Anaerobic methanotrophy and the rise of atmospheric oxygen

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In modern marine sediments, the anoxic decomposition of organic matter generates a significant flux of methane that is oxidized microbially with sulphate under the seafloor and never reaches the atmosphere. In contrast, prior to ca 2.4 Gyr ago, the ocean had little sulphate to support anaerobic oxidation of methane (AOM) and the ocean should have been an important methane source. As atmospheric O2 and seawater sulphate levels rose on the early Earth, AOM would have increasingly throttled the release of methane. We use a biogeochemical model to simulate the response of early atmospheric O2 and CH4 to changes in marine AOM as sulphate levels increased. Semi-empirical relationships are used to parameterize global AOM rates and the evolution of sulphate levels. Despite broad uncertainties in these relationships, atmospheric O2 concentrations generally rise more rapidly and to higher levels (of order approx. 10^3 bar versus approx. 10^4 bar) as a result of including AOM in the model. Methane levels collapse prior to any significant rise in O2, but counter-intuitively, methane re-rises after O2 rises to higher levels when AOM is included. As O2 concentrations increase, shielding of the troposphere by stratospheric ozone slows the effective reaction rate between oxygen and methane. This effect dominates over the decrease in the methane source associated with AOM. Thus, even with the inclusion of AOM, the simulated Late Palaeoproterozoic atmosphere has a climatologically significant level of methane of approximately 50 ppmv.

Keywords: oxygen; methane; methanotrophy; Archaean; Proterozoic; atmospheric evolution

1. Introduction

Oxygen concentrations in the Earth’s atmosphere are inferred to be less than 1 ppmv prior to ca 2.4 Gyr ago (Pavlov & Kasting 2002; Bekker et al. 2004). In such an anoxic atmosphere, photochemical models show that methane has a

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One contribution of 18 to a Discussion Meeting Issue ‘Trace gas biogeochemistry and global change’. 
lifetime of approximately $10^4$ years and can reach levels of $10^2$–$10^3$ ppmv, given a biogenic source of approximately 0.1–1 times present (Pavlov et al. 2001; Zahnle et al. 2006). Methane at this abundance can provide sufficient greenhouse warming to counteract an early Sun that was 25–30% fainter (Pavlov et al. 2000; Kasting & Howard 2006). The ultraviolet decomposition of methane in the early upper atmosphere and the accompanying escape of hydrogen to space may have also been important for irreversibly oxidizing Earth’s surface environment and enabling the rise of oxygen (Catling et al. 2001; Claire et al. 2006).

Carbon and sulphur isotopes suggest that there was abundant methane in the Archaean. A global distribution of $^{12}$C-enriched kerogens of 2.5–2.8 Ga age can be attributed to isotopically light CH$_4$, greater than 20 ppmv abundance, generated by methanogens and incorporated into methanotrophs (Hayes 1994; Hinrichs 2002; Hayes & Waldbauer 2006). Strictly speaking, this evidence only indicates that methane had to be plentiful within worldwide sediments, but independent evidence for high methane in the atmosphere is provided by mass-independent fractionation (MIF) of Archaean sedimentary sulphur isotopes (Farquhar et al. 2000). Abundant MIF is thought to occur only when sulphur exits the atmosphere in soluble and insoluble forms: in particular, soluble SO$_4^{2-}$ and insoluble elemental polymerized sulphur (S$_8$) at different ends of the sulphur redox distribution (Pavlov & Kasting 2002). Models show that both low levels of oxygen and a sufficiently high abundance of methane are required for insoluble S$_8$ to be a significant photochemical product of the ancient anoxic atmosphere (Ono et al. 2003; Zahnle et al. 2006). Sufficient methane enables the photochemical reduction of sulphur-bearing gases to S$_8$. Thus, Zahnle et al. (2006) show that MIF is indirect evidence for high Archaean methane.

Evidence from biomarkers suggests that oxygenic photosynthesis arose long before the rise of atmospheric O$_2$ around 2.4 Gyr ago (Brocks et al. 2003; Summons et al. 2006), a puzzle that can be explained if the O$_2$ was efficiently scavenged by a glut of reductants in the early environment (e.g. Walker et al. 1983; Holland 2002; see Catling & Claire (2005) for a review). Given little O$_2$ and abundant CH$_4$ in the Archaean atmosphere, how did the atmosphere become oxygenated?

One way to understand the factors that influence the history of O$_2$ is through time-dependent biogeochemical box models that simulate changes in atmospheric O$_2$ levels as a result of redox fluxes in the Earth system. In such models, it is necessary to pay particular attention to atmospheric photochemistry in order to simulate realistic levels of O$_2$ or CH$_4$. In Catling et al. (2004), we presented preliminary results of a biogeochemical model where we parameterized an effective bimolecular reaction between CH$_4$ and O$_2$ with a rate constant that depended on the levels of CH$_4$ and O$_2$. We noted then that shielding of the troposphere by stratospheric ozone acts as a positive feedback on O$_2$ as O$_2$ rises (Catling et al. 2004). Claire et al. (2006) (a paper which we henceforth refer to as ‘CCZ’) have subsequently enhanced this model and described its sensitivities and results in considerable detail (e.g. fig. 3 in CCZ shows the effect of increasing stratospheric ozone on the effective reaction of O$_2$ and CH$_4$ from photochemical modelling). Goldblatt et al. (2006) present a similar model that also uses the idea of an effective bimolecular reaction between O$_2$ and CH$_4$; as in Catling et al. (2004), they found that ozone shielding acts as a positive feedback on the rise of O$_2$.
While the shielding effect of the ozone layer is important in understanding the steady-state differences between oxic and anoxic atmospheres, CCZ demonstrated that this feedback alone does not cause an abrupt rise in oxygen. Instead, we hypothesized that the biosphere provided a strong positive feedback on atmospheric O\(_2\) by diminishing the CH\(_4\) flux to the atmosphere relative to the O\(_2\) flux (Zahnle et al. 2006). In particular, we hypothesized that the increase in oceanic sulphate (and nitrate) levels was accompanied by the increased activity of methanotrophs, which facilitated a rapid transition to an oxic atmosphere by lowering the ratio of CH\(_4\) : O\(_2\) fluxes to the atmosphere.

In this paper, we demonstrate the plausibility of this idea using our box model. Goldblatt et al. (2006) included aerobic methanotrophs in their model, i.e. microbes that directly use atmospheric O\(_2\) to consume CH\(_4\), but this has no effect on the CH\(_4\) : O\(_2\) flux ratio and so is neutral with respect to atmospheric redox. In contrast, anaerobic methanotrophs are known to use sulphate or nitrate when O\(_2\) is unavailable in the metabolic processes of ‘anaerobic oxidation of methane’ (AOM). In this paper, we demonstrate how AOM was likely to have been important in determining the rapidity and magnitude of the ca 2.4 Gyr ago rise of O\(_2\). We also show how AOM modulates the evolution of CH\(_4\) levels, which has implications for Earth’s climate.

2. Method: the box model and anaerobic oxidation of methane

In §2a–c, we describe our biogeochemical model, how AOM should influence the rise of oxygen, and how we parameterize AOM in the model.

(a) Model description

As our point of departure, we consider the atmosphere only after the advent of oxygenic photosynthesis. A full description of our biogeochemical model is given in CCZ. Here, we briefly reiterate the key equations so that modifications to take anaerobic methanotrophy into account can be appreciated.

In our model, the amount of O\(_2\) in the atmosphere is determined by a kinetic competition between source (\(F_{\text{SOURCE}}\)) and sink (\(F_{\text{SINK}}\)) fluxes of O\(_2\), i.e.

\[
\frac{d}{dt}[O_2] = F_{\text{SOURCE}} - F_{\text{SINK}} = (F_B + F_E) - (F_V + F_M + F_W), \tag{2.1}
\]

where \([O_2]\) is the total reservoir of atmospheric O\(_2\), which we express in units of teramoles \((10^{12}\) mol), sometimes converting to partial pressure units of bars for figures. We implement all source and sink fluxes in the model in units of Tmol O\(_2\) yr\(^{-1}\) production or consumption. We divide \(F_{\text{SOURCE}}\) into \(F_B\), the flux of oxygen due to organic carbon burial, and \(F_E\), the flux of oxygen to the Earth as a whole due to hydrogen escape. The oxygen sinks \(F_V\) and \(F_M\) represent oxygen-consuming gases (i.e. H\(_2\), H\(_2\)S, SO\(_2\), CO, CH\(_4\)) from volcanic/hydrothermal and metamorphic/geothermal processes, respectively, while \(F_W\) is the oxygen sink due to oxidative weathering of continental rocks. Equation (2.1) is illustrated by summing fluxes in and out of the atmosphere–ocean–biosphere (‘AOB’) box in figure 1.

We ignore the gross photosynthesis–respiration cycle because this rapid, closed cycle generates no net O\(_2\) (e.g. see Garrels & Perry (1974) or Walker (1980)). However, in order to calculate the levels of methane in the Archaean
atmosphere, it is necessary to consider the fraction of photosynthesized carbon from gross primary productivity that gets converted to methane. The net effect of methanogenic recycling of organic carbon produced photosynthetically is found by summing the respective net reactions of oxygenic photosynthesis and methanogenesis, as follows:

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} &\rightarrow \text{CH}_2\text{O} + \text{O}_2 \cdots \times 2 \\
+ 2\text{CH}_2\text{O} &\rightarrow \text{CH}_4 + \text{CO}_2 \\
\text{CO}_2 + 2\text{H}_2\text{O} &\rightarrow \text{CH}_4 + 2\text{O}_2
\end{align*}
\]

Thus, the combination of oxygenic photosynthesis and methanogenesis generates \( \text{O}_2 \) and \( \text{CH}_4 \) in the ratio of 2 : 1. Consequently, a flux of methane, \( \phi_{\text{CH}_4} \), to the atmosphere is accompanied by a stoichiometrically balanced flux of \( \text{O}_2 \) of \( 2\phi_{\text{CH}_4} \). This enables us to expand equation (2.1) to coupled time-dependent equations for the first-order evolution of atmospheric methane and oxygen

\[\frac{\text{d}}{\text{d}t}[\text{CH}_4] = \phi_{\text{CH}_4} - k_{\text{eff}}[\text{O}_2][\text{CH}_4] - k_{\text{esc}}[\text{CH}_4],\]

\[\frac{\text{d}}{\text{d}t}[\text{O}_2] = 2\phi_{\text{CH}_4} - 2k_{\text{eff}}[\text{O}_2][\text{CH}_4] - k_{\text{esc}}[\text{CH}_4] + F_B - (F_V + F_M + F_W),\]

where \( k_{\text{eff}} \) (Tmol\(^{-1}\) yr\(^{-1}\)) is the effective rate constant for a net bimolecular kinetic destruction of \( \text{O}_2 \) and \( \text{CH}_4 \). This reaction is ‘effective’ because it is not a real bimolecular reaction but the net result of many other reactions, starting with an attack on \( \text{CH}_4 \) by \( \text{OH} \), the hydroxyl radical. We have numerically parameterized \( k_{\text{eff}} \) from over a thousand photochemical model runs as a function of \( \text{CH}_4 \) and \( \text{O}_2 \) levels, as described in CCZ. The constant \( k_{\text{esc}} = 3.7 \times 10^{-5} \) Tmol \( \text{O}_2 \) equivalents yr\(^{-1}\) \((\text{Tmol CH}_4)^{-1}\) parameterizes the net photochemical destruction of methane associated with diffusion-limited hydrogen escape, \( F_E = k_{\text{esc}} [\text{CH}_4] \). As four H atoms

Figure 1. A schematic of the three-box model. Arrows represent fluxes of reducing material in Tmol \( \text{O}_2 \) equivalents yr\(^{-1}\). Consequently, arrows leaving a box represent oxidizing processes. Equation (2.1) for the evolution of \( \text{O}_2 \) is obtained by subtracting incoming reductant fluxes from outgoing reductant fluxes. The unfilled arrows represent crustal mixing due to erosion, uplift and tectonics.
escape, a CH$_4$ molecule is subtracted from our tally of methane in equation (2.3) by the term $-k_{\text{esc}}[\text{CH}_4]$. The remaining carbon atom (in both anoxic and oxic atmospheres) ultimately form CO$_2$ by a series of photochemical reactions, which acts as a net sink for atmospheric O$_2$. Owing to this, one O$_2$ redox equivalent is subtracted from our model atmosphere in equation (2.4) in the term $-k_{\text{esc}}[\text{CH}_4]$. However, since one molecule of methane ordinarily consumes two molecules of O$_2$ (the reverse of equation (2.2)), the net effect of methane-induced hydrogen escape is that the Earth gains an O$_2$ equivalent (Catling et al. 2001). Parameterizations for the following (and their corresponding sensitivities in the model) are described in CCZ and will not be repeated here: (i) evolution of the metamorphic reducing gas flux $F_M$ as a function of crustal redox state and (ii) evolution of volcanic reducing gas flux $F_V$. The oxidative weathering loss is parameterized as $F_W = k_W[\text{O}_2]^{b_w}$, where $b_w = 0.4$ is a dimensionless constant (see CCZ for justification) and the constant $k_W = 0.0065 \text{Tmol}^{0.6} \text{yr}^{-1}$ is based on the estimated modern flux, $F_W \approx 7 \text{Tmol} \text{O}_2 \text{yr}^{-1}$ and the known modern concentration of oxygen, $[\text{O}_2] = 0.21 \text{bar} \times (1.78 \times 10^8 \text{Tmol} \text{bar}^{-1}) = 3.7 \times 10^7 \text{Tmol}$.

(b) How methanotrophic feedback should influence the rise of O$_2$

Microbial methanotrophy results in the oxidation of methane with O$_2$, sulphate or nitrate. When sufficient methane and O$_2$ coexist, methane-oxidizing bacteria (methanotrophs) live off the reverse of equation (2.2). But in anoxic conditions, AOM is performed by a consortium of archaea and bacteria and requires either SO$_4^{2-}$ (e.g. Barnes & Goldberg (1976) and Reeburgh (1976) for pioneering papers or Valentine (2002) for a recent review) or NO$_3^-$ (Raghoebar-sing et al. 2006). The main source of oceanic SO$_4^{2-}$ today is O$_2$-dependant oxidative weathering (Holland 1978; Walker & Brimblecombe 1985). The lack of $\delta^{34}$S fractionation in Archaean marine sediments indicates low oceanic sulphate levels, which is consistent with very small fluxes of oxidative weathering (Canfield et al. 2000; Habicht et al. 2002). In terms of our model, the $F_W$ term in equation (2.4) was very small during the Archaean. Fixation of N$_2$ to NH$_4^+$ is considered to be genetically ancient, but O$_2$ is required to further oxidize the ammonia to nitrate, so NH$_4^+$ was probably the dominant nitrogen species in Archaean oceans (Beaumont & Robert 1999; Berman-Frank et al. 2003).

Owing to the lack of sulphate and nitrate in the Archaean, we assumed Archaean AOM to be fully limited in the CCZ paper. Thus, all CH$_4$ that was likely to be made from organic carbon production was fluxed to the atmosphere. In this paper, we explore the idea that any sulphate produced as the atmosphere transits to an oxic state would allow AOM to act as a significant throttle on methane fluxes through the following net reaction for AOM, which is performed by a consortium of CH$_4$-oxidizing archaea and sulphate-reducing bacteria (Boetius et al. 2000):

$$\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HS}^- + \text{HCO}_3^- + \text{H}_2\text{O}. \quad (2.5)$$

In the Archaean ocean, which had abundant ferrous iron at depth, such sulphide generated by methanotrophy would be rapidly removed as iron sulphides (Walker & Brimblecombe 1985). We focus on sulphate rather than nitrate because methanotrophy with sulphate occurs at a lower redox state and
The available evidence suggests that the nitrogen would predominantly be in the ammonium state prior to the oxic transition. Incorporation of nitrate methanotrophy and the nitrogen cycle is beyond the scope of this paper. The key point for the evolution of the environment is that with the presence of sulphate, the reducing partner that accompanies O$_2$ production in equation (2.2) is changed from volatile CH$_4$ to involatile sulphide. Clearly, O$_2$ and CH$_4$ would no longer flux to the atmosphere in the ratio of 2 : 1 under these circumstances. We would expect this flux imbalance to help O$_2$ win control of the redox state of the early atmosphere. The flux imbalance should also amplify in positive feedback at the oxic transition as more sulphate is produced.

With a given outgassing flux of reduced gases, the difference between an oxic and anoxic atmosphere can result from just a few per cent increase in the ratio of O$_2$ : CH$_4$ fluxes, according to the calculations with the one-dimensional photochemical model that we have described in Zahnle et al. (2006). In this model, the O$_2$ : CH$_4$ flux required to support a given atmospheric composition is slightly different from 2 : 1 because atmospheric redox balance is not just between O$_2$ and CH$_4$, but modulated by rainout of photochemical oxidants and reductants, as well as the escape of hydrogen to space. Figure 2 shows results from the photochemical model for assumed sulphur outgassing fluxes of approximately 1 Tmol S yr$^{-1}$ (a modern, high-end estimate of outgassing with SO$_2$ : H$_2$S fluxes in the ratio of 10 : 1, discussed in Zahnle et al. 2006), a fixed methane mixing ratio of 100 ppmv, and fixed outgassing flux of H$_2$ (2.7 Tmol yr$^{-1}$) and CO (0.3 Tmol yr$^{-1}$). The plot shows the O$_2$, CH$_4$, SO$_4^{2-}$ and S$_8$ fluxes which the photochemistry requires for a steady-state solution when the O$_2$ mixing ratio is set to that shown on the z-axis. The plus symbols (+) are the ratio of the O$_2$ and CH$_4$ flux curves, which map to the right-hand ordinate axis. Shaded regions in figure 2

Figure 2. Major atmospheric fluxes of chemical species (in molecules cm$^{-2}$ s$^{-1}$) as a function of the ground-level O$_2$ mixing ratio for a fixed CH$_4$ mixing ratio of 100 ppmv and fixed volcanic outgassing fluxes of sulphur gases and reducing gases (see text). Plus symbols (+) map to the right-hand ordinate axis and indicate the net ratio of the biogenic O$_2$ flux ($\phi_{O_2}$) to CH$_4$ flux ($\phi_{CH_4}$) as a function of the ground-level O$_2$ mixing ratio (equivalent to a partial pressure in bars to a 1 bar atmosphere). The shaded regions represent cases when the biogenic O$_2$ fluxes are either implausibly high or low.
are considered ‘forbidden’ because they require biogenic fluxes that are unreasonable according to arguments presented by Zahnle et al. (2006). Denoting O\(_2\) and CH\(_4\) fluxes by the symbols \(\phi_{O_2}\) and \(\phi_{CH_4}\), respectively, the oxic solutions in figure 2 have slightly higher \(\phi_{O_2}/\phi_{CH_4}\) ratios than the anoxic solutions. The mean value of \(\phi_{O_2}/\phi_{CH_4}\) in the stable anoxic regime (O\(_2\) with a mixing ratio of \(1 \times 10^{-10} - 2 \times 10^{-7}\)) is 2.014, while the mean ratio in the stable oxic regime (O\(_2\) with a mixing ratio of \(6 \times 10^{-4} - 0.1\)) is 2.11, which is an average increase of 4.8%. The flux ratio change between the most oxic anoxic atmosphere and the least oxic oxygenated atmosphere (i.e. from both sides of the forbidden, shaded region of \(2 \times 10^{-5} < O_2 < 6 \times 10^{-4}\)) is approximately 3%.

It is important to realize that for the results of our biogeochemical model, we are considering a non-steady-state, time-dependent Earth system. Consequently, one should avoid falling into a ‘steady-state trap’ of thinking that consumption of O\(_2\) associated with continental sulphide weathering (which is included as a proportion of flux \(F_W\) in equation (2.4) in our model) must exactly balance any reduction of sulphate. Sulphate built up in the ocean going from the Archaean to the Proterozoic, so that the summed flux of sulphate-producing weathering plus input from photochemical sulphate rainout must have outpaced sulphide deposition in the ocean. Indeed, during the Archaean, the primary input of sulphate to the oceans would have been photochemical production in the atmosphere, as originally suggested by Walker & Brimblecombe (1985) and verified by our photochemical calculations (e.g. the sulphate rainout flux in figure 2 in the anoxic regime is approx. 0.25 Tmol S yr\(^{-1}\)). Thus, a curious subtlety is that marine microbial sulphate reduction should have exceeded the flux of sulphate from weathering in the Archaean because the sulphate at this time primarily derived from photochemical oxidation of volcanic gases. Hydrogen escape to space supported a sulphate rainout flux.

Finally, another potential subtlety is that with the wider availability of sulphate during the oxic transition, the gaseous reduced partner of O\(_2\) may have changed from CH\(_4\) to biogenic sulphur gases. These sulphur gases, unlike methane, are kinetically much more unstable than O\(_2\). The photochemistry of such an atmosphere would clearly favour higher concentrations of O\(_2\). Biogenic sulphur gases include CH\(_3\)SCH\(_3\), OCS and CS\(_2\). According to the review by Warneck (2000, p. 611), today’s biogenic S flux of dimethyl sulphide is approximately 1.1 Tmol S yr\(^{-1}\), which exceeds estimated volcanic sulphur fluxes ranging approximately 0.3–1 Tmol S yr\(^{-1}\). However, the potential feedback of biogenic sulphur gases falls beyond the scope of the present paper because they are not yet implemented in either our photochemical or biogeochemical models.

(c) The magnitude of AOM and its parameterization

AOM with sulphate takes place in a narrow vertical zone in sediments called the sulphate–methane transition zone (SMTZ). Generally, in modern sediments, the sulphate–methane boundary lies at some distance (typically 0.1–4 m) below the seawater–seafloor interface. In this zone, virtually all the methane generated within marine anaerobic sediments is consumed by AOM before it can escape (Reeburgh 1996). Today, significant methane fluxes into the oceanic water column from sediments are produced only at rare places where very high methane fluxes, such as those from mud volcanoes, push the sulphate–methane boundary to within a few
centimetres or less of the seafloor (Luff & Wallmann 2003). Consequently, today’s oceans are estimated to be a relatively minor source of methane whereas land-based freshwater wetlands are relatively significant owing to their lack of sulphate.

In the Archaean and during the oxic transition, the vertical redox profile of marine sediments is likely to have been markedly different from today. Figure 3 shows a schematic of the modern profile of sulphate and methane in marine sediments. Modern seawater contains around 29 mM of sulphate, which is often well mixed by fauna into a bioturbation zone at the top of sediments. Below this bioturbation zone, the sulphate concentration starts to decline due to microbial sulphate reduction. Typically, methane concentrations are found to increase below the depth where sulphate concentrations fall below approximately 0.5–5 mM (Iversen & Jorgensen 1985; Whiticar 2002). The crossover depth, where sulphate and methane concentrations are small and roughly similar, is generally close to where the peak rate of AOM occurs (figure 3b; Devol 1983; Haese et al. 2003). In Archaean sediments, there would be no bioturbation zone. Moreover, Archaean oceanic sulphate concentrations were less than 0.2 mM (Habicht et al. 2002), so methane

![Figure 3](image_url)

**Figure 3.** (a) A schematic showing typical profiles of methane and sulphate in modern marine sediments, where SMTZ is the sulphate–methane transition zone. Solid line, methane concentration in pore waters (mM); dashed line, sulphate concentration in pore waters (mM). Depth is relative. (b) A schematic showing the profile of AOM rate that corresponds to (a). (c) A schematic of relative methane concentration (solid line) and sulphate concentration (dashed line in millimolar) for the Palaeoproterozoic.
would be abundant in sediments all the way to the seafloor, where methane would flux out. During the rise of oxygen, the SMTZ would be a narrow interface just below the seafloor (figure 3c).

The flux of methane consumed in modern marine sediments per unit area, \( f_{\text{AOM}} \), can be estimated from empirical data as

\[
f_{\text{AOM}} \sim H r_{\text{AOM}}.
\]  

(2.6)

Generally, there is a bell-shaped curve with depth of the AOM rate (figure 3b), and in equation (2.6), \( H \) is its characteristic half-width. The rate of AOM, \( r_{\text{AOM}} \), is given by

\[
r_{\text{AOM}} = K_{\text{AOM}} C_{\text{SO}_4} C_{\text{CH}_4},
\]  

(2.7)

where \( K_{\text{AOM}} \) is an empirical kinetic rate constant, and \( C_{\text{SO}_4} \) and \( C_{\text{CH}_4} \) are the concentrations within the SMTZ (Luff & Wallmann 2003; Wallmann et al. 2006). \( K_{\text{AOM}} \) depends on the abundance and activity of the AOM microbial community (Wallmann et al. 2006) but a reasonable average value is \( K_{\text{AOM}} \approx 8 \text{ mM}^{-1} \text{ yr}^{-1} = 8 \text{ mol} \text{ m}^{-3} \text{ yr}^{-1} \) (Van Cappellen & Wang 1996). Typical concentrations at the sulphate–methane transition are \( C_{\text{SO}_4} \approx 3 \text{ mM} = 3 \text{ mol} \text{ m}^{-3} \), \( C_{\text{CH}_4} \approx 1 \text{ mM} = 1 \text{ mol} \text{ m}^{-3} \) and \( H = 0.04 \text{ m} \) (Devol 1983; Iversen & Jorgensen 1985; Haese et al. 2003), giving an estimate of \( f_{\text{AOM}} = (0.04 \text{ m})(8 \text{ mol} \text{ m}^{-3} \text{ yr}^{-1})(3 \text{ mol} \text{ m}^{-3}) (1 \text{ mol} \text{ m}^{-3}) \approx 1 \text{ mol CH}_4 \text{ m}^{-2} \text{ yr}^{-1} \). This value is consistent with the observation that a typical shelf sediment has a total C mineralization of about 10 \text{ mol C m}^{-2} \text{ yr}^{-1}, of which about 10% is due to methanogenesis, giving approximately 1 \text{ mol CH}_4 \text{ m}^{-2} \text{ yr}^{-1} (Canfield 1991; Middelburg et al. 1997). Most organic matter accumulates in coastal sediments or ocean margin sediments that represent approximately 7 and 9% of the ocean area, respectively (Middelburg et al. 1997), with the former probably more important for methane generation. Given that the total ocean area is \( 1.8 \times 10^{14} \text{ m}^2 \), if roughly 10% of it generated an estimated 1 \text{ mol CH}_4 \text{ m}^{-2} \text{ yr}^{-1}, the global amount of methane consumed today by marine AOM would be \( (0.1)(1.8 \times 10^{14} \text{ m}^2)(1 \text{ mol m}^{-2} \text{ yr}^{-1}) \sim 18 \text{ Tmol CH}_4 \text{ yr}^{-1} \). This value is broadly consistent with an independent estimate of the global AOM rate from Hinrichs & Boetius (2002). They estimate mean AOM rates of 0.37, 0.22, 0.22 and 0.073 \text{ mol m}^{-2} \text{ yr}^{-1}, for inner shelf, outer shelf, inner margin and outer margin regions, respectively, and derive a global flux of approximately 24 \text{ Tmol CH}_4 \text{ yr}^{-1} when high flux seepage areas are also added. Thus, a potentially large flux of methane of a few tens of \text{Tmol CH}_4 \text{ yr}^{-1} magnitude apparently never escapes from the marine sediments; this flux can be compared with the estimated total global flux of methane from all sources that actually reaches the modern atmosphere, which ranges from 31 to 38 \text{Tmol CH}_4 \text{ yr}^{-1} (Prather et al. 2001).

The estimate of a few tens of \text{Tmol CH}_4 \text{ yr}^{-1} from modern AOM rates may underestimate the amount of methane that was generated in the largely anoxic Archaean after the advent of oxygenic photosynthesis. Methane is produced from organic carbon that would otherwise be buried or used for reduction of local oxygen carriers such as sulphate; in anaerobic sediments, organic carbon reduces sulphate directly, i.e. \( \text{SO}_4^{2-} + 2 \text{ CH}_2\text{O} = \text{H}_2\text{S} + 2 \text{ HCO}_3^- \). The average ratio of the AOM rate to the rate of sulphate reduction by organic matter in modern continental margins is estimated to be approximately 30% (Hinrichs & Boetius 2002). Taking the modern rate of methanogenesis as approximately 24 \text{Tmol CH}_4 \text{ yr}^{-1}, in the absence of sulphate, the potential rate of

Phil. Trans. R. Soc. A (2007)
methanogenesis could have been approximately 100 Tmol CH$_4$ yr$^{-1}$. We adopt this value as a baseline estimate for the global flux of methane from all sediments, $\phi_{CH_4}$, in our biogeochemical model for the Archaean and Early Proterozoic, as expressed in equations (2.3) and (2.4). In §3, we describe the sensitivity of the model to this parameter. When methane fluxes are high and sulphate levels low, data from modern environments suggest that almost all sulphate couples to the AOM (Aharon & Fu 2000; Boetius et al. 2000). Thus, in the Archaean and the Early Proterozoic, as a first-order approximation, we assume that AOM was the major process coupled with sulphate reduction, as argued by Hinrichs (2002) and Hinrichs & Boetius (2002).

We have previously suggested that the Archaean ocean could have provided a large flux of methane approximately $10^2$ Tmol CH$_4$ yr$^{-1}$ to the atmosphere owing to the lack of global reservoirs of sulphate and oxygen (Claire et al. 2006). How would the methane flux vary in time when sulphate levels increased? During the rise of oxygen, methane would be consumed at the seafloor in proportion to small amounts of increasing sulphate, according to equation (2.6). But once sulphate concentrations exceeded approximately 5 mM, the SMTZ would be pushed far below the seafloor into sediments, as it generally is today. At this point, virtually all the methane would be consumed by AOM and further increases in sulphate would not be expected to make any significant difference to the methane flux that escapes from sediments. Thus, the characteristic shape of the response of total AOM to sulphate may look like that schematically shown in figure 4. Proterozoic levels of sulphate after the rise of O$_2$ are constrained from sulphur isotopes to have been between 1.5 and 4.5 mM for ca 1 Gyr (Shen et al. 2003; Kah et al. 2004). Our proposed shape of the high sulphate end of the curve in figure 4 is probably relevant only to the Late Proterozoic ‘second rise of O$_2$’ at ca 0.6 Gyr ago (Fike et al. 2006; Canfield et al. 2007), because once sulphate levels exceeded approximately 5 mM, there is potential for rapid growth in oceanic sulphate and atmospheric O$_2$ levels. In this paper, we leave the second rise of O$_2$ to future work and restrict ourselves to examining the ca 2.4 Gyr ago Palaeoproterozoic oxic transition.

To a first approximation, the global flux of CH$_4$ to the atmosphere is modulated by subtracting the flux of CH$_4$ consumed by anaerobic methanotrophy. Thus, we modify equation (2.3) as follows:

$$\frac{d}{dt}[CH_4] = (\phi_{CH_4} - F_{AOM}) - k_{eff}[O_2][CH_4] - k_{esc}[CH_4],$$

where $F_{AOM}$ is the global AOM in Tmol O$_2$ equivalents yr$^{-1}$, which is related to sulphate availability and hence the amount of O$_2$ in the atmosphere. To relate average oceanic sulphate concentrations to atmospheric O$_2$ levels, we use a semi-empirical approximation. Kah et al. (2004) derive a curve for the evolution of Precambrian oceanic sulphate levels based on sulphur isotope data and carbonate-associated sulphate from ancient sediments. For the period of interest, the Late Archaean to Paleoproterozoic, marine sulphate concentrations range from less than 0.2 mM before 2.2 Ga, to approximately 0.7 mM at 1.7 Ga and 1.9–2.0 mM at 1.5 Ga. A power-law parameterization that crudely captures this behaviour for the Archaean and Palaeoproterozoic is

$$C_{SO_4} = k_{SO_4}[O_2]^{0.4},$$

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where \( k_{SO_4} \sim 0.003 \text{ mM Tmol}^{-0.4} \); \([O_2]\) is in Tmol; and \( C_{SO_4} \) is in mM. Here, \([O_2]\) is consistent with estimates and models for the Archaean and Late Palaeoproterozoic (Catling & Claire 2005; Canfield 2005), but we note that there is considerable uncertainty in this regard.

To relate ocean sulphate concentrations to the global rate of AOM, we consider a simple AOM model. AOM can be modelled given methane and sulphate profiles, along with sediment porosity (Martens & Berner 1977). A common method of estimating AOM rates is to assume that all AOM takes place in an infinitely thin layer at the depth where sulphate concentrations vanish (Haese et al. 2003; Jorgensen et al. 2004). In the simplest possible model, we ignore advection through fractures and faults, since most marine sediments are dominated by diffusion. Thus, the rate of methane consumption must be balanced by the downward diffusion of sulphate (\( J \), e.g. in mol m\(^{-2}\) yr\(^{-1}\)) into the seafloor by Fick’s first law (Berner 1980)

\[
J_{SO_4} = -\phi D_s \frac{\partial C}{\partial x} \bigg|_{AOM},
\]

where \( \phi \) is the sediment porosity; \( C \) is the sulphate concentration in mol m\(^{-3}\) (numerically equivalent to millimolar); \( x \) is the depth in the sediment; and \( D_s \) is the diffusion coefficient in marine sediments. Porosity \( \phi \) varies from 1.0 at the seafloor–water interface to smaller values with depth due to sediment compaction; for our model, where we are concerned with shallow penetration depths of low sulphate oceans, we assume a value of \( \phi \sim 0.8 \). The sediment diffusion coefficient for sulphate depends on temperature and porosity. Taking a typical sediment temperature of approximately 4°C, we use \( D_s \sim 3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \) (Iversen & Jorgensen 1993). The concentration gradient of sulphate is \( \partial C/\partial x \), which goes from the seafloor to the depth \( x_{AOM} \), of the maximum rate of AOM where \( C \rightarrow 0 \). Sulphate reduction and oxidation of methane at the sulphate–methane transition is arguably the most important factor for the depth of the sulphate profile and its often quasi-linear shape when AOM dominates sulphate reduction (Jorgensen et al. 2004). Owing to this, we adopt a simple linear approximation to equation (2.10)

\[
J_{AOM} = -J_{SO_4} = \phi D_s \frac{\partial C}{\partial x} \bigg|_{AOM} = \phi D_s \frac{C_{SO_4}}{x_{AOM}}.
\]

Figure 4. A schematic of the global rate of consumption of methane from AOM as the oceanic sulphate concentration increases.
This area flux is multiplied by area $A$, which we take as 10% of the ocean area, to give an estimated global flux $F_{AOM}$ of AOM. We note that coastal and shelf sediment area $A$ should depend on the amount of continental landmass. The time evolution of the growth of the continents remains a controversial, open field of inquiry but most models predict that at least 70% of the current continental volume was in place by 2 Ga (Patchett & Arndt 1986; Rogers & Santosh 2004, p. 48), which is close to the time of interest for this paper.

The AOM flux in equation (2.11) depends on sulphate concentrations and the depth of the sulphate–methane transition, i.e. $x_{AOM}$. In modern sediments, there is commonly a bioturbation zone that mixes sulphate downwards uniformly (figure 3a), and in this case, $x_{AOM}$ is the depth beneath the base of the bioturbation zone rather than below the sediment–water interface. Defined in this way, $x_{AOM}$ varies from a few centimetres depth in shallow coastal sediments to metres depth on the continental slope (Borowski et al. 1999; Kruger et al. 2005). In the modern ocean, $x_{AOM}$ appears to be a function of organic content of sediments and methane supply (Borowski et al. 1996). Hence, $x_{AOM}$ is a few centimetres depth around Black Sea mud volcanoes (Wallmann et al. 2006) when compared with many metres depth in oceanic sediments in regions of low methane flux. Since we are concerned with an anoxic, low sulphate ocean in the Archaean that progresses to an ocean with a few millimolar sulphate in the Proterozoic, we note that for some globally averaged methane flux from sediments, at low sulphate levels, $x_{AOM}$ must primarily depend on sulphate concentrations in the overlying water to a first approximation. For example, in lakes with anoxic bottom waters and sulphate approximately 2–5 mM, $x_{AOM}$ depths are very close to the water–sediment interface (Ingvorsen & Brock 1982), while freshwater stratified lakes with less than 0.01 mM sulphate essentially have negligible AOM (Reeburgh & Heggie 1977). Consequently, we parameterize the globally averaged depth of maximum AOM, as follows:

$$x_{AOM} = k_{SMTZ}C_{SO_4}^a,$$  \hspace{1cm} (2.12)

where $k_{SMTZ}$ and $a$ are constants. The connection of the average depth of AOM to sulphate concentrations in marine sediments has received little detailed investigation because modern seawater sulphate concentrations are uniform at 29 mM. Thus, the choice of $k_{SMTZ}$ and $a$ is arbitrary; consequently, we investigate the sensitivity of the model to these parameters when considering the results. We choose baseline values of $k_{SMTZ} = 0.1$ and $a = 0.4$, for which $x_{AOM}$ varies from approximately 1–15 cm over sulphate concentrations of approximately 0.005–3 mM. Taking equation (2.12) and inserting into equation (2.11) gives the parameterization for the global AOM flux for the Archaean to the Proterozoic, as follows:

$$F_{AOM} = A\phi D_s \frac{C_{SO_4}^{(1-a)}}{k_{SMTZ}}.$$  \hspace{1cm} (2.13)

A full general treatment of the effect of AOM on the rise of O$_2$ would involve isolating the ocean from the atmosphere in our box model and examining all sulphur fluxes in and out of the ocean constrained by the isotopic record, i.e. integrating a complete sulphur cycle to our biogeochemical model. However, even adding one process such as AOM introduces two new free parameters,
therefore a full model would obviously introduce many more. For present purposes, our rough approximations are sufficient to demonstrate the potential of AOM feedback to affect the history of O₂ and CH₄.

3. Results and discussion

We present the results of two numerical experiments that both perform a modulation of the methane flux according to equation (2.8). The first uses a simplistic approximation without the AOM model developed above. The second makes use of the AOM model captured in equation (2.13).

(a) Method 1: simple modulation of the CH₄ flux

For the first numerical experiment, we modulate the methane flux according to equation (2.8) with a factor that depends directly on oxidative weathering. Let us take the estimate that 45% of the oxidative weathering flux is used to mobilize sulphate (Holland 2002) and assume that the sulphate washed to the ocean by rivers is immediately available for methanotrophy. Thus, we take \( F_{\text{AOM}} = 0.45F_W \) where \( F_W \) is the oxidative weathering flux, which is parameterized as a function of atmospheric O₂ levels as described in §2. The advantage of this crude experiment is that it allows us to investigate the potential effects of any positive feedback and understand them algebraically.

Figure 5a shows the results of including this AOM feedback when compared with the reference model of CCZ with \( \phi_{\text{CH₄}} = 100 \) Tmol CH₄ yr⁻¹, as discussed in §2c. Figure 5b shows the corresponding AOM fluxes and seawater sulphate concentrations. O₂ rises more rapidly when AOM is included and to a level about an order of magnitude higher than that without AOM. Surprisingly, methane ‘re-rises’ faster after the oxic transition and to a higher value in this new scheme, despite the consumption of methane by AOM. Algebraic analysis helps explain this apparently counter-intuitive behaviour of methane.

We can solve equation (2.3) in the steady state \( (d[CH₄]/dt = 0) \) by assuming that the hydrogen escape term is a minor term after the rise of O₂ (i.e. \( F_{\text{E}} = k_{\text{esc}}[CH₄] \rightarrow 0) \)

\[
[CH₄]_{\text{Oxic}} \bigg| = \frac{\phi_{\text{CH₄}} - F_{\text{AOM}}}{k_{\text{eff}}[O₂]}.
\] (3.1)

The effective rate constant, \( k_{\text{eff}} \), has a nonlinear dependence on CH₄ and O₂ levels, particularly below an O₂ level of \( 10^{-6} \) bar and for CH₄ levels more than \( 10^{-4} \) bar (see fig. 3 in the CCZ paper). However, in the region \( O₂ > 10^{-6} \) bar and \( CH₄ < 10^{-4} \) bar, the dependence of \( k_{\text{eff}} \) on \([O₂]\) is approximately linear on a log–log plot so that a least-squares fit provides a power-law relationship, as follows (with correlation coefficient \( R^2 = 0.994\)):

\[
k_{\text{eff}}(O₂) = 1.8368[O₂]^{-1.2448},
\] (3.2)

where \([O₂]\) is the global amount of atmospheric O₂ in Tmol. Equation (3.2) is applicable for \([O₂]\) amounts in the atmosphere greater than approximately 100 Tmol, where this amount of oxygen is equivalent to a partial pressure of
approximately $10^{-6}$ bar in a 1 bar atmosphere. Substituting equation (3.2) into equation (3.1) gives

$$[\text{CH}_4]_{\text{Oxic}} = \frac{\phi_{\text{CH}_4} - F_{\text{AOM}}}{k_{\text{eff}}[O_2]} = 0.544(\phi_{\text{CH}_4} - F_{\text{AOM}})[O_2]^{0.2448}.$$ (3.3)

In the absence of anaerobic methanotrophs, $F_{\text{AOM}}=0$, hence post-transition $\text{CH}_4$ levels in the reference model are a monotonically increasing function of $O_2$. In other words, for a given methane flux, the effective rate constant for the oxidation of methane by oxygen in the atmosphere decreases with increasing $[O_2]$ according to equation (3.2), an effect that can be traced to the influence of a thickening stratospheric ozone layer (Catling et al. 2004; Claire et al. 2006; Goldblatt et al. 2006). If we substitute $F_{\text{AOM}} = 0.45F_W = 0.45k_W[O_2]^{\beta}$ with $\beta = 0.4$ and $k_W = 0.006$.

Figure 5. (a) A comparison of the evolution of $O_2$ and $\text{CH}_4$ from the biogeochemical model with and without the inclusion of AOM using ‘method 1’ (see text). The model with AOM is labelled method 1 and the model without AOM is the reference model of Claire et al. (2006), labelled ‘rm’. (b) Corresponding plot of simulated seawater sulphate concentrations AOM rates versus time for method 1.
into equation (3.3), we obtain

\[
[\text{CH}_4]_{\text{Oxic}} = \phi_{\text{CH}_4}0.544\left(\frac{[O_2]^{0.2448} - 0.45k_W}{\phi_{\text{CH}_4}[O_2]^{0.6448}}\right)
= 108.8([O_2]^{0.2448} - 1.35 \times 10^{-5}[O_2]^{0.6448}). \tag{3.4}
\]

In evaluating the numerical constant, we take the gross production flux of methane $\phi_{\text{CH}_4}$, as a 200 Tmol O$_2$ yr$^{-1}$ sink, equivalent to a worldwide production of 100 Tmol CH$_4$ yr$^{-1}$ in all Archaean–Proterozoic anaerobic sediments, as discussed earlier. Comparing the two terms on the right-hand side reveals that the first term is a factor of $10^2$–$10^3$ higher over the range of O$_2$ values considered for the Proterozoic after the oxic transition. Thus, in the methanotroph-modified world, CH$_4$ levels increase at higher O$_2$ levels in the Palaeoproterozoic despite the lower CH$_4$ flux; this is primarily a result of atmospheric chemistry as captured by $k_{\text{eff}}$. Overall, the results of our numerical experiment are consistent with the idea that CH$_4$ continued to be a significant greenhouse gas in the Proterozoic, albeit at a lower concentration than in the Archaean (Pavlov et al. 2003; Claire et al. 2006; Zahnle et al. 2006).

(b) Method 2: modulation of CH$_4$ fluxes by parameterized AOM

In our second numerical experiment, we modulate the methane flux to the atmosphere in equation (2.8) based on relationships given in §3a where sulphate diffusion into sediments balances the flux of methane consumed by AOM.

Figure 6a shows the results of using the parameterizations described by equations (2.11) and (2.12) (‘method 2′), compared to the results presented in §3a. The O$_2$ and CH$_4$ curves are qualitatively similar in shape and slope, although the curves generated from computing $F_{\text{AOM}}$ using method 2 hasten the time of oxic transition by ca 0.1 Gyr. Figure 6b shows the two curves referenced to the oxic transition; with method 2, O$_2$ rises from less than 10$^{-6}$ to 10$^{-4}$ bar in ca 0.05 Gyr, about twice as rapidly as ‘method 1’.

The effect on the timing of the transition can be understood with algebra. In CCZ, we discussed the timing of the oxic transition in terms of the fluxes of organic burial ($F_B$) versus the flux of O$_2$-consuming species from volcanism/hydrothermal ($F_V$) plus metamorphism/geothermal reductants ($F_M$), following an argument originally advanced by Walker et al. (1983). Essentially, the oxic transition occurs at the point when the O$_2$ produced by the organic burial flux, $F_B$, exceeds the sum of the reductant fluxes, $F_V + F_M$. Consequently, in CCZ, we defined an oxygenation parameter $K_{\text{OXY}}$, based on kinetically active reduced gases in the ground-level atmosphere and reduced cations in the ocean

\[
K_{\text{OXY}} = \frac{F_{\text{SOURCE}}}{F_{\text{REDUCED SINKS}}} \sim \frac{F_B}{F_V + F_M}. \tag{3.5}
\]

We define the atmosphere as oxygenated when $K_{\text{OXY}} > 1$. If we include methanotrophy, it can impact $K_{\text{OXY}}$ and hence the timing of the oxic transition in the following manner. An approximate steady-state solution for the evolution of CH$_4$ at the time of the oxic transition can be found by setting the hydrogen escape term,
\( F_E = k_{\text{esc}} [\text{CH}_4] \), to zero in equation (2.3) to obtain

\[
\phi_{\text{CH}_4|\text{trans}} = F_{\text{AOM}} + k_{\text{eff}}[\text{O}_2][\text{CH}_4].
\]  

(3.6)

Taking \( F_E = 0 \) and substituting twice equation (3.6) into equation (2.4) yields an equation for the evolution of \( \text{O}_2 \) at the time of the oxic transition

\[
\frac{d}{dt}[\text{O}_2]|_{\text{trans}} = 2F_{\text{AOM}} + F_B - (F_V + F_M + F_W).
\]  

(3.7)

The balance on the right-hand side of equation (3.7) provides an expanded version of the oxygenation parameter (\( K_{\text{OXY}}^* \)) that includes the AOM flux, \( F_{\text{AOM}} \)

\[
K_{\text{OXY}}^* \sim \frac{F_B + 2F_{\text{AOM}}}{F_V + F_M + F_W}.
\]  

(3.8)

Figure 6. (a) A comparison of the evolution of \( \text{O}_2 \) and \( \text{CH}_4 \) in the model using method 1 and ‘method 2’ (see text). (b) The plots for each model run where the time axis has been referenced to the time (equal to 0) of the oxic transition.
Method 1 used $F_{AOM} = 0.45F_W$ so that $2F_{AOM} \sim F_W$ and $K_{OXY}^*$ is approximately equal to $K_{OXY}$ in the reference model. Thus, by coincidence, the timing of the oxic transition was essentially the same. In method 2, the numerical values of $F_{AOM}$ were approximately equal in magnitude to $F_W$ at the time of the oxic transition so that $K_{OXY}^*$ reached unity somewhat before $K_{OXY}^*$ of method 1.

Equation (2.12), which forms part of the parameterization of AOM, has two free parameters ($k_{SMTZ}$ and $\alpha$) and we can examine how the model responds to their choice. For the comparison between different parameter choices, we ignore the effect on the timing of the oxic transition because this actually lacks real significance: the timing of this transition in the model is primarily determined by the choice of the parameterization of $F_V$ and $F_M$, as described in the CCK paper, and so it is necessarily a tuned parameter. Instead, we reference the time to the oxic transition when $K_{OXY}^* = 1$. In this manner, figure 7 shows the model sensitivities to changing $k_{SMTZ}$ and $\alpha$ from our reference values of 0.1 and 0.4. Figure 7a shows that decreasing $k_{SMTZ}$ sharpens the rate of the oxic transition.

Figure 7. (a) Sensitivity of the model to changes in parameter $k_{SMTZ}$. (b) Sensitivity of the model to changes in parameter $\alpha$. 

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and increases the post-oxic atmospheric O\textsubscript{2} and CH\textsubscript{4} concentrations. Effectively, when \( k_{\text{SMTZ}} \) is decreased, \( k_{\text{SMTZ}} \) AOM rates increase. In contrast, figure 7b shows that the model is relatively insensitive to the choice of \( \alpha \).

Finally, the qualitative results of the model are insensitive to the exact value chosen for the global methane flux generated in all sediments, \( \phi_{\text{CH}_4} \), which we have nominally taken as 100 Tmol CH\textsubscript{4} yr\textsuperscript{-1} (see §2c). The main effect of changing \( \phi_{\text{CH}_4} \) is to alter the level of the minor gas (O\textsubscript{2} or CH\textsubscript{4}) in the anoxic or oxic worlds. In the case of lower \( \phi_{\text{CH}_4} \), O\textsubscript{2} is lower in the Archaean, while CH\textsubscript{4} is proportionately lower in the Proterozoic, as predicted by equation (3.1).

4. Conclusions

Empirical data show that a significant flux of CH\textsubscript{4} is consumed by AOM in modern marine sediments before the methane even reaches the seafloor. This flux is estimated as roughly 20 Tmol CH\textsubscript{4} yr\textsuperscript{-1} (§2c). Consequently, a large amount of biogenic methane never reaches the modern atmosphere. However, in the Archaean ocean with less than 0.2 mM sulphate, AOM and other forms of sulphate reduction would have been limited by the lack of oxidized substrate so that methanogenesis would arguably have dominated recycling of organic carbon. In this case, a very large flux of methane approximately 100 Tmol CH\textsubscript{4} yr\textsuperscript{-1} produced in anaerobic marine sediments could have fluxed out to the atmosphere. For some perspective, this flux is only 1% of modern net primary productivity approximately \( 10^4 \) Tmol C yr\textsuperscript{-1}.

Approaching, during and after the oxic transition, the $\delta^{34}$S record in marine sediments suggests that the flux of sulphate to the oceans from continental oxidative weathering increased, consistent with the physical expectation that dissolved oxygen in rainwater and rivers would oxidize continental pyrite to sulphate (Habicht \textit{et al}. 2002). We have shown how methanotrophy can act to diminish methane fluxes to the Late Archaean atmosphere in the presence of increasing oceanic sulphate. This feedback means that gas fluxes to the atmosphere of O\textsubscript{2} and CH\textsubscript{4} increase slightly from the 2 : 1 ratio predicted from equation (2.2) because the reducing power of methane is converted to involatile sulphide.

When we include a simple AOM feedback in our model, O\textsubscript{2} rises more rapidly and to a higher value than in the model without the AOM feedback. The time-scale for the oxic transition is shortened, while O\textsubscript{2} rises to a level of a few $\times 10^{-3}$ bar (a few per cent of present levels) by 2.1 Gyr ago instead of approximately $10^{-4}$ bar in the reference model. Methane also re-rises faster and to a value of approximately 50 ppmv by the end of the Palaeoproterozoic, which is higher than that in the model without AOM feedback. At first sight, obtaining a higher level of Proterozoic methane when AOM is included in the model seems counter-intuitive because AOM diminishes the CH\textsubscript{4} flux to the atmosphere. However, the dominant effect of AOM is to enable O\textsubscript{2} to rise more rapidly to a higher level; consequently, methane levels also rise more rapidly to a higher level because they are enhanced more strongly by the effect of increased shielding effect of the stratospheric ozone layer than decreased by the lowering of the methane flux by AOM. We note that the effect of the nonlinear dependence of AOM at higher O\textsubscript{2} levels (figure 4) is not included in the model and may have been important for the Late Proterozoic second rise of O\textsubscript{2} \( ca \) 0.6 Gyr ago.
We have shown previously that CH$_4$ levels should have collapsed in the Early Proterozoic before there was sufficient atmospheric O$_2$ to be detectable through conventional geologic indicators such as red beds and palaeosols (Zahnle et al. 2006). The counter-intuitive twist that methanotrophy allows CH$_4$ to re-rise after the oxic transition to higher levels in the Proterozoic is relevant to the Proterozoic climate. Stable, relatively high levels of methane in the Proterozoic may help account for a prolonged period exceeding 1 Gyr where there is no reliable evidence for glaciation (Eyles 1993). Moderately abundant methane could have provided a greenhouse effect that compensated for a fainter Proterozoic Sun (Pavlov et al. 2003). The total oxidation of the Earth from the slow leak of hydrogen via methane-induced hydrogen escape may also be important when integrated over more than 1 Gyr of the Proterozoic, as mentioned in Catling & Claire (2005).

Finally, our computational experiments provide motivation for laboratory experiments and fieldwork. Clearly, more field data would constrain controls on AOM in sediments and the globally averaged magnitude of AOM, while, in principle, an O$_2$-free chamber in the laboratory could simulate the response of AOM in marine sediments to increasing levels of seawater sulphate.

M.W.C. acknowledges support of NSF IGERT award DGE09870713 awarded to the University of Washington’s Astrobiology Program and NASA Exobiology Program grant NNG05GGQ25G awarded to D.C.C. at the University of Washington. D.C.C. also acknowledges the support of a European Union Marie Curie Chair award. K.J.Z. acknowledges support from NASA’s Exobiology Program. The authors thank two anonymous referees whose comments much improved the manuscript.

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