Methane-Carbon Budget of a Ferruginous Meromictic Lake and Implications for Marine Methane Dynamics on Early Earth

Sajjad A. Akam[1]✉, Pei-Chuan Chuang[2,3]✉, Sergei Katsev[4], Chad Witkop[5], Michelle Chamberlain[3], Andrew W Dale[2], Klaus Wallmann[2], Adam J. Heathcote[6], Elizabeth D. Swanner[1]

[1]Geological and Atmospheric Sciences, Iowa State University, Ames, IA, *USA*

[2]GEOMAR, Helmholtz Centre for Ocean Research, Kiel, Germany

[3]Department of Earth Sciences, National Central University, Taoyuan City, Taiwan

[4]Department of Physics, University of Minnesota Duluth, Duluth, MN, USA

[5]Biochemistry, Chemistry, and Geology, Minnesota State University, Mankato, MN, USA

[6] St. Croix Watershed Research Station, Science Museum of Minnesota, Marine on St. Croix, MN, USA

✉ sajjad@iastate.edu; peichuanchuang@ncu.edu.tw

ABSTRACT

The greenhouse gas methane (CH_4) contributed to a warm climate that maintained liquid water and sustained Earth's habitability in the Precambrian despite the Faint Young Sun. The viability of methanogenesis (ME) in ferruginous environments, however, is debated, as iron reduction can potentially outcompete ME as a pathway of organic carbon remineralization (OCR). Here we document that ME is a dominant OCR process in Brownie Lake in Minnesota, USA, a ferruginous (iron-rich, sulfate-poor) and meromictic (stratified with permanent anoxic bottom waters) system. We report ME accounting for ≥90 and >9±7% of the anaerobic OCR in the water column and sediments, respectively, and an overall POC loading to CH_4 conversion efficiency of ≥18±7% in the anoxic zone of Brownie Lake. Our results, along with previous reports from ferruginous systems, suggest that even under low primary productivity in Precambrian oceans, the efficient conversion of organic carbon to CH_4 would have enabled a major role of marine CH_4.

INTRODUCTION

The greenhouse gas methane (CH_4), with a present atmospheric concentration of 1.8 ppmv, contributes ≤25% of postindustrial global warming (Etminan et al., 2016). The importance of CH_4 to Precambrian climate may have been considerably higher, with estimated atmospheric concentration ranging from 600-3000 ppmv in Archean and 1-100 ppmv in Proterozoic (Olson et al., 2016; Fakhraee et al., 2019; Fig. 1). Methane concentrations may have exerted multiple roles in early Earth's biogeochemical evolution, among others: in contributing to greenhouse gas warming under a faint young sun to maintain warm surface temperature, liquid water, and Earth's habitability (Haqq-Misra et al., 2008); in producing an anti-greenhouse organic haze layer (Pavlov et al., 2001); in drawing down the H_2-based greenhouse warming leading to a late Archean (2.9 Ga) glaciation event (Wordsworth and Pierrehumbert, 2013); in contributing to hydrogen escape to space leading to oxidation of Earth's surface environment (Catling et al., 2001); in decreasing microbial methanogenesis (ME) leading to oxygen buildup in the atmosphere (Konhauser et al., 2009); and in decreasing atmospheric CH_4 levels contributing to the onset of Proterozoic glaciations (Zahnle et al., 2006). All these hypotheses require an active CH_4 cycle, likely with biological mediation. ME is one of the oldest microbial metabolic pathways, whose origin is dated back to >3.5 Ga, and is considered to have played an essential role in CH_4 supply to the atmosphere during Earth's early history (Kharecha et al., 2005). Ferruginous conditions were a dominant feature of Earth's early oceans (Poulton, 2021; Fig 1), and so an understanding of the role of ME under ferruginous conditions is essential to our understanding of marine carbon cycling in early Earth.

Fig. 1

Meromictic ferruginous lakes are considered convenient analogs to Precambrian oceans (Swanner et al., 2020). Such lakes generally have large reservoirs of CH_4 (1–4 mM in bottom waters; Crowe et al., 2011; Lopes et al., 2011). However, estimates of how much organic carbon (OC) is degraded by ME have only been calculated for a handful of lakes with estimated POC-to-CH_4 remineralization efficiency varying even within a single lake, i.e., Lake Matano, from 3 to 80% (Crowe et al., 2011; Kuntz et al., 2015). Ferruginous conditions, or rather the scarcity of sulfate, likely promote ME as the dominant pathway of organic carbon remineralization (OCR) (Friese et al., 2021). Yet, some have proposed ME plays only a minor role in ferruginous oceans (Laakso and Schrag, 2019). The efficiency of ME during OCR in ancient ferruginous oceans is thus poorly constrained. Here, we report the carbon budget for OCR and ME in Brownie Lake, a ferruginous meromictic lake with a biogeochemical analogy to Precambrian oceans (Lambrecht et al., 2018), and evaluate the implications for Precambrian CH_4-carbon dynamics. Our results highlight that ME is a dominant OCR pathway in sulfate-poor ferruginous aquatic systems, suggestive of large CH_4 storage and fluxes from the Precambrian ferruginous oceans, thereby supporting models that invoke the importance of CH_4 in Earth's early climate.

STUDY SITE

Brownie Lake (44°58'04" N, 93°19'26" W) is the northernmost lake in the Minneapolis Chain of Lakes, Minnesota, USA (Fig. 2) and is characterized in detail by Lambrecht et al. (2018). It is a eutrophic lake with abundant iron in the anoxic water column and sediments. This lake has been meromictic since 1925, and its long-term water column stratification results in strong physicochemical gradients of sunlight, oxygen, and iron (Lambrecht et al., 2018). Brownie Lake currently has a maximum depth of 14 m and a surface area of 5 ha. The conductivity, dissolved O_2, and temperature profiles indicate an oxic mixolimnion (0–3.5 m) and a dense anoxic monimolimnion below 5 m, separated by a chemocline (4–5 m), which often coincides with the oxycline (Fig. 2). 16S rRNA sequencing revealed that Methanogens, primarily of the order *Methanobacteriales,* are abundant in the water column (Lambrecht et al., 2020). At 11-12 m water depth, Methanogen sequences accounted for ~31% of sequences, with a biogenic $\delta^{13}C_{CH4}$ signature (-64 ‰) and a higher CH_4 concentration compared to nearest the sediment—pointing to active water column methanogenesis (Lambrecht et al., 2020). Aerobic methanotrophy is the dominant CH_4 oxidation mechanism (Lambrecht et al., 2020). We build on these previous results from this lake by incorporating organic carbon fluxes, sediment burial rates, and OCR rates, along with a reaction transport model, to evaluate the role of ME in OC cycling.

METHODS

Water column profiles of concentrations and stable carbon isotopes of CH_4 ($\delta^{13}C_{CH4}$), dissolved and particulate organic carbon ($\delta^{13}C_{DOC}$, $\delta^{13}C_{POC}$), and dissolved inorganic carbon ($\delta^{13}C_{DIC}$), along with concertation of major nutrients, anions, and cations in Brownie Lake were collected over several years (Swanner, 2022). This study utilizes previously reported CH_4, DIC, major nutrients, anions, and cations data (Lambrecht et al., 2018; Lambrecht et al., 2020) along with new data, including concentrations of POC, DOC, particulate organic nitrogen (PON), and dissolved organic nitrogen (DON), along with their isotopic compositions to quantify the Lake's OC budget. Primary productivity and external carbon loading were quantified using rapid light curves and the external chemical input model available for Brownie Lake (Supp. Section 2). A 1.5 m long sediment piston core was collected from the deep basin for ^{210}Pb dating using the constant rate of supply model to quantify dry mass accumulation rates (Appleby and Oldfield, 1978; Supp. Section 3). To investigate and quantify the processes controlling the distribution of dissolved and particulate species as well as the turnover of C, S, Fe, and P in the water column, the data from the lake were simulated with an existing biogeochemical reaction-transport model (Dale et al., 2009; Supp. Section 4). The August 2018 dataset was the most comprehensive for the above chemical species and was used for reaction transport modeling. OCR in the sediment column was constrained by mass-balancing the measured sediment OC burial and modeled OC rain rate to the lake floor.

RESULTS AND DISCUSSION

The POC loading was 107–264 mmol C m^{-2} d^{-1} with contribution from primary productivity (100–250 mmol C m^{-2} d^{-1}) and runoff (7–14 mmol C m^{-2} d^{-1}; Supp. Section 2). Water column profiles showed a subsurface chlorophyll maximum at 3.5 m, characteristic of ferruginous meromictic lakes, along with a positive spike in POC, PON, and DOC, and a low C:N ratio (TOC/TN mass/mass) (Fig. 3; Supp. Section 1), indicating a predominantly autochthonous labile OC flux sinking to the deeper water column. The increase in ammonium and DIC concentrations with depth in the monimolimnion (below 4–5 m) indicate OCR. Increasing $\delta^{13}C_{DIC}$ values (−11.53‰ at 3.5 m to −2.92 ‰ at 13 m depth) and CH_4 concentrations (max 0.2 mM above 3.5 m to max 1.5 mM in monimolimnion) with depth indicate active ME below the chemocline. The DOC concentration profile below the chemocline did not show comparable variation with DIC and CH_4 concentrations, indicating that only a portion of the organic carbon is available for ME and the existence of a sizeable recalcitrant DOC pool. A depletion of $^{13}C_{DIC}$, $^{13}C_{DOC}$, and $^{13}C_{POC,}$ along with enrichment in $^{13}C_{CH4}$ at the chemocline, suggest strong aerobic CH_4 oxidation above the chemocline (Fig. 2; c.f. Lambrecht et al., 2020). CH_4 storage was estimated by integrating measured CH_4 concentration to water volume data per depth and lake surface area, yielding 25.85 g C m-2, which is very high compared to other lakes with similar surface areas (Supp. Section 7).

Our reaction-transport model-based simulation for POC remineralization in the water column returned a good fit to the measured chemical parameters (Fig. 3; Supp. Section 4). Results yielded a total OCR rate of 67–224 mmol C m^2 d^{-1} (62–85% of POC loading), of which 28–37 mmol C m^2 d^{-1} (14–26% of POC loading) occurs in the water column (Table 1). 75±1% of water column OCR occurred anaerobically, of which ME accounted for 92–95% (19–27 mmol C m^2 d^{-1}; Table 1). OCR via sulfate reduction and dissimilatory iron reduction in the water column was limited in comparison (1.6±0.1 mmol C m^2 d^{-1}; 5–8% of anaerobic OCR). The excess ammonium observed below the redoxcline compared to the modeled result could be due to nitrogen fixation (Philippi et al., 2021) or dissimilatory nitrate reduction to ammonium instead of N_2 (Michiels et al., 2017), two processes that have been observed in ferruginous lakes. While iron reduction could be thermodynamically favorable in the Brownie Lake water column, our results suggest a minimal role of dissimilatory iron reduction in OCR. Previous studies have shown that methanogens can outcompete iron reducers during OCR under non-carbon-limited settings due to the transformation of iron oxide minerals to stable forms or due to surface passivation of reactive iron oxides by Fe(II) (Friese et al., 2021; Gadol et al., 2022). The presence of iron oxide minerals in sediments (Supp. Section 6) indicates they are escaping water column remineralization processes, thereby favoring ME as the dominant mode of OCR in monimolimnion.

Modeled OC rain rate at the lake floor (79–226 mmol C m^2 d^{-1}; 74–86% of total OC load) combined with measured OC burial (40.38 mmol C m^{-2} d^{-1} for top 11 cm and 37.78 mmol C m^{-2} d^{-1} for top 70 cm) points to 38–186 mmol C m^{-2} d^{-1} OCR in the sediment column and that only 18–51% of the OC rain is being buried. This OCR in the ferruginous sediment column would occur via dissimilatory iron reduction and ME (Bray et al., 2017). The modeled CH_4 flux from the sediment column towards the lake floor (1–3 mmol CH_4 m^2 d^{-1}) implies a minimum methanogenic OCR of 2–6 mmol C m^2 d^{-1} in the sediment column. We emphasize that this is the minimum ME estimate in the sediment since a portion of CH_4 produced in the sediment column could be consumed by Fe-dependent AOM (Supp. Section 6). The low C:N ratio and low $\delta^{13}C_{org}$ in the benthic nepheloid layer and sediment column, along with highly enriched $\delta^{13}C_{DIC}$ for the top 40 cm of measured porewater (Supp. Fig. 5), support the interpretation of active ME in shallow sediments. Taken together, ME accounted for at least 13–42% of anaerobic OCR in the ferruginous water column and sediments.

Fig. 2; Table 1

Evaluation of the role of ME in ancient ferruginous oceans will provide critical insights into the carbon cycling dynamics during the Precambrian and Earth's early climate evolution. Comparison of Brownie Lake's CH_4-carbon budget with other published datasets (Fig 3) suggests that the reported OC loading to CH_4 conversion efficiency in anaerobic OCR under ferruginous settings averages 36% (18–59%), with Brownie Lake at the lower end of this range but still significantly higher than modern (oxic) oceans with 0.1% efficiency. OC burial and ME can impact Earth's early oxygenation in different ways—the former removes a reductant from the Earth's surface. The latter injects a reductant into the atmosphere, inducing greenhouse warming and contributing to top-down oxygenation via hydrogen escape to space (after CH_4 photolysis) from the atmosphere (Catling et al., 2001). A dominant role of CH_4 in the Precambrian climate has been widely proposed in the past three decades of literature (Catling and Zahnle, 2020). A few recent studies have argued for a limited role of CH_4 in the Precambrian climate (Laakso and Schrag, 2019), citing a case example of high OC burial in ferruginous Lake Matano (Kuntz et al., 2015). Our results from Brownie Lake rather support a lower proportion of OC being buried in sediments under ferruginous settings and a dominant role of CH_4 in the Archean carbon cycle (Thompson et al., 2019).

In the modern oceans, an average net primary productivity (NPP) of 50 Gt C yr^{-1} results in 2 Gt C yr^{-1} deposited in the seafloor, leading to ~0.05 Gt CH_4 yr^{-1} ME via OCR (Akam et al., 2023), with an OC loading to CH_4 generation efficiency of 0.1%. Estimates for a late Archean setting range from 0.1% to 14% of modern NPP (Ward et al., 2019; Farr et al., 2023). An OC to CH_4 conversion efficiency of 36% would yield 2 to 210 (extended range of 1–344 considering 18–59% efficiency) Tmol CH_4 yr^{-1} or 0.4–56 times modern annual marine ME rates (Supp. Section 8). Interestingly, Ozaki and Reinhard (2018) modeled an increased efficiency of CH_4 cycling under a hybrid ecosystem composed of H_2 and Fe^{2+}-based anoxygenic photoautotrophy. Under low sulfate and low oxygen surface waters, this CH_4 would have entered the atmosphere easily, compared to >90% CH_4 being oxidized in the modern ocean with high sulfate and oxygen (Habicht et al., 2002).

Photochemical models predict that the lifetime of CH_4 in a low-O_2 atmosphere is 5,000–10,000 years, as opposed to ∼12 years today (Catling et al., 2001). Hence, anoxic Archean atmosphere could hold 1000s of parts per million by volume of CH_4, provided a sufficient CH_4 supply, and even a smaller CH_4 flux over time (e.g., 2 Tmol CH_4 yr^{-1} in Archean over thousands of years) can increase CH_4-induced warming on early Earth. The gradual oxidation of Earth's surface would have limited ME to anoxic deep water and sediment column as well as a reduced lifetime of CH_4 in the atmosphere, limiting their warming control (Olson et al., 2016). Our results point to efficient ME in ancient ferruginous oceans supporting the climate models, suggesting a significant climate warming by CH_4 (Haqq-Misra et al., 2008). In contrast, a lower role of CH_4-warming was proposed recently, primarily based on high OC burial rates in Lake Matano (Laakso and Schrag, 2019). Our results hence emphasize that the ferruginous oceans were conducive to high rates of ME, and thus, the availability of OC loading and oxidants like sulfate and oxygen would have been the key controlling factor determining the marine CH_4 fluxes to Earth's early atmosphere. The amount of

CH_4 produced would have closely followed the trend of NPP in the early Earth until the advent of surface oxygenation, at which time the efficiency of ME with reference to NPP would have decreased gradually leading to current efficiency of 0.1%. Lastly, we highlight the need to constrain the OC budget and the relative efficiency of ME from additional ferruginous systems to improve on our understanding of the biogeochemical significance of iron-rich systems at present and in the geological past.

Fig. 3

CONCLUSION

We document that ME is a dominant OCR process in ferruginous meromictic Brownie Lake, accounting for ≥90 and >9±7% of the anaerobic OCR in the water column and sediments, respectively, and an overall POC loading to CH_4 conversion efficiency of ≥18±7% in the anoxic zone of Brownie Lake. Our results, combined with available results from other ferruginous systems, point to a very high efficiency (36 ± 21%) of POC to CH_4 conversion in these systems, compared to 0.1% in the modern sulfatic and oxic ocean. Hence, we conclude that even under a low primary productivity scenario, Archean oceans would have produced sufficient CH_4, in agreement with climate models suggesting CH_4-induced greenhouse warming in early Earth.

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FIGURE CAPTIONS

Figure 1: Atmospheric A) CH_4 concentration B) and O_2 concentration (Fakhraee et al., 2019). C) Spatially predominant ocean-redox conditions over Earth's history (Poulton, 2021). PAL = present atmospheric level.

Figure 2: A) Study site. B) Temperature, conductivity, and dissolved O_2 and Fe profiles of the water column. C) isotopic composition; D) measured and modeled water column concentration profiles; E) Crossplot of TOC:N and $\delta^{13}C_{org}$ suggestive of labile carbon availability (Meyers, 1994). F) Overall carbon budget schematic.

Table 1: Summary of modeled carbon cycling parameters in Brownie Lake.

Figure 3: Comparison of A) anaerobic organic carbon remineralization (OCR) rates for Archean ferruginous settings and analogs, B) efficiency of methanogenesis (ME) in OCR, and C) ME efficiency to OC loading (data from Supp. Table 7) D) simplified schematic of C-CH_4 cycling in ancient ferruginous oceans.

[Please include this text at the end of your paper if you are including an item in the Supplemental

[1]Supplemental Material. *[Please provide a brief description of your material.]*

Supplementary file contains additional information on lake setting, water chemistry measurements, Organic carbon loading calculation, sediment-coring, age-dating, mass accumulation rates, reaction-transport model description, $\delta^{13}C$ and C:N composition for organic carbon source identification; oxidation state of iron in sediments; methane storage comparison with lakes of similar size, and overall carbon cycling schematic.