

# Massive release of hydrogen sulfide to the surface ocean and atmosphere during intervals of oceanic anoxia

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## ABSTRACT

Simple calculations show that if deep-water H<sub>2</sub>S concentrations increased beyond a critical threshold during oceanic anoxic intervals of Earth history, the chemocline separating sulfidic deep waters from oxygenated surface waters could have risen abruptly to the ocean surface (a chemocline upward excursion). Atmospheric photochemical modeling indicates that resulting fluxes of H<sub>2</sub>S to the atmosphere (>2000 times the small modern flux from volcanoes) would likely have led to toxic levels of H<sub>2</sub>S in the atmosphere. Moreover, the ozone shield would have been destroyed, and methane levels would have risen to >100 ppm. We thus propose (1) chemocline upward excursion as a kill mechanism during the end-Permian, Late Devonian, and Cenomanian–Turonian extinctions, and (2) persistently high atmospheric H<sub>2</sub>S levels as a factor that impeded evolution of eukaryotic life on land during the Proterozoic.

**Keywords:** anoxia, extinction, hydrogen sulfide, atmosphere, Proterozoic, Phanerozoic.

## INTRODUCTION

Abundant geologic evidence indicates that oceanic anoxia in shelf and abyssal environments was a recurring feature of Earth history (e.g., Schlanger and Jenkyns, 1976; Berry and Wilde, 1978; Holland, 1984; Grotzinger and Knoll, 1995). Under such conditions, sulfate-reducing bacteria would have used sulfate, if available, as an electron acceptor in their metabolism, producing hydrogen sulfide. Thus, anoxic oceans might have become sulfide rich; as such, the Black Sea provides a useful analog (e.g., Arthur and Sageman, 1994).

Might sulfide introductions into the oxygenated layer of the ocean or more persistent intervals of surface-water euxinia (high sulfide concentrations) have accompanied the most extreme oceanic anoxic intervals? If so, what would have been their biological and chemical consequences? In anoxic basins today, mildly sulfidic deep waters are separated from the atmosphere by an oxygenated surface layer, at the base of which is a sulfide chemocline through which O<sub>2</sub> concentrations fall to zero. Here we explore the conditions that lead to a stable sulfide chemocline and the consequences for the atmosphere of destabilization of the chemocline by sulfide buildup or oxygen decline, a process we call chemocline upward excursion to the sea surface. We find that significant buildup of H<sub>2</sub>S in the deep sea could have led to toxic emissions of H<sub>2</sub>S to the atmosphere, methane accumulation and attendant global warming, and loss of the ozone

shield. We then consider implications for mid-Cretaceous and Late Devonian oceanic anoxic events, the Late Permian, when the largest mass extinction of animal life on Earth occurred, and the Proterozoic, which may have included a billion year period of persistent oceanic anoxia under a low O<sub>2</sub> atmosphere (Canfield, 1998).

## ESTABLISHMENT AND STABILITY OF AN OCEANIC CHEMOCLINE

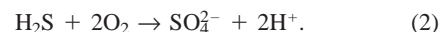
Deep-water anoxia requires low atmospheric O<sub>2</sub> concentrations, warm and thus poorly oxygenated bottom-water source regions, or nutrient-rich deep waters that, after ascending, stimulate productivity and carbon export and thus create a large O<sub>2</sub> demand for the deep sea (e.g., Sarmiento et al., 1988; Hotinski et al., 2000, 2001). The establishment of highly sulfidic conditions, however, requires an even larger change in oxidant demand or electron-donor flux. We can quantify this by adopting the approach of Broecker and Peng (1982). Assume that surface water has no P or H<sub>2</sub>S, but that the flux of organic matter to the deep sea is limited by the upwelling of P to the surface ocean. Deep water with [H<sub>2</sub>S] = 1 mmol·kg<sup>-1</sup> (a critical value; see following) is produced by downwelling surface water and adding 2 mmol·kg<sup>-1</sup> of settling organic matter that is utilized in sulfate reduction:



(We neglect the small amount of organic matter that is oxidized in the deep sea by O<sub>2</sub> and NO<sub>3</sub> under anoxic conditions.) If we assume

Redfield ratio proportions of carbon to phosphorus of 106 for the organic matter oxidized, then ~0.02 mmol·kg<sup>-1</sup> of P is also released. This is the steady-state P concentration, and it is ~10 times the average concentration in today's oceanic deep water. The establishment of a P-enriched ocean likely would result from positive feedback between anoxia and the release of P from marine sediments (Van Cappellen and Ingall, 1996; Murphy et al., 2000). The recent finding that much of the P contributing to the measured composition of marine plankton is adsorbed onto Mn-oxide coatings even in living plankton (Sañudo-Wilhelmy et al., 2004) may explain why P is so readily liberated from organic matter in euxinic environments.

The fundamental characteristic of a stable chemocline is that the supply of O<sub>2</sub> from the atmosphere across the air-sea interface and its transport through the surface layer must exceed the upwelling and diffusive flux of reductant (H<sub>2</sub>S) from below; the flux of O<sub>2</sub> must be at least twice as high given the stoichiometry of the reaction



(This treatment recognizes that the rate of this reaction [Cline and Richards, 1969] is rapid relative to the physical processes involved.) The exchange of gases including O<sub>2</sub> between the atmosphere and ocean is often treated by using a piston-velocity formulation, whereby the flux of gases occurs at a rate (in this case,  $F_{\text{O}_2}$ ) that is proportional to the contrast in gas concentrations between the atmosphere and surface ocean with the proportionality constant being the piston velocity ( $k$ ):

$$F_{\text{O}_2} = \rho_{\text{oce}} \cdot k \cdot K_{\text{H}} (p_{\text{O}_2\text{atm}} - p_{\text{O}_2\text{oce}}), \quad (3)$$

where  $K_{\text{H}}$  is the Henry's law constant for O<sub>2</sub>, a function of temperature and salinity, and  $\rho_{\text{oce}}$  is the density of seawater (~1002 kg·m<sup>-3</sup>). For warm surface waters,  $K_{\text{H}}$  is ~10<sup>-3</sup> mol·kg<sup>-1</sup>·bar<sup>-1</sup> (Pilson, 1998). The piston velocity is ~1000 m·yr<sup>-1</sup> (Pilson, 1998). Although net primary production is a source of surface-layer O<sub>2</sub>, gas exchange with the atmosphere is a much larger source, as evidenced by the minor levels of O<sub>2</sub> supersatura-

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ration that develop in surface waters. Thus, we can ignore biological O<sub>2</sub> production in the calculations that follow.

The supply of H<sub>2</sub>S from below by upwelling ( $F_{\text{H}_2\text{S}}$ ) can be written as

$$F_{\text{H}_2\text{S}} = \rho_{\text{oce}} \cdot u \cdot [\text{H}_2\text{S}]_{\text{deep}}, \quad (4)$$

where  $u$  is the upwelling rate (in  $\text{m}\cdot\text{yr}^{-1}$ ) and  $[\text{H}_2\text{S}]_{\text{deep}}$  is the concentration of H<sub>2</sub>S in deep waters (in  $\text{mol}\cdot\text{kg}^{-1}$ ). As long as the mixing down of O<sub>2</sub> exceeds the mixing up of H<sub>2</sub>S, the surface layer remains oxygenated. We can determine the critical conditions beyond which the surface layer becomes H<sub>2</sub>S rich by setting these two fluxes equal:

$$\begin{aligned} k \cdot K_{\text{H}} \cdot \rho_{\text{occ}} \cdot (P_{\text{O}_2, \text{atm}} - P_{\text{O}_2, \text{oce}}) \\ = 2u \cdot \rho_{\text{oce}} \cdot [\text{H}_2\text{S}]_{\text{deep}}. \end{aligned} \quad (5)$$

Given these values, and setting the surface-water O<sub>2</sub> partial pressure ( $p_{\text{O}_2, \text{oce}}$ ) to zero, the critical ratio of H<sub>2</sub>S in the deep to atmospheric O<sub>2</sub>, above which the steady-state surface-water O<sub>2</sub> concentration is zero, is

$$\begin{aligned} \left( \frac{[\text{H}_2\text{S}]_{\text{deep}}}{P_{\text{O}_2, \text{atm}}} \right)_{\text{crit}} \\ = \frac{k \cdot K_{\text{H}}}{2u} \\ = \frac{1000(\text{m}\cdot\text{yr}^{-1}) \cdot 10^3 \text{ mol}\cdot\text{kg}^{-1}\cdot\text{bar}^{-1}}{2 \cdot 4 \text{ m}\cdot\text{yr}^{-1}} \\ = 0.1 \frac{\text{mol}}{\text{kg}\cdot\text{bar}} \end{aligned} \quad (6)$$

for a globally averaged upwelling velocity of  $\sim 4 \text{ m}\cdot\text{yr}^{-1}$  (e.g., Broecker and Peng, 1982). With  $p_{\text{O}_2, \text{atm}} = 0.21 \text{ bar}$ , the deep ocean would have to contain  $\sim 20 \text{ mmol}\cdot\text{kg}^{-1}$  H<sub>2</sub>S to generate a chemocline upward excursion, a highly unlikely condition. However, regions of intense upwelling ( $\leq 100 \text{ m}\cdot\text{yr}^{-1}$ ; e.g., Tomczak and Godfrey, 1994) would become sulfidic at much lower  $[\text{H}_2\text{S}]_{\text{deep}}$ ,  $\sim 1 \text{ mmol}\cdot\text{kg}^{-1}$ . (Proper treatment of regional euxinia includes lateral transport as a nonlocal sink, but scale analysis demonstrates that this term is unimportant; see GSA Data Repository material<sup>1</sup>.) If atmospheric oxygen levels were substantially lower in the past, e.g., 50% of today's level in the Late Permian (Bernier and Canfield, 1989) and 1% or less in the Proterozoic (Canfield, 1998), then the required  $[\text{H}_2\text{S}]_{\text{deep}}$  for a chemocline upward excursion is proportionately reduced.

<sup>1</sup>GSA Data Repository item 2005072, scale analysis of nonlocal sink for H<sub>2</sub>S, is available online at [www.geosociety.org/pubs/ft2005.htm](http://www.geosociety.org/pubs/ft2005.htm). or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder CO, 80301-9140, USA.

## FLUX OF H<sub>2</sub>S TO THE ATMOSPHERE

Thus, if the  $[\text{H}_2\text{S}]$  of the deep sea increased during an anoxic interval beyond a critical value ( $\sim 1 \text{ mmol}\cdot\text{kg}^{-1}$ ), upwelling regions of the world ocean would become sulfidic, even with the modern  $p_{\text{O}_2, \text{atm}}$ . The H<sub>2</sub>S flux from an H<sub>2</sub>S-rich surface ocean could be considerably larger than the modern H<sub>2</sub>S flux ( $2 \text{ Tg S}\cdot\text{yr}^{-1}$  from volcanoes; Seinfeld and Pandis, 1998; Shooter, 1999) and can be estimated by using the piston-velocity formulation above. The maximum flux of H<sub>2</sub>S before significant H<sub>2</sub>S builds up in the atmosphere is

$$\begin{aligned} F_{\text{H}_2\text{S}}(\text{sea} \rightarrow \text{air}) \\ = k \cdot \rho_{\text{oce}} \cdot [\text{H}_2\text{S}]_{\text{deep}} \frac{\text{mol}}{\text{m}^2\cdot\text{yr}}. \end{aligned} \quad (7)$$

However, at steady state, the rate of release of H<sub>2</sub>S is limited not by the piston velocity but by the upwelling rate; for  $u = 100 \text{ m}\cdot\text{yr}^{-1}$ , the sustainable H<sub>2</sub>S flux is a factor of 10 smaller than that given by equation 7. A slightly more sulfidic ocean with  $[\text{H}_2\text{S}] = 3 \text{ mmol}\cdot\text{kg}^{-1}$  and a total upwelling area of  $\sim 0.4 \times 10^6 \text{ km}^2$  could sustain a flux of  $4000 \text{ Tg S}\cdot\text{yr}^{-1}$  ( $120 \text{ Tmol}\cdot\text{yr}^{-1}$ ), 2000 times the present-day flux and a critical value for the atmosphere (see following). The required upwelling area is a small fraction (0.1%) of the total surface area of the ocean and approximately equal to the upwelling area of the ocean today (McSweeney et al., 2003). If atmospheric  $p_{\text{O}_2}$  was lower in the past, the required  $[\text{H}_2\text{S}]$  would be proportionately smaller.

Photosynthetic and chemosynthetic activity of green, purple, and colorless S bacteria potentially regulate the release of H<sub>2</sub>S across the chemocline, whether it exists at depth or at the air-sea interface. However, as noted here, even the most productive pelagic ecosystems today generate only minor O<sub>2</sub> supersaturation in surface waters. By analogy, an equally productive anoxygenic photoautotrophic community would not be able to prevent H<sub>2</sub>S release, given that under such conditions, the upward flux of H<sub>2</sub>S exceeds the mixing-in flux of O<sub>2</sub>.

## IMPLICATIONS OF CHEMOCLINE DESTABILIZATION FOR THE ATMOSPHERE

To study the atmospheric consequences of such tremendous additions of H<sub>2</sub>S to the atmosphere, we have used an updated version of the one-dimensional photochemical atmospheric model from Kasting et al. (1985), fully described in Pavlov and Kasting (2002). In lieu of a spatially resolved flux calculation, we explore the atmospheric response to fluxes ranging as high as 10,000 times the present flux. In our model the present-day flux results in the steady-state mixing ratio of H<sub>2</sub>S, which is consistent with the average present-day free troposphere value of 6.5 ppt H<sub>2</sub>S (Seinfeld

and Pandis, 1998). Four 1000 yr simulations have been run; all start from our present-day atmosphere.

Figure 1 presents the results of these calculations. After 1000 yr the atmospheric composition is still evolving for large H<sub>2</sub>S fluxes, so reported values of H<sub>2</sub>S, CH<sub>4</sub>, and ozone should be considered as conservative ones. As the H<sub>2</sub>S flux increases relative to today's flux, so too does the tropospheric concentration of H<sub>2</sub>S (Fig. 1A). However, at an H<sub>2</sub>S flux between 1000 and 2000 times the present value, the H<sub>2</sub>S abundance increases abruptly from  $\sim 0.01 \text{ ppmv}$ , below the human limit of detection by smell, to  $100 \text{ ppmv}$ , near the level at which our olfactory nerve becomes paralyzed, and we lose the ability to detect the toxin. The reason for the threshold effect is apparent in Figure 1B: the OH radical abundance has fallen by several orders of magnitude as the H<sub>2</sub>S flux increased from 1000 to 2000 times the present value. At this point, the reaction with H<sub>2</sub>S reduces the OH abundance to very low levels. The H<sub>2</sub>S concentration in the marine boundary layer becomes limited only by transport to the upper layers of the atmosphere where sufficient OH exists to oxidize the H<sub>2</sub>S. Another interesting consequence of OH depletion is an abrupt increase in methane abundance to  $\sim 100 \text{ ppmv}$  (Fig. 1C). Finally, because H<sub>2</sub>S reacts rapidly with singlet O in the stratosphere, the O abundance falls abruptly. As an essential reactant in the formation of ozone, the loss of O from the stratosphere leads to the destruction of the ozone layer (Fig. 1D).

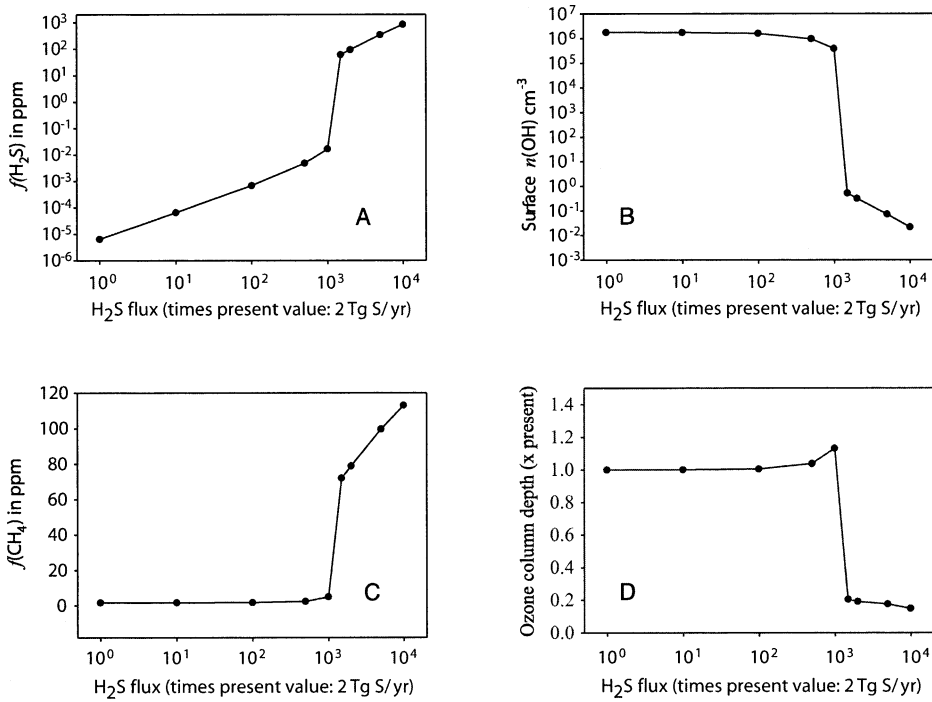
As shown here, the catastrophic release of H<sub>2</sub>S would require euxinic surface-water conditions over no more than just the upwelling regions of the world ocean. It would present only a small O<sub>2</sub> sink because the surface area is so small, a sink that would be easily matched by the O<sub>2</sub> liberated by oxygenic photosynthesis elsewhere.

## PALEOENVIRONMENTAL IMPLICATIONS

### Phanerozoic Anoxia and Extinctions

The calculations presented here indicate that chemocline upward excursions in upwelling zones and resultant massive H<sub>2</sub>S release to the atmosphere constitute a possible consequence of widespread and deep oceanic anoxia, consistent with the suggestion of Wilde et al. (1990). The condition is extreme, and thus likely to have been rarely achieved in Earth history. Is there any evidence that such conditions have occurred in the geologic past?

One indicator is the presence of isorenieratane, a biomarker for the original abundance of nonoxygenic photosynthetic green sulfur bacteria. Its abundance in deep-water sediments provides strong evidence for the presence of H<sub>2</sub>S in the photic zone; previous workers have tacitly assumed an oxygenated



**Figure 1.** Calculated change in atmospheric composition in response to increased flux of H<sub>2</sub>S to atmosphere. **A:** Tropospheric mixing ratio of H<sub>2</sub>S. **B:** Tropospheric hydroxyl radical abundance;  $n(\text{OH})$  is number of molecules of OH. **C:** Tropospheric mixing ratio of methane. **D:** Total ozone column depth (normalized to present value). Model domain extends from surface to altitude of 64 km and contains 34 chemical species that participate in 218 chemical reactions. We have assumed present-day atmospheric temperature profile, present-day rates of volcanic emissions of SO<sub>2</sub> and other gases, and present-day average atmospheric water-vapor abundance. Atmospheric  $p_{\text{CO}_2}$  is fixed at 340 ppm, and  $p_{\text{O}_2, \text{atm}}$  is set at its present value of 21%, which we consider a conservative approach. Length of simulation in all cases is 1000 yr.

surface ocean, but we find that euxinic surface waters are equally likely in upwelling zones. Isorenieratane has been identified in sedimentary rocks associated with extinctions in the Late Devonian (Frasnian–Famennian; Joachimski et al., 2001; Brown and Kenig, 2002) and mid-Cretaceous (Cenomanian–Turonian; Sinninghe Damste and Koester, 1998; Simons and Kenig, 2001; Pancost et al., 2004). In the mid-Cretaceous there was a marked extinction in corals and rudists in shallow-water and planktonic foraminifera, ammonites, and radiolaria (Erbacher et al., 1996) in the pelagic realm, perhaps the result of chemocline upward excursion.

The greatest extinction of the Phanerozoic occurred in the Late Permian (Erwin, 1995), and anoxia remains an important component of most proposed extinction mechanisms. The lack of bioturbation, presence of abundant framboidal pyrite, and trace-metal anomalies, including low Th/U ratios, indicate that anoxic and perhaps euxinic conditions became established in nearshore settings during the Late Permian (Wignall and Twitchett, 1996), and perhaps resulted from the expansion of such conditions in the deep sea (e.g., Isozaki, 1997). Anoxia and the biotic recovery period after extinction were anomalously long, extending millions of years into the Triassic

(e.g., Hallam, 1991; Woods et al., 1999; Payne et al., 2004).

Knoll et al. (1996) proposed catastrophic upwelling of CO<sub>2</sub>-rich bottom waters as the end-Permian kill mechanism, and presented fossil data supportive of hypercapnia as the specific agent of death. However, a physical mechanism for catastrophic upwelling was admittedly lacking in their hypothesis. Chemocline upward excursion requires no change in the physical characteristics of the ocean circulation, as it results entirely from buildup of H<sub>2</sub>S in the deep sea or reduction in atmospheric  $p_{\text{O}_2}$ . It provides a link to the terrestrial extinctions, because H<sub>2</sub>S accumulates in the troposphere to lethal levels for plants and animals (Bagarinao, 1992) under relatively modest fluxes of H<sub>2</sub>S from the ocean, and perhaps more important, the ozone shield is destroyed. Spores from the extinction interval in Greenland sediments show evidence of the mutation expected from extended exposure to high ultraviolet fluxes attendant on the loss of the ozone layer (Visscher et al., 2004). An abrupt increase in methane concentrations in the atmosphere significantly amplifies the greenhouse warming from the attendant CO<sub>2</sub> buildup. These environmental disturbances work together with hypercapnia (Knoll et

al., 1996) to produce a very effective kill mechanism.

To date, isorenieratane has not been identified in Upper Permian pelagic black cherts. However, a marked negative excursion in  $\delta^{34}\text{S}$  of marine sulfate may have been caused by the addition to surface waters of <sup>34</sup>S-depleted H<sub>2</sub>S from below the chemocline (Newton et al., 2004), and S enrichment of paleosols (Marouka et al., 2003) may have resulted from the rainout of tropospheric H<sub>2</sub>S.

### Proterozoic Canfield Ocean

Canfield (1998) proposed that the Paleoproterozoic and Mesoproterozoic ocean (1.8–0.8 Ga) was strongly chemically stratified, with sulfidic deep waters and modestly oxygenated surface waters in contact with a low  $p_{\text{O}_2, \text{atm}}$ . Fe chemistry and S isotopes of 1.5 Ga rocks from Australia (Shen et al., 2003) and Mo isotope ratios in Mesoproterozoic sedimentary rocks (Arnold et al., 2004) are consistent with deep-water euxinia.

Whether such conditions were indeed widespread and characteristic of the global ocean remains to be demonstrated. The arguments presented here, however, would indicate that widespread surface-water euxinia, rather than modestly oxygenated surface waters, could have existed under Proterozoic atmospheric conditions. A reasonable scenario for the Proterozoic ocean would have purple and green sulfur bacteria dominating productivity in upwelling regions (with persistently euxinic surface waters) and cyanobacteria dominating productivity in the more oligotrophic regions of the world's oceans with chemoclines at the base of the surface layer, under an atmosphere with O<sub>2</sub> levels 3%–4% of what they are today. The flux of H<sub>2</sub>S to the atmosphere would be significant and may have been the factor that sustained  $p_{\text{O}_2, \text{atm}}$  intermediate between those of the Archean and Phanerozoic. Moreover, the maintenance of elevated H<sub>2</sub>S concentrations in the Proterozoic atmosphere may have delayed the establishment of terrestrial ecosystems until the late Neoproterozoic.

### CONCLUSION

The necessary conditions for oceanic euxinia are well within the range of expected variability over Earth history. As the deep ocean becomes particularly euxinic and deep waters approach millimolar concentration of H<sub>2</sub>S at modern atmospheric  $p_{\text{O}_2}$ , a threshold is reached beyond which the H<sub>2</sub>S flux in upwelling zones exceeds the in-mixing of atmospheric O<sub>2</sub>, and the surface layer becomes euxinic. Lower levels of O<sub>2</sub> require proportionately lower levels of H<sub>2</sub>S for a chemocline upward excursion. Then, fluxes of H<sub>2</sub>S to the atmosphere from upwelling regions can exceed the oxidant-production rate, and atmospheric H<sub>2</sub>S mixing ratios jump abruptly to

lethal levels, the ozone shield is destroyed, and CH<sub>4</sub> levels rise abruptly.

We propose that such conditions may have existed during particular intervals of the Phanerozoic and much of the Proterozoic (from ca. 1.8 to 0.8 Ga). During the Phanerozoic, H<sub>2</sub>S buildups may have been a contributing factor in mass extinction and biotic turnover. A persistently sulfidic Proterozoic atmosphere may have delayed the establishment of eukaryotic life on land.

**Note Added in Proof:** Biomarker evidence consistent with the hypothesis of chemocline upward excursion at the Permian-Triassic boundary has just been reported online in *Science Express* (Grice et al., 2005).

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