

# Terrestrial methane fluxes and Proterozoic climate

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## ABSTRACT

**High concentrations of the greenhouse gases CO<sub>2</sub> and CH<sub>4</sub> have long been invoked to explain a largely ice-free climate despite lower solar luminosity during the Precambrian. However, recently a “methane paradox” has emerged, whereby the atmospheric CH<sub>4</sub> abundances required to buffer the Proterozoic climate system are difficult to reproduce in global biogeochemical models. Here, we use a biogeochemical model of a microbial mat ecosystem to examine whether terrestrial cyanobacteria-rich sediments (mats) could have released significant amounts of CH<sub>4</sub> to the atmosphere under the low pO<sub>2</sub> conditions characteristic of most of Precambrian time. We then use these fluxes to inform an Earth system model inversion of the extent of microbial mat coverage on Earth’s land surface that would be required to buffer mid-Proterozoic climate. Terrestrial mats on as little ~8%–10% of the exposed land surface result in a clement climate state. Further, although the photochemical stability of CH<sub>4</sub> in the atmosphere increases as atmospheric oxygen levels rise, methane fluxes from mat ecosystems drop dramatically, suggesting novel links between planetary oxygenation and catastrophic climate instability during the Proterozoic.**

## INTRODUCTION

The mid-Proterozoic Earth (ca. 1.6–1.0 Ga) was apparently characterized by a warm climate state without evidence for glaciation, despite a solar luminosity ~5%–20% lower than the modern value (Gough, 1981). High levels of atmospheric greenhouse gases are conventionally hypothesized to account for this “faint young Sun” paradox (Owen et al., 1979), with carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) assuming a prominent role in models for buffering the mid-Proterozoic climate system (e.g., Pavlov et al., 2003). However, recent proxy reconstructions based on evidence for cyanobacterial carbon-concentrating mechanisms (Kah and Riding, 2007) and paleosol mass balance arguments (Sheldon, 2013) suggest that pCO<sub>2</sub> was <10× the pre-industrial atmospheric level (PIAL) ca. 1.1–1.2 Ga, suggesting a potentially crucial role for alternative greenhouse gases.

Although high CH<sub>4</sub> levels in a low-oxygen ocean-atmosphere system are commonly invoked (e.g., Pavlov et al., 2003), this paradigm has recently been challenged. First, a strong case can be made that reduced rates of productivity and organic carbon burial are required to maintain a low-oxygen atmosphere (Laakso and Schrag, 2014, 2017). Biogenic methane fluxes should drop concordantly with productivity, likely limiting marine methane output (Laakso and Schrag, 2014, 2017). Further, Olson et al. (2016) recently quantified marine fluxes of CH<sub>4</sub> using an intermediate-complexity Earth system model and argued that the biogenic marine CH<sub>4</sub> flux in the

Proterozoic would have been throttled by anaerobic oxidation, similar to what is observed in the modern oceans. The most recent estimates suggest near-modern atmospheric methane concentrations (CH<sub>4</sub> ~1–10 ppmv) at mid-Proterozoic values of pO<sub>2</sub> and oceanic sulfate (Olson et al., 2016; Laakso and Schrag, 2017).

Simulations using the state-of-the-art Community Earth System Model (CESM; <http://www.cesm.ucar.edu>) suggest that CH<sub>4</sub> levels >28 ppmv at 10 PIAL CO<sub>2</sub> are required to prevent ice sheets from expanding beyond ~80° (north/south latitude), and even higher CH<sub>4</sub> levels are required for an ice-free state (Fiorella and Sheldon, 2017). Although other solutions for the faint young Sun paradox have been proposed (e.g., Rosing et al., 2010), they have been questioned (e.g., Goldblatt and Zahnle, 2011) and require additional verification. In this light, a “methane paradox” has emerged: climate models call for elevated atmospheric CH<sub>4</sub> levels while carbon cycle models suggest that these cannot be maintained by the ocean biosphere. Resolving this contradiction is essential for understanding Earth’s climate history and the evolution of atmospheric biosignatures (e.g., Olson et al., 2016; Reinhard et al., 2017).

Here, we explore the possibility that terrestrial microbial ecosystems could have sustained high atmospheric CH<sub>4</sub> levels by supplementing fluxes from the ocean biosphere (Olson et al., 2016). Wetlands are the largest single natural methane source in the modern global methane cycle, despite occupying a land area of only ~3%–6% (Mitra et al., 2005), and account for ~60%–80% of natural CH<sub>4</sub> release (IPCC, 2013)

despite the fact that >90% of the methane generated in wetlands ecosystems is estimated to be consumed by aerobic methanotrophic bacteria before emission (Frenzel et al., 1990; Bender and Conrad, 1992). In addition, there is direct evidence that before the rise of land plants, wetlands and water-logged soils were occupied by cyanobacterial mats (e.g., Sheldon, 2012).

The presence of oxygen in the upper pore waters of modern soil systems strongly inhibits methanogenesis (Peters and Conrad, 1995; Angel et al., 2011), and the release of methane is limited by methane oxidation within soils (Gauthier et al., 2015). However, under the low atmospheric O<sub>2</sub> levels characteristic of much of Precambrian time, soil mats would be essentially anoxic at night (Herman and Kump, 2005). The activity of methanogenic bacteria would thus transiently increase and methanotrophy would drop, resulting in a substantial release of methane to the atmosphere (e.g., Angel et al., 2011). Here, we use a biogeochemical model designed to mimic a water-saturated cyanobacterial mat in order to provide estimates of possible methane fluxes from terrestrial microbial ecosystems during the mid-Proterozoic. We then use these fluxes in an Earth system model inversion to estimate the land surface coverage required to achieve various atmospheric CH<sub>4</sub> levels and climate states.

## METHODS

Our microbial mat model is developed based on de Wit et al. (1995) and Herman and Kump (2005). In these models, the growth and loss of primary producers such as cyanobacteria (CYA), purple sulfur bacteria (PSB), and colorless sulfur bacteria (CSB) are driven by environmental factors such as photosynthetically active radiation, near-infrared radiation, and the availability of substrates such as sulfate (SO<sub>4</sub>), sulfide (H<sub>2</sub>S), and oxygen (O<sub>2</sub>). We modify this framework by adding a microbial CH<sub>4</sub> cycle, including fermentative methanogenesis, methanotrophy, and ebullition (see the GSA Data Repository<sup>1</sup>)

Following Herman and Kump (2005), we use a saturation function with respect to microbial biomass to describe the availability of substrates

<sup>1</sup>GSA Data Repository item 2018031, supplementary text, figures, and tables, is available online at <http://www.geosociety.org/datarepository/2018/> or on request from [editing@geosociety.org](mailto:editing@geosociety.org).

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for methanogenesis. Methanogenesis and sulfate reduction compete for the same substrates (e.g.,  $H_2$  and acetate) and sulfate reduction will out-compete methanogenesis under high sulfate concentrations. Therefore, a Monod scheme is used to describe the influence of sulfate reduction on the methane cycle. The presence of oxygen in the upper region of modern soils strongly inhibits methanogenesis, which is a strictly anaerobic process (Peters and Conrad, 1995; Angel et al., 2011). Thus, oxygen inhibition on methanogenesis is also included (Arah and Stephen, 1998). Finally, we use a two-substrate Michaelis-Menten formulation to describe the microbial oxidation of methane with oxygen (e.g., Arah and Stephen, 1998) and  $CH_4$  expulsion due to ebullition, following Walter et al. (1996).

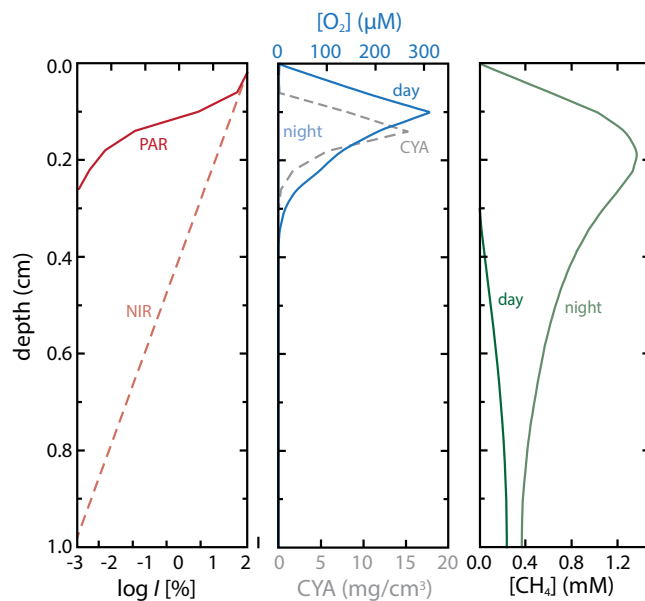
The model was written in R with the use of the ReacTran package (R Core Team, 2006; Soetaert and Herman, 2009), which uses the method of lines to solve the resulting partial differential equations. Following a spin-up period of 31 days to allow the colonization of the mat only by cyanobacteria (following de Wit et al., 1995; Herman and Kump, 2005), the model was then run for 60 days to reach a quasi-steady state with all of the components included. All parameter values can be found in Table DR1 in the Data Repository.

To quantify the expected methane fluxes from terrestrial cyanobacterial mats during the mid-Proterozoic, we first calibrate the model parameters using a mean methane flux of  $3 \mu\text{mol m}^{-2} \text{min}^{-1}$  as observed in a well-characterized Antarctic modern soil cyanobacteria mat (Gregorich et al., 2006). We then fix atmospheric  $pO_2$  as a boundary condition, with values characteristic of the mid-Proterozoic (Lyons et al., 2014; Cole et al., 2016), to calculate the area-normalized methane emission to the atmosphere. As our model is calibrated to an Antarctic ecosystem, we consider our estimates to be conservative.

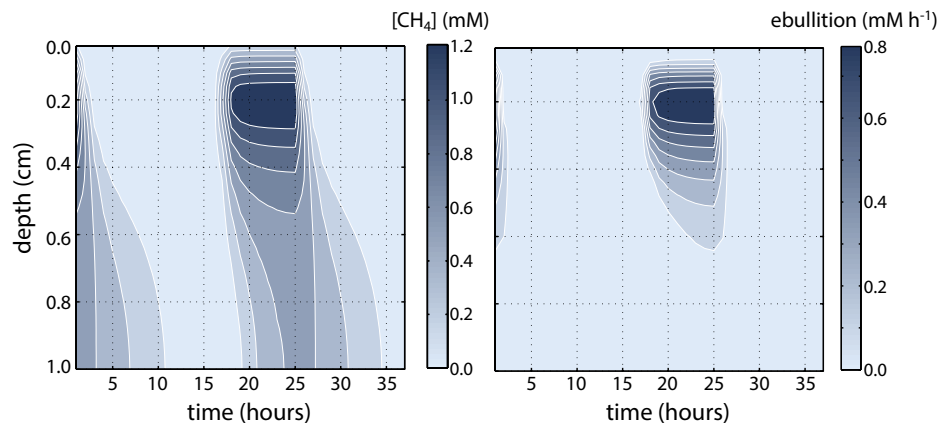
We use cGENIE (<http://genie.seao2.org>), an Earth system model of intermediate complexity, to invert for the terrestrial  $CH_4$  fluxes required to achieve a given atmospheric  $pCH_4$  value. The  $CH_4$  cycle is configured as in Olson et al. (2016), and includes fermentative methanogenesis, aerobic and anaerobic methanotrophy, and a parameterized  $O_2$ - $O_3$ - $CH_4$  photochemical scheme (Goldblatt et al., 2006). Marine productivity is assumed to be limited by available phosphorus, and is constrained according to Michaelis-Menten-type kinetics. The simulations shown here use a variable phosphate inventory and a marine sulfate concentration of  $500 \mu\text{mol kg}^{-1}$ .

## RESULTS AND DISCUSSION

The results for the 60 days baseline runs of our mat model are shown in Figures 1 and 2 and in Figures DR1–DR5 in the Data Repository. Due to low sulfate concentrations, the CSB and PSB biomass is very low relative to



**Figure 1.** Results of our baseline simulation of Proterozoic terrestrial cyanobacteria (CYA) mat. The thickness of model domain (depth) is 1 cm, with 0 cm representing the mat surface. Left: Penetration of photosynthetically available (PAR) and near-infrared (NIR) radiation; note the log scale. I is the intensity of PAR or NIR. Middle: Dissolved oxygen concentration during the day and at night (blue solid) and CYA biomass (gray dashed) as a function of depth. Right: Dissolved methane concentration as a function of depth during the day and at night.



**Figure 2.** Diurnal cycling of methane concentrations (left) and expulsion of methane due to ebullition (right) for the baseline simulation of a Proterozoic terrestrial cyanobacterial mat. The thickness of model domain (depth) is 1 cm, with 0 cm representing the mat surface.

CYA. The distributions of CYA are similar in the two runs (Fig. 1; Fig. DR2). CYA mainly occurs from 0.5 to 2.5 mm depth with a peak biomass of  $\sim 19 \text{ mg/cm}^3$  at  $\sim 1 \text{ mm}$ , comparable to observations from modern mat ecosystems (de Wit et al., 1995). Photosynthetically active radiation penetrates deeper in the modern run (3.4 mm) than the Proterozoic run (1.5 mm), likely because of the higher concentration of CYA biomass near the top of the Proterozoic mats as a result of less oxygen inhibition. Near-infrared radiation penetrates much deeper than photosynthetically active radiation (Fig. 1; Fig. DR2), due to its low sediment attenuation coefficient and low biological absorption as a result of low PSB.

Oxygen and methane show striking diurnal dynamics (Fig. 2; Figs. DR1, DR2, and DR5). The oxygen dynamics of our modeled cyanobacterial mats under modern conditions are similar

to the results for hypersaline mats from de Wit et al. (1995) and Herman and Kump (2005). For example, oxygen penetrates to  $\sim 3.5 \text{ mm}$  during the day and  $\sim 1 \text{ mm}$  at night (Fig. DR2), comparable to observations of wet soil crusts (Garcia-Pichel and Belnap, 1996; Angel et al., 2011). The maximum oxygen concentrations during the day ( $\sim 300 \mu\text{M}$ ; Figs. DR2 and DR5) are also comparable to those observed in incubation experiments of wet soil crusts (Garcia-Pichel and Belnap, 1996). Under Proterozoic conditions, oxygen penetrates to  $\sim 2.6 \text{ mm}$  during daylight hours (Fig. 1). However, for the baseline run, there is essentially no oxygen during the night (Fig. 1; Fig. DR1) due to the low levels of oxygen in the overlying atmosphere and the lack of oxygenic photosynthesis.

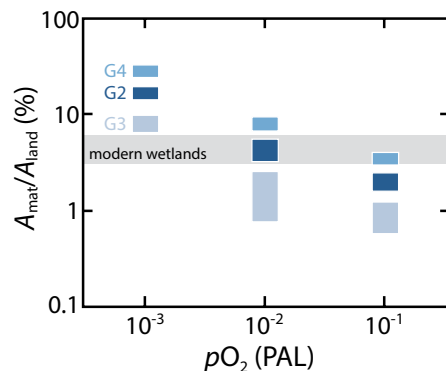
The overall diurnal dynamics of  $CH_4$  are similar under both modern and Proterozoic conditions, although we observe significantly different

CH<sub>4</sub> concentrations and ebullition rates (Fig. 2; Figs. DR3 and DR4). Daytime methane emission to the atmosphere is strongly attenuated under both modern and Proterozoic conditions. Rates of methanogenesis increase and rates of aerobic methanotrophy decrease during the night due to the sharp decrease in oxygen production, but the overall CH<sub>4</sub> emission under Proterozoic conditions is much greater due to lower oxygen penetration. The methane flux from the Proterozoic mat in our baseline run is 1613 μmol m<sup>-2</sup> h<sup>-1</sup> (Table DR2), i.e., nearly 9× that of its modern counterpart. The diurnal dynamics in our modeled methane fluxes are similar to those observed in modern wetland systems (King, 1990), though we note that more pronounced methane increases have been observed in incubation experiments of desert soil crusts (Angel et al., 2011), again suggesting that, if anything, our modeling approach is conservative.

In order to account for the influence of spatial heterogeneity in key model variables, we use the model to estimate methane fluxes sampled from probability distributions of underlying parameters. We have done a series of runs for several factors including the inhibition coefficient of methanogenesis by oxygen, maximum rate of methane oxidation, sediment attenuation coefficient of photosynthetically active radiation, the maximum rate of methanogenesis, and porosity (Tables DR2–DR4). We then use discrete probability density functions to calculate expected methane fluxes for each parameter (Table DR5).

The area-normalized CH<sub>4</sub> fluxes from our modeled mat ecosystems allow us to estimate the area of Earth's land surface required to support a given CH<sub>4</sub> flux to the atmosphere. In order to place these results in a climatological context, we build on results from a coupled atmosphere-ocean general circulation model (GCM) obtained by Fiorella and Sheldon (2017) for the mid-Proterozoic climate system. We take their simulation results that are most consistent with the geologic record—specifically, simulations G2 (*p*CO<sub>2</sub> of 5× PIAL and atmospheric *p*CH<sub>4</sub> of 70 ppmv), G3 (*p*CO<sub>2</sub> of 10× PIAL and atmospheric *p*CH<sub>4</sub> of 28 ppmv), and G4 (*p*CO<sub>2</sub> of 10× PIAL and atmospheric *p*CH<sub>4</sub> of 140 ppmv). We restore the atmospheric *p*CH<sub>4</sub> value in cGENIE and use the model to calculate the terrestrial CH<sub>4</sub> fluxes required to maintain a given steady-state atmospheric *p*CH<sub>4</sub> (e.g., in excess of the flux already provided by the marine biosphere in each simulation). Finally, we assume that continental freeboard during the mid-Proterozoic was roughly similar to the modern (e.g., Korenaga et al., 2017) and compute the relative land area that must be covered by our model mat ecosystem in order to buffer atmospheric *p*CH<sub>4</sub> at values consistent with the GCM simulations (Fig. 3).

We find that terrestrial microbial mats can result in globally significant fluxes of CH<sub>4</sub> to the atmosphere if they cover a relatively modest



**Figure 3. Model inversion of relative terrestrial mat area required to stabilize Earth's climate system at a range of atmospheric *p*O<sub>2</sub> and marine nutrient levels. *A*<sub>mat</sub> and *A*<sub>land</sub> represent the area of cyanobacteria mats and Earth's land surface during the mid-Proterozoic, respectively. Results show relative mat area required to support the terrestrial CH<sub>4</sub> flux associated with atmospheric *p*CH<sub>4</sub> in each simulation as a function of atmospheric *p*O<sub>2</sub> relative to the present atmospheric level (PAL). Symbol colors correspond to the G2, G3, and G4 climate simulations from Fiorella and Sheldon (2017), all of which represent clement surface temperatures and limited sea ice extent as demanded by the geologic record. G2: *p*CO<sub>2</sub> = 1400 ppmv, *p*CH<sub>4</sub> = 70 ppmv; G3: *p*CO<sub>2</sub> = 2800 ppmv, *p*CH<sub>4</sub> = 28 ppmv; G4: *p*CO<sub>2</sub> = 2800 ppmv, *p*CH<sub>4</sub> = 140 ppmv. Range in area shown for each simulation depicts the effect of varying the oceanic phosphate inventory between 0.25× and 1.0× the modern value. Shaded bar shows the extent of wetland environments on the modern land surface for reference.**

area of the land surface. For example, at an atmospheric *p*O<sub>2</sub> value of 1% of the present atmospheric level (PAL), mat ecosystems would only need to cover roughly the same relative land surface as modern wetlands to stabilize the G2 simulation with an atmospheric *p*CH<sub>4</sub> value of 70 ppmv (Fig. 3). This can be compared with the ~3%–6% land surface coverage represented by modern wetlands. Although terrestrial cyanobacterial mats are found in wet and dry environments today (e.g., Angel et al., 2011), cyanobacterial mats would have thrived foremost in wetlands and water-logged soils, the latter of which are common in large swaths of equatorial regions (Dirmeyer et al., 2006). This estimated mat area need only be increased to ~10% of the land surface to result in an atmospheric *p*CH<sub>4</sub> of 140 ppmv at the same *p*O<sub>2</sub> level (Fig. 3, G4 simulation). However, because the photochemical stability of CH<sub>4</sub> drops as atmospheric O<sub>2</sub> decreases from 1% PAL to 0.1% PAL (Pavlov et al., 2003; Olson et al., 2016), stabilizing an atmospheric *p*CH<sub>4</sub> value of 140 ppmv at the lower end of estimated mid-Proterozoic *p*O<sub>2</sub> values would require a mat coverage of ~30% of the land surface.

In sum, we find that fluxes of CH<sub>4</sub> from terrestrial microbial mats would be significant

enough to result in a warm mid-Proterozoic climate system under a wide range of conditions with mat areal coverage of ~10% or lower depending on atmospheric *p*O<sub>2</sub> (Fig. 3). In this light, large terrestrial methane fluxes provide a potential solution to the Proterozoic CH<sub>4</sub> paradox: despite limited marine methane fluxes, relatively high atmospheric methane concentrations can be maintained by terrestrial microbial ecosystems in a low-oxygen world. Importantly, organic matter oxidation within the mat and during transport of mat-derived organic matter to marine settings (even at low *p*O<sub>2</sub>) likely provides a mechanism for sustaining high methane fluxes with the low organic carbon burial rates required to maintain low atmospheric O<sub>2</sub> (e.g., Laakso and Schrag, 2017). Long sediment transport times in terrestrial systems (>10,000 yr; DePaolo et al., 2012) are likely to result in significant oxidation of mat-derived organics with increased oxidation efficiency relative to that observed in marine systems (Reinhard et al., 2013). In this light, this work also suggests that net productivity in the Precambrian was likely higher than previous mass balance model-derived estimates that consider only a marine biosphere (e.g., Laakso and Schrag, 2017).

## CONCLUSION

Climate simulations of the mid-Proterozoic Earth, combined with the geochemical proxy record, suggest that high atmospheric methane levels would have been required to buffer the climate system against a less luminous younger Sun. However, methane fluxes from the ocean biosphere were likely significantly muted by internal microbial methane consumption. We propose that terrestrial microbial mat ecosystems supplied a globally significant flux of methane to a relatively low O<sub>2</sub> atmosphere during the mid-Proterozoic, buffering the atmospheric CH<sub>4</sub> inventory and warming the climate system. Our results suggest a complex and novel series of interactions between the microbial O<sub>2</sub>, CH<sub>4</sub>, and S cycles and between the terrestrial biosphere and Earth's climate system.

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