

1 **Atmospheric oxygen abundance, marine nutrient availability, and organic carbon fluxes to**
2 **the seafloor**

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8
9 **Key Points**

- 10 • The CANOPS model was used to explore marine oxygenation, productivity, and organic
11 carbon flux to the seafloor across atmospheric O₂ levels.
- 12 • The deep ocean remains largely reducing until atmospheric oxygen levels reach ~40% of
13 present levels.
- 14 • Nutrients, productivity, and benthic carbon fluxes are severely restricted while atmospheric
15 oxygen is below ~40% of present levels.

16 **Abstract**

17 The global-scale oxygenation of Earth's surface represents one of the most fundamental chemical
18 transformations in our planet's history. There is empirical and theoretical evidence for at least two
19 distinct and stable regimes of Earth surface oxygenation—a 'low-O₂ world' characterized by
20 pervasively reducing deep ocean waters, and a 'high-O₂ world' with dominantly well-oxygenated
21 deep ocean waters represented by our modern surface environment. Numerous biogeochemical
22 processes and feedbacks control the redox state of the marine system, particularly when considered
23 globally and on geologic timescales. It has therefore proven challenging to provide quantitative
24 and internally consistent estimates of the atmospheric oxygen levels (and thereby, productivity,
25 nutrient availability, and reductant consumption) necessary to oxygenate the deep seas. Here, we
26 leverage an Earth-system biogeochemical model that tracks the carbon, nitrogen, oxygen,
27 phosphorus, and sulfur cycles (CANOPS) to provide new quantitative constraints on this

28 relationship. We explore ocean biogeochemistry and fluxes of reduced carbon to the seafloor
29 across a wide range of atmospheric oxygen levels from 0.01 – 100% of the present atmospheric
30 level (PAL), and implement a stochastic approach to provide formal estimates of uncertainty on
31 our results. We find that deep ocean waters remain largely reducing, and ocean productivity
32 remains significantly muted relative to the modern marine biosphere, until pO_2 levels reach ~40%
33 PAL. These results have major implications for quantitative constraints on atmospheric pO_2 levels
34 during the latest Proterozoic and Paleozoic, both in terms of environmental habitability for early
35 animals and with respect to potential energetic constraints on growing and diversifying benthic
36 communities.

37

38 **Keywords:** Oxygenation, primary productivity, phosphorus, Proterozoic, Paleozoic

39

40 **1 Introduction**

41 The long-term oxygenation of Earth's surface environments has been a topic of sustained interest
42 for more than half a century (e.g., Burkner and Marshall, 1965; Brinkmann, 1969; Rubey, 1955;
43 Cloud, 1968). On Earth, oxygen is supplied to surface environments principally by oxygenic
44 photosynthesizers, with these primary producers then becoming the source of organic material
45 required for all heterotrophic life. The redox evolution of our planet and the evolution of the
46 biosphere are thus fundamentally linked. However, barring a few unique examples (e.g., Belcher
47 et al., 2010; Farquhar et al., 2000; Glasspool et al., 2004; Johnston, 2011; Mitchell and Sheldon,
48 2010; Zbinden et al., 1988) virtually no geochemical proxies are capable of providing direct
49 information about atmospheric composition, and instead reflect localized marine conditions during
50 and subsequent to sediment deposition. As a result, attempting to quantitatively link proxy-derived

51 information about marine redox conditions to atmospheric composition has long been a central
52 challenge in efforts to reconstruct the chemical evolution of Earth's ocean-atmosphere system.

53
54 Following the initial rise in oxygen during the Paleoproterozoic Great Oxidation Event (GOE;
55 Holland, 2006), atmospheric oxygen levels eventually increased by more than four orders of
56 magnitude over the last ~2.3 billion years (Ga). There has been a sustained focus in recent decades
57 on oxygen levels during Earth's middle history (~1.8-0.8 Ga), leading to much debate and progress
58 in our quantitative understanding of atmospheric composition prior to the diversification of
59 animals. Recent work has suggested that baseline atmospheric oxygen levels during much of the
60 mid-Proterozoic likely did not exceed ~10% PAL, and may have been well below this for much
61 or most of mid-Proterozoic time (e.g., Bellefroid et al., 2018; Cole et al., 2016; Liu et al., 2016;
62 Planavsky et al., 2014; Planavsky et al., 2018; Planavsky et al., 2020). More recent constraints on
63 atmospheric composition have been tied to the onset of the charcoal record in the Late Silurian
64 (~420 Ma) (Glasspool et al., 2004), with more recent work indicating that atmospheric oxygen
65 levels of ~ 75% PAL may have been required for self-sustaining fire propagation (Belcher et al.,
66 2010; Belcher and McElwain, 2008). As a result, the transition of the Earth system from a
67 relatively stable mid-Proterozoic world to something closer to the modern state, perhaps by the
68 late Paleozoic (e.g., Dahl et al., 2010; Lenton et al., 2016; Wallace et al., 2017), represents a vast
69 period of time across which we have a relatively poor understanding of atmospheric oxygen levels.

70
71 Our primary source of information about the evolving state of Earth's surface redox conditions
72 comes from a range of proxies that reflect the biogeochemistry of marine environments. This
73 includes geochemical redox proxies (e.g., Lu et al., 2018; Partin et al., 2013; Reinhard et al., 2013;

74 Sperling et al., 2015; Stockey et al., 2020; Wallace et al., 2017; Zhang et al., 2018) as well as
75 paleontological evidence for evolving ecosystem structure and environmental habitability (e.g.,
76 Bowyer et al., 2017; Liu et al., 2015; Tarhan, 2018). These records provide substantial information
77 about marine biogeochemical conditions; however, these signals are difficult to quantitatively link
78 to atmospheric oxygen abundance. For example, there is currently no consensus on the
79 concentration of atmospheric oxygen that would be required to observe pervasively ‘oxic’
80 signatures in the trace metal records of marine systems, nor are there firm quantitative links
81 between the environmental oxygen levels implied by a given proxy or set of proxies and the levels
82 required for a particular degree of organism or ecosystem complexity (Cole et al., 2020).

83
84 There has been recent work exploring the relationship between primary productivity and proxy-
85 based estimates of mid-Proterozoic oxygen levels (Crockford et al., 2018; Laakso and Schrag,
86 2019; Ozaki et al., 2019). However, these analyses have been focused on the fairly limited range
87 of atmospheric oxygen levels expected for Earth’s middle history. Employing large-scale
88 biogeochemical models across more than ~2-3 orders of magnitude of atmospheric oxygen levels
89 is challenging, since highly non-linear feedbacks are expected as the ocean becomes oxygenated.
90 Modeling these feedbacks requires explicit coupling of the Earth’s carbon, oxygen, nitrogen,
91 phosphorus, and sulfur cycles, resulting in significant computational expense. In addition, explicit
92 quantification of key model uncertainties often requires a large ensemble of model runs. Together,
93 these constraints have prevented explicit investigation of ocean ventilation on productivity across
94 a large oxygen range except in very simple model architectures (e.g., Alcott et al., 2019; Laakso
95 et al., 2017).

96

97 Beyond oxygenation of the water column, the transition to a well-oxygenated deep ocean has major
98 implications for nutrient cycling and dramatic shifts in nutrient availability across the food chain—
99 and is thus likely to impact the viability of evolving benthic ecosystems. As a result, it is important
100 to establish a framework for the possible range of potential Earth system states that would be
101 consistent with observations from the rock record. By applying tested biogeochemical modeling
102 methods to this question using increased computing capacity and a moderate complexity model,
103 we provide a framework to quantitatively tie atmospheric conditions to nutrient availability, global
104 marine redox conditions, and biospheric productivity across the pO_2 space relevant for the last
105 ~2.3 billion years of Earth's history.

106

107 **2 Methods**

108 Here we utilize a biogeochemical Earth system model (CANOPS) in order to identify
109 biogeochemical regimes stable on geologic time scales at atmospheric oxygen levels between 0.01-
110 100% PAL. The CANOPS model couples a biogeochemical model with a diffusion-advection
111 model of the global ocean, a parameterized sediment model, and a stagnant film model for air-sea
112 gas exchange. The ocean circulation model robustly reproduces modern profiles of ocean
113 circulation tracers, and the biogeochemical and marine sediment diagenesis models include
114 explicit representations of photosynthetic primary production, a complete series of heterotrophic
115 respiratory pathways, a series of primary and secondary redox reactions, and the deposition,
116 decomposition, and burial of biogenic material in marine sediments. The physical configuration of
117 the CANOPS model is shown in Fig. 1a, while our modern “benchmark” simulation is compared
118 to observations from the modern oceans in Fig. 1b-c. A detailed description of the model and
119 modern Earth system calibration can be found in Ozaki and Tajika (2013) and Ozaki et al. (2019).

120

121 We build on the previously employed structure of CANOPS in two ways. First, we extend the
 122 model's treatment of pyrite (FeS_2) formation to include the formation of pyrite in the water column
 123 in addition to formation in marine sediments. We consider this a particularly relevant addition to
 124 the model framework given our interest in a very wide range of oxygen and sulfate levels and in
 125 the biogeochemical transition between largely reducing and strongly oxygenated systems, which
 126 is likely to be accompanied by an attendant large shift in the dynamics of global sulfur cycling.
 127 We parameterize water column FeS_2 formation at a given depth as a function of the local
 128 availability of dissolved sulfide and an assumed concentration of dissolved Fe^{2+} (Dale et al., 2009;
 129 2015):

130

$$131 \quad j_{py}^{WC} = k_{py} \cdot [\text{Fe}^{2+}] \cdot [\Sigma \text{H}_2\text{S}] , \quad \text{Eq. (1)}$$

132

133 where J_{py}^{WC} represents the water column pyrite formation flux, k_{py} represents a rate constant for
 134 pyrite formation, and brackets denote concentration.

135

136 Second, we employ a revised parameterization for the efficiency of nutrient P scavenging (σ_{scav})
 137 by Fe-bearing minerals as a function of the redox state of the ocean interior. Specifically, and in
 138 contrast to Ozaki et al. (2019), we specify that the relative efficiency of nutrient P scavenging is
 139 dependent on the abundance of dissolved O_2 below the photic zone according to:

140

$$141 \quad \sigma_{scav} = \sigma_{scav}^{\max} \cdot \left(1 - \tanh \left[\frac{[\text{O}_2]_{j=1}}{[\text{O}_2]_0} \right] \right) , \quad \text{Eq. (2)}$$

142
143 where σ_{scav}^{\max} denotes a maximum scavenging efficiency, sampled randomly from an inclusive
144 range between 0 and 1 during the stochastic analysis, $[O_2]_{j=1}$ denotes the dissolved oxygen
145 abundance in the ocean layer below the photic zone, and $[O_2]_0$ represents a reference dissolved O_2
146 concentration that initiates redox dependence of nutrient P scavenging. This is set by default to
147 $[O_2] = 1 \mu\text{mol kg}^{-1}$, following Reinhard et al. (2017). Mechanistically, this parameterization is
148 meant to describe the scavenging and removal of nutrient P below the photic zone when the ocean
149 interior becomes pervasively reducing. The P scavenging flux is thus equal to the upwelling flux
150 of P to the photic zone multiplied by σ_{scav} . This removal could be due to scavenging and
151 coprecipitation by Fe-oxide mineral phases at the oxic-anoxic interface (Bjerrum and Canfield,
152 2002; Jones et al., 2015), or the removal of nutrient P as a constituent of other reduced Fe-bearing
153 minerals such as Fe-phosphates, green rust, or Fe-silicate phases (Derry, 2015; Zegeye et al.,
154 2012). It is critical to point out that the specifics of Fe-associated P removal when the oceans are
155 pervasively oxygen-poor are not well constrained, especially in two key respects; (1) the sensitivity
156 of P removal efficiency to water column oxygen; and (2) the impact of changes in ocean chemistry
157 (i.e., carbonate chemistry, pH, etc.) on the efficiency and viability of each of these mechanisms
158 (e.g., Jahnke, 1984; Reinhard et al., 2017). This highlights the need for a robust statistical approach
159 and examination of the sensitivity of this parameter in our model (Fig. 3).

160
161 An additional key difference between our analysis and previous work (Reinhard et al., 2017; Ozaki
162 et al., 2019) is that we make the simplifying assumption that the C:P ratio of photosynthetic
163 biomass is constant at the classical “Redfield” value of 106:1. There is evidence to suggest that
164 biomass C:P should respond dynamically to environmental conditions (e.g., Galbraith and

165 Martiny, 2015; Reinhard et al., 2017), such that the C:P ratio of primary producers increases as
166 nutrient P availability drops (Quigg et al., 2003). However, for simplicity and transparency we
167 retain the simple “Redfield” assumption in our analysis. Better understanding the quantitative
168 relationship between the globally integrated C:P ratio of the ocean biosphere and environmental
169 boundary conditions is an important topic for future work, as is the attempt to provide empirical
170 constraints on biomass C:P in ancient oceans.

171
172 The centerpiece of our overall approach is to run a very large ensemble of model simulations in
173 which multiple key parameters are simultaneously sampled randomly from an assumed prior
174 distribution, with the model subsequently run with atmospheric pO_2 enforced as a constant
175 boundary condition until the S and P cycles reach steady state, although because S residence time
176 is much longer, model run times are determined primarily by S balance. We focus here on six key
177 parameters, chosen for their potential to significantly impact global oxygen and nutrient cycling,
178 and their likely roles in controlling the mechanistic links between atmospheric pO_2 , nutrient
179 biogeochemistry, marine redox, and energy fluxes to marine sediments. In contrast with Ozaki et
180 al. (2019), we do not vary the size of the crustal sulfur reservoirs for simplicity and because
181 reservoir size was not found to have a strong effect on the results. The key control parameters in
182 our analysis along with their constrained ranges and assumed prior distributions are provided in
183 Table 1. The specified ranges and prior distributions are discussed briefly below. Large ensembles
184 were implemented within the Georgia Institute of Technology Partnership for an Advanced
185 Computing Environment (PACE), with downstream data analysis performed using a custom
186 pipeline built in python. All model code, output data, and analytical pipeline can be found at the
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188

189 The key boundary condition for our analysis is atmospheric pO_2 . We examine atmospheric oxygen
190 levels ranging between 0.01 – 100% PAL, assuming a log-uniform prior distribution. By exploring
191 atmospheric oxygen levels across five orders of magnitude, we are able to provide both a repeated
192 analysis of low pO_2 levels and confirm earlier findings of Ozaki et al. (2019) with our newly
193 updated version of CANOPS, as well as place these results into larger context relative to the
194 modern Earth system with stable biogeochemical solutions up to 100% PAL O_2 . Most
195 significantly, this pO_2 range is significantly expanded beyond that of Ozaki et al. (2019) on the
196 high- O_2 end, and is expected to cover the dynamics of the transition to the well-ventilated and
197 highly productive “modern” ocean state.

198

199 The half-saturation constant for microbial sulfate reduction (K_{MSR}) controls the rate at which
200 organic matter is broken down via MSR at a given concentration of SO_4^{2-} . Because estimates of
201 K_{MSR} in natural environments and pure cultures vary over several orders of magnitude (Tarpgaard
202 et al., 2011; Pallud & Van Cappellen, 2006), we implement a relatively wide range of K_{MSR} values
203 of 0.002 – 2.0 mM, again assuming a log-uniform prior distribution. Based previous work (Ozaki
204 et al., 2019), it is expected that our results are not particularly sensitive to any plausible expansion
205 of this range. However, given that in this study we are examining a much larger range and higher
206 concentrations of sulfate we have chosen to maintain this parameter as a component of our
207 stochastic analysis.

208

209 The vast majority of P is delivered to the oceans via rivers, making the riverine P flux (R_P) a key
210 control on the size of the marine P reservoir. To account for relatively unconstrained variability in

211 this flux—tied to changes in the composition of weathering crust or the colonization of the
212 continents by land plants, for example—we have varied this flux from 0.2 – 2.0 times the modern
213 value, assuming a uniform normal prior distribution. Our range is similar to that of Ozaki et al.
214 (2019), although we limit our minimum value to 0.2 rather than 0 under the pretense that there
215 should always be some non-trivial riverine reactive P flux once there are significant continental
216 land masses above sea level. We note that this parameter is included separately from the
217 erosion/sedimentation rate (see below) as composition and chemical weathering environments will
218 play an independent (albeit not totally decoupled) role in the release of P from the continents.

219
220 Given the centrality of the marine P reservoir size to biospheric productivity and the chemistry of
221 the ocean interior, we also include a parameter designed to explore uncertainty associated with the
222 primary sink of P—burial in marine sediments. This parameter, which can be thought of
223 mechanistically as a nutrient P scavenging efficiency (σ_{scav}), is a proportionality coefficient
224 between 0 – 1 that dictates the efficiency of P scavenging (removal from the water column) by
225 oxidized and reduced iron species in anoxic settings (Bjerrum and Canfield, 2002; Derry, 2015;
226 Laakso and Schrag 2019; Ozaki et al., 2019; Reinhard et al., 2017). It is important to note that, as
227 shown in Eq. (2), this efficiency coefficient is implemented within a parameterization that
228 describes the dependence of P scavenging on oxygen availability within the water column. That
229 is, regardless of the randomly selected efficiency coefficient, if the water column is well-
230 oxygenated P scavenging will not be operative. The sensitivity of our results to this
231 parameterization is explored below. We explore an inclusive range of this parameter (0-1),
232 assuming a log-uniform prior distribution.

233

234 The sinking velocity of marine organic matter (V_{POM}) is a critical parameter regulating the
235 distribution of O_2 demand and nutrient release through the oceanic water column (e.g., De La
236 Rocha and Passow, 2007; Devol and Hartnett, 2001; Kwon et al., 2009; Meyer et al., 2016). It has
237 also been suggested that this parameter would have changed dramatically over time in step with
238 major changes to the ecological structure of the surface marine biosphere (e.g., Butterfield, 1997;
239 Lenton et al., 2014), although recent work casts doubt on major changes to particle sinking
240 velocities through time (Fakhraee et al., 2020). Nevertheless, we assign the global sinking velocity
241 of particulate organic matter to be between 10-100 m d^{-1} , assuming a uniform normal prior
242 distribution, to quantify the large uncertainty associated with settling rates of organic matter to the
243 deep ocean floor, as well as the idea that sinking velocities during the Proterozoic may have been
244 slower due to the lack of larger eukaryotic cells and limited packaging in zooplankton fecal pellets.
245 Our range is similar to that of Ozaki et al. (2019), although we limit our minimum value to 10 m
246 d^{-1} rather than 0 m d^{-1} .

247
248 We implement a single scaling parameter for continental erosion and marine sedimentation rates
249 (f_{sr}), as these should be closely linked on a global scale when the rock cycle is at steady state. This
250 parameter is normalized to that of the modern Earth (e.g., $f_{sr}^0 = 1.0$). This is a key variable in our
251 model since these rates modify the rate of oxidative weathering of organic carbon and pyrite, as
252 well as the rate of burial of these species in marine sediments. The sediment accumulation rate at
253 the seafloor also affects the burial efficiency of P and organic matter and the O_2 penetration depth
254 in the sediment column. Here, we vary this parameter from 0.5 to 1.5, assuming a uniform normal
255 prior distribution, based on the premise that it is equally reasonable for globally integrated rates of
256 erosion and sediment burial to have been either lower than the modern—particularly during the

257 Precambrian (e.g., Husson and Peters, 2017)—or higher, such as during the Pliocene-Pleistocene
258 (e.g., Herman et al., 2013).

259

260 After the generation of our complete dataset ($n = 20,589$ models), the data were subsampled to
261 produce a suite of results that are also consistent with our basic understanding of the Earth system
262 as derived from the geochemical record. This includes constraints on marine SO_4 concentrations
263 and an upper limit on globally integrated rates of N fixation. Specifically, at atmospheric oxygen
264 levels between 0.01-10% PAL we subsampled the model ensemble such that $0.05 \text{ mM} < [\text{SO}_4] \leq$
265 10.0 mM , while at atmospheric oxygen levels above 10% PAL, we subsampled such that 1.0 mM
266 $< [\text{SO}_4] \leq 60.0 \text{ mM}$. This upper limit reflects the maximum sulfate concentration the model
267 achieved (i.e., no runs were excluded by this limit), however this limit should reflect the existence
268 of an ‘evaporite ceiling’ (e.g., Canfield & Farquhar, 2009) which is poorly constrained in natural
269 systems. These conservative and overlapping ranges were chosen specifically to remove
270 mathematically viable solutions for which there is no evidence in the rock record. In particular,
271 this scheme was designed to remove cases of high atmospheric oxygen and extremely high
272 productivity resulting in extremely low SO_4 and eutrophic oceans. We emphasize that this SO_4
273 constraint was imposed in an effort to remove unrealistic end-member scenarios, and the
274 overlapping ranges were chosen so as not to impose a false apparent bistability in SO_4 . We discuss
275 the impact of this methodology on our primary conclusions below.

276

277 We also subsample our overall model ensemble for cases in which globally integrated rates of N
278 fixation are less than ten times the modern level. Although we consider this cutoff reasonable, and
279 note that our primary results are not particularly sensitive to this assumption (for instance,

280 increasing the cutoff to 15 times modern only increases the size of our final SO₄ filtered dataset by
281 0.4%), it is important to point out that this upper limit is almost completely unconstrained for the
282 Earth system. While P is widely considered the ultimate limiting nutrient on geologic timescales
283 (Tyrell, 1999), the mathematical potential for extremely high N fixation rates indicates that there
284 may be instances where global primary productivity could possibly be N-limited at high
285 atmospheric oxygen levels. This would likely occur via more proximate limitation on the
286 bioavailability of iron which is required as a catalyst in nitrogenase (Falkowski, 1997; Raven,
287 1988). There is also some potential that in a high oxygen, high productivity world trending towards
288 eutrophic oceans, trace element (Mo, V) limitation of N fixation as a result of expanding reducing
289 environments could act as a negative feedback on runaway eutrophication. The potential for N-
290 limited productivity tied to availability of cofactors (Fe, Mo, and in some cases V) for nitrogenase
291 or the loss of fixed N has been explored previously (Falkowski, 1997; Fennel et al., 2006; Reinhard
292 et al., 2013) but not in the context of extremely high rates of productivity well beyond the modern.
293 This represents a promising avenue for future work.

294

295

296 **3 Results**

297 Subsampling of our overall model ensemble yields the primary dataset used in our analysis ($n =$
298 1,672 models). Although the subsampled ensemble is still very large, subsampling results in a
299 significant drop in the overall model ensemble size. Nevertheless, median values of global
300 diagnostics in our subsampled ensemble suggest a stochastic ensemble of sufficient size to attain
301 a stationary distribution (Fig. 2b). We thus expect our subsampled results to be statistically
302 representative.

303
304 At atmospheric oxygen levels from 0.01-1.0% PAL, we find a median export production (flux of
305 photosynthetic carbon from the mixed layer) of 32.20 ± 25.56 (1σ) Tmol C yr⁻¹, and from 1 – 10%
306 PAL median export production 99.96 ± 78.79 Tmol C yr⁻¹ (Fig. 4a). Above 40% PAL median
307 export productivity increases significantly to 651.88 ± 348.14 Tmol C yr⁻¹. The binned median
308 values correspond to approximately 4%, 12%, and 77% of average published values for modern
309 export production ($708 - 1000$ Tmol C yr⁻¹) (Dunne et al., 2007; Laws et al., 2000; Sarmiento &
310 Gruber, 2006; Heinze et al., 2009).

311
312 These same trends for each bin are reflected the in PO₄³⁻ reservoir size which directly controls
313 levels of productivity (Fig. 4b). At atmospheric oxygen levels from 0.01-1.0% PAL, our results
314 yield a median marine PO₄³⁻ reservoir of 0.13 ± 0.09 (1σ) 10^{15} mol, and from $pO_2 = 1 - 10\%$ PAL
315 a median PO₄ reservoir of 0.35 ± 0.25 10^{15} mol. Above 40% PAL the median PO₄³⁻ reservoir
316 increases to 2.14 ± 1.08 10^{15} mol. The binned median values are approximately 4%, 12%, and 71%
317 of published estimates for the PO₄³⁻ reservoir ($\sim 3 \times 10^{15}$ mol; Delaney, 1998; Guidry et al., 2000)
318 (Fig. 4b).

319
320 There is negligible dissolved O₂ within the water column at pO_2 below $\sim 10\%$ PAL (Fig. 5). At
321 abyssal depths we begin to observe appreciable levels of O₂ between 10-20% PAL, with the most
322 dramatic increase above 40% PAL. Nevertheless, our model results do not achieve a mean [O₂]
323 that would be considered fully oxic at abyssal depths until atmospheric oxygen levels are above
324 60% PAL. Correspondingly, below 1% PAL, [PO₄³⁻] is extremely low with a mean of 0.2 μmol,
325 roughly less than 10% of modern values (Fig. 5). Mean deep water phosphate concentrations

326 remain below 1 μmol up to 30% PAL and only approach roughly modern values when atmospheric
327 oxygen levels are above $\sim 60\%$ PAL.

328

329 The benthic flux of organic carbon is about an order of magnitude lower at all water depths while
330 $p\text{O}_2$ levels are below 10% PAL (Fig. 6). At 200 m depth, median benthic C_{org} flux is 0.062 ± 0.088
331 (1σ) $\text{Tmol C m}^{-2} \text{ yr}^{-1}$, and at 4000 m depth median C_{org} flux is $0.005 \pm 0.006 (1 \sigma)$ $\text{Tmol C m}^{-2} \text{ yr}^{-1}$.
332 ¹. Above 10% PAL, the median flux increases substantially; when $p\text{O}_2$ is 10-30% PAL, median
333 benthic C_{org} flux is $0.439 \pm 0.086 (1 \sigma)$ $\text{Tmol C m}^{-2} \text{ yr}^{-1}$ at 200 m depth and $0.025 \pm 0.006 (1 \sigma)$
334 $\text{Tmol C m}^{-2} \text{ yr}^{-1}$ at 4000 m depth. These values are within roughly 1σ of medians when $p\text{O}_2$ is
335 above 70% PAL. At these highest $p\text{O}_2$ levels, median benthic C_{org} flux is $0.944 \pm 0.466 (1 \sigma)$ Tmol
336 $\text{C m}^{-2} \text{ yr}^{-1}$ at 200 m depth and $0.066 \pm 0.031 (1 \sigma)$ $\text{Tmol C m}^{-2} \text{ yr}^{-1}$ at 4000 m depth. We note that
337 these are zonally averaged values and benthic C_{org} flux is very heterogeneous in the modern ocean,
338 however these values are within range of modern data (e.g., Sweetman et al., 2017).

339

340

341

342 **4 Discussion**

343

344 *4.1 Ventilation of the deep ocean*

345 Our model results indicate that until atmospheric oxygen levels increase above $\sim 40\%$ PAL, the
346 deep ocean remains largely oxygen-poor, nutrient depleted, and significantly less productive
347 relative to the modern ocean (Fig. 4, 5). It is important to note that the impacts of oxygen limitation
348 on benthic ecosystems and the expression of this limitation in the geochemical proxy record differ

349 substantially. Specifically, as atmospheric oxygen levels increase and the marine system begins to
350 respond more dramatically, most geochemical proxies will tend to act as an ‘on-off switch’ at the
351 onset of this transition. In contrast, marine fauna—particularly larger, more complex organisms
352 and ecosystems—will likely feel the effects of lower-than-modern atmospheric oxygen
353 concentrations up to a pO_2 of ~60% PAL.

354
355 Below ~10% PAL, deep water $[O_2]$ concentrations are essentially negligible, or would on average
356 be low enough to suppress aerobic respiration and result in geochemical proxy signatures
357 diagnostic of reducing environments—that is, environments characterized by denitrification,
358 reduced iron, or sulfide and traditionally labeled as anoxic to suboxic (Fig. 5). At these low
359 atmospheric oxygen levels, we also find that water column phosphate is strongly limited, with
360 $[PO_4^{3-}]$ concentrations in deep waters similar to or lower than surface waters in the modern ocean
361 (Fig. 5a). We note that the basin-averaged water column chemistry of CANOPS is not equipped
362 to model the possibility of localized and/or temporally variable weakly oxygenated conditions in
363 the ocean interior at relatively low atmospheric pO_2 . Nevertheless, these findings are consistent
364 with the consensus of typical background mid-Proterozoic conditions, at least globally averaged
365 and on long time scales (e.g. Laakso and Schrag, 2019; Ozaki et al., 2019; Partin et al., 2013;
366 Poulton and Canfield, 2011; Reinhard et al., 2017; Reinhard et al., 2013; Scott et al., 2008).

367
368 As atmospheric oxygen levels increase, we observe the onset of a more dramatic response in the
369 marine biogeochemical system. From 10% to ~40% PAL, oxygen availability in globally averaged
370 deep waters remains quite limited, with oxygen concentrations that would conventionally be
371 classified as dysoxic (Cole et al., 2020; Tyson and Pearson, 1991). At these concentrations, there

372 is enough oxygen present in the water column to remove ferrous iron and inhibit anaerobic
373 respiration, but negative impacts on benthic ecology would still be potentially significant. While
374 we see the most dramatic increase in $[O_2]$ above ~40% PAL, oxygen availability is likely to have
375 impacted benthic organisms even up to ~60% PAL (Fig. 5). Within this range of atmospheric
376 oxygen levels, localized conditions such as increased temperature or salinity would not only
377 decrease O_2 solubility, but would also push metabolic rates higher thereby compounding the
378 impacts of oxygen availability (Boag et al., 2018; Cole et al., 2020; Portner, 2012; Reinhard et al.,
379 2016). Similarly, we find $[PO_4^{3-}]$ remains strongly limited up to 40% PAL, and somewhat less so
380 up to 60% PAL (Fig. 5a). This indicates that the potential of significant environmental impacts of
381 ocean redox on the habitability of benthic environments for larger, more complex organisms
382 should be expected below ~60% PAL. We highlight that this is for globally averaged values,
383 suggesting that these effects would impact the majority of the marine environment. In contrast, at
384 atmospheric oxygen levels above 60% PAL, both $[O_2]$ and $[PO_4^{3-}]$ are consistent with the range of
385 concentrations in deep waters of the modern oceans, with enough phosphate is available to support
386 roughly modern levels of primary productivity (Fig. 5). However, non-trivial albeit increasingly
387 localized portions of the marine environment will still likely have oxygen levels low enough to
388 substantially impact the extent of habitable space for larger, more complex organisms. This is true
389 even up to 100% PAL, as is observed with recent deoxygenation and impacts on the world's
390 fisheries (e.g., Pauly and Cheung, 2017; Stortini et al., 2017), although three-dimensional ocean
391 biogeochemistry models with higher spatial resolution are required to explore these effects.

392

393 *4.2 Nutrient availability and productivity dynamics*

394 Our model results suggest global export production is strongly muted at atmospheric oxygen levels
395 below 10% PAL relative to the modern (median value $\sim 7\%$ of modern estimates) in agreement
396 with previous work (Ozaki et al., 2019; Laakso and Schrag 2019) (Fig. 4; Table 2). As atmospheric
397 oxygen levels increase, median productivity remains depressed below $\sim 50\%$ of modern estimates
398 until $pO_2 > 40\%$ PAL. These limited levels of primary productivity can be tied directly to a lack
399 of available nutrients (specifically PO_4^{3-}) in the marine system (Fig. 4). The flux of riverine P
400 delivered to the ocean is included in our stochastic analysis, however this is not the primary control
401 on the marine P reservoir size across four orders of magnitude in atmospheric pO_2 . Instead, marine
402 PO_4^{3-} availability is dictated by the efficacy of removal from the marine system, which in our
403 model is parameterized based on the hypothesis that pervasively reducing and Fe-rich oceans will
404 give rise to a deep sea P trap (e.g., Bjerrum & Canfield, 2002; Laakso & Schrag, 2014; Derry,
405 2015; Reinhard et al., 2017). Our results further highlight the development of a better
406 understanding of the mechanistic links between pO_2 , ocean Fe inventory, and marine P availability
407 as an important topic of future work.

408
409 While it is widely thought that P was the ultimate limiting nutrient for primary productivity
410 globally and on geologic timescales through the mid-Proterozoic (Derry, 2015; Laakso and Schrag,
411 2014, 2017, 2018; Ozaki et al., 2019; Reinhard et al., 2017), there are instances where N or other
412 trace nutrients such as Fe, Mo, or V may play a key role in capping marine productivity. In our
413 model results, we examine the response of the N cycle to increasing pO_2 and find that below 10%
414 PAL median N fixation is $<10\%$ of modern estimates (median of $0.92 \pm 3.5 (1\sigma) \text{ Tmol N yr}^{-1}$),
415 indicating that trace nutrient limitation is unlikely under these conditions, given that denitrification
416 would be limited in a largely reducing ocean. Above 10% PAL, N fixation rates increase most

417 dramatically, reaching within error of modern estimates; from 10-40% PAL, median N fixation is
418 9.24 ± 6.66 (1σ) Tmol N yr⁻¹, or ~95% of modern estimates. As atmospheric oxygen levels increase
419 further, so too do median rates of N fixation. However, for a given level of export productivity,
420 we observe that N fixation rates are highest at moderate levels of pO_2 (~ 10-40% PAL) similar to
421 the relationship observed by Reinhard et al. (2017).

422

423 While the oxygenation of the marine system would lead to a significantly increased supply of
424 dissolved and bioavailable trace nutrients critical for nitrogenase (Mo, V), this would lead to a
425 decrease in dissolved and bioavailable Fe—also a necessary cofactor for nitrogenase (Falkowski,
426 1997; Raven, 1988). We find that some scenarios at higher atmospheric oxygen levels can result
427 in extremely high rates of N fixation (see *Methods*). In these cases, Fe availability could limit the
428 capacity of N fixation which in turn may have played a key role in preventing the Earth system
429 from moving into an extremely high productivity/low O₂ (eutrophic) regime. In the event of
430 substantial water column deoxygenation there is potential for a further stabilizing negative
431 feedback whereby increasing productivity and N fixation could lead to higher demand for trace
432 nutrients while this shift to a eutrophic system would lead to an increased drawdown of necessary
433 trace nutrients Mo and V, though this would likely be more localized. While we only have a
434 qualitative sense of this type of productivity cap tied to nitrogenase-limited N fixation, our results
435 highlight a promising avenue for future work. This work would be aided by implementation of a
436 complete iron cycle in this or similar biogeochemical models (e.g., van de Velde, in review, GMD),
437 as well as incorporation of trace metal cycling, and would have applications for both Earth system
438 evolution and predictions regarding Earth-like exoplanetary productivity regimes.

439

440 *4.3 An evolving biosphere*

441 While oxygen availability is traditionally the focus for thinking about habitability of benthic
442 environments and the evolution and diversification of animals, considering the availability of food
443 is also critically important (Cole et al., 2020; Reinhard et al., 2020; Sperling and Stockey, 2018).
444 At low pO_2 (<10% PAL), we find that the PO_4^{3-} reservoir is limited to ~7% of modern estimates.
445 This extremely nutrient-limited regime—possibly characteristic of much of the mid-Proterozoic—
446 is expected to strongly favor the dominance of small phytoplankton cells, limiting the expansion
447 of eukaryotic ecosystems (Reinhard et al., 2020). In contrast, increased nutrient availability
448 inherently tied to ocean ventilation may have acted as an important ‘bottom up’ driver, providing
449 a strong control on dominant cell size (e.g., cyanobacteria vs. photosynthetic eukaryotes) as well
450 as the extent of the size spectrum, and expansion to higher trophic levels (Armstrong, 1999; Ward
451 et al., 2014; Reinhard et al., 2020). Reinhard et al. (2020) suggested that this transition would
452 require marine nutrient inventories above ~10% of modern [PO_4^{3-}], and in line with this prediction,
453 we observe roughly an order of magnitude increase in median benthic carbon flux between the
454 0.01-10% and 10-40% PAL binned results (Fig. 6). As such, it is likely that algal expansion,
455 increasing micro predation, and increasing heterotrophic complexity—mechanistically linked to
456 the expansion of the nutrient reservoir—can be tied to atmospheric oxygen levels of at least ~10%
457 PAL (Fig. 5). Significantly, at pO_2 of 10% PAL, water column oxygen would have still been
458 vanishingly low in the global average, and yet possibly still higher than estimated requirements of
459 the earliest metazoans (Mills et al., 2014; Sperling et al., 2013). The resolvability of these nutrient-
460 redox dynamics in our results provides further strong support for the notion that ventilation-
461 associated changes to nutrient availability may have been more important for the evolutionary
462 progress of early animals than the oxygenation of the benthic environment itself.

463
464 This expansion of the nutrient reservoir and subsequently of trophic structure and heterotrophic
465 complexity would have been a necessary precursor to the arrival of more complex animals with
466 relatively higher oxygen demands towards the late Neoproterozoic and Cambrian. This is
467 especially relevant as an improved understanding of oxygen requirements for early animals and
468 their communities is emerging (e.g., Boag et al. 2018; Levin 2003; Sperling et al., 2016). As energy
469 fluxes and water column [O₂] continue to increase as pO_2 rises, this dramatic shift may act as a
470 positive feedback to support increasingly large and diverse fauna well into the Paleozoic.

471
472 Even in the modern ocean, the majority of the marine environment and especially the abyss is
473 characterized by substantial food limitation ($< 0.167 \text{ mol C m}^{-2} \text{ y}^{-1}$; Lutz et al., 2007) (Watling et
474 al., 2013). Despite major variation in benthic C_{org} flux across depth, latitude, seasonality, and sea-
475 ice regimes, this is roughly double the median flux retrieved by our model ensemble for 200 m
476 depth when $pO_2 < 10\%$ PAL. Broadly, this suggests that food limitation would have been a major
477 factor in controlling benthic biodiversity throughout the ocean and strongly favored the microbial
478 community (Sweetman et al., 2017). Recent studies have explored the effects of declining POC
479 flux as a result of climate change and suggest that a 3-fold reduction in POC may reduce nematode
480 and benthic microbial biomass by ~50%, macrofaunal biomass by 80%, and lead to major
481 decreases in bioturbation, benthic respiration, and sediment mixed-layer depth (Jones et al., 2014;
482 Laws et al., 2000; Smith et al., 2008). While our results lack spatial resolvability, it is clear that
483 with an increase to higher pO_2 , especially above ~50% PAL, benthic food supply would increase
484 substantially and the area of severely food-limited regions of the ocean would shrink, potentially
485 leading to increased ecological space for non-microbial life.

486

487 **5 Conclusions and Key Findings**

488 Across four orders of magnitude of pO_2 , ranging from levels representative of the Proterozoic Eon
489 to the modern Earth, our analysis identifies viable biogeochemical regimes that are potentially
490 capable of sustaining prescribed atmospheric conditions. We find that the most dramatic
491 transformation of the marine biogeochemical system occurs between 10% and 40% PAL, with the
492 water column not reaching modern-like oxygen and nutrient levels until atmospheric oxygen
493 exceeds 60% PAL. The onset of ocean ventilation also marks a critical increase in energy flux to
494 the benthic environment as export productivity increases in response to a muted Fe-P trap.
495 Heightened food supply across this transition likely helped to drive the expansion of increasingly
496 complex life across the Neoproterozoic and well into the Paleozoic. Our results provide a new
497 quantitative framework for linking insights about marine redox-productivity dynamics gleaned
498 from the rock record with atmospheric composition across an interval that marks one of Earth's
499 most transformative biogeochemical transitions.

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511

512 **Author Contributions**

513 D.B.C. and C.T.R. designed the study. D.B.C adapted the code, performed experiments and
514 analyses, and wrote the manuscript with input from K.O and C.T.R. K.O. designed the original
515 codebase.

516

517 **Samples and Data**

518 Data and code archiving is in compliance with FAIR data guidelines. All relevant data generated
519 for this study and the code used to generate and analyze the data can be found at DOI:
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521
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771 **Figure Captions**

772

773 **Figure 1:** (a) CANOPS model schematic adapted from Ozaki et al. (2019). (b - c) Kernel density
 774 estimate heatmaps of modern ocean observations (blue) and our baseline model simulation results
 775 under modern conditions for low-mid latitude (solid black line) and high latitude (black dashed
 776 line). Data from Olsen et al. (2016); Olsen et al. (2019).

777

778 **Figure 2:** (a-c) Increasingly strict lower bounds for the $[\text{SO}_4^{2-}]$ filtering requirement for the low
 779 $p\text{O}_2$ (0.01 – 10% PAL) group applied to the complete dataset with (a) 0.01-10 mM; (b) 0.025 – 10
 780 mM; and (c) 0.05 – 10 mM. (d-f) Cumulative median values showing convergence for (d) marine
 781 phosphate reservoir size; (e) organic C burial; and (f) export production for our filtered dataset.

782

783 **Figure 3:** Sensitivity of model export productivity to phosphorus scavenging efficiency. Shades
 784 of blue reflect scavenging efficiency as a function of σ_{scav} , while dashed lines show variation in
 785 $[\text{O}_2]_0$ (see eq. 2) over two orders of magnitude.

786

787 **Figure 4:** (a) Export production and (b) marine phosphate reservoir size as a function of
 788 atmospheric oxygen levels. Gray bar denotes range of modern estimates for export production
 789 (Dunne et al., 2007; Laws et al., 2000; Sarmiento and Gruber, 2006; Heinze et al., 2009) and the
 790 marine phosphate reservoir (Delaney, 1998; Guidry et al., 2000).

791

792 **Figure 5:** Globally averaged low-mid latitude water column profiles of a) phosphate and b) oxygen.
 793 All data are binned by atmospheric oxygen levels. (a) Mean $[\text{PO}_4^{3-}]$ at 10% present ocean
 794 levels (POL) corresponds to 10% of the total reservoir averaged across the water column or 0.216
 795 μM . South Pacific surface waters correspond to the approximate range of the upper 500 m at 32 °
 796 S (Kolterman et al., 2011), while South Atlantic deep waters correspond to the approximate range
 797 below 2000 m depth at 45 ° S (Kolterman et al., 2011; WOCE atlas). (b) Redox classifications are
 798 from the traditional classification of Tyson and Pearson (1991), and further elaborated on by Cole
 799 et al. (2020). Anoxic/Suboxic refers to vanishingly low $[\text{O}_2]$, the presence of anaerobic
 800 metabolisms, heterotrophic aerobic bacteria. Dysoxic refers to a lack of anaerobic respiration but
 801 oxygen levels low enough to impact benthic ecology. Oxic is similar to modern surface waters.

802

803 **Figure 6:** Organic carbon flux to the sediment-seawater interface as a function of ocean depth. All
 804 data are binned by atmospheric oxygen levels. (a) depth profiles of benthic C_{org} flux. (b-c) Violin
 805 plots of binned data from 200 m and 4000 m depth.

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Tables

Table 1 – Monte Carlo sampling parameters and ranges

Sampled Parameter	Sampling Range	Unit	Sampling Method
pO_2	0.0001-1	normalized to modern	log uniform
K_{MSR}	0.002-2	mM	log uniform
R_p	0.2-2	normalized to modern	uniform
V_{POM}	10-100	$m\ d^{-1}$	uniform
f_{sr}	0.5-1.5	normalized to modern	uniform
σ_{scav}	0.01-1	-	log uniform

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Table 2 – Global data summary

pO_2 bin (% PAL)	Count	Median PO_4 reservoir (10^{15} mol)	1σ	Median Export Production (Tmol C/yr)	1σ	Median N Fixation (Tmol N yr ⁻¹)	1σ
0.01-1	438	0.126	0.088	32.196	25.555	0.374	0.340
1-10	352	0.348	0.253	99.958	78.792	3.010	4.204
10-40	122	1.201	0.425	357.750	143.170	9.243	6.666
40-100	760	2.138	1.084	651.875	348.142	12.736	13.764

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