redox state of bottom-water and sediments, Neilsen and Shen (2004) were the first to apply this technique to the Permian-Triassic boundary and use this as another method to support evidence for oceanic anoxia. Since pyrite framboids form close to the anoxic/oxic interface, the location of the chemocline determines the size preserved in sediments, and modern environments are used to understand the different methods of formation in palaeoenvironments. In oxic environments, pyrites are formed in the sediments directly below the chemocline. These pyrites have a lower growth rate and a longer growth time, which allows for the formation of larger framboids. This contrasts euxinic environments, where the chemocline is higher, in the water column. When pyrites are formed just below the chemocline in these environments, they are not able to grow to significant sizes before they quickly sink and are no longer in conditions favorable to their growth. Although many previous studies successfully used only the framboid size as a proxy for redox state of the water column, Neilsen and Shen found that with bioturbation of sediments under oxic water columns disturbing the chemocline and pyrite microenvironments, there was also a much larger range of sizes in the framboids representing oxic water columns than those from euxinic. When looking at the range of framboids from the East Greenland basin, they found evidence of sulfidic conditions.

Fig 1. A representation of the size and size distribution of pyrite framboids from the Ravnfjeld formation, Eastern Greenland. (Nielsen and Shen 2004)

A different method that has been used as a proxy for the presence of euxinic water columns, and the chemocline upward excursions at the Permian-Triassic boundary. Riccardi et al. (2006), looking at $\delta^{34}S$ isotopes in carbonate associated sulfate found that the values reach a maximum right before the extinction horizon, and then fall precipitously afterwards that would require additions of low $\delta^{34}S$ in either basinal waters or diagenetic pore fluids. This they interpreted as being a result of chemocline upward
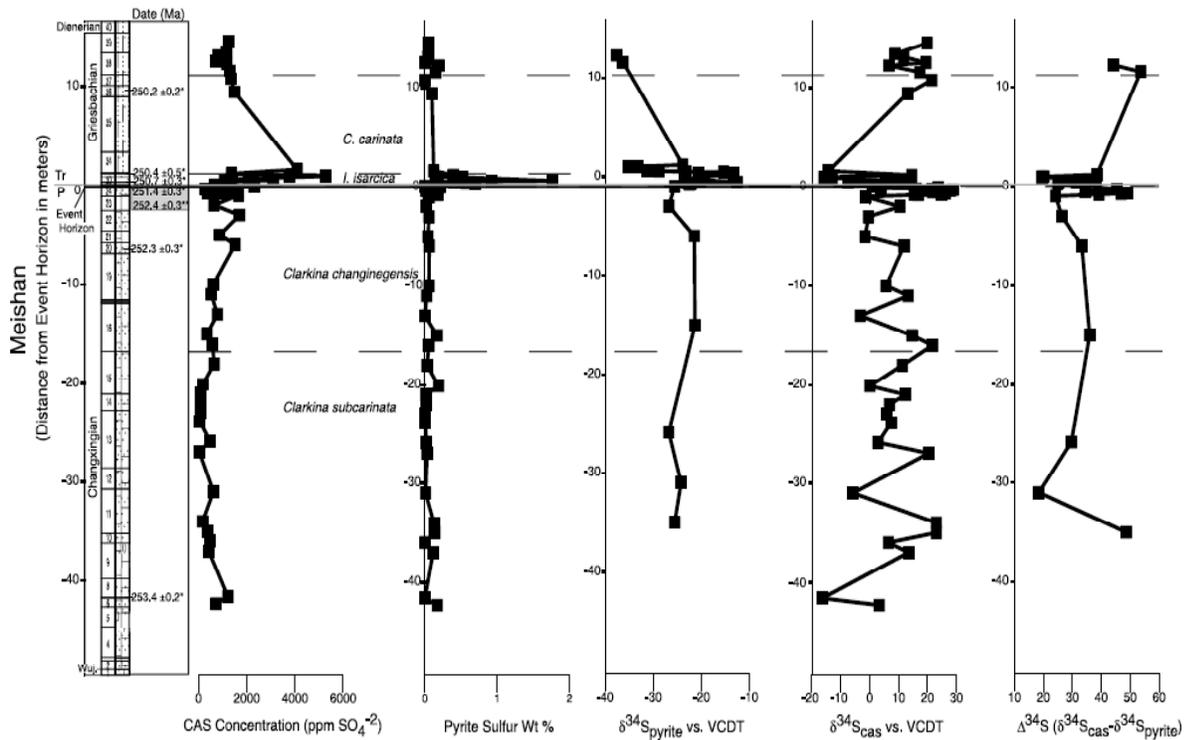
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Fig 2. Meishan records of CAS concentration, Pyrite sulfur, $\delta^{34}S$ pyrite, $\delta^{34}S$ CAS and $\Delta^{34}S$. Well shown is the peak in $\delta^{34}S$ of CAS at the extinction horizon. (Riccardi et al. 2006)

excursions in the oceans at this time period. When the chemocline was high in the water, it favored the growth of phototrophic sulfur bacteria, which produced elemental sulfur from a distinctively isotopically light bacterial source. At the end of the chemocline upward excursion events, the elemental sulfur produced would be oxidized, creating sulfate from the sulfur and low pH pore waters, which would dissolve part of the carbonate in the sediments and allow for the incorporation of the $\delta^{34}S$ depleted sulfate as

CAS. Therefore they interpret the fluctuations in the δ^{34}S of CAS during the Permian-Triassic boundary to be indicative perturbations of sulfur cycle dynamics.

Looking only at the lithology and mineralogy of deep-sea sediments, Isozaki found the first evidence from the greater Panthalassic for euxinic waters at the Permian-Triassic boundary (Isozaki 1995; Isozaki 1997). In two papers, Isozaki examines sediments deposited in mid-ocean deep waters that had been accreted onto the continental margin of China during the Jurassic. The sediments from the early- or mid-Permian as well as those from the late Triassic are cherts composed mainly of radiolarian tests, where the primary oxidized form of iron is hematite; all of these features are considered evidence for the presence of oxic conditions throughout these time periods. However during the late Permian and the early- to mid-Triassic, in the sediments directly adjacent to the distinctive unit spanning the PTB, the cherts are grey to black in color and contain framboidal pyrite grains. In what is termed the PTBU, or the Permian-Triassic boundary unit, are claystones, stratigraphically divided into a lower siliceous claystone, a jet-black carbonaceous claystone and an upper siliceous claystone that contains interbeddings of the middle section. Taken as a whole, these features suggest that this unit was deposited in an anoxic environment. Interestingly, the lithostratigraphy shows that the introduction and retreat of these features were similar, indicating that these conditions, though long-term and likely global were ultimately reversible.

Figure 3 removed due to copyright restrictions.
Citation: Isozaki, Y. (1997). Permo-Triassic Boundary Superanoxia and Stratified Superocean: Records from Lost Deep Sea. Science 276(5310): 235-238.

Fig 3. Stratigraphic column of the Permian-Triassic boundary unit found in Japan. On the left are the lithologies of the various sections and on the right are the interpretations. (Isozaki 1997)

The last major method for identifying euxinic water columns at the Permian-Triassic involves the study of biomarker data. The green sulfur bacteria, or Chlorobiaceae, are anoxygenic phototrophs that, by using hydrogen sulfide as an electron donor for photosynthesis, live obligately in conditions of photic zone euxinia. There are two different types of biomarkers that are used for identification of these organisms in the rock record – maleimides, degradation products of bacteriochlorophyll, and a range of degradation products of aromatic carotenoids. Both of these compounds are part of the photosystems in these organisms, which live at low-light environments and necessarily produce significant quantities of these compounds as a matter of course.
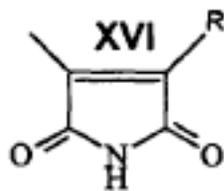

Fig 4. General maleimide.
Me Et: R =Et
Me i-Bu: R=i-Bu
Me n-Pr: R=n-Pr
(Grice et al. 1996)

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Although the exact method of formation is not known, maleimides are pyrroles formed from degradation of photosynthetic tetrapyrrole pigments. In Grice et al. (1996) two groups of maleimides were considered. The first, Me Et maleimide was found in large abundances around the PTB, and is likely derived from the chlorophyll of phytoplankton origin. The second group, Me n-Pr and Me i-Bu maleimides, are thought to be derived from the bacteriochlorophyll of Chlorobiaceae on structural grounds. Further confirmation of the different origins of these similar compounds comes from their $\delta^{13}C$ ratios. The compounds from Chlorobiaceae were found to be enriched by 10-11‰; a feature to be expected as a result of the distinctively heavy $\delta^{13}C$ ratio imparted on their compounds by the reverse TCA cycle used for carbon fixation. In a later paper by Grice et al. (1997), these compounds were also measured in a core from the Kupferschiefer basin. The elevated levels of the maleimides derived from Chlorobiaceae relative to those from phytoplankton in the core indicates that when these sediments were deposited, there were pervasive conditions of photic zone euxinia.

Figure 5 removed due to copyright restrictions.
Citation: Grice, K., et al. (2005). Photic Zone Euxinia During the Permian-Triassic Superanoxic Event. Science 307(5710): 706-709.

Fig 5. Aryl isoprenoid and isorenieratene concentrations from the Perth Basin (left) and Meishan (right) across the Permian-Triassic boundary. (Grice et al. 2005)

Samples from Meishan, China and the Perth Basin in Australia were examined for other biomarker evidence for Chlorobiaceae, specifically derivatives from the distinctive aromatic carotenoids produced by these organisms (Grice et al. 2005). Isorenieratene and chlorobactane are reduced compounds produced from diagenesis of isorenieratene and chlorbactene, aromatic compounds part of the photosynthetic machinery of Chlorbiaeceae. Also produced during diagenesis were a suite of aryl isoprenoids, compounds that have a single aromatic ring with a distinctive substitution pattern as well as an isoprenoid chain of varying lengths. Both isorenieratene and aryl isoprenoids were identified in these sections, and their relative abundances were found to be elevated in correlation to the boundary and extinction event.

With this plethora of evidence supporting the existence of a euxinic ocean at the Permian-Triassic boundary, it is important to model the environment that would allow for the formation of this condition, as well as establish methods that would allow for a euxinic ocean to release hydrogen sulfide causing for the toxicity. A model was established by Hotinski et al. (2001) to understand how such a large body of water could become anoxic and euxinic. They used an established global circulation model modified to include basic ocean biochemistry with the goal of understanding how latitudinal temperature gradients may have contributed to the establishment of anoxia. Figure 6 shows their model results. They found that deep-ocean anoxia is an expected result from

Fig 6. Two-dimensional representation of three-dimensional results from high and low pole-to-equator temperature gradients in the late Permian ocean. The high gradient case is analogous to modern-day temperature gradient and shows oxic conditions throughout. The low temperature gradient is similar to paleoclimatic conditions at the PTB and shows anoxia – represented by negative oxygen equivalents in the deep to mid ocean, with only a small oxic level in the mixed layer at the surface. After Hotinski et al. 2001.
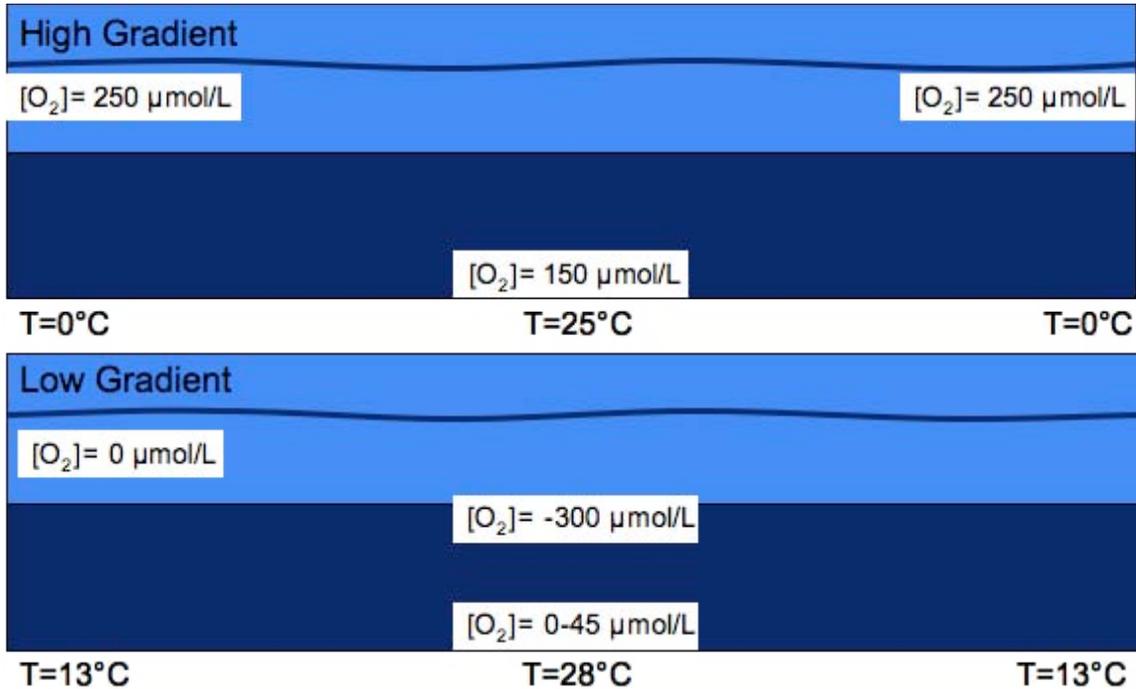
reduced thermohaline circulation during conditions of reduced pole-to-equator temperature gradients, but that a more significant factor in profound anoxia was the reduced oxygen solubility in the deep-water forming regions.

      Another modeling study performed by Kump et al. (2005) looked at the conditions required to produce and maintain a chemocline in shallow water, as well as how to create chemocline upward excursions that would allow for the release of hydrogen sulfide into the atmosphere. To create a stable chemocline, there must be a balance between the oxygen flux into the water column F_O and the hydrogen sulfide flux upward from the deep water, F_{H2S}. These can be written as a combination of factors:

$$F_{O2} = \rho_{oce} * k * K_H * (P_{O2,atm} - P_{O2,oce}) \qquad \text{(I)}$$
$$F_{H2S} = \rho_{oce} * \mu * [H_2S]_{deep} \qquad \text{(II)}$$

To maintain a stable chemocline, equations I and II must be equal which creates a critical value of:

$$([H_2S]_{deep}/P_{O2,atm})_{crit} = 0.1 \text{ mol/kg*bar}$$

When this is calculated for $P_{O2,atm}$ of 0.2 and an global average upwelling rate of 4m/yr, a deep-water sulfide concentration is required to be 20 mmol/kg H_2S – very high. In upwelling zones though, where the rate is higher, only 1 mmol/kg H_2S is required to have

chemocline upward excursions and releasing hydrogen sulfide to the atmosphere. At steady state, however, the release of hydrogen sulfide is dependent on the upwelling rate, not the piston velocity. In this case, to model the release quantities of hydrogen sulfide to the atmosphere with a deep sea hydrogen sulfide concentration of 3 mmol/kg H_2S and an upwelling condition in only 0.1% of oceanic surface waters, the flux of hydrogen sulfide to the atmosphere can be as high as 4000 Tg S/yr – a value 2000 times the modern flux from volcanoes.

The presence of significant physical data indicating that a euxinic ocean, likely extending upwards to the photic zone, existed at the Permian-Triassic boundary is substantial. All of the proxies show not only the presence of an euxinic ocean at the PTB, but one that existed for a significant period of time and reached a climax at the same point as the peak in extinction. Models, including the two examined here, support these palaeoenvironmental conditions. The presence of an ocean with profound anoxia indicated by the first model is supported by all of the data showing euxinia, but seems to be most supported by the lithologic and mineralogical evidence found in the deep-water sections from the open ocean examined by Isozaki. The indication of the second model – that upwelling of a euxinic ocean could result in significant chemocline upwards excursions – seems to correspond particularly well with the $\delta^{34}S$ isotope ratios of carbonate associated sulfates, but also with the evidence of Chlorobiaceae in upwelling environments. Both the evidence and the models indicate that the euxinic ocean at the Permian-Triassic boundary was pervasive and profound. The real question that remains is how it contributed to the largest extinction event in the Phanerozoic.

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