

# Methane-rich Proterozoic atmosphere?

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## ABSTRACT

**Methane mixing ratios of 100–300 ppm in the Proterozoic atmosphere (0.75–2.3 Ga) would have been sufficient to offset the climatic effects of the faint early sun and maintain the warm climate during those ~1.5 b.y. The major argument against this type of the atmosphere is the short atmospheric oxidation time of methane after the first oxygenation event ca. 2.3 Ga. Here we argue that the net methane flux from the oxygen-poor Proterozoic ocean could have been 10–20 times higher than the present total biological methane flux. We demonstrate that increased methane production would have been sufficient to maintain methane concentrations at 100–300 ppm, which would keep the surface warm throughout the Proterozoic without invoking high CO<sub>2</sub> levels (although the CO<sub>2</sub> abundance could have been higher as well). A second oxygenation event at the end of the Proterozoic would have resulted in a decrease of methane flux and could have caused the first Neoproterozoic “snowball” glaciation.**

**Keywords:** methane abundance, Proterozoic climate, atmospheric greenhouse, snowball Earth.

## INTRODUCTION

Decreased solar luminosity in the distant past would have implied a globally glaciated Earth throughout the Archean and Proterozoic, unless the concentrations of atmospheric greenhouse gases were much higher at that time (Owen et al., 1979; Walker et al., 1981; Kasting et al., 1988; Pavlov et al., 2000). Although CO<sub>2</sub> and H<sub>2</sub>O were probably the two dominant greenhouse gases on the prebiotic Earth, methane should have become important as well once life had evolved (Kiehl and Dickinson, 1987; Pavlov et al., 2000). The CH<sub>4</sub> produced by methanogenic bacteria could have accumulated to high concentrations, because the major atmospheric sink of methane (oxidation by OH radical) would have been suppressed in the anoxic Archean atmosphere (Pavlov et al., 2001). Once free oxygen became a major atmospheric constituent (2.1–2.3 Ga), the atmospheric lifetime of methane would have become short, and its abundance should have decreased dramatically. However, the lack of glaciations in the subsequent 1.5 b.y. of Earth history suggests the presence of a strong atmospheric greenhouse effect long after the atmosphere became oxidized. The conventional explanation for the long period of warm climate between 0.75 and 2.3 Ga assumes high levels of CO<sub>2</sub> in an oxidizing Proterozoic atmosphere (Kasting, 1993). Here we argue that if oxygen had increased to lower than the present atmospheric level (PAL) at 2.3 Ga and stayed at the reduced levels in the 0.75–2.3 Ga, methane could still have been a major greenhouse gas, even in the Late Proterozoic.

## PROTEROZOIC OXYGEN CONCENTRATIONS

The evidence for a major transition in the atmospheric oxidation state ca. 2.1–2.3 Ga is now very strong (Holland, 1994; Farquhar et al., 2000, 2001). The absence of mass-independent fractionation in sulfur isotopes in sediments younger than 2.3 Ga (Farquhar et al., 2000)

indicates that the atmospheric oxygen mixing ratio must have increased to at least 21 ppm or higher at that time (Pavlov and Kasting, 2002). Sulfur isotopes do not tell us, however, whether the O<sub>2</sub> concentration was 21 ppm or 21% following the 2.3 Ga event.

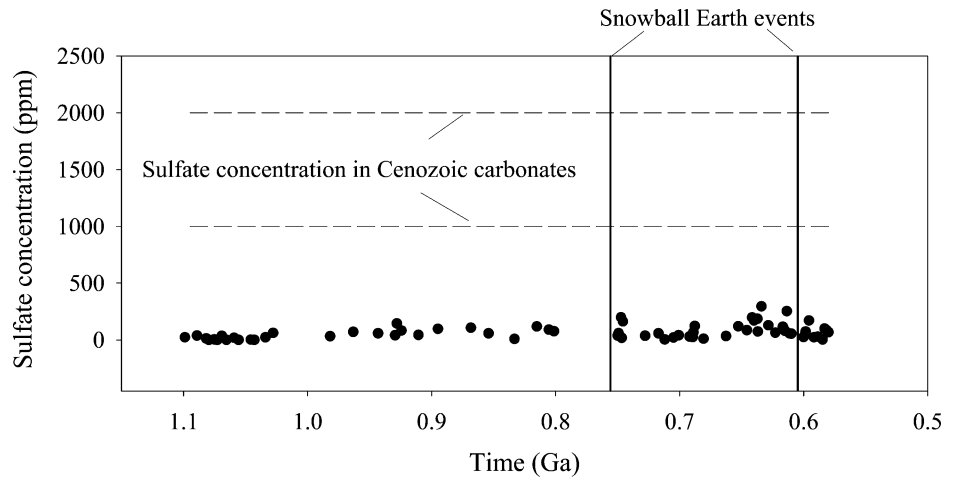
Two indirect arguments suggest that Proterozoic O<sub>2</sub> levels were significantly less than today's concentration. Canfield and Teske (1996) used sedimentary sulfur isotope ratios to argue that *p*O<sub>2</sub> remained below 5%–18% PAL until 0.64–1.05 Ga. They suggested that nonphotosynthetic sulfide-oxidizing bacteria were absent until this time because continental shelf sediments were overlain by anoxic waters. A second line of evidence in favor of low oxygen concentrations during the Proterozoic comes from measurements of trace sulfates in carbonates (Hurtgen et al., 2002). The amount of trace sulfate substituting for the carbonate ion appears to be primarily dictated by the sulfate concentration in the original solution and by the rate of crystal growth (Busenberg and Plummer, 1985). Faster rates of carbonate precipitation and higher amounts of available sulfate lead to increased sulfate substitution into the calcite and aragonite. Figure 1 shows that sulfate concentrations in carbonates (and therefore in ocean water) were an order of magnitude lower during the Proterozoic than at present (Hurtgen et al., 2002). This value agrees with sulfate concentrations inferred from isotopic differences between coexisting sulfates and sulfides and from rapid, temporal  $\delta^{34}\text{S}$  variations in Proterozoic gypsum and anhydrite (Shen et al., 2002; Anbar and Knoll, 2002). Lower oceanic sulfate concentrations imply lower rates of pyrite weathering and, therefore, lower levels of atmospheric oxygen.

## PROTEROZOIC METHANE FLUXES

Given low oxygen abundances in the Proterozoic atmosphere and ocean, the biogenic methane flux into the atmosphere could have been very different from today. In the modern marine ecosystem, more than 90% of the CH<sub>4</sub> produced by methanogens is consumed by methano-

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**Figure 1.** Trace sulfate concentrations of Neoproterozoic carbonates plotted against time in billions of years (data from Hurtgen et al., 2002, and this study). Nearly pure carbonates were collected in Death Valley, California (Crystal Springs and Beck Springs Formations), and Namibia (Rasthoff, Gruis, Ombaatjie, and Maeiberg Formations). Sulfate concentration in carbonates is function of sulfate concentration of ocean water. Sulfate concentrations in carbonates were order of magnitude lower than at present, which implies that oxygen concentrations should also have been lower.



trophic bacteria within the sediments. The efficiency of methane consumption by methanotrophic bacteria depends on oxygen (aerobic methanotrophs) and sulfate (anaerobic methanotrophs) abundance. Experiments on pure cultures of aerobic methanotrophic bacteria (Ren et al., 1997) have shown that oxygen becomes a limiting factor for methane oxidation at a dissolved  $O_2$  concentration of  $5.7 \mu M$ , corresponding to an atmospheric  $O_2$  mixing ratio of 0.45% by volume. The methane consumption decreases dramatically at a mixing ratio of 0.37% oxygen, or  $1.9 \times 10^{-2}$  PAL. Moreover, in the present sulfate-rich ocean, methanogens living in sediments are outcompeted by sulfate reducers and constrained to live in nutrient-poor environments. Methane is also consumed in marine sediments by anaerobic methanotrophs living in consortium with sulfate-reducing bacteria (Hinrichs et al., 1999). If the Proterozoic ocean was anoxic at depth and sulfate poor, as suggested earlier (Canfield and Teske, 1996; Canfield, 1998; Shen et al., 2002), the net flux of methane into the atmosphere could have been significantly higher than today. Here we provide a rough estimate of the Proterozoic methane flux.

We assume that most of the organic carbon ( $CH_2O$ ) was initially produced by photosynthesis:  $CO_2 + H_2O \rightarrow CH_2O + O_2$ . Because  $O_2$  and sulfate were low in the deep ocean, most of the organic carbon exported from the photic zone (net primary productivity, NPP) would have been converted into simpler compounds (e.g., acetate) by fermentation. These compounds would, in turn, have been utilized by methanogens. The overall reaction can be written as  $2CH_2O \rightarrow CH_4 + CO_2$ .

In the anoxic Proterozoic ocean, methanogenesis could have taken place not only in sediments, as it does now, but also in the water column. Opportunities for degradation within the water column were enhanced because organic particles would be expected to sink more slowly if not packaged as fecal pellets (Logan et al., 1995), unless such transport mechanisms as "marine snow" operated effectively (Ransom et al., 1998).

We assume that consumption of methane by methanotrophic bacteria was ineffective in the low-oxygen-sulfate ocean. The fraction of outgassed  $CO_2$  buried as organic carbon in sediments was approximately the same as the modern burial fraction of 20%, as indicated by the near constancy of the  $\delta^{13}C$  content of marine carbonates and kerogens (Des Marais, 1997). This constancy probably reflects limitation by phosphorus availability (Junge et al., 1975). For the  $CO_2$  outgassing rate similar to today's value (which would be a conservative estimate for Proterozoic), the average organic carbon burial rate should have been  $\sim 10^{13}$  mol/yr (Holland, 1978). We further assume that the fraction of NPP buried in sediments,  $f$ , was between the modern value of  $\sim 0.2\%$  (Berner, 1982) and the value of  $\sim 2\%$  (Arthur et al., 1994)

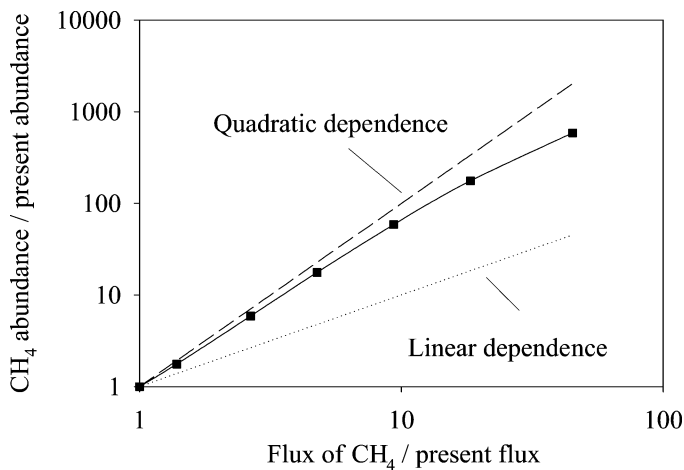
inferred from studies of the anoxic Black Sea. Other factors, such as sediment focusing and high sedimentation rates, may contribute to the higher  $f$  values in the Black Sea (Arthur et al., 1994). However, we take  $f = 2\%$  because this gives us a conservative estimate of the Proterozoic methane flux. If  $f$  was lower than 2%, then the methane flux would have been correspondingly higher.

We can estimate the Proterozoic methane production rate as follows: net primary productivity equals the organic carbon burial rate divided by the burial fraction:  $NPP = BR/f$ . So, for  $f = 2\%$ ,  $NPP = \sim 6 \times 10^{15}$  gC/yr. If half of this goes to methane (see preceding), the resulting  $CH_4$  flux is  $4 \times 10^{15}$  g( $CH_4$ )/yr. By comparison, the total current methane flux from land and sea is  $\sim 5.35 \times 10^{14}$  g( $CH_4$ )/yr (Houghton et al., 1994). So, our estimated Proterozoic flux from marine sediments alone is 7.5 times the modern global  $CH_4$  production rate. If  $f$  was closer to the modern value of 0.2%, then NPP was  $\sim 50 \times 10^{15}$  gC/yr (similar to today's value) and the estimated  $CH_4$  flux is 100 times higher than at present. The reality most likely is between these two estimates. Thus, a  $CH_4$  flux of 10–20 times the modern value in the Proterozoic is reasonable.

### PROTEROZOIC METHANE CONCENTRATIONS

The concentration of  $CH_4$  in the Proterozoic atmosphere would have depended on the biogenic flux and the photochemical lifetime of  $CH_4$  in a low (but not zero)  $O_2$  atmosphere. Previous photochemical calculations (Pavlov and Kasting, 2002; Kasting and Donahue, 1980) have shown that the photochemical lifetime of  $CH_4$  increases slightly as  $pO_2$  drops from 1 PAL to  $10^{-1}$  PAL, then decreases sharply at  $10^{-2}$  PAL  $O_2$ . This counterintuitive behavior is caused by increased production of the hydroxyl radical, OH, by tropospheric  $H_2O$  photolysis as ultraviolet shielding by  $O_3$  is reduced. These calculations, however, were done for a biogenic  $CH_4$  flux equal to the modern value. Previous researchers have also demonstrated that the  $CH_4$  abundance in the present atmosphere is a nonlinear function of its source strength (Thompson and Cicerone, 1986; Prather, 1996). The reason for this behavior is well known:  $CH_4$  is one of the major sinks for OH, and OH is the dominant sink for  $CH_4$ . Thus, the photochemical lifetime of  $CH_4$  increases as its abundance increases.

We explored this nonlinearity using a one-dimensional photochemical model adapted from Kasting et al. (1985) and fully described by Pavlov and Kasting (2002). This model extends from the surface to an altitude of 64 km and contains 34 chemical species that participate in 218 chemical reactions. We began by fixing the atmospheric  $O_2$  concentration at its present value of 21% by volume and increasing the biogenic  $CH_4$  flux from 1 to 100 times its present value. The results of this calculation are shown in Figure 2. Evidently, atmospheric  $CH_4$



**Figure 2. Nonlinear dependence of atmospheric methane abundance vs. methane flux.** For this simulation we assumed oxygen level at 1 present atmospheric level. We normalized Proterozoic methane abundance and flux against their present values. We kept fluxes of other biogenic species ( $H_2$ ,  $CO$ ,  $N_2O$ , and  $CH_3Cl$ ) fixed at their present values.

increases almost quadratically with  $CH_4$  flux throughout this range. More precisely, a 10-fold increase in  $CH_4$  flux resulted in an  $\sim 60$ -fold increase in  $CH_4$  concentration, from 1.6 ppm to nearly 100 ppm.

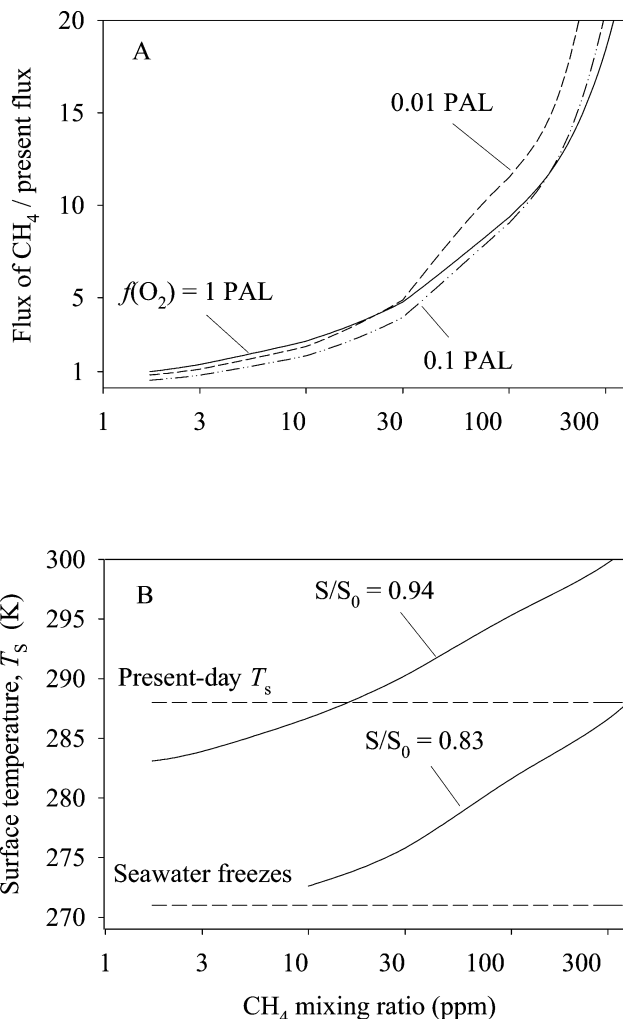
We next performed similar calculations at  $O_2$  concentrations of 0.1 and 0.01 PAL. In doing so we kept the fluxes of other biogenic species ( $H_2$ ,  $CO$ ,  $N_2O$ , and  $CH_3Cl$ ) fixed at their present values. We found that the same nonlinear behavior persists at the lower  $O_2$  levels thought to characterize the Proterozoic atmosphere (Fig. 3A).

To estimate the possible effect of these higher  $CH_4$  levels on surface temperature, we performed calculations using our one-dimensional climate model (Pavlov et al., 2000). The results are shown in Figure 3B. We used solar constants of 0.94 and 0.83 times present, representing the Neoproterozoic (700 Ma) and Paleoproterozoic (2.3 Ga), respectively (Gough, 1981).  $O_2$  does not substantially affect the radiative properties of the atmosphere and was therefore fixed at the present-day level in these calculations. We found that  $<6\%$  decreased solar luminosity, and assuming the present  $CO_2$  level, an increase of methane abundance from 1.7 ppm (present day) to 100 ppm would result in a 12 K increase in surface temperature, from 283 to 295 K. Higher  $CH_4$  concentrations would have been needed to keep the climate warm during the Paleoproterozoic if  $CO_2$  levels were as low as today. In reality, both  $CH_4$  and  $CO_2$  may have been more abundant at that time.

## CONCLUSIONS AND IMPLICATIONS FOR SNOWBALL EARTH

A Proterozoic atmospheric greenhouse bolstered by excess  $CH_4$  could explain why the climate remained ice free for more than 1 b.y. during this interval (2.3–0.75 Ga). This could also be accounted for by enhanced concentrations of atmospheric  $CO_2$ . However, a  $CH_4$  greenhouse effect has the additional advantage of being self-sustaining, because  $CH_4$  participates in a positive feedback loop. The doubling times for thermophilic methanogens are shorter than for mesophilic methanogens (Cooney, 1975); therefore, high temperatures favor increased rates of  $CH_4$  production, which in turn favor high temperatures. By contrast, the main long-term feedback between  $CO_2$  and climate is thought to be negative (Walker et al., 1981).

Our hypothesis also provides a possible mechanism for triggering “snowball” Earth (low-latitude) glaciations at the end of the Proterozoic. Schrag et al. (2002) suggested that a high  $CH_4$  flux from clathrate hydrate decomposition warmed the climate briefly just prior to 0.75



**Figure 3. A: Atmospheric methane concentrations vs. methane flux in Proterozoic atmosphere.** Calculations were performed for different oxygen fractions [ $f(O_2)$ ]: 0.01, 0.1, and 1 PAL (present atmospheric level). For all simulations methane abundance exhibited nonlinear dependence on its source flux. B: Global mean surface temperature ( $T_s$ ) vs. methane abundance. Two curves represent calculations for two solar luminosities: 83% and 94% of present value  $S_0$ .  $CO_2$  has been assumed at preindustrial value of  $\sim 320$  ppm.

Ga. Higher surface temperatures resulted in increased rates of silicate weathering, leading to drawdown of atmospheric  $CO_2$ . When the methane hydrate reservoir became depleted,  $CH_4$  levels dropped, leaving Earth vulnerable to runaway glaciation. To make this mechanism work, however, Schrag et al. assumed a  $CH_4$  lifetime of more than 1000 yr, roughly 100 times longer than the lifetime in the modern atmosphere. We have shown that the  $CH_4$  lifetime increases by a factor of 6 for a 10-fold increase in  $CH_4$  input flux. The proposed flux increase from methane clathrates is much smaller than this. The 12,000 Gt C in  $10^5$  yr, or  $1.6 \times 10^{14}$  g( $CH_4$ )/yr, for their nonlinear model represents only a 30% perturbation to the modern  $CH_4$  flux quoted earlier. Schrag et al. (2002) predicted that this flux increase could have produced an atmospheric  $CH_4$  concentration of 240 ppm, but this result is clearly a consequence of their unrealistically long  $CH_4$  lifetime.

Our model could produce a similar destabilization of climate, without involving methane hydrates, if oceanic dissolved  $O_2$  and sulfate increased just prior to 0.75 Ga, bringing net methane production down to values more like those at present. Unfortunately, there are no sulfate data (Fig. 1) spanning this time interval. Ongoing studies of

trace sulfates with higher time resolution ca. 0.8 Ga will provide a test of this mechanism.

#### ACKNOWLEDGMENTS

We are very grateful to K. Zahnle and D. Catling for valuable discussions. We thank the National Aeronautics and Space Administration Astrobiology Institute for the support of this research.

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Manuscript received July 19, 2002

Revised manuscript received September 17, 2002

Manuscript accepted September 23, 2002

Printed in USA