

1 **The effect of widespread early aerobic marine ecosystems on methane cycling and the Great**
2 **Oxidation**

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6 **Abstract**

7 The balance of evidence suggests that oxygenic photosynthesis had evolved by 3.0–2.7 Ga, several
8 hundred million years prior to the Great Oxidation ≈ 2.4 Ga. Previous work has shown that if oxygenic
9 photosynthesis spread globally prior to the Great Oxidation, this could have supported widespread
10 aerobic ecosystems in the surface ocean, without oxidizing the atmosphere. Here we use a suite of
11 models to explore the implications for carbon cycling and the Great Oxidation. We find that recycling
12 of oxygen and carbon within early aerobic marine ecosystems would have restricted the balanced
13 fluxes of methane and oxygen escaping from the ocean, lowering the atmospheric concentration of
14 methane in the Great Oxidation transition and its aftermath. This in turn would have minimised any
15 bi-stability of atmospheric oxygen, by weakening a stabilising feedback on oxygen from hydrogen
16 escape to space. The result would have been a more reversible and probably episodic rise of oxygen
17 at the Great Oxidation transition, consistent with existing geochemical evidence. The resulting drop
18 in methane levels to ≈ 10 ppm is consistent with climate cooling at the time but adds to the puzzle of
19 what kept the rest of the Proterozoic warm. A key test of the scenario of abundant methanotrophy
20 in oxygen oases before the Great Oxidation is its predicted effects on the organic carbon isotope
21 ($\delta^{13}\text{C}_{\text{org}}$) record. Our open ocean general circulation model predicts $\delta^{13}\text{C}_{\text{org}} \approx -30$ to -45 ‰ consistent
22 with most data from 2.65–2.45 Ga. However, values of $\delta^{13}\text{C}_{\text{org}} \approx -50$ ‰ require an extreme scenario
23 such as concentrated methanotroph production where shelf-slope upwelling of methane-rich water
24 met oxic shelf water.

25 **Keywords**

26 Great Oxidation; modelling; methane; oxygen; methanotrophy; carbon isotope record

27 **1. Introduction**

28 Multiple lines of evidence suggest that oxygenic photosynthesis evolved long before the oxygenation
29 of the atmosphere (Farquhar et al., 2011), and spread to oxygenate regions of the surface
30 environment in the late Archean (Buick, 1992; Czaja et al., 2012; Eigenbrode and Freeman, 2006;
31 Kasting, 1991; Kendall et al., 2010; Lalonde and Konhauser, 2015; Olson et al., 2013; Riding et al.,
32 2014). There is evidence for oxidative weathering on the continents, perhaps as early as 3.0-2.9 Ga
33 from chromium (Crowe et al., 2013) and molybdenum (Planavsky et al., 2014) isotope fractionation.
34 By 2.7-2.5 Ga, rising sedimentary concentrations of Mo and Re and Mo isotope fractionation indicate
35 oxidative weathering (Siebert et al., 2005; Wille et al., 2007), trends in sulphur isotopes suggest
36 localised oxygen production (Zerkle et al., 2012), and by 2.5 Ga sulphide accumulation in the ocean
37 suggests more intense oxidative weathering (Reinhard et al., 2009). In the oceans, rare earth
38 element analyses reveal a shallow shelf sea oxygen oasis 2.8 Ga (Riding et al., 2014). Coupled iron
39 and molybdenum isotope fractionation provides evidence of surface ocean oxygen oases 2.68-2.5 Ga
40 (Czaja et al., 2012), and changes in the abundance of Mo and Re with sediment depth 2.6–2.5 Ga
41 indicate dissolved O₂ at shallow depth along ocean margins (Kendall et al., 2010). Consistent with the
42 appearance of oxygen, protein fold evolution (Wang et al., 2011) and gene phylogeny (David and
43 Alm, 2011) both show a rapid burst of evolutionary innovation including aerobic metabolisms in the
44 Late Archean >2.5 Ga and possibly >2.85 Ga (David and Alm, 2011). Others have postulated a late
45 origin of oxygenic photosynthesis ≈2.4 Ga leading immediately to the Great Oxidation (Kopp et al.,
46 2005), but we find the geochemical evidence for oxygen production compelling by at latest ≈2.7 Ga,
47 and we take this as our working hypothesis in trying to explain the geochemical record.

48 The observed Mass Independent Fraction of Sulphur isotopes (MIF of S) until at least 2.45 Ga
49 (Farquhar et al., 2011), indicates a very low atmospheric $pO_2 < 10^{-5}$ PAL (Present Atmospheric Level),
50 and a high atmospheric concentration of methane (Zahnle et al., 2006). This can be reconciled with
51 abundant evidence for oxygen production, at least from an atmospheric point of view. Previous
52 modelling work has shown that the key overall determinant of atmospheric redox state in the Late
53 Archean would have been the net overall oxidant/reductant balance of fluxes to and from the
54 surface Earth system, including hydrogen escape to space, organic carbon burial, and exchange with
55 the crust and mantle (Claire et al., 2006; Goldblatt et al., 2006). Provided this net flux was sufficiently
56 reducing, a low atmospheric $pO_2 < 10^{-5}$ PAL would have been maintained even in the presence of a
57 productive oxygenic ecosystem (Goldblatt et al., 2006; Zahnle et al., 2006), because the balanced
58 atmospheric oxygen and methane fluxes escaping from the biosphere would have been rapidly
59 consumed by atmospheric photochemistry.

60 What is not fully understood is how surface ecosystems operated in the Late Archean prior to the
61 Great Oxidation (GOE) 2.45–2.32 Ga, in particular how the geochemical evidence for a strongly
62 reducing atmosphere and an oxygenated surface environment can be reconciled. This requires
63 either oxidative weathering at low atmospheric oxygen levels $pO_2 < 10^{-5}$ PAL, transient ‘whiffs’ of
64 oxygen as yet unresolved in the sulphur MIF record, or localized oxygen production and
65 consumption. Microbial mats represent an environment where the production and consumption of
66 oxygen and organic carbon were very closely coupled, potentially reconciling the occurrence of
67 oxidative weathering on land with a very reducing atmosphere (Herman and Kump, 2005; Lalonde
68 and Konhauser, 2015). In the ocean, following the evolution of planktonic oxygenic photosynthesis, a
69 partially oxygenated surface ocean could have coexisted with a reducing atmosphere and an anoxic
70 deep ocean, in a state of disequilibrium maintained by high rates of oxygen production in the water
71 and relatively slow air-sea gas exchange (Kasting, 1991; Olson et al., 2013).

72 Multiple biogeochemical pathways potentially could have contributed directly or indirectly to
73 oxygen cycling within early ecosystems. Aerobic respiration of organic carbon may have been
74 ubiquitous (Towe, 1990), especially if aerobic respiration is a more ancient metabolism than
75 oxygenic photosynthesis. This has received some recent support from measurements of aerobic
76 growth occurring at nanomolar O₂ concentrations (Stolper et al., 2010), where modelling has
77 indicated that such concentrations could have been reached even via abiotic mechanisms prior to
78 the origin of oxygenic photosynthesis (Haqq-Misra et al., 2011). A fraction of the organic carbon
79 fixed by oxygenic photosynthesis would have been converted to methane by fermentation and
80 methanogenesis, and then potentially consumed by aerobic methanotrophs, giving a mechanism to
81 explain isotopically very light Late Archean kerogens (Hayes, 1983; Hayes, 1994). In the Hamersley
82 Province, Western Australia, where evidence for oxygenic photosynthesis is compelling (Buick,
83 1992), these kerogens have minimum $\delta^{13}\text{C}_{\text{org}} \approx -60\text{‰}$ from shallower water sediments 2.72 Ga, and
84 minimum $\delta^{13}\text{C}_{\text{org}} \approx -50\text{‰}$ from deeper water sediments 2.65–2.6 Ga, weakening to a minimum $\delta^{13}\text{C}_{\text{org}}$
85 $\approx -35\text{‰}$ by 2.45 Ga (Czaja et al., 2012; Eigenbrode and Freeman, 2006; Thomazo et al., 2009).
86 Similar but less extreme environment-dependent patterns in $\delta^{13}\text{C}_{\text{org}}$ are seen in the 2.96-2.82 Ga
87 Witwatersrand Supergroup, Transvaal, South Africa (Guy et al., 2012), and in the 2.65-2.5 Ga Ghaap
88 Group (Zerkle et al., 2012). Any build-up of sulphate in the Late Archean ocean (Reinhard et al.,
89 2009) could potentially have supported anaerobic oxidation of methane (AOM), but recent work
90 suggests low sulphate concentrations $\sim 10\ \mu\text{M}$ (Crowe et al., 2014; Zhelezinskaia et al., 2014).
91 Previous models of Earth's long-term redox evolution in the Archean-Proterozoic (Catling et al.,
92 2007; Claire et al., 2006; Goldblatt et al., 2006), have not resolved such aerobic ecosystems and have
93 made different assumptions regarding methane cycling and atmospheric methane and oxygen
94 fluxes. These models agree that the eventual rise of atmospheric oxygen in the Great Oxidation
95 (GOE) 2.45–2.32 Ga, can be understood as being triggered by the overall balance of fluxes to and
96 from the ocean-atmosphere (including hydrogen escape) shifting to net oxidising, for which there

97 are several candidate causes (Kasting, 2013). They also agree that once a modest redox imbalance
98 produced enough oxygen for the ozone layer to begin to form, the resulting slowing in the
99 photochemical consumption of oxygen via reaction with methane would have produced a strong
100 positive feedback, driving an abrupt oxygen rise (Claire et al., 2006; Goldblatt et al., 2006). Where
101 existing models disagree is over the nature of the GOE transition. The apparently irreversible loss of
102 the MIF of S signal, which has not reappeared since 2.32 Ga, could be explained by a bi-stability of
103 atmospheric oxygen, in which for a range of values of the overall redox balance of the surface Earth,
104 both low and high oxygen states are stable (Goldblatt et al., 2006). However, this model assumes a
105 spatial and temporal decoupling within the ocean such that marine net primary production was
106 almost entirely converted into large balanced fluxes of oxygen and methane into the atmosphere
107 prior to the Great Oxidation. An alternative model (Claire et al., 2006) assumes lower atmospheric
108 methane/oxygen fluxes and generates an abrupt but reversible GOE transition. The size of the
109 balanced methane/oxygen flux also controls the atmospheric concentration of the minority gas
110 (oxygen prior to the Great Oxidation, methane afterwards), hence it determines the methane
111 contribution to the Proterozoic greenhouse (Pavlov et al., 2003), and it may have influenced the
112 Archean sulphur MIF signature (Zerkle et al., 2012).

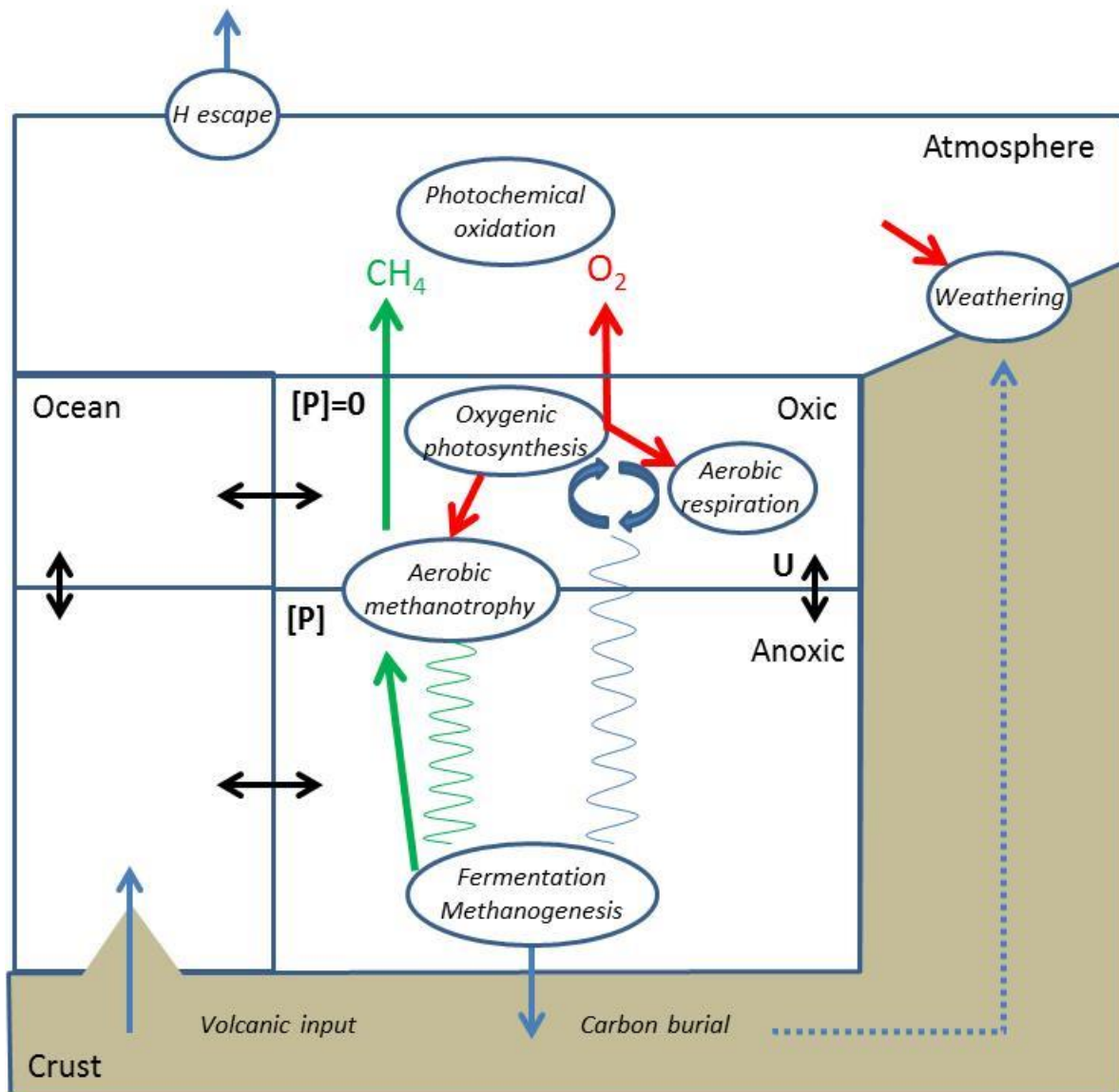
113 Here we seek to understand the controls on oxygen and methane cycling in Late Archean marine
114 ecosystems, and the implications for the nature of the GOE and for interpreting the carbon isotope
115 record. We take as a working hypothesis that planktonic oxygenic photosynthesis and therefore
116 oxygen oases were present in the Late Archean surface ocean. First we use an ocean general
117 circulation model and a multi-box ocean model to explore the potential for oxygen build-up in the
118 surface ocean. Then we simulate the effects of including aerobic methanotrophy in the surface
119 ocean on oxygen and methane concentrations and their balanced fluxes escaping to the
120 atmosphere. Next we used an existing model of the atmospheric redox balance (Goldblatt et al.,
121 2006) to examine the implications of the predicted oxygen/methane balanced fluxes for the nature
122 of the Great Oxidation transition. We exclude climate feedbacks (Claire et al., 2006) in the interests

123 of first clarifying our understanding of the key biological and chemical controls on oxygen and
124 methane through the Great Oxidation transition. Finally, we return to the ocean models to test the
125 hypothesis that aerobic methanotrophy was responsible for isotopically very light Late Archean
126 kerogens (Hayes, 1983; Hayes, 1994). This leads into a discussion of the potential for spatial
127 concentration of aerobic methanotrophy in shelf/slope upwelling regions and/or microbial mats, the
128 effects of additional redox shuttles (such as via sulphate), and the overall implications of our results
129 for controls on oxygen and methane concentrations before and after the Great Oxidation.

130 **2. Materials and Methods**

131 Figure 1 shows a schematic of the key processes considered in our modelling. We use a hierarchy of
132 models to cover the wide range of space and timescales. To account for the spatially and seasonally-
133 variable effects of potentially widespread early aerobic ecosystems, we extended the representation
134 of biogeochemistry in the MITgcm ocean general circulation model to include methane cycling. We
135 used the results of the GCM to inform the construction of a spatially-resolved box model utilising the
136 same biogeochemical scheme. Then we used this ocean box model together with an existing model
137 of the atmospheric redox balance (Goldblatt et al., 2006) to examine the effect of the predicted
138 balanced fluxes of methane and oxygen on the Great Oxidation transition. More complete details of
139 the models are given in the Supplementary Material. Here we concentrate on the key
140 biogeochemical processes that govern the results.

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Figure 1. Key processes in the Late Archean-Paleoproterozoic Earth system. [P] is the concentration of limiting nutrient in the deep ocean, which is mixed upwards at rate U to the surface ocean, fuelling oxygenic photosynthesis. Some of the oxygen liberated is consumed by aerobic respiration, recycling nutrient and boosting net primary production. The upwelling nutrient flux determines the sinking export flux of carbon (blue wiggly). In the deep ocean this is converted by fermentation and methanogenesis to methane (and CO₂). Methane upwells to the surface waters where it is partially consumed with oxygen by aerobic methanotrophy resulting in an additional isotopically light sinking flux (green wiggly). The remaining balanced fluxes of methane and oxygen escape to the atmosphere and are consumed by photochemically-driven oxidation. Reductant input into the atmosphere from the crust and mantle, and from any time-dependent imbalance between carbon burial and oxidative weathering, is balanced by escape to space of hydrogen produced by methane photolysis. See Figure A1 for a more complete description.

153 **2.1. Marine biogeochemistry**

154 Oxygenic photosynthesis limited by a single nutrient (P) is represented by



156 where $x = 1/r_{c:p}$ and $r_{c:p}$ is a 'Redfield ratio' of carbon to phosphorus in marine phytoplankton
157 biomass.

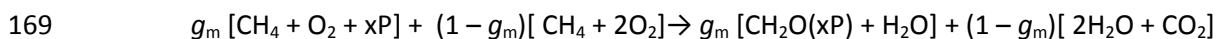
158 Aerobic respiration results in a null cycle with no net oxygen production:



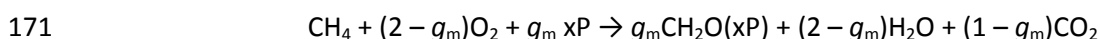
160 The remaining biomass carbon *EP* (export production) is exported to anoxic deeper waters with a
161 balancing net O₂ release in the surface ocean. *EP* is remineralized by fermentation and
162 methanogenesis (in the absence of alternative electron acceptors in the low sulphate Late Archean
163 environment), producing isotopically light methane:



165 Upwelling methane may then come into contact with surface O₂ and be consumed by aerobic
166 methanotrophy. We define a methanotroph growth efficiency g_m (biomass produced divided by
167 methane consumed) such that the stoichiometry is given by the combination of biomass production
168 and energy releasing reactions:



170 hence the overall methanotroph stoichiometry is given by:



172 The isotopic composition of the net organic carbon flux to anoxic deep waters and to sediments is
173 then determined by the relative proportion of methanotroph and autotroph sinking biomass, hence

174 is dependent on the fraction of methane captured by methanotrophs and the methanotroph growth
175 efficiency (Hayes, 1983; Hayes, 1994).

176 The remaining oxygen and methane then support a balanced flux escaping to the atmosphere, $f_{\text{bal}} =$
177 $f_{\text{O}_2} = 2 f_{\text{CH}_4}$.

178 The marine biosphere reaches equilibrium on an ocean circulation timescale on the order of 10^4 yr
179 hence (for the GCM) we assume it is in steady-state relative to tectonic or evolutionary forcings.

180 **2.2. Atmospheric redox balance**

181 Biosphere/geosphere inputs into the atmosphere are represented by two control parameters: the
182 balanced flux of oxygen and methane escaping the ocean, f_{bal} , and the oxygen-independent part of
183 overall Earth surface reductant input f_{surf} (i.e. not including the oxygen sensitivity of oxidative
184 weathering). f_{bal} is mostly consumed by atmospheric photochemical oxidation with net reaction:



186 with a non-linear dependency of the reaction rate on atmospheric oxygen concentration due to the
187 formation of the ozone layer (Goldblatt et al., 2006), and a fast equilibration timescale, on the order
188 of 10^2 yr.

189 The oxidation state of the atmosphere is determined by net oxidant and reductant budgets. A small
190 fraction of export production ($f_{\text{Cburial}} \approx 10^{13}$ mol O_2 equiv yr^{-1}) is buried as reduced organic carbon,
191 cycled via tectonic processes on timescales $\approx 10^8$ yr contributing to metamorphic flux f_{metr} and then
192 exposed and oxidised contributing to a surface oxidation flux f_{ox} . Volcanic input of reduced species
193 from the mantle provides a net reductant input of $f_{\text{mantle}} \approx 10^{11}$ mol O_2 equiv yr^{-1} . Hydrogen escape to
194 space via methane photolysis occurs with net overall reaction:



196 This provides a net oxidant input f_{hesc} (as methane and oxygen are produced in the ratio 1:2, but
197 consumed in the ratio 1:1). This drives a slow overall oxidation of the Earth's surface.

198 The redox budget f_{redox} of the atmosphere is then (all fluxes in mol O₂ equiv yr⁻¹):

$$199 \quad f_{\text{redox}} = -f_{\text{hesc}} (p\text{CH}_4) + f_{\text{met}}(t) + f_{\text{mantle}}(t) - f_{\text{cburial}}(t) + f_{\text{ox}}(t, p\text{O}_2)$$

200 To separate the dynamics of atmospheric oxygen and methane from the tectonically and biologically
201 driven inputs, we separate surface oxidation into time-dependent and oxygen-sensitive components
202 $f_{\text{ox}}(t, p\text{O}_2) = f_{\text{ox}}(t) + f_{\text{oxfb}}(p\text{O}_2)$, define a summary flux $f_{\text{surf}}(t) = f_{\text{met}}(t) + f_{\text{mantle}}(t) - f_{\text{cburial}}(t) + f_{\text{ox}}(t)$, and
203 rewrite as:

$$204 \quad f_{\text{redox}} = -f_{\text{hesc}} (p\text{CH}_4) + f_{\text{surf}}(t) + f_{\text{oxfb}}(p\text{O}_2) \quad (1).$$

205 Here $f_{\text{surf}}(t)$ represents any time-dependent imbalance between carbon burial f_{cburial} , metamorphic
206 and mantle inputs, and oxidation f_{ox} , treated as an exogenous driver of the system. f_{oxfb} is a
207 parameterization of any oxygen-dependence of carbon burial and oxidation rates. The timescale for
208 equilibration of atmospheric oxygen is long ($\approx 10^6$ yr), hence we explicitly consider the dynamics and
209 stability driven by a combination of stochastic forcing from changes in the carbon burial rate, and
210 slow secular change in f_{mantle} .

211 Time-dependent solutions were derived by integration using a variable-step size Runge-Kutta
212 algorithm (as implemented by the Matlab ode23 function) and steady-state solutions were derived
213 by integrating to convergence.

214 **3. Results**

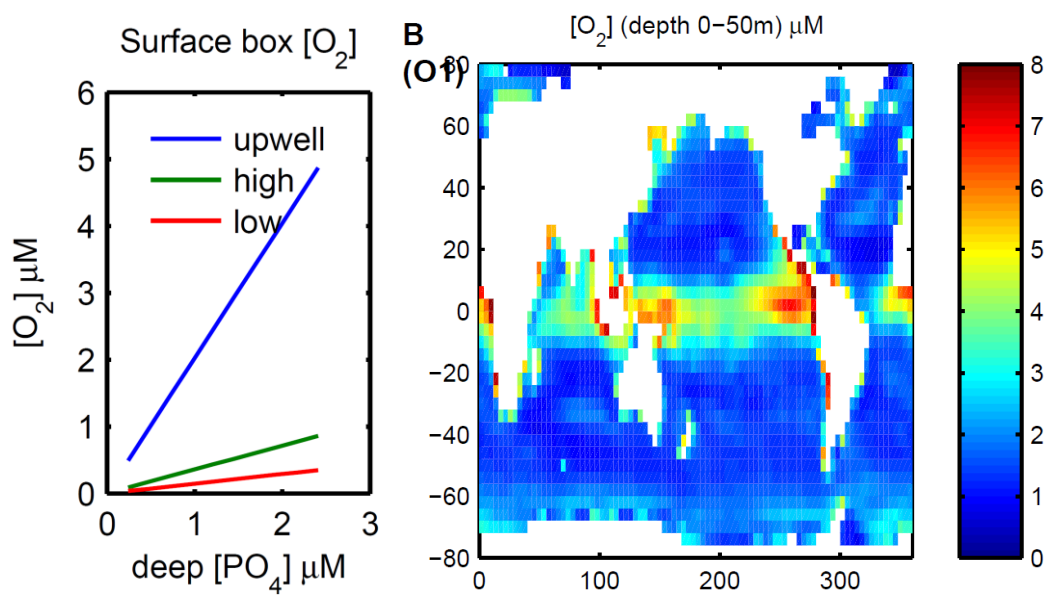
215 **3.1. Oxygenation of the surface ocean and marine export production**

216 Once the advent of oxygen photosynthesis lifts constraints from electron donor supply (Kharecha et
217 al., 2005), light and nutrients remain as the (abiotic) constraints on productivity. An upper limit on
218 Late Archean surface ocean oxygen concentration [O₂] (μM) (in the absence of methanotrophy) is

219 then determined by the balance between export production from oxygenic photosynthesis to anoxic
 220 depths, EP (which represents a net oxygen source to the surface ocean), and escape to the
 221 atmosphere represented by piston velocity κ_w (m hr^{-1}):

$$222 \quad [O_2]_s \approx 4.7 (EP / EP_0) / (\kappa_w / \kappa_{w0}) \mu\text{M} \quad (2)$$

223 where $EP_0 = 8.5 \text{ mol m}^{-2} \text{ yr}^{-1}$ is a global mean for highly productive ocean margin regions today and
 224 the global mean $\kappa_{w0} = 0.2 \text{ m hr}^{-1}$.



225
 226 **Figure 2. Upper limit on surface oxygen concentration (in the absence of methanotrophy) with nutrient limited oxygenic**
 227 **photosynthesis and atmospheric oxygen restored to zero. (A) Box model (Supplementary Methods). (B) GCM scenario**
 228 **'S1' with present-day nutrient level and aerobic respiration occurring in the oxygen oases created (Supplementary Table**
 229 **A-3 and Fig. A-9).**

230 The primary controls on EP are nutrient supply via the combination of nutrient concentration and
 231 the ocean circulation, and seasonal light limitation at high latitudes. GCM and box model simulations
 232 (Figure 2 and Supplementary Fig. A-9) confirm that the resulting upper limits on surface oxygen
 233 concentrations are of the order $[O_2]_s \approx 1\text{-}10 \mu\text{M}$ with maxima expected in upwelling regions. We use
 234 the present-day continental configuration and ocean circulation because these details and the Late
 235 Archean climate are largely unknown. However, the physical processes driving wind-driven

236 upwelling and stratification will still result in open-ocean wind-driven gyres and hence equatorial
237 and high-latitude upwelling, coastal upwelling regions, and low-latitude stratification with high-
238 latitude seasonal deep mixed-layer depths. EP and hence $[O_2]_s$ is approximately proportional to
239 nutrient level (Fig 2A) and nutrient levels are also uncertain (Konhauser et al., 2007), but even
240 nutrient levels as little as 10% of present provide sufficient productivity to support an aerobic
241 ecosystem ($[O_2]_s \approx 1 \mu M$) in upwelling regions (Supplementary Fig A-12).

242 NPP is a less well constrained multiple of EP , as a result of surface-ocean recycling in the microbial
243 loop. This recycling increases predicted NPP (and hence oxygen production) relative to export
244 production by at least a factor of 3 in the contemporary ocean (Laws et al., 2000). Bacterial aerobic
245 growth has been demonstrated down to nanomolar oxygen concentrations (Stolper et al., 2010),
246 with the limiting concentration close to the cellular diffusion limit. We therefore assume that aerobic
247 heterotrophic carbon and nutrient cycling in a microbial loop would have operated with an efficiency
248 at least comparable to that in present-day ecosystems, and potentially larger (limited ultimately by
249 light availability) given the absence of eukaryotic predation to package large sinking particles.
250 Changing the depth dependency of nutrient recycling, such that nutrients are recycled aerobically at
251 shallower depths in a prokaryote-dominated world increases NPP . However, as this cycling produces
252 and consumes oxygen in equal measure it leaves EP and hence $[O_2]_s$ and balanced fluxes unchanged
253 (Supplementary Table A-3, Section A-5.4).

254 **3.2. Biosphere methane cycling**

255 Nutrient, $[P]$, supply to the mixed layer from ocean upwelling and high latitude convection (U)
256 determines export production, via a 'Redfield ratio' ($r_{c:p}$). In the Late Archean this export production
257 would have determined the maximum methane flux produced in deeper anoxic layers, setting an
258 upper limit on the balanced fluxes of methane and oxygen that can leave the ocean in the absence
259 of methanotrophy:

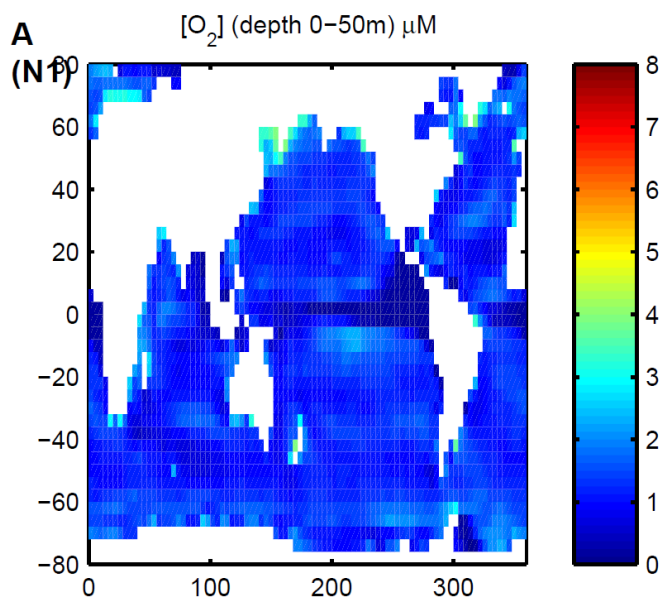
$$f_{\text{bal}} \leq EP \approx U [P]_{\text{d}} r_{\text{c;p}} \approx 2U [\text{CH}_4]_{\text{d}} \text{ mol O}_2 \text{ yr}^{-1} \quad (3)$$

261 Taking modern day $[P] = 2.17 \mu\text{M}$ as an upper limit, $U \approx 100 \text{ Sv}$ (Supplementary Table A-1) and $r_{\text{c;p}} =$
 262 117, typical for modern cyanobacteria, the resulting flux is $\approx 8 \times 10^{14} \text{ mol O}_2 \text{ yr}^{-1}$, which is only $\approx 20\%$ of
 263 contemporary NPP. Here we are assuming no alternative electron acceptors in the low sulphur Late
 264 Archean environment, but we expect that iron would have contributed (Kharecha et al., 2005).
 265 Whilst $r_{\text{c;p}}$ could conceivably have been higher or lower in the Late Archean ocean, $[P]$ is generally
 266 expected to have been lower, so our upper limit is unlikely to have been exceeded. In the presence
 267 of aerobic methanotrophy, $[\text{O}_2]_{\text{s}}$ and $[\text{CH}_4]_{\text{s}}$ are then reduced to levels above a minimum determined
 268 by the limiting concentration required to support methanotrophy, $[\text{O}_2]_{\text{s}} \approx 0.01\text{--}0.1 \mu\text{M}$ and $[\text{CH}_4]_{\text{s}} <$
 269 R^* , where $R^* \leq R^*_0 = 0.1 \mu\text{M}$ (Tavormina et al., 2010; Valentine, 2011) (Supplementary Material
 270 Section A-1). This limits the rate of methane escape to the atmosphere, leading to a lower limit
 271 (assuming local balance of methane and oxygen supply):

$$f_{\text{bal}} \geq 1.2 \times 10^{14} (k_w/k_{w0}) (R^*/R^*_0) \text{ mol O}_2 \text{ yr}^{-1} \quad (4)$$

273 Three mechanisms will increase the atmospheric flux above this limit. Firstly, spatial and temporal
 274 decoupling of export production from fermentation and methanogenesis mean that methane and
 275 oxygen are not equally available at the redoxcline. Seasonal high-latitude production therefore
 276 results in excess summer oxygen production and winter methane escape. Secondly, accumulation
 277 and consumption of oxygen over a diel cycle leads to a minimum daily mean concentration $[\text{O}_2]_{\text{diel}} \approx$
 278 $0.14 (NPP/10 \text{ mol C m}^{-2} \text{ yr}^{-1}) / (z_{\text{ml}} / 50 \text{ m}) \mu\text{M}$ (Supplementary Material Section A-1.3), where for
 279 typical open-ocean values of net primary productivity NPP and mixed layer depth z_{ml} this is a
 280 relatively small effect. Third, methane ebullition may result in atmospheric escape of methane
 281 produced in sediments. This likely provided a major mechanism in shallow-water environments, as it
 282 does today (Valentine, 2011), but we do not include it in our open ocean models.

283 The effect of methanotrophy and spatial and temporal decoupling on surface oxygen concentration
284 is illustrated using the GCM simulations in Figure 3. Oxygen levels approach the methanotroph-
285 determined limiting concentration at low latitudes (with methane in small excess as a result of
286 spatial decoupling), but are higher at seasonal high latitudes. Crucially, however, aerobic ecosystems
287 are still widespread in the model. The overall pattern of surface oxygen concentration is consistent
288 with previous work (Olson et al., 2013).

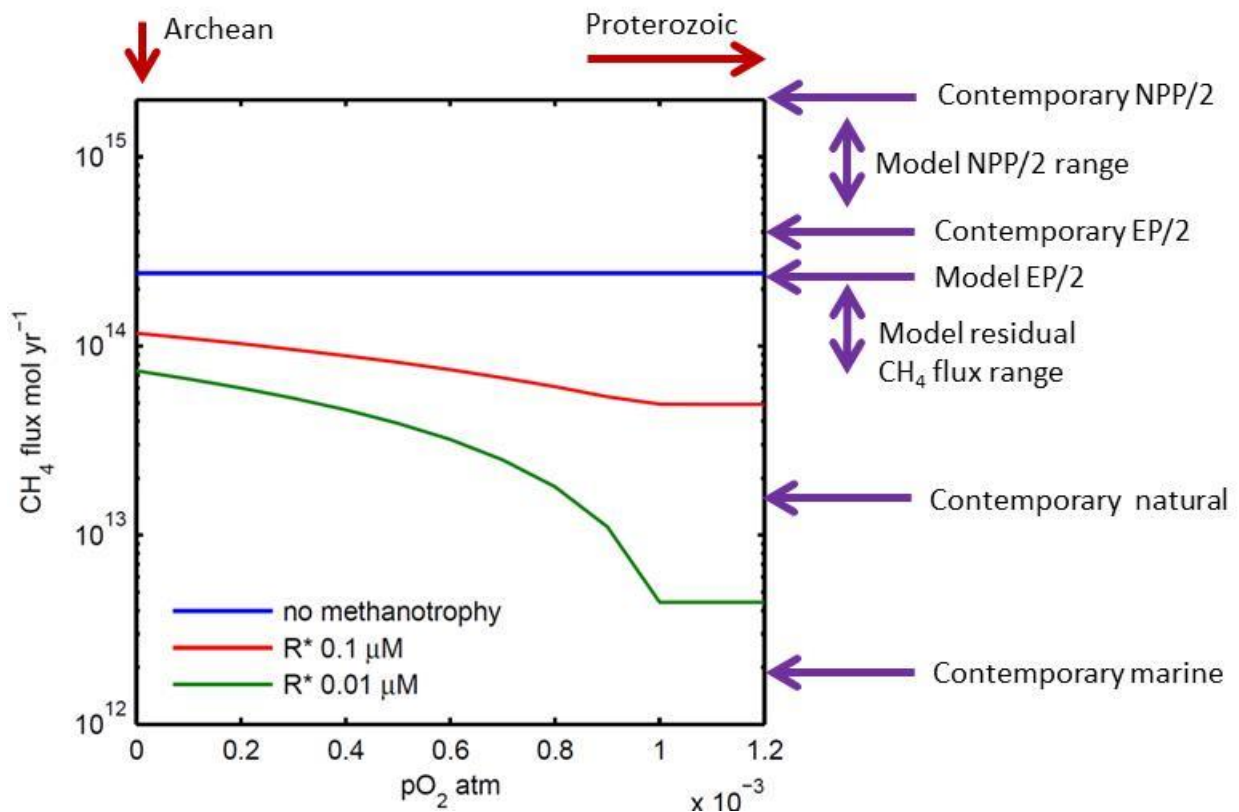


289

290 **Figure 3. Annual mean surface oxygen concentration for GCM scenario 'N1', including aerobic methanotrophy.**

291 Our GCM simulations also predict that roughly 40% of upwelling methane would have been
292 consumed by aerobic methanotrophy in the Late Archean and therefore the balanced flux of
293 methane and oxygen leaving the ocean would have been roughly 60% of export production
294 (Supplementary Table A-3 and Figures A-12). This result is due to a combination of spatial decoupling
295 of methane and oxygen supply in low latitude regions and temporal decoupling in seasonal high
296 latitudes (Supplementary Figures A-10, A-11). The range of balanced flux $\approx 1-5.7 \times 10^{14}$ mol O_2 yr^{-1} for
297 0.1–1 modern day nutrient levels is most directly linked to *EP* rather than *NPP* and hence is only
298 $\approx 20\%$ of that considered in some previous box models (Goldblatt et al., 2006). The fraction of *NPP*
299 converted to a balanced flux is less well constrained, because *NPP* depends on the degree of

300 nutrient cycling within oxygen oases. With a conservative, modern day assumption that around two-
 301 thirds of NPP is recycled and one-third is exported to depth, the balanced flux is about one-fifth of
 302 NPP (Figure 4). The balanced flux range considered here includes the 4.0×10^{14} mol O_2 yr^{-1} assumed
 303 by Claire et al. (2006) and the 2.0×10^{14} mol O_2 yr^{-1} assumed by Catling et al. (2007).

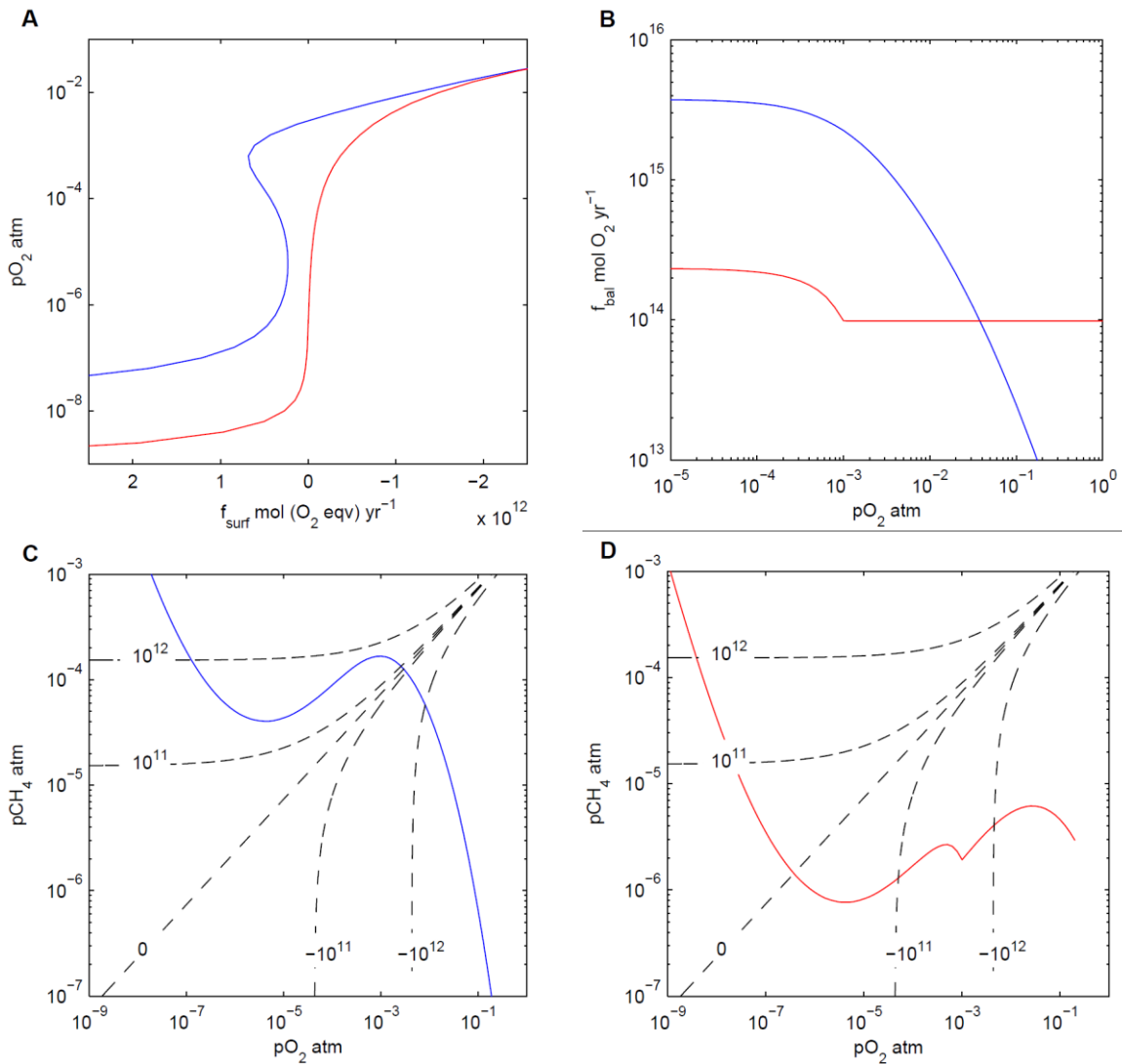


304
 305 **Figure 4.** Atmospheric methane fluxes ($0.5 f_{bal}$) from the marine biosphere box model, compared to contemporary fluxes
 306 and demonstrating the effect of increase in atmospheric oxygen to Proterozoic levels following the Great Oxidation. Net
 307 oxygen and methane production from the oxygenated surface layer is most directly related to export production *EP*. The
 308 balanced flux escaping to the atmosphere is reduced below *EP* by aerobic methanotrophy, depending on limiting oxygen
 309 and methane concentration (R^*). The advent of atmospheric oxygen provides an additional oxygen transport pathway,
 310 supporting additional consumption by aerobic methanotrophy and reducing f_{bal} .

311 **3.3. Effect on the Great Oxidation**

312 The two existing models for the Great Oxidation transition while demonstrating the same overall
 313 redox control on atmospheric oxygen, and highly non-linear response, differ in the assumed
 314 biosphere methane/oxygen balanced flux, and in the driving mechanism included. The model of

315 Goldblatt et al. (2006) assumed nearly all NPP translates into a balanced flux (with a parameterized
316 decline in balanced flux with increasing atmospheric pO_2 , Figure 5B), and generated a bistable
317 transition with two atmospheric oxygen states available for a range of Earth-surface reductant input.
318 The model of Claire et al. (2006) argued for a lower biosphere flux of 2.0×10^{14} mol O_2 yr^{-1} and also
319 calculated the effect of hydrogen escape on oxidation of the crust, and hence the redox state of
320 metamorphic flux and the secular evolution of atmospheric oxygen. Our approach here is to
321 examine the effect of the balanced flux of methane and oxygen on the Great Oxidation transition,
322 while prescribing the time-dependent evolution of Earth-surface redox input as a forcing parameter.
323



324

325

326 **Figure 5. Controls on atmospheric stability. (A)** Steady state solutions for pO_2 as a function of reductant input f_{surf} , for
 327 two models for oxygen/methane balanced flux. Blue corresponds to the model of Goldblatt et al. (2006), with $f_{bal} = N\Omega_{O_2}$
 328 where $N = 3.75 \times 10^{15} \text{ mol O}_2 \text{ yr}^{-1}$ is NPP and $\Omega_{O_2}(pO_2)$ is a parameterized decrease with increasing pO_2 . Red is for the box
 329 model shown in Figure 4 with $R^* = 0.1 \mu\text{M}$ and $f_{bal} = 2.3 \times 10^{14} \text{ mol O}_2 \text{ yr}^{-1}$ at low pO_2 decreasing to $1.0 \times 10^{14} \text{ mol O}_2 \text{ yr}^{-1}$ at
 330 high pO_2 . (B) Corresponding values of the balanced flux of methane and oxygen escaping the ocean. The revised lower
 331 value of balanced flux eliminates the bistability of pO_2 . (C) Phase space portrait for the model of Goldblatt et al. (2006)
 332 where dashed lines are values of $f_{surf} + f_{oxfb}$ with $f_{surf} = 10^{12}, 10^{11}, 0, -10^{11}, -10^{12} \text{ mol O}_2 \text{ eqv yr}^{-1}$ as indicated. (D) Phase
 333 space portrait for the marine biosphere box model. See Supplementary Fig A4, A6 for additional sensitivity studies.

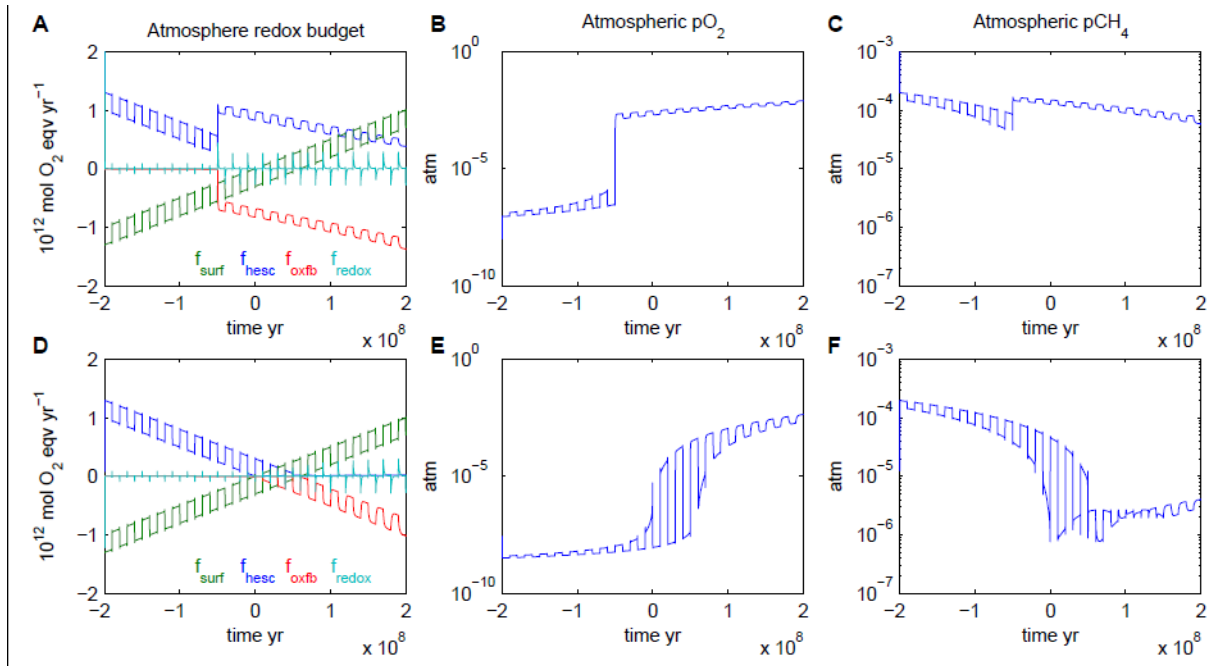
334 We first consider the steady state solutions for atmospheric oxygen concentration (Figure 5A). The
 335 high balanced-flux case (Goldblatt et al., 2006) produces a broad region of bi-stability for O_2 ,

336 whereas with our revised estimate including aerobic recycling in the surface ocean, the bi-stability is
337 eliminated leaving a sharp non-linear transition.

338 The non-linearity of the atmospheric transition is due to the effect of the formation of the ozone
339 layer on the atmospheric photochemical methane oxidation rate (Claire et al., 2006; Goldblatt et al.,
340 2006). There is a positive feedback regime in which as the ozone layer starts to form, this suppresses
341 oxygen consumption, accelerating ozone accumulation, and this tends to separate low and high
342 stable states for oxygen. However, the degree of bi-stability or hysteresis also depends on the
343 strength of the negative feedback involving hydrogen escape to space (an oxygen source). This is
344 particularly important in the high oxygen state: if some factor tends to reduce the oxygen
345 concentration, this generates a counterbalancing increase in methane concentration and hydrogen
346 escape, which resists the initial change. With a lower balanced flux of methane and oxygen, the
347 methane concentration and hydrogen escape rate are lower, hence the negative feedback is weaker.
348 Thus, reducing the balanced flux of oxygen and methane from the ocean (Figure 5B) shrinks the
349 basin of attraction of the high oxygen state and suppresses the bi-stability (Figure 5A).

350 The controls on atmospheric stability can be further understood by considering the phase space of
351 oxygen and methane concentrations (Figure 5C,D). Here solutions for the original model with high
352 balanced flux (Figure 5C) and the new model with low balanced flux (Figure 5D) are intersected by
353 different functions for the net Earth surface input of reductant ($f_{\text{surf}} + f_{\text{oxfb}}$) to the atmosphere (or
354 oxidant input if the value is negative). These dashed lines correspond to different fixed values of f_{surf}
355 but are curved because f_{oxfb} is sensitive to atmospheric composition. In the original model, with a
356 high balanced flux (Figure 5C), the oxygen source from hydrogen escape can still exceed the sink
357 from oxidative weathering for $p\text{O}_2 < 10^{-3}$ atm. This allows two steady states to exist for $f_{\text{surf}} = 0.25$ –
358 0.7×10^{12} mol O_2 equiv yr^{-1} , in both of which net reductant input is balanced by hydrogen escape to
359 space. In contrast, in the new model with low balanced flux (Figure 5D) there is only ever one steady
360 state. This oxygen-methane steady-state in Figure 5D is similar to that of Claire et al. (2006) and

361 Zahnle et al. (2006), as our balanced flux is comparable to what they assume (see Supplementary
 362 Section A-3 for additional comparison and sensitivity studies). We note that the high balanced flux
 363 from Goldblatt et al. (2006) exceeds the upper limit of $2.7 \times 10^{15} \text{ mol O}_2 \text{ yr}^{-1}$ considered by Zahnle et
 364 al. (2006) hence Fig 5C is in their ‘inaccessible region’.



365

366 **Figure 6. Atmosphere evolution for the two models for oxygen/methane balanced flux described in Figure 5: (A,B,C) the**
 367 **model of Goldblatt et al. (2006) with $f_{\text{bal}} = N\Omega_{\text{O}_2}$ where $N = 3.75 \times 10^{15} \text{ mol O}_2 \text{ yr}^{-1}$ is NPP, and (D,E,F) the box model shown**
 368 **in Figure 4 with $R^* = 0.1 \mu\text{M}$. Left panels (A,D) show components of overall net reductant input, f_{redox} as defined by**
 369 **Equation (1). The models are forced by a secular decrease in reductant input representing a slow overall oxidation of the**
 370 **Earth surface, and an pulsed imbalance between carbon burial and oxidative weathering of $\pm 1.5 \times 10^{11} \text{ mol O}_2 \text{ yr}^{-1}$ with**
 371 **time period 20 My. Time zero corresponds to $f_{\text{surf}} = 0$ (cf $K_{\text{OXY}} = 0$ in Claire et al. 2006).**

372 This is explored further with two scenarios for atmospheric evolution (Figure 6) based on the same
 373 pair of models for balanced methane/oxygen flux, from NPP (Goldblatt et al., 2006) and our revised
 374 lower estimate. The Earth surface reductant input f_{surf} is treated as an exogenous time-dependent
 375 forcing term, representing both a stochastic imbalance between carbon burial, metamorphic and
 376 volcanic inputs, and oxidative weathering (a pulsed input of $\pm 1.5 \times 10^{11} \text{ mol O}_2 \text{ yr}^{-1}$ and time period 20

377 My), and a secular decrease in reductant input representing a slow overall oxidation of the Earth
378 surface.

379 As a function of time, atmosphere evolution shows three regimes (Claire et al., 2006): (i) Prior to the
380 Great Oxidation, the atmosphere is in a stable, steady-state regime with methane level set by a
381 balance between reductant input and hydrogen escape, hence the two scenarios show the same
382 methane concentration. Oxygen is a trace gas, with concentration is set to balance oxygen input and
383 atmospheric oxidation, and is therefore lower in the lower balanced flux scenario. (ii) During the
384 transition to an oxic atmosphere, the atmosphere is in a non-steady state with falling methane and
385 rising oxygen levels, and methane/oxygen balance is controlled by the short-timescale atmospheric
386 methane oxidation process. As oxygen levels rise, methane levels must drop (Zahnle et al., 2006) and
387 pass through a minimum at $pO_2 \sim 10^{-5}$ atm (Fig A-3) determined only by the balanced flux input,
388 hence minimum methane level is lower in the low balanced flux scenario. Hydrogen escape feedback
389 stabilises the high oxygen state in the high balanced flux scenario, whereas in the low balanced flux
390 scenario the imposed tectonic forcing of reductant input drives multiple transitions in atmospheric
391 oxygen. (iii) After the Great Oxidation, the atmosphere approaches a higher oxygen steady-state,
392 where the oxygen level is set by oxygen-sensitive oxidative weathering balancing reductant input.
393 Methane is the trace gas, and the methane level is set by balancing methane input and atmospheric
394 oxidation. Hence methane concentration is much lower in the low balanced flux scenario, and
395 hydrogen escape is correspondingly much smaller in this scenario than in the high balanced flux
396 case.

397 The increase in atmospheric oxygen concentration following the Great Oxidation would have further
398 reduced the marine methane flux (Figure 4, Figure 5B), because oxygen redistribution via the
399 atmosphere would have compensated for the spatial decoupling of methanogenesis from marine
400 oxygen production, bringing oxygen to where methane was available for consumption by
401 methanotrophs. An estimated lower limit on Proterozoic $pO_2 \approx 0.01$ PAL (Rye and Holland, 1998) is

402 comparable to the atmospheric oxygen concentration (set by transport limitation at the air-sea
403 interface) that would have been sufficient to prevent oxygen limitation of methanotrophy (Figure 3).
404 Hence the flux of methane $0.5 f_{\text{bal}}$ from the ocean in the early Proterozoic could have been reduced
405 to the limit given by Equation (4), which assuming $R^* = 0.01 \mu\text{M}$ is near the contemporary marine
406 flux (Figure 4). As in the present, methane flux would then have been dominated by shallow water
407 wetlands (Figure 4). This results in a methane concentration of $\approx 1\text{--}5$ ppm and represents a
408 Phanerozoic type of methane control where surface input is balanced by atmospheric oxidation.

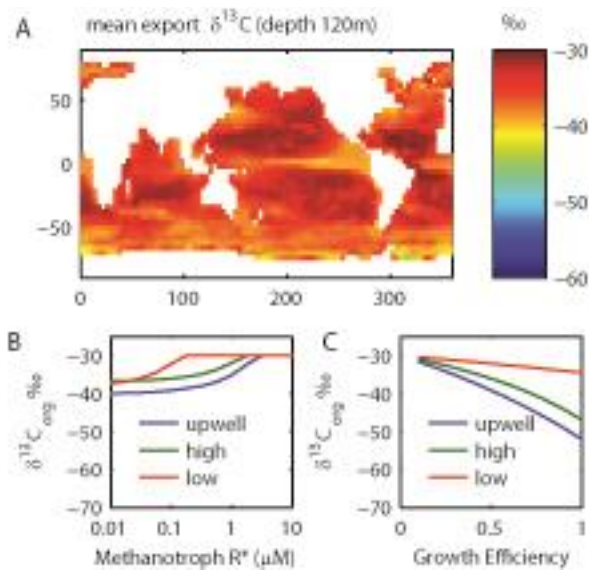
409 **3.4. $\delta^{13}\text{C}_{\text{org}}$ signature of methane cycling**

410 A key test of the hypothesis of abundant aerobic methanotrophy in oxygen oases before the Great
411 Oxidation are its predicted effects on the $\delta^{13}\text{C}_{\text{org}}$ record (Eigenbrode and Freeman, 2006; Hayes,
412 1994). The key control on the local isotopic composition $\delta^{13}\text{C}_{\text{org}}$ of sedimentary organic carbon is the
413 ratio of primary autotrophic production ($\delta^{13}\text{C}_{\text{org}} \approx -30 \text{‰}$) to secondary methanotroph production
414 ($\delta^{13}\text{C}_{\text{org}} < -70 \text{‰}$) in the organic carbon supply. In the limit where all autotroph production is locally
415 recycled, methanotroph growth efficiency $g_m = 1$, and EP is high so atmospheric escape is negligible,
416 $\delta^{13}\text{C}_{\text{org}}$ will approach $\delta_p - \varepsilon_m/2 \approx -70 \text{‰}$ where $\varepsilon_m \approx 80 \text{‰}$ is the fractionation produced by
417 fermentation and methanogenesis (Hayes, 1994). However, realistic methanotroph growth
418 efficiencies are $g_m < 0.5$, and the fraction of export production reprocessed via methanotrophy is
419 further reduced by spatial/temporal imbalances between export production and methanotrophy, and
420 by atmospheric escape.

421 The combination of these factors in our models leads to predictions of $\delta^{13}\text{C}_{\text{org}}$ ranging over ≈ -30 to -
422 45‰ (Figure 7), which are consistent with most deeper water data from 2.65–2.45 Ga (Eigenbrode
423 and Freeman, 2006; Fischer et al., 2009). The models give the lowest $\delta^{13}\text{C}_{\text{org}}$ of sinking organic matter
424 where upwelling nutrients fuel the most productive communities and oxygen oases. In oligotrophic
425 gyres, $\delta^{13}\text{C}_{\text{org}}$ remains close to that of photosynthetic matter, because little aerobic methanotrophy
426 can be supported. To reproduce the most extreme inferred deeper water $\delta^{13}\text{C}_{\text{org}} \approx -50 \text{‰}$ (from 2.65–

427 2.6 Ga) requires extreme assumptions, e.g. that methanotrophs have growth efficiency $g_m = 1$
428 allowing them to convert all the methane available to them in upwelling zones into biomass
429 (Supplementary Fig. A-14).

430



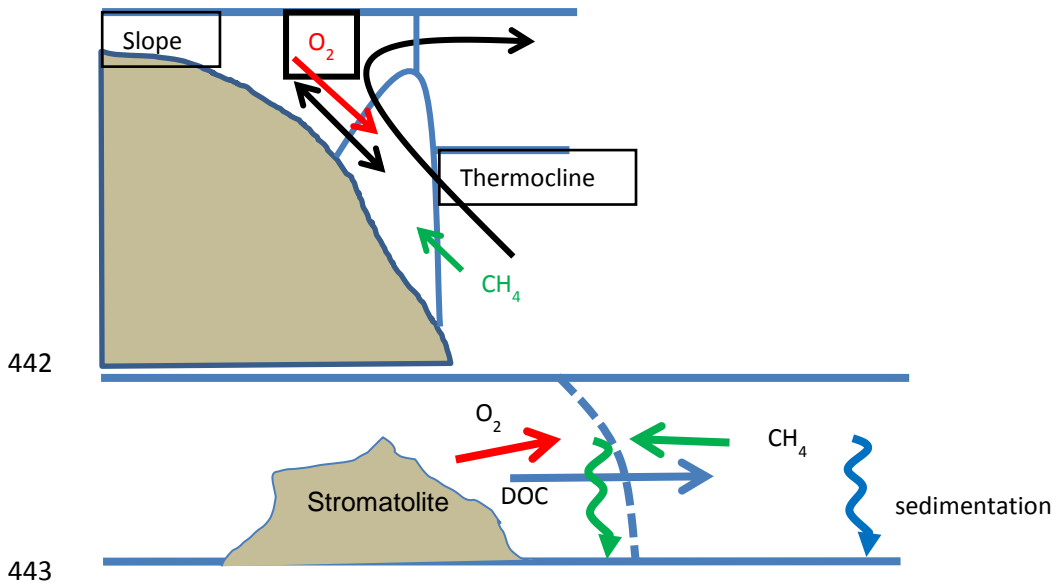
431

432 **Figure 7. Predicted $\delta^{13}\text{C}$ of sinking organic matter. (A) GCM scenario 'G1' with methanotroph growth efficiency 0.5**
433 **(Supplementary Methods). Box model dependency on (B) methanotroph limiting oxygen and methane concentration,**
434 **and (C) growth efficiency, for upwelling, high-latitude and low-latitude surface boxes.**

435 4. Discussion

436 4.1 Geochemical signature of marine aerobic ecosystems

437 By ≈ 2.6 Ga (if not before) oxygenic photosynthesis was creating oxygen oases in the open ocean
438 (Czaja et al., 2012), which fuelled aerobic ecosystems including methanotrophs that produced $\delta^{13}\text{C}_{\text{org}}$
439 ≈ -30 to -50 ‰ in deeper sediments (Eigenbrode and Freeman, 2006). We suggest the most negative
440 $\delta^{13}\text{C}_{\text{org}}$ could have been produced in shelf-slope upwelling regions, where upwelling methane-rich
441 water met oxic shelf water concentrating methanotroph production (Figure 8A).



442
443
444 **Figure 8. Two scenarios for the generation of extremely isotopically light $\delta^{13}\text{C}_{\text{org}}$ through the spatial concentration of**
445 **aerobic methanotrophy. (A) Shelf-slope upwelling region. (B) Microbial mat scenario.**

446 $\delta^{13}\text{C}_{\text{org}}$ values become generally less negative 2.6–2.45 Ga on approaching the Great Oxidation
447 (Eigenbrode and Freeman, 2006). This could have been because increasing sulphur concentration
448 due to sulphur input from oxidative weathering caused the spread of anaerobic oxidation of
449 methane (AOM), at the expense of aerobic methanotrophy. Sulphate provides an electron shuttle
450 across the redoxcline, which would initially have driven a fraction of methane consumption to
451 deeper depths in the water column – as seen in low-sulphate contemporary Lake Tanganyika
452 (Durisch-Kaiser et al., 2011). Ultimately, rising sulphate concentrations would have driven methane
453 consumption into the sediments, as assumed by Catling et al. (2007). AOM has low growth efficiency
454 (Hinrichs, 2002), hence its spread would have reduced the contribution of methanotroph biomass to
455 sedimentary organic carbon, producing less negative $\delta^{13}\text{C}_{\text{org}}$. Alternatively, as sulphate built up in the
456 ocean, sulphate reducers could have out-competed methanogens for sinking organic matter and
457 out-competed anaerobic methane oxidisers for sulphate, tending to reduce the cycling of carbon
458 through methanotrophs and thus produce less negative $\delta^{13}\text{C}_{\text{org}}$.

459 Increasing sulphur and AOM would have provided an additional redox shuttle and oxidant buffer
460 within the water column and sediments, potentially further reducing the atmospheric methane flux

461 (Beal et al., 2011; Catling et al., 2007). For example, a marine sulphate concentration of $\sim 100 \mu\text{M}$
462 would be sufficient to buffer high-latitude seasonality (lack of oxygen production over winter)
463 effectively turning a methane atmospheric flux into sulphide. However, our central result is
464 unaffected; this methane flux, and the associated balanced oxygen flux, would have been relatively
465 low, due to oxygen and methane cycling within the ocean, making the Great Oxidation more
466 reversible and probably episodic in nature. Our low balanced flux estimate (e.g. $2.3 \times 10^{14} \text{ mol O}_2 \text{ yr}^{-1}$
467 at low $p\text{O}_2$ in Figures 4 and 5) is close to that assumed by Catling et al. (2007) in the presence of
468 sedimentary AOM ($2.0 \times 10^{14} \text{ mol O}_2 \text{ yr}^{-1}$), and below that assumed by Claire et al. (2006) (4.0×10^{14}
469 $\text{mol O}_2 \text{ yr}^{-1}$). These authors' alternative model can also show an episodic rise of atmospheric O_2 at
470 the Great Oxidation in the presence of climate feedbacks (Claire et al., 2006), consistent with oxygen
471 rise being more reversible in a low balanced flux scenario.

472 **4.2 Microbial mat systems and their geochemical signature**

473 A complementary model of the Late Archean and Proterozoic world is that microbial mats in shallow
474 waters and on the land surface were major players in the cycling of oxygen and methane.
475 Cyanobacterial phylogeny suggests a freshwater origin for oxygenic photosynthesis (Blank and
476 Sánchez-Baracaldo, 2009), consistent with the interpretation that it was occurring in shallow water
477 lacustrine or estuarine environments, recorded in the Tumbiana formation at 2.72 Ga (Buick, 1992).
478 These same 2.72 Ga sediments host the most negative $\delta^{13}\text{C}_{\text{org}} \approx -60 \text{ ‰}$ (Eigenbrode and Freeman,
479 2006), which cannot be reproduced under realistic assumptions in our open ocean models. The
480 signal probably reflects methanotrophy at the edges of shallow-water stromatolites (Thomazo et al.,
481 2009), where oxygen from microbial mats meets methane produced from exported dissolved
482 organic carbon (DOC) (Figure 8B) allowing methanotroph secondary production to locally dominate
483 the biomass. This is consistent with the isotopically light $\delta^{13}\text{C}_{\text{org}}$ being located in mudstones, not just
484 stromatolites (Thomazo et al., 2009).

485 Atmospheric fluxes from microbial mat systems would have depended on spatial and temporal
486 decoupling of oxygenic photosynthesis and carbon cycling, as in the pelagic marine ecosystem.
487 Benthic mats where water depth exceeds $\sim 5\text{m}$ (the air-sea exchange piston velocity in m d^{-1}) would
488 have been buffered against daily atmospheric exchange by oxygen accumulation and consumption in
489 the water column. However mats in land-surface or intertidal environments (Lalonde and
490 Konhauser, 2015) could have provided an atmospheric oxygen and reduced gas source over a diel
491 cycle. The median net daytime oxygen production rate ($0.16 \text{ nmol cm}^{-2} \text{ s}^{-1}$) from the compilation of
492 Lalonde and Konshauer (2015), with a 50% correction for diel cycle mean and integrated over a
493 modern wetland area of 10^7 km^2 ($\sim 7\%$ of land area) corresponds to a global annual flux of 2.5×10^{14}
494 $\text{mol O}_2 \text{ yr}^{-1}$. However direct measurements of mat fluxes under anoxic conditions (which restricts
495 oxidant availability hence may limit night-time carbon and hence nutrient recycling) are scarce.
496 Hoehler et al. (2001) measured reduced flux (hydrogen) over a diel cycle from an intertidal mat
497 under laboratory anoxic conditions equivalent to $3.2 \times 10^{13} \text{ mol O}_2 \text{ eq yr}^{-1}$ when scaled to 10% of
498 contemporary marine NPP (their Table 2).

499 **4.3 Controls on Archean methanotrophy and atmospheric oxygen and methane.**

500 Sulphur isotope data show correlations between changes in the mass-independent fractionation
501 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope and negative $\delta^{13}\text{C}_{\text{org}}$ excursions at multiple locations (2.65 Ga Ghaap Group and ~ 2.5
502 Ga Gamohaam Formation, South Africa, ~ 2.5 Ga Mount McRae Shale and ~ 2.7 Ga Tumbiana
503 Formation, Western Australia) (Zerkle et al., 2012). This was interpreted as the result of transiently
504 increased biogenic methane production increasing both methanotrophy, and atmospheric methane
505 concentration leading to the formation of organic haze with corresponding changes in atmospheric
506 sulphur exit channels.

507 However, we find in our atmospheric model that an increase in balanced flux – nominally due to an
508 increase in productivity, methanogenesis and methanotrophy – leaves atmospheric pCH_4 unchanged
509 and increases pO_2 (and in fact would be likely to also generate increased carbon burial hence reduce

510 pCH₄). In contrast, an increase in reductant input – plausibly driven by a tectonic volcanic or
511 metamorphic perturbation – increases pCH₄ and reduces pO₂. We therefore suggest that
512 correlations between δ¹³C_{org} and sulphur MIF are more likely to be the result of tectonic
513 perturbations, with a reductant input (volcanic or metamorphic methane production) increasing
514 pCH₄, and an accompanying methane or CO₂-driven temperature, weathering and nutrient supply
515 increase driving increased productivity and methanotrophy.

516 **4.4 Proterozoic methane**

517 In the aftermath of the Great Oxidation, we predict a reduction in the methane flux from the ocean
518 to the Proterozoic atmosphere to $\approx 1.0 \times 10^{14}$ mol O₂ yr⁻¹, because oxygen was no longer limiting to
519 aerobic methane consumption anywhere in the surface ocean. Atmospheric methane input in the
520 Proterozoic was likely dominated instead by shallow-water and mat-based environments – just as
521 contemporary net biospheric methane production is dominated by wetlands. However, this
522 methane flux would have been reduced by sulphate input. Our estimate of post-Great Oxidation
523 methane flux is an order-of-magnitude less than the $7.5\text{--}15 \times 10^{14}$ mol O₂ yr⁻¹ suggested in arguments
524 for a methane-rich Proterozoic atmosphere (Pavlov et al., 2003; Roberson et al., 2011). Hence rather
525 than 100 ppm of CH₄ in the Proterozoic atmosphere (Pavlov et al., 2003; Roberson et al., 2011), we
526 predict <10 ppm (Figure 6F). The warming potential of methane was originally over-estimated
527 (Pavlov et al., 2003) due to an error in the model code (Byrne and Goldblatt, 2014; Roberson et al.,
528 2011). Lowering CH₄ concentration by at least an order-of-magnitude further adds to the problem of
529 explaining Proterozoic warmth, suggesting that a combination of CH₄, N₂O and CO₂ (Roberson et al.,
530 2011) is not sufficient and other contributions should be considered (Byrne and Goldblatt, 2014). A
531 low Proterozoic methane concentration also suggests ongoing hydrogen escape would have been
532 modest and is unlikely to have greatly reinforced the transition to a permanently oxic atmosphere.
533 Instead, other feedback mechanisms must have made the Great Oxidation permanent, such as land-

534 surface oxidative weathering of nutrients fuelling marine productivity and organic carbon burial
535 (Bekker and Holland, 2012).

536 **4.5 Further work**

537 The scenario of widespread oxygen oases prior to the Great Oxidation can be further tested. One
538 route would be to simulate the combined effects of our revised Late Archean oxygen and methane
539 fluxes on the MIF of S signature (Claire et al., 2014). A potentially strong constraint on the degree of
540 oxygenation of the surface ocean could come from process-based models of sulphur species
541 oxygenation in the water column (Halevy, 2013).

542 Our results demonstrate that quantitatively representing carbon, oxygen and methane cycling within
543 the marine environment is key to both interpreting the organic carbon isotope record, and to
544 understanding the evolution and stability of atmospheric composition. Future work should extend
545 this approach to quantify the relationship between marine redox-sensitive proxies and the oxidation
546 state of the water column (which is only indirectly coupled to atmospheric oxidation state), to
547 include microbial mats and understand their contribution to oxygen and methane cycling, and to test
548 hypotheses for Earth-system-level feedbacks during and after the Great Oxidation, including the role
549 of climate feedbacks.

550

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