



Role of hydrogen sulfide in a Permian-Triassic boundary ozone collapse

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[1] Using a three-dimensional chemistry-climate model of the troposphere and stratosphere, we find that hydrogen sulfide alone is unlikely to directly affect stratospheric ozone, even for hydrogen sulfide emission rates as large as 5000 Tg(S) per year. However, we also find that large quantities of hydrogen sulfide create a significant decrease in tropospheric hydroxyl radical, leading to a commensurate increase in atmospheric methane. Therefore a large methane flux (possibly from methane clathrate destabilization, Siberian traps or hydrothermal vent complexes) combined with a large hydrogen sulfide oceanic flux is much more likely to lead to an ozone collapse than methane or hydrogen sulfide alone with implications to the Permian-Triassic boundary extinction 250 million years ago. **Citation:** Lamarque, J.-F., J. T. Kiehl, and J. J. Orlando (2007), Role of hydrogen sulfide in a Permian-Triassic boundary ozone collapse, *Geophys. Res. Lett.*, *34*, L02801, doi:10.1029/2006GL028384.

1. Introduction

[2] In a recent study, *Kump et al.* [2005] (hereinafter KPA) have shown the potential role of hydrogen sulfide (H₂S), possibly released in large quantities by the ocean under anoxic conditions, as an ozone-destroying agent. According to KPA, in the case of large emission rates (of at least 2000 Tg(S) per year, see their Figure 1d), sufficiently large amounts of hydrogen sulfide could actually cause the disappearance of most of the atmospheric ozone, leading to toxic living conditions and a cataclysmic increase in UV-B radiation reaching the surface. KPA argue that this scenario could have led to the mass extinction at the Permian-Triassic boundary approximately 250 million years ago [*Erwin*, 1994; *Twitcheit*, 2006].

[3] While it is clear that large amounts of hydrogen sulfide released into the atmosphere will significantly perturb the tropospheric chemistry (mainly through its reaction with the hydroxyl radical OH, see section 2), its very short lifetime (a few days under present-day conditions [*Warneck*, 2000]) renders unlikely any substantial transport of hydrogen sulfide into the stratosphere, where most of the ozone resides.

[4] In this paper, we analyze the role of hydrogen sulfide using a global three-dimensional chemistry-climate model. While this model has a simpler chemical mechanism than KPA (the main differences are discussed in section 2), its three-dimensional representation of transport (and its dependence on the greenhouse gas distributions) makes it an

ideal tool to further study the role of hydrogen sulfide on atmospheric chemistry.

[5] The paper is organized as follows: in section 2, we describe the model and chemical equations used to simulate the hydrogen sulfide chemistry. In section 3 we present and discuss the results of the simulations with a small (present-day) and large hydrogen sulfide flux. Conclusions are drawn in section 4.

2. Model Description

[6] We use here a comprehensive atmospheric model with interactive stratospheric/tropospheric chemistry; consequently the model radiation uses the simulated greenhouse gas distributions as affected by chemistry and climate. This model is described in detail by *Sassi et al.* [2005] and only the main characteristics and differences are discussed here. We also discuss in this section major differences between our model and the KPA model.

[7] Our model extends from the surface to approximately 85 km, with a vertical resolution of 52 levels. In the present configuration it uses a horizontal resolution of 4°(latitude) × 5°(longitude). All physical and chemical processes are calculated using a 30 min time step. At the surface the atmospheric model uses the land/sea distribution and vegetation cover from the Latest Permian climate study by *Kiehl and Shields* [2005]. The CO₂ concentration is set to 3550 parts per million per volume (ppmv) as in work by *Kiehl and Shields* [2005]. The surface condition for methane is expressed in terms of a constant flux of 140 Tg/year, leading to a steady-state atmospheric methane concentration of approximately 700 parts per billion per volume (ppbv) when no hydrogen sulfide flux is considered.

[8] In addition to a chemistry configuration valid for the representation of methane and ozone chemistry in the troposphere and stratosphere [*Sassi et al.*, 2005], we have included a set of chemical reactions (Table 1) that describes the chemistry of H₂S [*Warneck*, 2000; *Sander et al.*, 2003]. In the troposphere, H₂S reacts rapidly with the hydroxyl radical (OH) to form HS. Subsequent reactions with ozone and NO₂ lead to the formation of SO₂ and ultimately sulfate. In addition, a relatively slow removal by precipitation is included on the basis of the H₂S Henry's law coefficient [*Sander et al.*, 2003]. In the stratosphere, the remaining H₂S that has been transported across the tropical tropopause can react with OH (reaction 1), O(³P) (reaction 5) and O(¹D) (reactions 2–4).

[9] The formation of sulfate from SO₂ (without any consideration of direct sources of SO₂ in this study) is done through both gas-phase (reaction of SO₂ with OH, #15 in Table 1) and aqueous-phase oxidation (reactions 16 and 17) by ozone and hydrogen peroxide, as in work by *Tie et al.*

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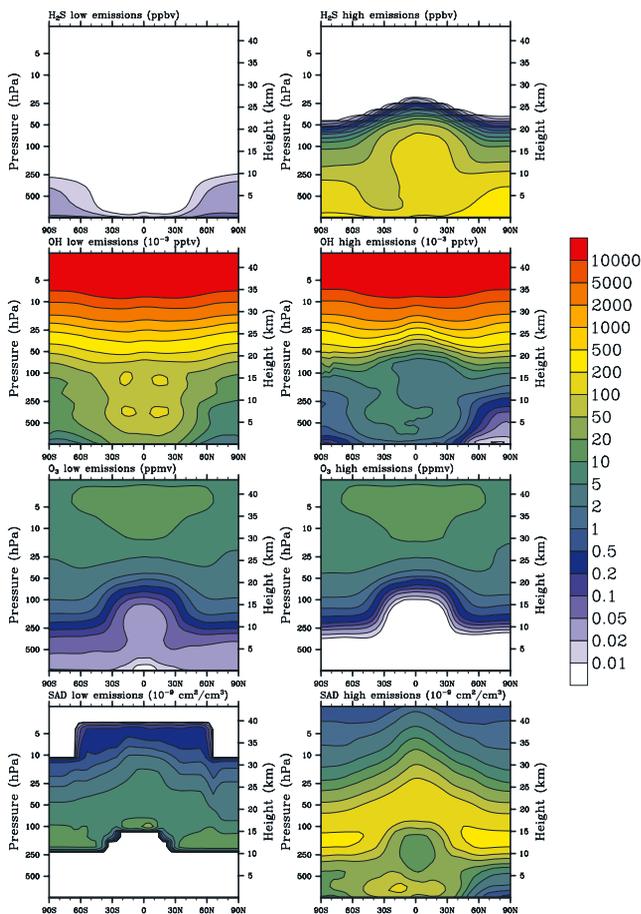


Figure 1. Annual and zonal average of the volume mixing ratio of H₂S (top row, parts per billion), OH (second row, parts per trillion, scaled by 10³) and ozone (third row, parts per million) and sulfate aerosol surface area density (bottom row, cm²/cm³, scaled by 10⁹). The left column is for the low H₂S emission case (2 Tg(S)/year) and the right column is for the high emission case (5000 Tg(S)/year).

[2001]. The aqueous-phase reactions only occur when clouds are present; consequently, under the warm and moist conditions prevalent in the latest Permian [Kiehl and Shields, 2005], this reaction pathway will be quite active. The modeled sulfate is used to calculate the surface area density available for heterogeneous chemistry in the troposphere and stratosphere. This is in addition to a background surface area density in the stratosphere typical of low volcanic conditions.

[10] Our sulfur chemical mechanism is slightly simpler than the one used in KPA (see Pavlov *et al.* [2001] and Pavlov and Kasting [2002] for a description of their chemical mechanism). Regarding the H₂S chemistry, which is the focus of this paper, both schemes have the main removal process for H₂S in the troposphere through its reaction with OH; however, when few oxidants are present, wet removal becomes its primary tropospheric loss. In the stratosphere, we include the reactions of H₂S with O(¹D) to the reaction with O(³P), while only the latter is present in KPA; the overall reaction rate with O(¹D) is based on work by Iagonsen *et al.* [1993], while the branching ratios are based on the recent measurements of Balucani *et al.* [2004].

Finally, our scheme does not have the H₂S chemical production terms listed in work by Pavlov *et al.* [2001]; this simplification is based on our analysis of the very low concentration of the reactants (HS and HSO) and on the proposed H₂S chemistry from Warneck [2000] and Sander *et al.* [2003]. It is believed that these differences will have little impact on the simulated abundance of H₂S in the atmosphere (we actually have slightly more H₂S in the troposphere than KPA, see section 3); on the other hand, in the stratosphere, our additional reaction of H₂S with O(¹D) (and to a lesser extent the absence of H₂S photolysis in our scheme) significantly increases the potential for H₂S to destroy ozone in our model.

[11] In addition to differences in the chemical mechanism, our fully interactive three-dimensional model differs from KPA in that the transport of chemical species in the atmosphere is explicitly calculated instead of being parameterized by a diffusive flux [Kasting and Donahue, 1980]. Indeed, because of the short H₂S lifetime (a few days in the troposphere), only a small fraction will cross the tropical tropopause into the stratosphere. However, the use of one-dimensional diffusive transport for H₂S [Pavlov *et al.*, 2001] has the potential to transport much more rapidly such a short-lived chemical species across the tropopause. In addition, a one-dimensional model only provides a limited representation of the tropospheric and stratospheric circulations, which strongly affect the distribution of chemical species such as ozone and methane.

[12] To identify the role of H₂S fluxes on atmospheric chemistry, we have selected two emission scenarios: the first one is representative of H₂S emissions under present-day conditions (2 Tg(S)/year), the second one is for H₂S emissions that are large enough (5000 Tg(S)/year) to be significantly above the value (approximately 2000 Tg(S)/year) in KPA at which their model produces a step-like increase in H₂S and a cataclysmic ozone reduction (see their Figure 1d). These emissions are released uniformly over the oceanic distribution from Kiehl and Shields [2005], valid for the Permian-Triassic boundary. This uniform distribution is clearly a simplification as several studies have indicated that the lowest oxygen concentrations were found in the eastern Equatorial Panthalassa, the equivalent to present-day Equatorial Pacific [Zhang *et al.*, 2001; Hotinski

Table 1. List of Chemical Reactions Related to the Sulfur Cycle^a

	Reaction	Reaction Rate, cm ³ molecule ⁻¹ s ⁻¹
1	H ₂ S + OH → HS	rate = 6.00E-12*exp(-75/T)
2	H ₂ S + O ¹ D → OH + HS	rate = 5.50E-11
3	H ₂ S + O ¹ D → HSO + H	rate = 1.40E-10
4	H ₂ S + O ¹ D → SO + H ₂	rate = 2.20E-11
5	H ₂ S + O → OH + HS	rate = 9.20E-12*exp(-1800/T)
6	H ₂ S + Cl → HCl + HS	rate = 3.70E-11*exp(210/T)
7	HS + O ₃ → HSO + O ₂	rate = 9.00E-12*exp(-280/T)
8	HS + NO ₂ → HSO + NO	rate = 2.90E-11*exp(240/T)
9	HSO + O ₃ → HS + 2*O ₂	rate = 2.70E-13*exp(-400/T)
10	HSO + O ₃ → HO ₂ + SO ₂	rate = 1.00E-12*exp(-1000/T)
11	HSO + NO ₂ → SO ₂ + HO ₂ + NO	rate = 9.60E-12
12	SO + O ₂ → SO ₂ + O	rate = 2.60E-13*exp(-2400/T)
13	SO + O ₃ → SO ₂ + O ₂	rate = 3.60E-12*exp(-1100/T)
14	SO + NO ₂ → SO ₂ + NO	rate = 1.40E-11
15	SO ₂ + OH + M → SO ₄	see Sander <i>et al.</i> [2003]
16	SO ₂ + O ₃ → SO ₄	aqueous-phase reaction
17	SO ₂ + H ₂ O ₂ → SO ₄	aqueous-phase reaction

et al., 2001; *Kiehl and Shields*, 2005]. This simplified hydrogen sulfide emission distribution has however the advantage of being directly comparable to KPA. Our two simulations are run long enough (over 20 years) to establish a steady state in the concentrations of H₂S, OH and ozone; the steady-state assumption was verified by looking at the evolution of the concentration of these chemical species and the sulfur budget (balance of surface fluxes and deposition losses) over multiple years. Indeed, a fully coupled chemistry-climate model cannot achieve a true steady-state, only in a statistical sense.

3. Results

3.1. H₂S Under Present-Day Emissions

[13] Under present-day emissions (2 Tg(S)/year), the monthly globally-averaged tropospheric (mass-weighted integral from the ground to 200 hPa) mixing ratio of H₂S (Figure 1, top left) is on the order of 10 parts per trillion per volume (pptv), slightly larger than the 6.5 pptv quoted in KPA; compared to present-day observations, our mean tropospheric concentration is also slightly larger than the 8.5 pptv marine boundary layer average of *Saltzman and Cooper* [1998] and in good agreement with the continental surface and free tropospheric measurements of *Andreae et al.* [1990]. In addition, the tropospheric lifetime of H₂S is estimated to be 9 days, slightly longer than *Warneck* [2000] and KPA, indicating a realistic representation of the main processes affecting the H₂S concentration in our model. Under these conditions, the annual average mixing ratio of H₂S at the tropical tropopause (i.e., where tropospheric air enters the stratosphere) is of the order of 0.01 pptv, much too small to have any significant impact on stratospheric ozone.

3.2. H₂S Under Elevated Emissions

[14] Under elevated emissions (5000 Tg(S)/year), the tropospheric mixing ratio of H₂S increases to 140 ppbv (Figure 1, top row) and its surface mixing ratio to approximately 250 ppbv; this increase is larger than 2500 times (i.e. the ratio of emissions) the low emission case (average tropospheric mixing ratio of 10 pptv, see section 3.1) because of the 5-fold increase in the H₂S lifetime, to approximately 45 days. Indeed, at steady-state, the burden of a chemical species is simply the product of its production rate (in this case surface emissions; units: Tg/year) by its lifetime (units: years). An increase by a factor of 5 in the lifetime therefore directly translates into an equivalent increase in the burden.

[15] The increase in the H₂S lifetime is a direct consequence of the large decrease in tropospheric OH (Figure 1, second row); by the time the H₂S has reached a steady state, the tropospheric OH has decreased by approximately a factor of 15 from the low emission case. This OH decrease, while substantial, is still much smaller than what KPA report. The reason for our smaller OH decrease is the following: in our model simulation, while tropospheric ozone and OH are very efficiently removed by the emission of H₂S, tropospheric ozone (and consequently OH) is also significantly replenished by a flux of stratospheric ozone (which is mostly unaffected by H₂S) in the extratropical regions; this flux occurs every year primarily in the spring in the southern hemisphere and in the fall in the northern

hemisphere. Even under present-day conditions, this stratosphere to troposphere transport of ozone accounts for a significant fraction (approximately 500 Tg(O₃)/year) of the annual tropospheric ozone budget [*Lamarque et al.*, 2005, and references therein]. The importance of this flux becomes even more critical when the ozone is rapidly destroyed in the troposphere, as is the case under the high H₂S emission scenario. As the occurrence and characteristics of this transport of ozone from the stratosphere can only be realistically simulated by three-dimensional models, this could be a reason for the difference in the tropospheric OH behavior between KPA and this study. In addition, the use in KPA of fixed present-day conditions (i.e., colder and drier than in the Latest Permian) probably limits the ability for OH (with its production mainly from O(¹D) + H₂O) to recover from the increase in hydrogen sulfide emissions. Interestingly, in the event of a stratospheric ozone collapse, this tropospheric ozone refilling mechanism described above will become less effective, providing a positive or amplifying feedback and leading to an additional decrease in tropospheric OH and further ozone-destruction potential.

[16] Under elevated emissions, the H₂S at the tropical tropopause (taken here as the 50 hPa surface) now reaches 100 ppbv. While this is much larger than in the low emission case, there is no indication that it has any significant impact on stratospheric ozone in this region or above (Figure 1, third row). Similarly, the increase of surface area density from sulfate aerosols (Figure 1, bottom row) associated with the hydrogen sulfide oxidation does not lead to an impact on stratospheric ozone there or anywhere else; this is due to the small chlorine loading assumed in this set of simulations, with a fixed surface concentration of 550 pptv, based on estimates for pre-industrial conditions. It has actually been shown that the sulfate increase from large volcanic eruptions under low-chlorine levels can lead to an ozone increase [*Tie and Brasseur*, 1995]. Overall, our analysis indicates that, for hydrogen sulfide emissions up to 5000 Tg(S)/year, there is no indication, in our model, of the tropospheric OH collapse and associated H₂S and methane increases found in KPA.

[17] The importance of considering a distribution for H₂S emissions limited to the Equatorial region instead of our assumed uniform distribution [*Zhang et al.*, 2001; *Hotinski et al.*, 2001; *Kiehl and Shields*, 2005] will have to be pursued in another study. However, it is unclear how, based on our simulations, a concentration of emissions would raise the surface mixing ratio of H₂S (from the simulated 250 ppbv) to toxic levels (considered to be > 10 ppmv) over a significant fraction of the globe, unless emissions were substantially greater than the 5,000 Tg(S)/year considered here.

4. Discussion and Conclusions

[18] In this paper, we use a three-dimensional chemistry-climate model of the troposphere and stratosphere to study the importance of hydrogen sulfide at the Permian-Triassic boundary through two simulations, with present-day and large hydrogen sulfide emissions respectively; the large emissions (5,000 Tg(S)/year) were picked as these are above the threshold for which ozone starts collapsing in the work by *Kump et al.* [2005]. We show that, in our large

emission simulation, the hydrogen sulfide does not produce a stratospheric ozone collapse such as the one described by Kump *et al.* [2005]; also it does not reach surface concentrations that could lead to toxic conditions (considered to be > 10 ppmv). In our high-emission simulation, the hydroxyl radical is always present in sufficient quantities to remove hydrogen sulfide from the troposphere (in addition to wet removal) owing to the regular influx of ozone from the stratosphere. We believe that this different behavior (between Kump *et al.* [2005] and this study) is mostly related to differences in the way transport into and from the stratosphere is handled by the respective models and, to a lesser extent, to differences in the climate state. It is however clear that a sufficiently large H_2S flux will eventually lead to a collapse of OH and the same catastrophic behavior as in KPA. In our model, these fluxes were not reached in the experiments described here and are associated with values of the H_2S flux that seem unreasonably high; indeed, a short additional experiment with our models indicate that this flux would have to be larger than 10,000 Tg(S)/year.

[19] More importantly, as can be also seen in work by Kump *et al.* [2005, Figure 1c], the significant decrease in tropospheric OH from large H_2S emissions increases the atmospheric methane lifetime; for any methane surface flux (S), an increase in its lifetime (τ) directly translates into a commensurate increase in the steady-state methane burden (B) as $B = S * \tau$. Consequently, the impact of a methane flux becomes amplified, by at least an order of magnitude in the 5000 Tg(S)/year hydrogen sulfide flux case and likely more for even larger fluxes. In a separate study [Lamarque *et al.*, 2006] with the same model (focusing on methane only and therefore without H_2S emissions), we have shown that a large increase of tropospheric methane (of at least 2500 times the pre-industrial surface concentration, corresponding to a direct injection of approximately 3900 Gt(C) (from the destabilization of methane clathrates [Dickens *et al.*, 1995], hydrothermal vent complexes [Svensen *et al.*, 2004] or Siberian traps [Wignall, 2001]) leads to a very large stratospheric ozone depletion; this depletion is due to an increase in water vapor (from methane photochemistry) in the middle and upper stratosphere, with additional ozone loss from OH and HO_2 chemistry in the lower stratosphere. Large emissions of H_2S (with their impact on the methane lifetime) can therefore increase the likelihood of a methane-driven ozone collapse by decreasing by more than one order of magnitude the amount of methane flux necessary for large ozone destruction. Consequently, the combined emissions of hydrogen sulfide and methane are much more likely to lead to a cataclysmic ozone destruction than in the case of methane or hydrogen sulfide emissions alone; the associated increase in UV-B [Lamarque *et al.*, 2006] provides a possible explanation for the Permian-Triassic boundary mass extinction [Erwin, 1994].

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