

Positive Reinforcement, H₂S, and the Permo-Triassic Extinction: Comment and Reply

COMMENT doi: 10.1130/G22641.1

Robert A. Berner

Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06520-8109, USA

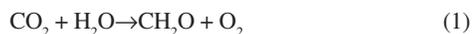
Peter D. Ward

University of Washington, Earth and Space Sciences, P.O. Box 351310, Seattle, Washington 98195, USA

Kump et al. (2005) have suggested that the emission of H₂S to the atmosphere from a Late Permian to Early Triassic euxinic (anoxic deep waters) ocean helped to bring about the massive extinction of organisms. Berner (1989; 2005) has suggested that the rate of burial of terrestrially derived organic matter during this period decreased considerably. We demonstrate here how decreased terrestrial organic burial should have led to positive feedback and reinforcement of H₂S release, due to both a drop in atmospheric O₂ and a rise in atmospheric CO₂.

Positive feedback is best illustrated in terms of a systems analysis diagram (Fig. 1). To start, consider the eruption of the Siberian plateau basalts (e.g., Benton and Twitchett, 2003; Grard et al., 2005). These authors suggest that this eruption should have led to an increase in atmospheric CO₂ and global warming, including warming of the ocean, via the atmospheric greenhouse effect (Fig. 1, arrows a and b). A coupled ocean-atmosphere general circulation model (Kiehl and Shields, 2005) has shown that high CO₂ and ocean warming at this time likely led to decreased circulation and the development of a stratified anoxic ocean (arrow c). Stratification then should have brought about increased oceanic areas of bacterial sulfate reduction, a process that takes place only at depth in the absence of dissolved oxygen (arrow d). Hydrogen sulfide is produced by bacterial sulfate reduction. If the zone of H₂S production gets close enough to the ocean surface, the H₂S may escape into the atmosphere and kill organisms (Kump et al., 2005). Thus, as sulfate reduction increased, occasional emissions of H₂S into the air led to increased die-offs of land plants (arrows e and f).

Protracted lethal H₂S episodes should have led to a decrease in the standing crop of land plants, resulting in less production and less burial over time of organic debris derived from plants (arrow g). During the Permian, land plants were a major contributor to global organic matter deposition and burial (Berner, 2005). For every mole of organic matter buried, one mole of CO₂ is removed from the atmosphere via the overall reaction:



therefore, decreased organic burial should have led to an increase in atmospheric CO₂ (arrow h). (The production of dead debris following short-term sporadic lethal episodes would exert only a minor long-term effect on CO₂). Because this cycle began with an increase in CO₂ and ends with a further increase in CO₂, the whole cycle is reinforced and should have led to further poisoning of plants by H₂S.

There is another positive feedback cycle shown by the succession of arrows e-f-g-i-j-k. More sulfate reduction led to increased H₂S emission to the atmosphere, increased die-off of plants, and less terrestrially derived organic burial. Less organic burial should have led to less O₂ production (Eq. 1) and a reduction of atmospheric O₂ (Berner, 2005) (arrow i). Less atmospheric O₂, upon gas exchange between the atmosphere and ocean, would then have led to reduced oceanic O₂ and the enhancement of sulfate reduction (arrows j and k). Thus, increased sulfate reduction, by way of

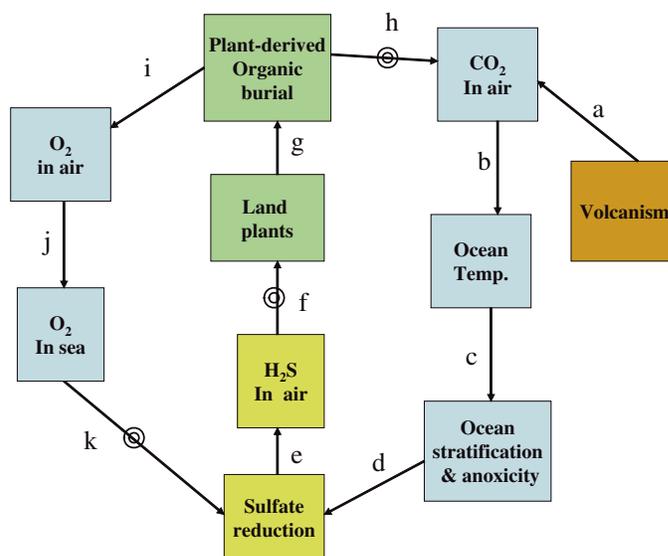


Figure 1. Systems analysis diagram for Permo-Triassic extinction. Plain arrows denote positive responses; arrows with attached bullseyes indicate negative responses. After going entirely around a loop, if the total of bullseyes is zero or an even number, the cycle leads to positive feedback and reinforcement. An odd number of bullseyes leads to negative feedback and stabilization. Cycles b-c-d-e-f-g-h and e-f-g-i-j-k both lead to positive reinforcement.

the poisoning of plants and lowering of atmospheric O₂, led to a further increase in sulfate reduction.

In summary, the two cycles (b-c-d-e-f-g-h and e-f-g-i-j-k) both lead to the increased die-off of plants (and animals) due to the emission of H₂S to the atmosphere. If H₂S poisoning was an important cause of extinction across the Permo-Triassic boundary, then the cycles shown here illustrate that this process was self-reinforcing.

REFERENCES CITED

- Benton, M.J., and Twitchett, R. J., 2003, How to kill (almost) all life: The end-Permian extinction event: Trends in Ecology and Evolution, v. 18, p. 358-365
- Berner, R.A., 1989, Drying, O₂ and mass extinction: Discussion: Nature, v. 340, p. 603, doi: 10.1038/340603b0.
- Berner, R.A., 2005, The carbon and sulfur cycles and atmospheric oxygen from Middle Permian to Middle Triassic: Geochimica et Cosmochimica Acta, v. 69, p. 3211–3217, doi: 10.1016/j.gca.2005.03.021.
- Grard, A., Francois, L.M., Dessert, C., Dupre, B., and Godderis, Y., 2005, Basaltic volcanism and mass extinction at the Permo-Triassic boundary: Environmental impact and modeling of the global carbon cycle: Earth and Planetary Science Letters, v. 234, p. 207–221, doi: 10.1016/j.epsl.2005.02.027.
- Kiehl, J.T., and Shields, C.A., 2005, Climate simulation of the latest Permian: Implications for mass extinction: Geology, v. 33, p. 757–760, doi: 10.1130/G21654.1.
- Kump, L.R., Pavlov, A., and Arthur, M.A., 2005, Massive release of hydrogen sulfide to the surface ocean and atmosphere during intervals of oceanic anoxia: Geology, v. 33, p.397–400, doi: 10.1130/G21295.1.

REPLY doi: 10.1130/G22836.1

Lee R. Kump

Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, USA

Alex Pavlov

*Department of Planetary Sciences, Lunar and Planetary Laboratory,
University of Arizona, Tucson, Arizona 85721, USA*

Michael A. Arthur

*Department of Geosciences, Pennsylvania State University, University
Park, Pennsylvania 16802, USA*

We welcome the comment by Berner and Ward on our 2005 paper, and appreciate the double meaning of “positive reinforcement” in its title, reflecting the absence of criticism of our work. The feedbacks they describe are likely components of the end-Permian biosphere upheaval, and the positive sign of the feedback loops are likely correct. However, the strength and response time of individual couplings among system components in their diagram are uncertain, but these are amenable to evaluation through numerical modeling. Perhaps the long biotic recovery time and persistence of extreme oceanic conditions through the early Triassic (e.g., Woods et al., 1999; Payne et al., 2004) was at least in part a consequence of the stifling effects of these self-enforcing feedback loops.

One subtle issue is the cause of oceanic anoxia. Berner and Ward link ocean warming and anoxia through the vigor of ocean circulation, but we, among others, have shown that the more important factor is warming of deep-water source regions, because of the inverse solubility of O₂ in seawater as a function of temperature (Hotinski et al., 2001). Reductions in meridional overturning rate, in and of themselves, have less effect on deep-water oxygen concentrations because the reduction in O₂ supply is matched by a reduction in O₂ demand: reduced upwelling limits the export of organic material from the surface ocean and thus the rate of consumption in the deep sea (Broecker and Peng, 1982). Moreover, stagnation of circulation is not synonymous with ocean stratification; the modern ocean is vigorously circulating but strongly stratified in nutrient concentrations and modestly stratified in O₂ concentration. The biological pump is a worthy competitor to the thermohaline circulation of the ocean.

A number of important issues remain to be resolved before the hypothesis of H₂S as the proximal kill mechanism for the end-Permian mass extinction will be widely accepted, including 1) whether phosphate

concentrations can build up to the necessarily very high concentrations needed to sustain such deep anoxia (the ocean would have to be highly supersaturated with respect to various apatite phases; however, Framvaren Fjord and the Black Sea currently demonstrate high levels of supersaturation); 2) whether during the transition from oxic to anoxic conditions, denitrification would rob the ocean of all nutrient nitrogen (however, recent analysis indicates that nitrogen fixation may well be able to keep pace with denitrification, given a much lower Fe requirement than previously thought; Arrigo, 2005); and 3) whether H₂S has a selective lethality (relatively little is known about H₂S toxicity, especially among important groups such as insects, which suffered their only mass extinction in geologic history during the Late Permian; Erwin, 2006). Moreover, fundamental uncertainty exists concerning the nature of the pre-Mesozoic biological pump: in the absence of planktonic calcifiers that produce the bulk of the ballast for settling biogenic particles in the ocean today, would there be an effective transfer of organic matter to the deep sea that could keep pace with increased upwelling of nutrients from below? All of these issues are prime for research, and we look forward to the results of ongoing and future investigations.

REFERENCES CITED

- Arrigo, K.R., 2005, Marine microorganisms and global nutrient cycles: *Nature*, v. 437, p. 349–355, doi: 10.1038/nature04159.
- Broecker, W.S., and Peng, T.-H., 1982, *Tracers in the sea*: New York, Eldigio Press, 690 p.
- Erwin, D.H., 2006. *Extinction: How life on Earth nearly ended 250 million years ago*: Princeton, New Jersey, Princeton University Press, 296 p.
- Hotinski, R.M., Bice, K.L., Kump, L.R., Najjar, R.G., and Arthur, M.A., 2001, Ocean stagnation and end-Permian anoxia: *Geology*, v. 29, p. 7–10, doi: 10.1130/0091-7613(2001)029<0007:OSAEPA>2.0.CO;2.
- Payne, J.L., Lehrmann, D.J., Wei, Y.Y., Orchard, M.J., Schrag, D.P., and Knoll, A.H., 2004, Large perturbations of the carbon cycle during recovery from the end-Permian extinction: *Science*, v. 305, p. 506–509, doi: 10.1126/science.1097023.
- Woods, A.D., Bottjer, D.J., and Mutti, M., 1999, Lower Triassic large sea-floor carbonate cements: Their origin and a mechanism for the prolonged biotic recovery from the end-Permian mass extinction: *Geology*, v. 27, p. 645–648, doi: 10.1130/0091-7613(1999)027<0645:LTLFC>2.3.CO;2.