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Modeling the carbon cycle in Lake Matano

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ABSTRACT

Lake Matano, Indonesia, is a stratified anoxic lake with iron-rich waters that has been used as an analogue for the Archean and early Proterozoic oceans. Past studies of Lake Matano report large amounts of methane production, with as much as 80% of primary production degraded via methanogenesis. Low δ^{13}C values of DIC in the lake are difficult to reconcile with this notion, as fractionation during methanogenesis produces isotopically heavy CO_2. To help reconcile these observations, we develop a box model of the carbon cycle in ferruginous Lake Matano, Indonesia, that satisfies the constraints of CH_4 and DIC isotopic profiles, sediment composition, and alkalinity. We estimate methane fluxes smaller than originally proposed, with about 9% of organic carbon export to the deep waters degraded via methanogenesis. In addition, despite the abundance of Fe within the waters, anoxic ferric iron respiration of organic matter degrades <3% of organic carbon export, leaving methanogenesis as the largest contributor to anaerobic organic matter remineralization, while indicating a relatively minor role for iron as an electron acceptor. As the majority of carbon exported is buried in the sediments, we suggest that the role of methane in the Archean and early Proterozoic oceans is less significant than presumed in other studies.

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INTRODUCTION

The Archean ocean is thought to have been ferruginous, as abundant dissolved iron is required to explain the deposition of Archean banded iron formations (Holland, 1984; Bekker *et al.*, 2014). The biogeochemistry of an iron-rich Archean ocean is still very poorly understood. Lake Matano in Indonesia is a stratified anoxic lake with ferrous iron concentrations of more than 100 μM below its pycnocline. Lake Matano has been put forward as an analogue of Archean biogeochemical cycling (Crowe *et al.*, 2008). Crowe *et al.* (2011) estimated that as much as 80% of primary production in Lake Matano is degraded through methanogenesis, suggesting a quantitatively important role for methanogens in controlling organic carbon fluxes in low-oxygen, low-sulfate environments such as the Archean. If true, this suggests organic matter can be very efficiently remineralized in environments that lack electron acceptors. This contrasts a number of studies of organic carbon burial efficiency in anoxic marine sediments (e.g., Cowie *et al.*, 1995) and terrestrial wetlands (Shoemaker *et al.*, 2012); furthermore, an increase in burial efficiency under low-oxygen conditions is an important stabilizing feedback in a number of models of Phanerozoic pO_2 (e.g., Kump & Garrel, 1986; Lasaga & Ohmoto, 2002; Laakso & Schrag, 2014). Therefore, any evidence for efficient remineralization in anoxic environments is of great significance to our understanding of the carbon and oxygen cycles over geologic time scales.

The methanogenesis rates of Crowe *et al.* (2011) are derived from the methane profile of Lake Matano. The flux of methane to the oxidized surface layer is calculated by applying an eddy diffusion coefficient derived from the Brunt–Väisälä stability frequency to the methane gradient, and the depth-integrated methanogenesis rate is assumed equal to this diffusive loss at steady state. The resulting methane production rate is 1.6 mmol C m^{-2} d^{-1}, corresponding to a total organic carbon degradation rate of 3.2 mmol C m^{-2} d^{-1} (given a simplified stoichiometry $2CH_2O \rightarrow CO_2 + CH_4$). The reported primary production rate for the lake is 3.8 mmol C m^{-2} d^{-1}, and the organic carbon burial rate is reported to be 0.85–1.3 mmol C m^{-2} d^{-1}. Thus, the methane fluxes calculated by Crowe *et al.* (2011) imply that essentially all of organic carbon degradation occurs through methanogenesis.

Organic carbon degradation through methanogenesis produces CO_2 and CH_4 in equal amounts, whether it occurs through acetoclastic methanogenesis or CO_2 reduction. As methanogenesis is associated with a large isotopic fractionation (Crowe *et al.* report methane $\delta^{13}C$ near −70‰), the $\delta^{13}C$ of CO_2 released to the deep lake should be roughly +10‰, assuming an average $\delta^{13}C$ value of organic carbon of −30‰ (Crowe, unpublished data). Given that the calculated fluxes leave no room for significant degradation of organic carbon through other types of heterotrophic respiration, the $\delta^{13}C$ of the dissolved inorganic carbon (DIC) of the deep water in the lake should be slightly <+10‰, drawn down by diffusive exchange with the surface. However, the reported $\delta^{13}C_{DIC}$ at depth in Lake Matano is between −7 and −8‰, which is actually *depleted* relative to the surface value. This implies that the methanogenesis rate may be an overestimate and that there is substantial input of CO_2 from other types of heterotrophic respiration or other sources in the deep lake and is inconsistent with the calculated methane fluxes.

In this study, we revisit the carbon cycling in Lake Matano using a simple box model to estimate a rate of methanogenesis that is consistent with all of the constraints. These include the $\delta^{13}C$ of DIC, and an iron burial flux twice that calculated by Crowe *et al.* (2011), which stems from remedying an inconsistency between the length scales used to determine sedimentation rate and sediment water content. We calculate a methane flux that is roughly 15 times lower than proposed by Crowe *et al.* (2011). We discuss the implications these revised estimates have for understanding carbon cycling in the anoxic deep oceans of the Archean or Proterorozic.

METHODS

Our model of Lake Matano consists of two well-mixed layers, separated by an implicit pycnocline between 100 and 200 m, which has an unknown effective diffusivity. Such a simple model is consistent with many of the chemical profiles through the lake that show essentially no gradients above and below the pycnocline. Given the absence of chemical gradients in the deeper part of the lake, we cannot determine whether the chemical fluxes including methanogenesis and ferric iron respiration are occurring in the water column or in sediments. One can consider the sediments and the deep water together represented by the deeper layer in our model and the well-mixed surface water represented by the shallower layer. Species concentration values, for the surface and deep layers are given in Table 1, simplified from the data of Crowe *et al.* (2011) and presented in Fig. 1.

The mixed box treatment of Lake Matano allows for all methane and DIC production to occur in the well-mixed bottom portion. The flux between the surface and deep layers of the lake is controlled by an eddy diffusion coefficient, D, and the concentration gradient across the pycnocline. The diffusivity is taken to be constant across chemical species, as it is controlled through eddy mixing rather than molecular diffusion. The deep water is taken to be in steady state, with degradation of organic matter balanced by the flux of DIC and CH_4 from the bottom to the top of the lake. We also allow DIC to be removed via precipitation of carbonate minerals, primarily siderite. Degradation of organic matter occurs through methanogenesis and via iron reduction. The latter pathway is supported by an observed increase in $[Fe^{2+}]$ with depth below the pycnocline (Crowe *et al.*, 2008). Given the $\delta^{13}C$ and concentration of both methane and DIC at depth, it is possible to solve for the diffusion constant and the rates of carbonate precipitation, Fe(III) reduction, and methanogenesis.

Based on local observations, we assume that the incoming organic matter has an isotopic composition of −30‰ and that the carbonate precipitates out of the system with the same isotopic composition of the bottom waters ($\delta_P = -7.5‰$), the amount of carbonate precipitation P can be calculated as a function of the diffusivity:

$$\begin{aligned} \mathrm{P} = \mathrm{D}\Bigg(& \frac{\delta_{\mathrm{org}} + 1000}{\delta_{\mathrm{P}} - \delta_{\mathrm{org}}} \frac{(\mathrm{DIC}_B - \mathrm{DIC}_T) + (\mathrm{CH4}_B - \mathrm{CH4}_T)}{\mathrm{d}_{\mathrm{mid}}} \\ & - 1000 \frac{({}^{13}\mathrm{DIC}_B - {}^{13}\mathrm{DIC}_T) + ({}^{13}\mathrm{CH4}_B - {}^{13}\mathrm{CH4}_T)}{\mathrm{d}_{\mathrm{mid}} \mathrm{R}_{\mathrm{std}} (\delta_{\mathrm{P}} - \delta_{\mathrm{org}})} \Bigg) \\ = {} & 0.0101\mathrm{D} \end{aligned} \tag{1}$$

A complete derivation of this formula is provided in Appendix A. The isotopic composition of the organic matter necessary to sustain the measured isotopic profiles can be calculated as:

Table 1 Concentration and isotope values for the top and bottom portions of Lake Matano (Crowe *et al.*, 2011)

Species	DIC(mmol L^{-1})	CH_4(mmol L^{-1})	δDIC(‰)	δCH_4(‰)	^{13}DIC(mmol L^{-1})	$^{13}CH_4$(mmol L^{-1})
Top	2.0	0	−10	0	0.02	0
Bottom	3.7	1.2	−7.5	−70	0.041	0.013

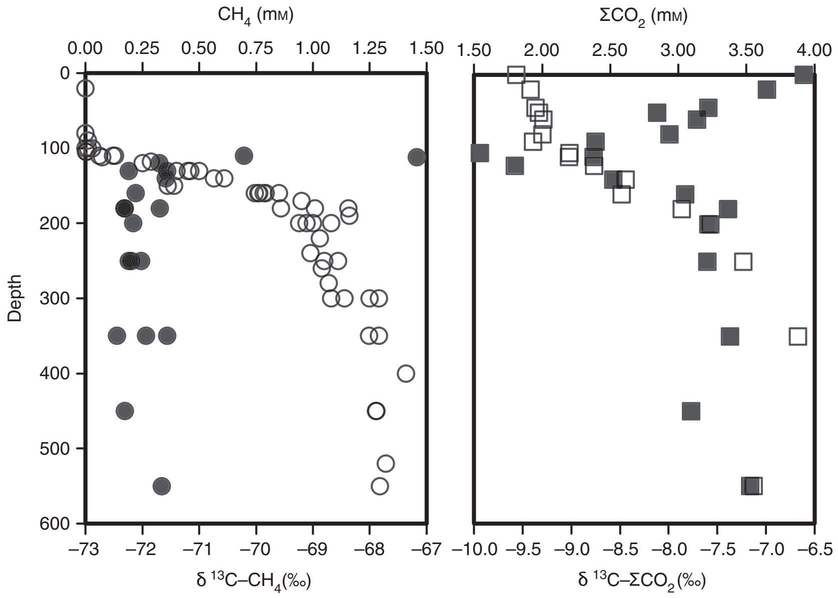

Fig. 1 Profiles of methane (circles) and DIC (squares) concentrations (open) and carbon isotopic compositions (filled). Modified from Crowe *et al.*, 2011.

$$R_{\mathrm{org}} = \frac{J_{13\mathrm{DIC}} + J_{13\mathrm{CH4}} + {}^{13}\mathrm{P}}{J_{\mathrm{DIC}} + J_{\mathrm{CH4}} + \mathrm{P}} \tag{2}$$

where P and ^{13}P are the amount of precipitation of carbonate with ^{12}C and ^{13}C, respectively, and R_{org} is defined by

$$\delta_{\mathrm{org}} = 1000\left(\frac{R_{\mathrm{org}}}{R_{\mathrm{std}}} - 1\right) \tag{3}$$

J_N is the diffusive flux of a species N between the top and bottom of the lake, given by:

$$J_N = \mathrm{D}\frac{[N]_B - [N]_T}{\mathrm{d}_{\mathrm{mid}}} \tag{4}$$

where d_{mid} is the thickness of the pycnocline and the subscripts B and T denote the bottom and top mixed portions of the lake, respectively.

At steady state, the net degradation rate must equal the loss of DIC and CH$_4$ from diffusion and carbonate precipitation:

$$\begin{aligned} r_{\mathrm{degradation}} &\approx \mathrm{P} + J_{\mathrm{DIC}} + J_{\mathrm{CH4}} \\ &= \mathrm{D}\left(0.0101 + \frac{(\mathrm{DIC}_B - \mathrm{DIC}_T) + (\mathrm{CH4}_B - \mathrm{CH4}_T)}{d_{\mathrm{mid}}}\right) \end{aligned} \tag{5}$$

where the contributions from ^{13}C species are neglected. Rearranging, it is possible to solve for the diffusion coefficient. Methane production is then set equal to J_{CH4}.

The chemical and isotopic mass balances in this simple model do not by themselves constrain the eddy diffusion coefficient through the pycnocline. Rather, the magnitude of the eddy diffusion coefficient depends on the total amount of carbon degraded through methanogenesis and respiration. The diffusivity scales with the degradation rate of organic matter – greater amounts of degradation require higher fluxes, implying higher diffusivities. An accurate measure of the degradation rate within Lake Matano is necessary to constrain the absolute value of the diffusivity.

The organic matter export to the deep waters that is not degraded is buried in the sediments. Hence, the rates of organic matter export and sedimentation can constrain the organic matter degradation rate. The primary production reported in Crowe *et al.* (2011), however, is not equivalent to organic matter export, as it does not account for allochthonous organic carbon, most likely from terrestrial plant debris, or respiration within the oxic top portion of the lake. Without estimates for organic matter export, it is impossible to fully constrain the diffusivity through a mass and isotopic balance alone. However, the sedimentation rate of iron can be used as an additional constraint on the system to determine diffusivity. Fe(III) reduction, using a simplified stoichiometry for Fe to C of 4:1, adds alkalinity to the lake. In our model, this alkalinity is removed through precipitation of siderite and mixed ferrous and ferric oxyhydroxides, ultimately ending up as magnetite. The observed accumulation of ferrous iron in the sediment therefore provides an upper bound on the rate of Fe(III) reduction, which in turn constrains the rate of methanogenesis through the isotopic mass balance.

Crowe *et al.* (2011) use sedimentation rate (0.08 cm y^{-1}; Crowe *et al.*, 2004), particle density (2.97 g cm^{-3}), Fe content (9–20 wt.%), and sediment water content (90% by mass) to calculate an iron burial rate of 0.38–0.85 mmol Fe m^{-2} d^{-1}. This calculation, however, used an estimated sediment water content value for the top 1 cm of sediment, although the sedimentation rate was calculated from ^{210}Pb data over the upper 10–30 cm (unpublished data). Instead, using a value for the sediment water content of 80% (by mass; 92% by volume) measured at 10 cm to reflect an average over the length scale of ^{210}Pb dating leads to Fe accumulation rates of 0.81–1.86 mmol Fe m^{-2} d^{-1}.

$$\begin{aligned} R_{Fe} &= R_{sed}(1-\theta)\rho_{sed}\,wt.\%_{Fe}\frac{1}{M_{Fe}} \\ &= 0.08\frac{cm}{yr}\cdot(1-0.92)\cdot 2.97\frac{g}{cm^3}\cdot 0.2\cdot\frac{1}{55.85\frac{g}{mol}} \\ &= 6.8\times10^{-5}\frac{molFe}{cm^2yr} = 1.86\frac{mmolFe}{m^2day} \end{aligned} \tag{6}$$

Similarly, the organic carbon content of 5–8 wt.% yields a sedimentation rate of 2.1–3.4 mmol C m^{-2} d^{-1}, or roughly 2.5 times the value reported in Crowe *et al.* (2011).

The Fe accumulation rates include both reduced and ferric iron. However, only precipitation of iron minerals with reduced iron (i.e., siderite and magnetite) balances the alkalinity budget. Thus, only a fraction of the Fe in the sediment plays a role in the carbon cycle and constrains the alkalinity budget. Assuming that 27% the iron burial is in the reduced state, based on estimates of reactive iron more generally (Canfield, 1988), and that all of this iron is processed through anaerobic Fe(III) reduction, then only 0.2–0.5 mmol Fe m^{-2} d^{-1} is available to balance the alkalinity budget. In this study, median values for reduced Fe availability (0.35 mmol Fe m^{-2} d^{-1}) and organic C burial (2.7 mmol C m^{-2} d^{-1}) are used in the carbon cycle model. Future measurements of the exported organic carbon into the deep waters and oxidation state of Fe in the sediments could be used to further constrain the system. However, the basic mass balance constraints of this analysis would still hold.

RESULTS

Figure 2 depicts the carbon cycle we calculate for Lake Matano. Roughly 0.39 mmol organic C m^{-2} d^{-1} is respired in the anoxic portion of the lake. Combined with the organic carbon sedimentation rate of 2.7 mmol m^{-2} d^{-1}, this results in a burial efficiency over 87%. The methanogenesis pathway degrades 0.30 mmol C m^{-2} d^{-1}, or 9 to 10% of organic matter export, producing CO_2 and CH_4 in equal amounts. This accounts for roughly 75% of the organic matter respiration, while an additional 0.09 mmol C m^{-2} d^{-1}, or 2 to 3% of organic matter export, undergoes Fe(III) reduction (the remaining 25% of organic carbon respiration). At steady state, methane diffuses up to the chemocline at a rate equal to methane production (0.15 mmol C m^{-2} d^{-1}). 0.21 mmol DIC m^{-2} d^{-1} diffuses to the top waters, while 0.03 mmol C m^{-2} d^{-1} is buried in the sediment as siderite, and 0.33 mmol Fe m^{-2} d^{-1} is buried as iron oxyhydroxides, eventually ending up as magnetite. The eddy diffusivity, assuming that all of the reactive iron is used in the reactions, is 1.4×10^{-7} m^2 s^{-1}.

Although changes in burial rate of reduced iron alters the amount of organic matter degradation, and subsequently the fluxes of methanogenesis and respiration and the

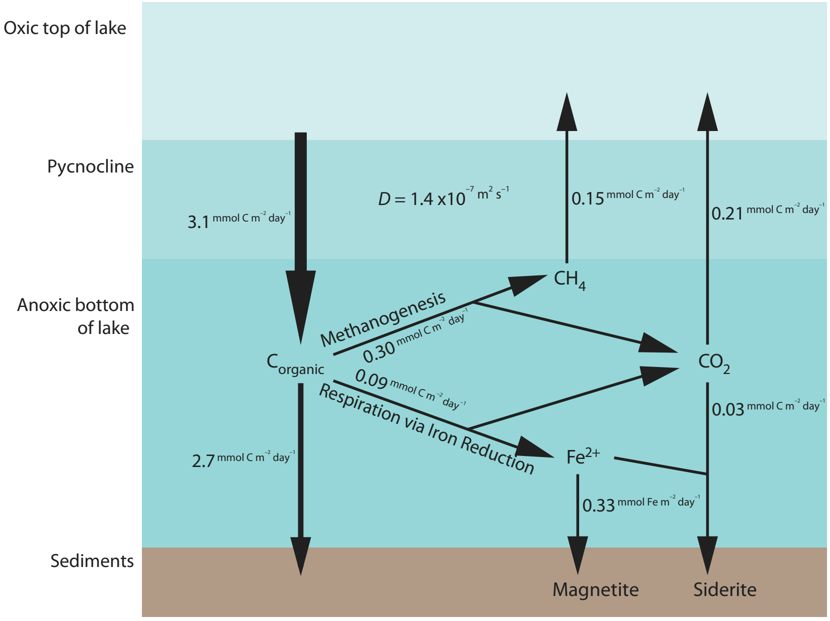

Fig. 2 A schematic representation of the organic matter burial and degradation pathways in Lake Matano with respective fluxes for each pathway listed. Although the methanogenesis and respiration reactions are depicted as occurring within the water column, we cannot distinguish whether these reactions occur there or within the sediments.

diffusivity, the results scale together. The ratio of respiration via Fe(III) reduction to methanogenesis is preserved irrespective of the burial rate, at a value of 1 to 3.4. Diffusivity is proportional to the flux of carbon degraded through methanogenesis; halving the rate of methanogenesis halves the diffusivity.

The numerical results are sensitive to changes in the isotopic composition of the organic matter, sediment-reduced iron content, and sediment organic matter content. A system with lighter organic matter has higher diffusivity, greater amounts of organic matter degradation, and a smaller ratio of respiration via Fe(III) reduction to methanogenesis. For instance, if the organic matter exported to the deep waters had an isotopic composition of $-31‰$, organic matter degradation increases to 14% of export, with methanogenesis accounting for 80% of this degradation. In this case, the diffusivity increases roughly 19%. Similarly, larger amounts of reduced iron in the sediment lead to increases in degradation and diffusivity. In the limiting case where all of the iron in the sediment was anaerobically respired and is in the reduced state, 34% of the organic matter is degraded and the diffusivity is about $5 \times 10^{-7}\ \mathrm{m}^2\ \mathrm{s}^{-1}$. The ratio of respiration via Fe(III) reduction to methanogenesis is unaltered, with methanogenesis still accounting for roughly 75% of the degradation. Although a simplified stoichiometry for Fe(III) reduction is assumed (4:1 for Fe to C), changes to the ratio of Fe to C have a minimal impact on the results. Using the stoichiometry of Bergmann *et al.* (2013) of 4.85:1 for Fe to C changes the numerical results by <15%. Finally, changes in the organic carbon content of the sediment only impact the burial efficiency. Sediment with 5 wt.% organic carbon would give a minimum burial efficiency of 86% while 8 wt.% organic carbon leads to a maximum burial efficiency of 90%.

DISCUSSION

Our model of Lake Matano reveals an anaerobic respiration pathway, presumably with Fe(III) as the electron acceptor. Iron reduction provides DIC that is isotopically depleted, while adding alkalinity. Carbonate precipitation alone cannot completely balance this alkalinity flux, implying that additional iron precipitation occurs, likely as ferrous oxyhydroxides. Alternative respiratory pathways such as denitrification and sulfate reduction produce changes in alkalinity sufficiently small to maintain a self-consistent system through carbonate precipitation alone. However, as only trace amounts of oxidized nitrogen and sulfur are present below the pycnocline in Lake Matano, it is doubtful that these reactions occur to any appreciable extent. In addition, a study of sediment composition in Lake Matano reveals that siderite is present in the sediments with as much as 40–60% of the sediments composed of iron oxyhydroxides (Crowe *et al.*, 2004), supporting the possibility of siderite precipitation via Fe(III) reduction. Subsequent investigations of Lake Matano can test the proposed iron reduction pathway and subsequent siderite and iron oxyhydroxide precipitation. By examining the redox state and chemical composition of iron within the lake sediments, burial rates can further constrain the model predictions.

The model results are valid irrespective of the particular biochemical pathway of methanogenesis. As long as the hydrogen (used as the primary electron donor) originates from organic matter degradation, the net stoichiometry is equivalent between pathways. Another possibility is that there are external sources of H_2 or CH_4 that do not come from organic matter degradation nearby. In our model, the isotopic constraints on DIC dictate the ratio of methanogensis to Fe(III) reduction of organic carbon. An additional methane source that does not affect the isotopic budget, such as from deep sediments or volcanic activity, would not impact our calculated degradation fluxes. Such a source could increase the net methane flux, suggesting a higher diffusivity than calculated by the model and consequently requiring a greater DIC flux and less carbonate precipitation, but it would not affect our calculation of methanogenesis rate. The presence of methylotrophic methanogenesis would have a similar effect, as it would not impact the isotropic balance, yet would add methane to the system. This possibility is neglected in the model, as methylotrophic methanogenesis is unlikely to result in large-scale organic matter degradation (Penger *et al.*, 2012).

An external source of hydrogen, such as from serpentinization, would necessitate a greater portion of degradation via Fe(III) reduction. Similar to the isotopic effects of methanogenesis, an external H_2 supply would react with CO_2 to fractionate toward heavier DIC, essentially acting as an additional source of heavy DIC. A smaller ratio of methanogenesis to Fe(III) reduction of organic carbon would be necessary to explain the isotopically light DIC in the bottom waters, implying even lower rates of methanogenesis.

Limestone dissolution may also have an effect on our calculation of methanogenesis rate by acting as an additional source of heavy DIC. Any dissolution of limestone would shift our calculations toward a smaller ratio of methanogenesis to Fe(III) reduction rates, and thus a smaller overall methanogenesis rate. Limestone is present in the region, so some dissolution of carbonates is possible. However, the concentration of DIC is roughly an order of magnitude higher than the concentration of Ca^{2+}, implying that the impact on our calculated carbon budget in Lake Matano is small.

The Lake Matano carbon cycle described here is characterized by extremely efficient burial of organic carbon, representing nearly 90% of organic carbon export to the deep waters. Organic matter degradation is dominated by

Table 2 Diffusivity through pycnocline of meromictic lakes

Location	Diffusivity ($m^2 s^{-1}$)	Source
Lac Pavin, France	5×10^{-8}	Aeschbach-Hertig *et al.*, 2002
Merseburg-Ost 1b, Germany	~10^{-8}	von Rohden & Ilmerger, 2001
Waldensee, Germany	~10^{-9}	Boehrer *et al.*, 2009
Lake Lugano, Switzerland	2×10^{-5}	Aeschbach-Hertig *et al.*, 2007

methanogenesis, but the total flux is quite small compared to >99% recycling of organic carbon in oxic marine settings. This is consistent with a number of studies showing that organic carbon burial efficiency rises with decreasing levels of oxygen (Canfield, 1993; Cowie *et al.*, 1995; Hedges *et al.*, 1999).

While our calculated diffusivity of 1.4×10^{-7} m^2 s^{-1} is in close agreement with other meromictic lakes as presented in Table 2, it is over an order of magnitude smaller than the diffusivity calculated by Katsev *et al.* (2010) and is also outside of the range presented in Crowe *et al.* (2014) for the pycnocline in Lake Matano, although the uncertainty in these values is high. Katsev *et al.* (2010) uses a variety of empirical and modeling methods to calculate the diffusivity. Empirical formulas, however, rely on a variety of parameters that are sensitive to the physics of a specific location and can span a wide range. Without accurate constraints on these parameters, empirical formulas are limited in their ability to provide absolute values of diffusivity. In addition, the 1-D and 3-D models employed in Katsev *et al.* (2010) use the heat budget to constrain the diffusivity. Although this can provide a reliable estimate of thermal diffusivity, it is not necessarily equivalent to the turbulent diffusivity. Studies of other meromictic lakes indicate a higher diffusivity for heat than dissolved substances (von Rohden & Ilmerger, 2001; Aeschbach-Hertig *et al.*, 2002, 2007), which could explain the discrepancy with the value calculated by Katsev *et al.* (2010). In the future, chemical tracer experiments in Lake Matano could be performed to test this possibility and further constrain the carbon budget.

Our results have important implications for our understanding of biogeochemical cycling in the low-oxygen oceans hypothesized for the Archean and Proterozoic. Highly efficient burial of organic carbon in these anoxic oceans would result in a larger-than-modern source of oxygen, as long as nutrient availability remained the same. This opens up the possibility that nutrient limitation could have stabilized the redox budget, a concept employed in recent modeling of Proterozoic oxygen (Laakso & Schrag, 2014). If methanogens were in fact capable of remineralizing the bulk of primary productivity in ferruginous waters, this feedback would be much less significant, and it would be reasonable to assume a fixed organic carbon burial efficiency at any time, an approach that has been used in previous models of the Proterozoic (Fennel *et al.*, 2005) and the Archean (Habicht *et al.*, 2002). The low rates of methanogenesis support the theory that the rate-limiting factor for methanogenesis is the breakdown of organic matter into simple sugars rather than the availability of organic carbon (Shoemaker *et al.*, 2012). Our model for Lake Matano provides further evidence that organic carbon is buried more efficiently in anoxic environments, and that the role of methanogenesis has been overstated. This result emphasizes the need to re-examine the basis for requiring a greenhouse gas other than CO_2 to resolve the Faint Young Sun paradox (Halevy *et al.*, 2009).

A final point is that, despite very high Fe(III) supply, respiration of organic carbon using it as an electron acceptor in Lake Matano is very small; only 2–3% of the organic carbon export is degraded through Fe(III) reduction. Despite experimental evidence that this process can proceed rapidly (Lovely & Phillips, 1988), the kinetics appear to be too slow to make a substantial contribution to the overall carbon budget in Lake Matano. Iron reduction can be important in other environments, such as Danish coastal sediments (Canfield *et al.*, 1993) or the Amazon shelf (Aller & Blair, 2006) where many cycles of Fe(III) reduction and Fe(II) reoxidation occur at a highly oxidized carbon-rich interface (e.g., Canfield *et al.*, 1993; Lovley *et al.*, 2004). This implies that the efficiency of Fe(III) reduction as a process for remineralizing organic carbon in an anoxic ocean in the Archean or Proterozoic is likely to have been very low. The presence of magnetite in organic carbon-poor banded iron formations (BIFs) of Archean and Paleoproterozoic ages has been taken as a possible indication of the importance of Fe(III) reduction in organic matter degradation at that time (Konhauser *et al.*, 2005). Our results suggest that if BIFs were initially organic carbon rich, and if the organic carbon was remineralized through Fe(III) reduction, then this process may have occurred much later in the burial process, or during metamorphism.

CONCLUSIONS

We present a quantitative model of carbon cycling in Lake Matano that matches isotopic, concentration, and sedimentation constraints. We calculate a methanogenesis rate of 0.30 mmol C m^{-2} d^{-1} or 9–10% of organic carbon export. We show that methanogenesis is the most important contributor to anaerobic carbon remineralization, but that the vast majority of organic carbon export is buried in the sediments, with burial efficiency near 90%. This supports the idea that without adequate availability of electron acceptors, methanogenesis is substrate limited, perhaps by the availability of simple sugars to drive fermentation. We calculate a maximum rate of respiration using Fe(III) reduction of 2–3% of the organic carbon export. If Lake

Matano is a good analogue for the Archean and Proterozoic oceans, then the role of methane and iron in the marine carbon cycle at these times has likely been overstated.

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APPENDIX A PRECIPITATION RATE ALGEBRA

Beginning with the equation for isotopic composition of organic matter

$$\delta_{\mathrm{org}} = 1000\left(\frac{\mathrm{R_{org}}}{\mathrm{R_{std}}} - 1\right) \tag{7}$$

where

$$R_{\mathrm{org}} = \frac{J_{13\mathrm{DIC}} + J_{13\mathrm{CH4}} + {}^{13}\mathrm{P}}{J_{\mathrm{DIC}} + J_{\mathrm{CH4}} + \mathrm{P}} \tag{8}$$

the goal was to solve for P, the precipitation rate, as a function of the diffusion coefficient, D. ^{13}P can be written in terms of P by assuming that the isotopic composition of the precipitate of δ_{P} which is taken to be equal to the isotopic composition of the bottom waters, or $-7.5‰$:

$${}^{13}\mathrm{P} = \left(\frac{\delta_{\mathrm{P}}}{1000} + 1\right) \mathrm{R}_{\mathrm{std}} \mathrm{P} \tag{9}$$

Plugging Equations (8) and (9) into (7) gives:

$$\delta_{\mathrm{org}} = 1000 \left[\frac{\frac{J_{13\mathrm{DIC}} + J_{13\mathrm{CH4}} + \left(\frac{\delta_{\mathrm{P}}}{1000} + 1\right) \mathrm{R}_{\mathrm{std}} \mathrm{P}}{J_{\mathrm{DIC}} + J_{\mathrm{CH4}} + \mathrm{P}}}{\mathrm{R}_{\mathrm{std}}} - 1 \right] \tag{10}$$

Rearranging to get the P terms on one side:

$$\mathrm{P}\mathrm{R}_{\mathrm{std}} \left(\frac{\delta_{\mathrm{P}} - \delta_{\mathrm{org}}}{1000}\right) = \mathrm{R}_{\mathrm{std}} \left(\frac{\delta_{\mathrm{org}}}{1000} + 1\right) (J_{\mathrm{DIC}} + J_{\mathrm{CH4}}) - (J_{13\mathrm{DIC}} + J_{13\mathrm{CH4}}) \tag{11}$$

$$\mathrm{P} = \left(\frac{\delta_{\mathrm{org}} + 1000}{\delta_{\mathrm{P}} - \delta_{\mathrm{org}}}\right) (J_{\mathrm{DIC}} + J_{\mathrm{CH4}}) - 1000 \frac{(J_{13\mathrm{DIC}} + J_{13\mathrm{CH4}})}{\mathrm{R}_{\mathrm{std}} (\delta_{\mathrm{P}} - \delta_{\mathrm{org}})} \tag{12}$$

Factoring D out of the fluxes gives the result presented in Equation (1):

$$\mathrm{P} = \mathrm{D} \left(\frac{\delta_{\mathrm{org}} + 1000}{\delta_{\mathrm{P}} - \delta_{\mathrm{org}}} \frac{(\mathrm{DIC}_B - \mathrm{DIC}_T) + (\mathrm{CH4}_B - \mathrm{CH4}_T)}{\mathrm{d}_{\mathrm{mid}}} - 1000 \frac{({}^{13}\mathrm{DIC}_B - {}^{13}\mathrm{DIC}_T) + ({}^{13}\mathrm{CH4}_B - {}^{13}\mathrm{CH4}_T)}{\mathrm{d}_{\mathrm{mid}} \mathrm{R}_{\mathrm{std}} (\delta_{\mathrm{P}} - \delta_{\mathrm{org}})} \right) \tag{13}$$

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