Limited role for methane in the mid-Proterozoic greenhouse

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Pervasive anoxia in the subsurface ocean during the Proterozoic may have allowed large fluxes of biogenic CH4 to the atmosphere, enhancing the climatic significance of CH4 early in Earth’s history. Indeed, the assumption of elevated pCH4 during the Proterozoic underlies most models for both anomalous climatic stasis during the mid-Proterozoic and extreme climate perturbation during the Neoproterozoic; however, the geologic record cannot directly constrain atmospheric CH4 levels and attendant radiative forcing. Here, we revisit the role of CH4 in Earth’s climate system during Proterozoic time. We use an Earth system model to quantify CH4 fluxes from the marine biosphere and to examine the capacity of biogenic CH4 to compensate for the faint young Sun during the “boring billion” years before the emergence of metazoan life. Our calculations demonstrate that anaerobic oxidation of CH4 coupled to SO42− reduction is a highly effective obstacle to CH4 accumulation in the atmosphere, possibly limiting atmospheric pCH4 to less than 10 ppm by volume for the second half of Earth history regardless of atmospheric pO2. If recent pO2 constraints from Cr isotopes are correct, we predict that reduced UV shielding by O3 should further limit pCH4 to very low levels similar to those seen today. Thus, our model results likely limit the potential climate warming by CH4 for the majority of Earth history—possibly revisiting the faint young Sun paradox during Proterozoic time and challenging existing models for the initiation of low-latitude glaciation that depend on the oxidative collapse of a steady-state CH4 greenhouse.

Adearth of glacial deposits during much of the Proterozoic is traditionally interpreted as evidence that Earth’s surface was as warm as, or warmer than, modern Earth throughout the mid-Proterozoic, 1.8 to 0.8 billion years ago (Ga) (1). This relatively warm climate state has conventionally been considered to require enhanced greenhouse warming to compensate for reduced solar luminosity early in Earth’s history (2, 3). Although the composition of the ancient greenhouse is still debated, the temporal proximity of extensive, low-latitude glaciation and oxygenation in the Paleoproterozoic (2.5 Ga to 1.6 Ga) supports speculation that a reduced greenhouse gas, such as biogenic CH4, played an important role in the Precambrian climate system (1, 4). This relationship has been envisaged in two ways for the Paleoproterozoic Snowball Earth glaciations: (i) the Paleoproterozoic Great Oxidation Event (GOE) rapidly evolved a potent CH4 greenhouse, and oxidative collapse of the CH4 reservoir allowed the Earth system to plunge into snowball glaciation (5); or (ii) declining biogenic CH4 fluxes allowed the collapse of a CH4 greenhouse, extreme climate perturbation, and the initial rise of atmospheric O2 by reducing the atmospheric sink for O2 (6, 7). Several authors have similarly suggested that the oxidative collapse of a CH4 greenhouse could have also triggered climate destabilization during the Neoproterozoic (1.0 Ga to 0.54 Ga) if biogenic CH4 fluxes were elevated throughout the Proterozoic Eon, as assumed before the GOE (8–11).

Despite its conceptual convenience, the existence and/or effectiveness of a CH4 greenhouse at any time during the Proterozoic remains speculative. Although relatively small surface oxidant reservoirs (e.g., O2 and SO42−) during Proterozoic time may have allowed large CH4 fluxes from the marine biosphere (9), the geologic record does not provide quantitative constraints on either CH4 fluxes or the CH4 content of the atmosphere, and some models suggest only modest CH4 accumulation in the Proterozoic atmosphere compared with the Archean (12, 13). Characterization of the Proterozoic greenhouse is further complicated by (i) strong nonlinearity in biospheric CH4 fluxes as a function of marine SO42− concentrations, which arises because CH4 consumption and CH4 production are increased and decreased, respectively, with increasing [SO42−] (14, 15); and (ii) strong nonlinearity in the atmospheric lifetime of CH4 as a function of atmospheric pO2, which reflects the competing effects on CH4 stability from O2 content of the ocean–atmosphere system and correspondingly greater UV shielding by O3 in oxidizing atmospheres (16, 17). In other words, both the production and preservation of CH4 are disfavored by high levels of O2, but some low threshold level of O2 enhances CH4 preservation in the atmosphere because its photochemical destruction is muted when a protective O3 layer is well established (16, 17). These challenges for quantifying atmospheric CH4 (pCH4) are exacerbated by the nonlinear relationships between atmospheric pO2, crustal sulfide oxidation, and marine pyrite burial, muddling the relationship between atmospheric pO2 and oceanic [SO42−] (18, 19). Thus, the quantitative relationships between O2, SO42−, and CH4, on a global scale, are poorly understood for much of Earth’s history.

Potential Constraints for Proterozoic Methane

In the modern ocean, SO42−, not O2, is the primary oxidant for CH4 because of the coupling between SO4 and CH4 during anaerobic oxidation of methane (AOM) by microbes. Consequently,
freshwater, terrestrial ecosystems (e.g., wetlands) are the most important source of CH₄ to the modern atmosphere (excluding anthropogenic sources) because the vast quantity of CH₄ produced deep within reducing marine sediments does not readily evade oxidation in overlying SO₄²⁻-rich pore waters (20). Quantitative isotopic constraints on seawater SO₄²⁻ concentrations limit Proterozoic [SO₄²⁻] to only a few millimoles per liter (21), or possibly several hundred micromoles per liter (22)—a small fraction of the 28 mM characteristic of the modern ocean. Although less than ~10% of the modern marine SO₄²⁻ inventory is certainly low in relative terms, a seawater SO₄²⁻ concentration of 1 mM still carries a far greater electron accepting capacity than the entire O₂ reservoir of the generally well-oxygenated modern ocean. Thus, even at comparatively low concentrations, SO₄²⁻ in pore waters and in an anoxic Proterozoic water column could have been a major obstacle preventing biogenic CH₄ from escaping the ocean environment and entering the atmosphere.

Early arguments for elevated pCH₄ during the Proterozoic were predicated on the notion that surface CH₄ fluxes could have been >10⁴ to 20x modern values due to enhanced methanogenesis and complete inhibition of methanotrophy under low [SO₄²⁻] conditions (9, 10), but this assumption has been challenged both experimentally and through the recognition of extensive anaerobic CH₄ recycling in modern analog environments. For example, efficient microbial oxidation of CH₄ coupled to SO₄²⁻ reduction has been documented at SO₄²⁻ concentrations as low as 100 µM (23), which is potentially much lower than the [SO₄²⁻] conditions that typified the Proterozoic ocean (21). Recent work has also shown that CH₄ oxidation can be metabolically coupled to a range of alternate electron acceptors [e.g., Mn(III/IV) and Fe(III)] in freshwater lake systems (24) and in SO₄²⁻-deficient marine sediments (25). These metabolic pathways are theoretically more energetically favorable than SO₄²⁻-based AOM and are likely to have been important for Precambrian CH₄ cycling given the apparent abundance of Fe and Mn in the Precambrian ocean (23, 26); however, there have been few attempts to include these metabolic sinks for CH₄ in quantitative biogeochemical models, with attempts, to date, focusing on photochemical models that do not explicitly resolve redox cycling within the ocean (23–27).

Somewhat counterintuitively, low pO₂ in the Proterozoic may have also been an obstacle to CH₄ accumulation in the atmosphere due to strongly diminished UV shielding by O₃ at low pO₂—which would act to greatly decrease the photochemical lifetime of atmospheric CH₄. For this reason, atmospheres with low pO₂ can be more oxidizing toward CH₄ than higher pO₂ atmospheres (16, 17). Thus, there is an optimization of the lifetime of atmospheric CH₄ associated with having sufficient O₂ to promote UV shielding by O₃ but at O₂ levels still low enough to minimize oxidative CH₄ destruction. Previous models that have suggested the existence of a CH₄ greenhouse during the Proterozoic have assumed that pO₂ stabilized at, or above, ~10% present atmospheric levels (PAL) following the GOE (9), but several diverse proxy records collectively indicate that pO₂ may have eventually stabilized at much lower levels than those seen during the GOE and associated Lomagundi event (28). Recently, the absence of Cr isotope fractionation in mid-Proterozoic marine sediments suggests that atmospheric pO₂ may have been as low as 0.1% PAL, an order of magnitude lower than envisioned by some authors (29). Consequently, it is possible that previous attempts to characterize the Proterozoic greenhouse have overestimated the lifetime for atmospheric CH₄.

Ocean-Resolving Methane Cycle Model

In response to recent revelations regarding the high efficiency of anaerobic CH₄ oxidation under low [SO₄²⁻] conditions (23–25) and refined constraints on atmospheric O₂ levels during the mid-Proterozoic (29), we have revisited the role of CH₄ in mid-Proterozoic climate stabilization and Neoproterozoic climate perturbation. Our calculations were performed using the grid-enabled integrated Earth system model (GENIE), an Earth system model of intermediate complexity. GENIE considers a 3D marine biosphere, including nutrient-limited export production, aerobic respiration, sulfate reduction, and methanogenesis. The marine biogeochemical module also includes aerobic methanotrophy and sulfide oxidation (see ref. 30 for a detailed description). The ocean is divided as a 36 × 36 equal-area grid with 16 depth layers, and the ocean system is coupled to a 2D energy and moisture balance model, a sea ice model, and a 2D model for

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**Fig. 1.** Oxidant controls on CH₄ cycling. (A) CH₄ production flux (methanogenesis; blue squares) and CH₄ consumption flux (the sum of aerobic methanotrophy and AOM; red circles) as a function of marine SO₄²⁻. The difference between methanogenesis and methanotrophy is equal to the net biogenic CH₄ flux (i.e., the flux of CH₄ that enters the atmosphere through sea–air exchange). Note that the SO₄²⁻ experiments shown here assume pO₂ = 10⁻³ PAL (29). (B) Net biogenic CH₄ flux to the atmosphere (red squares) and atmospheric pCH₄ (blue circles) as a function of atmospheric pO₂. Net biogenic CH₄ production declines with increasing O₂ due to enhanced methanotrophic oxidation of CH₄, but CH₄ accumulation in the atmosphere increases despite reduced CH₄ supply due to the establishment of an increasingly effective O₃ layer (see figure 7 from ref. 34). Note that pO₂ experiments shown here assume [SO₄²⁻] = 280 µM.
the calculation of atmospheric chemistry and spatially resolved, bidirectional sea–air exchange fluxes (31).

For our Proterozoic simulations, we have expanded GENIE’s representation of the CH4 cycle compared with previously published versions of the model. In particular, we have (i) parameterized dynamic calculation of CH4 photoproduction (incorporated after ref. 17); (ii) refined the competition between methanogens and sulfate reducers (improved from ref. 32); and (iii) added AOM coupled to SO4\(^{2-}\) reduction, the rate law for which we derived from radio-labeled CH4 oxidation rates and chemical profiles from the anoxic water column of the Black Sea (Eq. S1) (33). In combination, these upgrades add strong nonlinearity to both CH4 fluxes and CH4 accumulation as a function of oxidant availability, allowing for an oceanographically realistic calculation of CH4 cycling during oxidant-deficient intervals of Earth history.

We calculated steady-state biogenic CH4 fluxes and resulting atmospheric pCH4 for >75 model configurations, differing primarily in the prescribed sizes of their surface oxidant reservoirs (e.g., O2 and SO4\(^{2-}\)). We systematically quantified the influence of pO2 (from 10\(^{-3}\) PAL to 10\(^{-1}\) PAL) and oceanic [SO4\(^{2-}\)] (from 0 to 2.8 mM). We then performed a wide range of sensitivity analyses (Supporting Information), starting from our baseline oxidant levels (10\(^{-3}\) PAL pO2; 280 µM SO4\(^{2-}\)) and examining the effects of varying (i) prescribed CH4 fluxes from terrestrial environments (0 Tmol CH4-yr\(^{-1}\) to 22 Tmol CH4-yr\(^{-1}\)), (ii) the oceanic PO4\(^{3-}\) inventory (i.e., export production, from 0.25x to 2x modern), (iii) whether or not N limitation is considered, (iv) the depth distribution of organic carbon (Corg) remineralization, (v) the rate constants for both aerobic and anaerobic microbial CH4 oxidation, and (vi) the half-saturation constant for SO4\(^{2-}\) reduction. We also explored model sensitivity to the parameterization of CH4 oxidation within the atmosphere.

Importantly, our modeling experiments were designed to conservatively err in favor of overestimating pCH4 by calculating generous CH4 production fluxes while minimizing CH4 destruction. In our baseline model, we assume complete remineralization of exclusively P-limited export production in a closed ocean–atmosphere system; because this base model stipulates a modern PO4\(^{3-}\) inventory while neglecting potential N stress and C removal through organic burial, these calculations tend to overestimate the amount of organic matter remineralized via methanogenesis. This potential for overestimating CH4 production is further amplified by our use of a relatively high half-saturation constant for SO4\(^{2-}\) reduction (500 µM SO4\(^{2-}\)), which effectively reduces the competitive advantage of SO4\(^{2-}\) reducers over methanogens. Furthermore, because we neglect anaerobic oxidation of CH4 coupled to electron acceptors other than SO4\(^{2-}\) (e.g., oxidized Fe and Mn), it is unlikely that we overestimate CH4 oxidation by the marine biosphere. Consequently, the sea-to-air CH4 fluxes and subsequent pCH4 calculations presented here should be considered conservative upper limits (see Supporting Information for further details).

**Oxidant Controls on Methane Cycling**

We find that, during the Proterozoic, SO4\(^{2-}\) would have been the primary control on biogenic CH4 fluxes from the ocean, not unlike today. Methane production by methanogenesis rapidly declines as SO4\(^{2-}\) reduction, the more energetically favorable metabolism, becomes increasingly competitive at higher [SO4\(^{2-}\)] and remineralizes a correspondingly greater fraction of organic material exported from the surface ocean. Meanwhile, CH4 destruction via AOM increases with increasing [SO4\(^{2-}\)], until low CH4 availability ultimately limits AOM kinetics and slows CH4 oxidation. The combined result of these effects is that net biogenic CH4 fluxes to the atmosphere plummet as oceanic [SO4\(^{2-}\)] increases (Fig. 1A), and the extreme sea-to-air CH4 fluxes suggested by Pavlov et al. (9) are not achievable for any of our model configurations. Thus, relatively modest oceanic SO4\(^{2-}\) levels can, in principle, preclude significant warming by CH4 on early Earth, regardless of atmospheric pO2.

At higher atmospheric O2 levels, net biogenic CH4 fluxes also decline as a consequence of higher rates of methanotrophy—both aerobic (i.e., through direct metabolic consumption of CH4 with O2) and anaerobic (i.e., through more effective regeneration of SO4\(^{2-}\) via S\(^{2-}\) oxidation). Globally, however, aerobic methanotrophy is quantitatively much less significant than AOM because, when pO2 is low, oxygenation and aerobic methanotrophy are spatially restricted to the photic zone (Fig. 2A), which represents less than a few percent of the ocean by volume, whereas
AOM occurs throughout the ocean interior in closer association with CH$_4$ production (Fig. 2C). Consequently, CH$_4$ oxidation linked to SO$_4^{2-}$ reduction in a broadly anoxic Proterozoic ocean greatly exceeds CH$_4$ oxidation by O$_2$ globally. The influence of atmospheric pO$_2$ on aqueous CH$_4$ oxidation is further muted when atmospheric pO$_2$ is low because the surface ocean—the site of O$_2$ production—is widely supersaturated with O$_2$ with respect to the atmosphere when pO$_2$ is less than ∼2.5% PAL. Under these conditions, sea–air exchange of O$_2$ is effectively unidirectional, which partially decouples atmospheric pO$_2$ from dissolved O$_2$ and aerobic metabolism in the surface ocean.

Despite limited influence on net biogenic CH$_4$ fluxes, atmospheric pO$_2$ exerts strong control on the accumulation of CH$_4$ in the atmosphere when [SO$_4^{2-}$] is sufficiently low to allow significant CH$_4$ escape to the atmosphere. For the range of atmospheric pO$_2$ that is consistent with the absence of mass-independent fractionation of S isotopes and unfractonated Cr in Proterozoic marine sediments (10$^{-5}$ to 10$^{-9}$ PAL) (29, 34), the atmospheric lifetime of CH$_4$ increases with increasing pO$_2$ as the result of an increasingly effective O$_3$ UV shield (Fig. S2). This effect ultimately dominates at steady state over enhanced methanotrophic oxidation of CH$_4$ when pO$_2$ is very low, with the result that atmospheric CH$_4$ is greater despite reduced production of CH$_4$ in an increasingly oxygenated Earth system. For example, as pO$_2$ increases from 0.1 to 1% PAL, net biogenic CH$_4$ production declines more than 20% whereas atmospheric pCH$_4$ increases more than 200% as a consequence of muted photochemistry and a correspondingly greater lifetime for atmospheric CH$_4$ (Fig. 1B).

Combining the opposing effects of [SO$_4^{2-}$] and pO$_2$, we find that a robust steady-state CH$_4$ greenhouse is plausible for only a very narrow window of pO$_2$–[SO$_4^{2-}$] parameter space (Fig. 3A). Atmospheric pCH$_4$ values greater than ∼10 ppm by volume (ppmv) do not occur for [SO$_4^{2-}$] > 1 mM, whereas pCH$_4$ values greater than ∼100 ppmv are restricted to pO$_2$ between 1 and 10% PAL. Thus, substantial accumulation of CH$_4$ in the atmosphere requires the unique combination of exceptionally low [SO$_4^{2-}$] (<1 mM), which allows sufficiently large CH$_4$ fluxes from the marine biosphere, and relatively high pO$_2$ (1 to 10% PAL), which optimizes the atmospheric lifetime of CH$_4$. Although uncertainties remain regarding the coevolution of pO$_2$ and marine [SO$_4^{2-}$], this requirement for modest pO$_2$ and very low SO$_4^{2-}$ is not consistent with the most recent [SO$_4^{2-}$] and pO$_2$ proxy records and likely would have been difficult to maintain over geologic timescales considering the coupling between atmospheric pO$_2$, crustal sulfide oxidation, and SO$_4^{2-}$ fluxes. These conclusions regarding oxidant controls on pCH$_4$ are insensitive to uncertainty in other model parameters (Fig. 3 B–E and Table S1), indicating that our salient results are robust, and these constraints challenge the paradigm of persistently elevated pCH$_4$ throughout the Precambrian.

**Consequences for Proterozoic Climate**

Elevated pCH$_4$ on the order of 100 ppmv could provide ~6 K of greenhouse warming, which would substantially, although not completely, compensate for reduced solar luminosity if Proterozoic Earth was persistently warmer than today (10); thus we consider ~6 K to be the minimum radiative deficit implied by our model if the Proterozoic [SO$_4^{2-}$] approach 1 mM or if pO$_2$ was lower than previously appreciated. This deficit is a substantial one that is difficult to reconcile with the absence of glaciation and the suggestion that Proterozoic pCO$_2$ was <10x modern (35).

Other reduced greenhouse gases that are not explicitly considered by our model may have bolstered the mid-Proterozoic greenhouse, helping to alleviate the radiative deficit produced by low atmospheric pCH$_4$. Most notably, atmospheric levels of nitrous oxide (N$_2$O) during the Proterozoic may have been much higher if widespread euxinia limited Cu availability and inhibited effective conversion of N$_2$O to N$_2$ during the final stage of denitrification (36), potentially yielding ~5 K of supplemental warming (10). Although SO$_4^{2-}$ would not severely throttle N$_2$O fluxes, N$_2$O—like CH$_4$—is rapidly photolyzed at low pO$_2$. Nitrous oxide, therefore, is only a viable greenhouse contributor for a partial range of the proposed pO$_2$ conditions for the
Proterozoic (10). Higher hydrocarbons, particularly ethane (C₂H₆), can be photochemically produced from CH₄ and may have been important for regulating the climate of Archean Earth (37), but our model results generally preclude the elevated pCH₄/pCO₂ conditions required for substantial hydrocarbon polymerization. Thus, greenhouse contributions from other hydrocarbons are unlikely during Proterozoic time.

In combination with evidence for relatively low pCO₂ during much of the Proterozoic (35), we conclude that the faint young Sun paradox may still be a problem for the Proterozoic if relatively high CH₄ levels are precluded by current estimates of oceanic SO₂⁻²⁻ and/or atmospheric pO₂. Continued exploration of the metabolic limitations of CH₄ oxidizing consortia (11), revised pCO₂ calculations, or more realistic consideration of heat transport in increasingly sophisticated 3D coupled climate models may eventually reconcile our suggestion of low pCH₄ with element conditions during the mid-Proterozoic, but, given current constraints on the warming potential of CO₂ during Proterozoic time, the paradox remains unresolved.

Given the possibility that baseline Proterozoic pCH₄ was much lower than previously envisioned, the role of CH₄ in triggering Neoproterozoic climate collapse also requires revisiting. Several authors have previously suggested that the oxidative collapse of a CH₄ greenhouse was involved in the initiation of Neoproterozoic snowball glaciations (1, 8, 9). Indeed, emerging trace metal proxies suggest atmospheric oxygenation in advance of the glaciation (29, 38), despite unclear evidence for oxygenation within the marine realm (39–41). The climatic consequences of the oxygenation of a low pCH₄ atmosphere, however, have not been previously considered.

We suggest that a Neoproterozoic oxygenation event might have triggered a CH₄-based climate collapse, despite low steady-state pCH₄ as a result of the vastly differing timescales over which photochemical, biological, and weathering processes modulate Earth’s greenhouse. For example, the immediate consequence of an atmospheric oxygenation event would be an increase in the photochemical lifetime of CH₄ via UV shielding by O₃, and thus an initial increase in atmospheric pCH₄. Subsequent destabilization of CH₄ hydrates as the result of a warming climate may amplify this initial accumulation of CH₄ in the atmosphere (12, 42). The resulting greenhouse, however, would be inherently unstable because CH₄-induced warming would promote the drawdown of CO₂ on weathering timescales (12, 42); thus, the climate system would then be vulnerable to any disruption of the CH₄ source to the atmosphere (42), including the gradual accumulation of oceanic SO₂⁻²⁻ that would accompany oxygenation (9). A CH₄ greenhouse would also be sensitive to CH₄ instability arising as the result of either further oxygenation or even deoxygenation.

Although conceptually similar to the “methane shotgun” scenario advanced by Schrag et al. (42), our snowball initiation scenario has the advantage of eliminating the need for a large, sustained external source of CH₄ to the ocean–atmosphere system and does not rely on either enhanced biological CH₄ production or high steady-state pCH₄ before climate de-stabilization. Glacial initiation through the buildup and collapse of a CH₄ greenhouse in response to an oxygenation event may also provide an explanation for the enigmatic C isotope excursions of the late Neoproterozoic (12, 42). Future geochemical and model analyses that clarify the relationship between oxygenation, glaciation, and isotopic perturbation in the Neoproterozoic will be required to validate our proposed snowball scenario and could provide implicit support for our conclusion that baseline pCH₄ was very low during much of the Proterozoic.

Summary

We have shown that long-term stabilization of Earth’s climate system by CH₄ is challenging for much of Earth history, despite the likelihood of greatly enhanced CH₄ cycling within the broadly anoxic Proterozoic ocean. Even at very low SO₂⁻²⁻ concentrations, anaerobic oxidation of CH₄ in the ocean is sufficient to severely throttle CH₄ fluxes to the atmosphere, precluding the stability of an atmosphere with >100 ppm CH₄ as previously suggested for Proterozoic Earth. If recent pO₂ constraints from Cr isotopes are correct, reduced UV shielding by O₃ may exacerbate this issue, further limiting the potential accumulation of CH₄ in the atmosphere—with the implication that mid-Proterozoic pCH₄ may not have been markedly different from the low levels present today. In this scenario, our results suggest that elevated CH₄ should not be invoked to reconcile existing constraints on the composition of the mid-Proterozoic greenhouse with the absence of glaciation in the mid-Proterozoic. Thus, the faint young Sun paradox remains unresolved.

Although our model results imply relatively low steady-state pCH₄ (<10 PAL) during the second half of Earth history, they do not preclude a significant role for O₂ and CH₄ in destabilizing the Neoproterozoic climate system. Rather than occurring as the result of the demise of a steady-state CH₄ greenhouse, we suggest that the extreme low-latitude glaciations during the Neoproterozoic are the consequence of non–steady-state CH₄–oxidant dynamics produced by the interplay of the marine biosphere, photochemistry, weathering, and climate.

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