Greenhouse warming by nitrous oxide and methane in the Proterozoic Eon

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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 N₂O to N₂. Today, only about 5–6% of denitrification results in release of N₂O. If all denitrification stopped at N₂O during the Proterozoic, the N₂O flux could have been 15–20 times higher than today, producing N₂O concentrations of several ppmv, but only if O₂ levels were relatively high (>0.1 PAL). At lower O₂ levels, N₂O is rapidly photodissociated. Methane concentrations may also have been elevated during this time, as has been previously suggested. A lack of dissolved O₂ and sulfate in the deep ocean could have produced a high methane flux from marine sediments, as much as 10–20 times today’s methane flux from land. The photochemical lifetime of CH₄ increases as more CH₄ is added to the atmosphere, so CH₄ concentrations of up to 100 ppmv are possible during this time. The combined greenhouse effect of CH₄ and N₂O could have provided up to 10⁶°C of warming, thereby keeping the surface warm during the Proterozoic without necessitating high CO₂ levels. A second oxygenation event near the end of the Proterozoic would have resulted in a reduction in both atmospheric N₂O and CH₄, perhaps triggering the Neoproterozoic “Snowball Earth” glaciations.

Received 02 February 2011; accepted 31 May 2011

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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% dimmer at the beginning of the Proterozoic and still 5% dimmer at its end (Gough, 1981). Greenhouse warming by CO₂ and H₂O could conceivably have compensated for the faint Sun and kept the climate warm if CO₂ concentrations were sufficiently high, 30–300 PAL (PAL means times the Present Atmospheric Level, here taken to be 300 ppmv, or 3 x 10⁻⁴ bar; Kasting, 1987; von Paris et al., 2008). However, data from paleosols (Sheldon, 2006) and from the degree of calcification of cyanobacterial sheaths (Kah and Riding, 2007) suggest that atmospheric CO₂ concentrations may have been only 10–20 PAL during much of this time. Data from banded iron-formations (BIFs) suggest even lower CO₂ levels during parts of the Precambrian (Rosing et al., 2010). Both the paleosol data and the BIF data can be disputed (see Discussion), but the calcification data, if correctly interpreted, limit CO₂ 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, CH₄, 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 CH₄ near the end of the Mid-Proterozoic, but their estimated CH₄ fluxes are probably too small to have had any significant climate impact (see discussion in Pavlov et al., 2003). By contrast, Pavlov et al. suggested that high surface CH₄ fluxes (10–20 times the present flux of ~600 Tg(CH₄) year⁻¹; Prather and Ehhalt, 2001) and even higher atmospheric CH₄ concentrations (up to 100 ppmv, compared to the present 1.6 ppmv) could have been maintained continuously throughout the Mid-Proterozoic. The (nonlinear) relationship between CH₄ flux and atmospheric concentration in the Pavlov et al. study was based
on detailed photochemical modeling. Their argument for a high Proterozoic CH₄ flux was based on an analysis of organic matter decomposition in marine sediments. Today, most organic matter decomposes either by aerobic respiration or by dissimilatory 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 CH₄; however, little or no CH₄ 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 et al., 1999). The absence of aerobic methanotrophs from the Proterozoic ocean, combined with the smaller amount of available sulfate (Hurtgen et al., 2003), may have allowed higher fluxes of CH₄ to the atmosphere.

This said, it is unclear that the rate of CH₄ production was high enough to maintain these high fluxes, given that in the absence of atmospheric O₂ theoxic degradation of organic matter that appears to be necessary for some methanogens would have been absent (Shoemaker and Schrag, 2010). High Mid-Proterozoic CH₄ fluxes have also been questioned on other grounds. Bjerrum & Canfield (2011, Supp. Info.) argue that marine sediments underlying a low-sulfate, Mid-Proterozoic CH₄ ocean would have produced only about (2–3) × 10⁻¹⁴ mol CH₄ year⁻¹ (320–480 Tg(CH₄) year⁻¹), or about double the preanthropogenic methane flux. Their much lower estimate for CH₄ production from marine sediments is based on sediment modeling work by Habicht et al. (2002). The Habicht et al. model shows that 30–70% of carbon remineralization goes through methanogenesis at the very low (0.2 mM) compared to the present concentration of 28 mM) sulfate concentrations considered typical of the Archean oceans, but that this fraction decreases rapidly at higher sulfate concentrations. The fraction of carbon recycled as methane depends strongly on the organic carbon flux to the sediments, though, and can be as high as 50% even at the ~1 mM sulfate concentrations thought to have been present in the Mid-Proterozoic (Habicht et al., 2002; Fig. 2B). Clearly, if the supply of organic matter to sediments outstrips the supply of sulfate, then sulfate reduction cannot keep up, and the Pavlov et al. argument for high CH₄ production rates stands. Self-consistent, redox-balanced modeling of the Proterozoic carbon and sulfur cycles is needed to resolve the discrepancies between these different models.

Overall, the favorable conditions for high CH₄ 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 CH₄ absorption coefficients, later described and resolved by Haqq-Misra et al. (2008). We demonstrate here that their calculated surface warming from CH₄ was too high by a factor of ~2. Some of this warming may be recovered, however, by considering the effect of nitrous oxide, N₂O, which was not included in the model of Pavlov et al.

THE PROTEROZOIC MARINE NITROGEN CYCLE AND THE FLUX OF N₂O

With the rise of atmospheric oxygen at 2.4 Ga (Holland, 2006), the ocean chemistry would 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 & 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 Mid-Proterozoic oceans should have had a profound influence on the marine nitrogen cycle. According to Fuhrman & 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 year⁻¹ (Naqvi, 2006). Today, most denitrification proceeds all the way to N₂ (Fig. 1). However, a small fraction of denitrification, about one-twentieth of the total, stops at N₂O, creating a global N₂O flux of about 4–7 Tg N year⁻¹ (Naqvi, 2006).

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 N₂O to N₂, which is catalyzed by the nitric oxide synthase (NOS) enzyme. 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 N₂O, creating an N₂O flux that might have been as much as 20 times that of today (Buick, 2007).

Fig. 1 Simplified view of the marine nitrogen cycle, showing the nitrification and denitrification pathways. The denitrification pathway has two possible paths, leading to N₂O and N₂. Copper is needed for the enzyme NOS in the N₂ pathway.
To support a biological $\text{N}_2\text{O}$ 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 & Knoll (2002) argue that Proterozoic nitrogen fixation rates would have been inhibited by the 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 (Saito et al., 2003; Zerkle et al., 2006).

Below, we explore the possible effect of higher $\text{N}_2\text{O}$ and $\text{CH}_4$ 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 6 two-stream scattering algorithm (Toon et al., 1989) to calculate fluxes and uses four-term, correlated $k$ coefficients to parameterize absorption by $\text{O}_3$, $\text{CO}_2$, $\text{H}_2\text{O}$, $\text{O}_2$, and $\text{CH}_4$ in each of 38 spectral intervals (Kasting & Ackerman, 1986). At thermal-IR wavelengths, we use eight-term correlated $k$ coefficients for $\text{CO}_2$ and $\text{H}_2\text{O}$ and six-term coefficients for $\text{CH}_4$, 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 (2008). 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 & 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%. The reason is that the 8–12 µm 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 study of Goldblatt and Zahnle was performed for dense CO$_2$ atmospheres, but their conclusions probably hold for increased CH$_4$ and N$_2$O concentrations as well, as both of these gases absorb partly within the window region. Thus, the greenhouse warming calculated here could be as much as 25% too high. 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 six-term, correlated $k$ coefficients for $\text{N}_2\text{O}$ at five pressures ($10^{-4}$, $10^{-3}$, $10^{-2}$, 0.1, and 1 bar) and three 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 cm$^{-1}$, out to a cutoff distance of 50 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 & 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 $10^{-6}$ 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°, 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 N₂O are described as they arise in the calculations.

RESULTS

We began by repeating the climate calculations for CH₄ published originally by Pavlov et al. (2003). To do this, we allowed fCH₄ to vary from its present value of 1.6 ppmv up to a maximum of 100 ppmv, while holding N₂O and CO₂ constant at their present concentrations, 0.3 and 320 ppmv, respectively. We used 320 ppmv of CO₂ 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 Fig. 2. At either time, an increase in fCH₄ from 1.6 to 100 ppmv yields about 6° 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 fCH₄ corresponds roughly to a 10-fold increase in the biological methane source, perhaps within the range of plausible values. So, 6° of greenhouse warming from methane during the Mid-Proterozoic seem possible.

We then performed similar calculations for N₂O. In this case we varied N₂O concentrations from 0.3 to 30 ppm (a factor of 100 increase), while fCH₄ and fCO₂ were held constant at their present values. N₂O was assumed to be well mixed with altitude in these calculations. The results are shown in Fig. 3A. According to our model, an increase in N₂O by a factor of 100 would yield about 8° of surface warming. A factor of 60 increase, like that assumed for methane, would yield 6–7° of warming, similar to that from CH₄. Thus, at identical concentrations, N₂O 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) CH₄ and N₂O are equally potent. A more realistic increase in fN₂O of 10–20 times would have produced 3–5° of warming. This is not enough to make the Proterozoic warm by itself. But when added to the effect of CH₄, the net warming is about 10°. Because the absorption bands of CH₄ and N₂O overlap, we calculated their combined effect explicitly (Fig. 3B).

One of the uncertainties in this climate calculation is the atmospheric O₂ concentration. After the so-called Great Oxidation Event (Holland, 2006) at 2.4 Ga, O₂ levels began to rise. However, numerous authors have speculated that the O₂ concentration did not reach the present atmospheric level until near the end of the Proterozoic (see, e.g. Berkner & Marshall, 1964; Knoll, 1979; Canfield & Teske, 1996). The atmospheric lifetime of methane does not depend strongly on the atmospheric O₂ concentration, for O₂ levels between 0.01 and 1 PAL (Pavlov et al., 2003), implying that the Proterozoic atmospheric concentration of CH₄ would have depended mostly on the magnitude of its source flux. But this is not the case for N₂O. The main photochemical sink for N₂O is photolysis (N₂O + hv → N₂ + O) at wavelengths shorter than about 230 nm (Kaiser et al., 2003). Those wavelengths are blocked by O₂ (in the Herzberg bands), so as atmospheric O₂ decreases, fN₂O decreases along with it. This is demonstrated explicitly in Fig. 4, which shows fN₂O as a function of N₂O flux, relative to today, for three different O₂ levels. The dashed
line shows the present $N_2O$ concentration. Evidently, for $N_2O$ to have played a significant role in Proterozoic climate, $O_2$ concentrations must have been greater than 0.1 PAL.

In Fig. 5 we show how $N_2O$ volume mixing ratio (ppbv) changes with altitude for three different $O_2$ levels. In our calculations for Fig. 2, we assumed $N_2O$ 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 $N_2O$ vertical profile for the 1 PAL $O_2$ case into the climate model and performed calculations at 94% present solar luminosity for near-surface concentrations of 30 ppmv $N_2O$, 1 PAL $O_2$, and 1.6 ppmv CH$_4$. This calculation was then compared with the result shown in Fig. 2A for the same case. In Fig. 2A, the 30 ppmv $N_2O$ case was about 8°C warmer than the 0.3 ppmv case (290 K vs. 282 K). When the $N_2O$ mixing ratio was allowed to vary with altitude, the warming for the 30 ppmv case was reduced by 0.1°C. Clearly, nearly all of the greenhouse warming from $N_2O$ is coming from the lowest 20 km of the atmosphere where $N_2O$ is well mixed. With such a small difference between the two profiles, we can safely say that it was an acceptable assumption to consider $N_2O$ to be well mixed in all of the climate model calculations.

**DISCUSSION**

Constraints (or lack thereof) on Proterozoic $CO_2$ concentrations

Figures 2 and 3 suggest that $CO_2$ 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 Figs 2 and 3 were computed for modern $CO_2$ levels, and they are almost all below the modern mean surface temperature, 288 K. Additional $CO_2$ is especially needed during the early Proterozoic when solar luminosity was substantially lower.

Paleosol data indicate that $CO_2$ 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 $CO_2$ 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 $pCO_2$ values come from an equation originally derived by Holland & Zbinden (1988). Sheldon allows the ratio of the $CO_2$ diffusion coefficient in air to that in soil, $a$, to vary from 0.1 by ±20%. Holland and Zbinden, however, assign a much larger uncertainty to $a$ – 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$^{-1}$, or half the globally averaged modern rainfall rate, whereas Sheldon uses $r$ = 100 cm year$^{-1}$. This makes Sheldon’s estimate for $pCO_2$ lower by a factor of 2 in cases where percolation of rainwater dominates. Holland and Zbinden themselves list the uncertainty in calculated $pCO_2$ as being a factor of 10 in either direction (their equation 19). Finally, all of these authors effectively assume that weathering by $CO_2$ is 100% efficient, that is, that all of the $CO_2$ that makes it into the soil results in mineral dissolution. In reality, some of this $CO_2$ probably does not react, and hence this equation should yield only a lower limit on $pCO_2$, and a highly uncertain one at that.

Additional, very tight constraints on Precambrian $CO_2$ concentrations have been proposed by Rosing et al. (2010). Their analysis is based on the mineralogy of BIFs. Rosing et al. argue that magnetite (Fe$_3$O$_4$) in BIFs would have been quantitatively converted to siderite (FeCO$_3$) if $pCO_2$ were greater than about 3 PAL, or ~1000 ppmv. BIFs were not deposited...
between 1.8 Ga and 0.8 Ga, so these constraints do not apply directly to the Mid-Proterozoic, which is the time period of interest here. Nevertheless, extremely low CO₂ levels in the Archean and Paleoproterozoic would imply low CO₂ in the Mid-Proterozoic, as well. The Rosing *et al.* argument has been criticized on the grounds that siderite formation was limited by the supply of reductant, i.e. organic matter, and not by the thermodynamics of carbonate formation (Dauphas & Kasting, 2011). Although this argument is not settled, we believe that the Rosing *et al.* pCO₂ limit is invalid.

If we discount the paleosol and BIF constraints on pCO₂, there is no difficulty in explaining nonglacial climates. A CO₂ mixing ratio of ~0.2 and ~0.01 would have sufficed in the early and late Proterozoic, respectively, if CH₄ and N₂O were at their present, low concentrations. In combination with 1 ppmv N₂O and 100 ppmv CH₄, however, a CO₂ mixing ratio of only ~0.06 would have been sufficient to keep *T*ᵣ > 293 K (Fig. 6) during the Paleoproterozoic. In the Late Proterozoic, 3000 ppmv of CO₂, along with similar amounts of N₂O and CH₄, 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 CO₂ 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.

**Snowball Earth initiation in the Neoproterozoic**

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 & Schrag, 2002). The question of what caused these glaciations remains unresolved (for a recent review, see Pierrehumbert *et al.*, 2011). Possible triggering mechanisms include CO₂ drawdown (Hoffman *et al.*, 1998; Hoffman & Schrag, 2002) or a sudden decrease in non-CO₂ greenhouse gases (Schrag *et al.*, 2002; Pavlov *et al.*, 2003). In the first hypothesis, CO₂ 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 (Marshall *et al.*, 1988; Hoffman *et al.*, 1998; Donnadieu *et al.*, 2004). But if significant continental area existed at all paleolatitudes, as suggested by paleomagnetic data (Hyde *et al.*, 2000; Hoffman & Schrag, 2002), the normal silicate weathering feedback should have operated (Walker *et al.*, 1981), making it difficult to lower CO₂ too far. Thus, reduction of non-CO₂ greenhouse gases – CH₄ in particular – may well have been the trigger. The sudden loss of 100 ppmv of CH₄ would result in the loss of ~10 W m⁻² of radiative forcing (Appendix, Fig. S3), causing about 6° of cooling in our climate model (Fig. 2). Pierrehumbert *et al.* (2011) estimate about 12 W m⁻² of radiative forcing for this same CH₄ change – enough, by their estimation, to trigger a Snowball Earth in 3-D climate model simulations. This change in CH₄ could have been precipitated by changes in atmospheric O₂ concentrations. As discussed earlier, an increase in O₂ 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 toward N₂ production at the expense of N₂O. Though it has been recently suggested that there was a rise in atmospheric O₂ as early as about 1.2 Ga (Parnell *et al.*, 2010), most sulfur isotope evidence (e.g. Canfield & Teske, 1996) supports the hypothesis of a marked O₂ rise in the Neoproterozoic. We therefore consider a late Proterozoic rise in oxygen to be a plausible way of triggering Snowball Earth episodes. This hypothesis could be tested by constructing a box model of the Proterozoic carbon cycle and determining whether a perturbation of this nature could explain the marked carbon isotope excursions that occur in Neoproterozoic carbonates (see, e.g. Schrag *et al.*, 2002).

**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 existed during the Mid-Proterozoic to keep the climate nonglacial. We have shown that both N₂O and CH₄ could have contributed to
this greenhouse, although given its probable higher flux and longer lifetime under moderately low O$_2$ conditions, CH$_4$ is by far the more potent of the two. When 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 oceans. This would have reduced the biogenic fluxes of N$_2$O and CH$_4$, possibly triggering the Neoproterozoic Snowball Earth glaciations. While the greenhouse contributions from N$_2$O and 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 CO$_2$ concentrations would also be helpful in testing the validity of this hypothesis.

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**SUPPORTING INFORMATION**

Additional Supporting Information may be found in the online version of this article:

**Fig. S1.** Calculated temperature profiles for 94% solar luminosity. Calculations were performed for NH2O = 0 and 30 ppmv, with fCH4 fixed at 100 ppmv.

**Fig. S2.** Radiative forcing of NH2O vs. N2O mixing ratio (ppmv) calculated using our climate model and the IPCC formula. The solar constant is set at present solar luminosity and CH4 is shown at 0 ppmv (A) and 100 ppmv (B).

**Fig. S3.** Radiative forcing of CH4 vs. CH2 mixing ratio (ppmv) calculated using our climate model and the IPCC formula. The solar constant is set at present solar luminosity and N2O is fixed at 0 ppmv.

**Fig. S4.** Radiative forcing of CH4 vs. CH2 mixing ratio (ppmv) calculated using our climate model and the IPCC formula. The solar constant is set at present solar luminosity and N2O is fixed at 0.3 ppmv.

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**APPENDIX**

To test the behavior of our 1-D climate model, we computed the change in temperature with altitude for 30 ppmv change in fN2O (0–30 ppmv) (Fig. S1). As expected, stratospheric temperatures cooled while the surface temperature warmed. We also compared the radiative forcing (in W m$^{-2}$) of our model to the radiative forcing calculated in Chapter 6 of the 2001 IPCC report (Ramaswamy et al., 2001). The formulae for N2O and CH4, 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 CH4 in ppb and N is N2O 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 fN2O = 0.3 ppmv and fCH4 = 1.6 ppmv, while varying CH4 and N2O concentrations, respectively. Results are shown in Figs S2–S4. In most cases, our model agrees well with the radiative forcing 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 N2O and CH4 by approximately the same amount, if the IPCC formulae are correct. Thus, the maximum warming produced by the combination of these gases near the end of the Proterozoic could have led to drastic climate cooling.