

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

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Key Points

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

Abstract

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

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

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

1 Introduction

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

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

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

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

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

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

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

2 Methods

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

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

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

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

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

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

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

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

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

The centerpiece of our overall approach is to run a very large ensemble of model simulations in which multiple key parameters are simultaneously sampled randomly from an assumed prior distribution, with the model subsequently run with atmospheric pO_2 enforced as a constant boundary condition until the S and P cycles reach steady state, although because S residence time is much longer, model run times are determined primarily by S balance. We focus here on six key parameters, chosen for their potential to significantly impact global oxygen and nutrient cycling, and their likely roles in controlling the mechanistic links between atmospheric pO_2 , nutrient biogeochemistry, marine redox, and energy fluxes to marine sediments. In contrast with Ozaki et al. (2019), we do not vary the size of the crustal sulfur reservoirs for simplicity and because reservoir size was not found to have a strong effect on the results. The key control parameters in our analysis along with their constrained ranges and assumed prior distributions are provided in Table 1. The specified ranges and prior distributions are discussed briefly below. Large ensembles were implemented within the Georgia Institute of Technology Partnership for an Advanced Computing Environment (PACE), with downstream data analysis performed using a custom pipeline built in python. All model code, output data, and analytical pipeline can be found at the DOI: 10.5281/zenodo.4716158

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

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

The vast majority of P is delivered to the oceans via rivers, making the riverine P flux (R_P) a key 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.

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

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

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

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

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

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

3 Results

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

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

These same trends for each bin are reflected the in PO₄³⁻ reservoir size which directly controls levels of productivity (Fig. 4b). At atmospheric oxygen levels from 0.01-1.0% PAL, our results yield a median marine PO₄³⁻ reservoir of 0.13 ± 0.09 (1σ) 10¹⁵ mol, and from $pO_2 = 1 - 10\%$ PAL a median PO₄ reservoir of 0.35 ± 0.25 10¹⁵ mol. Above 40% PAL the median PO₄³⁻ reservoir increases to 2.14 ± 1.08 10¹⁵ mol. The binned median values are approximately 4%, 12%, and 71% of published estimates for the PO₄³⁻ reservoir ($\sim 3 \times 10^{15}$ mol; Delaney, 1998; Guidry et al., 2000) (Fig. 4b).

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

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

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

4 Discussion

4.1 Ventilation of the deep ocean

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

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

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

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

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

4.2 Nutrient availability and productivity dynamics

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

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

dramatically, reaching within error of modern estimates; from 10-40% PAL, median N fixation is $9.24 \pm 6.66 (1\sigma) \text{ Tmol N yr}^{-1}$, or ~95% of modern estimates. As atmospheric oxygen levels increase further, so too do median rates of N fixation. However, for a given level of export productivity, we observe that N fixation rates are highest at moderate levels of $p\text{O}_2$ (~ 10-40% PAL) similar to the relationship observed by Reinhard et al. (2017).

While the oxygenation of the marine system would lead to a significantly increased supply of dissolved and bioavailable trace nutrients critical for nitrogenase (Mo, V), this would lead to a decrease in dissolved and bioavailable Fe—also a necessary cofactor for nitrogenase (Falkowski, 1997; Raven, 1988). We find that some scenarios at higher atmospheric oxygen levels can result in extremely high rates of N fixation (see *Methods*). In these cases, Fe availability could limit the capacity of N fixation which in turn may have played a key role in preventing the Earth system from moving into an extremely high productivity/low O_2 (eutrophic) regime. In the event of substantial water column deoxygenation there is potential for a further stabilizing negative feedback whereby increasing productivity and N fixation could lead to higher demand for trace nutrients while this shift to a eutrophic system would lead to an increased drawdown of necessary trace nutrients Mo and V, though this would likely be more localized. While we only have a qualitative sense of this type of productivity cap tied to nitrogenase-limited N fixation, our results highlight a promising avenue for future work. This work would be aided by implementation of a complete iron cycle in this or similar biogeochemical models (e.g., van de Velde, in review, GMD), as well as incorporation of trace metal cycling, and would have applications for both Earth system evolution and predictions regarding Earth-like exoplanetary productivity regimes.

4.3 An evolving biosphere

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

This expansion of the nutrient reservoir and subsequently of trophic structure and heterotrophic complexity would have been a necessary precursor to the arrival of more complex animals with relatively higher oxygen demands towards the late Neoproterozoic and Cambrian. This is especially relevant as an improved understanding of oxygen requirements for early animals and their communities is emerging (e.g., Boag et al. 2018; Levin 2003; Sperling et al., 2016). As energy fluxes and water column $[O_2]$ continue to increase as pO_2 rises, this dramatic shift may act as a positive feedback to support increasingly large and diverse fauna well into the Paleozoic.

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

5 Conclusions and Key Findings

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

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Author Contributions

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

Samples and Data

Data and code archiving is in compliance with FAIR data guidelines. All relevant data generated for this study and the code used to generate and analyze the data can be found at DOI: 10.5281/zenodo.4716158

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Figure Captions

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

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

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

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

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

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

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

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











