

The Pennsylvania State University  
The Graduate School  
College of Earth and Mineral Sciences

**GREENHOUSE WARMING BY NITROUS OXIDE AND METHANE IN THE  
PROTEROZOIC EON**

A Thesis in  
Geosciences

by

April L. Roberson

© 2011 April L. Roberson

Submitted in Partial Fulfillment  
of the Requirements  
for the Degree of

Master of Science

August 2011

The thesis of April L. Roberson was reviewed and approved\* by the following:

James F. Kasting  
Distinguished Professor of Geosciences and Meteorology  
Thesis Adviser

Lee R. Kump  
Professor of Geosciences

Jerry Y. Harrington  
Associate Professor of Meteorology

Chris J. Marone  
Department Head and Professor of Geosciences

\*Signatures are on file in the Graduate School.

## ABSTRACT

An anoxic, sulfidic ocean that may have existed during the Proterozoic Eon (0.54-2.4 Ga) would have had limited trace metal abundances because of the low solubility of metal sulfides. The lack of copper, in particular, could have had a significant impact on marine denitrification. Copper is needed for the enzyme that controls the final step of denitrification, from  $\text{N}_2\text{O}$  to  $\text{N}_2$ . Today, only about 5-6 percent of denitrification results in release of  $\text{N}_2\text{O}$ . If all denitrification stopped at  $\text{N}_2\text{O}$  during the Proterozoic, the  $\text{N}_2\text{O}$  flux could have been 15-20 times higher than today, producing  $\text{N}_2\text{O}$  concentrations of several ppmv.  $\text{CH}_4$  concentrations may also have been elevated during this time, as has been previously suggested. A lack of dissolved  $\text{O}_2$  and sulfate in the deep ocean should have produced a high methane flux from marine sediments, as much as 10-20 times today's methane flux from land. Climate and photochemical modeling show that the combined greenhouse effect of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  could have provided ~10 degrees of warming, thereby keeping the surface warm during the Proterozoic without necessitating high  $\text{CO}_2$  levels. A second oxygenation event near the end of the Proterozoic would have resulted in a reductions of both atmospheric  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , perhaps triggering the Neoproterozoic "Snowball Earth" glaciations.

## TABLE OF CONTENTS

List of Figures.....	v
Acknowledgements.....	vi
Chapter 1. INTRODUCTION.....	1
The Proterozoic marine nitrogen cycle and the flux of N <sub>2</sub> O.....	2
Model Description.....	4
<i>1-D climate model</i> .....	4
<i>1-D photochemical model</i> .....	6
Chapter 2. RESULTS.....	7
Discussion.....	10
Conclusion.....	13
Appendix: .....	14
References.....	17

## List of Figures

Figure 1.....	3
Simplified view of the marine nitrogen cycle, showing the nitrification and denitrification pathways. The denitrification pathway has two possible paths, leading to N <sub>2</sub> O and N <sub>2</sub> . Copper is needed for the enzyme NOS in the N <sub>2</sub> pathway.	
Figure 2 .....	7
Global mean surface temperature as a function of methane abundance. The two solid curves represent climate model calculations for two solar luminosities: 83% and 94% of present value S <sub>0</sub> . The CO <sub>2</sub> concentration is fixed at 320 ppmv.	
Figure 3 .....	8
Global mean surface temperature as a function of nitrous oxide abundance for two different CH <sub>4</sub> concentrations, 1.6 ppmv (panel ‘a’) and 100 ppmv (panel ‘b’). Other parameters are the same as in Figure 2.	
Figure 4.....	9
N <sub>2</sub> O volume mixing ratio as a function of N <sub>2</sub> O flux (relative to today’s value). Calculations were performed for different O <sub>2</sub> mixing ratios: 0.01, 0.1, and 1 PAL (present atmospheric level). The present N <sub>2</sub> O concentration is shown for comparison.	
Figure 5.....	10
Calculated N <sub>2</sub> O mixing ratio profiles for different O <sub>2</sub> levels. The N <sub>2</sub> O flux is assumed to be 10 times the present N <sub>2</sub> O flux.	
Figure 6.....	11
Global mean surface temperature as a function of carbon dioxide abundance. The two solid curves represent climate model calculations for two solar luminosities: 83% and 94% of present value S <sub>0</sub> . The N <sub>2</sub> O and CH <sub>4</sub> concentrations are fixed at 1 ppm and 100 ppm, respectively.	
Figure A1.....	14
Calculated temperature profiles for 94% solar luminosity. Calculations were performed for fN <sub>2</sub> O = 0 ppmv and fN <sub>2</sub> O = 30 ppmv, with fCH <sub>4</sub> fixed at 100 ppmv.	
Figure A2.....	15
Radiative Forcing of N <sub>2</sub> O vs. N <sub>2</sub> O mixing ratio (ppmv) calculated using our climate model and the IPCC formula. The solar constant is set at present solar luminosity and CH <sub>4</sub> is shown at 0 ppmv (panel ‘a’) and 100 ppmv (panel ‘b’).	
Figure A3.....	16
Radiative Forcing of CH <sub>4</sub> vs. CH <sub>4</sub> mixing ratio (ppmv) calculated using our climate model and the IPCC formula. The solar constant is set at present solar luminosity and N <sub>2</sub> O is fixed at 0 ppmv.	
Figure A4.....	16
Radiative Forcing of CH <sub>4</sub> vs. CH <sub>4</sub> mixing ratio (ppmv) calculated using our climate model and the IPCC formula. The solar constant is set at 86% present solar luminosity and N <sub>2</sub> O is fixed at 0.3 ppmv.	

## Acknowledgements

- ▶ Funding by:
  - NASA Astrobiology Institute
  - Exobiology Program
  - Ohmoto Graduate Fellowship in Geosciences
  - And smaller contributions from: Krynine award & Chevron Travel Award for Fall AGU
  
- ▶ Thanks to: Jim Kasting, Lee Kump, Jerry Harrington, Itay Halevy, Janis Roadt, Ravikumar Kopparapu, Jacob Haqq-Misra, Jamie Brainard
  
- ▶ I would like to thank Kenneth Riddile for his unwavering support and encouragement throughout this entire project.

## Chapter 1: INTRODUCTION

The Proterozoic Eon appears to have been a time of warmth, based on the absence of evidence for glaciation for almost a billion and a half years, from 2.2 Ga to 0.75 Ga (Crowell, 1999). This is surprising, taken at face value, as the Sun was some 17 percent dimmer at the beginning of the Proterozoic and still 5 percent dimmer at its end (Gough, 1981). Greenhouse warming by CO<sub>2</sub> and H<sub>2</sub>O could conceivably have compensated for the faint Sun and kept the climate warm if CO<sub>2</sub> concentrations were sufficiently high, 30-300 PAL (Kasting, 1987; von Paris et al., 2008). ('PAL' means times the Present Atmospheric Level, here taken to be 300 ppmv, or  $3 \times 10^{-4}$  bar.) However, data from paleosols (Sheldon, 2006) and from the degree of calcification of cyanobacterial sheaths (Kah and Riding, 2007) suggest that atmospheric CO<sub>2</sub> concentrations may have been only 10-20 PAL during much of this time. The paleosol data can be disputed (see Discussion), but the calcification data, if correctly interpreted, limit CO<sub>2</sub> concentrations to 10 PAL at 1.2 Ga. With this in mind, additional warming from other greenhouse gases or from changes in planetary albedo would have been needed to keep the climate warm.

Methane, CH<sub>4</sub>, has already been suggested to have been an important greenhouse gas during the Proterozoic (Schrag et al., 2002; Pavlov et al., 2003). Schrag et al. were concerned primarily about triggering of Snowball Earth episodes near the end of this time interval. Their proposed mechanism of clathrate formation and destruction might have yielded transient increases in atmospheric CH<sub>4</sub> near the end of the Mesoproterozoic, but the estimated CH<sub>4</sub> fluxes appear to have been rather small (Pavlov et al., 2003). By contrast, Pavlov et al. suggested that high surface CH<sub>4</sub> fluxes (10-20 times present) and even higher atmospheric CH<sub>4</sub> concentrations (up to 100 ppmv) could have been maintained continuously throughout the Mesoproterozoic. (The present atmospheric CH<sub>4</sub> concentration is 1.6 ppmv, and the present CH<sub>4</sub> flux is ~600 Tg(CH<sub>4</sub>)/yr (Prather et al., 2001)). Their argument was based on an

analysis of organic matter decomposition in marine sediments. Today, most organic matter decomposes either by aerobic respiration, denitrification, or dissimilatory iron, manganese, and sulfate reduction within tens of centimeters of the sediment-water interface. Some organic matter that is buried even more deeply decays by fermentation and methanogenesis, with subsequent release of CH<sub>4</sub>; however, little or no CH<sub>4</sub> makes its way into the ocean because it is consumed either by aerobic methanotrophs or by methane-oxidizing Archaea that live in consortia with sulfate reducing bacteria (Hinrichs, 1999). The absence of aerobic methanotrophs from the Proterozoic ocean, combined with the smaller amount of available sulfate (Hurtgen et al., 2002), may have allowed higher fluxes of CH<sub>4</sub> to the atmosphere. This said, it is unclear that the rate of CH<sub>4</sub> production was high enough to maintain these high fluxes, given that in the absence of atmospheric O<sub>2</sub> the oxic degradation of organic matter that appears to be necessary for some methanogens would have been absent (Shoemaker and Schrag, 2010). Overall, the favorable conditions for high CH<sub>4</sub> fluxes to the atmosphere justify testing its effect on climate. Unfortunately, the climate calculations of Pavlov et al. (2003) have been shown to be incorrect, as a consequence of an error in the CH<sub>4</sub> absorption coefficients, later described and resolved by Haqq-Misra et al. (2008). We demonstrate here that their calculated surface warming from CH<sub>4</sub> was too high by a factor of ~2. Some of this warming may be recovered, however, by considering the effect of nitrous oxide, N<sub>2</sub>O, which was not included in the model of Pavlov et al.

### **The Proterozoic marine nitrogen cycle and the flux of N<sub>2</sub>O**

With the rise of atmospheric oxygen at 2.4 Ga (Holland, 2006), the ocean chemistry may have begun shifting from the anoxic, iron-rich waters of the Archean to the chemically stratified and euxinic oceans of the Proterozoic (Canfield, 1998; Anbar and Knoll, 2002). Sulfate produced from oxidative weathering of sulfide minerals on the continents was reduced in the deep oceans, making them sulfidic. Not all deep ocean basins need to have



followed this same pattern. Holland (2006) argued that at least some ocean basins were oxic, based on the presence of oxidized manganese deposits. The argument that follows requires only that significant portions of the oceans were euxinic.

Widespread anoxia in the Mesoproterozoic oceans should have had a profound influence on the marine nitrogen cycle. According to Fuhrman and Capone (1991), significant amounts of bacterial denitrification occur at oxic-anoxic marine interfaces. The present global rate of denitrification must approximately balance the rate of nitrogen fixation, estimated to be approximately 135 Tg N/yr (Naqvi, 2006). Today, most denitrification proceeds all the way to N<sub>2</sub> (Fig. 1). However, a small fraction of denitrification, about 1/20<sup>th</sup> of the total, stops at N<sub>2</sub>O, creating a global N<sub>2</sub>O flux of about 4-7 Tg N/yr (*ibid.*).

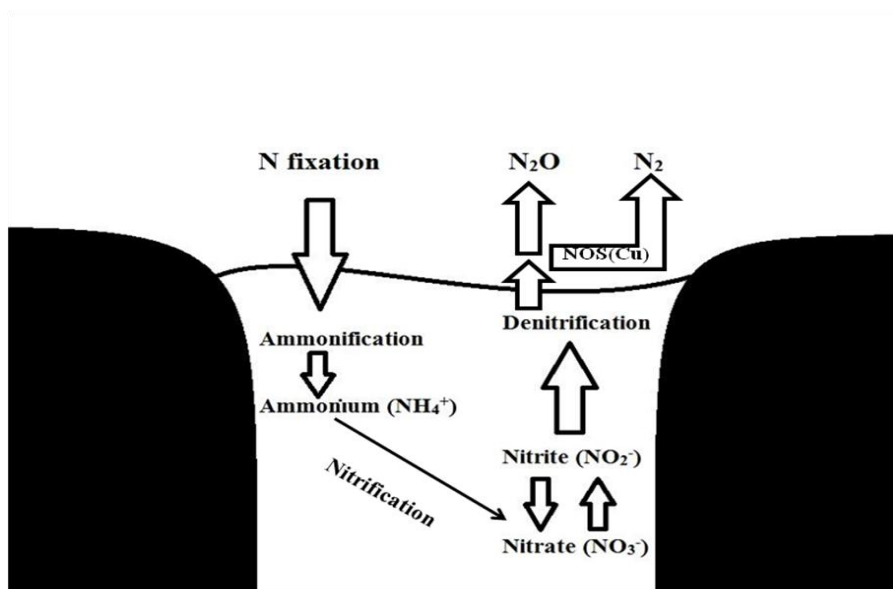


Figure 1: Simplified view of the marine nitrogen cycle, showing the nitrification and denitrification pathways. The denitrification pathway has two possible paths, leading to N<sub>2</sub>O and N<sub>2</sub>. Copper is needed for the enzyme NOS in the N<sub>2</sub> pathway.

Buick (2007) pointed out that the process of denitrification would have been very different during the Proterozoic. The final step of this process is the transition from N<sub>2</sub>O to N<sub>2</sub>, which is

catalyzed by the enzyme NOS. However, the active site for this enzyme contains copper, which complexes strongly with sulfide, and hence would have been severely depleted in the Proterozoic oceans (Saito et al., 2003; Zerkle et al., 2006). In the absence of Cu and NOS, most denitrification may have stopped at N<sub>2</sub>O, creating an N<sub>2</sub>O flux that might have been as much as 20 times that of today.

To support a biological N<sub>2</sub>O flux of this magnitude, the global rate of bacterial nitrogen fixation would need to have been as fast in the Proterozoic as it is today. This was not necessarily the case. Anbar and Knoll (2002) argued that Proterozoic nitrogen fixation rates would have been inhibited by availability of molybdenum, which should also have been impacted by the euxinic Proterozoic oceans. However, unlike the terminal step in the denitrification pathway, which relies solely on copper, nitrogen fixation does not depend on molybdenum alone. Some alternative nitrogenase enzymes (*i.e.*, Fe-only and Fe-V) do not involve Mo at all. These alternative nitrogenase enzymes would have been less severely affected by oceanic euxinia and should therefore have been readily available (Saito et al., 2003). Consequently, even with reduced metal concentrations in the Proterozoic oceans, nitrogen fixation rates could have been close to modern values (Zerkle et al., 2006; Saito et al., 2003).

Below, we explore the possible effect of higher N<sub>2</sub>O and CH<sub>4</sub> fluxes on Proterozoic climate.

## **Model Description**

### *1-D climate model*

For our purposes we use a 1-D, cloud-free, radiative-convective model, which is actually a hybrid of two separate models. The time-stepping procedure and the solar (visible/near-IR) portion of the radiation code are from the model of Pavlov et al. (2000). The code incorporates a  $\delta$  2-stream scattering algorithm (Toon et al., 1989) to calculate fluxes and uses four-term, correlated k-coefficients to parameterize absorption by O<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, and CH<sub>4</sub> in each of 38 spectral intervals (Kasting and Ackerman, 1986). At thermal-IR wavelengths, we use 8-term correlated-k coefficients for CO<sub>2</sub> and H<sub>2</sub>O and 6-term coefficients for CH<sub>4</sub>, as described by Haqq-Misra et al. (2008). The corrected IR subroutine generates radiative fluxes that agree reasonably well with fluxes calculated using the SMART

line-by-line model (*ibid.*). The latest version of our radiative-convective model incorporates 101 atmospheric levels, extending from 1 bar at the surface to  $3 \times 10^{-5}$  bar at altitude. The present model produces slightly greater greenhouse warming for dense atmospheres than our earlier, 25-level models, because of better vertical resolution within the region where the temperature is rapidly changing (Tian et al., 2010).

Clouds are not included explicitly in the model; however, their effect is taken into account implicitly by using an artificially high surface albedo. The surface albedo is obtained by running the model for present Earth conditions and adjusting the albedo until the surface temperature converges to its observed mean value of 288 K. The surface albedo used in these calculations was 0.275. Recently, Goldblatt and Zahnle (2010) analyzed the effect of treating clouds in this manner. They concluded that putting the cloud layer at the surface, as we do, may overestimate the additional warming of other greenhouse gases by as much as 25 percent. The reason is that the 8-12  $\mu\text{m}$  window region is partially blocked by cloud absorption in the real atmosphere; hence, when that region is assumed to be clear, any gaseous absorption in this wavelength region is relatively more important than it would be in reality. The Goldblatt and Zahnle study was performed for dense  $\text{CO}_2$  atmospheres, but their conclusions probably hold for increased  $\text{CH}_4$  and  $\text{N}_2\text{O}$  concentrations as well, as both of these gases absorb partly within the window region. Thus, the greenhouse warming calculated here could be high by as much as 25 percent. This is still smaller than other uncertainties in this problem, and so we simply acknowledge the possible error.

For our current study we added in 6-term, correlated k-coefficients for  $\text{N}_2\text{O}$  at 5 pressures ( $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$ , 0.1, and 1 bar) and 3 temperatures (150, 225, and 300 K) to the climate model. The coefficients were derived from an air-broadened absorption spectrum for  $\text{N}_2\text{O}$ , calculated with a line-by-line radiative transfer model, described in Halevy et al. (2009), and using absorption line parameters from the 2008 HITRAN spectroscopic database

(Rothman et al., 2009). Absorption by the lines was calculated at a spectral resolution of  $0.001 \text{ cm}^{-1}$ , out to a cutoff distance of  $50 \text{ cm}^{-1}$  from line centers, and using the Voigt line shape. We do not account for possible non-Lorentzian behavior of far-wing absorption, though at the abundances of  $\text{N}_2\text{O}$  considered the effect is likely negligible.

### *1-D photochemical model*

The photochemical model, originally developed by Kasting et al. (1985), is more fully described in Pavlov and Kasting (2002). We used the “high- $\text{O}_2$ ” version of the model, which is valid for atmospheric  $\text{O}_2$  concentrations down to about  $10^{-5}$  PAL. Our photochemical model contained 73 chemical species involved in 359 reactions and spanned the region from the planetary surface up to 64 km in 1-km steps. The solar zenith angle was fixed at  $50^\circ$ , and a two-stream approach was used for the radiative transfer (Toon et al., 1989). The combined flux and continuity equations were cast in centered finite difference form and solved at each height for each of the long-lived species, including transport by eddy diffusion only. (Molecular diffusion can be neglected at these altitudes.) Boundary conditions for each species were applied at the top and bottom of the model atmosphere and the resulting set of coupled differential equations was integrated to steady state using the reverse Euler method. Specific boundary conditions used for  $\text{N}_2\text{O}$  are described as they arise in the calculations.

## Chapter 2: RESULTS

We began by repeating the climate calculations for CH<sub>4</sub> published originally by Pavlov et al. (2003). To do this, we allowed fCH<sub>4</sub> to vary from its present value of 1.6 ppmv up to a maximum of 100 ppmv, while holding N<sub>2</sub>O and CO<sub>2</sub> constant at their present concentrations, 0.3 ppmv and 320 ppmv, respectively. (We used 320 ppmv of CO<sub>2</sub> to remain consistent with Pavlov et al. (2003).) Calculations were performed for two different solar luminosities: 83% and 94% of present. These two values correspond to the beginning and the end of the Proterozoic, respectively (Gough, 1981). Results are shown in Figure 2. At either time, an increase in fCH<sub>4</sub> from 1.6 ppmv to 100 ppmv yields about 6 degrees of greenhouse warming—roughly half that calculated with the incorrect model of Pavlov et al. (2003). According to Pavlov et al., this factor of 60 increase in fCH<sub>4</sub> corresponds roughly to a 10-fold increase in the biological methane source, perhaps within the range of plausible values. So, six degrees of greenhouse warming from methane during the Mesoproterozoic seem possible.

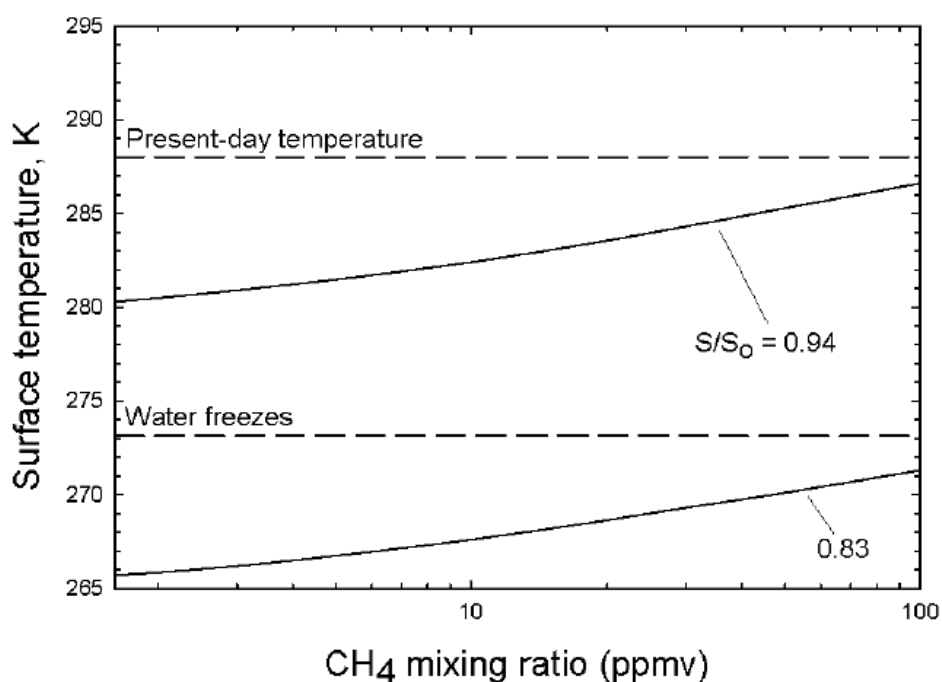


Figure 2: Global mean surface temperature as a function of methane abundance. The two solid curves represent climate model calculations for two solar luminosities: 83% and 94% of present value  $S_0$ . The CO<sub>2</sub> concentration is fixed at 320 ppmv.

Next, we performed similar calculations for N<sub>2</sub>O. In this case we varied N<sub>2</sub>O concentrations from 0.3 to 30 ppm (a factor of 100 increase), while fCH<sub>4</sub> and fCO<sub>2</sub> were held constant at

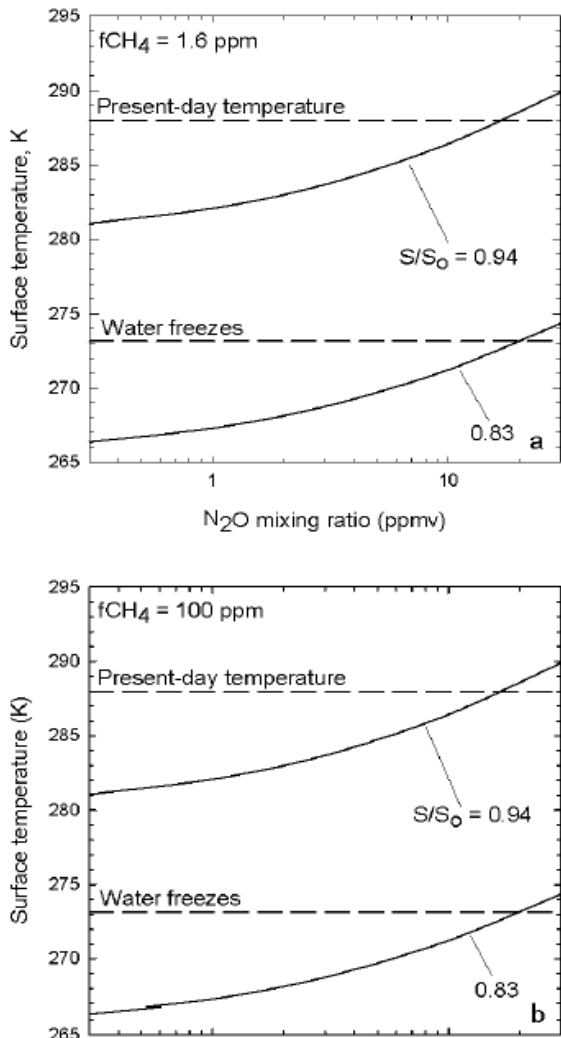


Figure 3: Global mean surface temperature as a function of nitrous oxide abundance for two different CH<sub>4</sub> concentrations, 1.6 ppmv (panel 'a') and 100 ppmv (panel 'b'). Other parameters are the same as in Figure 2.

their present values. N<sub>2</sub>O was assumed to be well mixed with altitude in these calculations. The results are shown in Figure 3a. According to our model, an increase in N<sub>2</sub>O by a factor of 100 would yield about 8 degrees of surface warming. A factor of 60 increase, like that assumed for methane, would yield 6-7 degrees of warming, similar to that from CH<sub>4</sub>. Thus, at identical concentrations, N<sub>2</sub>O is a stronger greenhouse gas when added to a putative Proterozoic atmosphere, but in terms of climate sensitivity (expressed in degrees warming per concentration doubling) CH<sub>4</sub> and N<sub>2</sub>O are equally potent. A more realistic increase in fN<sub>2</sub>O of 10-20 times would have produced 3-5 degrees of warming. This is not enough to make the Proterozoic warm (above modern temperatures) by itself. But when added to the effect of CH<sub>4</sub>, the net warming

is about 10 degrees. Because the absorption bands of CH<sub>4</sub> and N<sub>2</sub>O overlap, we calculated their combined effect explicitly (Figure 3b).

One of the uncertainties in this climate calculation is the atmospheric O<sub>2</sub> concentration. After the so-called Great Oxidation Event (Holland, 2006) at 2.4 Ga, O<sub>2</sub> levels began to rise. However, numerous authors have speculated that the O<sub>2</sub> concentration did not reach the present atmospheric level until near the end of the Proterozoic (see, *e.g.*, Berkner

and Marshall, 1964; Knoll, 1979; Canfield and Teske, 1996). The atmospheric lifetime of methane does not depend strongly on the atmospheric O<sub>2</sub> concentration, for O<sub>2</sub> levels between 0.01 PAL and 1 PAL (Pavlov et al., 2003). But this is not the case for N<sub>2</sub>O. The main photochemical sink for N<sub>2</sub>O is photolysis ( $N_2O + h\nu \rightarrow N_2 + O$ ) at wavelengths shorter than about 230 nm (Kaiser et al., 2003). Those wavelengths are blocked by O<sub>2</sub> (in the Herzberg bands), so as atmospheric O<sub>2</sub> decreases, fN<sub>2</sub>O decreases along with it. This is demonstrated explicitly in Figure 4, which shows fN<sub>2</sub>O as a function of N<sub>2</sub>O flux, relative to today, for three different O<sub>2</sub> levels. The dashed line shows the present N<sub>2</sub>O concentration. Evidently, for N<sub>2</sub>O to have played a significant role in Proterozoic climate, O<sub>2</sub> concentrations must have been greater than 0.1 PAL.

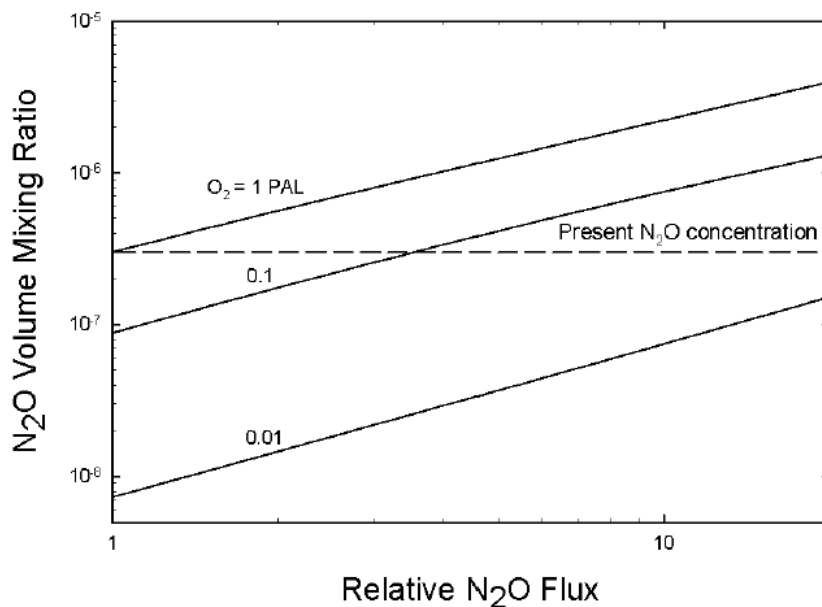


Figure 4 (left): N<sub>2</sub>O volume mixing ratio as a function of N<sub>2</sub>O flux (relative to today's value). Calculations were performed for different O<sub>2</sub> mixing ratios: 0.01, 0.1, and 1 PAL (present atmospheric level). The present N<sub>2</sub>O concentration is shown for comparison.

In Figure 5 we show how N<sub>2</sub>O volume mixing ratio (ppbv) changes with altitude for three different O<sub>2</sub> levels. In our calculations for Figure 3, we assumed N<sub>2</sub>O to be well-mixed throughout the atmosphere. Clearly, this is not the case, and so we need to test whether this assumption biases our climate calculations. To do this, we incorporated the calculated N<sub>2</sub>O vertical profile for the 1-PAL O<sub>2</sub> case into the climate model and performed calculations at 94% present solar luminosity for concentrations of 30 ppmv N<sub>2</sub>O, 1 PAL O<sub>2</sub>, and 1.6 ppmv CH<sub>4</sub>. This calculation was then compared with the result shown in Figure 3a for the same

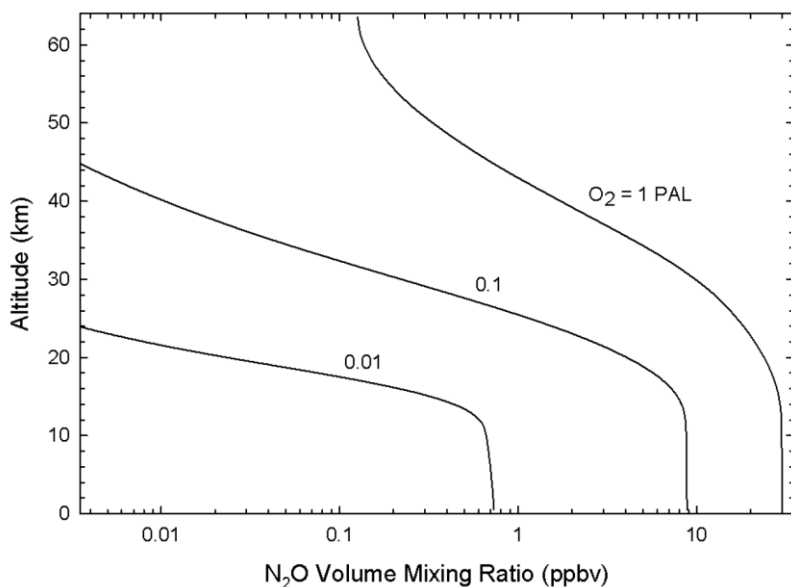


Figure 5: Calculated N<sub>2</sub>O mixing ratio profiles for different O<sub>2</sub> levels. The N<sub>2</sub>O flux is assumed to be 10 times the present N<sub>2</sub>O flux.

case. In Fig. 3a, the 30-ppmv N<sub>2</sub>O case was about 8 degrees warmer than the 0.3-ppmv case (290 K versus 282 K). When the N<sub>2</sub>O mixing ratio was allowed to vary with altitude, the warming for the 30-ppmv case was reduced by 0.1 degrees. Clearly, nearly all of the greenhouse warming from N<sub>2</sub>O is coming from the lowest 20 km of the atmosphere where N<sub>2</sub>O

is well mixed. With such a small difference between the two profiles, we can safely say that it was an acceptable assumption to consider N<sub>2</sub>O to be well-mixed in all of the climate model calculations.

## Discussion

Figures 2 and 3 suggest that CO<sub>2</sub> levels must have been significantly higher than today to produce nonglacial climates. Following Kasting (1987) we assume that nonglacial climates correspond to mean surface temperatures ( $T_s$ ) >293 K. The temperatures shown in Figures 2 and 3 were computed for modern CO<sub>2</sub> levels, and they are almost all below the modern mean surface temperature, 288 K. Additional CO<sub>2</sub> is especially needed during the early Proterozoic when solar luminosity was substantially lower.

Paleosol data indicate that CO<sub>2</sub> concentrations were 20-30 PAL at 2 Ga and 2-3 PAL at 1.2 Ga, with no data available in between (Sheldon, 2006). The quoted error bars on these estimates are roughly a factor of 3 in either direction, so CO<sub>2</sub> levels could have been as high as 100 PAL at the beginning of the Proterozoic and 10 PAL near its end. Even these broader limits may be inaccurate, however. Sheldon's calculations for pCO<sub>2</sub> values come from an



equation originally derived by Holland and Zbinden (1988). Sheldon allows the ratio of the  $\text{CO}_2$  diffusion coefficient in air to that in soil,  $\alpha$ , to vary from 0.1 by plus or minus 20 percent. Holland and Zbinden, however, assign a much larger uncertainty to  $\alpha$ --a factor of 10 in either direction. Holland and Zbinden also assume that the amount of rainfall absorbed by the soil,  $r$ , is 50 cm/yr, or half the globally averaged modern rainfall rate, whereas Sheldon uses  $r = 100$  cm/yr. This makes Sheldon's estimate for  $p\text{CO}_2$  lower by a factor of 2 in cases where percolation of rainwater dominates. Holland and Zbinden, themselves, list the uncertainty in calculated  $p\text{CO}_2$  as being a factor of 10 in either direction (their equation 19). Finally, all of these authors effectively assume that weathering by  $\text{CO}_2$  is 100 percent efficient, that is, that all of the  $\text{CO}_2$  that makes it into the soil results in mineral dissolution. In reality, some of this  $\text{CO}_2$  probably does not react, and hence this equation should yield only a lower limit on  $p\text{CO}_2$ , and a highly uncertain one at that.

If we discount the paleosol constraints on  $p\text{CO}_2$ , there is no difficulty in explaining nonglacial climates. In the Paleoproterozoic, a  $\text{CO}_2$  mixing ratio of  $\sim 0.06$ , combined with 1

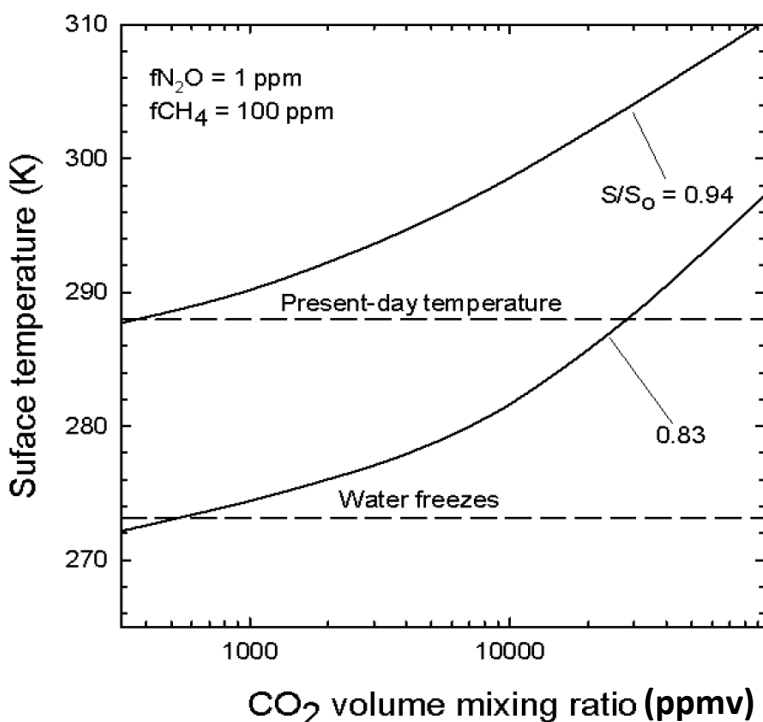


Figure 6: Global mean surface temperature as a function of carbon dioxide abundance. The two solid curves represent climate model calculations for two solar luminosities: 83% and 94% of present value  $S_0$ . The  $\text{N}_2\text{O}$  and  $\text{CH}_4$  concentrations are fixed at 1 ppm and 100 ppm, respectively.

ppmv of  $\text{N}_2\text{O}$  and 100 ppmv of  $\text{CH}_4$ , would have been sufficient to keep  $T_s > 293$  K (Figure 6). In the Late Proterozoic, 3000 ppmv of  $\text{CO}_2$ , along with similar amounts of  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , could have done it. This is below the 10 PAL limit implied by the calcification data (Kah and Riding, 2007). This, of course, does not prove that such  $\text{CO}_2$

concentrations were present, especially as the actual mean surface temperatures are not known, but it shows that self-consistent climate solutions do exist throughout the Proterozoic.

This lack of information about absolute surface temperatures does not prevent us from speculating about what may have happened near the end of this time period. Several studies have suggested that the Earth entered periods of severe glaciations (termed “Snowball Earth” episodes) during the Neoproterozoic (Kirschvink, 1992; Hoffman et al., 1998; Hoffman and Schrag, 2002). The question of what caused these glaciations remains unresolved. Possible triggering mechanisms include CO<sub>2</sub> drawdown (Hoffman et al., 1998; Hoffman and Schrag, 2002) or a sudden decrease in non-CO<sub>2</sub> greenhouse gases (Schrag et al., 2002; Pavlov et al., 2003). In the first hypothesis, CO<sub>2</sub> is assumed to have been drawn down either by increased burial of organic carbon (Hoffman et al., 1998) or by clustering of continents in the tropics, causing enhanced silicate weathering (Hoffman et al., 1998; Marshall et al., 1987; Donnadieu et al., 2004). But if significant continental area existed at all paleolatitudes, as suggested by paleomagnetic data (Hyde et al., 2000; Hoffman and Schrag, 2002), the normal silicate weathering feedback should have operated (Walker et al., 1981), making it difficult to lower CO<sub>2</sub> too far. Thus, reduction of non-CO<sub>2</sub> greenhouse gases—CH<sub>4</sub> and N<sub>2</sub>O, in particular—may well have been the trigger. An increase in atmospheric O<sub>2</sub> in the Neoproterozoic could have caused most of the ocean to become oxic, shutting down the flux of methane from marine sediments and causing denitrification to shift towards N<sub>2</sub> production at the expense of N<sub>2</sub>O. Though it has been recently suggested that there was a rise in atmospheric O<sub>2</sub> as early as about 1.2 Ga (Parnell et al., 2010), most sulfur isotope evidence (e.g. Canfield and Teske, 1996) supports the hypothesis of a marked O<sub>2</sub> rise in the Neoproterozoic. We therefore consider this hypothesis to be a plausible way of triggering Snowball Earth episodes.

## Conclusion

The early Earth managed to avoid global glaciations for much of its history, which is contrary to what we might expect, given the greatly reduced solar luminosity. An intense greenhouse effect must have been existed during the Mesoproterozoic to keep the climate nonglacial. We have shown that both  $\text{N}_2\text{O}$  and  $\text{CH}_4$  could have contributed significantly to this greenhouse. When  $\text{O}_2$  concentrations increased near the end of this time, the euxinic ocean chemistry that may have dominated during much of the Proterozoic would have been transformed into something similar to that in today's oxic oceans. This could have reduced the biogenic fluxes of  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , possibly triggering the Neoproterozoic Snowball Earth glaciations. While the greenhouse contributions from  $\text{N}_2\text{O}$  and  $\text{CH}_4$  can be quantified, the transitions in ocean chemistry that lead to changes in their fluxes could use further clarification. Additional data on Proterozoic  $\text{CO}_2$  concentrations would also be helpful in testing the validity of this hypothesis.

## Appendix

To test the behavior of our 1-D climate model, we computed the change in temperature with altitude for 30 ppmv change in fN<sub>2</sub>O (0-30 ppmv) (Figure A1). As

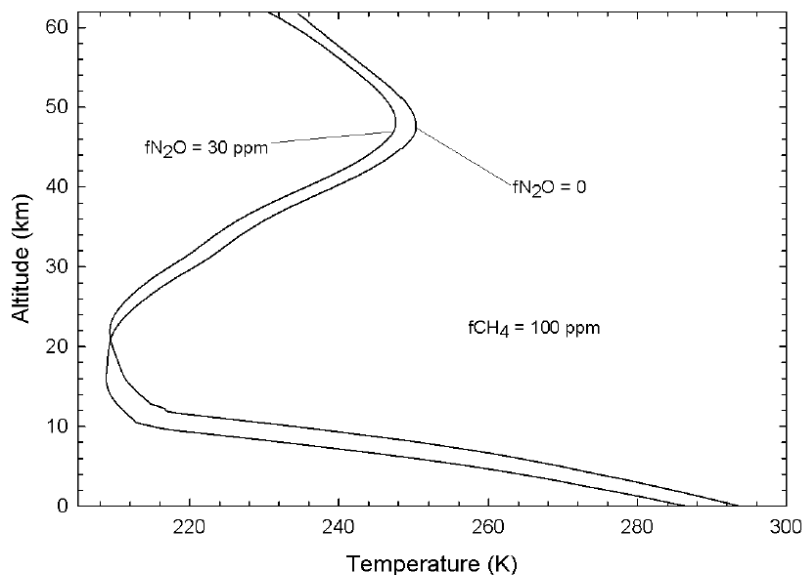


Figure A1: Calculated temperature profiles for 94% solar luminosity. Calculations were performed for fN<sub>2</sub>O = 0 ppmv and fN<sub>2</sub>O = 30 ppmv, with fCH<sub>4</sub> fixed at 100 ppmv.

expected, stratospheric temperatures cooled while the surface temperature warmed. We also compared the radiative forcing of our model to the radiative forcing calculated in

Chapter 6 of the 2001 IPCC report (Ramaswamy et al., 2001). The formulae for N<sub>2</sub>O and CH<sub>4</sub>, respectively,

are as follows:  $\Delta F = \alpha(\sqrt{N} - \sqrt{N_0}) - (f(M_0, N) - f(M_0, N_0))$ ,  $\alpha = 0.12$  and  $\Delta F = \alpha(\sqrt{M} - \sqrt{M_0}) - (f(M, N_0) - f(M_0, N_0))$ ,  $\alpha = 0.036$ , where M is CH<sub>4</sub> in ppb and N is N<sub>2</sub>O in ppb. We used the total infrared flux at the tropopause to measure the net radiative forcing. Calculations were done at present solar luminosity, as well as 0.86 solar luminosity, with fN<sub>2</sub>O = 0.3 ppmv and fCH<sub>4</sub> = 1.6 ppmv, while varying CH<sub>4</sub> and N<sub>2</sub>O concentrations, respectively. Results are shown in Figures A2-A4 (below). In most cases, our model agrees well with the radiative forcing (Wm<sup>-2</sup>) calculated by the 2001 IPCC report. Differences of up to 20% between our results and the IPCC formulae suggest that we may overestimate the greenhouse effects of both N<sub>2</sub>O and CH<sub>4</sub> by approximately this same amount, if the IPCC formulae are correct. Thus, the maximum warming produced by the combination of these gases could be reduced

from 10 K to ~8 K. None of this alters our conclusion that elimination of these gases near the end of the Proterozoic could have led to drastic climate cooling.

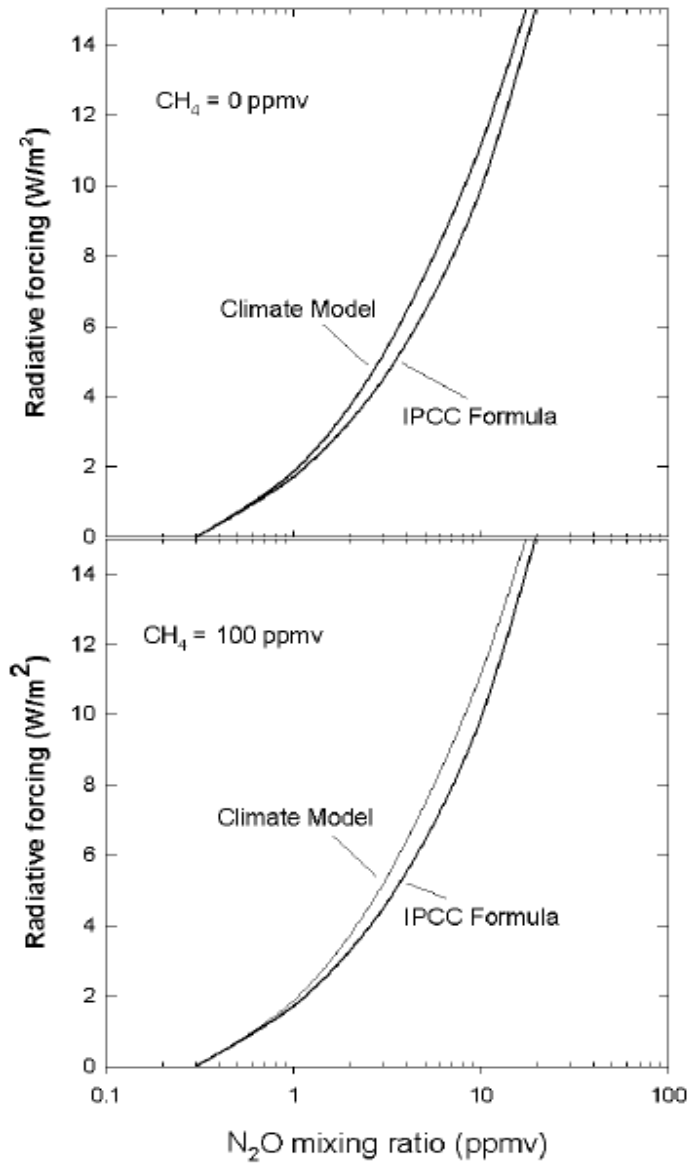


Figure A2: Radiative Forcing of N<sub>2</sub>O vs. N<sub>2</sub>O mixing ratio (ppmv) calculated using our climate model and the IPCC formula. The solar constant is set at present solar luminosity and CH<sub>4</sub> is shown at 0 ppmv (panel 'a') and 100 ppmv (panel 'b').

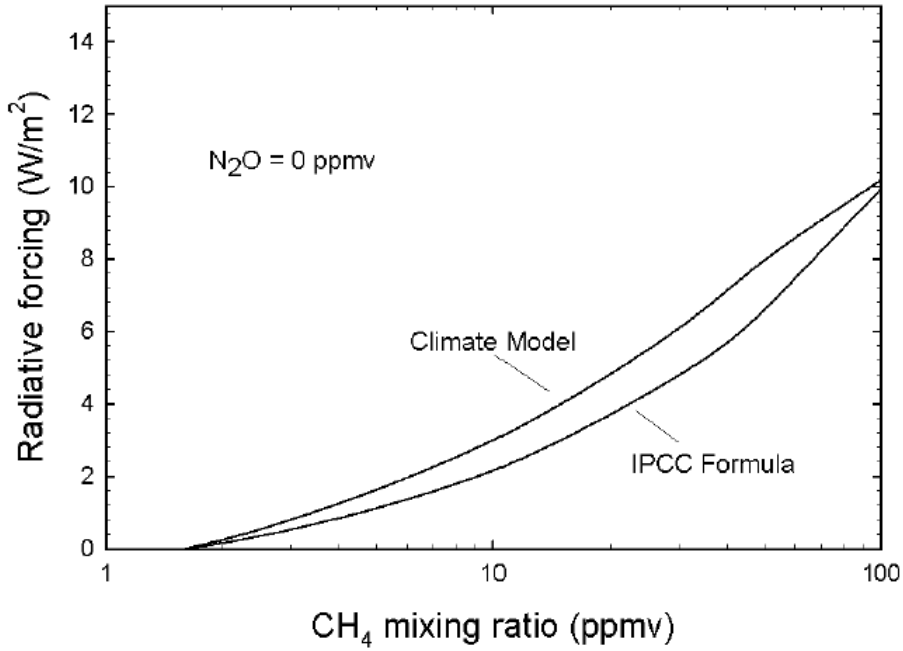


Figure A3: Radiative Forcing of CH<sub>4</sub> vs. CH<sub>4</sub> mixing ratio (ppmv) calculated using our climate model and the IPCC formula. The solar constant is set at present solar luminosity and N<sub>2</sub>O is fixed at 0 ppmv.

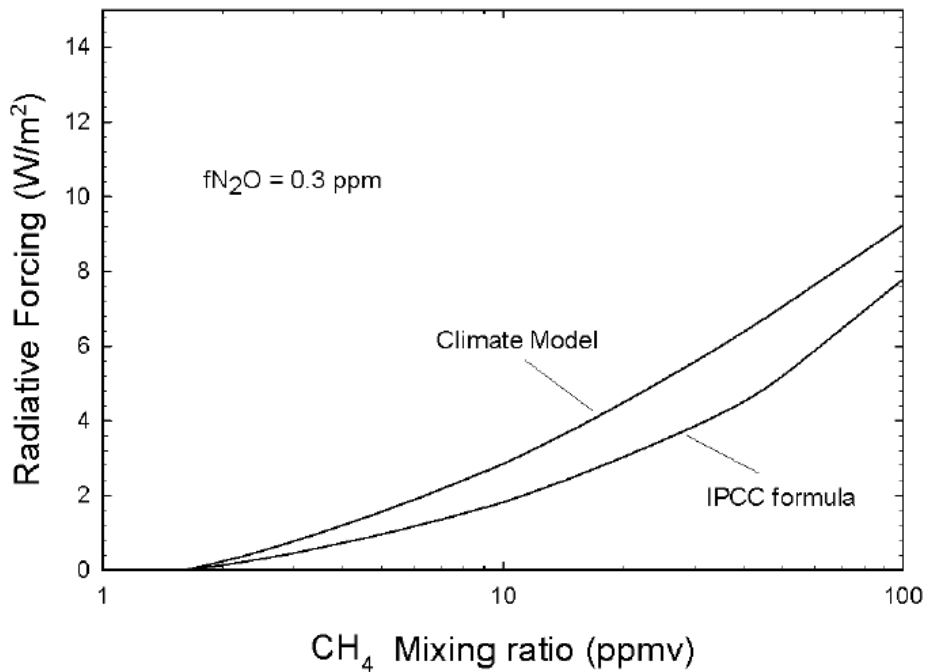


Figure A4: Radiative Forcing of CH<sub>4</sub> vs. CH<sub>4</sub> mixing ratio (ppmv) calculated using our climate model and the IPCC formula. The solar constant is set at 86% present solar luminosity and N<sub>2</sub>O is fixed at 0.3 ppmv.

## References

- Anbar AD, Knoll AH (2002) Proterozoic Ocean Chemistry and Evolution: A Bioinorganic Bridge? *Science*, 297, 1137-1142.
- Berkner LV, Marshall LL (1964) The history of oxygenic concentration in the Earth's atmosphere. *Disc. Faraday Soc.*, 34, 122-141.
- Buick R (2007) Did the Proterozoic 'Canfield Ocean' cause a laughing gas greenhouse? *Geobiology*, 5, 97-100.
- Canfield DE (1998) A new model for Proterozoic ocean chemistry. *Nature*, 396, 450-453.
- Canfield DE, Teske A (1996) Late-Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulfur isotope studies. *Nature*, 382, 127-132.
- Crowell JC (1999) Pre-Mesozoic Ice Ages: Their Bearing on Understanding the Climate System. Boulder, CO: Geological Society of America.
- Donnadieu Y, Godderis Y, Ramstein G (2004) A 'snowball Earth' climate triggered by continental break-up through changes in runoff. *Nature*, 428, 303-306.
- Fuhrman JA, Capone DG (1991) What Controls Phytoplankton Production in Nutrient-Rich Areas of the Open Sea? *Limnology and Oceanography*, 36, 1951-1959.
- Goldblatt C, Zahnle KJ (2010) Clouds and the faint young Sun problem. *Climate of the Past Discussions*, 6, 1163-1207.
- Gough DO (1981) Solar interior structure and luminosity variations. *Solar Phys.*, 74, 21-34.
- Haqq-Misra JD, Domagal-Goldman SD, Kasting PJ, Kasting JF (2008) A Revised, Hazy Methane Greenhouse for the Archean Earth. *Astrobiology*, 8, 1127-1137.

- Halevy I, Pierrehumbert RT, Schrag DP (2009) Radiative transfer in CO<sub>2</sub>-rich paleoatmospheres. *Journal of Geophysical Research* 114, D18112.
- Hinrichs KU, Hayes JM, Sylva SP, Brewer PG, DeLong EF (1999) Methane-consuming archaeobacteria in marine sediments. *Nature*, 398, 802-805.
- Hoffman PF, Kaufman AJ, Halverson GP, Schrag DP (1998) A Neoproterozoic Snowball Earth. *Science*, 281, 1342-1346.
- Hoffman PF, Schrag DP (2002) The Snowball Earth hypothesis: testing the limits of global change. *Terra Nova*, 14, 129-155.
- Holland HD (2006) The oxygenation of the atmosphere and oceans. *Philosophical Transactions of the Royal Society B-Biological Sciences*, 361, 903-915.
- Holland HD, Zbinden EA (1988) Paleosols and the evolution of the atmosphere: Part I. In: *Physical and Chemical Weathering in Geochemical Cycles* [A Lerman, M Meybeck (eds.)], 61-82.
- Hurtgen MT, Arthur MA, Suits N, Kaufman AJ (2002) The sulfur isotopic composition of Neoproterozoic seawater sulfate: implications for a Snowball Earth? *Earth Planet. Sci. Lett.*, 203, 413-429.
- Hyde WT, Crowley TJ, Baum SK, Peltier WR (2000) Neoproterozoic 'snowball Earth' simulations with a coupled climate/ice-sheet model. *Nature*, 405, 425-429.
- Kah LC, Riding R (2007) Mesoproterozoic carbon dioxide levels inferred from calcified cyanobacterial. *Geology*, 35, 799-802.
- Kaiser J, Röckmann T, Brenninkmeijer CAM, Crutzen PJ (2003) Wavelength dependence of isotope fractionation in N<sub>2</sub>O photolysis. *Atmos. Chem. Phys.*, 3, 303-313.



Kasting JF (1987) Theoretical constraints on oxygen and carbon dioxide concentrations in the Precambrian atmosphere. *Precambrian Res.*, 34, 205-229.

Kasting JF, Holland HD, Pinto JP (1985) Oxidant abundances in rainwater and the evolution of atmospheric oxygen. *Journal of Geophysical Research*, 90, 10,497-10,510.

Kasting JF, Ackerman TP (1986) Climatic consequences of very high CO<sub>2</sub> levels in the earth's early atmosphere. *Science*, 234, 1383-1385.

Kirschvink JL (1992) Late Proterozoic low-latitude global glaciation: the snowball Earth. In *The Proterozoic Biosphere: A Multidisciplinary Study*, ed. JW Schopf, C Klein, 51-52.

Cambridge: Cambridge University Press

Knoll AH (1979) Archean photoautotrophy: some alternatives and limits. *Origins of Life*, 9, 313-327.

Marshall HG, Walker JCG, Kuhn WR (1988) Long-term climate change and the geochemical cycle of carbon. *J. Geophys. Res.*, 93, 791-802.

Naqvi, W (2006) Marine Nitrogen Cycle. In: *Encyclopedia of Earth* (ed. Cleveland CJ). Environmental Information Coalition, National Council for Science and the Environment, Washington.

Pavlov AA, Kasting JF, Brown LL, Rages KA, Freedman R (2000) Greenhouse warming by CH<sub>4</sub> in the atmosphere of early Earth. *Journal of Geophysical Research*, 105, 11,981-11,990.

Pavlov AA, Kasting JF (2002) Mass-Independent Fractionation of Sulfur Isotopes in Archean Sediments: Strong Evidence for an Anoxic Archean Atmosphere. *Astrobiology*, 2, 27-41

Pavlov AA, Hurtgen MT, Kasting JF, Arthur MA (2003) Methane-rich Proterozoic atmosphere? *Geology*, 31, 87-90.

Prather M, al. el. 2001. Atmospheric chemistry and greenhouse gases. In *Climate Change 2001: the Scientific Basis*, ed. JT Houghton, e al., pp. 239–88. New York: Cambridge Univ. Press

Ramaswamy V, Boucher O, Haigh J, Hauglustaine D, Haywood J, Myhre G, Nakajima T, Shi GY, Solomon S (2001) Radiative Forcing of Climate Change. In: *Climate Change 2001: The Scientific Basis*. The Contribution of Working Group I to the Third Assessment Report of the International Panel on Climate Change [Joos F, Srinivasan J (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 357-359.

Rosing M, Bird D, Sleep N, Bjerrum C (2010) No climate paradox under the faint early Sun. *Nature*, 464, 744-747.

Rothman LS, Gordon LE, Barbe A, Benner DC, Bernath PF, Birk M, Boudon V, Brown LR, Campargue A, Champion JP, Chance K, Coudert LH, Dana V, Devi VM, Fally S, Flaud JM, Gamache RR, Goldman A, Jacquemart D, Kleiner I, Lacombe N, Lafferty WJ, Mandin JY, Massie ST, Mikhailenko SN, Miller CE, Moazzen-Ahmadi N, Naumenko OV, Nikitin AV, Orphal J, Perevalov VI, Perrin A, Predoi-Cross A, Rinsland CP, Rotger M, Simeckova M, Smith MAH, Sung K, Tashkun SA, Tennyson J, Toth RA, Vandaele AC, Auwera JV (2009) The *HITRAN* 2008 molecular spectroscopic database. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 110, 553-572.

Saito MA, Sigman DM, Morel FMM (2003) The bioinorganic chemistry of the ancient ocean: the co-evolution of cyanobacterial metal requirements and biogeochemical cycles at the Archean-Proterozoic boundary? *Inorganica Chimica Acta*, 356, 308–318.

Schrag DP, Berner RA, Hoffman PF, Halverson GP (2002) On the initiation of a snowball Earth. *Geochem. Geophys. Geosystems*, 3.

Sheldon ND (2006) Precambrian paleosols and atmospheric CO<sub>2</sub> levels. *Precambrian Res.*,

147, 148-155.

Tian, F., M. W. Claire, J. D. Haqq-Misra, M. Smith, D. C. Crisp, D. Catling, K. Zahnle, and J. F. Kasting (2010) Photochemical and climate consequences of sulfur outgassing on early Mars, *Earth Planet. Sci. Lett.*, 295, 412-418.

Toon OB, McKay CP, Ackerman TP, Santhanam K (1989) Rapid calculation of radiative heating rates and photodissociation rates in inhomogeneous multiple scattering atmospheres. *Journal of Geophysical Research*, 94, 16,287-16,301.

von Paris P, Rauer H, Lee Grenfell J, Patzer B, Hedelt P, et al. (2008) Warming the early earth--CO<sub>2</sub> reconsidered. *Planetary and Space Science*, 56, 1244-1259.

Walker JCG, Hays PB, Kasting JF (1981) A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. *J. Geophys. Res.*, 86, 9776-9782.

Zerle AL, House CH, Cox RP, Canfield DE (2006) Metal limitation of cyanobacterial N<sub>2</sub> fixation and implications for the Precambrian nitrogen cycle. *Geobiology*, 4, 285-297.