# CANOPS-GRB v1.0: a new Earth system model for simulating the evolution of ocean-atmosphere chemistry over geologic timescales

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#### 12 Abstract

A new version of the Earth system model of intermediate complexity — (CANOPS-GRB v1.0)— iwas 13 presented<del>developed</del> for use in quantitatively assessing the dynamics and stability of atmospheric and 14 oceanic chemistry on Earth and Earth-like planets over geologic timescales. The new release is designed to 15 represent the coupled major element cycles of C, N, P, O, and S, as well as the global redox budget (GRB) 16 in Earth's exogenic (ocean-atmosphere-crust) system, using a process-based approach. This framework 17 provides a mechanistic model of the evolution of atmospheric and oceanic O<sub>2</sub> levels on geologic timescales 18 and enables comparison with a wide variety of geological records to further constrain the processes driving 19 Earth's oxygenation. A complete detailed description of the resulting Earth system model and its new 20 features are provided. The performance of CANOPS-GRB is then evaluated by comparing a steady-state 21 simulation under present-day conditions with a comprehensive set of oceanic data and existing global 22 estimates of bio-element cycling. The dynamic response of the model is also examined by varying 23 phosphorus availability in the exogenic system. CANOPS-GRB reliably simulates the short- and long-term 24 evolution of the coupled C-N-P-O<sub>2</sub>-S biogeochemical cycles and is generally applicable across any-most 25 period of Earth's history given suitable modifications to boundary conditions and forcing regime. The 26 simple and adaptable design of the model also makes it useful to interrogate a wide range of problems 27 related to Earth's oxygenation history and Earth-like exoplanets more broadly. The model source code is 28

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- 29 available on GitHub, and represents a unique community tool for investigating the dynamics and stability of
- 30 atmospheric and oceanic chemistry on long timescales.

## 31 Short summary:

32 A new biogeochemical model (CANOPS-GRB v1.0) for assessing the redox stability and dynamics of the 33 ocean-atmosphere system on geologic timescales has been developed. In this paper, we present a full 34 description of the model and its performance. CANOPS-GRB is a useful tool for understanding the factors 35 regulating atmospheric  $O_2$  level and has the potential to greatly refine our current understanding of Earth's 36 oxygenation history.

## 37 1 Introduction-

A quarter century has passed since the first discovery of exoplanets (Mayor and Queloz, 1995). In the next 38 39 quarter century, a full-scale search for signs of life\_\_\_biosignatures\_\_on Earth-like exoplanets is one of the 40 primary objectives of the next generation of exoplanetary observational surveys (National Academies of Sciences and Medicine, 2019; The LUVOIR Team, 2019). The definition of biosignatures includes a variety 41 42 of signatures that require biological activity for their origin (Des Marais et al., 2002; Lovelock, 1965; Sagan et al., 1993; Schwieterman et al., 2018; National Academies of Sciences and Medicine, 2019), but 43 44 atmospheric composition has received the most interdisciplinary attention since the dawn of the search for 45 life beyond our own planet (Hitchcock and Lovelock, 1967; Lovelock, 1965, 1972, 1975; Sagan et al., 1993) because of its potential for remote detectability. Indeed, it is likely that deciphering of exoplanetary 46 47 atmospheric composition based on spectroscopic information will, at least for the foreseeable future, be our only promising means for life detection beyond our solar system. However, the detection of atmospheric 48 49 composition cannot immediately answer the question of the presence or absence of a surface biosphere 50 because significant gaps remain in our understanding of the relationships between atmospheric composition and biological activity occurring at the surface on life-bearing exoplanets. Many of these gaps arise from a 51 52 lack of robust theoretical and quantitative frameworks for the emergence and maintenance of remotely detectable atmospheric biosignatures in the context of planetary biogeochemistry. 53

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55 It is also important to emphasize that the abundance of atmospheric biosignature gases of living planets will 56 evolve via an intimate interaction between life and global biogeochemical cycles of bio-essential elements 57 across a range of timescales. Indeed, the abundances of biosignature gases such as molecular oxygen (O<sub>2</sub>) **書式変更:** タブ位置: 36.9 字, 左揃え+ 39.32 字(なし)

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and methane (CH<sub>4</sub>) in Earth's atmosphere have evolved dramatically through coevolutionary interaction with Earth's biosphere for nearly 4 billion years\_—\_through remarkable fluctuations in atmospheric chemistry and climate (Catling and Kasting, 2017; Lyons et al., 2014; Catling and Zahnle, 2020). To the extent that the coupled evolution of life and the atmosphere is a universal property of life-bearing planets that maintain robust atmospheric biosignatures, the construction of a biogeochemical framework for diagnosing atmospheric biosignatures should be a subject of urgent interdisciplinary interest.

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Establishing a mechanistic understanding of our own planet's evolutionary history is also an important 65 milestone for the construction of a search strategy for life beyond our solar system, as it provides the first 66 step towards understanding how remotely detectable biosignatures emerge and are maintained on a planetary 67 scale. While numerous atmospheric biosignature gases have been proposed, the most promising candidates 68 have been 'redox-based' species, such as  $O_2$ , ozone ( $O_3$ ), and CH<sub>4</sub> (Meadows, 2017; Meadows et al., 2018; 69 Reinhard et al., 2017a; Krissansen-Totton et al., 2018). In particular, O<sub>2</sub> is of great interest to astrobiologists 70 71 because of its crucial role in metabolism on Earth. Thus, a considerable effort has been devoted over recent 72 decades toward quantitatively and mechanistically understanding Earth's oxygenation history. In particular, a recent surge in the generation of empirical records for Earth's redox evolution has yielded substantial 73 progress in our 'broad stroke' understanding of Earth's oxygenation history and has shaped our view of 74 biological evolution (Kump, 2008; Lyons et al., 2014). One of the intriguing insights obtained from the 75 accumulated geochemical records is that atmospheric O<sub>2</sub> levels might have evolved more dynamically than 76 previously thought — our current paradigm of Earth's oxygenation history suggests that atmospheric  $O_2$ 77 levels may have risen and then plummeted during the early Proterozoic, then remained low (probably <10%) 78 of the present atmospheric level; PAL) for much of the  $\sim 1$  billion years leading up to the catastrophic 79 climate system perturbations and the initial diversification of complex life during the late Proterozoic. 80

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The possibility of low but 'post-biotic' atmospheric  $O_2$  levels during the mid-Proterozoic has important ramifications not only for our basic theoretical understanding of long-term  $O_2$  cycle stability on a planet with biological  $O_2$  production, but also for biosignature detectability (Reinhard et al., 2017a). However, our quantitative and mechanistic understanding of the Earth's  $O_2$  cycle in deep time is still rudimentary at

present. For example, one possible explanation for low atmospheric O<sub>2</sub> levels during the mid-Proterozoic is 86 simply a less active or smaller biosphere (Crockford et al., 2018; Derry, 2015; Laakso and Schrag, 2014; 87 Ozaki et al., 2019a). However, mechanisms for regulating biotic O<sub>2</sub> generation rates and stabilizing 88 atmospheric  $O_2$  levels at low levels on billion-year timescales remain obscure. As a result, the level of 89 atmospheric O<sub>2</sub> and its stability during the early-mid Proterozoic are the subject of vigorous debate 90 (Bellefroid et al., 2018; Canfield et al., 2018; Cole et al., 2016; Planavsky et al., 2018; Planavsky et al., 91 2016; Tang et al., 2016; Zhang et al., 2016). Perhaps even more importantly, a relatively rudimentary 92 quantitative framework for probing the dynamics and stability of the oxygen cycle leads to the imprecision 93 of geochemical reconstructions of ocean-atmosphere O<sub>2</sub> levels. 94

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Planetary atmospheric  $O_2$  levels are governed by a kinetic balance between sources and sinks. Feedback 96 97 arises because the response of source/sink fluxes to changes in atmospheric  $O_2$  levels is intimately interrelated to each other. Since the biogeochemical cycles of C, N, P, and S exert fundamental control on 98 99 the redox budget through non-linear interactions and feedback mechanisms, a mechanistic understanding of these biogeochemical cycles is critical for understanding Earth's O<sub>2</sub> cycle. However, the wide range of 100 timescales that characterize C, N, P, O<sub>2</sub> and S cycling through the reservoirs of the Earth system makes it 101 difficult to fully resolve the mechanisms governing the dynamics and stability of atmospheric O<sub>2</sub> levels from 102 geologic records. From this vantage, developing new quantitative tools that can explore biogeochemical 103 cycles under conditions very different from those of the present Earth is an important pursuit. 104

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This study is motivated by the conviction that an ensemble of 'open' Earth system modeling frameworks 106 with explicit and flexible representation of the coupled C-N-P-O<sub>2</sub>-S biogeochemical cycles will ultimately 107 be required to fully understand the dynamics and stability of Earth's O<sub>2</sub> cycle and its controlling factors. In 108 particular, a coherent mechanistic framework for understanding the global redox (O<sub>2</sub>) budget (GRB) is 109 critical for filling remaining gaps in our understanding of Earth's oxygenation history and the cause-and-110 effect relationships with an evolving biosphere. Here, we develop a new Earth system model, named 111 CANOPS-GRB, which implements the coupled biogeochemical cycles of C-N-P-O<sub>2</sub>-S within the Earth's 112 surface system (ocean-atmosphere-crust). The core of this model is an ocean biogeochemical model, 113

CANOPS (Ozaki et al., 2011; Ozaki and Tajika, 2013; Ozaki et al., 2019a) (Ozaki, 2011, Conditions 114 required for oceanic anoxia/euxinia: Constraints from a one dimensional ocean biogeochemical cycle 15 model;Ozaki, 2013, Biogeochemical effects of atmospheric oxygen concentration', phosphorus weathering', 16 and sea level stand on oceanic redox chemistry: Implications for greenhouse climates;Ozaki, 2019, A 17 sluggish mid Proterozoic biosphere and its effect on Earth's redox balance]. This model has been used to 18 examine conditions for the development of widespread oceanic anoxia/euxinia during the Phanerozoic 119 120 (Ozaki et al., 2011; Ozaki and Tajika, 2013; Kashiyama et al., 2011) and to quantitatively constrain 121 biogeochemical cycles during the Precambrian (Cole et al., 2022; Ozaki et al., 2019a; Ozaki et al., 2019b; Reinhard et al., 2017b). In this study, we extend this model to simulate the biogeochemical dynamics of the 122 coupled ocean-atmosphere-crust system. The model design (such as the complexity of the processes and 123 spatial-temporal resolution of the model) is constrained by the requirement of simulation length (>100 124 million years) and actual model run-time. A lack of understanding of biogeochemistry in deep-time and 125 availability and quality of geologic records also limit the model structure. With this in mind, we aim for a 126 comprehensive, simple, yet realistic representation of biogeochemical processes in the Earth system, 127 yielding a unique tool for investigating coupled biogeochemical cycles within the Earth system over a wide 128 range of time scales. We have placed particular emphasis on the development of a global redox budget in the 129 ocean-atmosphere-crust system given its importance in the secular evolution of atmospheric  $O_2$  levels. 130 CANOPS-GRB is an initial step towards developing the first large-scale biogeochemistry evolution model 131 suited for the wide range of redox conditions, including explicit consideration of the coupled C-N-P-O<sub>2</sub>-S 132 cycles and the major biogenic gases in planetary atmospheres (O<sub>2</sub> and CH<sub>4</sub>). 133

## 134 2 Model description

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Here we present a full description of a new version of the Earth system model CANOPS\_—\_CANOPS-GRB v1.0 —\_which is designed to facilitate simulation for a wide range of biogeochemical conditions so as to permit quantitative examination of evolving ocean-atmosphere chemistry throughout Earth's history. Below we first describe the concept of model design (Sect. 2.1). Next, we describe the overall structure of the model and the basic design of global biogeochemical cycles (Sect. 2.2 and 2.3). That is followed by a detailed description of each sub-model.

## 141 2.1 CANOPS-GRB in the hierarchy of biogeochemical models

A full understanding of Earth's evolving  $O_2$  cycle requires a quantitative framework that includes 142 mechanistic links between biological metabolism, ocean-atmosphere chemistry, and geologic processes. 143 Such a framework must also represent the feedbacks between ocean-atmosphere redox state and 144 biogeochemical cycles of redox-dependent bio-essential elements. Over recent decades, considerable 145 progress has been made in quantifying the feedbacks between atmospheric O<sub>2</sub> levels and the coupled C-N-P-146 O2-S biogeochemical cycles over geological timescales (Berner, 2004a; Lasaga and Ohmoto, 2002; Betts 147 and Holland, 1991; Holland, 1978; Bolton et al., 2006; Slomp and Van Cappellen, 2007; Van Cappellen and 148 Ingall, 1994; Colman et al., 2000; Belcher and Mcelwain, 2008). Refinements to our understanding of 149 mechanisms regulating Earth's surface redox state have been implemented in low-resolution box models 150 where the ocean-atmosphere system is expressed by a few boxes (Bergman et al., 2004; Laakso and Schrag, 151 2014; Lenton and Watson, 2000b, a; Van Cappellen and Ingall, 1996; Handoh and Lenton, 2003; Petsch and 152 Berner, 1998; Claire et al., 2006; Goldblatt et al., 2006; Alcott et al., 2019). These models offer insights into 153 basic system behavior and can illuminate the fundamental mechanisms that exert the most leverage on 154 biogeochemical cycles because of their simplicity, transparency and low computational demands. However, 155 these model architectures also have important quantitative limitations. For example, with low spatial 156 resolution the modeler needs to assume reasonable (but a priori) relationships relating to internal 157 biogeochemical cycles in the system. For instance, because of a lack of high vertical resolution, oceanic box 158 models (Knox and Mcelroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984) usually 159 overestimate the sensitivity of atmospheric CO<sub>2</sub> levels to biological activity at high-latitude surface ocean 160

relative to projections by general circulation models (Archer et al., 2000). Oceanic biogeochemical cycles and chemical distributions are also characterized by strong vertical and horizontal heterogeneities, which have the potential to affect the strength of feedback processes (Ozaki et al., 2011). In other words, the lowresolution box modeling approach might overlook the strength and response of the internal feedback loops. Thus, the development of an ocean model with high resolution of ocean interior and reliable representation of water circulation is <u>preferredrequired</u> to investigate the mechanisms controlling atmospheric O<sub>2</sub> levels under conditions very different from those of the modern Earth.

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In the last decade, comprehensive Earth system models of intermediate complexity (EMICs) have also been 169 developed and extended to include ocean sediments and global C cycling (Ridgwell and Hargreaves, 2007; 170 Lord et al., 2016). Such models can be integrated over tens of thousands of years, allowing experimentation 171 172 with hypothetical dynamics of global biogeochemical cycles in the geological past (Reinhard et al., 2020; Olson et al., 2016). However, a key weakness of existing EMICs is the need to parameterize (or ignore) 173 174 boundary (input/output) fluxes\_-\_\_either due to the computational expense of explicitly specifying boundary 175 conditions or due to poorly constrained parameterizations. For example, the oceanic P cycle is usually treated as a closed system, limiting the model's applicability to timescales less than the oceanic P residence 176 time (~15–20 kvr). Further, boundary conditions such as continental configuration and oceanic bathymetry 177 are variable or poorly constrained in deep time and the use of highly complex models is difficult to justify 178 the computational cost. Finally, exploration of hypotheses concerning the biogeochemical dynamics in deep 179 time often require large model ensembles across broad parameter space given the scope of uncertainty. This 180 makes the computational cost of EMICs intractable at present for many key questions. 181

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The CANOPS-GRB model is designed to capture the major components of Earth system biogeochemistry on timescales longer than <u>a millennium~10<sup>3</sup> years</u>, but is simple enough to allow for runs on the order of <u>a</u> billion10<sup>9</sup> model years. The model structure is also designed so that the model captures the essential biogeochemical processes regulating the global O<sub>2</sub> budget, while keeping the calculation cost as moderate as possible. For example, the simple relationships of biogeochemical transport processes at the interface of <u>the</u> Earth system (hydrogen escape to space, early diagenesis in marine sediments, and weathering) are

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employed based on the systematic application of 1-D models -in previous studies (Bolton et al., 2006; 189 Daines et al., 2017; Middelburg et al., 1997; Claire et al., 2006; Wallmann, 2003a), providing a powerful, 190 computationally efficient means for exploring the Earth system under a wide range of conditions. The 191 resultant CANOPS-GRB model can be run on a standard personal computer on a single CPU with an 192 efficiency of approximately 6 million model years per CPU hour. In other words, model runs in excess of 193  $10^9$  model years are tractable with modest wall times (approximately 7 days). The model is thus not as 194 efficient as simple box models, but is highly efficient relative to EMICs, making sensitivity experiments and 195 exploration of larger parameter space over a billion years feasible, particularly with implementation on a 196 high-performance computing cluster (see (Cole et al., 2022)Cole et al., accepted). CANOPS-GRB thus 197 occupies a unique position within the hierarchy of global biogeochemical cycle models, rendering it a useful 198 tool for the development of more comprehensive, low- to intermediate-complexity models of Earth system 199 200 on very long timescales.

## 201 2.2 Overall model structure

The overall structure of the model is shown in Fig. 1. The model consists of ocean, atmosphere and 202 sedimentary reservoirs. The core of the model is an ocean model, comprising a high-resolution 1-D 203 intermediate-complexity box model of the global ocean (Sect. 2.4). The ocean model is coupled to a 204 parameterized marine sediment module (Sect. 2.4.4) and a one box model of the atmosphere (Sect. 2.6). The 205 atmospheric model includes O2 and CH4 as chemical components, and abundances of these molecules are 206 calculated based on the mass balance between sources and sinks (e.g., biogenic fluxes of O2 and CH4 from 207 the ecosystems and photochemical reactions). The net air-sea gas exchange of chemical species (O<sub>2</sub>, H<sub>2</sub>S, 208 NH<sub>3</sub> and CH<sub>4</sub>) is quantified according to the stagnant film model (Liss and Slater, 1974; Kharecha et al., 209 2005) (Sect. 2.4.5). The ocean and atmosphere models are embedded in a 'rock cycle' model that simulates 210 the evolution of sedimentary reservoir sizes on geologic timescales (Sect. 2.5). Three sedimentary reservoirs 211 (organic carbon, ORG; pyrite sulfur, PYR; and gypsum sulfur, GYP) are considered in the CANOPS-GRB 212 model. These reservoirs interact with the ocean-atmosphere system through weathering, outgassing, and 213 burial. 214



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217 Figure 1<sub>a</sub> CANOPS-GRB model configuration. (a) The schematic of material cycles in the surface (ocean-218 atmosphere-crust) system. Three sedimentary reservoirs, organic carbon (ORG), pyrite sulfur (PYR), and gypsum sulfur (GYP), are considered. Sedimentary reservoirs interact with the ocean-atmosphere system via 219 weathering, volcanic degassing, and burial. No interaction with the mantle is included, except for the input 220 221 of reduced gases from the mantle. Total mass of sulfur is conserved in the surface system. (b) Schematic of ocean and atmosphere modules. "L" and "H" denote the low-mid latitude mixed surface layer and high-222 latitude surface layer, respectively. An ocean area of 10% is assumed for H. River flux for each region is 223 proportional to the areal fraction. Ocean interior is divided into two sectors, high-latitude deep water (HD) 224 and low-mid latitude deep water (LD), which are vertically resolved. The area of HD is 25% of the whole 225 ocean. The deep overturning circulation,  $\dot{V}$ , equals the poleward flow in the model surface layer (from L to 226 H).  $K_v^{\rm l}(z)$  and  $K_v^{\rm h}(z)$  are the vertical eddy diffusion coefficients in the LD and HD regions, respectively.  $K_{\rm hor}$ 227 and  $V_{\rm h}$  are the horizontal diffusion coefficient and polar convection, respectively. The black hatch represents 228 229 the seafloor topography assumed. The parameters regarding geometry and water transport are tabulated in 230 Table 3.

The ocean model is a vertically resolved transport-reaction model of the global ocean, which was originally developed by Ozaki et al. (2011) and Ozaki and Tajika (2013). The model consists of 122 boxes across two regions\_\_\_\_\_\_; a low-mid latitude region and a high-latitude region (Fig. 1b). The ocean model describes water transport processes as exchange fluxes between boxes and via eddy diffusion terms. More specifically, ocean circulation is modelled as an advection-diffusion model of the global ocean\_\_\_\_a general and robust scheme that is capable of producing well-resolved modern profiles of circulation tracers using realistic parameter values (the physical set up of the model can be found in Sect. 2.4.1 and 2.4.2). The

239	biogeochemical sub-model provides a mechanistic description of the marine biogeochemical cycles of C, P,
240	N, O <sub>2</sub> , and S (Sect. 2.4.3). This includes explicit representation of a variety of biogeochemical processes
241	such as biological productivity in the sunlit surface oceans, a series of respiration pathways and secondary
242	redox reactions under oxic and anoxic conditions (Sect. 2.4.3), and deposition, decomposition, and burial of
243	biogenic materials in marine sediments (Sect. 2.4.4), allowing a mechanistically based examination of
244	biogeochemical processes. The suite of metabolic reactions included in the model is listed in Table 1. Ocean
245	biogeochemical tracers considered in the CANOPS-GRB model are phosphate (PO4 <sup>3-</sup> ), nitrate (NO3 <sup>-</sup> ), total
246	ammonia ( $\Sigma NH_3$ ), dissolved oxygen (O <sub>2</sub> ), sulfate (SO <sub>4</sub> <sup>2-</sup> ), total sulfide ( $\Sigma H_2S$ ), and methane (CH <sub>4</sub> ). <u>Note that</u>
247	biogeochemical cycling of trace metals (e.g., Fe and Mn) is not included in the current version of the model.
248	All H <sub>2</sub> S and NH <sub>3</sub> degassing from the ocean to the atmosphere is assumed to be completely oxidized by O <sub>2</sub> to
249	$SO_4^{2-}$ and $NO_3^{-}$ and returns to the ocean surface. These simplifications limit application of the model to very
250	poorly oxygenated Earth system states ( $pO_2 < 10^{-5}$ PAL). Ocean model performance was tested for the
251	modern-day ocean field observational data (Sect. 3). Simulation results were also compared to previously
252	published integrated global flux estimates.

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254	Table 1: Biogeochemical reactions	considered in the CANOPS-GRB model
201	ruble 1. Biogeoenenneur reactions	considered in the ern (of b) of the model

Process	Stoichiometry*	Reaction #
Ammonia assimilation	$\alpha \text{CO}_2 + \beta \text{NH}_4^+ + \text{H}_3\text{PO}_4 + \alpha \text{H}_2\text{O} \rightarrow \text{OM} + \alpha \text{O}_2$	R1
Nitrate assimilation	$\alpha \mathrm{CO}_2 + \beta \mathrm{NO}_3^{'} + \mathrm{H_3PO_4} + (\alpha + \beta) \mathrm{H_2O} + 2\beta \mathrm{H^+} \rightarrow \mathrm{OM} + \left(\alpha + 2\beta\right) \mathrm{O_2}$	R2
Nitrogen fixation	$N_2 + 5H_2O \rightarrow 2NH_4^+ + 2OH^- + \frac{3}{2}O_2$	R3
Aerobic respiration	$\mathrm{OM} + \alpha \mathrm{O}_2 \rightarrow \alpha \mathrm{CO}_2 + \beta \mathrm{NH}_4^+ + \mathrm{H}_3 \mathrm{PO}_4 + \alpha \mathrm{H}_2 \mathrm{O}$	R4
Denitrification	$OM + \frac{4}{5}\alpha NO_3^{\circ} + \frac{4}{5}\alpha H^+ \rightarrow \alpha CO_2 + \beta NH_4^{\circ} + H_3PO_4 + \frac{7}{5}\alpha H_2O + \frac{2}{5}\alpha N_2$	R5
Sulfate reduction	$\mathrm{OM} + \frac{1}{2} \alpha \mathrm{SO}_4^{2*} + \alpha \mathrm{H}^+ \rightarrow \alpha \mathrm{CO}_2 + \beta \mathrm{NH}_4^* + \mathrm{H_3PO}_4 + \alpha \mathrm{H_2O} + \frac{1}{2} \alpha \mathrm{H_2S}$	R6
Methanogenesis	$\mathrm{OM} \rightarrow \frac{1}{2} \alpha \mathrm{CO}_2 + \frac{1}{2} \alpha \mathrm{CH}_4 + \beta \mathrm{NH}_4^* + \mathrm{H}_3 \mathrm{PO}_4$	R7
Nitrification	$\mathrm{NH}_4^+ + \mathrm{2O}_2 \rightarrow \mathrm{NO}_3^- + \mathrm{H}_2\mathrm{O} + \mathrm{2H}^+$	R8
Aerobic H <sub>2</sub> S oxidation <sup>†</sup>	$\Sigma H_2 S + 2O_2 \rightarrow SO_4^{2\cdot} + 2H^+$	R9

Aerobic CH <sub>4</sub> oxidation	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	R10
Anaerobic CH4 oxidation	$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O$	R11
Photooxidation of CH4	$\rm CH_4 + 2O_2 \rightarrow \rm CO_2 + 2H_2O$	R12
Hydrogen escape to space	$\mathrm{CH}_4 + \mathrm{O}_2 \rightarrow \mathrm{CO}_2 + 4\mathrm{H} \uparrow$	R13

255 \*OM denotes organic matter,  $(CH_2O)_{\alpha}(NH_4^+)_{\beta}H_3PO_4$ 

 $256 \quad ^{\dagger}\Sigma H_2 S = H_2 S + H S^{-1}$ 

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258	The CANOPS model has been extended and altered a number of times since first publication. The
259	description of biogeochemical cycles in the original version of CANOPS (Ozaki and Tajika, 2013; Ozaki et
260	al., 2011) does not include the S and CH <sub>4</sub> cycles because of their aims to investigate the conditions for the
261	development of oceanic anoxia/euxinia on timescales less than a million years during the Phanerozoic. More
262	recently, Ozaki et al. (2019) implemented an open system modeling approach for the global S and CH <sub>4</sub>
263	cycles, enabling quantitative analysis of global redox budget for given atmospheric O2 levels and crustal
264	reservoir sizes. In this version of CANOPS atmospheric O2 levels and sedimentary reservoirs are treated as
265	boundary conditions because imposing them simplifies the model and significantly reduces computing time.
266	However, this approach does not allow exploration of the dynamic behavior of atmospheric O <sub>2</sub> in response
267	to other boundary conditions. In the newest version presented here, significant improvements in the
268	representation of global biogeochemistry were achieved by (1) an explicit calculation of atmospheric $O_2$
269	levels based on atmospheric mass balance (Sect. 2.6), (2) expansion of the model framework to include
270	secular evolution of sedimentary reservoirs (Sect. 2.5.5), and (3) simplification of the global redox budget
271	between the surface (ocean-atmosphere-crust) system and the mantle (Sect. 2.3.5). These improvements are
272	in line with the requirement of an 'open' Earth system model, which is necessary for a systematic,
273	quantitative understanding of Earth's oxygenation history.
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recently, Ozaki et al. (2019) implemented an open system modeling approach for the global S and CH4 279 cycles, enabling quantitative analysis of global redox budget for given atmospheric O2 levels and crustal 280 reservoir sizes. In this version of CANOPS atmospheric O2 levels and sedimentary reservoirs are treated as 281 boundary conditions because imposing them simplifies the model and significantly reduces computing time. 282 283 However, this approach does not allow exploration of the dynamic behavior of atmospheric O<sub>2</sub> in response to other boundary conditions. In the newest version presented here, significant improvements in the 284 285 representation of global biogeochemistry were achieved by (1) an explicit calculation of atmospheric O<sub>2</sub> levels based on atmospheric mass balance (Sect. 2.6), (2) expansion of the model framework to include 286 secular evolution of sedimentary reservoirs (Sect. 2.5.5), and (3) simplification of the global redox budget 287 between the surface (ocean atmosphere crust) system and the mantle (Sect. 2.3.5). These improvements are 288 in line with the requirement of an 'open' Earth system model, which is necessary for a systematic, 289 quantitative understanding of Earth's oxygenation history. 290

## 291 2.3 Global biogeochemical cycles

We construct a comprehensive biogeochemical model in order to investigate the interaction between dynamic behaviors of Earth's oxygenation history and its biogeochemical processes, as well as redox structure of the ocean. Here we provide the basic implementation of global biogeochemical cycles of C, P, N, and S, with particular emphasis on processes of mass exchange between reservoirs that play a critical role in global redox budget (Fig. 2). Our central aim here is to <u>make\_describe\_</u>the overall design of <u>the</u> biogeochemical cycles-<u>clear</u>. The details of each sub-model are provided in the following sections.









Figure 2. Schematics of global biogeochemical cycling in CANOPS-GRBes. (a) Global C cycle. The 300 primary source of C for the ocean-atmosphere system is volcanic degassing and oxidative weathering of 301 302 sedimentary organic carbon, whereas primary sink is burial of marine and terrigenous organic matter into sediments. Inorganic carbon reservoirs (depicted as dashed boxes) and DOC are not considered. NPP<sub>ocn</sub> = 303 marine net primary production. DIC = dissolved inorganic carbon. POC = particulate organic carbon. MSR 304 = microbial sulfate reduction. AOM = anoxygenic\_anaerobic oxidation of methane. CANOPS-GRB includes 305 CH<sub>4</sub> generation via methanogenesis and its oxidation reactions via methanotrophy and AOM in the ocean 306 interior, as well as CH<sub>4</sub> degassing flux to the atmosphere and its photooxidation. The rates of CH<sub>4</sub> 307 photooxidation and hydrogen escape to space are calculated based on parameterizations proposed by 308 309 previous studies (Goldblatt et al., 2006; Claire et al., 2006). Note that CH<sub>4</sub> flux from land biosphere is not 310 shown here. (b) Global P cycle schematic. Weathering of reactive P ( $P_{reac}$ ) is the ultimate source, whereas burial in sediments is the primary sink. A part of the weathered P is buried as terrigenous organic P, and the 311 remaining is delivered to the ocean. The redox-dependent P burial in marine sediments is modelled by 312 313 considering three phases (organic P, Fe-boundsorbed P, and authigenic P). DIP = dissolved inorganic phosphorus. POP = particulate organic phosphorus. The hypothetical P scavenging via Fe-species in anoxic-314 ferruginous waters is depicted, but it is not modelled in our standard model configuration. (c) Global N cycle 315 316 schematic. The abundance of Two-inorganic nitrogen species (ammonium and nitrate), which are lumped 317 into DIN (dissolved inorganic nitrogen), is affected byare transformed each other via denitrification and 318 nitrification. The primary source is nitrogen fixation and riverine flux, whereas primary sink is denitrification and burial in marine sediments. PON = particulate organic nitrogen. The nitrogen 319 320 weathering/riverine flux is assumed to be equal to the burial flux so that there is no mass imbalance in global N budget. Aeolian delivery of N from continent to the ocean is not included. (d) Global S cycle schematic. 321 322 The reservoir sizes of wo sedimentary reservoirs sulfur (pyrite sulfur, PYR, and gypsum sulfur, GYP) and two sulfur species (SO<sub>4</sub><sup>2-</sup> and  $\Sigma$ H<sub>2</sub>S) in the ocean are transformed each other are controlled by-via volcanic 323 outgassing, weathering, burial, MSR, AOM, and sulfide oxidation reactions. Weathering and volcanic inputs 324 are the primary source of S to the ocean, and burial of pyrite and gypsum in marine sediments is the primary 325 326 sink. It is assumed that hydrogen sulfide escaping from the ocean to the atmosphere is completely oxidized 327 and returns to the ocean as sulfate. The organic sulfur cycle is ignored in this study.

## 328 2.3.1 Carbon cycle

The CANOPS-GRB model includes particulate organic carbon (POC), atmospheric CH<sub>4</sub>, dissolved CH<sub>4</sub> in the ocean, and sedimentary organic carbon (ORG) as carbon reservoirs (Fig. 2a). Atmospheric CO<sub>2</sub>, dissolved inorganic carbon (DIC), and dissolved organic carbon (DOC) are not explicitly modelled in the current version of the model. <u>Although we ignore the inorganic carbon cycle here for clarity and in order to</u> simplify interpretation of model results, the full coupling of the inorganic carbon cycle within CANOPS-GRB is an important topic for future work. The primary sources of carbon for the ocean-atmosphere system

- 335 are volcanic degassing and oxidative weathering of sedimentary organic carbon, while the primary sink is
- 336 burial of marine and terrigenous organic matter in sediments.

## 337 Organic carbon cycle

The biogeochemical model is driven by the cycling of the primary nutrient phosphorus, which is assumed to be the ultimate limiting factor for biological productivity (see Sect. 2.4.3). Previous versions of CANOPS do not take into account the impact of the activity of terrestrial ecosystem on the global  $O_2$  budget. In the CANOPS-GRB model, we improve on this by evaluating the activity levels of terrestrial and marine ecosystems separately: The global net primary production (NPP),  $J_{NPP}$  (in terms of organic C), is given as a sum of the oceanic ( $J_{NPP}^{ocn}$ ) and terrestrial ( $J_{NPP}^{Ind}$ ) NPP:

$$J_{\rm NPP} = J_{\rm NPP}^{\rm ocn} + J_{\rm NPP}^{\rm ind} \tag{1}$$

Biological production in the ocean surface layer depends on P availability while nutrient assimilation efficiency is assumed to be lower in the high latitude region (Sect. 2.4.3). Terrestrial NPP is affected by the atmospheric  $O_2$  level (Sect. 2.5.1). In this study, the flux (in terms of moles per year) is expressed with a capital *J*, whereas the flux density (in terms of moles per square meter per year) is expressed with a lowercase *j*.

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In our standard model configuration, oceanic primary production follows canonical Redfield stoichiometry 350 (C:N:P = 106:16:1) (Redfield et al., 1963). Flexible C:N:P stoichiometry of particulate organic matter 351 352 (POM) can be explored by changing a user-flag. Nutrients (P and N) are removed from seawater in the photic zone via biological uptake, and exported as POM to deeper aphotic layers. The exported POM sinks 353 through the water column with a speed of  $v_{POM}$  (the reference value is 100 m d<sup>-1</sup>). As it settles through the 354 water column, POM is subject to decomposition via a series of respiration pathways dependent on the redox 355 state of proximal seawater (Sect. 2.4.3). This gives rise to the release of dissolved constituent species back 356 into seawater. Within each layer a fraction of POM is also intercepted by a sediment layer at the bottom of 357 each water depth. Fractional coverage of every ocean layer by seafloor is calculated based on the prescribed 358 359 bathymetry (Sect. 2.4.1). Settling POM reaching the seafloor undergoes diagenetic alteration (releasing additional dissolved species into seawater) and/or permanent burial. The ocean model has 2×60 sediment 360 segments (HD and LD have 60 layers, respectively), and for each segment the rates of organic matter 361 decomposition and burial are calculated by semi-empirical relationships extracted from ocean sediment data 362

and 1-D modelling of early diagenesis (Sect. 2.4.4). Specifically, the organic C ( $C_{org}$ ) burial at each water depth is calculated based on the burial efficiency ( $BE_{org}$ ), which is defined as the fraction of POC buried in sediments relative to that deposited on the seafloor at each water depth and is also a function of sedimentation rate and bottom water O<sub>2</sub> levels. Organic matter not buried is subject to decomposition.

The key biogeochemical fluxes of our reference state (mimicking the present condition) are summarized in 368 Table 2. The reference value for burial rate of terrigenous  $C_{org}$  is set at 3 Tmol C yr<sup>-1</sup>, assuming that burial of 369 terrigenous organic matter accounts for ~20% of the total burial. Combined with the burial rate of marine 370 Corg in our standard run, the total burial rate is 14.3 Tmol C yr<sup>-1</sup>, representing the dominant O<sub>2</sub> source flux to 371 the modern ocean-atmosphere system. At steady-state, this is balanced by oxidative weathering and volcanic 372 outgassing of sedimentary Core: The reference value of oxidative weathering of organic matter is determined 373 as 13.0 Tmol C yr<sup>-1</sup> based on the global O<sub>2</sub> budget (Sect. 2.3.5). Previous versions of CANOPS (Ozaki et al., 374 2019a) treat sedimentary reservoirs as a boundary condition. This model limitation is removed in the 375 CANOPS-GRB model\_\_\_the reservoir size of sedimentary Corg (ORG) freely evolves based on the mass 376 balance through burial, weathering, and volcanic outgassing (Sect. 2.5.5). We adopted an oft-quoted value of 377 1250 Emol (E =  $10^{18}$ ) for our reference value of the ORG, based on literature survey (Berner, 1989; Garrels 378 and Lerman, 1981). 379

 $\frac{\textbf{Table 2}}{2} \text{ Key biogeochemical fluxes obtained from the reference run. * denotes the reference value. Tmol = 10^{12} \text{ mol.}$ \_

Fluxes	Label	Value	Comments
Carbon cycle (Tmol C yr <sup>-1</sup> )			
Marine NPP	$J_{\rm NPP}^{\rm ocn,*}$	3794	Simulated (Eq. 24)
Terrestrial NPP	$J_{\mathrm{NPP}}^{\mathrm{Ind},*}$	5000	Prescribed (Prentice et al., 2001)
Marine organic C burial	$J_{\mathrm{org}}^{\mathrm{b,ocn},*}$	11.28	Simulated (Eq. 40)
Terrestrial organic C burial	$J_{\rm org}{}^{\rm b,lnd,*}$	3.0	Prescribed (This study)
Oxidative organic C weathering	$J_{\mathrm{org}}{}^{\mathrm{w},*}$	13.03	Tuned (Eq. 15)
Organic C degassing	$J_{\mathrm{org}}{}^{\mathrm{m},*}$	1.25	Prescribed (Bergman et al., 2004)
Phosphorus cycle (Tmol P yr <sup>-1</sup> )			
Reactive P weathering	$J_{\mathrm{P}}{}^{\mathrm{w},*}$	0.158	Eqs. (4) and, (84)
Terrestrial organic P burial	$J_{\mathrm{P}}^{\mathrm{b,lnd,*}}$	0.003	Eq. (85)
Riverine reactive P flux	$J_{\mathrm{P}}{}^{\mathrm{r},*}$	0.155	Tuned (This study)
Marine organic P burial	$J_{\mathrm{Porg}}{}^{\mathrm{b},*}$	0.0438	Simulated (Eq. 51)
Fe-boundsorbed P burial	$J_{\mathrm{PFe}}{}^{\mathrm{b},*}$	0.0323	Simulated (Eq. 53)
Ca-bound P burial	$J_{\mathrm{PCa}}{}^{\mathrm{b},*}$	0.0788	Simulated (Eq. 54)
Nitrogen cycle (Tg N yr <sup>-1</sup> )			
Nitrogen fixation	${J_{ m Nfix}}^*$	180.5	Simulated
Denitrification in the water column	$J_{ m deni}{}^{ m wc,*}$	102.5	Simulated
Benthic denitfirification	$J_{ m deni}{}^{ m sed,*}$	62.4	Simulated (Eq. 55)
Marine organic N burial	$J_{ m Norg}{}^{ m b,*}$	15.8	Simulated (Eq. 56)
Organic N weathering	$J_{ m Norg}{}^{ m w,*}$	15.8	$= J_{ m Norg}{}^{ m b,*}$
Sulfur cycle (Tmol S yr <sup>-1</sup> )			
Pyrite weathering	$J_{ m pyr}{}^{ m w,*}$	1.0	Prescribed (This study)
Gypsum weathering	$J_{\mathrm{gyp}}{}^{\mathrm{w},*}$	1.6	Prescribed (This study)
Pyrite degassing	$J_{\mathrm{pyr}}{}^{\mathrm{m,*}}$	0.3	Prescribed (This study)
Gypsum degassing	$J_{\mathrm{gyp}}{}^{\mathrm{m},*}$	0.5	Prescribed (This study)
Pyrite burial	$J_{ m pyr}{}^{ m b,*}$	1.3	Simulated
Gypsum burial	$J_{\mathrm{gyp}}{}^{\mathrm{b},*}$	2.1	Prescribed (This study)

書式を変更: フォント:太字

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## 384 Methane cycle

The ocean model includes biogenic CH<sub>4</sub> generation via methanogenesis and its oxidation reactions via 385 methanotrophy and anoxygenie-anaerobic oxidation of methane (AOM) in the ocean interior (R10 and R11 386 in Table 1), as well as a CH<sub>4</sub> degassing flux to the atmosphere. The land model also calculates the biogenic 387 CH<sub>4</sub> flux from the terrestrial ecosystem to the atmosphere using a transfer function (Sect. 2.5.2). The 388 abundance of CH<sub>4</sub> in the atmosphere is explicitly modelled as a balance of its source (degassing from marine 389 and terrestrial ecosystems) and sink (photooxidation and hydrogen escape), where CH<sub>4</sub> sink fluxes are 390 391 calculated according to parameterized  $O_2$  dependent functions proposed by previous studies. More specifically, the oxidation rate of  $CH_4$  in the upper atmosphere is calculated based on the empirical 392 parameterization obtained from a 1-D photochemistry model (Claire et al., 2006). The rate of hydrogen 393 escape to space is evaluated with the assumption that it is diffusion limited and that CH<sub>4</sub> is a major H-394 containing chemical compound carrying hydrogen to the upper atmosphere (Goldblatt et al., 2006). No 395 continental abiotic or thermogenic CH4 fluxes are taken into account, because previous estimates of the 396 modern fluxes are negligible relative to the biogenic flux, although we realize that it could have played a 397 role in the global redox budget (<0.3 Tmol yr<sup>-1</sup>; (Fiebig et al., 2009)). We also note that the current version 398 of the model does not include the possibility of aerobic CH<sub>4</sub> production in the sea (Karl et al., 2008). Our 399 reference run calculates atmospheric CH<sub>4</sub> to be 0.16 ppmv (Sect. 3.3), slightly lower than that of the 400 preindustrial level of 0.7 ppmv (Raynaud et al., 1993; Etheridge et al., 1998), but we consider this to be 401 within reasonable error given unknowns in the CH<sub>4</sub> cycle. 402

#### 403 2.3.2 Phosphorus cycle

Phosphorus is an essential element for all life on Earth and it is regarded as the 'ultimate' bio-limiting nutrient for primary productivity on geologic time scales (Tyrrell, 1999). Thus, the P cycle plays a prominent role in regulating global  $O_2$  levels. In the CANOPS-GRB model, we model the reactive (i.e., bioavailable) P (P<sub>reac</sub>) cycling in the system and ignore non-bioavailable P. Specifically, dissolved inorganic P (DIP) and particulate organic P (POP) are explicitly modelled (Fig. 2b), whereas dissolved organic P (DOP) is ignored.

411 On geologic timescales, the primary source of P to the ocean-atmosphere system is continental weathering: a 412 pPhosphorus is released through the dissolution of apatite which exists as a trace mineral in silicate and 413 carbonate rocks (~0.1wt%; (Föllmi, 1996)). The total  $P_{reac}$  flux via weathering,  $J_P^w$ , is given as follows:

$$J_{\rm P}^{\rm w} = f_{\rm P} f_{\rm R} J_{\rm P}^{\rm w,*} \tag{2}$$

where \* denotes the reference value, and  $f_P$  and  $f_R$  are parameters that control the availability of P in the system. Specifically,  $f_R$  is a global erosion factor representing the impact of tectonic activity on total terrestrial weathering rate, and  $f_P$  represents the availability of P<sub>reac</sub>, which is used in a sensitivity experiment to assess the response of atmospheric O<sub>2</sub> levels to changing P<sub>reac</sub> availability (Sect. 4.1). A fraction of the weathering flux  $J_P^w$  is removed via burial on land, while the remainder is transported to the ocean (Sect. 2.5.2):

$$J_{\rm P}^{\rm b, \rm Ind} = k_{11} V J_{\rm P}^{\rm w} \tag{3}$$

$$J_{\rm P}^{\rm r} = (1 - k_{11}V)J_{\rm P}^{\rm w} \tag{4}$$

where  $J_P^{b,lnd}$  and  $J_P^r$  denote the burial rate of terrigenous organic P and riverine P<sub>reac</sub> flux to the ocean, 420 respectively, k<sub>11</sub> is a reference value for the fraction of the total P flux removed by the terrestrial biosphere, 421 and V denotes the vegetation mass normalized to the modern value. These treatments are based on the Earth 422 system box model COPSE (Bergman et al., 2004; Lenton et al., 2016; Lenton et al., 2018; Lenton and 423 Watson, 2000b) which has been extensively tested and validated against geologic records during the 424 425 Phanerozoic. In the CANOPS-GRB model,  $J_P^r$  is tuned so that modelled oceanic P inventory of the reference state is consistent with modern observations of the global ocean (Sect. 3.2.4). Our resulting tuned value is 426 0.155 Tmol P yr<sup>-1</sup> falling in the mid-range of published estimates of 0.11–0.33 Tmol P yr<sup>-1</sup>, although 427 428 previous estimates of the riverine Preac flux show large uncertainty (Sect. 3.2.4).

429

<sup>30</sup> Note that our representation of P weathering ignores the effect of climate (Eq. 2). In the current version of

<sup>431</sup> the model the rate of P weathering is treated as one of the model forcings. Although ignoring the climate

<sup>432</sup> feedback on P mobility makes interpretation of the model results more straightforward, the incorporation of

<sup>433 &</sup>lt;u>a climate-sensitive crustal P cycle is an important avenue for future work.</u>

Since atmospheric P inputs are equivalent to less than 10% of the continental P supply to the modern oceans and much of this flux is not bioavailable (Graham and Duce, 1979), we neglect the aeolian flux in this study. Therefore, riverine input is the primary source of  $P_{reac}$  to the ocean. We highlight that open-system modelling is crucial for realistic simulations of ocean biogeochemistry on timescales longer than the residence time of P in the ocean (15–20 kyr for the modern ocean) (Hotinski et al., 2000), and in this framework the riverine input of  $P_{reac}$  must be balanced over the long-term by loss to sediments via burial. The change in total marine  $P_{reac}$  inventory,  $M_P$ , is given as follows:

$$\frac{dM_{\rm P}}{dt} = J_{\rm P}^{\rm r} - J_{\rm P}^{\rm b,cm} , \qquad (5)$$

where  $J_P^{b,ocn}$  denotes the total burial flux of  $P_{reac}$  in the marine system which is the sum of the burial fluxes d43 of three reactive phases, i.e. organic P ( $P_{org}$ ), Fe-<u>boundsorbed</u> P ( $P_{-Fe}$ ), and Ca-bound P ( $P_{-Ca}$ ) (Sect. 2.4.4):

$$J_{\rm P}^{\rm b,cen} = J_{\rm Porg}^{\rm b} + J_{\rm P-Fe}^{\rm b} + J_{\rm P-Ca}^{\rm b}$$
(6)

O2-dependent P burial is taken into account using empirical relationships from previous studies (Slomp and 444 Van Cappellen, 2007; Van Cappellen and Ingall, 1996, 1994). The burial of Porg at each water depth is a 445 function of burial efficiency, which is controlled by the burial efficiency of organic matter, C/P 446 447 stoichiometry of POM, sedimentation rate and bottom water  $[O_2]$ . We note that the strength of anoxia-448 induced P recycling in marine sediments is very poorly constrained, especially in the Precambrian oceans (Reinhard et al., 2017b). Recent studies also suggest that the P retention potential in marine sediments could 449 be affected not only by bottom water  $O_2$  levels but by redox states (sulfidic vs. ferruginous) and and the Ca<sup>2+</sup> 450 451 concentration of bottom waters, as well as various environmental conditions such as temperature, and pH (Zhao et al., 2020; Algeo and Ingall, 2007; Papadomanolaki et al. 2022). These are fruitful topics for future 452 453 research.

454

We do not explicitly account for P removal via hydrothermal processes, because it is estimated that this contribution is secondary in the modern marine P cycle (0.014–0.036 Tmol P yr<sup>-1</sup>; (Wheat et al., 1996; Wheat et al., 2003)). We note, however, that the hydrothermal contribution to the total P budget in the geologic past remains poorly constrained. We also note that in anoxic, ferruginous oceans, P scavenging by Fe-minerals could also play an important role in controlling P availability and the overall budget (Reinhard

et al., 2017b; Derry, 2015; Laakso and Schrag, 2014). Modern observations (Dellwig et al., 2010; 460 Turnewitsch and Pohl, 2010; Shaffer, 1986) and modeling efforts (Yakushev et al., 2007) of the redoxcline 461 in the Baltic Sea and the Black Sea suggest an intimate relationship between Mn, Fe, and P cycling. 462 Trapping efficiencies of DIP by settling authigenic Fe and Mn-rich particles were found to be as high as 463 0.63 (the trapping efficiency is defined as the downward flux of P in Mn-, and Fe-oxides divided by the 464 upward flux of DIP) (Turnewitsch and Pohl, 2010). Although coupled Mn-Fe-P dynamics might have been a 465 key aspect of the biogeochemical dynamics in the Precambrian oceans, we exclude this process in our 466 standard model due to poor constraints and provide a clear and simplified picture of basic model behavior. 467 The key features between the P availability and atmospheric O<sub>2</sub> levels are explored by changing  $f_P$  in this 468 study (Sect. 4). 469

#### 470 2.3.3 Nitrogen cycle

In the CANOPS-GRB model, two dissolved inorganic nitrogen (DIN) species (total ammonium  $\Sigma NH_4^+$  and nitrate NO<sub>3</sub><sup>-</sup>) and particulate organic nitrogen (PON) are explicitly calculated (Fig. 2c). Atmospheric nitrogen gas is assumed to never limit biospheric carbon fixation, and is not explicitly calculated. Dissolved organic N (DON) and terrestrial N cycling (e.g., N fixation by terrestrial ecosystems and riverineterrigenious organic N transfer) are ignored.

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In the surface ocean N assimilation via nitrate and ammonium depends on the availability of these compounds. If the N required for sustaining a given level of biological productivity is not available, the additional N required is assumed to be provided by atmospheric N<sub>2</sub> via nitrogen fixers. The ocean model explicitly calculates denitrification and nitrification reactions in the water column and marine sediments (R5 and R8 in Table 1). The benthic denitrification rate is estimated using a semi-empirical parameterized function obtained from a 1-D early diagenetic model (see Sect. 2.4.4), while nitrification is modelled as a single step reaction (R8). N<sub>2</sub>O and its related reactions, such as anammox, are not currently included.

484

The oceanic N cycle is open to external inputs of nitrogen. While the ultimate source of N to the oceanatmosphere system is weathering of organic N, nitrogen fixation represents the major input flux to the ocean with the capacity to compensate for N loss due to denitrification. The time evolution of DIN inventory,  $M_N$ , in the ocean can be written as follows:

$$\frac{dM_{\rm N}}{dt} = \left(J_{\rm Nfix} - J_{\rm deni}^{\rm wc} - J_{\rm deni}^{\rm sed}\right) + \left(J_{\rm Norg}^{\rm w} - J_{\rm Norg}^{\rm b}\right),\tag{7}$$

where  $J_{\rm Nfix}$  denotes the N fixation rate, and  $J_{\rm deni}^{\rm wc}$  and  $J_{\rm deni}^{\rm sed}$  are denitrification rates in the water column 489 and sediments, respectively. The first set of terms on the right-hand side represent the internal N cycle in the 490 ocean-atmosphere system, while the second set of terms represent the long-term N budget which interacts 491 with sedimentary reservoir. Ultimately, loss of fixed N from the ocean-atmosphere system only occurs via 492 burial of organic N (Norg) in sediments, J<sub>Norg</sub><sup>b</sup>. This loss is compensated for by continental weathering, J<sub>Norg</sub><sup>w</sup>, 493 which is assumed to be equal to the burial rate of Norg so that the N cycle has no impact on the global redox 494 budget. In the current version of the model, we ignore aeolian flux and all riverine N fluxes other than 495 weathering since these are minor relative to N fixation (Wang et al., 2019). As a result, modelled N fixation 496 required for oceanic N balance can be regarded as an upper estimate. 497

## 498 2.3.4 Sulfur cycle

The original CANOPS ocean model (Ozaki and Tajika, 2013; Ozaki et al., 2011) treated two sulfur species, 499  $SO_4^{2-}$  and  $\Sigma H_2S$ , in a closed system: Neither inputs to the ocean from rivers, hydrothermal vents, and 500 submarine volcanoes, nor outputs due to evaporite formation and sedimentary pyrite burial were simulated. 501 This simplification can be justified when the timescale of interest is less than the residence time of the S 502 cycle (~10-20 Myr). The recently-revised CANOPS model (Ozaki et al., 2019a) extends the framework by 503 504 incorporating the S budget in the ocean. In their model framework, the sedimentary S reservoirs are treated as boundary conditions: The size of sedimentary gypsum and pyrite reservoirs are prescribed and no explicit 505 calculations of mass balance are performed. In CANOPS-GRB, we removed this model limitation and the 506 sedimentary reservoirs are explicitly evaluated based on mass balance which is controlled by burial, 507 outgassing and weathering (see Sect. 2.4). Specifically, seawater  $SO_4^2$ ,  $\Sigma H_2S$ , and sedimentary sulfur 508 reservoirs of pyrite sulfur (PYR) and gypsum sulfur (GYP) are explicitly evaluated in the current version of 509 the model. No atmospheric sulfur species are calculated-all H<sub>2</sub>S degassing from the ocean to the 510

atmosphere is assumed to be oxidized to sulfate and return to the ocean. The organic sulfur cycle is not considered in this study.

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Sulfur enters the ocean mainly from river runoff,  $J_{\rm S}^{\rm r}$ , with minor contributions from volcanic outgassing of 514 sedimentary pyrite,  $J_{pyr}^{m}$  and gypsum,  $J_{gyp}^{m}$ . The reference value for the riverine flux is set at 2.6 Tmol S yr<sup>-1</sup>, 515 consistent with the published estimate of 2.6±0.6 Tmol S yr<sup>-1</sup> (Raiswell and Canfield, 2012). The riverine 516 flux is written as the sum of gypsum weathering and oxidative weathering of pyrite:  $J_{\rm S}^{\rm r} = J_{\rm gyp}^{\rm w} + J_{\rm pyr}^{\rm w}$ . 517 Sulfur weathering fluxes are also assumed to be proportional to the sedimentary reservoir size. Estimates of 518 modern volcanic input fall within the range of 0.3-3 Tmol S yr<sup>-1</sup> (Catling and Kasting, 2017; Kagoshima et 519 al., 2015; Raiswell and Canfield, 2012; Walker and Brimblecombe, 1985). We adopted a value of 0.8 Tmol 520 S yr<sup>-1</sup> for this flux (Kagoshima et al., 2015). Our total input of 3.4 Tmol S yr<sup>-1</sup> is also within the range of the 521 previous estimate of 3.3±0.7 Tmol S yr<sup>-1</sup> (Raiswell and Canfield, 2012). Sulfur is removed from the ocean 522 either via pyrite burial,  $J_{pyr}^{b}$ , or gypsum deposition,  $J_{gyp}^{b}$  (Fig. 2d). The time evolution of the inventory of 523 total S in the ocean can thus be written, as follows: 524

$$\frac{d\left(M_{\rm SO_4} + M_{\rm H_2S}\right)}{dt} = \left(J_{\rm S}^{\rm r} + J_{\rm pyr}^{\rm m} + J_{\rm gyp}^{\rm m}\right) - \left(J_{\rm pyr}^{\rm b} + J_{\rm gyp}^{\rm b}\right),\tag{8}$$

where  $M_{SO4}$  and  $M_{H2S}$  denote the inventory of sulfate and hydrogen sulfide in the ocean, respectively. Two sulfur species (SO<sub>4</sub><sup>2-</sup> and  $\Sigma$ H<sub>2</sub>S) are transformed via microbial sulfate reduction (MSR) (R6), AOM (R11), and aerobic sulfide oxidation reactions (R9). The above equation thus can be divided into following equations:

$$\frac{dM_{\rm SO_4}}{dt} = J_{\rm S}^{\rm r} + J_{\rm pyr}^{\rm m} + J_{\rm gyp}^{\rm m} + J_{\rm H_2S}^{\rm ox} - J_{\rm MSR\&AOM} - J_{\rm gyp}^{\rm b},$$
(9)

$$\frac{dM_{\rm H_2S}}{dt} = -J_{\rm H_2S}^{\rm ox} + J_{\rm MSR\&AOM} - J_{\rm pyr}^{\rm b},\tag{10}$$

where  $J_{\text{H2S}}^{\text{ox}}$  denotes the oxidation of hydrogen sulfide and  $J_{\text{MSR&AOM}}$  is sulfate reduction via MSR and AOM. Pyrite burial is represented as the sum of pyrite precipitation in the water column and sediments:  $J_{\text{pyr}}^{\text{b}}$  $= J_{\text{pyr}}^{\text{b,wc}} + J_{\text{pyr}}^{\text{b,sed}}$ , where the pyrite burial rate in marine sediments is assumed to be proportional to the rate of benthic sulfide production. The proportional coefficient, pyrite burial efficiency ( $e_{\text{pyr}}$ ), is one of the tunable constants of the model: For normal (oxic) marine sediments  $e_{pyr}$  is tuned such that the seawater SO4<sup>2-</sup> concentration for our reference run is consistent with modern observations (Sect. 2.4.3). Pyrite precipitation in the water column is assumed to be proportional to the concentration of  $\Sigma$ H<sub>2</sub>S.

536

Although the present-day marine S budget is likely out of balance because of a lack of major gypsum 537 formation, the S cycle can be considered to operate at steady state on timescales longer than the residence 538 time of sulfur in the ocean. According to S isotope mass balance calculations, ~10-45% of the removal flux 539 540 is accounted for by pyrite burial, and the remainder is removed via formation of gypsum/anhydrite in the 541 near-modern oceans (Tostevin et al., 2014). Although gypsum deposition would have been strongly influenced by tectonic activity (Halevy et al., 2012), we assume that the rate of gypsum deposition on 542 geologic time scales is proportional to the ion product of  $Ca^{2+}$  and  $SO_4^{2-}$  (Berner, 2004b) in the low- to mid-543 latitude surface layer (L), and is defined as follows: 544

$$J_{gyp}^{b} = \left(\frac{[Ca^{2+}]_{l}[SO_{4}^{2-}]_{l}}{[Ca^{2+}]^{*}[SO_{4}^{2-}]^{*}}\right) J_{gyp}^{b,*} = f_{Ca}\left(\frac{[SO_{4}^{2-}]_{l}}{[SO_{4}^{2-}]^{*}}\right) J_{gyp}^{b,*}$$
(11)

where *l* denotes the low- to mid-latitude surface layer and  $f_{Ca}$  is a parameter that represents the seawater Ca<sup>2+</sup> concentration normalized by the present value ( $f_{Ca} = 1$  for the reference run). The reference value of gypsum burial  $J_{gyp}^{b,*}$  is determined by assuming that gypsum deposition accounts for ~60% of the total S removal from the near-modern ocean.

## 549 2.3.5 Global redox budget

In the previous version of the CANOPS model (Ozaki et al., 2019a), the atmospheric  $O_2$  level was prescribed as a boundary condition, rather than modeled in order to limit computational demands. In this study, we remove this model limitation by introducing an explicit mass balance calculation of atmospheric  $O_2$  (Sect. 2.6.3). This improvement allows us to explore the dynamic response of  $O_2$  levels in the oceanatmosphere system (Sect. 4).



## 555

**Figure 3**<sub>2</sub> Schematics of global redox (O<sub>2</sub>) budget. Arrows represent the O<sub>2</sub> flux. The primary source is burial of organic carbon and pyrite sulfur in sediments and hydrogen escape to space. The primary sink is volcanic outgassing and weathering of crustal organic matter and pyrite. PYR = sedimentary reservoir of pyrite sulfur. ORG = sedimentary reservoir of organic carbon. CANOPS-GRB tracks the global redox (O<sub>2</sub>) budget for each simulation.

The newly released CANOPS-GRB v1.0 is designed to be a part of a comprehensive global redox budget 562 (GRB) framework (Fig. 3) (Catling and Kasting, 2017; Ozaki and Reinhard, 2021). Here GRB is defined for 563 the combined ocean-atmosphere system. In this study we track GRB in terms of  $O_2$  equivalents. The 564 ultimate source of  $O_2$  is the activity of oxygenic photosynthesis (and subsequent burial of reduced species, 565 such as organic matter and pyrite sulfur, in sediments), whereas the primary sink of  $O_2$  is the oxidative 566 weathering of organic carbon and pyrite which are assumed to be O2-dependent (Sect. 2.5.3). On timescales 567 longer than the residence time of  $O_2$  in the ocean-atmosphere system,  $O_2$  source fluxes should be balanced 568 569 by sink fluxes. Specifically, the  $O_2$  budget in the coupled ocean-atmosphere system can be expressed as 570 follows:

$$GRB = \left(J_{\text{org}}^{\text{b,cen}} + J_{\text{org}}^{\text{b,lnd}} - J_{\text{org}}^{\text{w}} - J_{\text{org}}^{\text{m}}\right) + 2\left(J_{\text{pyr}}^{\text{b}} - J_{\text{pyr}}^{\text{w}} - J_{\text{pyr}}^{\text{m}}\right) + \left(J_{\text{Hesc}} - J_{\text{man}}\right),$$
(12)

where the first and second set of terms on the right-hand side represent the redox balance via organic carbon and pyrite sulfur subcycles, respectively.  $J_{\text{Hesc}}$  in the third term denotes hydrogen escape to space, representing the irreversible oxidation of the system. For well-oxygenated atmospheres this process plays a minor role in the redox budget, but for less oxygenated atmospheres with high levels of CH<sub>4</sub> this flux could

lead to redox imbalance. In this study we include the input of reducing power (e.g., H<sub>2</sub> and CO) from the 575 Earth's interior to the surface,  $J_{\text{man}}$ , which is assumed to be equal to the value of  $J_{\text{Hesc}}$  ( $J_{\text{man}} = J_{\text{Hesc}}$ ) to avoid 576 redox imbalance in the exogenic system. In reality, mantle degassing and the rate of hydrogen escape are not 577 necessarily equal, resulting in redox imbalance that may exert a fundamental control on atmospheric redox 578 chemistry on geologic timescales (Hayes and Waldbauer, 2006; Ozaki and Reinhard, 2021; Canfield, 2004; 579 Eguchi et al., 2020), however to maintain simplicity we have left this as a topic for future work. As a result, 580 the terms on the right-hand side must be balanced at steady state. Our model can meet this criterion. Note 581 that the effects of the Fe cycle on the  $O_2$  budget (e.g., the oxidative weathering of Fe(II)-bearing minerals; 582 (Ozaki et al., 2019a)) are not eurrently-included in the core version of the CANOPS-GRB v1.0 code and in 583 the analyses presented here for the sake of simplicity. 584

585

2

586 The CANOPS-GRB model also tracks the  $O_2$  budgets for the atmosphere (<u>ARB</u>) and ocean (<u>ORB</u>) 587 independently, and these can be evaluated by the following relationships:

$$ARB = \Phi_{\rm ex}^{\rm air-sea} + \left(J_{\rm org}^{\rm b,lnd} - J_{\rm org}^{\rm w} - J_{\rm org}^{\rm m}\right) - 2\left(J_{\rm pyr}^{\rm w} + J_{\rm pyr}^{\rm m}\right) + \left(J_{\rm Hesc} - J_{\rm man}\right),$$
(13)

$$ORB = -\Phi_{\rm ex}^{\rm air-sea} + J_{\rm org}^{\rm b,ocn} + 2J_{\rm pyr}^{\rm b}, \tag{14}$$

where *ARB* and *ORB* denote the redox budget in the atmosphere and ocean, respectively,  $\Phi_{ex}^{air-sea}$  represents the net exchange of oxidizing power between the ocean and atmosphere via gas exchange (O<sub>2</sub> with minor contributions of NH<sub>3</sub>, H<sub>2</sub>S and CH<sub>4</sub>). These separate redox budgets are also tracked in order to validate global budget calculations.

592

For our reference condition, we obtain the reference value for the oxidative weathering rate of  $C_{org} (J_{org}^{w,*})$ using the redox budget via  $C_{org}$  subcycle:

$$J_{\rm org}^{\rm w,*} = J_{\rm org}^{\rm b, ccn,*} + J_{\rm org}^{\rm b, Ind,*} - J_{\rm org}^{\rm m,*}.$$
(15)

Given flux values based on the calculated  $(J_{\text{org}}^{\text{b,ccn},*} = 11.28 \text{ Tmol C yr}^{-1})$  and prescribed  $(J_{\text{org}}^{\text{b,lnd},*} = 3 \text{ Tmol})$ 596 C yr<sup>-1</sup>,  $J_{\text{org}}^{\text{m},*} = 1.25 \text{ Tmol C yr}^{-1})$  values on the right-hand side,  $J_{\text{org}}^{\text{w},*}$  is estimated as 13.03 Tmol C yr<sup>-1</sup> 597 (Table 2). **書式を変更:** フォント: 斜体 **書式を変更:** フォント: 斜体

## 598 2.4 Ocean model

Here we undertake a thorough review, reconsideration and revision (where warranted), of all aspects of the
ocean model, including bringing together developments of the model <u>followingsince</u> the original papers
<u>describing the CANOPS ocean model framework</u> (Ozaki and Tajika, 2013; Ozaki et al., 2011).

602

The ocean model includes exchange of chemical species with external systems via several processes such as air-sea exchange, riverine input, and sediment burial. The biogeochemical model also includes a series of biogeochemical processes, such as the ocean biological pump and redox reactions under oxic-anoxic-sulfidic conditions. Our ocean model is convenient for investigating Earth system changes on timescales of hundreds of years or longer and it can be relatively easily integrated, rendering the model unique in terms of biogeochemical cycle models. CANOPS is also well suited for sensitivity studies and can be used to obtain useful information upstream of more complex models.

610

Development of the ocean model included two initial goals: The first goal is First, to adopt a general and 611 robust ocean circulation scheme capable of producing well-resolved modern distributions of circulation 612 tracers, using realistic ventilation rates with a limited number of free parameters. The model<sup>2</sup> outputs for 613 circulation tracers are validated by comparison with modern observations (see Sect. 3). This confirms that 614 615 our ocean circulation scheme is adequate for representing the global patterns of water mass transport. AThe second key goal wais to couple the circulation model with an ocean biogeochemical model, and to evaluate 616 performance by comparison with modern ocean biogeochemical data (see Sect. 3.2). Examination of the 617 distributions and globally-integrated fluxes of C, N, P, S, and O<sub>2</sub> for the modern ocean reveals that the ocean 618 model can capture the fundamentals of marine biogeochemical cycling. 619

## 620 2.4.1 Structure

CANOPS ocean model is a 1-D (vertically resolved) intermediate complexity box model of ocean
biogeochemistry (see Fig. 1b for the schematic structure) originally developed by (Ozaki and Tajika, 2013;
Ozaki et al., 2011). Our model structure is an improved version of the HILDA model (Joos et al., 1991;
Shaffer and Sarmiento, 1995). Unlike simple one-dimensional global ocean models (e.g., (Southam et al.,

1982)), the HILDA-type model includes explicit high-latitude dynamics whereby the high-latitude surface 625 layer exchanges properties with the deep ocean. This treatment is crucial for simulating preformed 626 properties and observed chemical distributions, especially for phosphate and dissolved O<sub>2</sub> in a self-627 consistent manner. Unlike simple box-type global ocean models, the model has high vertical resolution. This 628 is needed for representing proper biogeochemical processes which show strong depth dependency. 629 Furthermore, HILDA type models (Arndt et al., 2011; Shaffer et al., 2008), unlike multi-box-type global 630 ocean models (Hotinski et al., 2000), use a small number of free parameters to represent ocean physics and 631 biology. The simple and adaptable structure of the model should make it applicable to a wide range of 632 paleoceanographic problems. The ocean model t couples a diffusion-advection model of the global ocean 633 surface and interior with a biogeochemical model (Sect. 2.4.3) and a parameterized sediment model (Sect. 634 2.4.4). 635

636

The ocean surface consists of a mixed layer at low-mid latitude (L) and high-latitude (H). Below the surface 637 layers, we adopt the present-day averaged seafloor topography of (Millero, 2006), with the h-(Hypsometric 638 639 profile is shown in Fig. 4a). Below the surface water layers, the ocean interior comprises two regions: the 640 high-mid latitude region (HD) and low-mid latitude region (LD). Each region is subdivided vertically, with high resolution ( $\Delta z = 100$  m). Each of the 60 ocean layers in each latitude region (120 total) is assigned 641 ocean sediment properties. The cross-sectional area, volume, and sediment surface area of each box is 642 calculated from the benthic hypsometry. Inclusion of the bathymetry allows evaluation of the flux of 643 biogenic materials which settle on, and are buried in, seafloor sediments at each water depth (Sect. 2.3.3 and 644 2.3.4). 645



**Figure 4**. Ocean bathymetry and water transport. (**a**) Seafloor topography (cumulative seafloor area) (Millero, 2006) adopted in the CANOS-GRB model. (**b**) Lateral water advection from HD to LD section assumed in the standard run (in Sv). Total advection rate  $\dot{V}$  was set at 20 Sv. (**c**) Upwelling rate in the LD region (in m yr<sup>-1</sup>) of the standard run.

## 652 2.4.2 Transport

The ocean circulation model represents a general and robust scheme that is capable of producing wellresolved modern profiles of circulation tracers using realistic parameter values, and the coupled biogeochemical model (Sect. 2.4.3) and the parameterized sediment model (Sect. 2.4.4).

656

657 The time-space evolution of model variables in the ocean is described by a system of horizontally integrated 658 vertical diffusion equations for non-conservative substances. The tracer conservation equation establishes the relationship between change of tracer concentration at a given grid point and the processes that can 659 660 change that concentration. These processes include water transport by advection and mixing, as well as<del>nd</del> sources and sinks due to biological and chemical transformations. The temporal and spatial evolution of the 661 concentration of a dissolved component in the aphotic zone is described by a horizontally integrated vertical 662 diffusion equation, which relates the rate of change of tracer concentration at a given point to the processes 663 that act to change the tracer concentration: 664

$$\frac{\partial [X]}{\partial t} = \frac{\partial [X]}{\partial t} \bigg|_{\text{trans}} + \Theta_{\text{bio}} + \Theta_{\text{react}},$$
(16)

where [X] represents horizontally integrated physical variables (such as potential temperature, salinity or  $^{14}$ C) or concentration of a chemical component, *t* denotes time, and  $\Theta_{bio}$  and  $\Theta_{react}$  represents internal sources and sinks associated with the biological pump and chemical reactions, respectively. An external source/sink term  $\Theta_{ex}$ , which represents riverine input and/or air-sea gas exchange, is added to the surface layers. The first term on the right\_hand side of equation (16) represents the physical transport:

$$\frac{\partial[X]}{\partial t}\Big|_{\text{trans}} = -A^{\text{l,h}}(z)w^{\text{l,h}}(z)\frac{\partial[X]}{\partial z} + \frac{\partial}{\partial z}\left(A^{\text{l,h}}(z)K_{\nu}^{\text{l,h}}(z)\frac{\partial[X]}{\partial z}\right) + K_{\text{hor}}\frac{\partial^{2}[X]}{\partial y^{2}}.$$
(17)

The terms on the right-hand side express (from left to right) the advection, vertical diffusion, and horizontal diffusion. Here, 1 and h indicate the LD and HD, respectively. The factors  $K_v^{1,h}(z)$ ,  $K_{hor}$ ,  $A^{1,h}(z)$ , and  $w^{1,h}(z)$ denotes the vertical and horizontal diffusion coefficients, the areal fraction of the water layer at water depth *z* to the sea surface area, and upwelling (for LD) or downwelling (for HD) velocity, respectively.

In the CANOPS ocean model, ocean circulation and mixing are characterized by five physical parameters: 675 (1) water transport via thermohaline circulation, V, associated with high latitude sinking and low-mid 676 latitude upwelling; (2) constant horizontal diffusion between the aphotic zones, K<sub>hor</sub>; (3) strong, depth-677 678 dependent vertical diffusion between the aphotic zones in the high latitude region,  $K_v^{\rm h}(z)$ ; (4) high latitude convection,  $\dot{V}_{\rm h}$ ; and (5) depth-dependent vertical diffusion in the low-mid latitude region,  $K_{\rm v}^{\rm l}(z)$ . These 679 parameters are tuned to give tracer distributions consistent with present-day observations. Thermohaline 680 681 circulation and high-latitude convection are considered to be general physical modes on any rotating planet, 682 and our simplified water transport scheme allows us to represent them with a limit number of free 683 parameters. However, we emphasize that the water transport scheme explored here is designed to represent 684 the modern ocean mportant nn on Earth. As a result, some of these parameterizations may need to be modified when applying to ancient oceans or oceans on exoplanets. Nevertheless, given our simple design, 685 our water transport scheme is relatively flexible to modify the water circulations that are markedly different 686 from the modern ocean. 687

#### 688 Advection

Advective water transport in the ocean model represents the major features of modern meridional overturning circulation. The rate of production of ventilated ocean waters ranges from 14 to 27 Sv (1 Sv = 691  $10^6 \text{ m}^3 \text{ s}^{-1}$ ) in the North Atlantic and from 18 to 30 Sv in the Southern Ocean (e.g., (Doney et al., 2004; 692 Lumpkin and Speer, 2007)). The formation of deepwater effectively supplies "fresh" ventilated water to the 693 abyss. We choose  $\dot{V} = 20$  Sv as a reference value, giving a mean overturning time of about 2,140 yr, 694 consistent with the ventilation time estimated from observations (Broecker and Peng, 1982).

The downwelling of the surface waters at H forms HD that flows into the intermediate to deep oceanic 696 layers of LD, which, in turn, upwells over L (Fig. 1b). In many one-dimensional ocean models, downwelling 697 water enters the ocean interior via the deepest model layer (e.g., (Southam et al., 1982; Shaffer and 698 Sarmiento, 1995; Volk and Hoffert, 1985)). In the real ocean, downwelling waters are transported along 699 isopycnal layers below approximately 1,000 m (e.g., (Doney et al., 2004; Lumpkin and Speer, 2007; Shaffer 700 and Sarmiento, 1995; Volk and Hoffert, 1985)). Hence, we assume that high-latitude deep water flows into 701 each ocean layer below 1,100 m. While there is some uncertainty in the pattern of lateral advection, the flow 702 is determined in our model assuming a constant upwelling rate below a depth of 1,100 m in the LD region. 703 The upwelling/downwelling rate  $w^{l,h}(z)$  is then determined by the seafloor topography and the deep water 704 lateral inflow, assuming continuity. Figure 4b shows the lateral advection of deep waters with a reference 705 circulation rate  $\dot{V}$  of 20 Sv. This assumption provides a plausible upwelling rate, which is consistent with 706 the oft-quoted value of  $2-3 \text{ m vr}^{-1}$  (Broecker and Peng, 1982) (Fig. 4c). 707

## 708 Vertical mixing

Ocean circulation is dominated by turbulent processes driven by wind and tidal mixing. These processes 709 occur as eddies which occur at a wide range of spatial scales, from centimeters to whole ocean basins. In 710 numerical models of ocean circulation, turbulent mixing in the ocean interior is commonly represented as a 711 diffusion process, characterized by an eddy diffusion coefficient. The vertical eddy diffusion coefficient 712  $K_{\rm x}(z)$  is typically on the order of 10<sup>-5</sup> to 10<sup>-4</sup> m<sup>2</sup> s<sup>-1</sup> and it is common to assume a depth-dependence which 713 smoothly increases from the thermocline ( $\sim 10^{-5} \text{ m}^2 \text{ s}^{-1}$ ) to the abyss ( $\sim 10^{-4} \text{ m}^2 \text{ s}^{-1}$ ) using an inverse or 714 hyperbolic tangent function (e.g., (Shaffer et al., 2008; Yakushev et al., 2007)). To account for thermocline 715 ventilation, we assumed a relatively high vertical diffusion coefficient in mid-water depth ( $K_1 = 6.3 \times 10^{-5} \text{ m}^2$ 716 s<sup>-1</sup> for water depth 500–1500 m). We also adopted a higher value for the vertical diffusion coefficient ( $K_u$  = 717

718  $1.6 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ ) in the upper most 500 m of the ocean in order to represent the highly convective Ekman 719 layer in the upper part of the ocean.

$$K_{v}^{1}(z) = \begin{cases} K_{u} & (z \ge -500 \text{ m}) \\ K_{1} & (-500 \ge z \ge -1500 \text{ m}) \\ \kappa^{s} + \frac{\kappa^{d} - \kappa^{s}}{2} \left( 1 + \tanh\left(\frac{z - z^{1}}{z^{1}}\right) \right) & (\text{otherwise}) \end{cases}$$
(18)

where  $\kappa^{s}$  and  $\kappa^{d}$  are vertical mixing coefficients, and  $z^{l}$  is the transition length scale (Romaniello and Derry, 2010). In the high latitude region where no permanent thermocline exists, more rapid communication with deepwaters can occur. Previous studies have pointed out that the vertical diffusivities at high latitude can be very high (up to  $O(10^{-2} \text{ m}^2 \text{ s}^{-1})$ ) (e.g., (Sloyan, 2005)). To account for this we include high-latitude convection between H and YD ( $\dot{V}_{h} = 57.4 \text{ Sv}$ ) and higher vertical diffusion ( $K_{v}^{h}(z) = 2 \times K_{v}^{1}(z)$ ).

# 725 Horizontal diffusion

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The horizontal diffusivity is included according to Romaniello and Derry (2010). On basin scales, the horizontal (isopycnal) eddy diffusivity is  $10^7-10^8$  times larger than the vertical (diapycnal) eddy diffusivity due to anisotropy of the density field. For a spatial scale of 1,000 km, horizontal eddy diffusion is estimated to be  $O(10^3 \text{ m}^2 \text{ s}^{-1})$  (e.g., (Ledwell et al., 1998)). We adopt this value. As Romaniello and Derry (2010) did, we assume horizontal mixing follows the pathways of advective fluxes between laterally adjacent regions. The reciprocal exchange fluxes may be written as

$$Y_{\rm hor}^{\rm ex} = K_{\rm hor} A_{\perp} \frac{\partial [X]}{\partial y} = \frac{K_{\rm hor} A_{\perp}}{L} \Delta [X], \qquad (19)$$

where  $J_{hor}^{ex}$  denotes the exchange fluxes between the layers (in mol yr<sup>-1</sup>),  $A_{\perp}$  represents the cross-sectional area separating two adjacent reservoirs, *L* is a characteristic spatial distance separating the reservoirs,  $\Delta[X]$  is the difference in concentration between two reservoirs (Romaniello and Derry, 2010). By assuming that *L* is of the same order as the length of the interface separating the two regions, we can approximate  $A_{\perp} \approx \Delta z \times O(L)$ , where  $\Delta z$  is the thickness of the interface separating the two regions. Then we obtain

$$J_{\rm hor}^{\rm ex} = K_{\rm hor} \Delta z \Delta [X] \,. \tag{20}$$

Therefore, when we discretize the ocean interior at 100 m spacing approximately 0.1 Sv of reciprocalmixing occurs between adjacent layers.

## 739 Ocean circulation tracers

748

We use potential temperature  $\theta$ , salinity S, and radioactive carbon <sup>14</sup>C, as physical tracers. Distributions of 740 these tracers are determined by the transport mechanisms described above. In this study, we adopt the values 741 at the surface layers (L and H) as upper boundary conditions:  $\dot{\theta} = 15^{\circ}$ C,  $\dot{\theta}^{h} = 0^{\circ}$ C,  $S^{l} = 35$  psu,  $S^{h} = 34$  psu, 742  $\Delta^{14}C^{1} = -40\%$ , and  $\Delta^{14}C^{h} = -100\%$ . The radioactive decay rate for  ${}^{14}C$  is  $1.21 \times 10^{-4}$  yr<sup>-1</sup>. Although  ${}^{14}C$  can be 743 incorporated in the biogenic materials and transported into deep water, we ignore this biological effect for 744 745 simplicity. The associated error is ~10% of the profiles produced by circulation and radioactive decay (Shaffer and Sarmiento, 1995). The parameter values used in the ocean circulation model are listed in Table 746 747 3.

Parameters	Label	Value	Unit	Ref.
Ocean surface area	Α	3.62×10 <sup>14</sup>	m <sup>2</sup>	(Ozaki and Tajika, 2013)
Surface area of high-latitude layer (H)	$A^{\mathrm{h}}$	0.362×1014	$m^2$	(Ozaki and Tajika, 2013)
Depth of mixed layer	$h_{ m m}$	100	m	(Ozaki and Tajika, 2013)
Grid spacing	$\Delta z$	100	m	(Ozaki and Tajika, 2013)
Water depth of ocean bottom	Zb	6,100	m	(Ozaki and Tajika, 2013)
Ocean overturning rate	Ŵ	20	Sv	(Ozaki and Tajika, 2013)
Vertical mixing coefficient ( $z < 500 \text{ m}$ )	$K_{\mathrm{u}}$	5,000	m <sup>2</sup> yr <sup>-1</sup>	(Ozaki and Tajika, 2013)
Vertical mixing coefficient (500 m $< z < 1,500$ m)	$K_1$	2,500	m <sup>2</sup> yr <sup>-1</sup>	(Ozaki and Tajika, 2013)
Mixing coefficient	Ks	473	m <sup>2</sup> yr <sup>-1</sup>	(Romaniello and Derry, 2010
Mixing coefficient	Kd	3,154	m <sup>2</sup> yr <sup>-1</sup>	(Romaniello and Derry, 2010
Transition depth for vertical mixing coefficient	Zı	1,000	m	(Romaniello and Derry, 2010

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High-latitude convection rate	$\dot{V_{ m h}}$	57.4	$\mathbf{Sv}$	(Ozaki and Tajika, 2013)
Horizontal diffusion coefficient	$K_{ m hor}$	1,000	$m^2 s^{-1}$	(Romaniello and Derry, 2010)

## 749 2.4.3 Ocean biogeochemical framework

750 The ocean circulation model is coupled to a biogeochemical model, which includes an explicit

751 representation of a variety of biogeochemical processes in the ocean. The parameters used in the oceanic

752 biogeochemical model are listed in Table 4.

**Table 4.** Parameter values used in the oceanic biogeochemistry module of CANOPS-GRB.

Parameter	Label	Value	Unit	Ref.
Efficiency factor for phosphate uptake at L	ε <sup>l</sup>	1.0	-	(Ozaki and Tajika, 2013)
Efficiency factor for phosphate uptake at H	$\varepsilon^{\rm h}$	0.15	-	(Ozaki and Tajika, 2013)
Phosphate half saturation constant	$K_{\mathrm{P}}$	1×10-6	mM	(Ozaki and Tajika, 2013)
Export ratio	$f_{\exp}$	0.2	_	(Ozaki et al., 2019a)
Redfield C/P ratio	$\alpha^*$	106	mol mol-1	(Redfield et al., 1963)
Redfield N/P ratio	$\beta^*$	16	mol mol-1	(Redfield et al., 1963)
POM sinking velocity	VPOM	100	m d <sup>-1</sup>	(Ozaki et al., 2011)
Mass fraction of G <sub>1</sub>	$m_1$	0.72	_	(Ozaki and Tajika, 2013)
Mass fraction of G <sub>2</sub>	$m_2$	0.25	_	(Ozaki and Tajika, 2013)
Mass fraction of G <sub>3</sub>	<i>m</i> <sub>3</sub>	0.03	_	(Ozaki and Tajika, 2013)
Decomposition rate of G <sub>1</sub>	$k_1$	0.6	d-1	(Ozaki et al., 2011)
Decomposition rate of G <sub>2</sub>	$k_2$	0.1	d-1	(Ozaki et al., 2011)
Decomposition rate of G <sub>3</sub>	<i>k</i> <sub>3</sub>	0.0	d-1	(Ozaki et al., 2011)
Half saturation constant for aerobic respiration	$K_{O2}$	8×10-3	mM	(Boudreau, 1996)
Half saturation constant for denitrification	$K_{\rm NO3}$	3×10-2	mM	(Boudreau, 1996)
Half saturation constant for MSR	$K_{\rm MSR}$	0.2	mM	This study
Half saturation constant for AOM	K <sub>AOM</sub>	0.093	mM	(Beal et al., 2011)
Aerobic oxidation rate of ammonium	$k_{\rm R8}$	$1.825 \times 10^{4}$	mM <sup>-1</sup> yr <sup>-1</sup>	(Oguz et al., 2001)
Aerobic oxidation rate of sulfide	$k_{\rm R9}$	3.65×10 <sup>3</sup>	mM <sup>-1</sup> yr <sup>-1</sup>	(Oguz et al., 2001)
A such is mother an ideal on the	$k_{\rm R10}$	1,107	mM <sup>-1</sup> yr <sup>-1</sup>	(Van Cappellen and
Aerobic methane oxidation fate		1×10		Wang, 1996)
Anaerobic methane oxidation rate	<i>k</i> <sub>R11</sub>	3×10-4	yr-1	(Ozaki et al., 2019a)
	35			

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Pyrite formation rate in the water column	$k_{\rm pyr}^{\rm wc}$	0.01	yr <sup>-1</sup>	This study
Reference value of seawater sulfate concentration	$[SO_4^{2-}]^*$	28.9	mM	(Ozaki et al., 2019a)

#### 754 Biological production

The overall biogeochemical cycling scheme is based on the cycling of primary nutrient (phosphate;  $PO_4^{3-}$ ), which limits biological productivity—export production is related to the availability of P within the euphotic zone (Maier-Reimer, 1993; Yamanaka and Tajika, 1996; Shaffer et al., 2008):

$$j_{\exp}^{l,h} = \alpha^{l,h} h_m \varepsilon^{l,h} [PO_4^{3-}]^{l,h} \frac{[PO_4^{3-}]^{l,h}}{[PO_4^{3-}]^{l,h} + K_p},$$
(21)

where  $j_{exp}$  represents new/export production of POC (in unit of mol C m<sup>-2</sup> yr<sup>-1</sup>),  $\alpha$  denotes C:P stoichiometry of POM,  $h_m$  is the mixed layer depth,  $\varepsilon$  denotes the assimilation efficiency factor for P uptake, and  $K_P$ denotes the half-saturation constant. The value of  $\varepsilon$  for the low-mid latitude region is assumed to be 1. In contrast, we assume a lower efficiency for high latitude region because biological production tends to be limited by environmental factors other than phosphate availability (e.g., amount of solar radiation, mixed layer thickness, sea-ice formation, and iron availability). This is used as one of the fitting parameters in the model. Downwelling waters contain a certain level of nutrients (i.e., preformed nutrients).

765

In our standard run, the stoichiometry of organic matter is parameterized using the canonical Redfield ratio 766 (C:N:P = 106:16:1) (Redfield et al., 1963). However, we note that flexible C:N:P stoichiometry has been the 767 subject of recent discussion. In the modern oceans, C:N:P ratios of exported POM vary across latitude, 768 reflecting ecosystem structure (Galbraith and Martiny, 2015). Local observations (and laboratory 769 experiments) suggest that the C:N:P ratio of cyanobacteria is a function of seawater  $PO_4^{3-}$  concentration 770 (Larsson et al., 2001). The evolutionary perspective has also been discussed (Quigg et al., 2003; Sharoni and 771 Halevy, 2022). In the previous version of the CANOPS model, the C-N-P stoichiometry of primary 772 producers responds dynamically to P availability in the surface layer (Reinhard et al., 2017b): 773

$$\alpha = \alpha^* + \frac{\alpha_{\max} - \alpha^*}{2} \left( 1 + \tanh\left(\frac{\gamma_{P0} - [PO_4^{3-}]}{\gamma_{P1}}\right) \right), \tag{22}$$
$$\beta = \beta^* + \frac{\beta_{\max} - \beta^*}{2} \left( 1 + \tanh\left(\frac{\gamma_{P0} - [PO_4^{3-}]}{\gamma_{P1}}\right) \right),$$
(23)

where  $\alpha$  and  $\beta$  represent the C/P ratio and N/P ratio of POM, \* denotes the canonical Redfield ratios, max denotes the maximum value ( $\alpha_{max} = 400$  and  $\beta_{max} = 60$ ), and  $\gamma_{P0}$  and  $\gamma_{P1}$  are tunable constants ( $\gamma_{P0} = 0.1 \ \mu M$ and  $\gamma_{P1} = 0.03 \ \mu M$ ) (Kuznetsov et al., 2008). In the CANOPS-GRB model, this dynamic response of POM stoichiometry can be explored by changing the user-flag from the standard static response. In this study, we do not explore the impacts of flexible POM stoichiometry on global biogeochemistry (i.e.,  $\alpha_{max} = \alpha^*$  and  $\beta_{max} = \beta^*$ ).

780

Biological production in the surface mixed layer increases the concentration of dissolved  $O_2$  and reduces the concentrations of DIP and DIN according to the stoichiometric ratio (R1 and R2; Table 1). DIN consumption is partitioned between nitrate and ammonium, assuming that ammonium is preferentially assimilated. CANOPS-GRB evaluates the availability of fixed N in the surface ocean, and any N deficiency required for a given level of productivity is assumed to be compensated for on geologic time scales by N fixers. In other words, it is assumed that biological N fixation keeps pace with P availability, so that P (not N) ultimately determines oceanic biological productivity.

788

To date, models of varying orders of complexity have been developed to simulate oceanic primary production and nutrient cycling in the euphotic layer, from a single nutrient and single phytoplankton component system to the inclusion of multiple nutrients and trophic levels in the marine ecosystem, usually coupled to physical models (e.g., (Yakushev et al., 2007; Oguz et al., 2000)). To avoid this level of complexity, we introduce a parameter,  $f_{exp}$ , called export ratio (Sarmiento and Gruber, 2006), which relates the flux densities of export production and NPP, as follows:

$$j_{\rm NPP}^{\rm ocn} = \frac{J_{\rm exp}}{f_{\rm exp}},\tag{24}$$

where  $j_{\text{NPP}}^{\text{ocn}}$  denotes the NPP in terms of mol C m<sup>-2</sup> yr<sup>-1</sup>. In the modern ocean globally averaged value of  $f_{\text{exp}}$ is estimated at 0.2 (Laws et al., 2000), and we assumed this value in this study. The rate of recycling of organic matter in the photic zone is thus given by

$$j_{\text{recy}} = j_{\text{NPP}}^{\text{ocn}} - j_{\text{exp}} = \frac{1 - f_{\text{exp}}}{f_{\text{exp}}} j_{\text{exp}}.$$
 (25)

The respiration pathway of  $j_{recy}$  depends on the availability of terminal electron acceptors (O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>). Following exhaustion of these species as terminal electron acceptors, organic matter remineralization occurs by methanogenesis (R7). See below for the treatment of organic matter remineralization in the water column.

#### 802 Biological pump

Most POM exported to the deep sea is remineralized in the water column before reaching the seafloor (e.g., (Broecker and Peng, 1982)). Nutrients returning to seawater at intermediate depths may rapidly return to the surface ocean and support productivity. The remaining fraction of POM that reaches the sediment ultimately exerts an important control on oceanic inventories of nutrients and O<sub>2</sub>. An adequate representation of the strength of biological pump is therefore critical to any descriptions of global biogeochemical cycles.

808

809 The governing equation of the concentration of biogenic particles G is

$$\frac{\partial G}{\partial t} + v_{\text{POM}} \frac{\partial G}{\partial z} = -rG \tag{26}$$

where r is a decomposition rate and  $v_{POM}$  is the settling velocity of POM in the water column. We assume a 810 settling velocity of 100 m d<sup>-1</sup> for our reference value (e.g., (Suess, 1980)), although a very wide range of 811 values and depth-dependency have been reported (e.g., (Berelson, 2001a)). Therefore, the settling velocity is 812 fast enough to neglect advective and diffusive transport of biogenic particles. Note that the settling velocity 813 814 would affect the intensity of biological pump and chemical distribution in the ocean interior. Considering the 815 ballast hypothesis in the modern ocean (Armstrong et al., 2001; Francois et al., 2002; Ittekkot, 1993; Klaas and Archer, 2002), the settling velocity of POM in the geological past would very likely have been different 816 from the modern ocean. As (Kashiyama et al., 2011) pointed out, there would be a critical aspect among 817

sinking rate of POM, intensity of biological pump and chemical distribution in the ocean. The quantitative
and comprehensive evaluation of their effect is an important issue for the future work (Fakhraee et al., 2020).

In order to solve equation (26) explicitly, a relatively small time step (~1 day) would be required. However, because the sinking velocity and remineralization of biogenic material are fast processes, we assume that the POM export and remineralization occurs in the same time step (ignoring the term  $\partial G/\partial t$ ). Then the concentration of biogenic particles can be solved as follows:

$$G(z + \Delta z) = G(z) \exp\left(-\frac{r\Delta z}{v_{\text{POM}}}\right).$$
(27)

825 where  $\Delta z$  is a spatial resolution of the model.

#### 826 Organic matter decomposition

As POM settles through the water column, it is nearly entirely decomposed back to dissolved tracers. 827 Therefore, decomposition of POM is a key process for modelling biogeochemistry in the ocean. To avoid 828 the complex treatment of this process (such as repackaging and aggregation/dispersal of particles), various 829 empirical schemes for POM sinking flux have been proposed, such as exponential (Volk and Hoffert, 1985) 830 or power law (Martin et al., 1987) functions (Fig. 5). However, the estimation of Volk and Hoffert generally 831 tends to overestimate in the upper water column (<1.5 km) and underestimate at depth. It is important to 832 note that data series of sediment trap measurements were obtained from a limited geographic and depth 833 range. (Berelson, 2001b) and (Lutz et al., 2002) conducted further estimates of the sediment flux and found 834 regional variability in the sinking flux. Broadly, these data indicate that commonly applied flux relationships 835 generally tend to overestimate flux to depth. 836



838

Figure 5. Empirical relationships between POC settling flux normalized to export production (Lutz et al., 2002) and water depth (Archer et al., 1998; Berelson, 2001b; Martin et al., 1987; Volk and Hoffert, 1985).
The profile of the CANOPS-GRB model is depicted as a red line. The black dots represent observational data (Honjo and Manganini, 1993; Lutz et al., 2002; Tsunogai and Noriki, 1991; Honjo, 1980) (and references therein).

The microbial degradation of different groups of organic matter with different labilities differs over 845 timescales ranging from hours to millions of years. In order to represent the decrease in POM lability with 846 time and water depth, we adopt the so-called multi-G model (Westrich and Berner, 1984) that describes the 847 detailed kinetics of organic matter decomposition (Ozaki and Tajika, 2013; Ozaki et al., 2011). In the 848 CANOPS model, POM is described using two degradable fractions ( $G_1$  and  $G_2$ ) and one inert ( $G_3$ ) fraction 849 using different rate constants  $k_i$  (i=1, 2, 3) for each component. Rate constants are tuned on the basis of 850 consistency with the typical profile of the POM sinking flux estimated from sediment trap studies (Fig. 5). 851 In this study, constant stoichiometries between C, N, and P during the remineralization of POM are assumed 852 throughout the water column, taking values equal to those characterizing mean export production. 853

The electron acceptor used in the respiration reaction changes from dissolved O<sub>2</sub> to other oxidants (e.g., 855  $NO_3^-$  and  $SO_4^{2-}$ ) as  $O_2$  becomes depleted. The respiration pathway is controlled by the free energy change 856 per mole of organic carbon oxidized. The organic matter decomposition is performed by the oxidant which 857 yields the greatest free energy change per mole of organic carbon oxidized. When the oxidant is depleted, 858 further decomposition will proceed utilizing the next most efficient (i.e., the most energy producing) oxidant 859 until either all oxidants are consumed or oxidizable organic matter is depleted (e.g., (Froelich et al., 1979; 860 Berner, 1989)). In oxic waters, organic matter is remineralized by an aerobic oxidation process (R4). As 861 dissolved O<sub>2</sub> is depleted,  $NO_3^{-1}$  and/or  $SO_4^{2-1}$  will be used (R5 and R6). Denitrification is carried out by 862 heterotrophic bacteria under low concentrations of dissolved O<sub>2</sub>, if there is sufficient nitrate. For anoxic, 863 sulfate-lean oceans, the methanogenic degradation of organic matter production from carbon dioxide 864 (methanogenesis) or fermentation of organic matter to produce methane and carbon dioxide will occur (R7). 865 In the CANOPS-GRB model, we parameterized the dependence of decomposition of POM with a 866 Michaelis-Menten type relationship with respect to the terminal electron acceptors: 867

$$R_4 = \frac{[O_2]}{K_{O_2} + [O_2]} (\Sigma k_i G_i)$$
(28)

$$R_{5} = \frac{K_{O_{2}}}{K_{O_{2}} + [O_{2}]} \frac{[NO_{3}]}{K_{NO_{3}} + [NO_{3}]} (\Sigma k_{i}G_{i})$$
(29)

$$R_{6} = \frac{K_{O_{2}}}{K_{O_{2}} + [O_{2}]} \frac{K_{NO_{3}}}{K_{NO_{3}} + [NO_{3}^{2}]} \frac{[SO_{4}^{2^{*}}]}{K_{MSR} + [SO_{4}^{2^{*}}]} (\Sigma k_{i}G_{i})$$
(30)

$$R_{7} = \frac{K_{O_{2}}^{'}}{K_{O_{2}}^{'} + [O_{2}]} \frac{K_{NO_{3}}^{'}}{K_{NO_{3}}^{'} + [NO_{3}^{'}]} \frac{K_{MSR}^{'}}{K_{MSR}^{'} + [SO_{4}^{2}]} (\Sigma k_{i}G_{i})$$

$$= (1 - R_{O_{2}} - R_{NO_{3}} - R_{SO_{4}}) (\Sigma k_{i}G_{i})$$
(31)

where  $K_{02}$ ,  $K_{NO3}$ , and  $K_{MSR}$  are Monod constants, and  $K'_{02}$ ,  $K'_{NO3}$ ,  $K'_{MSR}$  are inhibition constants. The Monod-type expressions are most-widely used in mathematical models of POM decomposition processes (e.g., (Boudreau, 1996)). The oxidants for organic matter decomposition change graduallywith, depending on the amount-availability of each oxidant, which vary with time and water depth. The parameter values are based on the previous studies on early diagenetic processes in marine sediments (Boudreau, 1996; Van

Cappellen and Wang, 1996). SO4<sup>2-</sup> has been one of the major components of the Phanerozoic oceans and has 873 been an important mortantt oxidizing agent in anaerobic systems. In the original CANOPS model (Ozaki 874 and Tajika, 2013; Ozaki et al., 2011), it was assumed that the saturation constant  $K_{\text{MSR}}$  is zero, meaning that 875 the  $SO_4^{2-}$  is never a limiting factor. In contrast, during the Precambrian, seawater  $SO_4^{2-}$  could have been 876 extremely low (Lyons and Gill, 2010). The half saturation constant for MSR ( $K_{MSR}$ ) determines the degree 877 to which MSR contributes to the total respiration rates. However, estimates for  $K_{MSR}$  in natural environments 878 and pure cultures vary over several orders of magnitude ( $\sim 0.002-3$  mM) (Tarpgaard et al., 2011; Pallud and 879 Van Cappellen, 2006). We assume a reference value of 0.2 mM for this study. 880

881

Finally, temperature may also have played an important role in organic matter decomposition rates. The dependence of ammonification on temperature is sometimes described by an exponential function or  $Q_{10}$ function (e.g., (Yakushev et al., 2007)). While we recognize that the temperature dependency of organic matter decomposition might have played an important role in oceanic biogeochemical cycles in the geological past (Crichton et al., 2021), these dynamics are not included in <u>our standard modelCANOPS-</u> <u>GRB v1.0</u>.

#### 888 Secondary redox reactions

889 Total ammonia ( $\Sigma NH_3$ ), total sulfide ( $\Sigma H_2S$ ), and methane (CH<sub>4</sub>), produced during organic matter degradation, are subject to oxidation toby NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and CO<sub>2</sub> via a set of secondary redox reactions (Table 890 1). Rate constants for these reactions are taken from the literature. The ocean model includes nitrification 891 (R8), total sulfide oxidation by  $O_2$  (R9), aerobic oxidation of CH<sub>4</sub> by  $O_2$  (R10), and AOM by  $SO_4^{2-}$  (R11). 892 Nitrification, the oxidation of ammonium to nitrate, occurs in several stages and is accomplished mainly by 893 chemolithotrophic bacteria (Sarmiento and Gruber, 2006). In this study, we treat all nitrification reactions as 894 a combined reaction (R8). The rate of this process is assumed to depend on the concentration of both oxygen 895 and ammonia as follows: 896

$$R_8 = k_{\rm R8} [\rm NH_4^+] [\rm O_2].$$
(32)

The oxidation of sulfide formed in anoxic waters by MSR can also be written as a series of reactions (e.g., (Yakushev and Neretin, 1997)), but we treat it as an overall reaction (R9). The rate of this secondary redox

900 reaction is also formulated using <u>a</u> bimolecular rate law:

$$R_{\rm g} = k_{\rm Rg} [\Sigma H_2 S] [O_2]. \tag{33}$$

The rate constant for this process has been shown to vary significantly as a function of several redoxsensitive trace metals which act as catalysts (Millero, 1991). Here we assume  $k_{R9} = 3650 \text{ mM}^{-1} \text{ yr}^{-1}$  based on the observations of suboxic layer the chemocline of the Black Sea (Oguz et al., 2001).

904

In the original CANOPS model (Ozaki et al., 2019a; Ozaki and Tajika, 2013), syngenetic pyrite formation in the water column was not considered. In a more recent revision of the model, this process was added (Cole et al., in review) and parameterized such that iron sulfide formation is assumed to be proportional to the hydrogen sulfide concentration:

$$R_{\rm pyr}^{\rm wc} = k_{\rm pyr}^{\rm wc} [\Sigma H_2 S], \qquad (34)$$

where  $k_{pyr}^{wc}$  is a model constant (its reference value is set at 0.01 yr<sup>-1</sup>). This constant is a function of the ferrous iron concentration in seawater, but it is the subject of large uncertainty. The total flux (in mol S yr<sup>-1</sup>) can be obtained by integrating the precipitation flux density over the whole ocean:

$$J_{\rm pyr}^{\rm wc} = \int R_{\rm pyr}^{\rm wc} \frac{dV}{dz} dz \,. \tag{35}$$

912

913 CH<sub>4</sub>-can be oxidized not only by O<sub>2</sub> in aerobic waters (R10) but by SO<sub>4</sub> in anoxic waters (R11). The aerobic

914 oxidation of CH<sub>4</sub> is formulated using a bimolecular rate law:

$$R_{10} = k_{\rm R10} [\rm CH_4] [\rm O_2]. \tag{36}$$

915 The rates of AOM is formulated using a Monod-type law (Beal et al., 2011):

Ì

$$R_{11} = k_{\text{R11}} [\text{CH}_4] \frac{[\text{SO}_4^{2^-}]}{K_{\text{AOM}} + [\text{SO}_4^{2^-}]}.$$
(37)

Rate constants for above reactions are taken from the literature (Table 4). Secondary redox reactions were calculated implicitly with an operator splitting scheme (Steefel and Macquarrie, 1996) so as to maintain numerical stability.

### 919 2.4.4 Sediment-water exchange

The burial of biogenic material in marine sediments plays a critical role in global biogeochemical cycles, 920 especially with respect to the marine budgets of nutrients, carbon, and sulfur. This is intimately linked to 921 922 atmospheric O2 levels on geologic timescales. Specifically, the burial rate of Corg in marine sediments exerts a primary control on the evolution of atmospheric O2 levels throughout Earth's history. Given the 923 complexity of biogeochemical processes within sediments and our limited knowledge on many of the early 924 diagenetic processes, we adopt some semi-empirical relationships extracted from ocean sediment data. This 925 approach, rather than explicit modelling, is also required to reduce the computational cost of the simulation 926 on timescales >100 Myr. The related parameter values are listed in Table 5. 927

929 **Table 5** Parameters used in the sediment-water interface module of CANOPS-GRB.

Parameters	Label	Value	Unit	Ref.
Scale constant for benthic aerobic respiration	k	0.02	yr-1	(Ozaki et al., 2019a)
Burial efficiency of $C_{\mbox{\scriptsize org}}$ at zero sediment accumulation rate	$be_1$	5.0	%	(Dale et al., 2012)
Burial efficiency of $C_{\mbox{\scriptsize org}}$ at infinite sediment accumulation rate	$be_2$	75	%	(Dale et al., 2012)
Centre of the regression for burial efficiency of organic C	а	0.01	g cm <sup>-2</sup> yr <sup>-1</sup>	(Dale et al., 2012)
Pyrite burial efficiency in oxic sediments	$e_{\rm pyr}^{\rm oxic}$	0.117	_	This study
Pyrite burial efficiency in anoxic sediments	$e_{\rm pyr}^{\rm anox}$	1	-	(Ozaki et al., 2019a)
O2 threshold value for P burial efficiency	oxic	0.25	mM	(Ozaki et al., 2011)
Corg/Norg ratio of buried sediments	$(C_{org}/N_{org})_b$	10	mol mol-1	(Ozaki and Tajika, 2013)

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#### 930 **POM deposition**

928

931 The fraction of settling POM that reaches the sediment surface,  $J_{org}^{dep}$  (in mol C yr<sup>-1</sup>) is a function of both

932 the settling flux density,  $j_{org}^{dep}$  (in mol C m<sup>-2</sup> yr<sup>-1</sup>), and topography (Fig. 4a):

$$J_{\text{org}}^{\text{dep}} = \int_{z_1}^{z_2} j_{\text{org}}^{\text{dep}}(z) \frac{dA}{dz} dz, \qquad (38)$$

933 where the settling flux density can be written as follows:

$$j_{\rm org}^{\rm dep} = v_{\rm POM} G \,. \tag{39}$$

where G is the concentration of POM, and  $v_{POM}$  denotes the sinking velocity.

## 935 Carbon cycling

Interactions between the ocean and underlying sediments play an important role in influencing whole-ocean chemical and nutrient inventories on geologic time scales. POM deposited to the seafloor is subject to decomposition during diagenetic processes associated with burial in marine sediments. Only a small fraction of organic matter will ultimately be buried and removed from the surface environment. However, understanding what factors control the preservation of organic matter in marine sediments has been a controversial topic, and we still lack a robust understanding of this process. With this issue in mind, we adopt an empirical approach obtained using the observational data from previous studies.

943

The burial flux density of  $C_{org}$  at each water depth,  $j_{org}^{b,ocn}$  (in terms of mol C m<sup>-2</sup> yr<sup>-1</sup>), is calculated based on burial efficiency,  $BE_{org}$ :

$$j_{\rm org}^{\rm b,ocn} = BE_{\rm org} j_{\rm org}^{\rm dep} \,. \tag{40}$$

Burial efficiency is defined as the fraction of organic matter buried in sediments relative to the total 946 depositional flux. Burial efficiency is described by simplified parametric laws based on empirical 947 relationships from modern day observations. Previous studies demonstrate strong dependency of this term 948 on total sedimentation rate, SR (e.g., (Henrichs and Reeburgh, 1987)). Figure 6 demonstrates the relationship 949 between BE<sub>org</sub> and SR compiled from literature surveys. The sedimentation rate in the modern ocean varies 950 over about five orders of magnitude, with a primary dependence on material supplied from the continents. 951 There is a strong relationship, especially for SR less than 0.01 cm yr<sup>-1</sup>. In contrast to the strong SR 952 dependence under oxic conditions, anoxic settings show a much weaker dependence of BEorg on SR (Betts 953 and Holland, 1991; Henrichs and Reeburgh, 1987) (Fig. 6). In this study, the following relationship 954

proposed by (Henrichs and Reeburgh, 1987) is adopted for sediments underlying well-oxygenated bottom water (O<sub>2</sub> concentration of bottom water,  $[O_2]_{bw} > 200 \ \mu M$ ):

$$BE_{\rm org} = \frac{SR^{0.4}}{2.1}.$$
 (41)

Given that  $BE_{\text{org}}$  depends on the  $[O_2]_{\text{bw}}$  (Lasaga and Ohmoto, 2002; Katsev and Crowe, 2015), we adopt the following formulation for sediments underlying less-oxygenated bottom waters ( $[O_2]_{\text{bw}} < 30 \ \mu\text{M}$ ) (Dale et al., 2012):

$$BE_{\rm org} = b_2 + \frac{b_1 - b_2}{1 + SR/a},$$
(42)

where a = 0.019,  $b_1 = 0.05$ , and  $b_2 = 0.7$ , respectively. For intermediate  $[O_2]_{bw}$  levels,  $BE_{org}$  is evaluated as a function of  $[O_2]_{bw}$  with a log-linear interpolation method. Note that the original CANOPS model (Ozaki and Tajika, 2013; Ozaki et al., 2011) adopted Eq. (41) without considering the O<sub>2</sub> dependency, whereas more recent versions employ Eq. (42) for both oxic and anoxic sediments with different values of *a*,  $b_1$  and  $b_2$ . In the CANOPS-GRB\_v1.0, we adopted both equations, because of the sake of more accurate reproduction of C<sub>org</sub> burial distribution in the modern ocean (Sect. 3.2.2).





concentration of bottom water,  $[O_2]_{bw}$ , with grey dots for the unknown  $[O_2]_{bw}$  value. <u>Blue and red lines are</u> the relationship for well-oxygenated ( $[O_2]_{bw} > 200 \ \mu$ M) (Henrichs and Reeburgh, 1987) and anoxic ( $[O_2]_{bw}$  $< 30 \ \mu$ M) marine sediments adopted in the CANOPS-GRB model, whereas <u>Black and</u> grey solid lines is are a previously proposed empirical relationship proposed by<del>s</del> (Betts and Holland, 1991), whereas blue and red lines are the relationship for well oxygenated ( $[O_2]_{bw} > 200 \ \mu$ M) and anoxic ( $[O_2]_{bw} < 30 \ \mu$ M) marine sediments adopted in the CANOPS-GRB model.

979 Sedimentation rate depends strongly on water depth and distance from shore (Hedges et al., 1999), and we 980 apply the relationship between water depth, *z*, and the reference value of *SR* shown by (Tromp et al., 1995) 981 (Fig. 7).

$$z = 2700 \times erfc \left( 2.1 + \log SR^* \right).$$
(43)

Using these formulas with seafloor topography (Fig. 4a) and  $j_{org}^{dep}$  (Eq. 39), we can calculate  $j_{org}^{b,ocn}$  for each ocean depth. In the CANOPS-GRB model, we also introduce an erosion factor,  $f_R$ , representing the global weathering/sedimentation rate (Sect. 2.4.3). Given the intimate coupling between global erosion rate and mass transfer from continents to the ocean, *SR* scales with the erosion factor ( $f_R = 1$  for our reference run):

$$SR(z) = f_{\rm R} SR(z)^{\dagger}. \tag{44}$$



**Figure 7.** Sedimentation rate as a function of water depth. Data (black dots) were compiled from literature survey (Colman et al., 2000; Baturin, 2007; Betts and Holland, 1991; Tromp et al., 1995; Cha et al., 2005; Reimers et al., 1992). Black line represents the relationship assumed in the CANOPS-GRB model. Previously estimated empirical relationships (Middelburg et al., 1997; Tromp et al., 1995) are also shown.

993 Organic matter that is not buried is subject to decomposition. The <u>benthic</u> decomposition rate at each water 994 depth is given as follows:

$$j_{\text{recy}}^{\text{sed}} = j_{\text{org}}^{\text{dep}} - j_{\text{org}}^{\text{b,ocn}} = \left(1 - BE_{\text{org}}\right) j_{\text{org}}^{\text{dep}}.$$
(45)

The respiration pathway used in the benthic decomposition is evaluated based on semi-empirical relationships obtained by 1-D early diagenesis models (see below). The degradation of organic matter in sediments is coupled to the availability of terminal electron acceptors, such as  $O_2$ ,  $NO_3^-$ , and  $SO_4^2$ - in the water column. The fraction of aerobic degradation in total sedimentary respiration,  $f_{aero}$ , is calculated based on oxygen exposure time ( $\tau_{OET}$ ):

$$f_{\text{aero}} = \left(1 - f_{\text{deni}}\right) \left(1 - e^{-k\tau_{\text{OET}}}\right),\tag{46}$$

1000 where  $f_{\text{deni}}$  denotes the fraction of denitrification and k is an empirical constant.  $\tau_{\text{OET}}$  is given by

i

$$\tau_{\rm OET} = \frac{\rm OPD}{SR},\tag{47}$$

where OPD is the oxygen penetration depth (cm) and SR denotes a linear sedimentation rate (cm yr<sup>-1</sup>). In the 1001 CANOPS-GRB model OPD is calculated by a simplified parametric law obtained from a 1-D early-1002 diagenetic model of C and O<sub>2</sub>. We performed a series of experiments (n = 5,652) in order to parameterize 1003 OPD as a polynomial function with the following variables: sedimentation rate SR (cm yr<sup>-1</sup>), bottom water 1004 O<sub>2</sub> concentration  $[O_2]_{bw}$  ( $\mu$ M), depositional flux of POC  $j_{org}^{dep}$  (mmol C cm<sup>-2</sup> yr<sup>-1</sup>) and bottom water 1005 temperature  $T_{\rm bw}$  (°C). The variables are allowed to vary over a parameter space spanning 10<sup>-4</sup> cm yr<sup>-1</sup> < SR < 1006  $10^{1}$  cm yr<sup>-1</sup>,  $10^{0}$   $\mu$ M < [O<sub>2</sub>]<sub>bw</sub> <  $10^{3}$   $\mu$ M,  $10^{-4}$  mmol C cm<sup>-2</sup> yr<sup>-1</sup> <  $j_{org}^{dep}$  <  $10^{1}$  mmol C cm<sup>-2</sup> yr<sup>-1</sup>, and 0 °C < 1007  $T_{\rm bw} < 30 \,{}^{\circ}{\rm C}.$ 1008

$$\log \text{OPD} = a_0 + a_1 \log SR + a_2 \log[O_2]_{bw} + a_3 \log j_{org}^{dep} + a_4 (\log SR)^2 + a_5 (\log[O_2]_{bw})^2 + a_6 (\log j_{org}^{dep})^2 + a_7 (\log SR) (\log[O_2]_{bw}),$$
(48)  
+  $a_8 (\log[O_2]_{bw}) (\log j_{org}^{dep}) + a_9 (\log SR) (\log j_{org}^{dep}) + a_{10} T_{bw}$ 

where  $a_0 = -2.24869$ ,  $a_1 = 0.110645$ ,  $a_2 = 1.12569$ ,  $a_3 = -0.281005$ ,  $a_4 = 0.014827$ ,  $a_5 = -0.124721$ ,  $a_6 = 0.0894604$ ,  $a_7 = 0.00279531$ ,  $a_8 = -0.127797$ ,  $a_9 = 0.0017995$ , and  $a_{10} = 0.0085171$ . This parametric fit provides a rapid means of obtaining OPD from a 1-D early diagenetic model of C and O<sub>2</sub> (Fig. 8). Note that Eq. (48) is verified for  $[O_2]_{bw} > 1 \ \mu$ M. When bottom water O<sub>2</sub> concentration is lower than 1 \ \muM, OPD is set at zero.

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## 1015



1018

### 1019 Phosphorus cycling

Marine P inventory is controlled not only by the riverine P input flux from land but also by the efficiency of P recycling in marine sediments (Van Cappellen and Ingall, 1994). Because the estimated P diffusive flux from seafloor sediments is much greater than the riverine P flux (Delaney, 1998; Hensen et al., 1998; Ruttenberg, 2003; Mcmanus et al., 1997; Wallmann, 2003a; Wallmann, 2010a), changes in diagenetic

- processes affecting P recycling and burial in marine sediments could have a significant impact on global 1024
- oceanic biogeochemical cycles. 1025



1029 Figure 9. Schematic of P burial in marine sediments. The primary source of P to the sediment is the deposition of organic matter, which represents the C:P ratio of primary producers,  $\alpha$ . Most of the deposited 1030 organic P is decomposed before burial and the DIP released to pore waters diffuses to the bottom water. A 1031 fraction of the liberated P is trapped by iron hydroxides or buried as authigenic minerals (e.g., carbonate 1032 1033 fluorapatite). Phosphorus deposited in sediments is a subject of decomposition and sink-switching. Three reactive phases, organic P (Porg), Fe-bound-sorbed P (PFe), and Ca-bound P (PCa), are considered in the 1034 CANOPS-GRB model. The burial of these species are redox-dependent: burial efficiency is affected by 1035

bottom water  $O_2$  concentration. Because of the sink-switching, sedimentary  $C_{org}/P_{reac}$ , rather than  $C_{org}/P_{org}$ ratios, provides a correct measure of the retention versus diffusive loss of remineralized P.

A schematic of benthic P cycling is shown in Fig. 9. The majority of organic matter delivered to the 1039 sediment-water interface is regenerated (Jahnke, 1996), but a fraction of DIP released via respiration to pore 1040 waters is redistributed to other phases such as iron-hydroxide or carbonate fluorapatite within the sediments. 1041 This mechanism is known as 'sink-switching' (e.g., (Anderson et al., 2001; Filippelli, 2001)), and results in 1042 1043 P burial other than organic P playing a more important role in the total P sink (Ruttenberg, 1993b, 2003; Compton et al., 2000). Three different P pools are considered in the CANOPS-GRB model: organic P (Porg), 1044 Fe-hydroxide-bound sorbed P ( $P_{Fe}$ ), and authigenic Ca-bound P ( $P_{Ca}$ ). The sum of these pools is defined as 1045 biologically reactive P (Preac) (bioavailable in the ocean to fuel primary productivity). The marine C and P 1046 cycles are coupled not only through the  $C_{org}/P_{org}$  ratio of POM ( $\alpha$ ) but also through the  $C_{org}/P_{reac}$  ratio of 1047 1048 marine sediments. It is important to note that as argued by Anderson et al. (2001), the fundamental measure 1049 of the retention versus diffusive loss of remineralized P is not the sedimentary Corg/Porg ratio, but the ratio of Corg/Preac. 1050

1051

1052 Field observations of marine and lacustrine sediments have revealed that the burial efficiency of P depends on the redox conditions of bottom waters (Ingall and Jahnke, 1994): Phosphorus retention potential is 1053 1054 suppressed under anoxic bottom water conditions. Elevated  $C_{org}/P_{reac}$  ratios observed in permanently anoxic environments suggest preferential regeneration of P relative to C under these conditions (Algeo and Ingall, 1055 1056 2007; Anderson et al., 2001; Colman et al., 2000; Filippelli, 2001; Ingall and Jahnke, 1997). In the 1057 CANOPS-GRB model, P benthic regeneration rate is calculated at each sediment segment based on the POP depositional flux density  $j_P^{dep}$  (= $j_{org}^{dep}/\alpha$ ) and P burial efficiency which is a function of both [O<sub>2</sub>]<sub>bw</sub> and SR. 1058 We assume the following formulation for the Corg/Porg ratio of the buried organic phase, on the basis of 1059 previous studies (Slomp and Van Cappellen, 2007; Van Cappellen and Ingall, 1994, 1996): 1060

$$\left(C_{\rm org}/P_{\rm org}\right)_{\rm b} = \begin{cases} \frac{\left(C_{\rm org}/P_{\rm org}\right)_{\rm b}^{\rm oxic}\left(C_{\rm org}/P_{\rm org}\right)_{\rm b}^{\rm anox}}{\left(C_{\rm org}/P_{\rm org}\right)_{\rm b}^{\rm axic}} f_{\rm r} & \text{for } \left[O_{2}\right]_{\rm bw} < oxic \\ \frac{\left(C_{\rm org}/P_{\rm org}\right)_{\rm b}^{\rm axic}}{\left(C_{\rm org}/P_{\rm org}\right)_{\rm b}^{\rm oxic}} + \left(1 - \frac{\left[O_{2}\right]_{\rm bw}}{\left(C_{\rm org}/P_{\rm org}\right)_{\rm b}^{\rm oxic}}} f_{\rm r} & \text{for } \left[O_{2}\right]_{\rm bw} < oxic \\ \frac{\left(C_{\rm org}/P_{\rm org}\right)_{\rm b}^{\rm oxic}}{\left(C_{\rm org}/P_{\rm org}\right)_{\rm b}^{\rm oxic}} f_{\rm r} & \text{for } \left[O_{2}\right]_{\rm bw} \ge oxic \end{cases}$$

$$\tag{49}$$

where (Corg/Porg)b<sup>oxic</sup> and (Corg/Porg)b<sup>anox</sup> denote organic C/P ratios for fully oxic and anoxic conditions, and 1061 oxic (=250  $\mu$ M) is a threshold value of [O<sub>2</sub>]<sub>bw</sub> below which preferential P regeneration occurs. (C<sub>org</sub>/P<sub>org</sub>)<sub>b</sub><sup>oxic</sup> 1062 is set to twice the value of the Redfield ratio, and (Corg/Porg)banox is an upper limit assumed for organic matter 1063 buried under fully anoxic overlying waters, estimated as 40 times larger than the Redfield value on the basis 1064 of previous studies on various ancient anoxic basin sediments (Slomp and Van Cappellen, 2007; Ingall et al., 1065 1066 1993). In Eq. (49), we also include the dependence of buried  $C_{org}/P_{org}$  ratio on SR, expressed as  $f_r$ . Modern observations suggest that SR is a one of the major factors influencing the preservation versus 1067 remineralization of sedimentary organic C and P. Organic C preservation in marine sediments tends to be 1068 enhanced at higher SR. In contrast, the Corg/Porg ratio of sedimentary organic matter shows a non-linear 1069 1070 relationship with respect to SR (Ingall and Cappellen, 1990) (Sect. 3.2.3), suggesting more complex 1071 behavior of benthic P cycling. Specifically, in the pelagic deep ocean, preferential P regeneration is not 1072 observed, likely due to the long timescale of diagenesis prior to burial (Ingall and Cappellen, 1990). In the CANOPS model,  $f_{\tau}$  is formulated as follows: 1073

$$f_{\tau} = 0.5 + 0.5 \exp\left(-\frac{0.001 \text{ cm}}{SR}\right).$$
 (50)

1074 Specifically, the  $C_{org}/P_{org}$  ratio approaches the Redfield value for oxygenated pelagic sediments. 1075

1076 The burial flux density of Porg can be calculated as the Corg burial flux density divided by (Corg/Porg)b:

$$j_{\text{Porg}}^{\text{b}} = \frac{j_{\text{org}}^{\text{b,con}}}{\left(C_{\text{org}}/P_{\text{org}}\right)_{\text{b}}}.$$
(51)

1077 The burial efficiency of Porg can be written as follows:

$$BE_{\text{Porg}} \equiv \frac{j_{\text{Porg}}^{\text{b}}}{j_{\text{p}}^{\text{dep}}} = \frac{j_{\text{Porg}}^{\text{b}}}{j_{\text{org}}^{\text{dep}}/\alpha} = \frac{\alpha BE_{\text{org}}}{j_{\text{Porg}}^{\text{b}}/j_{\text{Porg}}^{\text{b}}} = \frac{\alpha BE_{\text{org}}}{\left(C_{\text{org}}/P_{\text{org}}\right)_{\text{b}}},$$
(52)

where  $j_P^{\text{dep}}$  denotes the POP settling flux density to sediments, which is coupled to the C/P stoichiometry of POM (= $j_{\text{org}}^{\text{dep}}/\alpha$ ).

1080

1081 Under oxic bottom water conditions, remineralized organic P can be trapped efficiently at the sediment-

1082 water interface by ferric iron phases. In contrast, under anoxic bottom water conditions, a lack of ferric iron

phases allows most mineralized P to diffuse out of the sediment. This redox-dependent P burial is assumed to be linearly proportional to the  $[O_2]_{bw}$  (Slomp and Van Cappellen, 2007):

c

$$j_{\text{P-Fe}}^{\text{b}} = \begin{cases} BE_{\text{Porg}}^{\text{oxic}} \left( \frac{[O_2]_{\text{bw}}}{\text{oxic}} \right) j_{\text{Porg}}^{\text{dep}} \text{ for } [O_2]_{\text{bw}} < oxic \\ BE_{\text{Porg}}^{\text{oxic}} j_{\text{Porg}}^{\text{dep}} \text{ for } [O_2]_{\text{bw}} \ge oxic \end{cases},$$
(53)

where  $BE_{Porg}^{oxic}$  denotes the burial efficiency of P<sub>org</sub> under well-oxygenated bottom water conditions ([O<sub>2</sub>]<sub>bw</sub> 1086 > *oxic*). We assume that the retention potential of P<sub>Fe</sub> in <u>oxic</u>-sediments<u>overlain by oxic bottom waters</u> is 1087 comparable to that of P<sub>org</sub> (Ruttenberg, 1993a).

1088

Some authors have also proposed that authigenic P burial, the dominant process for P burial today (Ruttenberg, 1993a), depends on the redox conditions of the bottom water (Slomp and Van Cappellen, 2007; Slomp et al., 2002). In the CANOPS-GRB model, we adopt the following redox dependence used by Slomp and Van Cappellen (2007):

$$j_{P,Ca}^{b} = \begin{cases} 2BE_{Porg}^{oxic} \left( a_{auth} + \left(1 - a_{auth}\right) \frac{[O_2]_{bw}}{oxic} \right) j_{Porg}^{dep} \text{ for } [O_2]_{bw} < oxic \\ 2BE_{Porg}^{oxic} j_{Porg}^{dep} \text{ for } [O_2]_{bw} \ge oxic \end{cases}.$$
(54)

We assume that  $P_{org}$ ,  $P_{Fe}$  and  $P_{Ca}$  account roughly for 25%, 25%, and 50%, respectively, of the total reactive 1093 1094 P buried in oxygenated sediments (Ruttenberg, 1993a). Therefore, the burial efficiency of authigenic P phases is larger than that of Porg and PFe by a factor of 2. The redox-dependency of authigenic P burial is 1095 controlled by a parameter,  $a_{\text{auth}}$ . There is still great uncertainty as to the sensitivity of P retention efficiency 1096 of authigenic P phases to changing redox conditions. For instance, recent modeling study suggests that the 1097 burial of authigenic P is influenced not only by the redox state of bottom water, but also by the-seawater 1098 chemistry (especially Ca<sup>2+</sup>) (Zhao et al., 2020), temperature, and pH (Papadomanolaki et al. 2022). In our 1099 reference run, we set *a*<sub>auth</sub> at 1, *i.e.* no redox\_dependency for authigenic P burial. 1100

1101

1102 When above formulations are adopted, the ratio

$$\overline{C_{\text{org}}/P_{\text{reac}}} = \frac{\text{Marine } C_{\text{org}} \text{ burial rate}}{\text{Marine } P_{\text{reac}} \text{ burial rate}}$$
(55)

1103 varies between <u>63</u> and 370 as a function of ocean redox state. This is in the range of an estimation derived

1104 from various observations of modern and ancient sediments (Papadomanolaki et al. 2022; Algeo and Ingall,

1105 2007). Given that the continental shelves are a main locus of reactive P burial, the separate treatment of

1106 continental shelves and margin sediments from the pelagic ocean could affect the non-linearity of the redox-

1107 dependent P cycle. However, this was left as one of the subjects of future work.

## 1108 Nitrogen cycling

1109 The benthic denitrification rate is estimated with a semi-empirical relationship (Middelburg et al., 1996).

1110 Middelburg and colleagues performed a series of experiments (n = 2,000) with a 1-D early diagenetic model

1111 of C-N-O<sub>2</sub> to parameterize benthic denitrification  $j_{deni}^{sed}$  ( $\mu$ mol C cm<sup>-2</sup> d<sup>-1</sup>) as a polynomial function using

1112  $j_{\text{org}}^{\text{dep}}$  ( $\mu$ mol C cm<sup>-2</sup> d<sup>-1</sup>), z (m), and bottom water concentrations of dissolved O<sub>2</sub> and NO<sub>3</sub><sup>-</sup> ( $\mu$ M):

$$\log j_{\text{deni}}^{\text{sed}} = c_0 + c_1 \log j_{\text{org}}^{\text{dep}} + c_2 \left( \log j_{\text{org}}^{\text{dep}} \right)^2 + c_3 \log[\text{NO}_3^-]_{\text{bw}} \log[\text{O}_2]_{\text{bw}}$$
  
+  $c_4 \log[\text{NO}_3^-]_{\text{bw}} + c_5 \log[\text{O}_2]_{\text{bw}} + c_6 \log z + c_7 \log j_{\text{org}}^{\text{dep}} \log[\text{O}_2]_{\text{bw}}$ 

¥(56)

where  $c_0 = -2.2567$ ,  $c_1 = -0.1850$ ,  $c_2 = -0.2210$ ,  $c_3 = -0.3995$ ,  $c_4 = 1.2500$ ,  $c_5 = 0.4721$ ,  $c_6 = -0.0996$ ,  $c_7 = -0.0996$ , 1113 1114 0.4256. This polynomial function was obtained by examining a parameter space spanning 50 m < z < 6,000m, 10  $\mu M < [O_2]_{bw} < 350 \ \mu M$ , and 1  $\mu M < [NO_3]_{bw} < 60 \ \mu M$ .  $j_{org}^{dep}$  was allowed to vary within 2 orders of 1115 magnitude at each water depth (Middelburg et al., 1996). As pointed out by (Romaniello and Derry, 2010), 1116 the predicted contribution of denitrification to total decomposition  $f_{\text{denit}}$  (=  $j_{\text{denitr}}^{\text{sed}}/j_{\text{recy}}^{\text{sed}}$ ) can sometimes 1117 exceed 100% for  $[O_2]_{bw} < 10 \mu M$ . When the fraction of benthic denitrification to total decomposition exceeds 1118 90%, benthic denitrification is limited in order to avoid unphysical values (Ozaki and Tajika, 2013; 1119 Romaniello and Derry, 2010). 1120

1121

1122 The burial flux density of  $N_{org}$  is calculated by molar ratio of C to N of buried sediments,  $(C_{org}/N_{org})_b$ , and 1123 the burial flux of  $C_{org}$ :

$$j_{\text{Norg}}^{\text{b}} = \frac{j_{\text{org}}^{\text{b,cen}}}{\left(C_{\text{org}}/N_{\text{org}}\right)_{\text{b}}}$$
(56)(57)

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1124 We assumed an average ratio of 10, which is observed in the Washington and Mexico margin (Hedges et al.,

## 1126 Sulfur cycling

1127 The fractions of MSR and methanogenesis to total decomposition of organic matter in marine sediment are 1128 given by

$$f_{\rm MSR} = (1 - f_{\rm aerobic} - f_{\rm denitr}) \frac{[{\rm SO}_4^{2-}]_{\rm bw}}{[{\rm SO}_4^{2-}]_{\rm bw} + K_{\rm MSR}}, \qquad (58)$$

$$f_{\rm meth} = 1 - f_{\rm aero} - f_{\rm deni} - f_{\rm MSR}. \qquad (59)$$

1129 The production rate of hydrogen sulfide in sediment,  $j_{H2S}^{sed}$  (mol S m<sup>-2</sup> yr<sup>-1</sup>), is given by

$$j_{\rm H_2S}^{\rm sed} = \frac{1}{2} f_{\rm MSR} j_{\rm recy}^{\rm sed} + j_{\rm AOM} , \qquad (59)(6)$$

1130 where  $j_{AOM}$  denotes the production rate of sulfide via AOM:

$$j_{\rm AOM} = \frac{1}{2} f_{\rm meth} \frac{[SO_4^2]_{\rm bw}}{[SO_4^{-2}]_{\rm bw} + K_{\rm MSR}} j_{\rm recy}^{\rm sed}.$$
(60)(61)

- Here we assume that AOM is proportional to the CH<sub>4</sub> production rate with a sulfate-dependent term.
- 1133 The rate of pyrite precipitation in sediments would be proportional to the sulfide production rate at the 1134 sediment-water interface:

where the proportional coefficient,  $e_{pyr}$ , is the pyrite burial efficiency. The rate of MSR is a function of the marine redox state, [SO4<sup>2-</sup>], and the availability of degradable organic matter. In the well-oxygenated modern oceans most sulfide produced in sediments is reoxidized and only a few per cent of total sulfide is buried as pyrite (Canfield, 1991; Lin and Morse, 1991; Turchyn and Schrag, 2004; Bowles et al., 2014; Jørgensen, 1982). It has been pointed out that efficient oxidation of sulfide is promoted by animal bioturbation (Berner and Westrich, 1985; Canfield and Farquhar, 2009). In contrast, the value of  $e_{pyr}$  for anoxic sediments is much greater due to the absence of bioturbation and enhanced sulfide production. We assume that  $e_{pyr}$  asymptotes toward unity with decreasing the bottom water [O<sub>2</sub>] (Tarhan et al., 2015):

$$e_{\rm pyr} = e_{\rm pyr}^{\rm max} - \left(e_{\rm pyr}^{\rm max} - e_{\rm pyr}^*\right) \tanh[{\rm O}_2]_{\rm bw}, \qquad (62)(63)$$

where  $e_{pyr}^{max}$  (= 1 in our reference run) denotes the maximum pyrite precipitation efficiency in anoxic sediments. The reference value,  $e_{pyr}^*$ , was calibrated using a present-day control simulation such that the present-day seawater [SO<sub>4</sub><sup>2-</sup>] is ~29 mM. The obtained value of 0.117 is generally consistent with modern observations (Bottrell and Newton, 2006b; Tarhan et al., 2015; Turchyn and Schrag, 2006a) (see Sect. 3). Although our approach does not provide a mechanistic description of the complex process of pyrite precipitation, it is suitable for many purposes.

### 1149 Early diagenetic modeling for quantifying the OPD

A simple 1-D early diagenetic model of C and O<sub>2</sub> is employed to obtain the parameterization of OPD (Eq. (48)). The 100 cm thick sediment is vertically divided into 50 layers with an uneven grid. The grid size increases from the sediment-water interface ( $\Delta z = 0.25$  mm) to the maximum simulated sediment depth ( $\Delta z = 1.6$  cm). The diagenetic model calculates transport and biogeochemical transformation processes at each grid point within these sediment columns as well as the sedimentary burial and recycling fluxes at the model boundaries. The one-dimensional mass conservation equation for POC (wt. %) and dissolved O<sub>2</sub> is given by

$$\frac{\partial \text{POC}}{\partial t} = D_{\text{bio}} \frac{\partial^2 \text{POC}}{\partial z^2} - SR \frac{\partial \text{POC}}{\partial z} - k \text{POC}, \qquad (63)(64)$$

$$\frac{\partial [O_2]}{\partial t} = D_{O_2} \frac{\partial^2 [O_2]}{\partial z^2} - r_{O_2} k \text{POC} \left(\frac{\rho(1 \cdot \phi)}{1.2\phi}\right) \frac{[O_2]}{[O_2] + K_{O_2}}, \qquad (64)(65)$$

where  $D_{O2}$  is the diffusion coefficient of O<sub>2</sub>, *SR* is the sedimentation rate, and  $\phi$  is porosity, which is assumed to be constant over the entire sediment column for simplicity. Bioturbation is formulated as a diffusive process with a coefficient  $D_{\text{bio}}$ . The effective diffusion coefficient of O<sub>2</sub> is then given by

$$D_{O_2} = \frac{D_{O_2}^{T=0} \times \left(1 + \nu_{O_2} T_{bw}\right)}{\theta^2} + D_{bio}, \qquad (65)(66)$$

where  $D_{02}^{T=0}$  denotes a tracer diffusion coefficient in seawater of 0°C,  $v_{02}$  is a coefficient for temperature dependence of molecular diffusion coefficient. The in situ diffusion coefficient is further corrected for tortuosity  $\theta$ , which is related to pore water resistivity and porosity via the following expressions (Colman and Holland, 2000; Tromp et al., 1995; Berner, 1980):

$$\theta^2 = \phi F$$
 (66)(67)  
 $F = \phi^{-m}$  (67)(68)

where *F* is the formation factor—defined as the ratio of bulk sediment resistivity to interstitial water resistivity—and *m* is an empirical constant, varying with sediment type. We assumed the average value for unconsolidated muds (m = 2.7) in this work (Tromp et al., 1995). The particle mixing coefficient for bioturbation  $D_{\text{bio}}$  is formulated as a function of both sediment accumulation rate and bottom water O<sub>2</sub> concentration (Tromp et al., 1995; Wallmann, 2003b):

$$D_{\rm bio} = 10^{1.63+0.85\log SR} \frac{[O_2]_{\rm bw}}{[O_2]_{\rm bw} + K_{O_2}}.$$
(68)(69)

1168 At the bottom of the sediment column, a no-flux condition was applied. The parameters used in the 1-D 1169 early diagenetic model are tabulated in Table 6.

1170

1171 **Table 6.**- Parameters used in the 1-D early diagenetic model.

Parameters	Label	Value	Unit	Ref.
Porosity	$\phi$	0.8	-	
Dry bulk density	ρ	2.6	g cm <sup>-3</sup>	
O2:C ratio for aerobic respiration	$r_{O2}$	1.4	mol mol-1	
Half-saturation constant for aerobic respiration	$K_{O2}$	1	$\mu M$	
O2 diffusion coefficient at 0°C	$D_{\mathrm{O2}}{}^{\mathrm{T=0}}$	281	cm <sup>2</sup> yr <sup>-1</sup>	
Coefficient for a temperature dependence of molecular diffusion coefficient	V02	0.06	°C-1	
Exponent for the formation factor	т	2.7	-	

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# 1173 2.4.5 Air-sea exchange

1174 To calculate the gas exchange of  $O_2$ ,  $H_2S$ ,  $NH_3$ , and  $CH_4$  across the air–sea interface, we employed a 1175 stagnant film model (Liss and Slater, 1974). The flux of a gas X across the air–sea interface is controlled by

1176 the difference in partial pressure between the atmosphere and surface waters, which can be described by the 1177 following formula:

$$J_X^{\text{air-sea}} = v_X^{\text{pis}} \left( [X]_{\text{aq}} - [X]_{\text{sat}} \right), \tag{69)}$$

where  $v_X^{\text{pis}}$ ,  $[X]_{\text{aq}}$ , and  $[X]_{\text{sat}}$  denote piston velocity, the dissolved concentration of species *X*, and the saturation concentration of species *X*, respectively. For O<sub>2</sub>, the saturation concentration is calculated based on solubility (Garcia and Gordon, 1992; Sarmiento and Gruber, 2006) and partial pressure:

$$[\mathbf{O}_2]_{\text{sat}} = \left(\frac{1000}{22.3916}e^l\right) \left(\frac{p\mathbf{O}_2}{p\mathbf{O}_2^*}\right),\tag{70)}$$

1181 where

$$l = A_0 + A_1 T_s + A_2 T_s^2 + A_3 T_s^3 + A_4 T_s^4 + A_5 T_s^5 + S \times (B_0 + B_1 T_s + B_2 T_s^2 + B_3 T_s^3) + C_0 S^2, \tag{71)}$$

$$T_{\rm s} = \ln \left( \frac{298.15 - T}{273.15 + T} \right), \tag{72)(73)}$$

with *T* in °C. The constants are  $A_0 = 2.00907$ ,  $A_1 = 3.22014$ ,  $A_2 = 4.0501$ ,  $A_3 = 4.94457$ ,  $A_4 = -0.256847$ ,  $A_5 = 1.183$  3.88767,  $B_0 = -6.24523 \times 10^{-3}$ ,  $B_1 = -7.3761 \times 10^{-3}$ ,  $B_2 = -1.0341 \times 10^{-2}$ ,  $B_3 = -8.17083 \times 10^{-3}$ , and  $C_0 = -1.184$  4.88682×10<sup>-7</sup>. The erroneous  $A_3 \times T_s^2$  term in the original equation (Garcia and Gordon, 1992) was left out (Sarmiento and Gruber, 2006).

1186

1187 For CH<sub>4</sub>, H<sub>2</sub>S and NH<sub>3</sub>, [X]<sub>sat</sub> is given by (Kharecha et al., 2005)

$$[X]_{\text{sat}} = K_X^{\text{Henry}} pX, \qquad (73)(74)$$

1188 where  $K_X^{\text{Henry}}$ , and pX denote Henry's law coefficient and the partial pressure of species X, respectively. 1189 The temperature dependence of X's solubility is expressed as:

$$K_{\chi}^{\text{Henry}} = K_{\chi}^{\text{Henry}} \exp\left[K_{\chi}^{T}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right],$$
 (74)(75)

- where  $K_X^{\text{Henryo}}$  denotes the Henry's law coefficient of species X at 25°C, and  $K_X^T$  is the temperature dependence constant.
- 1192
- 1193 [X]<sub>aq</sub> is the dissolved concentration of X. [H<sub>2</sub>S]<sub>aq</sub> and [NH<sub>3</sub>]<sub>aq</sub> can be written as follows:

$$[\mathbf{H}_{2}\mathbf{S}]_{aq} = \frac{[\Sigma\mathbf{H}_{2}\mathbf{S}]}{1 + K_{\mathrm{H}_{2}\mathrm{S}}^{\mathrm{dis}}/[\mathbf{H}^{+}]}$$
(75)(76)

$$[NH_3]_{aq} = \frac{[\Sigma NH_3]}{1 + [H^+]/K_{NH_3}^{dis}}$$
(76)(77)

where  $[\Sigma H_2 S] = [H_2 S] + [HS^-]$  and  $[\Sigma NH_3] = [NH_4^+] + [NH_3]$ .  $K_{H2S}^{dis}$  and  $K_{NH3}^{dis}$  are the dissociation constant, defined as follows:

$$K_{\rm H_2S}^{\rm dis} = \frac{[\rm HS^{-}][\rm H^{+}]}{[\rm H_2S]_{\rm aq}}, \qquad (77)(78)$$

$$K_{\rm H_2S}^{\rm dis} = \frac{[\rm NH_3]_{aq}[\rm H^+]}{[\rm NH_4^+]} \cdot$$
(78)(79)

- Given values of  $K_{\text{H2S}}^{\text{dis}}$ ,  $K_{\text{NH3}}^{\text{dis}}$  and pH (Millero et al., 1988; Yao and Millero, 1995),  $[\text{H}_2\text{S}]_{aq}$  and  $[\text{NH}_3]_{aq}$ can be calculated.
- 1198

1199 In the CANOPS-GRB model, <u>aA</u>tmospheric concentrations of  $H_2S$  and  $NH_3$  are set at 0.  $H_2S$  and  $NH_3$  flow 1200 past the surface layer of the ocean to the atmosphere are converted to an equal influx of  $SO_4^{2-}$  and  $NO_3^{-}$  to 1201 the surface ocean. The parameters used in the stagnant film model are tabulated in Table 7.

1202

If atmospheric  $O_2$  levels are lower than ~1% PAL spatial heterogeneity of the gas exchange flux is expected (Olson et al., 2016); for example primary productivity (and  $O_2$  generation) would be more active in coastal regions than open-ocean gyres. Because our ocean model resolves only two regions for the surface oceans (low-mid latitude region L and high latitude region H), it tends to overestimate the oxidation of reductants in surface mixing layers. To mitigate this model limitation for the CH<sub>4</sub> degassing flux, the aerobic oxidation rate of CH<sub>4</sub> is decreased to  $1 \times 10^{-7}$  of the standard value in surface layers (Ozaki et al., 2019a).

12	10	Table 7	+ Parameters	used in the	he air-sea	exchange	module of	CANOPS-	GRB

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<b>D</b>	* 1 1	** 1	** •	
Parameters	Label	Value	Unit	Ref.
Piston velocity of O <sub>2</sub>	VO2 <sup>pis</sup>	1,000	m yr <sup>-1</sup>	This study
Piston velocity of NH <sub>3</sub>	V <sub>NH3</sub> <sup>pis</sup>	300	m yr-1	(Webbook
				, 2022)
Piston velocity of H <sub>2</sub> S	v <sub>H2S</sub> <sup>pis</sup>	1072	m yr <sup>-1</sup>	(Webbook
				, 2022)
Piston velocity of CH <sub>4</sub>	VCH4 <sup>pis</sup>	1419	m yr <sup>-1</sup>	(Webbook
				, 2022)
Solubility of NH3 at 25°C	$K_{ m NH3}^{ m Henry^\circ}$	$5.6 \times 10^{4}$	mol m-3 bar-1	
Solubility of H <sub>2</sub> S at 25°C	$K_{ m H2S}^{ m Henry^\circ}$	100	mol m <sup>-3</sup> bar <sup>-1</sup>	
Solubility of CH4 at 25°C	$K_{ m CH4}^{ m Henry^\circ}$	1.4	mol m-3 bar-1	
Temperature dependence of solubility of NH <sub>3</sub>	$K_{\rm NH3}{}^{\rm T}$	4,100	К	
Temperature dependence of solubility of $H_2S$	$K_{\rm H2S}{}^{\rm T}$	2,100	Κ	
Temperature dependence of solubility of CH <sub>4</sub>	$K_{\rm CH4}{}^{ m T}$	1,600	Κ	
Sea surface pH at low-mid latitude region	$p H^1$	8.17	-	This study
Sea surface pH at high latitude region	$p\mathrm{H}^{\mathrm{h}}$	8.16	-	This study
Partial pressure of atmospheric NH <sub>3</sub>	$pNH_3$	0	atm	This study
Partial pressure of atmospheric H <sub>2</sub> S	$pH_2S$	0	atm	This study

1211

## 1212 2.5 Land model

## 1213 2.5.1 Net primary productivity

1214 Terrestrial NPP is scaled by global land biomass *V* normalized to the modern value:

 $J_{\rm NPP}^{\rm Ind} = V \times J_{\rm NPP}^{\rm Ind,*}$ ,

<del>(79)<u>(</u>80)</del>

1215 where the present value of terrestrial NPP is set at 60 Gt C yr<sup>-1</sup> (Prentice et al., 2001). The global land

1216 biomass is a function of atmospheric  $O_2$  levels:

$$V = f_{\rm UV} f_{\rm fire} f_{\rm O_2}$$
,

<del>(80)</del>(81)

where  $f_{02}$  represents the direct effect of atmospheric O<sub>2</sub> concentration on the C<sub>3</sub> plant growth, and  $f_{\text{fire}}$ denotes the effect of fires on land biota (Bergman et al., 2004; Lenton and Watson, 2000b):

$$f_{O_2} = \max \left\{ 1.5 - 0.5 \, p O_2^{\text{PAL}}, 0 \right\}, \qquad (81)(82)$$

$$f_{\text{fire}} = \frac{k_{\text{fire}}}{k_{\text{fire}} - 1 + ignit}. \qquad (82)(83)$$

Here  $k_{\text{fire}}$  (= 3; (Lenton, 2013)) is the fire frequency constant, and *ignit* is an ignition factor representing the fire frequency as a function of oxygen (Lenton, 2013; Lenton et al., 2018; Lenton and Watson, 2000b):

$$ignit = \min \{\max \{c_1 p O_2 - c_2, 0\}, c_3\},$$
 (83)(84)

with  $c_1 = 48$ ,  $c_2 = 9.08$  and  $c_3 = 5$  (Lenton, 2013). CANOPS-GRB also includes an additional factor  $f_{UV}$ representing the effect of UV on the terrestrial biosphere as a function of atmospheric O<sub>2</sub> levels (Ozaki and Reinhard, 2021):

$$f_{\rm UV} = \tanh\left(\frac{pO_2^{\rm PAL}}{c_{\rm UV}}\right),\tag{84)(8)}$$

<del>84)(85)</del>

where  $c_{UV}$  is a model parameter, which, in our standard model is set at 1% PAL, meaning that terrestrial plant activity is suppressed when atmospheric O<sub>2</sub> is lower than a few % PAL.

### 1226 2.5.2 Terrestrial biogeochemical cycles

Phosphorus weathering flux,  $J_P^w$  (Eq. (2)), is treated as a boundary condition. A fraction of weathered P is ultimately buried as terrigenous organic matter (Eq. (3)), whereas the remaining fraction is delivered to the ocean via rivers (Eq. (4)). In the CANOPS-GRB model, the reference value of  $J_P^r$  (= 0.155 Tmol P yr<sup>-1</sup>) is tuned so that the oceanic P level of the reference state is consistent with modern observations. The burial rate of terrigenous organic matter (in terms of C) can be written as follows:

$$J_{\text{org}}^{\text{b,lnd}} = \left( C_{\text{org}} / P_{\text{org}} \right)^{\text{lnd}} J_{\text{P}}^{\text{b,lnd}}, \qquad (85)(86)$$

where  $(C_{org}/P_{org})^{lnd}$  (= 1000) is the average C/P burial ratio of terrigenous organic matter (Bergman et al., 2004). In this study, the reference value of  $J_{org}^{b,lnd}$  was set at 3 Tmol C yr<sup>-1</sup>. By combining Eqs. (3), (4), and 1234 (85) for the reference state, the proportional coefficient  $k_{11}$  of Eq. (3) is determined by the reference state, as 1235 follows:

$$k_{11} = \frac{J_{\rm org}^{\rm b.Ind,*}}{J_{\rm org}^{\rm b.Ind,*} + \left(C_{\rm org}/P_{\rm org}\right)^{\rm Ind}J_{\rm P}^{\rm r,*}} = 0.0189 \; .$$

1236 The value of  $k_{11}$  is treated as a constant in this study.

1237

Almost all organic matter produced by terrestrial NPP is decomposed before burial. The total decomposition rate is given by:

$$J_{\rm org}^{\rm r,Ind} = J_{\rm NPP}^{\rm Ind} - J_{\rm org}^{\rm b,Ind}$$
. (87)(88)

1240 CANOPS-GRB includes aerobic respiration and methanogensis as respiration pathways for terrigenous 1241 matter, and the CH<sub>4</sub> flux from the terrestrial ecosystem to the atmosphere is evaluated with the assumption 1242 that it is proportional to the burial rate of terrigenous organic matter:

where the reference value was set at 1 Tmol CH<sub>4</sub> yr<sup>-1</sup>. The net flux of CO<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub> from the terrestrial ecosystem to the atmosphere can be written, as follows:

$$J_{CO_{2}}^{\text{ind}} = \left(g_{O_{2}} + \frac{1}{2}(1+\delta)g_{CH_{4}}\right) J_{\text{org}}^{r,\text{ind}},$$

$$J_{O_{2}}^{\text{ind}} = J_{\text{NPP}}^{\text{ind}} - \left(g_{O_{2}} + \delta g_{CH_{4}}\right) J_{\text{org}}^{r,\text{ind}},$$

$$J_{CH_{4}}^{\text{ind}} = \frac{1}{2}(1-\delta)g_{CH_{4}}J_{\text{org}}^{r,\text{ind}},$$

$$(90)(91)$$

$$(91)(92)$$

1245 where  $g_{O2}$  and  $g_{CH4}$  denote the fraction of organic matter decomposed by aerobic respiration and 1246 methanogenesis, respectively.  $\delta$  represents the fraction of methane that is consumed by aerobic 1247 methanotrophy that is a function of O<sub>2</sub>:

(<u>88)(</u>89)

<del>(86)<u>(</u>87)</del>

$$\delta = \frac{M_{O_2}^{\text{atm}}}{M_{O_2}^{\text{atm}} + K_{O_2}}, \qquad (92)(93)$$

with  $K'_{02} = 0.273 \times 10^{18}$  mol (Goldblatt et al., 2006). A fraction of organic matter decomposed by methanogenesis,  $g_{CH4}$ , can be calculated based on Eqs. (89) and (91). Then,  $g_{02}$  is determined from 1- $g_{CH4}$ .

## 1250 2.5.3 Weathering

The oxidative weathering of continental crust is a major oxygen sink on geologic timescales, providing a fundamental control on atmospheric  $O_2$  levels. The weathering rate in the model is assumed to be proportional to sedimentary reservoir size and a global erosion factor,  $f_R$ , expressing the effect of continental denudation/erosion on terrestrial weathering:

$$J_{\text{org}}^{\text{w}} = f_{\text{R}} f_{\text{orgw}}^{O_2} \left( \frac{ORG}{ORG^*} \right) J_{\text{org}}^{\text{w},*}, \qquad (93)(94)$$
$$J_{\text{pyr}}^{\text{w}} = f_{\text{R}} f_{\text{pyrw}}^{O_2} \left( \frac{PYR}{PYR^*} \right) J_{\text{pyr}}^{\text{w},*}, \qquad (93)(94)$$

where  $J_{\text{org}}^{W}$  and  $J_{\text{pyr}}^{W}$  denotes the oxidative weathering of organic carbon and pyrite, respectively, and  $f_{\text{orgw}}^{O2}$ and  $f_{\text{pyrw}}^{O2}$  represent the O<sub>2</sub> dependency. For the oxidative weathering of organic matter, previous biogeochemical models have adapted a  $(pO_2^{\text{PAL}})^{0.5}$  relationship (Bergman et al., 2004; Lasaga and Ohmoto, 2002). In this study, we employ alternative empirical relationships based on results obtained from a 1-D weathering model (Bolton et al., 2006; Daines et al., 2017)<u>ENREF\_63</u>:

$$f_{\text{orgw}}^{O_2} = c_{\text{orgw}} \frac{pO_2^{\text{PAL}}}{pO_2^{\text{PAL}} + K_{\text{orgw}}},$$

$$f_{\text{pyrw}}^{O_2} = c_{\text{pyrw}} \frac{pO_2^{\text{PAL}}}{pO_2^{\text{PAL}} + K_{\text{orgw}}},$$
(95)(96)
(96)(97)

where  $K_{\text{orgw}}$  and  $K_{\text{pyrw}}$  denote half-saturation constants ( $K_{\text{orgw}} = 0.334$  and  $K_{\text{pyrw}} = 0.017$ ) and  $c_{\text{orgw}}$  and  $c_{\text{pyrw}}$ are normalized constants ( $c_{\text{orgw}} = 1.334$  and  $c_{\text{pyrw}} = 1.017$ ), respectively. The Monod-type relationship captures the fact that the rate of oxidative weathering reaches its maximum as determined by the erosion rate under highly oxygenated conditions (i.e., transport-limited regime). For example, due to the fast dissolution kinetics of pyrite, oxidative weathering can be regarded as transport-limited under modern conditions

- 1265 (Bolton et al., 2006) (Fig. 10). In the CANOPS-GRB model,  $J_{\text{org}}^{\text{w}^*}$  is calibrated based on the global redox 1266 budget of the reference run (see Sect. 2.2.5).
- 1267

1268 It is important to note that above equations ignore the possible importance of microbial activity and 1269 temperature on the rate of oxidative weathering (Petsch et al., 2001; Soulet et al., 2021). Both represent 1270 important topics for future research.

1271





**Figure 10**<sub>2</sub>  $O_2$  dependency of the oxidative weathering rate of organic matter and pyrite sulfur. Gray line denotes the  $(pO_2^{PAL})^{0.5}$  relationship assumed in previous biogeochemical models (Lasaga and Ohmoto, 2002; Daines et al., 2017). Solid and dashed black lines represent the empirical Monod-type relationships for oxidative weathering of organic matter (solid) and pyrite sulfur (dashed) based on the results obtained from a 1-D weathering model (Bolton et al., 2006; Daines et al., 2017), which are adopted in the standard model of the CANOPS-GRB model. PAL = present atmospheric level.

The present riverine flux of sulfur,  $J_{S}^{r^*}$ , is estimated at 2.6 Tmol S yr<sup>-1</sup> (Raiswell and Canfield, 2012), representing the dominant source to the oceans. Riverine flux is written as the sum of the gypsum weathering flux  $J_{gyp}^{w}$  and the oxidative weathering of pyrite  $J_{pyr}^{w}$  and depends directly or indirectly on the oxidation state of the atmosphere:

$$J_{\rm S}^{\rm r} = J_{\rm gyp}^{\rm w} + J_{\rm pyr}^{\rm w}$$
. (97)(98)

Based on previous studies (Berner, 2009; Wortmann and Paytan, 2012; Bergman et al., 2004; Markovic et al., 2015), a 3:1 ratio in modern rivers of  $SO_4^{2-}$  from gypsum versus pyrite weathering is assumed. Gypsum weathering flux is assumed to be proportional to its sedimentary reservoir size, *GYP*, and *f*<sub>R</sub>:

$$J_{gyp}^{w} = f_{R} \left( \frac{GYP}{GYP^{*}} \right) J_{gyp}^{w^{*}}, \qquad (98)(99)$$

1287 where \* represents the present value.

1288

In the previous version of the CANOPS (Ozaki et al., 2019a), oxidative weathering of pyrite was divided to biogenic and abiotic weathering fluxes. In this study, we simplify this (Eq. (94)). Also, oxidative weathering of Fe(II)-bearing minerals is ignored in this study, which simplifies the framework of the global  $O_2$  budget (Sect. 2.2.5).

### 1293 2.5.4 Volcanic degassing

Volcanic outgassing fluxes of carbon and sulfur are assumed to be proportional to their respective crustal reservoir sizes:

$$J_{\text{org}}^{\text{m}} = \left(\frac{ORG}{ORG^*}\right) J_{\text{org}}^{\text{m},*}, \qquad (99)(100)$$

$$J_{\text{pyr}}^{\text{m}} = \left(\frac{PYR}{PYR^*}\right) J_{\text{pyr}}^{\text{m},*}, \qquad (100)(101)$$

$$J_{\text{gyp}}^{\text{m}} = \left(\frac{GYP}{GYP^*}\right) J_{\text{gyp}}^{\text{m},*}. \qquad (101)(102)$$

We set the reference value of the volcanic outgassing flux of organic carbon,  $J_{\text{org}}^{\text{m},*}$ , at 1.25 Tmol C yr<sup>-1</sup> (Bergman et al., 2004). The estimates of modern volcanic fluxes of sulfur fall within the range of ~0.3–3 Tmol S yr<sup>-1</sup> (Kagoshima et al., 2015; Catling and Kasting, 2017; Raiswell and Canfield, 2012; Walker and Brimblecombe, 1985). We adopted a recent estimate of 0.8 Tmol S yr<sup>-1</sup> (Kagoshima et al., 2015).

#### 1300 2.5.5 Sedimentary reservoirs

1301 We extend the original model framework to the explicit calculation of the secular evolution of the

1302 sedimentary reservoirs, linking the biogeochemical cycles in the ocean-atmosphere system to the rock cycle.

1303 The mass balance equation for sedimentary organic carbon (*ORG*) can be written as follows:

$$\frac{dORG}{dt} = J_{\rm org}^{\rm b} - J_{\rm org}^{\rm w} - J_{\rm org}^{\rm m}, \qquad (102)(103)$$

where  $J_{\text{org}}^{b}$  denotes the sum of the burial rate of marine and terrigenous organic matter ( $J_{\text{org}}^{b,\text{ocn}} + J_{\text{org}}^{b,\text{lnd}}$ ), the primary source of sedimentary organic carbon. Primary outputs are oxidative weathering, volcanic outgassing and metamorphism. Previous estimates of the present reservoir size of *ORG* fall in the range of 1000–1300 Emol (1 E =10<sup>18</sup>) (Berner, 1989; Garrels and Perry, 1974; Mackenzie et al., 1993). We assumed 1250 Emol for the reference value of *ORG*.

1309

The sedimentary reservoir sizes of pyrite sulfur (*PYR*) and gypsum sulfur (*GYP*) are also written as the balance between the input (burial) and outputs (weathering and outgassing):

$$\frac{dPYR}{dt} = J_{pyr}^{b} - J_{pyr}^{w} - J_{pyr}^{m}, \qquad (103)(104)$$

$$\frac{dGYP}{dt} = J_{gyp}^{b} - J_{gyp}^{w} - J_{gyp}^{m}, \qquad (104)(105)$$

where  $J_{pyr}^{b,sed}$  represents the sum of pyrite precipitation rates in the water column and sediments,  $J_{pyr}^{b,wc}$  +  $J_{pyr}^{b,sed}$ . Previous estimates of present reservoir sizes of *GYP* and *PYR* fall in the range of 77–300 Emol and 155–300 Emol (Berner, 2006; Bottrell and Newton, 2006a; Yaroshevsky, 2006; Kump, 1989; Lasaga, 1989; Holser et al., 1989; Sleep, 2005; Schlesinger and Bernhardt, 2013), respectively. We adopted 200 Emol and 200 Emol for *GYP*<sup>\*</sup> and *PYR*<sup>\*</sup>.

## 1317 2.6 Atmosphere model

### 1318 2.6.1 Hydrogen escape

The rate of hydrogen escape is assumed to be diffusion-limited as it is today. Thus, the total concentration of all H-bearing compounds in the lower stratosphere determines the rate of hydrogen escape (Walker, 1977). For Proterozoic-Phanerozoic atmospheres, CH<sub>4</sub> appears to have been the dominant hydrogen-bearing species in the stratosphere, and the flux,  $J_{\text{Hesc}}$  (mol yr<sup>-1</sup>), is calculated as

$$I_{\rm Hesc} = s M_{\rm CH_4}^{\rm atm}$$

where  $M_{CH4}^{atm}$  denotes the abundance of CH<sub>4</sub> in the atmosphere (mol) and  $s = 3.7 \times 10^{-5} \text{ yr}^{-1}$  is a proportional coefficient (Goldblatt et al., 2006).

## 1325 2.6.2 Photochemistry

1326 CANOPS-GRB includes parameterized  $O_2-O_3-CH_4$  photochemistry that allows quantification of the 1327 abundances of atmospheric  $O_2$  and  $CH_4$ . The rate of oxidation of  $CH_4$  is calculated by the following 1328 empirical parameterization that was obtained from a 1-D photochemistry model (Claire et al., 2006):

$$J_{\rm CH_4ox} = k_{\rm CH_4ox} M_{\rm O_2}^{\rm atm} M_{\rm CH_4}^{\rm atm}, \qquad (106)(107)$$

(105)(106)

where  $M_{O2}^{\text{atm}}$  and  $M_{CH4}^{\text{atm}}$  denote the abundance of O<sub>2</sub> and CH<sub>4</sub> in the atmosphere (mol). The reaction rate  $k_{CH4ox}$  (mol<sup>-1</sup> yr<sup>-1</sup>) is expressed as a polynomial function of the reservoir sizes of O<sub>2</sub> and CH<sub>4</sub> (Ozaki and Reinhard, 2021):

$$gk_{CH_{4}ox} = \alpha_{0}^{j} + \alpha_{1}^{j} \cdot \varphi_{O_{2}} + \alpha_{2}^{j} \cdot \varphi_{O_{2}}^{2} + \alpha_{3}^{j} \cdot \varphi_{O_{2}}^{3} + \alpha_{4}^{j} \cdot \varphi_{O_{2}}^{4} + \alpha_{5}^{j} \cdot \varphi_{O_{2}}^{5} + \alpha_{6}^{j} \cdot \varphi_{O_{2}}^{6}$$

$$(107)(108)$$

where  $a_i^j$  are fitting coefficients for given atmospheric CH<sub>4</sub> levels and  $\varphi_{O2}$  is  $\log pO_2$  (in bar) (Supplementary Table 4 of Ozaki and Reinhard, 2021). The oxidation rate was evaluated using Fig. 3 of Claire et al. (2006), showing the oxidation rate as a function of  $pO_2$  and  $pCH_4$ . We took the relationship between  $k_{CH4ox}$  and  $pO_2$ for  $pCH_4$  of 10<sup>-6</sup>, 10<sup>-5</sup>, 10<sup>-4</sup>, 10<sup>-3</sup>, 2×10<sup>-3</sup> bar, and  $k_{CH4ox}$  is calculated as a function of  $pO_2$  and  $pCH_4$  with a log-linear interpolation method. Note that the default photochemical parameterization presented above limits the applicability of CANOPS-GRB v1.0 to Earth-like planets around the Sun-like host stars. Current work is focused on elaborating parameterized photochemistry across a wider range of spectral energy distributions.

#### 1339 2.6.3 Mass balance

lo

1340 CANOPS-GRB accounts for the atmospheric concentrations of  $O_2$  and  $CH_4$ . The atmospheric concentration 1341 of  $O_2$  is determined by the biogenic source (from the ocean and terrestrial ecosystems) and the consumption **書式を変更:** 蛍光ペン(なし)

through the series of oxidation reaction (the continental weathering of kerogen and pyrite, volcanicoutgassing, and photochemical oxidation of methane):

$$\frac{dM_{O_2}^{\text{atm}}}{dt} = J_{O_2\uparrow}^{\text{air-sea}} + J_{O_2\uparrow}^{\text{air-Ind}} - \left(J_{\text{Hesc}} + 2J_{\text{CH}_4\text{ox}}\right) - \left(J_{\text{org}}^{\text{w}} + J_{\text{org}}^{\text{m}}\right) - 2\left(J_{\text{pyr}}^{\text{w}} + J_{\text{pyr}}^{\text{m}}\right), \qquad (108)(109)$$

where  $M_{02}^{\text{atm}}$  denotes the mass of O<sub>2</sub> in the atmosphere (moles), and the first and second term on the righthand side represents the biogenic flux of O<sub>2</sub> from marine and terrestrial ecosystems. The third term denotes O<sub>2</sub> consumption via photochemistry, and the fourth and fifth terms are the O<sub>2</sub> consumption via organic C and pyrite S sub-cycles. Note that the hydrogen escape to space is represented as the O<sub>2</sub> sink, because the hydrogen escape via CH<sub>4</sub> followed by the oxidation of carbon to CO<sub>2</sub> is represented as:  $CH_4 + O_2 + h\nu \rightarrow 4H \uparrow + CO_2.$ (110)

 $CH_4 + 2O_2 + h\nu \rightarrow 2H_2O + CO_{2.}$ (111)

1350 Thus, the hydrogen escape to space represents the net gain of oxidizing power to the system (see Eq. (13)).
1351

- 1352 The abundance of CH<sub>4</sub> in the atmosphere,  $M_{CH4}^{atm}$ , is determined by input from the ecosystems and the
- 1353 consumption of CH<sub>4</sub> via photolysis, as well as by the hydrogen escape:

$$\frac{dM_{\rm CH_4}^{\rm atm}}{dt} = J_{\rm CH_4\uparrow}^{\rm air-sea} + J_{\rm CH_4\uparrow}^{\rm air-Ind} - \left(J_{\rm Hesc} + J_{\rm CH_4 ox}\right).$$

<del>(1)<u>(112)</u></del>

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1354 No abiotic CH<sub>4</sub> input via hydrothermal systems is included.

#### 1355 3 Validation against the modern global ocean

Here, a steady-state simulation mimicking the present-day condition was run to evaluate the overall performance of CANOPS-GRB. To do this, the ocean model was run until reaching the-steady state, assuming the present atmospheric  $O_2$  level and reference values of boundary fluxes (weathering and volcanic fluxes). The simulated circulation and biogeochemistry for the modern global ocean was compared with modern oceanographic observations from the Global Ocean Data Analysis Project (Key et al., 2015; Olsen et al., 2016).

#### 1362 3.1 Distribution of circulation tracers

Comparisons of model output with circulation tracers, such as potential temperature ( $\theta$ ) and radiocarbon 1363  $(\Delta^{14}C)$ , permit a test of the physical exchange scheme. Figure 11 depicts the simulated patterns of physical 1364 tracers with observational data. The physical circulation in the model generally agrees well with oceanic 1365 observations, although we note that model temperatures for low-mid latitudes above 1,000 m water depth 1366 tend to be higher than observed because temperature distribution in the real ocean is strongly controlled by 1367 vertical structure and advective processes that are not captured in our simple circulation scheme. Despite this 1368 model limitation, the modelled temperature distribution generally reproduces the observed distribution. The 1369  $\Delta^{14}$ C minimum in the model for the low-mid latitude region corresponds well with observations. The 1370 1371 modelled background radiocarbon for young deep waters (about  $-150\pm25\%$ ) is closer to the value for the Southern Ocean (approximately -150%) than for North Atlantic deep waters (approximately -80%), and old 1372 deep waters (-200±15‰) correspond to the South Pacific. We conclude that the simulated circulation tracers 1373 1374 generally match well with ocean data.



**Figure 11**<sub>2</sub> Simulated steady state depth-profiles of (**a**) potential temperature,  $\theta$ , (**b**) radio carbon,  $\Delta^{14}$ C, (**c**) DIP (dissolved inorganic phosphorus, PO<sub>4</sub><sup>3-</sup>), and (**d**) dissolved oxygen, O<sub>2</sub>. Solid and dashed white lines denote the simulated profiles for LD and HD regions, respectively. Simulation results are compared with the dataset from the Global Ocean Data Analysis Project (GLODAP) data base (GLODAPv2\_2019; (Key et al., 2015; Olsen et al., 2016)). The color represents the density of observational points.

### 1382 3.2 Ocean biogeochemistry

Having demonstrated that CANOPS-GRB's ocean circulation model does a reasonable job of representing water mass exchange, we next assess the performance of the oceanic biogeochemistry model by comparing its output to ocean biogeochemical data. Model-generated global fluxes and inventories of C, P, N and S cycles are summarized in Fig. 12. Those compare well with independent observational estimates. Below, we provide a brief discussion of globally-integrated biogeochemical flux estimates.

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**Figure 12** Schematics of the simulated material flow in the ocean for the reference run. (a) Organic carbon (in Gt C yr<sup>-1</sup>), (b) phosphorus (in Tmol P yr<sup>-1</sup>), (c) nitrogen (in Tg N yr<sup>-1</sup>), and (d) sulfur (in Tmol S yr<sup>-1</sup>). NPP<sub>ocn</sub> = oceanic net primary production. EX = export production.  $M_X$  = mass of X in the ocean.  $\tau_X$  = residence time of X in the ocean. Pmol = 10<sup>15</sup> mol.

### 1394 3.2.1 Distribution of nutrients and oxygen

1395 The simulated vertical profile of phosphate captures the characteristic features and values of observational 1396 data (Fig. 11c). More specifically, the distribution in the low-mid latitude region is more similar to that in 1397 the Pacific and Indian Ocean, and distribution of high-mid latitude region is similar to that in the Southern 1398 Ocean. This is a consequence of limiting high-latitude productivity (preformed DIP is 1.1  $\mu$ M) which results 1399 in higher concentrations in the ocean interior. The model dissolved O<sub>2</sub> profile for low-mid latitude shows a 1400 minimum of approximately 100  $\mu$ M at water depth of 1,000 m, corresponding to the oxygen minimum zone
(Fig. 11d). In contrast, dissolved O<sub>2</sub> for high-mid latitude sector (HD) shows a monotonically decreasing
trend. This is because of oxygen consumption via POM decomposition during downwelling.

# 1403 3.2.2 Carbon cycling

1412

1413

The marine export/new production in our model is 9.1 Gt C yr<sup>-1</sup> (8.36 Gt C yr<sup>-1</sup> at L and 0.74 Gt C yr<sup>-1</sup> at H). 1404 This is consistent with previously estimated global values of 8.5–12 Gt C yr<sup>-1</sup> (Dunne et al., 2007a; Laws et 1405 1406 al., 2000; Sarmiento and Gruber, 2006; Heinze et al., 2009). In particular, our estimate is close to the midpoint of the previously estimated range of 9.6±3.6 Gt C yr<sup>-1</sup> (Dunne et al., 2007b). This is a marked 1407 improvement from earlier studies with box models which have underestimated marine new production by a 1408 factor of 2 or more (Archer et al., 2000; Shaffer et al., 2008). Simulated global oceanic NPP is 45.5 Gt C yr<sup>-1</sup>. 1409 This is also consistent with the previous estimated range of 44-65 Gt C vr<sup>-1</sup> (Prentice et al., 2001; 1410 Woodward, 2007; Carr et al., 2006; Berelson et al., 2007). 1411



Figure 13. Simulated steady-state depth-profiles of organic C and reactive P flux density for the LD region. 1414 In (a), gray dots denote observations of depositional/settling flux density, whereas black dots represent 1415 observations of burial flux density compiled from literature survey (Baturin, 2007; Betts and Holland, 1991; 1416 1417 Colman et al., 2000; Lutz et al., 2002). Gray and black solid lines denote the simulated POC depositional and burial flux densities obtained from the reference run. (b) Gray dots denote the benthic P efflux density 1418 obtained from literature survey (Hartnett and Devol, 2003; Hensen et al., 1998; Ingall and Jahnke, 1994, 1419 1420 1997; Mcmanus et al., 1997; Colman et al., 2000; Schenau and De Lange, 2001; Zabel et al., 1998), whereas gray and black solid lines represent the simulated benthic P efflux density and burial flux density of reactive 1421

P obtained from the reference run. <u>The burial flux density of reactive P is not shown due to the sparseness of</u>
 <u>such observations.</u>
 1424

The global marine POC flux depends largely on water depth. Model-generated fluxes compare well with 1425 independent estimates of deposition, burial, and regeneration. The gray line in Fig. 13a shows the simulated 1426 sinking flux density of POC in the water column for LD region, compared with observations (Archer et al., 1427 2002; Betts and Holland, 1991; Lutz et al., 2002; Baturin, 2007). The preferential consumption of labile 1428 1429 compounds ( $G_1$  and  $G_2$ ) during the settling process leads to a continuous decrease in reactivity and therefore, remineralization rates from the surface ocean down to the deep. Our estimate lies well within the range of 1430 observations. The model tends to give lower fluxes than observed above 2,000 m water depth, and higher 1431 below 5,000 m water depth. This is probably because of the assumption of homogeneous productivity in the 1432 surface ocean. In the real ocean, oceanic productivity is generally greater at the continental margins than in 1433 the pelagic gyre regions (Lutz et al., 2002). This is a model limitation, but the simulated biological pump is 1434 sufficient to describe the general characteristics of global ocean biogeochemistry. 1435

1436

Of total exported POC, 91% (8.25 Gt C yr<sup>-1</sup>) is decomposed in the water column and the rest (0.85 Gt C yr<sup>-1</sup>) 1437 sinks to the sediment surface (Fig. 12a). The simulated global POC depositional flux is comparable not only 1438 with observational estimates of 0.93 Gt C yr<sup>-1</sup> (Muller-Karger et al., 2005) and 0.67 $\pm$ 0.48 Gt C yr<sup>-1</sup> for off-1439 shore regions (Dunne et al., 2007b), but also with an estimate using EMIC (0.87 Gt C yr<sup>-1</sup>) (Ridgwell and 1440 Hargreaves, 2007). The depositional fluxes of Corg in marginal (<2,000 m) and deep-sea sediments (>2,000 1441 m) are estimated at 0.58 Gt C yr<sup>-1</sup> and 0.27 Gt C yr<sup>-1</sup>, respectively. These estimates are slightly lower than 1442 previous estimates of 0.62–1.98 Gt C yr<sup>-1</sup> and 0.31–0.62 Gt C yr<sup>-1</sup> (Bohlen et al., 2012; Dunne et al., 2007a; 1443 Muller-Karger et al., 2005; Burdige, 2007). 1444

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In our standard run, benthic remineralization removes 7.9% of the exported POC (0.72 Gt C yr<sup>-1</sup>), equivalent of 84% of the global POC sedimentation rate. As a result, only 1.5% (0.135 Gt C yr<sup>-1</sup> or 11.3 Tmol C yr<sup>-1</sup>) of the global POC export production is ultimately buried in marine sediments. Our model demonstrates that much (91%) of the total burial occurs on the continental margins (<2,000 m water depth), where the settling flux and burial efficiency are relatively high. Previous studies (Dunne et al., 2007b; Muller-Karger et al., **書式を変更:** 蛍光ペン(なし)

2005) estimated a Corg burial rate of 0.29±0.15 Gt C yr<sup>-1</sup> and >0.06±0.06 Gt C yr<sup>-1</sup> at the margin. Our 1451 estimate of 0.123 Gt C yr<sup>-1</sup> lies between these values, whereas our estimate for the deep sea, 0.012 Gt C yr<sup>-1</sup>, 1452 is on the lower end of previous estimates of 0.012±0.02 Gt C yr<sup>-1</sup> (Dunne et al., 2007b) and 0.017±0.005 Gt 1453 C yr<sup>-1</sup> (Hayes et al., 2021). Also, (Sarmiento and Gruber, 2006; Hayes et al., 2021) estimated the burial rate 1454 below 1,000 m as 0.02±0.006 Gt C yr<sup>-1</sup>; our estimate of 0.019 Gt C yr<sup>-1</sup> is consistent with this. Combined 1455 with the prescribed burial rate of terrigenous Corg 0.036 Gt C yr<sup>-1</sup> (3 Tmol C yr<sup>-1</sup>), the total burial rate is 1456 calculated to be 0.17 Gt C yr<sup>-1</sup> (14.3 Tmol C yr<sup>-1</sup>). This is somewhat higher than previous estimates (Berner, 1457 1982; Burdige, 2005; Muller-Karger et al., 2005), but given the rather large uncertainty we consider it 1458 defensible. 1459

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Figure 14 shows OPD as a function of water depth. Although the benthic data could be biased towards highly specific environments, such as sediments underlying upwelling areas and continental margins, our estimates capture the general features of modern observations.

1464



**Figure 14.** Oxygen penetration depth (OPD) as a function of water depth. Color dots denote the observational data obtained from literature survey (Bradley et al., 2020; Donis et al., 2016; Nierop et al., 2017; Rowe et al., 2008; Mcmanus et al., 2005; Martin and Sayles, 2014; Pfeifer et al., 2002; Hyacinthe et al., 2001; Hartnett et al., 1998; Hedges et al., 1999; Morford and Emerson, 1999; Devol and Christensen,

1470 1993; Gundersen and Jorgensen, 1990; Sachs et al., 2009). Colors represent the  $O_2$  concentration of bottom 1471 water (Gray dots represents the unknown dissolved  $O_2$  concentration). The color represents the  $O_2$ 

1472 concentration of bottom water, [O2]bw, with grey dots for the unknown [O2]bw value. The simulated OPD

1473 obtained from the reference run is shown as a black line.

#### 1474

# 1475 3.2.3 Phosphorus cycling

The removal of phosphate from surface waters occurs through photosynthetic fixation by primary producers 1476 and subsequent export in the form of POP into deeper waters, where it is largely remineralized back into 1477 DIP. Through this process there is a vertical partitioning of DIP within the ocean with reduced surface 1478 concentrations. Phosphorus export production is 7.16 Tmol P yr<sup>-1</sup>, which is coupled with carbon according 1479 to the POM compositional ratio (C:P = 106:1 for our standard model). The remineralization in the water 1480 column (6.49 Tmol P yr<sup>-1</sup>) and total sedimentation rate (0.672 Tmol P yr<sup>-1</sup>) are also proportional to those of 1481 POC. In contrast, the benthic DIP flux is decoupled from the carbon flux. Figure 13b shows modelled DIP 1482 benthic efflux and burial flux together with observed fluxes. Some observational data showing a relatively 1483 large abyssal (4–6 km) benthic flux are from upwelling regions in the South Atlantic (Hensen et al., 1998). 1484 The deviation is therefore not critical for our globally averaged model. Our model gives the total benthic 1485 efflux of DIP as 0.517 Tmol P yr<sup>-1</sup>, which is roughly three times the riverine reactive P input rate. This is 1486 within the range of previous estimates of 0.05-1.25 Tmol P yr<sup>-1</sup> (Wallmann, 2003b; Wallmann, 2010b; 1487 Compton et al., 2000; Colman and Holland, 2000)\_ENREF\_25. 1488

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The preservation efficiency (here defined as burial flux divided by the export flux) of P is 2.1%. This is 1490 higher than that of organic carbon (1.5%), indicating that more P is trapped in marine sediments than might 1491 be expected from Redfield stoichiometry. In oxic marine sediments overlain by oxic bottom waters, a 1492 fraction of the DIP released to pore waters from POM decomposition can be absorbed by iron-oxyhydroxide 1493 or precipitated as authigenic fluorapatite (Fig. 9). Therefore, the global averaged  $C_{org}/P_{reac}$  ratio of buried 1494 sediments is generally less than the Redfield of 106 (approximately 65±25 based on observations; (Algeo 1495 and Ingall, 2007)). The modelled global average Corg/Preac ratio of buried sediment is 73, consistent with this. 1496 The P burial fluxes of organic P, Fe-bound P and authigenic P are estimated at 0.044 Tmol P yr<sup>-1</sup>, 0.032 1497 Tmol P yr<sup>-1</sup>, and 0.079 Tmol P yr<sup>-1</sup>, respectively. 1498

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The Corg/Porg ratio of burying organic matter shows a non-linear relationship with respect to sedimentation 1500 rate. The observed  $C_{org}/P_{org}$  ratios are generally greater than the Redfield value of 106, especially for 1501 sediments in oxygen minimum zones (OMZs), which are characterized by a high depositional flux of 1502 organic matter (Corg/Porg ratios up to 600 for the present open ocean) (Ingall and Cappellen, 1990). For 1503 example, the averaged Corg/Porg molar ratio at the Peru-Chile OMZ and Black Sea are 600, and the estimated 1504 burial ratio of sapropel S1 of Mediterranean Sea is in the range of 400-800 (Slomp et al., 2002). This reflects 1505 the preferential regeneration of P relative to C during microbial remineralization of marine organic matter 1506 and reflect the more labile nature of P-biochemicals relative to most non-phosphorus containing organic 1507 carbon compounds. Additional rationale for this observation is that P is preferentially targeted for 1508 remineralization to support subsequent biological productivity as an essential and potentially limiting 1509 nutrient. Our model demonstrates that we can reproduce the first-order relationship between Corg/Porg and 1510 sediment accumulation rate (Fig. 15). 1511

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The modelled marine DIP inventory is  $2.75 \times 10^{15}$  mol, consistent with the observational estimate of around 3×10<sup>15</sup> mol (e.g., (Delaney, 1998; Guidry et al., 2000)). Given the riverine reactive P input flux of 0.155 Tmol P yr<sup>-1</sup>, the phosphorus residence time is estimated at 18 kyr, which is also consistent with previous estimates of 20 kyr or shorter (Benitez-Nelson, 2000; Ruttenberg, 2003).

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- 1518





**Figure 15**<sub>2</sub>  $C_{org}/P_{org}$  ratios of buried sediments as a function of sedimentation rate. Black dots represent the observational data (Ingall and Cappellen, 1990). The simulated  $C_{org}/P_{org}$  ratios for the LD region obtained from our reference run is shown as a black line.

## 1524 3.2.4 Nitrogen cycling

Nitrogen export production is 1603 Tg N yr<sup>-1</sup>, which is coupled with carbon according to the C:N 1525 stoichiometry of organic matter. Simulated N fixation required for the N balance in the ocean is 180 Tg N 1526 yr<sup>-1</sup>, which is higher than the range of previous estimates of 110–150 Tg N yr<sup>-1</sup> (Luo et al., 2012; Gruber and 1527 Sarmiento, 1997; Galloway et al., 2004; Karl et al., 2002; Fowler et al., 2013; Duce et al., 2008; Deutsch et 1528 al., 2007), while a recent study (Großkopf et al., 2012) suggests a higher value of ~180 Tg N yr<sup>-1</sup>. This 1529 discrepancy is partly because atmospheric deposition is ignored in the CANOPS-GRB model, which 1530 contributes 25.8 Tg N yr<sup>-1</sup> (Wang et al., 2019). Gruber and Sarmiento (2002) (Gruber and Sarmiento, 2002) 1531 estimated the pre-industrial value of the total source of N as 188±44 Tg N yr<sup>-1</sup>. Our estimate of 196 Tg N yr<sup>-</sup> 1532 <sup>1</sup> is within this range. 1533

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Nitrogen fluxes in an oxic water column are tightly coupled with the  $C_{org}$  fluxes, whereas decoupling appears in suboxic environments. Simulated denitrification in the water column is 102 Tg N yr<sup>-1</sup>, within the

range of the observational estimates (50-150 Tg N yr<sup>-1</sup>) (Devries et al., 2012; Devries et al., 2013; Brandes 1537 and Devol, 2002; Gruber, 2008; Gruber and Sarmiento, 2002; Oschlies et al., 2008; Wang et al., 2019). 1538 Modelled benthic denitrification is  $62 \text{ Tg N yr}^{-1}$ , which is lower than the estimated range of  $90-300 \text{ Tg N yr}^{-1}$ 1539 (Devries et al., 2012; Devries et al., 2013; Brandes and Devol, 2002; Eugster and Gruber, 2012; Devol, 1540 2015; Wang et al., 2019) by a factor of 1.5-5, suggesting that further efforts are required to improve 1541 representation of this process. One possible explanation for this discrepancy is that our model is not 1542 sufficient to express benthic N cycling because we ignore localized upwelling regions (such as the eastern 1543 Tropical Pacific and the Arabian Sea) and coastal regions where benthic denitrification is significant POM 1544 decomposition pathway in favor of globally averaged parameterizations. The separate treatment of 1545 continental shelves and margin sediments from the pelagic ocean could improve this issue. We also ignore 1546 another denitrification mechanism: anaerobic ammonium oxidation (anammox), which will often play an 1547 important role in the loss of fixed nitrogen in marine sediments and pelagic anoxic zones (Karthäuser et al., 1548 2021; Kuypers et al., 2005). 1549

1550

The modelled DIN inventory is  $4.5 \times 10^5$  Tg N. Given the total source flux of 196 Tg N yr<sup>-1</sup>, the residence time of DIN is estimated at 2.3 kyr.

## 1553 3.2.5 Sulfur cycling

1554 MSR is a major early diagenetic pathway of carbon oxidation in organic-rich sediments deposited below oxygenated waters. For the standard run, aerobic oxidation is a dominant process in the water column, but 1555 MSR contributes 37% of benthic degradation. CANOPS-GRB estimates a global rate of benthic sulfate 1556 reduction at 11 Tmol S yr<sup>-1</sup>. This is lower than the previously reported value of gross MSR (40-75 Tmol S 1557 yr<sup>-1</sup>; (Canfield and Farquhar, 2009; Jørgensen and Kasten, 2006) but agrees better with net MSR (Bowles et 1558 al., 2014). Bowles et al. (Bowles et al., 2014) have estimated global net MSR at 6.2 Tmol S yr<sup>-1</sup> and 11.3 1559 Tmol S yr<sup>-1</sup> for z > 200 m depth and z > 0 m depth, respectively. Our estimate is within this range. MSR is 1560 most pronounced on the shelf where high fluxes of organic matter to the seafloor lead to shallow OPD, high 1561 sulfide production, and consequently high pyrite precipitation (Fig. 16). 1562





1564 Figure 16. MSR and pyrite burial flux density as a function of sedimentation rate. Gray and black dots depict observational data compilation of depth-integrated MSR flux density and pyrite burial flux density for 1565 normal (oxic) marine sediments (Berner and Canfield, 1989; Canfield, 1989; Raiswell and Canfield, 2012). 1566 The unit of sedimentation rate was converted from g cm<sup>-2</sup> yr<sup>-1</sup> to cm yr<sup>-1</sup> with assuming the dry bulk density 1567 of 2.5 g cm<sup>-3</sup> and porosity of 0.9. Solid lines are the results obtained from the reference run of the CANOPS-1568 GRB model. 1569

In the CANOPS-GRB model, pyrite burial efficiency e<sub>pyr</sub> (Sect. 2.3.4) for sediments underlying oxic bottom 1571 waters is set such that simulated seawater [SO4<sup>2-</sup>] of the reference run is consistent with the modern value of 1572 28.9 mM. The tuned value of 11.7% agrees well with observations suggesting that pyrite precipitation rate is 1573 1574 about 10-20% of the rate of MSR (Fig. 16). Our reference value is also consistent with other estimates of 11-20% (ref.(Bottrell and Newton, 2006a; Tarhan et al., 2015; Turchyn and Schrag, 2006b)). 1575

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The sulfate inventory of our reference state is  $39 \times 10^{18}$  mol. Given the total source flux of 3.4 Tmol S yr<sup>-1</sup>, 1577 the residence time of sulfate is 11.5 Myr. 1578

#### 3.3 Global oxygen cycling 1579

The global O<sub>2</sub> budget for our reference state is shown in Fig. 17. The simulated O<sub>2</sub> inventory in the ocean-1580 1581

burial represents a major O<sub>2</sub> source flux (marine = 11.3 Tmol O<sub>2</sub> equiv. yr<sup>-1</sup> and terrigenous = 3 Tmol O<sub>2</sub> equiv. yr<sup>-1</sup>). Pyrite burial and hydrogen escape to space contribute 2.6 Tmol O<sub>2</sub> equiv. yr<sup>-1</sup> and 0.001 Tmol O<sub>2</sub> equiv. yr<sup>-1</sup>, respectively. Given the total source/sink flux of 16.9 Tmol O<sub>2</sub> yr<sup>-1</sup>, the residence time of O<sub>2</sub>= in the ocean-atmosphere system of our reference state is estimated as 2.26 Myr, which is consistent with previous estimates of 2–4 Myr (Berner, 1989; Berner, 2004a; Garrels and Perry, 1974).



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**Figure 17**<sub>2</sub> Schematics of global redox (O<sub>2</sub>) budget for the reference run. Arrows represent the O<sub>2</sub> flux in terms of  $10^{12}$  mol O<sub>2</sub> equiv. yr<sup>-1</sup>. PAL = present atmospheric level. Pmol =  $10^{15}$  mol. Emol =  $10^{18}$  mol. ORG sedimentary organic carbon. PYR = sedimentary pyrite sulfur.

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## 1591 4 Sensitivity experiment

Based on the results obtained above, we conclude that the CANOPS-GRB model is sufficient to describe basic biogeochemical characteristics in the modern ocean-atmosphere system. As a next step, we assess the dynamic response of the full model by performing sensitivity experiments with respect to P availability in surface environments.

## 1596 4.1 Dynamic response to changes in P weathering

Here, we conduct a sensitivity experiment with respect to the P weathering rate in order to see how the atmospheric and oceanic  $O_2$  levels respond to changes in P availability in the exogenic system over a wide range of timescales. Specifically, we performed four simulations, varying the values of  $f_P$  in Eq. (2) over two orders of magnitude. The reference state presented in the previous section is assumed for the initial condition, and the full model is allowed to evolve freely for three billion model years. These experiments demonstrate how P availability in surface environments affects global biogeochemical cycles and redox states of the atmosphere and oceans over a diverse range of timescales.

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The simulated transient response is shown in Fig. 18. As expected, lower P availability leads to <u>a</u> lower oceanic P inventory (Fig. 18a), resulting in suppressed biological productivity in the ocean (Fig. 18b). Given the residence time of P in the ocean (20 kyr, see Sect. 3.2.4), these responses occur within  $10^5$  yr. The suppressed biological productivity leads to a decline of burial rate of organic matter in sediments (Fig. 18c). Specifically, 10% and 1% of  $f_P$  give rise to the burial rate of marine  $C_{org}$  of 1 Tmol C yr<sup>-1</sup> and 0.13 Tmol C yr<sup>-1</sup> at  $10^5$  yr, respectively (cf. the reference value of 11.3 Tmol C yr<sup>-1</sup>).

On the timescales of  $10^5-10^6$  yr, the system reaches a quasi-steady state, but there is still a large redox imbalance due mainly to the suppression of C<sub>org</sub> burial (Fig. 18i). This gives rise to deoxygenation of the atmosphere on a time scale of millions of years (Fig. 18d). Note that once the ocean interior becomes anoxic, the enhanced P recycling and preservation of organic matter in anoxic marine sediments tend to buffer the atmospheric deoxygenation (Figs. 18a and c). However, these passive responses do not alter the fundamental behavior: lower P availability results in lower atmospheric O<sub>2</sub> levels. After atmospheric deoxygenation (>~4

<sup>1611</sup> 

1618 Myr), the system again reaches its quasi-steady state. Specifically,  $f_P$  values of 10% and 1% result in 1619 atmospheric O<sub>2</sub> levels of 9% PAL and 0.6% PAL, respectively.



**Figure 18**<sub>2</sub> Biogeochemical responses obtained from the CANOPS-GRB model with different values of P availability,  $f_P$ . (a) Oceanic phosphate inventory,  $M_P$ . (b) Oceanic net primary production (NPP<sub>ocn</sub>). (c) Burial rate of organic carbon (C<sub>org</sub>) in marine sediments. (d) Atmospheric partial pressure of O<sub>2</sub>. PAL = present atmospheric level. (e) Atmospheric CH<sub>4</sub> mixing ratio. (f) Sulfate concentration in the surface ocean layer. (g) Sedimentary reservoir size of pyrite sulfur, *PYR*. (h) Sedimentary reservoir size of organic carbon, *ORG*. (i) Global redox budget, *GRB*. For the  $f_P = 1\%$  run (redblack line), the calculation stopped when the atmospheric O<sub>2</sub> level decreased to ~10<sup>-5</sup> PAL due to the numerical instability.

The following change is driven by the response of oceanic S cycle, which is characterized by the long 1629 residence time of 11.5 Myr (see Sect. 3.2.6). Ocean anoxia promotes the MSR and subsequent precipitation 1630 of pyrite in the ocean interior. However, our model demonstrates that the decline of seawater  $SO_4^{2-}$  on a 1631 timescale of tens of millions of years is small (Fig. 18f), because the rate of MSR depends not only on the 1632 oceanic redox state but on the availability of organic matter for the MSR. The significant reduction of 1633 seawater  $SO_4^{2-}$  occurs on the longer timescales (>100 Myr) for extremely low  $f_P$  scenarios (0.016 and 0.01), 1634 in which atmospheric  $O_2$  levels decrease to <1% PAL. These scenarios also accompany with a growth of 1635 sedimentary S from gypsum to pyrite (Fig. 18g). 1636

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1638 On longer timescales, sedimentary reservoirs affect the redox state of the atmosphere and oceans. The 1639 present result demonstrates that  $f_P$  of 1% finally leads to the catastrophic decrease in atmospheric O<sub>2</sub> level at 1640 around 0.9 billion years (Fig. 18d). The simulation was stopped at this point due to the numerical instability. 1641 For other scenarios, the system reaches a new steady state after roughly three billion model years.

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Biogenic CH<sub>4</sub> production tends to be enhanced in the anoxic oceans. However, the present result demonstrates that CH<sub>4</sub> degassing to the atmosphere is inhibited by both limited availability of organic matter for methanogenesis and the anaerobic oxidation of CH<sub>4</sub> by  $SO_4^{2-}$ . Once the seawater [ $SO_4^{2-}$ ] decreases below 1 mM, CH<sub>4</sub> can escape from oceans to the atmosphere, promoting the buildup of CH<sub>4</sub> in the atmosphere. Nevertheless, because of the limited biological activity, atmospheric CH<sub>4</sub> levels <u>remainare</u> comparable to the modern value (~1 ppmv) (Fig. 18e).

# 1649 4.2 O2 budget for the less oxygenated scenario

Figure 19 shows the O<sub>2</sub> budget of the less oxygenated state ( $f_P = 1.6\%$  scenario). Because P availability exerts a primary control on biospheric O<sub>2</sub> production, the strongly suppressed P delivery to the ocean leads to low oceanic P levels and commensurately low biological productivity (0.08 Pmol and 1.3 Gt C yr<sup>-1</sup>, respectively). As a consequence, the atmospheric O<sub>2</sub> level is low (0.75% PAL). In this scenario the ocean interior is globally anoxic, and the preservation of organic C in marine sediments is enhanced. However, the

suppressed biological productivity results in a low overall burial rate of organic C (0.9 Tmol O<sub>2</sub> equiv. yr<sup>-1</sup>; 1655  $\sim 9\%$  of the reference value). When combined with the burial rate of terrigenous organic C, total O<sub>2</sub> 1656 production by the organic C sub-cycle is 0.97 Tmol  $O_2$  equiv. yr<sup>-1</sup>. This  $O_2$  source is balanced by the sum of 1657 oxidative weathering and metamorphism. The role of the pyrite S sub-cycle in the global redox budget is 1658 also shown in Fig. 19. Most of the  $SO_4^{2^2}$  entering the anoxic ocean is buried as pyrite, representing a major 1659  $O_2$  source (2.64 Tmol  $O_2$  equiv. yr<sup>-1</sup>). This  $O_2$  source is balanced by oxidation of sedimentary pyrite S 1660 through weathering (1.33 Tmol O<sub>2</sub> equiv. yr<sup>-1</sup>) and metamorphism (1.31 Tmol O<sub>2</sub> equiv. yr<sup>-1</sup>). In other words, 1661 the O<sub>2</sub> budget for the weakly-oxygenated Earth system is largely controlled-affected by the crustal S sub-1662 cycle. This is in marked contrast to the well-oxygenated Earth system, on which the O<sub>2</sub> budget is mainly 1663 controlled by organic C sub-cycle. 1664

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The present result demonstrates that low atmospheric O<sub>2</sub> states (~1% PAL) can be achieved in scenarios where the availability of P is strongly limited. However, a slight decrease of  $f_P$  to 1% leads to the destabilization of global O<sub>2</sub> budget, providing implications for the stability and evolution of atmospheric O<sub>2</sub> levels during the Proterozoic. This point will be further systematically examined in future work.



**Figure 19.** Schematics of global redox (O<sub>2</sub>) budget for the  $f_P = 1.6\%$  (=10<sup>-1.8</sup>) run. Arrows represent the O<sub>2</sub> flux in terms of 10<sup>12</sup> mol O<sub>2</sub> equiv. yr<sup>-1</sup>. PAL = present atmospheric level. Pmol = 10<sup>15</sup> mol. Emol = 10<sup>18</sup> mol. Gt C = 10<sup>15</sup> g C. ORG = sedimentary organic C. PYR = sedimentary pyrite S.

## 1676 5 Discussion

The reference run under the present condition demonstrates generally good agreement with modern 1677 observations (Sect. 3). The water circulation scheme provides an adequate representation of general ocean 1678 circulation, resulting in robust and reliable tracer distributions that are comparable to the modern 1679 observations. This provides a mechanistic foundation for simulating generalized ocean biogeochemical 1680 cycles. The ocean biogeochemistry module includes a series of biogeochemical processes in oxic-anoxic-1681 sulfidic environments. The reference run gives rise to the distributions of nutrients and dissolved O<sub>2</sub> that 1682 1683 capture fundamental properties observed in the modern ocean. Integrated biogeochemical fluxes of the global ocean, such as biological productivity, material flow in the water column, and burial into sediments 1684 are also consistent with observational data. In our reference run the estimated organic carbon burial and 1685 oxidative weathering fluxes are relatively high compared to some previous estimates, though there remains 1686 1687 significant uncertainty in globally integrated organic carbon weathering and burial fluxes. Further work will also be needed to better quantify the biogeochemical cycling in the continental shelf, which is a major locus 1688 of organic matter burial. In addition, sSome future developments to the N cycle may be needed, especially 1689 with regard to denitrification (e.g., anammox, coastal benthic denitrification). Nevertheless Despite of these 1690 remaining challenges, our ocean-biogeochemical model is adequate for representing the general property of 1691 the coupled C-N-P-O<sub>2</sub>-S cycles. 1692

1693

A new scheme for oxidative weathering of organic matter and pyrite sulfur, mass balance calculation of  $O_2$ in the atmosphere, and time evolution of sedimentary reservoirs are explicitly included in the CANOPS-GRB model. These are a significant improvement from the previous versions of CANOPS (Lenton, 2020). The simplified framework for the global  $O_2$  budget is also useful to understand the response of complex biogeochemical systems. The computational efficiency of our CANOPS-GRB model allows us to conduct simulations over billions of model years with reasonable wall times (on the order of weeks), providing a useful tool for exploring the wide range of topics about the oxygenation history of Earth's atmosphere.

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Sensitivity experiments with respect to the terrestrial weathering rate of P were conducted in order to see how the redox state of the ocean-atmosphere system responds to varying P availability in the surface system 1704 (Sect. 4). The CANOPS-GRB model appears to adequately simulate the biogeochemical dynamics over a 1705 wide range of timescales and is applicable for quantitative assessment of the evolution and stability of 1706 Earth's  $O_2$  cycling. Perhaps even more importantly, our results encourage us to perform further systematic 1707 examinations with Earth system models which have different complexities. Such an 'Earth system model 1708 intercomparison' would be a critical step towards better mechanistic understanding of the stability and 1709 dynamics of atmospheric  $O_2$  levels over Earth's history.

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Due to a lack of explicit Fe cycling and anaerobic metabolisms (such as anoxygenic photosynthesis), the 1711 current version of the model cannot be applicable for the simulation under the Archean-like weakly-1712 oxygenated ( $pO_2 < 10^{-5}$  PAL) conditions. These topics are left to future studies, but it would be an achievable 1713 goal (Ozaki et al., 2018; Ozaki et al., 2019b; Van De Velde et al., 2021). The model design presented here 1714 also ignores the interaction between the surface system and the mantle (e.g., subduction) except for the 1715 degassing of reducing gases from the mantle. We note, however, that the surface-mantle interaction would 1716 1717 have exerted a primary control on the long-term redox budget of Earth's surface system through the Earth's history (Canfield, 2004; Eguchi et al., 2020; Hayes and Waldbauer, 2006) and may be important for the 1718 discussion about the distant future (Ozaki and Reinhard, 2021). The importance of mantle and solid Earth 1719 controls on surficial environments is a crucially important topic for future research. 1720

1721

1722 The CANOPS-GRB model has the basic capability to simulate the time evolution of the abundance of

1723 <u>atmospheric biosignature gases</u> ( $O_2$  and  $CH_4$ ), on a wide range of timescales. While the biogeochemical

1724 model is based on process studies to the extent possible, many processes are derived from empirical

calibrations to Earth-like planets around sun-like stars. Clearly, some these parameterizations, such as the

1726 photochemical parameterization among  $O_2$ - $O_3$ - $CH_4$  (Eq. 107), must be modified when applying the model to

1727 <u>a range of habitable Earth-like exoplanets.</u>

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# 1728 6 Conclusions

A new Earth system box model was developed\_-\_\_CANOPS-GRB v1.0. The new code release provides an 1729 improved description of the coupled C-N-P-O<sub>2</sub>-S biogeochemical cycles in the ocean-atmosphere-crust 1730 system, which can be utilized to examine the dynamics and stability of Earth's O<sub>2</sub> cycle over a wide range of 1731 timescales. The computational efficiency and simple model design of CANOPS-GRB make it relatively easy 1732 to modify existing processes or add entirely new processes and components. CANOPS-GRB is thus a new 1733 and uniquely flexible tool capable of providing a coherent mechanistic framework for quantifying the 1734 1735 biogeochemical cycles regulating Earth's O<sub>2</sub> cycle. CANOPS-GRB is also a useful tool for the development of more comprehensive, low- to intermediate-complexity Earth system box models of biogeochemistry. 1736

CANOPS-GRB-\_will-provides an important step forward when coupled to new and existing geochemical 1738 proxy data. The accumulating geological/geochemical records have led to new hypothesis for the evolution 1739 1740 of atmospheric O<sub>2</sub> levels on Earth. CANOPS-GRB was designed to facilitate simulation of a wide range of past conditions so as to permit more explicit testing of hypothesis about the function of biogeochemical 1741 cycles and its effect on the redox budget through Earth history. Through the model-data synergy, CANOPS-1742 GRB has a great potential to provide an integrated, quantitative, and statistically informative picture of 1743 biogeochemical states, opening new perspectives on a wide range of scientific questions in research seeking 1744 to understand the Earth's chemical evolution, and in particular the cause-and-effect relationships with 1745 evolving biosphere. 1746

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CANOPS-GRB also provides significant steps forward in our predictive understanding of the links between 1748 geology, biogeochemistry, and the evolution of Earth's biosphere. It will allow for a fundamentally new and 1749 more precise quantitative understanding of evolving atmospheric biosignatures  $(O_2, O_3, CH_4)$  on Earth, and 1750 will broaden the interpretive power of Earth system evolution in the search for life beyond our planet. 1751 1752 Additional elaboration of the CANOPS-GRB code could represent an important avenue for be a central piece for developing a more robust tool for diagnosing atmospheric biosignatures for future analysis of 1753 extrasolar worlds. In sum, it is anticipated that CANOPS-GRB will have many applications for problems 1754 linking the coupled evolution of life and the atmosphere on Earth and habitable rocky exoplanets. 1755

Code availability. The bulk of CANOPS-GRB is written in Fortran as a stand-alone model. The model code can be found at GitHub (doi:10.5281/zenodo.5893804(URL). This model is still undergoing regular development and it is recommended that potential users contact the corresponding author (Kazumi Ozaki; kazumi.ozaki@sci.toho-u.ac.jpozaki.k.ai@m.titech.ac.jp) to obtain the latest version. The CANOPS GRB eode is provided freely but with the requirement that prospective users contact the corresponding author with their research plans to avoid parallel projects emerging. Author contribution. KO designed the study, wrote the code, and ran model simulations. DBC and CTR contributed to code debugging. KO wrote the manuscript, with inputs from DBC, CTR, and ET. Competing interests. The authors declare that they have no conflict of interest. Acknowledgements. This work was supported by JSPS KAKENHI Grant Number JP16K05618, 19K21055, and JP20K04066. CTR acknowledges the NASA Exobiology Program (Grant Number 80NSSC19K0461) and the NASA Interdisciplinary Consortia for Astrobiology Research (ICAR) (Grant Number 80NSSC21K0594).

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