

Dear Dr. Kasting,

Thank you very much for the helpful review. We have addressed your comments individually below.

It would be useful if they surveyed the literature a bit more carefully and pointed out which, if any, of their greenhouse gases are predicted to have been present in published models of the early atmosphere. Haqq-Misra et al. (2008), referenced in the proposal, suggest that CO₂, H₂O, CH₄, and C₂H₆ could all have been quantitatively important during the Late Archean. Did these authors miss anything? It should not take long to figure out the answer.

We have expanded our review of the literature. The following has been added to the text:

“NH₃ was proposed as a solution to the FYSP soon after the problem was posed (Sagan and Mullen, 1972). NH₃ is a strong greenhouse gas and concentrations of 10 ppmv could have warmed the Archean surface by 12-15 K (Kuhn and Atreya, 1979). At the time NH₃ was proposed as a solution, it was thought that the early Earth was strongly reducing such that NH₃ could have built up to significant atmospheric concentrations. However, the Archean atmosphere is now thought to have been only mildly reducing. NH₃ would likely have photo-dissociated rapidly without UV protection (Kuhn and Atreya, 1979; Kasting, 1982). Furthermore, NH₃ is highly soluble and would have been susceptible to rain-out. Therefore, sustaining atmospheric concentrations of NH₃ at which there is significant absorption may not be as easy as originally thought. Considering the destruction of NH₃ by photolysis, Kasting (1982) found that concentrations as high as 10 ppbv could plausibly be attained by biotic sources. If NH₃ were shielded from UV radiation (by a possible organic haze layer) larger concentrations could be sustained, though concentrations above 1 ppbv seem unlikely (Pavlov et al., 2000).

....

C₂H₆ has been suggested to have been radiatively important in the Archean because it can form in significant concentrations from the photolysis of CH₄ at high partial pressures (Haqq-Misra, 2008). Haqq-Misra et al. (2008) find that 1 ppmv of C₂H₆ could increase the surface temp by ~2 K, and 10 ppmv by ~10 K. However, C₂H₆ is formed along with other organic compounds which form an organic haze. This organic haze is thought to provide a strong anti-greenhouse effect which limits the utility of C₂H₆ to warm the climate when produced in this manner.

Elevated OCS concentrations were proposed by Ueno (2009) to explain the negative Δ³³S observed in the Archean sulfate deposits. However, Hattori (2011) report measurements of ultraviolet OCS absorption cross-sections and find that OCS photolysis does not cause large mass independent fractionation in Δ³³S and is therefore not the source of the signatures seen in the geologic record.

Buick (2007) proposed that large amounts of N₂O could have been produced in the Proterozoic due to bacterial denitrification in copper depleted water, because copper is needed in the enzymatic production of N₂ from N₂O (which is the last step of denitrification). Roberson et al., (2011) find that increasing N₂O from 3x10⁻⁷ to 3x10⁻⁵ warms surface temperatures by ~8 K. However, Roberson et al., (2011) also show that N₂O would be rapidly photo-dissociated if O₂ levels were lower than 0.1~PAL and that N₂O was unlikely to have been radiatively important at O₂ levels below this.”

1. (Abstract) **“For CO₂ to resolve the FYSP alone, 0.21 bar is needed with 0.5 bar of atmospheric pressure, 0.13 bar with 1 bar of atmospheric pressures, or 0.07 bar with 2 bar of atmospheric pressure.” –At what time do these estimates apply? From reading the rest of the paper, the answer is 2.8 Ga, and the solar luminosity is 80% of present, but this info should accompany these results in the abstract.**

We have amended the abstract thus: “For CO₂ to resolve the FYSP alone at 2.8 Gyr BP (80% of present solar luminosity), 0.21 bar is needed with 0.5 bar...”

2. (p. 2015) **“Increasing pressure increases the moist adiabatic lapse rate.” –Say why. I presume this is because it pushes the lapse rate closer to the dry adiabat. This is not really a pressure effect, though; rather, it’s a dilution effect.**

Correct. The lapse rate is proportional to the mixing ratio of water vapour and dry air. The lapse rate increases with a decreasing mixing ratio and is a maximum for a mixing ratio of zero which is the dry adiabat. We have clarified this in the text by adding:

Increasing pressure increases the moist adiabatic lapse rate. The moist adiabatic lapse rate is a function of the saturation mixing ratio of water vapour. The saturation vapour pressure is independent of pressure. Increasing pressure means there is more dry air to absorb the latent heat released by condensation, making the moist adiabatic lapse rate larger (closer to the dry adiabatic lapse rate).

3. (p. 2021) **“...given that there is near-complete absence of evidence of glaciation during the Archean” –This is not really true. Evidence for the oldest glaciation occurs at 2.9 Ga in the Pongola Supergroup in S. Africa (Young et al., J. Geol., 1998). Later, 2.7 Ga glacial rocks are found in the Dharwar Supergroup, India (Ojakangas et al., Current Science, 2014). Given the sparse nature of the rock record during this time, it may not be surprising that few glaciations are recorded. This doesn’t necessarily mean that the Archean climate was warm.**

We may have overstated this point. We have revised this to:

“Glaciations appear rare in the Archean (Young, 1991), thus, it is expected that surface temperatures were likely as warm as today for much of the Archean. Therefore, modern day surface temperatures are a reasonable assumption for our profile.”

4. (p. 2022) **“If the stratosphere is optically thin and heated by upwelling radiation, it will be isothermal at the atmospheric skin temperature...” –The authors cite Pierrehumbert’s 2010 book to back up this statement. But Leconte et al. (Nature, 2013) cite Pierrehumbert as saying something quite different: upper atmospheres can be well below the grey gas skin temperature if they are non-grey. Which statement is correct? I’m almost sure it is the latter.**

For non-grey gases the skin temperature can be warmer or colder than the grey gas skin temperature depending on the positioning of absorption bands (pg 289-291, Pierrehumbert). We have clarified that this would be the grey gas skin temperature.

“For a grey gas, an optically thin stratosphere heated by upwelling radiation will be isothermal at the atmospheric skin temperature ($T=(I(1-\alpha)/8\sigma)^{1/4} \sim 203$ K, Pierrehumbert 2010). We take this to be the case in our calculations. In reality, non-grey gases can give a warmer or cooler stratosphere depending on the spectral positioning of the absorption lines. Furthermore, the stratosphere would not have been optically thin, as CO₂ (and possibly other gases) were likely optically thick for some wavelengths, which would have cooled the stratosphere.”

5. (p. 2024) “Large increases in CO₂...result in a cooling of the troposphere...” –This statement does not make sense. Do you mean the upper troposphere, the stratosphere, or what? The lower troposphere should be warmed by increases in CO₂.

Corrected, should be stratosphere.

6. The units ‘ppv’ are used for gas concentrations throughout the manuscript. I’m unfamiliar with this notation, although it is obvious what is meant. Does this stand for “parts per volume”? ‘ppmv’ makes sense, but ‘ppv’ does not.

In retrospect this is a confusing and ill-defined unit. We have replaced the use of 'ppv' throughout the manuscript with the unit-less abundance. We describe this unit in the text as follows:

Gas amounts are given in abundances, a , relative to the modern atmosphere (1 bar, molecular weight of 28.97 g/moles, total moles (n_0) of $\sim 1.8 \times 10^{20}$). Thus, $a = n_{gas}/n_0$. As an example, an abundance of 1 for CO₂ contains the same number of moles as the modern atmosphere but would give a surface pressure larger than 1 bar because of the higher molecular weight. For our experiments we add gas abundances to background N₂ partial pressure, increasing the atmospheric pressure.

7. (p. 2027) The authors mention the near-IR absorption by CH₄ and point out that it leads to surface cooling at high enough mixing ratios. But they fail to mention that high CH₄:CO₂ ratios lead to organic haze formation in low-O₂ atmospheres, and this leads to even greater cooling. The problem of haze formation should be mentioned.

We have included some discussion of this in the text:

“These calculations do not consider the products of atmospheric chemistry. Numerous studies have found that high CH₄:CO₂ ratios lead to the formation of organic haze in low O₂ atmospheres which exerts an anti-greenhouse effect (Kasting, 1983, Zahnle, 1986, Pavlov, 2000, Haqq-Misra, 2008). Organic haze has been predicted by photochemical modelling at CH₄:CO₂ ratios larger than 1 (Zahnle, 1986), and laboratory experiments have found that organic haze could form at CH₄:CO₂ ratios as low as 0.2-0.3 (Trainer et al, 2004, 2006).”