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

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Abstract

A new version of the Earth system model of intermediate complexity (CANOPS-GRB) was developed for use in quantitatively assessing the dynamics and stability of atmospheric and oceanic chemistry over geologic timescales. The new release is designed to represent the coupled major element cycles of C, N, P, O, and S, as well as the global redox budget (GRB) in Earth's exogenic (ocean-atmosphere-crust) system, using a process-based approach. This framework provides a mechanistic model of the evolution of atmospheric and oceanic O_2 levels on geologic timescales and enables comparison with a wide variety of geological records to further constrain the processes driving Earth's oxygenation. A complete detailed description of the resulting Earth system model and its new features are provided. The performance of CANOPS-GRB is then evaluated by comparing a steady-state simulation under present-day conditions with a comprehensive set of oceanic data and existing global estimates of bio-element cycling. The dynamic response of the model is also examined by varying phosphorus availability in the exogenic system. CANOPS-GRB reliably simulates the short- and long-term evolution of the coupled C-N-P-O_2-S biogeochemical cycles and is generally applicable across any period of Earth's history given suitable modifications to boundary conditions and forcing regime. The simple and adaptable design of the model also makes it useful to interrogate a wide range of problems related to Earth's oxygenation history and Earth-like exoplanets more broadly. The model source code is available on GitHub, and represents a unique community tool for investigating the dynamics and stability of atmospheric and oceanic chemistry on long timescales.

Short summary:

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

1 Introduction

A quarter century has passed since the first discovery of exoplanets (Mayor and Queloz, 1995). In the next quarter century, a full-scale search for signs of life—biosignatures—on Earth-like exoplanets is one of the 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 of signatures that require biological activity for their origin (Des Marais et al., 2002; Lovelock, 1965; National Academies of Sciences and Medicine, 2019; Sagan et al., 1993; Schwieterman et al., 2018), but atmospheric composition has received the most interdisciplinary attention since the dawn of the search for life beyond our own planet (Hitchcock and Lovelock, 1967; Lovelock, 1972, 1965, 1975; Sagan et al., 1993) because of its potential for remote detectability. Indeed, it is likely that deciphering of exoplanetary 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 composition cannot immediately answer the question of the presence or absence of a surface biosphere 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 lack of robust theoretical and quantitative frameworks for the emergence and maintenance of remotely detectable atmospheric biosignatures in the context of planetary biogeochemistry.

It is also important to emphasize that the abundance of atmospheric biosignature gases of living planets will evolve via an intimate interaction between life and global biogeochemical cycles of bio-essential elements across a range of timescales. Indeed, the abundances of biosignature gases such as molecular oxygen (O_2) and

55 methane (CH_4) in Earth's atmosphere have evolved dramatically through coevolutionary interaction with

56 Earth's biosphere for nearly 4 billion years—through remarkable fluctuations in atmospheric chemistry and

57 climate (Catling and Kasting, 2017; Catling and Zahnle, 2020; Lyons et al., 2014). To the extent that the

58 coupled evolution of life and the atmosphere is a universal property of life-bearing planets that maintain robust

59 atmospheric biosignatures, the construction of a biogeochemical framework for diagnosing atmospheric

60 biosignatures should be a subject of urgent interdisciplinary interest.

61

62 Establishing a mechanistic understanding of our own planet's evolutionary history is also an important

63 milestone for the construction of a search strategy for life beyond our solar system, as it provides the first step

64 towards understanding how remotely detectable biosignatures emerge and are maintained on a planetary scale.

65 While numerous atmospheric biosignature gases have been proposed, the most promising candidates have

66 been 'redox-based' species, such as O_2, ozone (O_3), and CH_4 (Krissansen-Totton et al., 2018; Meadows, 2017;

67 Meadows et al., 2018; Reinhard et al., 2017a). In particular, O_2 is of great interest to astrobiologists because

68 of its crucial role in metabolism on Earth. Thus, a considerable effort has been devoted over recent decades to

69 quantitatively and mechanistically understand Earth's oxygenation history. In particular, a recent surge in the

70 generation of empirical records for Earth's redox evolution has yielded substantial progress in our 'broad

71 stroke' understanding of Earth's oxygenation history and has shaped our view of biological evolution (Kump,

72 2008; Lyons et al., 2014). One of the intriguing insights obtained from the accumulated geochemical records

73 is that atmospheric O_2 levels might have evolved more dynamically than previously thought—our current

74 paradigm of Earth's oxygenation history suggests that atmospheric O_2 levels may have risen and then

75 plummeted during the early Proterozoic, then remained low (probably <10% of the present atmospheric level;

76 PAL) for much of the ~1 billion years leading up to the catastrophic climate system perturbations and the

77 initial diversification of complex life during the late Proterozoic.

78

79 The possibility of low but 'post-biotic' atmospheric O_2 levels during the mid-Proterozoic has important

80 ramifications not only for our basic theoretical understanding of long-term O_2 cycle stability on a planet with

81 biological O_2 production, but also for biosignature detectability (Reinhard et al., 2017a). However, our

82 quantitative and mechanistic understanding of the Earth's O_2 cycle in deep time is still rudimentary at present.

83 For example, one possible explanation for low atmospheric O_2 levels during the mid-Proterozoic is simply a

84 less active or smaller biosphere (Crockford et al., 2018; Derry, 2015; Laakso and Schrag, 2014; Ozaki et al.,

85 2019a). However, mechanisms for regulating biotic O_2 generation rates and stabilizing atmospheric O_2 levels

86 at low levels on billion-year timescales remain obscure. As a result, the level of atmospheric O_2 and its stability

87 during the early-mid Proterozoic are the subject of vigorous debate (Bellefroid et al., 2018; Canfield et al.,

88 2018; Cole et al., 2016; Planavsky et al., 2018; Planavsky et al., 2016; Tang et al., 2016; Zhang et al., 2016).

89 Perhaps even more importantly, a relatively rudimentary quantitative framework for probing the dynamics

90 and stability of the oxygen cycle leads to the imprecision of geochemical reconstructions of ocean-atmosphere

91 O_2 levels.

92

93 Planetary atmospheric O_2 levels are governed by a kinetic balance between sources and sinks. Feedback arises

94 because the response of source/sink fluxes to changes in atmospheric O_2 levels is intimately interrelated to

95 each other. Since the biogeochemical cycles of C, N, P, and S exert fundamental control on the redox budget

96 through non-linear interactions and feedback mechanisms, a mechanistic understanding of these

97 biogeochemical cycles is critical for understanding Earth's O_2 cycle. However, the wide range of timescales

98 that characterize C, N, P, O_2 and S cycling through the reservoirs of the Earth system makes it difficult to fully

99 resolve the mechanisms governing the dynamics and stability of atmospheric O_2 levels from geologic records.

100 From this vantage, developing new quantitative tools that can explore biogeochemical cycles under conditions

101 very different from those of the present Earth is an important pursuit.

102

103 This study is motivated by the conviction that an ensemble of 'open' Earth system modeling frameworks with

104 explicit and flexible representation of the coupled C-N-P-O_2-S biogeochemical cycles will ultimately be

105 required to fully understand the dynamics and stability of Earth's O_2 cycle and its controlling factors. In

106 particular, a coherent mechanistic framework for understanding the global redox (O_2) budget (GRB) is critical

107 for filling remaining gaps in our understanding of Earth's oxygenation history and the cause-and-effect

108 relationships with an evolving biosphere. Here, we develop a new Earth system model, named CANOPS-

109 GRB, which implements the coupled biogeochemical cycles of C-N-P-O_2-S within the Earth's surface system

110 (ocean-atmosphere-crust). The model design (such as the complexity of the processes and spatial-temporal

111 resolution of the model) is constrained by the requirement of simulation length (>100 million years) and actual

112 model run-time. A lack of understanding of biogeochemistry in deep-time and availability and quality of

113 geologic records also limit the model structure. With this in mind, we aim for a comprehensive, simple, yet

114 realistic representation of biogeochemical processes in the Earth system, yielding a unique tool for

115 investigating coupled biogeochemical cycles within the Earth system over a wide range of time scales. We

116 have placed particular emphasis on the development of a global redox budget in the ocean-atmosphere-crust

117 system given its importance in the secular evolution of atmospheric O_2 levels. CANOPS-GRB is an initial

118 step towards developing the first large-scale biogeochemistry evolution model suited for the wide range of

119 redox conditions, including explicit consideration of the coupled C-N-P-O_2-S cycles and the major biogenic

120 gases in planetary atmospheres (O_2 and CH_4).

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2 Model description

Here we present a full description of a new version of the Earth system model CANOPS—CANOPS-GRB— 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.

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 mechanistic links between biological metabolism, ocean-atmosphere chemistry, and geologic processes. Such a framework must also represent the feedbacks between ocean-atmosphere redox state and biogeochemical cycles of redox-dependent bio-essential elements. Over recent decades, considerable progress has been made in quantifying the feedbacks between atmospheric O_2 levels and the coupled C-N-P-O_2-S biogeochemical cycles over geological timescales (Belcher and McElwain, 2008; Berner, 2004b; Betts and Holland, 1991; Bolton et al., 2006; Colman et al., 2000; Holland, 1978; Lasaga and Ohmoto, 2002; Slomp and Van Cappellen, 2007; Van Cappellen and Ingall, 1994). Refinements to our understanding of mechanisms regulating Earth's surface redox state have been implemented in low-resolution box models where the ocean-atmosphere system is expressed by a few boxes (Alcott et al., 2019; Bergman et al., 2004; Claire et al., 2006; Goldblatt et al., 2006; Handoh and Lenton, 2003; Laakso and Schrag, 2014; Lenton and Watson, 2000a, b; Petsch and Berner, 1998; Van Cappellen and Ingall, 1996). These models offer insights into basic system behavior and can illuminate the fundamental mechanisms that exert the most leverage on biogeochemical cycles because of their simplicity, transparency and low computational demands. However, these model architectures also have important quantitative limitations. For example, with low spatial resolution the modeler needs to assume reasonable (but *a priori*) relationships relating to internal biogeochemical cycles in the system. For instance, because of a lack of high vertical resolution, oceanic box models (Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984) usually overestimate the sensitivity of atmospheric CO_2 levels to biological activity at high-latitude surface ocean relative to projections by general circulation models (Archer et al.,

148 2000). Oceanic biogeochemical cycles and chemical distributions are also characterized by strong vertical and

149 horizontal heterogeneities, which have the potential to affect the strength of feedback processes (Ozaki et al.,

150 2011). In other words, the low-resolution box modeling approach might overlook the strength and response

151 of the internal feedback loops. Thus, the development of an ocean model with high resolution of ocean interior

152 and reliable representation of water circulation is required to investigate the mechanisms controlling

153 atmospheric O_2 levels under conditions very different from those of the modern Earth.

154

155 In the last decade, comprehensive Earth system models of intermediate complexity (EMICs) have also been

156 developed and extended to include ocean sediments and global C cycling (Lord et al., 2016; Ridgwell and

157 Hargreaves, 2007). Such models can be integrated over tens of thousands of years, allowing experimentation

158 with hypothetical dynamics of global biogeochemical cycles in the geological past (Olson et al., 2016;

159 Reinhard et al., 2020). However, a key weakness of existing EMICs is the need to parameterize (or ignore)

160 boundary (input/output) fluxes—either due to the computational expense of explicitly specifying boundary

161 conditions or due to poorly constrained parameterizations. For example, the oceanic P cycle is usually treated

162 as a closed system, limiting the model's applicability to timescales less than the oceanic P residence time

163 (~15−20 kyr). Further, boundary conditions such as continental configuration and oceanic bathymetry are

164 variable or poorly constrained in deep time and the use of highly complex models is difficult to justify the

165 computational cost. Finally, exploration of hypotheses concerning the biogeochemical dynamics in deep time

166 often require large model ensembles across broad parameter space given the scope of uncertainty. This makes

167 the computational cost of EMICs intractable at present for many key questions.

168

169 The CANOPS-GRB model is designed to capture the major components of Earth system biogeochemistry on

170 timescales longer than a millennium, but is simple enough to allow for runs on the order of a billion model

171 years. The model structure is also designed so that the model captures the essential biogeochemical processes

172 regulating the global O_2 budget, while keeping the calculation cost as moderate as possible. For example, the

173 simple relationships of biogeochemical transport processes at the interface of Earth system (hydrogen escape

174 to space, early diagenesis in marine sediments, and weathering) are employed based on the systematic

175 application of 1-D models in previous studies (Bolton et al., 2006; Claire et al., 2006; Daines et al., 2017;

176 Middelburg et al., 1997; Wallmann, 2003a), providing a powerful, computationally efficient means for

177 exploring the Earth system under a wide range of conditions. The resultant CANOPS-GRB model can be run

178 on a standard personal computer on a single CPU with an efficiency of approximately 6 million model years

179 per CPU hour. In other words, model runs in excess of 10^9 model years are tractable with modest wall times

180 (approximately 7 days). The model is thus not as efficient as simple box models, but is highly efficient relative

181 to EMICs, making sensitivity experiments and exploration of larger parameter space over a billion years

182 feasible, particularly with implementation on a high-performance computing cluster (see Cole et al., 2022).

183 CANOPS-GRB thus occupies a unique position within the hierarchy of global biogeochemical cycle models,

184 rendering it a useful tool for the development of more comprehensive, low- to intermediate-complexity models

185 of Earth system on very long timescales.

2.2 Overall model structure

187 The overall structure of the model is shown in Fig. 1. The model consists of ocean, atmosphere and

188 sedimentary reservoirs. The core of the model is an ocean model, comprising a high-resolution 1-D

189 intermediate-complexity box model of the global ocean (Sect. 2.4). The ocean model is coupled to a

190 parameterized marine sediment module (Sect. 2.4.4) and a one box model of the atmosphere (Sect. 2.6). The

191 atmospheric model includes O_2 and CH_4 as chemical components, and abundances of these molecules are

192 calculated based on the mass balance between sources and sinks (e.g., biogenic fluxes of O_2 and CH_4 from the

193 ecosystems and photochemical reactions). The net air-sea gas exchange of chemical species (O_2, H_2S, NH_3

194 and CH_4) is quantified according to the stagnant film model (Kharecha et al., 2005; Liss and Slater, 1974)

195 (Sect. 2.4.5). The ocean and atmosphere models are embedded in a 'rock cycle' model that simulates the

196 evolution of sedimentary reservoir sizes on geologic timescales (Sect. 2.5). Three sedimentary reservoirs

197 (organic carbon, *ORG*; pyrite sulfur, *PYR*; and gypsum sulfur, *GYP*) are considered in the CANOPS-GRB

198 model. These reservoirs interact with the ocean-atmosphere system through weathering, outgassing, and burial.

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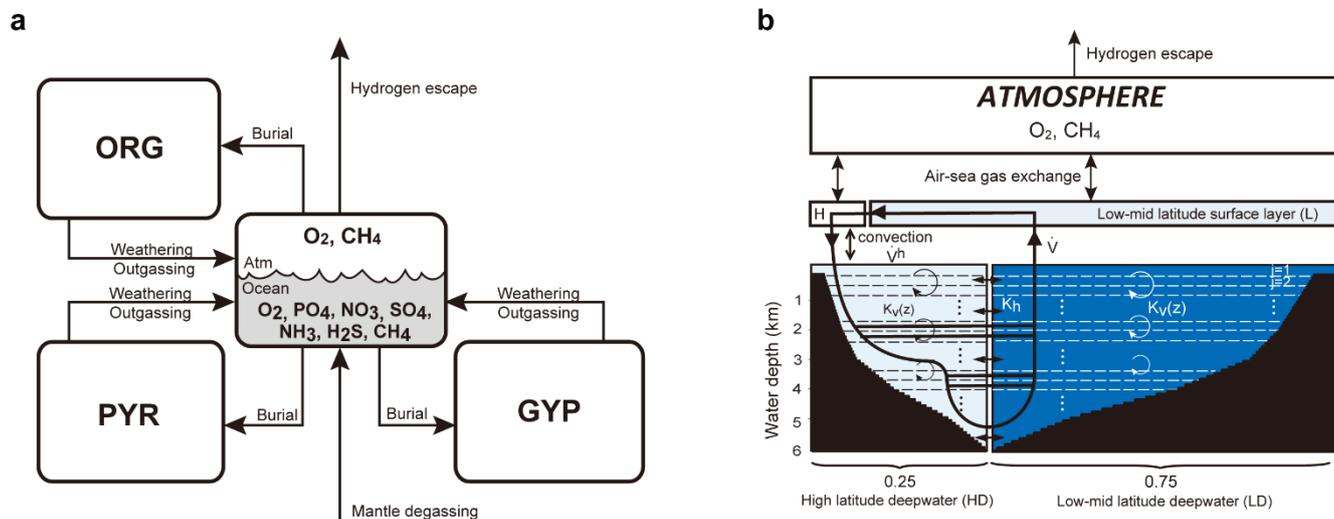
Figure 1 CANOPS-GRB model configuration. (**a**) The schematic of material cycles in the surface (ocean-atmosphere-crust) system. Three sedimentary reservoirs, organic carbon (*ORG*), pyrite sulfur (*PYR*), and gypsum sulfur (*GYP*), are considered. Sedimentary reservoirs interact with the ocean-atmosphere system via weathering, volcanic degassing, and burial. No interaction with the mantle is included, except for the input 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-latitude surface layer, respectively. An ocean area of 10% is assumed for H. River flux for each region is proportional to the areal fraction. Ocean interior is divided into two sectors, high-latitude deep water (HD) and low-mid latitude deep water (LD), which are vertically resolved. The area of HD is 25% of the whole ocean. The deep overturning circulation, $\dot{V}$, equals the poleward flow in the model surface layer (from L to H). $K_v^l(z)$ and $K_v^h(z)$ are the vertical eddy diffusion coefficients in the LD and HD regions, respectively. K_{hor} and $\dot{V}_h$ are the horizontal diffusion coefficient and polar convection, respectively. The black hatch represents the seafloor topography assumed. The parameters regarding geometry and water transport are tabulated in Table 3.

214

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 biogeochemical sub-model provides a mechanistic description of the marine biogeochemical cycles of C, P, N, O_2, and S (Sect. 2.4.3).

223 This includes explicit representation of a variety of biogeochemical processes such as biological productivity
224 in the sunlit surface oceans, a series of respiration pathways and secondary redox reactions under oxic and
225 anoxic conditions (Sect. 2.4.3), and deposition, decomposition, and burial of biogenic materials in marine
226 sediments (Sect. 2.4.4), allowing a mechanistically based examination of biogeochemical processes. The suite
227 of metabolic reactions included in the model is listed in Table 1. Ocean biogeochemical tracers considered in
228 the CANOPS-GRB model are phosphate (PO_4^{3-}), nitrate (NO_3^-), total ammonia (ΣNH_3), dissolved oxygen
229 (O_2), sulfate (SO_4^{2-}), total sulfide (ΣH_2S), and methane (CH_4). Ocean model performance was tested for the
230 modern-day ocean field observational data (Sect. 3). Simulation results were also compared to previously
231 published integrated global flux estimates.

232

233 Table 1: Biogeochemical reactions considered in the CANOPS-GRB model.

Process	Stoichiometry*	Reaction #
Ammonia assimilation	$\alpha CO_2 + \beta NH_4^+ + H_3PO_4 + \alpha H_2O \rightarrow OM + \alpha O_2$	R1
Nitrate assimilation	$\alpha CO_2 + \beta NO_3^- + H_3PO_4 + (\alpha + \beta)H_2O + 2\beta H^+ \rightarrow OM + (\alpha + 2\beta)O_2$	R2
Nitrogen fixation	$N_2 + 5H_2O \rightarrow 2NH_4^+ + 2OH^- + \frac{3}{2}O_2$	R3
Aerobic respiration	$OM + \alpha O_2 \rightarrow \alpha CO_2 + \beta NH_4^+ + H_3PO_4 + \alpha H_2O$	R4
Denitrification	$OM + \frac{4}{5}\alpha NO_3^- + \frac{4}{5}\alpha H^+ \rightarrow \alpha CO_2 + \beta NH_4^+ + H_3PO_4 + \frac{7}{5}\alpha H_2O + \frac{2}{5}\alpha N_2$	R5
Sulfate reduction	$OM + \frac{1}{2}\alpha SO_4^{2-} + \alpha H^+ \rightarrow \alpha CO_2 + \beta NH_4^+ + H_3PO_4 + \alpha H_2O + \frac{1}{2}\alpha H_2S$	R6
Methanogenesis	$OM \rightarrow \frac{1}{2}\alpha CO_2 + \frac{1}{2}\alpha CH_4 + \beta NH_4^+ + H_3PO_4$	R7
Nitrification	$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$	R8
Aerobic H$_2$S oxidation†	$\Sigma H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$	R9
Aerobic CH$_4$ oxidation	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	R10
Anaerobic CH$_4$ oxidation	$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O$	R11
Photooxidation of CH$_4$	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	R12
Hydrogen escape to space	$CH_4 + O_2 \rightarrow CO_2 + 4H\uparrow$	R13

234 *OM denotes organic matter, $(CH_2O)_\alpha(NH_4^+)_\beta H_3PO_4$
235 †$\Sigma H_2S = H_2S + HS^-$

236

237 The CANOPS model has been extended and altered a number of times since first publication. The description
238 of biogeochemical cycles in the original version of CANOPS (Ozaki and Tajika, 2013; Ozaki et al., 2011)
239 does not include the S and CH_4 cycles because of their aims to investigate the conditions for the development
240 of oceanic anoxia/euxinia on timescales less than a million years during the Phanerozoic. More recently, Ozaki
241 et al. (2019) implemented an open system modeling approach for the global S and CH_4 cycles, enabling
242 quantitative analysis of global redox budget for given atmospheric O_2 levels and crustal reservoir sizes. In this
243 version of CANOPS atmospheric O_2 levels and sedimentary reservoirs are treated as boundary conditions
244 because imposing them simplifies the model and significantly reduces computing time. However, this
245 approach does not allow exploration of the dynamic behavior of atmospheric O_2 in response to other boundary
246 conditions. In the newest version presented here, significant improvements in the representation of global
247 biogeochemistry were achieved by (1) an explicit calculation of atmospheric O_2 levels based on atmospheric
248 mass balance (Sect. 2.6), (2) expansion of the model framework to include secular evolution of sedimentary
249 reservoirs (Sect. 2.5.5), and (3) simplification of the global redox budget between the surface (ocean-
250 atmosphere-crust) system and the mantle (Sect. 2.3.5). These improvements are in line with the requirement
251 of an 'open' Earth system model, which is necessary for a systematic, quantitative understanding of Earth's
252 oxygenation history.

253 **2.3 Global biogeochemical cycles**

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

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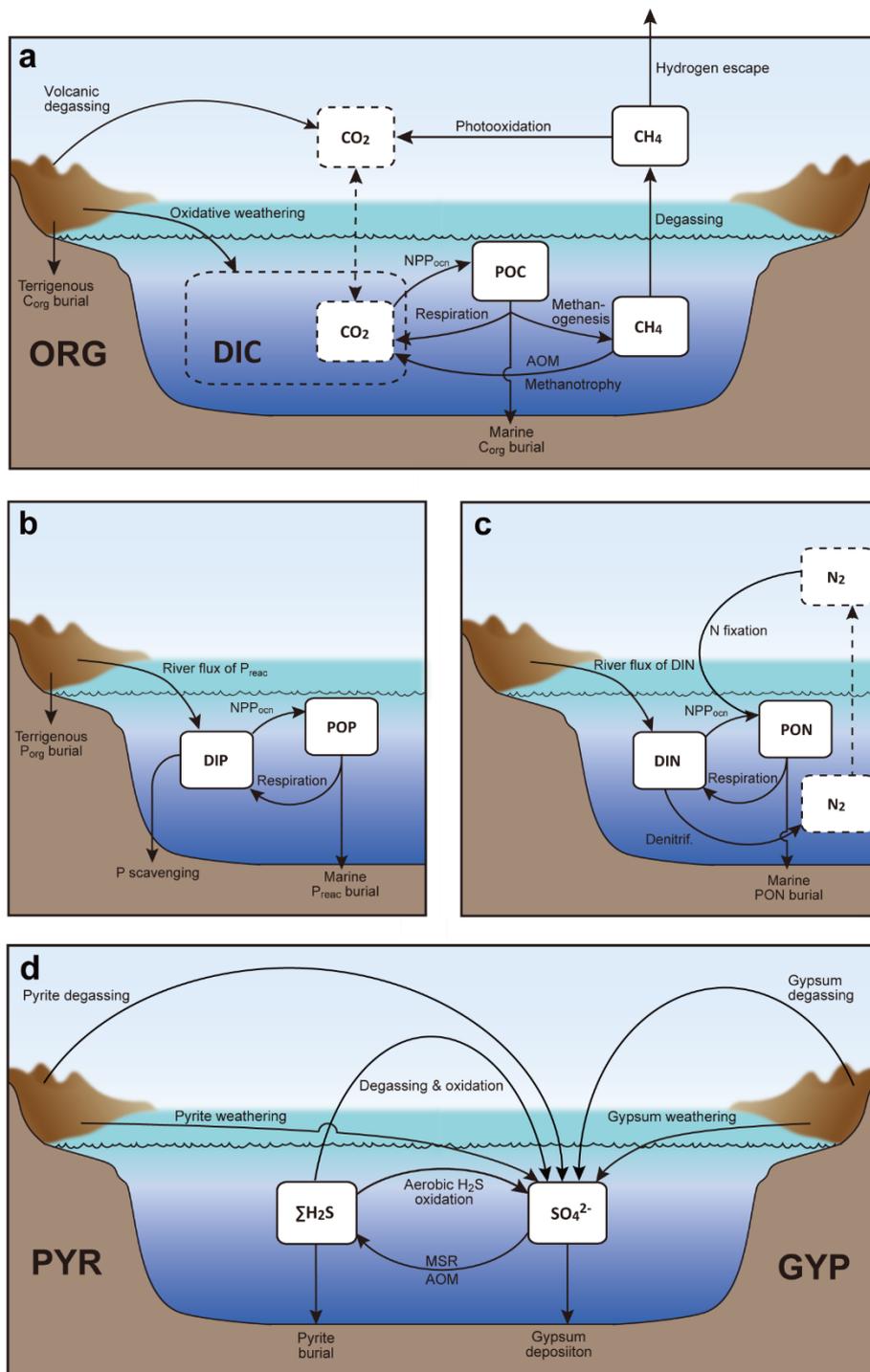
262 **Figure 2** Schematics of global biogeochemical cycles. (**a**) Global C cycle. The primary source of C for the
263 ocean-atmosphere system is volcanic degassing and oxidative weathering of sedimentary organic carbon,
264 whereas primary sink is burial of marine and terrigenous organic matter into sediments. Inorganic carbon
265 reservoirs (depicted as dashed boxes) and DOC are not considered. NPP_{ocn} = marine net primary production.
266 DIC = dissolved inorganic carbon. POC = particulate organic carbon. MSR = microbial sulfate reduction.
267 AOM = anoxygenic oxidation of methane. CANOPS-GRB includes CH_4 generation via methanogenesis and
268 its oxidation reactions via methanotrophy and AOM in the ocean interior, as well as CH_4 degassing flux to the
269 atmosphere and its photooxidation. The rates of CH_4 photooxidation and hydrogen escape to space are
270 calculated based on parameterizations proposed by previous studies (Claire et al., 2006; Goldblatt et al., 2006).
271 Note that CH_4 flux from land biosphere is not shown here. (**b**) Global P cycle schematic. Weathering of
272 reactive P (P_{reac}) is the ultimate source, whereas burial in sediments is the primary sink. A part of the weathered
273 P is buried as terrigenous organic P, and the remaining is delivered to the ocean. The redox-dependent P burial
274 in marine sediments is modelled by considering three phases (organic P, Fe-sorbed P, and authigenic P). DIP
275 = dissolved inorganic phosphorus. POP = particulate organic phosphorus. The hypothetical P scavenging via
276 Fe-species in anoxic-ferruginous waters is depicted, but it is not modelled in our standard model configuration.
277 (**c**) Global N cycle schematic. Two inorganic nitrogen species (ammonium and nitrate), which are lumped into
278 DIN (dissolved inorganic nitrogen), are transformed each other via denitrification and nitrification. The
279 primary source is nitrogen fixation and riverine flux, whereas primary sink is denitrification and burial in
280 marine sediments. PON = particulate organic nitrogen. The nitrogen weathering/riverine flux is assumed to
281 be equal to the burial flux so that there is no mass imbalance in global N budget. Aeolian delivery of N from
282 continent to the ocean is not included. (**d**) Global S cycle schematic. Two sedimentary reservoirs (pyrite sulfur,
283 PYR, and gypsum sulfur, GYP) and two sulfur species (SO_4^{2-} and ΣH_2S) in the ocean are transformed each
284 other via volcanic outgassing, weathering, burial, MSR, AOM, and sulfide oxidation reactions. Weathering
285 and volcanic inputs are the primary source of S to the ocean, and burial of pyrite and gypsum in marine
286 sediments is the primary sink. It is assumed that hydrogen sulfide escaping from the ocean to the atmosphere
287 is completely oxidized and returns to the ocean as sulfate. The organic sulfur cycle is ignored in this study.

288 **2.3.1 Carbon cycle**

289 The CANOPS-GRB model includes particulate organic carbon (POC), atmospheric CH_4, dissolved CH_4 in

290 the ocean, and sedimentary organic carbon (ORG) as carbon reservoirs (Fig. 2a). Atmospheric CO_2, dissolved

291 inorganic carbon (DIC), and dissolved organic carbon (DOC) are not explicitly modelled in the current version

292 of the model. The primary sources of carbon for the ocean-atmosphere system are volcanic degassing and

293 oxidative weathering of sedimentary organic carbon, while the primary sink is burial of marine and terrigenous

294 organic matter in sediments.

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}^{lnd}) NPP:

$$J_{NPP} = J_{NPP}^{ocn} + J_{NPP}^{lnd}. \tag{1}$$

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.

In our standard model configuration, oceanic primary production follows canonical Redfield stoichiometry (C:N:P = 106:16:1) (Redfield et al., 1963). Flexible C:N:P stoichiometry of particulate organic matter (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 through the water column with a speed of v_{POM} (the reference value is 100 m d^{-1}). As it settles through water column, POM is subject to decomposition via a series of respiration pathways dependent on the redox state of proximal seawater (Sect. 2.4.3). This gives rise to the release of dissolved constituent species back into seawater. Within each layer a fraction of POM is also intercepted by a sediment layer at the bottom of each water depth. Fractional coverage of every ocean layer by seafloor is calculated based on the prescribed 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 segments, and for each segment the rates of organic matter decomposition and burial are calculated by semi-empirical relationships extracted from ocean sediment data and 1-D modelling of early diagenesis (Sect. 2.4.4). Specifically, the

321 organic C (C_{org}) burial at each water depth is calculated based on the burial efficiency (BE_{org}), which is defined

322 as the fraction of POC buried in sediments relative to that deposited on the seafloor at each water depth and

323 is also a function of sedimentation rate and bottom water O_2 levels. Organic matter not buried is subject to

324 decomposition.

325

326 The key biogeochemical fluxes of our reference state (mimicking the present condition) are summarized in

327 Table 2. The reference value for burial rate of terrigenous C_{org} is set at 3 Tmol C yr^{-1}, assuming that burial of

328 terrigenous organic matter accounts for ~20% of the total burial. Combined with the burial rate of marine C_{org}

329 in our standard run, the total burial rate is 14.3 Tmol C yr^{-1}, representing the dominant O_2 source flux to the

330 modern ocean-atmosphere system. At steady-state, this is balanced by oxidative weathering and volcanic

331 outgassing of sedimentary C_{org}: The reference value of oxidative weathering of organic matter is determined

332 as 13.0 Tmol C yr^{-1} based on the global O_2 budget (Sect. 2.3.5). Previous versions of CANOPS (Ozaki et al.,

333 2019a) treat sedimentary reservoirs as a boundary condition. This model limitation is removed in the

334 CANOPS-GRB model—the reservoir size of sedimentary C_{org} (*ORG*) freely evolves based on the mass

335 balance through burial, weathering, and volcanic outgassing (Sect. 2.5.5). We adopted an oft-quoted value of

336 1250 Emol (E = 10^{18}) for our reference value of the *ORG*, based on literature survey (Berner, 1989; Garrels

337 and Lerman, 1981).

338

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339 Table 2: Key biogeochemical fluxes obtained from the reference run. * denotes the reference value. Tmol =
340 10^{12} mol.

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

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Methane cycle

The ocean model includes biogenic CH_4 generation via methanogenesis and its oxidation reactions via methanotrophy and anoxygenic oxidation of methane (AOM) in the ocean interior (R10 and R11 in Table 1), as well as CH_4 degassing flux to the atmosphere. The land model also calculates the biogenic CH_4 flux from the terrestrial ecosystem to the atmosphere using a transfer function (Sect. 2.5.2). The abundance of CH_4 in the atmosphere is explicitly modelled as a balance of its source (degassing from marine and terrestrial ecosystems) and sink (photooxidation and hydrogen escape), where CH_4 sink fluxes are 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 parameterization obtained from a 1-D photochemistry model (Claire et al., 2006). The rate of hydrogen escape to space is evaluated with the assumption that it is diffusion limited and that CH_4 is a major H-containing chemical compound carrying hydrogen to the upper atmosphere (Goldblatt et al., 2006). No continental abiotic or thermogenic CH_4 fluxes are taken into account, because previous estimates of the modern fluxes are negligible relative to the biogenic flux, although we realize that it could have played a role in the global redox budget (<0.3 Tmol yr^{-1}; Fiebig et al., 2009). We also note that the current version of the model does not include the possibility of aerobic CH_4 production in the sea (Karl et al., 2008). Our reference run calculates atmospheric CH_4 to be 0.16 ppmv (Sect. 3.3), slightly lower than that of the preindustrial level of 0.7 ppmv (Etheridge et al., 1998; Raynaud et al., 1993), but we consider this to be within reasonable error given unknowns in the CH_4 cycle.

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_{reac}) 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.

367 On geologic timescales, the primary source of P to the ocean-atmosphere system is continental weathering:

368 Phosphorus is released through the dissolution of apatite which exists as a trace mineral in silicate and

369 carbonate rocks (~0.1wt%; Föllmi, 1996). The total P_{reac} flux via weathering, J_P^w, is given as follows:

$$J_P^w = f_P f_R J_P^{w,*},$$
(2)

370 where * denotes the reference value, and f_P and f_R are parameters that control the availability of P in the system.

371 Specifically, f_R is a global erosion factor representing the impact of tectonic activity on total terrestrial

372 weathering rate, and f_P represents the availability of P_{reac}, which is used in a sensitivity experiment to assess

373 the response of atmospheric O_2 levels to changing P_{reac} availability (Sect. 4.1). A fraction of the weathering

374 flux J_P^w is removed via burial on land, while the remainder is transported to the ocean (Sect. 2.5.2):

$$J_P^{b,lnd} = k_{11} V J_P^w,$$
(3)

$$J_P^r = (1 - k_{11} V) J_P^w$$
(4)

375 where $J_P^{b,lnd}$ and J_P^r denote the burial rate of terrigenous organic P and riverine P_{reac} flux to the ocean,

376 respectively, k_{11} is a reference value for the fraction of the total P flux removed by the terrestrial biosphere,

377 and V denotes the vegetation mass normalized to the modern value. These treatments are based on the Earth

378 system box model COPSE (Bergman et al., 2004; Lenton et al., 2016; Lenton et al., 2018; Lenton and Watson,

379 2000b) which has been extensively tested and validated against geologic records during the Phanerozoic. In

380 the CANOPS-GRB model, J_P^r is tuned so that modelled oceanic P inventory of the reference state is consistent

381 with modern observations of the global ocean (Sect. 3.2.4). Our resulting tuned value is 0.155 Tmol P yr^{-1}

382 falling in the mid-range of published estimates of 0.11–0.33 Tmol P yr^{-1}, although previous estimates of the

383 riverine P_{reac} flux show large uncertainty (Sect. 3.2.4).

384

385 Since atmospheric P inputs are equivalent to less than 10% of the continental P supply to the modern oceans

386 and much of this flux is not bioavailable (Graham and Duce, 1979), we neglect the aeolian flux in this study.

387 Therefore, riverine input is the primary source of P_{reac} to the ocean. We highlight that open-system modelling

388 is crucial for realistic simulations of ocean biogeochemistry on timescales longer than the residence time of P

389 in the ocean (15–20 kyr for the modern ocean) (Hotinski et al., 2000), and in this framework the riverine input

390   of P_{reac} must be balanced over the long-term by loss to sediments via burial. The change in total marine P_{reac}

391   inventory, M_P, is given as follows:

$$\frac{dM_P}{dt} = J_P^r - J_P^{b,ocn}, \tag{5}$$

392   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 of

393   three reactive phases, i.e. organic P (P_{org}), Fe-sorbed P (P_{-Fe}), and Ca-bound P (P_{-Ca}) (Sect. 2.4.4):

$$J_P^{b,ocn} = J_{Porg}^b + J_{P-Fe}^b + J_{P-Ca}^b. \tag{6}$$

394   O_2-dependent P burial is taken into account using empirical relationships from previous studies (Slomp and

395   Van Cappellen, 2007; Van Cappellen and Ingall, 1994, 1996). The burial of P_{org} at each water depth is a

396   function of burial efficiency, which is controlled by the burial efficiency of organic matter, C/P stoichiometry

397   of POM, sedimentation rate and bottom water [O_2]. We note that the strength of anoxia-induced P recycling

398   in marine sediments is very poorly constrained, especially in the Precambrian oceans (Reinhard et al., 2017b).

399   Recent studies also suggest that the P retention potential in marine sediments could be affected not only by

400   bottom water O_2 levels but by redox states (sulfidic vs. ferruginous) and the Ca^{2+} concentration of bottom

401   waters (Zhao et al., 2020). These are fruitful topics for future research.

402

403   We do not explicitly account for P removal via hydrothermal processes, because it is estimated that this

404   contribution is secondary in the modern marine P cycle (0.014–0.036 Tmol P yr^{-1}; Wheat et al., 1996; Wheat

405   et al., 2003). We note, however, that the hydrothermal contribution to the total P budget in the geologic past

406   remains poorly constrained. We also note that in anoxic, ferruginous oceans, P scavenging by Fe-minerals

407   could also play an important role in controlling P availability and the overall budget (Derry, 2015; Laakso and

408   Schrag, 2014; Reinhard et al., 2017b). Modern observations (Dellwig et al., 2010; Shaffer, 1986; Turnewitsch

409   and Pohl, 2010) and modeling efforts (Yakushev et al., 2007) of the redoxcline in the Baltic Sea and the Black

410   Sea suggest an intimate relationship between Mn, Fe, and P cycling. Trapping efficiencies of DIP by settling

411   authigenic Fe and Mn-rich particles were found to be as high as 0.63 (the trapping efficiency is defined as the

412   downward flux of P in Mn-, and Fe-oxides divided by the upward flux of DIP) (Turnewitsch and Pohl, 2010).

413   Although coupled Mn-Fe-P dynamics might have been a key aspect of the biogeochemical dynamics in the

414   Precambrian oceans, we exclude this process in our standard model due to poor constraints and provide a clear

415 and simplified picture of basic model behavior. The key features between the P availability and atmospheric

416 O_2 levels are explored by changing f_P in this study (Sect. 4).

2.3.3 Nitrogen cycle

418 In the CANOPS-GRB model, two dissolved inorganic nitrogen (DIN) species (total ammonium ΣNH_4^+ and

419 nitrate NO_3^-) and particulate organic nitrogen (PON) are explicitly calculated (Fig. 2c). Atmospheric nitrogen

420 gas is assumed to never limit biospheric carbon fixation, and is not explicitly calculated. Dissolved organic N

421 (DON) and terrestrial N cycling (e.g., N fixation by terrestrial ecosystems and riverine-terrigenious organic N

422 transfer) are ignored.

423

424 In the surface ocean N assimilation via nitrate and ammonium depends on the availability of these compounds.

425 If the N required for sustaining a given level of biological productivity is not available, the additional N

426 required is assumed to be provided by atmospheric N_2 via nitrogen fixers. The ocean model explicitly

427 calculates denitrification and nitrification reactions in the water column and marine sediments (R5 and R8 in

428 Table 1). The benthic denitrification rate is estimated using a semi-empirical parameterized function obtained

429 from a 1-D early diagenetic model (see Sect. 2.4.4), while nitrification is modelled as a single step reaction

430 (R8). N_2O and its related reactions, such as anammox, are not currently included.

431

432 The oceanic N cycle is open to external inputs of nitrogen. While the ultimate source of N to the ocean-

433 atmosphere system is weathering of organic N, nitrogen fixation represents the major input flux to the ocean

434 with the capacity to compensate for N loss due to denitrification. The time evolution of DIN inventory, M_N,

435 in the ocean can be written as follows:

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

436 where J_{Nfix} denotes the N fixation rate, and J_{deni}^{wc} and J_{deni}^{sed} are denitrification rates in the water column and

437 sediments, respectively. The first set of terms on the right-hand side represent the internal N cycle in the ocean-

438 atmosphere system, while the second set of terms represent the long-term N budget which interacts with

439 sedimentary reservoir. Ultimately, loss of fixed N from the ocean-atmosphere system only occurs via burial

440 of organic N (N_{org}) in sediments, J_{Norg}^b. This loss is compensated for by continental weathering, J_{Norg}^w, which

441 is assumed to be equal to the burial rate of N_{org} so that the N cycle has no impact on the global redox budget.

442 In the current version of the model, we ignore aeolian flux and all riverine N fluxes other than weathering

443 since these are minor relative to N fixation (Wang et al., 2019). As a result, modelled N fixation required for

444 oceanic N balance can be regarded as an upper estimate.

2.3.4 Sulfur cycle

446 The original CANOPS ocean model (Ozaki and Tajika, 2013; Ozaki et al., 2011) treated two sulfur species,

447 SO_4^{2-} and $\Sigma H_2 S$, in a closed system: Neither inputs to the ocean from rivers, hydrothermal vents, and

448 submarine volcanoes, nor outputs due to evaporite formation and sedimentary pyrite burial were simulated.

449 This simplification can be justified when the timescale of interest is less than the residence time of the S cycle

450 (~10–20 Myr). The recently-revised CANOPS model (Ozaki et al., 2019a) extends the framework by

451 incorporating the S budget in the ocean. In their model framework, the sedimentary S reservoirs are treated as

452 boundary conditions: The size of sedimentary gypsum and pyrite reservoirs are prescribed and no explicit

453 calculations of mass balance are performed. In CANOPS-GRB, we removed this model limitation and the

454 sedimentary reservoirs are explicitly evaluated based on mass balance which is controlled by burial,

455 outgassing and weathering (see Sect. 2.4). Specifically, seawater SO_4^2, $\Sigma H_2 S$, and sedimentary sulfur

456 reservoirs of pyrite sulfur (*PYR*) and gypsum sulfur (*GYP*) are explicitly evaluated in the current version of

457 the model. No atmospheric sulfur species are calculated—all $H_2 S$ degassing from the ocean to the atmosphere

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

459 study.

460

461 Sulfur enters the ocean mainly from river runoff, J_S^r, with minor contributions from volcanic outgassing of

462 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^{-1},

463 consistent with the published estimate of 2.6±0.6 Tmol S yr^{-1} (Raiswell and Canfield, 2012). The riverine flux

464 is written as the sum of gypsum weathering and oxidative weathering of pyrite: $J_S^r = J_{gyp}^w + J_{pyr}^w$. Sulfur

465 weathering fluxes are also assumed to be proportional to the sedimentary reservoir size. Estimates of modern

466 volcanic input fall within the range of 0.3–3 Tmol S yr^{-1} (Catling and Kasting, 2017; Kagoshima et al., 2015;

467 Raiswell and Canfield, 2012; Walker and Brimblecombe, 1985). We adopted a value of 0.8 Tmol S yr^{-1} for

468 this flux (Kagoshima et al., 2015). Our total input of 3.4 Tmol S yr^{-1} is also within the range of the previous

469 estimate of 3.3±0.7 Tmol S yr^{-1} (Raiswell and Canfield, 2012). Sulfur is removed from the ocean either via

470 pyrite burial, $J_{pyr}{}^{b}$, or gypsum deposition, $J_{gyp}{}^{b}$ (Fig. 2d). The time evolution of the inventory of total S in the

471 ocean can thus be written, as follows:

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

472 where M_{SO4} and M_{H2S} denote the inventory of sulfate and hydrogen sulfide in the ocean, respectively. Two

473 sulfur species (SO_4^{2-} and ΣH_2S) are transformed via microbial sulfate reduction (MSR) (R6), AOM (R11),

474 and aerobic sulfide oxidation reactions (R9). The above equation thus can be divided into following equations:

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

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

475 where $J_{H2S}{}^{ox}$ denotes the oxidation of hydrogen sulfide and $J_{MSR\&AOM}$ is sulfate reduction via MSR and AOM.

476 Pyrite burial is represented as the sum of pyrite precipitation in the water column and sediments: $J_{pyr}{}^{b} = J_{pyr}{}^{b,wc}$

477 $+ J_{pyr}{}^{b,sed}$, where the pyrite burial rate in marine sediments is assumed to be proportional to the rate of benthic

478 sulfide production. The proportional coefficient, pyrite burial efficiency (e_{pyr}), is one of the tunable constants

479 of the model: For normal (oxic) marine sediments e_{pyr} is tuned such that the seawater SO_4^{2-} concentration for

480 our reference run is consistent with modern observations (Sect. 2.4.3). Pyrite precipitation in the water column

481 is assumed to be proportional to the concentration of ΣH_2S.

482

483 Although the present-day marine S budget is likely out of balance because of a lack of major gypsum formation,

484 the S cycle can be considered to operate at steady state on timescales longer than the residence time of sulfur

485 in the ocean. According to S isotope mass balance calculations, ~10–45% of the removal flux is accounted for

486 by pyrite burial, and the remainder is removed via formation of gypsum/anhydrite in the near-modern oceans

487 (Tostevin et al., 2014). Although gypsum deposition would have been strongly influenced by tectonic activity

488 (Halevy et al., 2012), we assume that the rate of gypsum deposition on geologic time scales is proportional to

489 the ion product of Ca^{2+} and SO_4^{2-} (Berner, 2004a) in the low- to mid-latitude surface layer (L), and is defined

490 as follows:

$$J_{\mathrm{gyp}}^{\mathrm{b}} = \left(\frac{[Ca^{2+}]_l [SO_4^{2-}]_l}{[Ca^{2+}]^* [SO_4^{2-}]^*} \right) J_{\mathrm{gyp}}^{\mathrm{b},*} = f_{\mathrm{Ca}} \left(\frac{[SO_4^{2-}]_l}{[SO_4^{2-}]^*} \right) J_{\mathrm{gyp}}^{\mathrm{b},*} \qquad (11)$$

491 where l denotes the low- to mid-latitude surface layer and f_{Ca} is a parameter that represents the seawater Ca^{2+}

492 concentration normalized by the present value ($f_{\mathrm{Ca}} = 1$ for the reference run). The reference value of gypsum

493 burial $J_{\mathrm{gyp}}^{\mathrm{b},*}$ is determined by assuming that gypsum deposition accounts for ~60% of the total S removal from

494 the near-modern ocean.

495 **2.3.5 Global redox budget**

496 In the previous version of the CANOPS model (Ozaki et al., 2019a), the atmospheric O_2 level was prescribed

497 as a boundary condition, rather than modeled in order to limit computational demands. In this study, we

498 remove this model limitation by introducing an explicit mass balance calculation of atmospheric O_2 (Sect.

499 2.6.3). This improvement allows us to explore the dynamic response of O_2 levels in the ocean-atmosphere

500 system (Sect. 4).
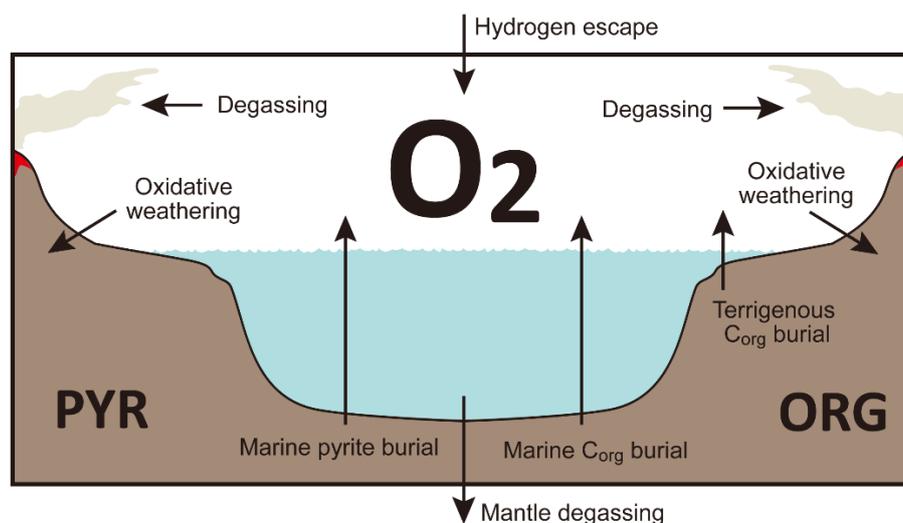
501

502 **Figure 3** Schematics of global redox (O_2) budget. Arrows represent the O_2 flux. The primary source is burial
503 of organic carbon and pyrite sulfur in sediments and hydrogen escape to space. The primary sink is volcanic
504 outgassing and weathering of crustal organic matter and pyrite. PYR = sedimentary reservoir of pyrite sulfur.
505 ORG = sedimentary reservoir of organic carbon. CANOPS-GRB tracks the global redox (O_2) budget for each
506 simulation.

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508 The newly released CANOPS-GRB is designed to be a part of a comprehensive global redox budget (GRB)

509 framework (Fig. 3) (Catling and Kasting, 2017; Ozaki and Reinhard, 2021). Here GRB is defined for the

510 combined ocean-atmosphere system. In this study we track GRB in terms of O_2 equivalents. The ultimate

511 source of O_2 is the activity of oxygenic photosynthesis (and subsequent burial of reduced species, such as

512 organic matter and pyrite sulfur, in sediments), whereas the primary sink of O_2 is the oxidative weathering of

513 organic carbon and pyrite which are assumed to be O_2-dependent (Sect. 2.5.3). On timescales longer than the

514 residence time of O_2 in the ocean-atmosphere system, O_2 source fluxes should be balanced by sink fluxes.

515 Specifically, the O_2 budget in the coupled ocean-atmosphere system can be expressed as follows:

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

516 where the first and second set of terms on the right-hand side represent the redox balance via organic carbon

517 and pyrite sulfur subcycles, respectively. J_{Hesc} in the third term denotes hydrogen escape to space, representing

518 the irreversible oxidation of the system. For well-oxygenated atmospheres this process plays a minor role in

519 the redox budget, but for less oxygenated atmospheres with high levels of CH_4 this flux could lead to redox

520 imbalance. In this study we include the input of reducing power (e.g., H_2 and CO) from the Earth's interior to

521 the surface, J_{man}, which is assumed to be equal to the value of J_{Hesc} ($J_{\text{man}} = J_{\text{Hesc}}$) to avoid redox imbalance in

522 the exogenic system. In reality, mantle degassing and the rate of hydrogen escape are not necessarily equal,

523 resulting in redox imbalance that may exert a fundamental control on atmospheric redox chemistry on geologic

524 timescales (Canfield, 2004; Eguchi et al., 2020; Hayes and Waldbauer, 2006; Ozaki and Reinhard, 2021),

525 however to maintain simplicity we have left this as a topic for future work. As a result, the terms on the right-

526 hand side must be balanced at steady state. Our model can meet this criterion. Note that the effects of the Fe

527 cycle on the O_2 budget (e.g., the oxidative weathering of Fe(II)-bearing minerals; Ozaki et al., 2019a) are not

528 currently included for the sake of simplicity.

529

530 The CANOPS-GRB model also tracks the O_2 budgets for the atmosphere and ocean independently, and these

531 can be evaluated by the following relationships:

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

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

532 where *ARB* and *ORB* denote the redox budget in the atmosphere and ocean, respectively, $\Phi_{ex}^{air\text{-}sea}$ represents

533 the net exchange of oxidizing power between the ocean and atmosphere via gas exchange (O_2 with minor

534 contributions of NH_3, H_2S and CH_4). These separate redox budgets are also tracked in order to validate global

535 budget calculations.

536

537 For our reference condition, we obtain the reference value for the oxidative weathering rate of C_{org} ($J_{org}^{w,*}$)

538 using the redox budget via C_{org} subcycle:

$$J_{org}^{w,*} = J_{org}^{b,ocn,*} + J_{org}^{b,lnd,*} - J_{org}^{m,*}. \tag{15}$$

539 Given flux values based on the calculated ($J_{org}^{b,ocn,*}$ = 11.28 Tmol C yr^{-1}) and prescribed ($J_{org}^{b,lnd,*}$ = 3 Tmol

540 C yr^{-1}, $J_{org}^{m,*}$ = 1.25 Tmol C yr^{-1}) values on the right-hand side, $J_{org}^{w,*}$ is estimated as 13.03 Tmol C yr^{-1} (Table

541 2).

2.4 Ocean model

543 Here we undertake a thorough review, reconsideration and revision (where warranted), of all aspects of the

544 ocean model, including bringing together developments of the model since the original paper (Ozaki and

545 Tajika, 2013; Ozaki et al., 2011).

546

547 The ocean model includes exchange of chemical species with external systems via several processes such as

548 air-sea exchange, riverine input, and sediment burial. The biogeochemical model also includes a series of

549 biogeochemical processes, such as the ocean biological pump and redox reactions under oxic-anoxic-sulfidic

550 conditions. Our ocean model is convenient for investigating Earth system changes on timescales of hundreds

551 of years or longer and it can be relatively easily integrated, rendering the model unique in terms of

552 biogeochemical cycle models. CANOPS is also well suited for sensitivity studies and can be used to obtain

553 useful information upstream of more complex models.

554

555 Development of the ocean model included two initial goals: The first goal is to adopt a general and robust

556 ocean circulation scheme capable of producing well-resolved modern distributions of circulation tracers, using

557 realistic ventilation rates with a limited number of free parameters. The model's output for circulation tracers
558 are validated by comparison with modern observations (see Sect. 3). This confirms that our ocean circulation
559 scheme is adequate for representing the global patterns of water mass transport. The second goal is to couple
560 the circulation model with an ocean biogeochemical model, and to evaluate performance by comparison with
561 modern ocean biogeochemical data (see Sect. 3.2). Examination of the distributions and globally-integrated
562 fluxes of C, N, P, S, and O_2 for the modern ocean reveals that the ocean model can capture the fundamentals
563 of marine biogeochemical cycling.

2.4.1 Structure

565 CANOPS ocean model is a 1-D (vertically resolved) intermediate complexity box model of ocean
566 biogeochemistry (see Fig. 1b for the schematic structure) originally developed by (Ozaki and Tajika, 2013;
567 Ozaki et al., 2011). Our model structure is an improved version of the HILDA model (Joos et al., 1991; Shaffer
568 and Sarmiento, 1995). Unlike simple one-dimensional global ocean models (e.g, Southam et al., 1982), the
569 HILDA-type model includes explicit high-latitude dynamics whereby the high-latitude surface layer
570 exchanges properties with the deep ocean. This treatment is crucial for simulating preformed properties and
571 observed chemical distributions, especially for phosphate and dissolved O_2 in a self-consistent manner. Unlike
572 simple box-type global ocean models, the model has high vertical resolution. This is needed for representing
573 proper biogeochemical processes which show strong depth dependency. Furthermore, HILDA type models
574 (Arndt et al., 2011; Shaffer et al., 2008), unlike multi-box-type global ocean models (Hotinski et al., 2000),
575 use a small number of free parameters to represent ocean physics and biology. The simple and adaptable
576 structure of the model should make it applicable to a wide range of paleoceanographic problems. It couples a
577 diffusion-advection model of the global ocean with a biogeochemical model (Sect. 2.4.3) and a parameterized
578 sediment model (Sect. 2.4.4).

579

580 The ocean surface consists of a mixed layer at low-mid latitude (L) and high-latitude (H). Below the surface
581 layers, we adopt the present-day averaged seafloor topography of (Millero, 2006) (Hypsometric profile is
582 shown in Fig. 4a). Below the surface water layers, the ocean interior comprises two regions: the high-mid
583 latitude region (HD) and low-mid latitude region (LD). Each region is subdivided vertically, with high

584 resolution (Δz = 100 m). Each of the 60 ocean layers in each latitude region (120 total) is assigned ocean

585 sediment properties. The cross-sectional area, volume, and sediment surface area of each box is calculated

586 from the benthic hypsometry. Inclusion of the bathymetry allows evaluation of the flux of biogenic materials

587 which settle on, and are buried in, seafloor sediments at each water depth (Sect. 2.3.3 and 2.3.4).

588
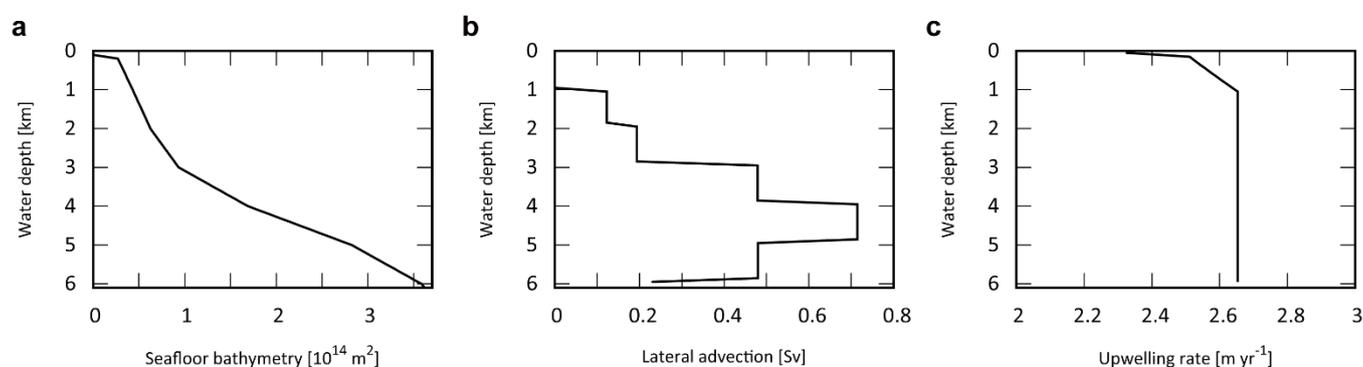
589

590 **Figure 4** Ocean bathymetry and water transport. (**a**) Seafloor topography (cumulative seafloor area) (Millero,
591 2006) adopted in the CANOS-GRB model. (**b**) Lateral water advection from HD to LD section assumed in
592 the standard run (in Sv). Total advection rate $\dot{V}$ was set at 20 Sv. (**c**) Upwelling rate in the LD region (in m
593 yr^{-1}) of the standard run.

594 **2.4.2 Transport**

595 The ocean circulation model represents a general and robust scheme that is capable of producing well-resolved

596 modern profiles of circulation tracers using realistic parameter values, and the coupled biogeochemical model

597 (Sect. 2.4.3) and the parameterized sediment model (Sect. 2.4.4).

598

599 The time-space evolution of model variables in the ocean is described by a system of horizontally integrated

600 vertical diffusion equations for non-conservative substances. The tracer conservation equation establishes the

601 relationship between change of tracer concentration at a given grid point and the processes that can change

602 that concentration. These processes include water transport by advection and mixing, and sources and sinks

603 due to biological and chemical transformations. The temporal and spatial evolution of the concentration of a

604 dissolved component in the aphotic zone is described by a horizontally integrated vertical diffusion equation,

605 which relates the rate of change of tracer concentration at a given point to the processes that act to change the

606 tracer concentration:

$$\frac{\partial [X]}{\partial t} = \left.\frac{\partial [X]}{\partial t}\right|_{\text{trans}} + \Theta_{\text{bio}} + \Theta_{\text{react}}, \tag{16}$$

607 where [X] represents horizontally integrated physical variables (such as potential temperature, salinity or ^{14}C)

608 or concentration of a chemical component, t denotes time, and Θ_{bio} and Θ_{react} represents internal sources and

609 sinks associated with the biological pump and chemical reactions, respectively. An external source/sink term

610 Θ_{ex}, which represents riverine input and/or air-sea gas exchange, is added to the surface layers. The first term

611 on the right hand side of equation (16) represents the physical transport:

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

612 The terms on the right-hand side express (from left to right) the advection, vertical diffusion, and horizontal

613 diffusion. Here, l and h indicate the LD and HD, respectively. The factors $K_v^{\text{l,h}}(z)$, K_{hor}, $A^{\text{l,h}}(z)$, and $w^{\text{l,h}}(z)$

614 denotes the vertical and horizontal diffusion coefficients, the areal fraction of the water layer at water depth z

615 to the sea surface area, and upwelling (for LD) or downwelling (for HD) velocity, respectively.

616

617 In the CANOPS ocean model, ocean circulation and mixing are characterized by five physical parameters: (1)

618 water transport via thermohaline circulation, $\dot{V}$, associated with high latitude sinking and low-mid latitude

619 upwelling; (2) constant horizontal diffusion between the aphotic zones, K_{hor}; (3) strong, depth-dependent

620 vertical diffusion between the aphotic zones in the high latitude region, $K_v^{\text{h}}(z)$; (4) high latitude convection,

621 $\dot{V}_{\text{h}}$; and (5) depth-dependent vertical diffusion in the low-mid latitude region, $K_v^{\text{l}}(z)$. These parameters are

622 tuned to give tracer distributions consistent with present-day observations.

Advection

624 Advective water transport in the ocean model represents the major features of modern meridional overturning

625 circulation. The rate of production of ventilated ocean waters ranges from 14 to 27 Sv (1 Sv = 10^6 m^3 s^{-1}) in

626 the North Atlantic and from 18 to 30 Sv in the Southern Ocean (e.g., Doney et al., 2004; Lumpkin and Speer,

627   2007). The formation of deepwater effectively supplies "fresh" ventilated water to the abyss. We choose $\dot{V} =$

628   20 Sv as a reference value, giving a mean overturning time of about 2,140 yr, consistent with the ventilation

629   time estimated from observations (Broecker and Peng, 1982).

630

631   The downwelling of the surface waters at H forms HD that flows into the intermediate to deep oceanic layers

632   of LD, which, in turn, upwells over L (Fig. 1b). In many one-dimensional ocean models, downwelling water

633   enters the ocean interior via the deepest model layer (e.g., Shaffer and Sarmiento, 1995; Southam et al., 1982;

634   Volk and Hoffert, 1985). In the real ocean, downwelling waters are transported along isopycnal layers below

635   approximately 1,000 m (e.g., Doney et al., 2004; Lumpkin and Speer, 2007; Shaffer and Sarmiento, 1995;

636   Volk and Hoffert, 1985). Hence, we assume that high-latitude deep water flows into each ocean layer below

637   1,100 m. While there is some uncertainty in the pattern of lateral advection, the flow is determined in our

638   model assuming a constant upwelling rate below a depth of 1,100 m in the LD region. The

639   upwelling/downwelling rate $w^{l,h}(z)$ is then determined by the seafloor topography and the deep water lateral

640   inflow, assuming continuity. Figure 4b shows the lateral advection of deep waters with a reference circulation

641   rate $\dot{V}$ of 20 Sv. This assumption provides a plausible upwelling rate, which is consistent with the oft-quoted

642   value of 2–3 m yr^{-1} (Broecker and Peng, 1982) (Fig. 4c).

643   **Vertical mixing**

644   Ocean circulation is dominated by turbulent processes driven by wind and tidal mixing. These processes occur

645   as eddies which occur at a wide range of spatial scales, from centimeters to whole ocean basins. In numerical

646   models of ocean circulation, turbulent mixing in the ocean interior is commonly represented as a diffusion

647   process, characterized by an eddy diffusion coefficient. The vertical eddy diffusion coefficient $K_v(z)$ is

648   typically on the order of 10^{-5} to 10^{-4} m^2 s^{-1} and it is common to assume a depth-dependence which smoothly

649   increases from the thermocline (~10^{-5} m^2 s^{-1}) to the abyss (~10^{-4} m^2 s^{-1}) using an inverse or hyperbolic tangent

650   function (e.g., Shaffer et al., 2008; Yakushev et al., 2007). To account for thermocline ventilation, we assumed

651   a relatively high vertical diffusion coefficient in mid-water depth ($K_l = 6.3 \times 10^{-5}$ m^2 s^{-1} for water depth

652   500–1500 m). We also adopted a higher value for the vertical diffusion coefficient ($K_u = 1.6 \times 10^{-4}$ m^2 s^{-1}) in

653 the upper most 500 m of the ocean in order to represent the highly convective Ekman layer in the upper part

654 of the ocean.

$$
K_v^1(z) = \begin{cases} K_u & (z \geq \text{-500 m}) \\[2mm] K_l & (\text{-500} \geq z \geq \text{-1500 m}) \\[2mm] \kappa^s + \dfrac{\kappa^d - \kappa^s}{2}\left(1 + \tanh\left(\dfrac{z - z^l}{z^l}\right)\right) & (\text{otherwise}) \end{cases}
\tag{18}
$$

655 where κ^s and κ^d are vertical mixing coefficients, and z^l is the transition length scale (Romaniello and Derry,

656 2010). In the high latitude region where no permanent thermocline exists, more rapid communication with

657 deep waters can occur. Previous studies have pointed out that the vertical diffusivities at high latitude can be

658 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

659 between H and YD ($\dot{V}_h = 57.4$ Sv) and higher vertical diffusion ($K_v^h(z) = 2 \times K_v^1(z)$).

Horizontal diffusion

661 The horizontal diffusivity is included according to Romaniello and Derry (2010). On basin scales, the

662 horizontal (isopycnal) eddy diffusivity is 10^7–10^8 times larger than the vertical (diapycnal) eddy diffusivity

663 due to anisotropy of the density field. For a spatial scale of 1,000 km, horizontal eddy diffusion is estimated

664 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

665 assume horizontal mixing follows the pathways of advective fluxes between laterally adjacent regions. The

666 reciprocal exchange fluxes may be written as

$$
J_{hor}^{ex} = K_{hor} A_\perp \frac{\partial [X]}{\partial y} = \frac{K_{hor} A_\perp}{L} \Delta[X],
\tag{19}
$$

667 where J_{hor}^{ex} denotes the exchange fluxes between the layers (in mol yr^{-1}), $A_\perp$ represents the cross-sectional

668 area separating two adjacent reservoirs, L is a characteristic spatial distance separating the reservoirs, $\Delta[X]$ is

669 the difference in concentration between two reservoirs (Romaniello and Derry, 2010). By assuming that L is

670 of the same order as the length of the interface separating the two regions, we can approximate $A_\perp \approx \Delta z \times O(L)$,

671 where Δz is the thickness of the interface separating the two regions. Then we obtain

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

672 Therefore, when we discretize the ocean interior at 100 m spacing approximately 0.1 Sv of reciprocal mixing

673 occurs between adjacent layers.

Ocean circulation tracers

675 We use potential temperature θ, salinity S, and radioactive carbon ^{14}C, as physical tracers. Distributions of

676 these tracers are determined by the transport mechanisms described above. In this study, we adopt the values

677 at the surface layers (L and H) as upper boundary conditions: $\theta^l = 15°C$, $\theta^h = 0°C$, $S^l = 35$ psu, $S^h = 34$ psu,

678 $\Delta^{14}C^l = -40‰$, and $\Delta^{14}C^h = -100‰$. The radioactive decay rate for ^{14}C is 1.21×10^{-4} yr^{-1}. Although ^{14}C can be

679 incorporated in the biogenic materials and transported into deep water, we ignore this biological effect for

680 simplicity. The associated error is ~10% of the profiles produced by circulation and radioactive decay (Shaffer

681 and Sarmiento, 1995). The parameter values used in the ocean circulation model are listed in Table 3.

682 Table 3: Physical set-up of the ocean circulation model.

Parameters	Label	Value	Unit	Ref.
Ocean surface area	A	3.62×10^{14}	m^2	(Ozaki and Tajika, 2013)
Surface area of high-latitude layer (H)	A^h	0.362×10^{14}	m^2	(Ozaki and Tajika, 2013)
Depth of mixed layer	h_m	100	m	(Ozaki and Tajika, 2013)
Grid spacing	Δz	100	m	(Ozaki and Tajika, 2013)
Water depth of ocean bottom	z_b	6,100	m	(Ozaki and Tajika, 2013)
Ocean overturning rate	$\dot{V}$	20	Sv	(Ozaki and Tajika, 2013)
Vertical mixing coefficient ($z < 500$ m)	K_u	5,000	m^2 yr^{-1}	(Ozaki and Tajika, 2013)
Vertical mixing coefficient (500 m $< z <$ 1,500 m)	K_l	2,500	m^2 yr^{-1}	(Ozaki and Tajika, 2013)
Mixing coefficient	κ_s	473	m^2 yr^{-1}	(Romaniello and Derry, 2010)
Mixing coefficient	κ_d	3,154	m^2 yr^{-1}	(Romaniello and Derry, 2010)
Transition depth for vertical mixing coefficient	z_l	1,000	m	(Romaniello and Derry, 2010)
High-latitude convection rate	$\dot{V}_h$	57.4	Sv	(Ozaki and Tajika, 2013)
Horizontal diffusion coefficient	K_{hor}	1,000	m^2 s^{-1}	(Romaniello and Derry, 2010)

2.4.3 Ocean biogeochemical framework

The ocean circulation model is coupled to a biogeochemical model, which includes an explicit representation of a variety of biogeochemical processes in the ocean. The parameters used in the oceanic 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^l	1.0	–	(Ozaki and Tajika, 2013)
Efficiency factor for phosphate uptake at H	ε^h	0.15	–	(Ozaki and Tajika, 2013)
Phosphate half saturation constant	K_P	1×10^{-6}	mM	(Ozaki and Tajika, 2013)
Export ratio	f_{exp}	0.2	–	(Ozaki et al., 2019a)
Redfield C/P ratio	α^*	106	mol mol^{-1}	(Redfield et al., 1963)
Redfield N/P ratio	β^*	16	mol mol^{-1}	(Redfield et al., 1963)
POM sinking velocity	v_{POM}	100	m d^{-1}	(Ozaki et al., 2011)
Mass fraction of G_1	m_1	0.72	–	(Ozaki and Tajika, 2013)
Mass fraction of G_2	m_2	0.25	–	(Ozaki and Tajika, 2013)
Mass fraction of G_3	m_3	0.03	–	(Ozaki and Tajika, 2013)
Decomposition rate of G_1	k_1	0.6	d^{-1}	(Ozaki et al., 2011)
Decomposition rate of G_2	k_2	0.1	d^{-1}	(Ozaki et al., 2011)
Decomposition rate of G_3	k_3	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_{NO3}	3×10^{-2}	mM	(Boudreau, 1996)
Half saturation constant for MSR	K_{MSR}	0.2	mM	This study
Half saturation constant for AOM	K_{AOM}	0.093	mM	(Beal et al., 2011)
Aerobic oxidation rate of ammonium	k_{R8}	1.825×10^4	mM^{-1} yr^{-1}	(Oguz et al., 2001)
Aerobic oxidation rate of sulfide	k_{R9}	3.65×10^3	mM^{-1} yr^{-1}	(Oguz et al., 2001)
Aerobic methane oxidation rate	k_{R10}	1×10^7	mM^{-1} yr^{-1}	(Van Cappellen and Wang, 1996)
Anaerobic methane oxidation rate	k_{R11}	3×10^{-4}	yr^{-1}	(Ozaki et al., 2019a)
Pyrite formation rate in the water column	k_{pyr}^{wc}	0.01	yr^{-1}	This study
Reference value of seawater sulfate concentration	$[SO_4^{2-}]^*$	28.9	mM	(Ozaki et al., 2019a)

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; Shaffer et al., 2008; Yamanaka and Tajika, 1996):

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

where j_{exp} represents new/export production of POC (in unit of mol C m^{-2} yr^{-1}), α denotes C:P stoichiometry of POM, h_m is the mixed layer depth, ε denotes the assimilation efficiency factor for P uptake, and K_P denotes the half-saturation constant. The value of ε 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).

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

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

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

708 where α and β represent the C/P ratio and N/P ratio of POM, * denotes the canonical Redfield ratios, max

709 denotes the maximum value ($\alpha_{\max} = 400$ and $\beta_{\max} = 60$), and γ_{P0} and γ_{P1} are tunable constants ($\gamma_{P0} = 0.1$ μM

710 and $\gamma_{P1} = 0.03$ μM) (Kuznetsov et al., 2008). In the CANOPS-GRB model, this dynamic response of POM

711 stoichiometry can be explored by changing the user-flag from the standard static response. In this study, we

712 do not explore the impacts of flexible POM stoichiometry on global biogeochemistry (i.e., $\alpha_{\max} = \alpha^*$ and $\beta_{\max}$

713 $= \beta^*$).

714

715 Biological production in the surface mixed layer increases the concentration of dissolved O_2 and reduces the

716 concentrations of DIP and DIN according to the stoichiometric ratio (R1 and R2; Table 1). DIN consumption

717 is partitioned between nitrate and ammonium, assuming that ammonium is preferentially assimilated.

718 CANOPS-GRB evaluates the availability of fixed N in the surface ocean, and any N deficiency required for a

719 given level of productivity is assumed to be compensated for on geologic time scales by N fixers. In other

720 words, it is assumed that biological N fixation keeps pace with P availability, so that P (not N) ultimately

721 determines oceanic biological productivity.

722

723 To date, models of varying orders of complexity have been developed to simulate oceanic primary production

724 and nutrient cycling in the euphotic layer, from a single nutrient and single phytoplankton component system

725 to the inclusion of multiple nutrients and trophic levels in the marine ecosystem, usually coupled to physical

726 models (e.g., Oguz et al., 2000; Yakushev et al., 2007). To avoid this level of complexity, we introduce a

727 parameter, $f_{\exp}$, called export ratio (Sarmiento and Gruber, 2006), which relates the flux densities of export

728 production and NPP, as follows:

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

729 where j_{NPP}^{ocn} denotes the NPP in terms of mol C m^{-2} yr^{-1}. In the modern ocean globally averaged value of $f_{\exp}$

730 is estimated at 0.2 (Laws et al., 2000), and we assumed this value in this study. The rate of recycling of organic

731 matter in the photic zone is thus given by

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

732   The respiration pathway of j_{recy} depends on the availability of terminal electron acceptors (O_2, NO_3^- and SO_4^{2-}).

733   Following exhaustion of these species as terminal electron acceptors, organic matter remineralization occurs

734   by methanogenesis (R7). See below for the treatment of organic matter remineralization in the water column.

Biological pump

736   Most POM exported to the deep sea is remineralized in the water column before reaching the seafloor (e.g.,

737   Broecker and Peng, 1982). Nutrients returning to seawater at intermediate depths may rapidly return to the

738   surface ocean and support productivity. The remaining fraction of POM that reaches the sediment ultimately

739   exerts an important control on oceanic inventories of nutrients and O_2. An adequate representation of the

740   strength of biological pump is therefore critical to any descriptions of global biogeochemical cycles.

741

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

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

743   where r is a decomposition rate and v_{POM} is the settling velocity of POM in the water column. We assume a

744   settling velocity of 100 m d^{-1} for our reference value (e.g., Suess, 1980), although a very wide range of values

745   and depth-dependency have been reported (e.g., Berelson, 2001b). Therefore, the settling velocity is fast

746   enough to neglect advective and diffusive transport of biogenic particles. Note that the settling velocity would

747   affect the intensity of biological pump and chemical distribution in the ocean interior. Considering the ballast

748   hypothesis in the modern ocean (Armstrong et al., 2001; Francois et al., 2002; Ittekkot, 1993; Klaas and Archer,

749   2002), the settling velocity of POM in the geological past would have been different from the modern ocean.

750   As Kashiyama et al. (2011) pointed out, there would be a critical aspect among sinking rate of POM, intensity

751   of biological pump and chemical distribution in the ocean. The quantitative and comprehensive evaluation of

752   their effect is an important issue for the future work (Fakhraee et al., 2020).

753

754 In order to solve equation (26) explicitly, a relatively small time step (~1 day) would be required. However,

755 because the sinking velocity and remineralization of biogenic material are fast processes, we assume that the

756 POM export and remineralization occurs in the same time step (ignoring the term $\partial G/\partial t$). Then the

757 concentration of biogenic particles can be solved as follows:

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

758 where Δz is a spatial resolution of the model.

759 **Organic matter decomposition**

760 As POM settles through the water column, it is nearly entirely decomposed back to dissolved tracers.

761 Therefore, decomposition of POM is a key process for modelling biogeochemistry in the ocean. To avoid the

762 complex treatment of this process (such as repackaging and aggregation/dispersal of particles), various

763 empirical schemes for POM sinking flux have been proposed, such as exponential (Volk and Hoffert, 1985)

764 or power law (Martin et al., 1987) functions (Fig. 5). However, the estimation of Volk and Hoffert generally

765 tends to overestimate in the upper water column (<1.5 km) and underestimate at depth. It is important to note

766 that data series of sediment trap measurements were obtained from a limited geographic and depth range.

767 Berelson (2001a) and Lutz et al. (2002) conducted further estimates of the sediment flux and found regional

768 variability in the sinking flux. Broadly, these data indicate that commonly applied flux relationships generally

769 tend to overestimate flux to depth.

770

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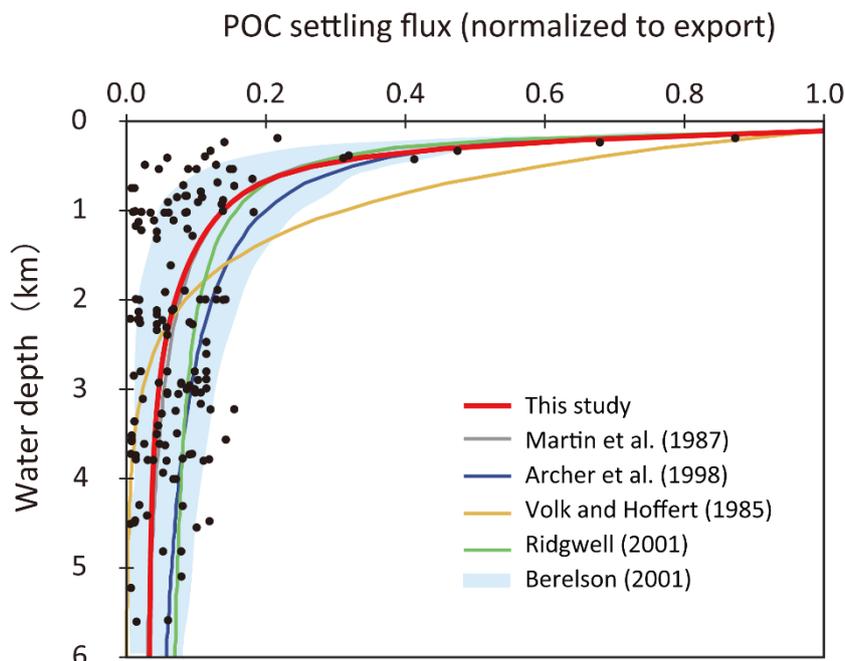
Figure 5 Empirical relationships between POC settling flux normalized to export production (Lutz et al., 2002) and water depth (Archer et al., 1998; Berelson, 2001a; Martin et al., 1987; Volk and Hoffert, 1985). The profile of the CANOPS-GRB model is depicted as a red line. The black dots represent observational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

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

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788 The electron acceptor used in the respiration reaction changes from dissolved O_2 to other oxidants (e.g., NO_3^-

789 and SO_4^{2-}) as O_2 becomes depleted. The respiration pathway is controlled by the free energy change per mole

790 of organic carbon oxidized. The organic matter decomposition is performed by the oxidant which yields the

791 greatest free energy change per mole of organic carbon oxidized. When the oxidant is depleted, further

792 decomposition will proceed utilizing the next most efficient (i.e., the most energy producing) oxidant until

793 either all oxidants are consumed or oxidizable organic matter is depleted (e.g., Berner, 1989; Froelich et al.,

794 1979). In oxic waters, organic matter is remineralized by an aerobic oxidation process (R4). As dissolved O_2

795 is depleted, NO_3^- and/or SO_4^{2-} will be used (R5 and R6). Denitrification is carried out by heterotrophic bacteria

796 under low concentrations of dissolved O_2, if there is sufficient nitrate. For anoxic, sulfate-lean oceans, organic

797 matter production from carbon dioxide (methanogenesis) or fermentation of organic matter to produce

798 methane and carbon dioxide will occur (R7). In the CANOPS-GRB model, we parameterized the dependence

799 of decomposition of POM with a Michaelis-Menten type relationship with respect to the terminal electron

800 acceptors:

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

$$R_5 = \frac{K'_{O_2}}{K'_{O_2} + [O_2]} \frac{[NO_3^-]}{K_{NO_3} + [NO_3^-]} (\textstyle\sum k_i G_i) \tag{29}$$

$$R_6 = \frac{K'_{O_2}}{K'_{O_2} + [O_2]} \frac{K'_{NO_3}}{K'_{NO_3} + [NO_3^-]} \frac{[SO_4^{2-}]}{K_{MSR} + [SO_4^{2-}]} (\textstyle\sum k_i G_i) \tag{30}$$

$$R_7 = \frac{K'_{O_2}}{K'_{O_2} + [O_2]} \frac{K'_{NO_3}}{K'_{NO_3} + [NO_3^-]} \frac{K'_{MSR}}{K'_{MSR} + [SO_4^{2-}]} (\textstyle\sum k_i G_i)$$
$$= \left(1 - R_{O_2} - R_{NO_3} - R_{SO_4}\right)(\textstyle\sum k_i G_i) \tag{31}$$

801 where K_{O2}, K_{NO3}, and K_{MSR} are Monod constants, and K'_{O2}, K'_{NO3}, K'_{MSR} are inhibition constants. The Monod-

802 type expressions are most widely used in mathematical models of POM decomposition processes (e.g.,

803 Boudreau, 1996). The oxidants for organic matter decomposition change gradually, depending on the amount

804 of each oxidant. The parameter values are based on the previous studies on early diagenetic processes in

805 marine sediments (Boudreau, 1996; Van Cappellen and Wang, 1996). SO_4^{2-} has been one of the major

806 components of the Phanerozoic oceans and has been an important oxidizing agent in anaerobic systems. In

807 the original CANOPS model (Ozaki and Tajika, 2013; Ozaki et al., 2011), it was assumed that the saturation

808 constant K_{MSR} is zero, meaning that the SO_4^{2-} is never a limiting factor. In contrast, during the Precambrian,

809 seawater SO_4^{2-} could have been extremely low (Lyons and Gill, 2010). The half saturation constant for MSR

810 (K_{MSR}) determines the degree to which MSR contributes to the total respiration rates. However, estimates for

811 K_{MSR} in natural environments and pure cultures vary over several orders of magnitude (~0.002–3 mM) (Pallud

812 and Van Cappellen, 2006; Tarpgaard et al., 2011). We assume a reference value of 0.2 mM for this study.

813

814 Finally, temperature may also have played an important role in organic matter decomposition rates. The

815 dependence of ammonification on temperature is sometimes described by an exponential function or Q_{10}

816 function (e.g., Yakushev et al., 2007). While we recognize that the temperature dependency of organic matter

817 decomposition might have played an important role in oceanic biogeochemical cycles in geological past

818 (Crichton et al., 2021), these dynamics are not included in our standard model.

819 Secondary redox reactions

820 Total ammonia (ΣNH_3), total sulfide (ΣH_2S), and methane (CH_4), produced during organic matter degradation,

821 are subject to oxidation by NO_3^-, SO_4^{2-}, and CO_2 via a set of secondary redox reactions (Table 1). Rate

822 constants for these reactions are taken from the literature. The ocean model includes nitrification (R8), total

823 sulfide oxidation by O_2 (R9), aerobic oxidation of CH_4 by O_2 (R10), and AOM by SO_4^{2-} (R11). Nitrification,

824 the oxidation of ammonium to nitrate, occurs in several stages and is accomplished mainly by

825 chemolithotrophic bacteria (Sarmiento and Gruber, 2006). In this study, we treat all nitrification reactions as

826 a combined reaction (R8). The rate of this process is assumed to depend on the concentration of both oxygen

827 and ammonia as follows:

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

828

829 The oxidation of sulfide formed in anoxic waters by MSR can also be written as a series of reactions (e.g.,

830 Yakushev and Neretin, 1997), but we treat it as an overall reaction (R9). The rate of this secondary redox

831 reaction is also formulated using bimolecular rate law:

$$R_9 = k_{R9}[\Sigma H_2 S][O_2]. \tag{33}$$

832 The rate constant for this process has been shown to vary significantly as a function of several redox-sensitive

833 trace metals which act as catalysts (Millero, 1991). Here we assume $k_{R9} = 3650$ mM^{-1} yr^{-1} based on the

834 observations of suboxic layer of the Black Sea (Oguz et al., 2001).

835

836 In the original CANOPS model (Ozaki et al., 2019a; Ozaki and Tajika, 2013), syngenetic pyrite formation in

837 the water column was not considered. In a more recent revision of the model, this process was added (Cole et

838 al., 2022) and parameterized such that iron sulfide formation is assumed to be proportional to the hydrogen

839 sulfide concentration:

$$R_{pyr}^{wc} = k_{pyr}^{wc}[\Sigma H_2 S], \tag{34}$$

840 where k_{pyr}^{wc} is a model constant (its reference value is set at 0.01 yr^{-1}). This constant is a function of the ferrous

841 iron concentration in seawater, but it is the subject of large uncertainty. The total flux (in mol S yr^{-1}) can be

842 obtained by integrating the precipitation flux density over the whole ocean:

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

843

844 CH$_4$ can be oxidized not only by O$_2$ in aerobic waters (R10) but by SO$_4$ in anoxic waters (R11). The aerobic

845 oxidation of CH$_4$ is formulated using a bimolecular rate law:

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

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

$$R_{11} = k_{R11}[CH_4]\frac{[SO_4^{2-}]}{K_{AOM} + [SO_4^{2-}]}. \tag{37}$$

847 Rate constants for above reactions are taken from the literature (Table 4). Secondary redox reactions were

848 calculated implicitly with an operator splitting scheme (Steefel and MacQuarrie, 1996) so as to maintain

849 numerical stability.

850 **2.4.4 Sediment-water exchange**

851 The burial of biogenic material in marine sediments plays a critical role in global biogeochemical cycles,

852 especially with respect to the marine budgets of nutrients, carbon, and sulfur. This is intimately linked to

853 atmospheric O_2 levels on geologic timescales. Specifically, the burial rate of C_{org} in marine sediments exerts

854 a primary control on the evolution of atmospheric O_2 levels throughout Earth's history. Given the complexity

855 of biogeochemical processes within sediments and our limited knowledge on many of the early diagenetic

856 processes, we adopt some semi-empirical relationships extracted from ocean sediment data. This approach,

857 rather than explicit modelling, is also required to reduce the computational cost of the simulation on timescales

858 >100 Myr. The related parameter values are in Table 5.

859

860 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_{org} at zero sediment accumulation rate	be_1	5.0	%	(Dale et al., 2012)
Burial efficiency of C_{org} at infinite sediment accumulation rate	be_2	75	%	(Dale et al., 2012)
Centre of the regression for burial efficiency of organic C	a	0.01	$g\ cm^{-2}\ yr^{-1}$	(Dale et al., 2012)
Pyrite burial efficiency in oxic sediments	e_{pyr}^{oxic}	0.117	–	This study
Pyrite burial efficiency in anoxic sediments	e_{pyr}^{anox}	1	–	(Ozaki et al., 2019a)
O_2 threshold value for P burial efficiency	$oxic$	0.25	mM	(Ozaki et al., 2011)
C_{org}/N_{org} ratio of buried sediments	$(C_{org}/N_{org})_b$	10	$mol\ mol^{-1}$	(Ozaki and Tajika, 2013)

861 **POM deposition**

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

863 settling flux density, j_{org}^{dep} (in mol C m^{-2} yr^{-1}), and topography (Fig. 4a):

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

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

$$j_{org}^{dep} = v_{POM} G.$$ (39)

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

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.

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

$$j_{org}^{b,ocn} = BE_{org}\, j_{org}^{dep}.$$ (40)

Burial efficiency is defined as the fraction of organic matter buried in sediments relative to the total depositional flux. Burial efficiency is described by simplified parametric laws based on empirical relationships from modern day observations. Previous studies demonstrate strong dependency of this term on total sedimentation rate, SR (e.g., Henrichs and Reeburgh, 1987). Figure 6 demonstrates the relationship between BE_{org} and SR compiled from literature surveys. The sedimentation rate in the modern ocean varies over about five orders of magnitude, with a primary dependence on material supplied from the continents. There is a strong relationship, especially for SR less than 0.01 cm yr^{-1}. In contrast to the strong SR dependence under oxic conditions, anoxic settings show a much weaker dependence of BE_{org} on SR (Betts and Holland, 1991; Henrichs and Reeburgh, 1987) (Fig. 6). In this study, the following relationship proposed by (Henrichs and Reeburgh, 1987) is adopted for sediments underlying well-oxygenated bottom water (O_2 concentration of bottom water, $[O_2]_{bw} > 200\ \mu M$):

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

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

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

891 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

892 function of $[O_2]_{bw}$ with a log-linear interpolation method. Note that the original CANOPS model (Ozaki and

893 Tajika, 2013; Ozaki et al., 2011) adopted Eq. (41) without considering the O_2 dependency, whereas more

894 recent versions employ Eq. (42) for both oxic and anoxic sediments with different values of a, b_1 and b_2. In

895 the CANOPS-GRB, we adopted both equations, because of the sake of more accurate reproduction of C_{org}

896 burial distribution in the modern ocean (Sect. 3.2.2).

897

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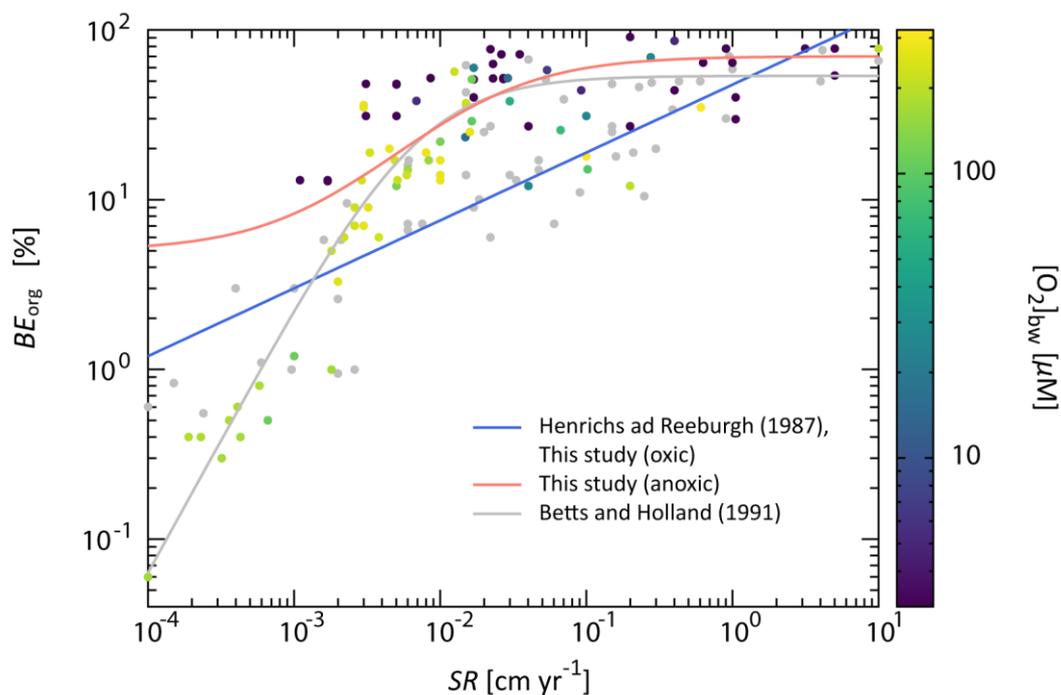
Figure 6 Burial efficiency of organic carbon (BE_{org}) as a function of sedimentation rate (SR). The dots denote
the observational data compiled from literature survey (Betts and Holland, 1991; Canfield, 1993; Hartnett et
al., 1998; Henrichs and Reeburgh, 1987; Tromp et al., 1995). The color represents the O_2 concentration of
bottom water, $[O_2]_{bw}$, with grey dots for the unknown $[O_2]_{bw}$ value. Black and grey solid lines are previously
proposed empirical relationships (Betts and Holland, 1991; Henrichs and Reeburgh, 1987), whereas blue and
red lines are the relationship for well-oxygenated ($[O_2]_{bw} > 200$ μM) and anoxic ($[O_2]_{bw} < 30$ μM) marine
sediments adopted in the CANOPS-GRB model.

906

43

907 Sedimentation rate depends strongly on water depth and distance from shore (Hedges et al., 1999), and we

908 apply the relationship between water depth, z, and the reference value of SR shown by Tromp et al. (1995)

909 (Fig. 7).

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

910 Using these formulas with seafloor topography (Fig. 4a) and j_{org}^{dep} (Eq. 39), we can calculate $j_{org}^{b,ocn}$ for each

911 ocean depth. In the CANOPS-GRB model, we also introduce an erosion factor, f_R, representing the global

912 weathering/sedimentation rate (Sect. 2.4.3). Given the intimate coupling between global erosion rate and mass

913 transfer from continents to the ocean, SR scales with the erosion factor ($f_R = 1$ for our reference run):

$$SR(z) = f_R \, SR(z)^*. \tag{44}$$

914

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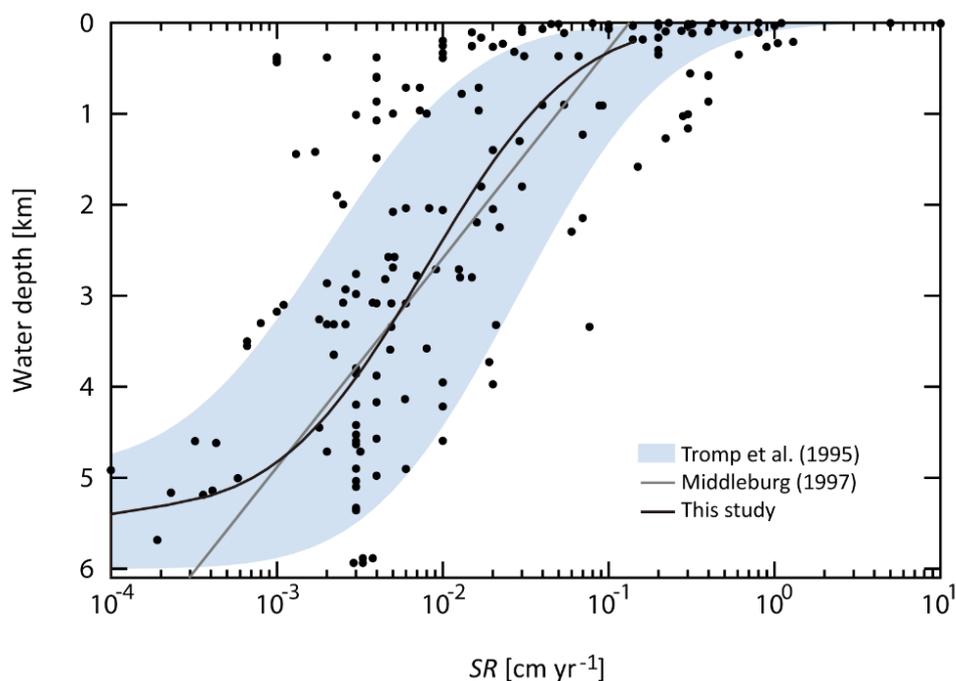
Figure 7 Sedimentation rate as a function of water depth. Data (black dots) were compiled from literature
survey (Baturin, 2007; Betts and Holland, 1991; Cha et al., 2005; Colman et al., 2000; Reimers et al., 1992;
Tromp et al., 1995). Black line represents the relationship assumed in the CANOPS-GRB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

920

921 Organic matter that is not buried is subject to decomposition. The decomposition rate at each water depth is
922 given as follows:

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

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

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

928 where f_{deni} denotes the fraction of denitrification and k is an empirical constant. τ_{OET} is given by

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

929 where OPD is the oxygen penetration depth (cm) and SR denotes a linear sedimentation rate (cm yr^{-1}). In the
930 CANOPS-GRB model OPD is calculated by a simplified parametric law obtained from a 1-D early-diagenetic
931 model of C and O_2. We performed a series of experiments ($n = 5,652$) in order to parameterize OPD as a
932 polynomial function with the following variables: sedimentation rate SR (cm yr^{-1}), bottom water O_2
933 concentration $[O_2]_{\text{bw}}$ (μM), depositional flux of POC $j_{\text{org}}^{\text{dep}}$ (mmol C cm^{-2} yr^{-1}) and bottom water temperature
934 T_{bw} (°C). The variables are allowed to vary over a parameter space spanning 10^{-4} cm yr^{-1} < SR < 10^1 cm yr^{-1},
935 10^0 μM < $[O_2]_{\text{bw}}$ < 10^3 μM, 10^{-4} mmol C cm^{-2} yr^{-1} < $j_{\text{org}}^{\text{dep}}$ < 10^1 mmol C cm^{-2} yr^{-1}, and 0 °C < T_{bw} < 30 °C.

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

936 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 =
937 0.0894604, a_7 = 0.00279531, a_8 = -0.127797, a_9 = 0.0017995, and a_{10} = 0.0085171. This parametric fit
938 provides a rapid means of obtaining OPD from a 1-D early diagenetic model of C and O_2 (Fig. 8). Note that
939 Eq. (48) is verified for $[O_2]_{\text{bw}}$ >1 μM. When bottom water O_2 concentration is lower than 1 μM, OPD is set at
940 zero.

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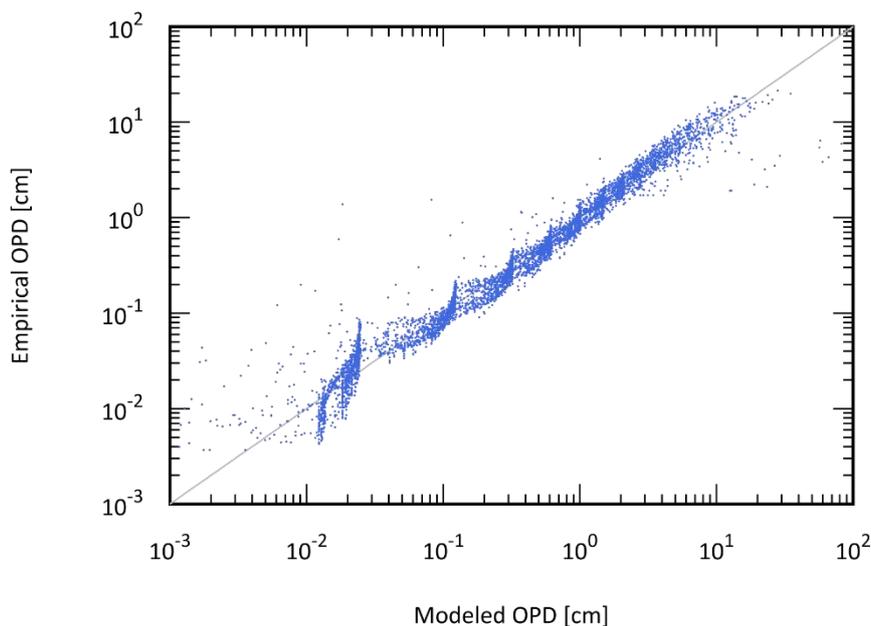
Figure 8 The correlation between the simulated OPD and the OPD obtained from an empirical relationship of equation (48) ($n = 5652$). Gray line denotes the 1:1 line. $r^2 = 0.9595$.

945

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; McManus et al., 1997; Ruttenberg, 2003; Wallmann, 2003a; Wallmann, 2010a), changes in diagenetic processes affecting P recycling and burial in marine sediments could have a significant impact on global oceanic biogeochemical cycles.

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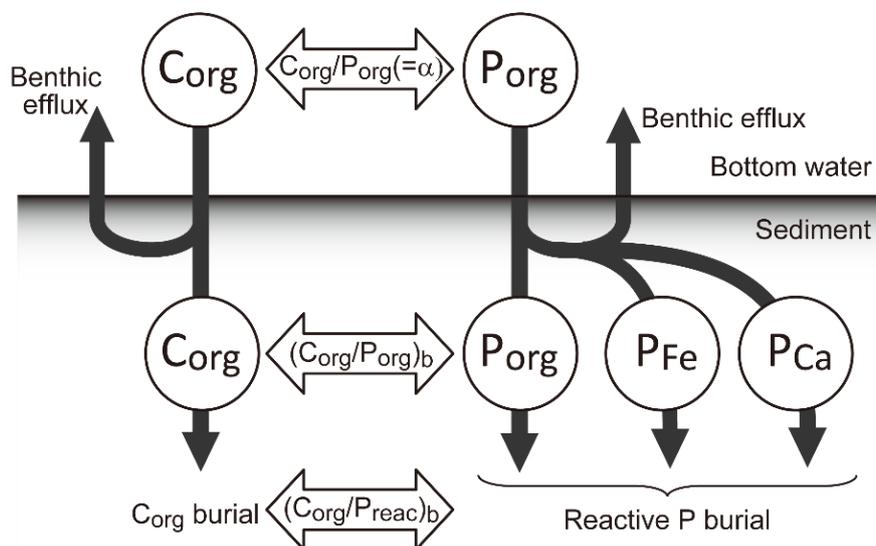
Figure 9 Schematic of P burial in marine sediments. The primary source of P to the sediment is the deposition of organic matter, which represents the C:P ratio of primary producers, α. Most of the deposited organic P is decomposed before burial and the DIP released to pore waters diffuses to the bottom water. A fraction of the liberated P is trapped by iron hydroxides or buried as authigenic minerals (e.g., carbonate fluorapatite). Phosphorus deposited in sediments is a subject of decomposition and sink-switching. Three reactive phases, organic P (P_{org}), Fe-sorbed P (P_{Fe}), and Ca-bound P (P_{Ca}), are considered in the CANOPS-GRB model. The burial of these species are redox-dependent: burial efficiency is affected by 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 sediment-water interface is regenerated (Jahnke, 1996), but a fraction of DIP released via respiration to pore waters is redistributed to other phases such as iron-hydroxide or carbonate fluorapatite within the sediments. This mechanism is known as 'sink-switching' (e.g., Anderson et al., 2001; Filippelli, 2001), and results in P burial other than organic P playing a more important role in the total P sink (Compton et al., 2000; Ruttenberg, 2003, 1993a). Three different P pools are considered in the CANOPS-GRB model: organic P (P_{org}), Fe-hydroxide-sorbed P (P_{Fe}), and authigenic Ca-bound P (P_{Ca}). The sum of these pools is defined as biologically reactive P (P_{reac}) (bioavailable in the ocean to fuel primary productivity). The marine C and P cycles are coupled not only through the C_{org}/P_{org} ratio of POM (α) but also through the C_{org}/P_{reac} ratio of marine sediments. It is important to note that as argued by Anderson et al. (2001), the fundamental measure of the retention versus diffusive loss of remineralized P is not the sedimentary C_{org}/P_{org} ratio, but the ratio of C_{org}/P_{reac}.

47

976

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 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, 2007; Anderson et al., 2001; Colman et al., 2000; Filippelli, 2001; Ingall and Jahnke, 1997). In the 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 $[O_2]_{bw}$ and SR. We assume the following formulation for the C_{org}/P_{org} ratio of the buried organic phase, on the basis of previous studies (Slomp and Van Cappellen, 2007; Van Cappellen and Ingall, 1994, 1996):

$$(C_{org}/P_{org})_b = \begin{cases} \dfrac{(C_{org}/P_{org})_b^{oxic}(C_{org}/P_{org})_b^{anox}}{(C_{org}/P_{org})_b^{anox}\dfrac{[O_2]_{bw}}{oxic}+\left(1-\dfrac{[O_2]_{bw}}{oxic}\right)(C_{org}/P_{org})_b^{oxic}}f_\tau & \text{for } [O_2]_{bw} < oxic \\ (C_{org}/P_{org})_b^{oxic}f_\tau & \text{for } [O_2]_{bw} \geq oxic \end{cases}, \quad (49)$$

where $(C_{org}/P_{org})_b^{oxic}$ and $(C_{org}/P_{org})_b^{anox}$ denote organic C/P ratios for fully oxic and anoxic conditions, and $oxic$ ($=250\ \mu M$) is a threshold value of $[O_2]_{bw}$ below which preferential P regeneration occurs. $(C_{org}/P_{org})_b^{oxic}$ is set to twice the value of the Redfield ratio, and $(C_{org}/P_{org})_b^{anox}$ is an upper limit assumed for organic matter buried under fully anoxic overlying waters, estimated as 40 times larger than the Redfield value on the basis of previous studies on various ancient anoxic basin sediments (Ingall et al., 1993; Slomp and Van Cappellen, 2007). In Eq. (49), we also include the dependence of buried C_{org}/P_{org} ratio on SR, expressed as f_τ. Modern observations suggest that SR is a one of the major factors influencing the preservation versus remineralization of sedimentary organic C and P. Organic C preservation in marine sediments tends to be enhanced at higher SR. In contrast, the C_{org}/P_{org} ratio of sedimentary organic matter shows a non-linear relationship with respect to SR (Ingall and Cappellen, 1990) (Sect. 3.2.3), suggesting more complex behavior of benthic P cycling. Specifically, in the pelagic deep ocean, preferential P regeneration is not observed, likely due to the long timescale of diagenesis prior to burial (Ingall and Cappellen, 1990). In the CANOPS model, f_τ is formulated as follows:

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

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

1000

1001 The burial flux density of P_{org} can be calculated as the C_{org} burial flux density divided by $(C_{org}/P_{org})_b$:

$$j_{Porg}^{b} = \frac{j_{org}^{b,ocn}}{\left(C_{org}/P_{org}\right)_b}. \tag{51}$$

1002 The burial efficiency of P_{org} can be written as follows:

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

1003 where j_P^{dep} denotes the POP settling flux density to sediments, which is coupled to the C/P stoichiometry of

1004 POM ($= j_{org}^{dep}/\alpha$).

1005

1006 Under oxic bottom water conditions, remineralized organic P can be trapped efficiently at the sediment-water

1007 interface by ferric iron phases. In contrast, under anoxic bottom water conditions, a lack of ferric iron phases

1008 allows most mineralized P to diffuse out of the sediment. This redox-dependent P burial is assumed to be

1009 linearly proportional to the $[O_2]_{bw}$ (Slomp and Van Cappellen, 2007):

$$j_{P\text{-}Fe}^{b} = \begin{cases} BE_{Porg}^{oxic}\left(\dfrac{[O_2]_{bw}}{\text{oxic}}\right)j_{Porg}^{dep} & \text{for } [O_2]_{bw} < oxic \\[2ex] BE_{Porg}^{oxic}\, j_{Porg}^{dep} & \text{for } [O_2]_{bw} \geq oxic \end{cases}, \tag{53}$$

1010 where BE_{Porg}^{oxic} denotes the burial efficiency of P_{org} under well-oxygenated bottom water conditions ($[O_2]_{bw}$

1011 $> oxic$). We assume that the retention potential of P_{Fe} in oxic sediments is comparable to that of P_{org}

1012 (Ruttenberg, 1993b).

1013

1014 Some authors have also proposed that authigenic P burial, the dominant process for P burial today (Ruttenberg,

1015 1993b), depends on the redox conditions of the bottom water (Slomp et al., 2002; Slomp and Van Cappellen,

1016 2007). In the CANOPS-GRB model, we adopt the following redox dependence used by Slomp and Van

1017 Cappellen (2007):

$$
j_{\text{P-Ca}}^{\text{b}} = \begin{cases} 2BE_{\text{Porg}}^{\text{oxic}} \left(a_{\text{auth}} + \left(1 - a_{\text{auth}}\right) \dfrac{[\text{O}_2]_{\text{bw}}}{\text{oxic}} \right) j_{\text{Porg}}^{\text{dep}} & \text{for } [\text{O}_2]_{\text{bw}} < oxic \\[2ex] 2BE_{\text{Porg}}^{\text{oxic}} j_{\text{Porg}}^{\text{dep}} & \text{for } [\text{O}_2]_{\text{bw}} \geq oxic \end{cases} \tag{54}
$$

1018 We assume that P_{org}, P_{Fe} and P_{Ca} account roughly for 25%, 25%, and 50%, respectively, of the total reactive

1019 P buried in oxygenated sediments (Ruttenberg, 1993b). Therefore, the burial efficiency of authigenic P phases

1020 is larger than that of P_{org} and P_{Fe} by a factor of 2. The redox-dependency of authigenic P burial is controlled

1021 by a parameter, a_{auth}. There is still great uncertainty as to the sensitivity of P retention efficiency of authigenic

1022 P phases to changing redox conditions. For instance, recent modeling study suggests that the burial of

1023 authigenic P is influenced not only by the redox state of bottom water, but also by the seawater chemistry

1024 (especially Ca^{2+}) (Zhao et al., 2020). In our reference run, we set a_{auth} at 1, no redox-dependency for authigenic

1025 P burial.

Nitrogen cycling

1027 The benthic denitrification rate is estimated with a semi-empirical relationship (Middelburg et al., 1996).

1028 Middelburg and colleagues performed a series of experiments ($n = 2{,}000$) with a 1-D early diagenetic model

1029 of C-N-O_2 to parameterize benthic denitrification $j_{\text{deni}}^{\text{sed}}$ (μmol C cm^{-2} d^{-1}) as a polynomial function using

1030 $j_{\text{org}}^{\text{dep}}$ (μmol C cm^{-2} d^{-1}), z (m), and bottom water concentrations of dissolved O_2 and NO_3^- (μM):

$$
\begin{aligned}
\log j_{\text{deni}}^{\text{sed}} &= c_0 + c_1 \log j_{\text{org}}^{\text{dep}} + c_2 \left(\log j_{\text{org}}^{\text{dep}} \right)^2 + c_3 \log[\text{NO}_3^-]_{\text{bw}} \log[\text{O}_2]_{\text{bw}} \\
&\quad + c_4 \log[\text{NO}_3^-]_{\text{bw}} + c_5 \log[\text{O}_2]_{\text{bw}} + c_6 \log z + c_7 \log j_{\text{org}}^{\text{dep}} \log[\text{O}_2]_{\text{bw}}
\end{aligned} \tag{55}
$$

1031 where $c_0 = -2.2567$, $c_1 = -0.1850$, $c_2 = -0.2210$, $c_3 = -0.3995$, $c_4 = 1.2500$, $c_5 = 0.4721$, $c_6 = -0.0996$, $c_7 = 0.4256$.

1032 This polynomial function was obtained by examining a parameter space spanning 50 m $< z <$ 6,000 m, 10 μM

1033 $< [\text{O}_2]_{\text{bw}} <$ 350 μM, and 1 μM $< [\text{NO}_3^-]_{\text{bw}} <$ 60 μM. $j_{\text{org}}^{\text{dep}}$ was allowed to vary within 2 orders of magnitude

1034 at each water depth (Middelburg et al., 1996). As pointed out by Romaniello and Derry (2010), the predicted

1035 contribution of denitrification to total decomposition f_{deni} ($= j_{\text{denitr}}^{\text{sed}}/j_{\text{recy}}^{\text{sed}}$) can sometimes exceed 100% for

1036 $[\text{O}_2]_{\text{bw}} <$ 10 μM. When the fraction of benthic denitrification to total decomposition exceeds 90%, benthic

1037 denitrification is limited in order to avoid unphysical values (Ozaki and Tajika, 2013; Romaniello and Derry,

1038 2010).

1039

1040 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 the

1041 burial flux of C_{org}:

$$j_{Norg}^{b} = \frac{j_{org}^{b,ocn}}{\left(C_{org}/N_{org}\right)_b} \tag{56}$$

1042 We assumed an average ratio of 10, which is observed in the Washington and Mexico margin (Hartnett and

1043 Devol, 2003; Hedges et al., 1999).

Sulfur cycling

1045 The fractions of MSR and methanogenesis to total decomposition of organic matter in marine sediment are

1046 given by

$$f_{MSR} = \left(1 - f_{aerobic} - f_{denitr}\right) \frac{[SO_4^{2-}]_{bw}}{[SO_4^{2-}]_{bw} + K_{MSR}}, \tag{57}$$

$$f_{meth} = 1 - f_{aero} - f_{deni} - f_{MSR}. \tag{58}$$

1047 The production rate of hydrogen sulfide in sediment, j_{H2S}^{sed} (mol S m^{-2} yr^{-1}), is given by

$$j_{H_2S}^{sed} = \frac{1}{2} f_{MSR} j_{recy}^{sed} + j_{AOM}, \tag{59}$$

1048 where j_{AOM} denotes the production rate of sulfide via AOM:

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

1049 Here we assume that AOM is proportional to the CH$_4$ production rate with a sulfate-dependent term.

1050

1051 The rate of pyrite precipitation in sediments would be proportional to the sulfide production rate at the

1052 sediment-water interface:

$$j_{pyr}^{b,sed} = e_{pyr} j_{H_2S}^{sed}, \tag{61}$$

1053 where the proportional coefficient, e_{pyr}, is the pyrite burial efficiency. The rate of MSR is a function of the

1054 marine redox state, $[SO_4^{2-}]$, and the availability of degradable organic matter. In the well-oxygenated modern

1055 oceans most sulfide produced in sediments is reoxidized and only a few per cent of total sulfide is buried as

1056 pyrite (Bowles et al., 2014; Canfield, 1991; Jørgensen, 1982; Lin and Morse, 1991; Turchyn and Schrag, 2004).

1057 It has been pointed out that efficient oxidation of sulfide is promoted by animal bioturbation (Berner and

1058 Westrich, 1985; Canfield and Farquhar, 2009). In contrast, the value of e_{pyr} for anoxic sediments is much

1059 greater due to the absence of bioturbation and enhanced sulfide production. We assume that e_{pyr} asymptotes

1060 toward unity with decreasing the bottom water [O_2] (Tarhan et al., 2015):

$$e_{pyr} = e_{pyr}^{max} - \left(e_{pyr}^{max} - e_{pyr}^{*} \right) \tanh[O_2]_{bw} , \qquad (62)$$

1061 where e_{pyr}^{max} (= 1 in our reference run) denotes the maximum pyrite precipitation efficiency in anoxic

1062 sediments. The reference value, e_{pyr}^{*}, was calibrated using a present-day control simulation such that the

1063 present-day seawater [SO_4^{2-}] is ~29 mM. The obtained value of 0.117 is generally consistent with modern

1064 observations (Bottrell and Newton, 2006b; Tarhan et al., 2015; Turchyn and Schrag, 2006a) (see Sect. 3).

1065 Although our approach does not provide a mechanistic description of the complex process of pyrite

1066 precipitation, it is suitable for many purposes.

1067 **Early diagenetic modeling for quantifying the OPD**

1068 A simple 1-D early diagenetic model of C and O_2 is employed to obtain the parameterization of OPD (Eq.

1069 (48)). The 100 cm thick sediment is vertically divided into 50 layers with an uneven grid. The grid size

1070 increases from the sediment-water interface (Δz = 0.25 mm) to the maximum simulated sediment depth (Δz =

1071 1.6 cm). The diagenetic model calculates transport and biogeochemical transformation processes at each grid

1072 point within these sediment columns as well as the sedimentary burial and recycling fluxes at the model

1073 boundaries. The one-dimensional mass conservation equation for POC (wt. %) and dissolved O_2 is given by

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

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

1074 where D_{O2} is the diffusion coefficient of O_2, SR is the sedimentation rate, and ϕ is porosity, which is assumed

1075 to be constant over the entire sediment column for simplicity. Bioturbation is formulated as a diffusive process

1076 with a coefficient D_{bio}. The effective diffusion coefficient of O_2 is then given by

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

1077 where $D_{O2}^{T=0}$ denotes a tracer diffusion coefficient in seawater of 0°C, v_{O2} is a coefficient for temperature

1078 dependence of molecular diffusion coefficient. The in situ diffusion coefficient is further corrected for

1079 tortuosity θ, which is related to pore water resistivity and porosity via the following expressions (Berner, 1980;

1080 Colman and Holland, 2000; Tromp et al., 1995):

$$\theta^2 = \phi F \tag{66}$$

$$F = \phi^{-m} \tag{67}$$

1081 where F is the formation factor—defined as the ratio of bulk sediment resistivity to interstitial water

1082 resistivity—and m is an empirical constant, varying with sediment type. We assumed the average value for

1083 unconsolidated muds ($m = 2.7$) in this work (Tromp et al., 1995). The particle mixing coefficient for

1084 bioturbation D_{bio} is formulated as a function of both sediment accumulation rate and bottom water O_2

1085 concentration (Tromp et al., 1995; Wallmann, 2003b):

$$D_{\text{bio}} = 10^{1.63 + 0.85 \log SR} \frac{[O_2]_{\text{bw}}}{[O_2]_{\text{bw}} + K_{O_2}}. \tag{68}$$

1086 At the bottom of the sediment column, a no-flux condition was applied. The parameters used in the 1-D early

1087 diagenetic model are tabulated in Table 6.

1088

1089 Table 6: Parameters used in the 1-D early diagenetic model.

Parameters	Label	Value	Unit	Ref.
Porosity	ϕ	0.8	–	
Dry bulk density	ρ	2.6	g cm^{-3}	
O_2:C ratio for aerobic respiration	r_{O2}	1.4	mol mol^{-1}	
Half-saturation constant for aerobic respiration	K_{O2}	1	μM	
O_2 diffusion coefficient at 0°C	$D_{O2}^{T=0}$	281	cm^2 yr^{-1}	
Coefficient for a temperature dependence of molecular diffusion coefficient	v_{O2}	0.06	°C^{-1}	
Exponent for the formation factor	m	2.7	–	

1090

2.4.5 Air-sea exchange

1092 To calculate the gas exchange of O_2, H_2S, NH_3, and CH_4 across the air–sea interface, we employed a stagnant

1093 film model (Liss and Slater, 1974). The flux of a gas X across the air–sea interface is controlled by the

1094 difference in partial pressure between the atmosphere and surface waters, which can be described by the

1095 following formula:

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

1096 where v_X^{pis}, $[X]_{\text{aq}}$, and $[X]_{\text{sat}}$ denote piston velocity, the dissolved concentration of species X, and the saturation

1097 concentration of species X, respectively. For O_2, the saturation concentration is calculated based on solubility

1098 (Garcia and Gordon, 1992; Sarmiento and Gruber, 2006) and partial pressure:

$$[O_2]_{\text{sat}} = \left(\frac{1000}{22.3916} e^l \right) \left(\frac{pO_2}{pO_2^*} \right), \tag{70}$$

1099 where

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

$$T_s = \ln \left(\frac{298.15 - T}{273.15 + T} \right), \tag{72}$$

1100 with T in °C. The constants are $A_0 = 2.00907$, $A_1 = 3.22014$, $A_2 = 4.0501$, $A_3 = 4.94457$, $A_4 = -0.256847$, $A_5 =$

1101 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 $C_0 = -$

1102 4.88682×10^{-7}. The erroneous $A_3 \times T_s^2$ term in the original equation (Garcia and Gordon, 1992) was left out

1103 (Sarmiento and Gruber, 2006).

1104

1105 For CH_4, H_2S and NH_3, $[X]_{\text{sat}}$ is given by (Kharecha et al., 2005)

$$[X]_{\text{sat}} = K_X^{\text{Henry}} pX, \tag{73}$$

1106 where K_X^{Henry}, and pX denote Henry's law coefficient and the partial pressure of species X, respectively. The

1107 temperature dependence of X's solubility is expressed as:

$$K_X^{\text{Henry}} = K_X^{\text{Henry°}} \exp\left[K_X^T \left(\frac{1}{T} - \frac{1}{298.15} \right) \right], \tag{74}$$

1108 where $K_X^{\text{Henry°}}$ denotes the Henry's law coefficient of species X at 25°C, and K_X^T is the temperature

1109 dependence constant.

1110

1111 $[X]_{\text{aq}}$ is the dissolved concentration of X. $[H_2S]_{\text{aq}}$ and $[NH_3]_{\text{aq}}$ can be written as follows:

$$[H_2S]_{\text{aq}} = \frac{[\Sigma H_2S]}{1 + K_{H_2S}^{\text{dis}}/[H^+]} \tag{75}$$

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

1112 where $[\Sigma H_2S] = [H_2S] + [HS^-]$ and $[\Sigma NH_3] = [NH_4^+] + [NH_3]$. K_{H2S}^{dis} and K_{NH3}^{dis} are the dissociation constant,

1113 defined as follows:

$$K_{H_2S}^{\text{dis}} = \frac{[HS^-][H^+]}{[H_2S]_{\text{aq}}}, \tag{77}$$

$$K_{H_2S}^{\text{dis}} = \frac{[NH_3]_{\text{aq}}[H^+]}{[NH_4^+]}. \tag{78}$$

1114 Given values of K_{H2S}^{dis}, K_{NH3}^{dis} and pH (Millero et al., 1988; Yao and Millero, 1995), $[H_2S]_{\text{aq}}$ and $[NH_3]_{\text{aq}}$ can

1115 be calculated.

1116

1117 In the CANOPS-GRB model, atmospheric concentrations of H_2S and NH_3 are set at 0. H_2S and NH_3 flow past

1118 the surface layer of the ocean to the atmosphere are converted to an equal influx of SO_4^{2-} and NO_3^- to the

1119 surface ocean. The parameters used in the stagnant film model are tabulated in Table 7.

1120

1121 If atmospheric O_2 levels are lower than ~1% PAL spatial heterogeneity of the gas exchange flux is expected

1122 (Olson et al., 2016); for example primary productivity (and O_2 generation) would be more active in coastal

1123 regions than open-ocean gyres. Because our ocean model resolves only two regions for the surface oceans

1124 (low-mid latitude region L and high latitude region H), it tends to overestimate the oxidation of reductants in

1125   surface mixing layers. To mitigate this model limitation for the CH_4 degassing flux, the aerobic oxidation rate

1126   of CH_4 is decreased to 1×10^{-7} of the standard value in surface layers (Ozaki et al., 2019a).

1127

1128   Table 7: Parameters used in the air-sea exchange module of CANOPS-GRB.

Parameters	Label	Value	Unit	Ref.
Piston velocity of O_2	v_{O2}^{pis}	1,000	m yr^{-1}	This study
Piston velocity of NH_3	v_{NH3}^{pis}	300	m yr^{-1}	(WebBook, 2022)
Piston velocity of H_2S	v_{H2S}^{pis}	1072	m yr^{-1}	(WebBook, 2022)
Piston velocity of CH_4	v_{CH4}^{pis}	1419	m yr^{-1}	(WebBook, 2022)
Solubility of NH_3 at 25°C	$K_{NH3}^{Henry°}$	5.6×10^4	mol m^{-3} bar^{-1}	
Solubility of H_2S at 25°C	$K_{H2S}^{Henry°}$	100	mol m^{-3} bar^{-1}	
Solubility of CH_4 at 25°C	$K_{CH4}^{Henry°}$	1.4	mol m^{-3} bar^{-1}	
Temperature dependence of solubility of NH_3	K_{NH3}^{T}	4,100	K	
Temperature dependence of solubility of H_2S	K_{H2S}^{T}	2,100	K	
Temperature dependence of solubility of CH_4	K_{CH4}^{T}	1,600	K	
Sea surface pH at low-mid latitude region	pH^l	8.17	–	This study
Sea surface pH at high latitude region	pH^h	8.16	–	This study
Partial pressure of atmospheric NH_3	pNH_3	0	atm	This study
Partial pressure of atmospheric H_2S	pH_2S	0	atm	This study

1129

1130   **2.5 Land model**

1131   **2.5.1 Net primary productivity**

1132   Terrestrial NPP is scaled by global land biomass V normalized to the modern value:

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

(79)

1133 where the present value of terrestrial NPP is set at 60 Gt C yr^{-1} (Prentice et al., 2001). The global land biomass

1134 is a function of atmospheric O_2 levels:

$$V = f_{UV} f_{fire} f_{O_2},$$ (80)

1135 where f_{O2} represents the direct effect of atmospheric O_2 concentration on the C_3 plant growth, and f_{fire} denotes

1136 the effect of fires on land biota (Bergman et al., 2004; Lenton and Watson, 2000b):

$$f_{O_2} = \max\left\{1.5 - 0.5 pO_2^{PAL}, 0\right\},$$ (81)

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

1137 Here k_{fire} (= 3; Lenton, 2013) is the fire frequency constant, and *ignit* is an ignition factor representing the fire

1138 frequency as a function of oxygen (Lenton, 2013; Lenton et al., 2018; Lenton and Watson, 2000b):

$$ignit = \min\left\{\max\left\{c_1 pO_2 - c_2, 0\right\}, c_3\right\},$$ (83)

1139 with $c_1 = 48$, $c_2 = 9.08$ and $c_3 = 5$ (Lenton, 2013). CANOPS-GRB also includes an additional factor f_{UV}

1140 representing the effect of UV on the terrestrial biosphere as a function of atmospheric O_2 levels (Ozaki and

1141 Reinhard, 2021):

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

1142 where c_{UV} is a model parameter, which, in our standard model is set at 1% PAL, meaning that terrestrial plant

1143 activity is suppressed when atmospheric O_2 is lower than a few % PAL.

2.5.2 Terrestrial biogeochemical cycles

1145 Phosphorus weathering flux, J_P^w (Eq. (2)), is treated as a boundary condition. A fraction of weathered P is

1146 ultimately buried as terrigenous organic matter (Eq. (3)), whereas the remaining fraction is delivered to the

1147 ocean via rivers (Eq. (4)). In the CANOPS-GRB model, the reference value of J_P^r (= 0.155 Tmol P yr^{-1}) is

1148 tuned so that the oceanic P level of the reference state is consistent with modern observations. The burial rate

1149 of terrigenous organic matter (in terms of C) can be written as follows:

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

1150 where $(C_{\text{org}}/P_{\text{org}})^{\text{lnd}}$ (= 1000) is the average C/P burial ratio of terrigenous organic matter (Bergman et al.,

1151 2004). In this study, the reference value of $J_{\text{org}}^{\text{b,lnd}}$ was set at 3 Tmol C yr^{-1}. By combining Eqs. (3), (4), and

1152 (85) for the reference state, the proportional coefficient k_{11} of Eq. (3) is determined by the reference state, as

1153 follows:

$$k_{11} = \frac{J_{\text{org}}^{\text{b,lnd,*}}}{J_{\text{org}}^{\text{b,lnd,*}} + \left(C_{\text{org}} / P_{\text{org}} \right)^{\text{lnd}} J_{\text{P}}^{\text{r,*}}} = 0.0189 \, . \tag{86}$$

1154 The value of k_{11} is treated as a constant in this study.

1155

1156 Almost all organic matter produced by terrestrial NPP is decomposed before burial. The total decomposition

1157 rate is given by:

$$J_{\text{org}}^{\text{r,lnd}} = J_{\text{NPP}}^{\text{lnd}} - J_{\text{org}}^{\text{b,lnd}} \, . \tag{87}$$

1158 CANOPS-GRB includes aerobic respiration and methanogensis as respiration pathways for terrigenous matter,

1159 and the CH$_4$ flux from the terrestrial ecosystem to the atmosphere is evaluated with the assumption that it is

1160 proportional to the burial rate of terrigenous organic matter:

$$J_{\text{CH}_4}^{\text{lnd}} = \left(\frac{J_{\text{org}}^{\text{b,lnd}}}{J_{\text{org}}^{\text{b,lnd,*}}} \right) J_{\text{CH}_4}^{\text{lnd,*}}, \tag{88}$$

1161 where the reference value was set at 1 Tmol CH$_4$ yr^{-1}. The net flux of CO$_2$, O$_2$ and CH$_4$ from the terrestrial

1162 ecosystem to the atmosphere can be written, as follows:

$$J_{\text{CO}_2}^{\text{lnd}} = \left(g_{\text{O}_2} + \frac{1}{2}(1+\delta) g_{\text{CH}_4} \right) J_{\text{org}}^{\text{r,lnd}}, \tag{89}$$

$$J_{\text{O}_2}^{\text{lnd}} = J_{\text{NPP}}^{\text{lnd}} - \left(g_{\text{O}_2} + \delta g_{\text{CH}_4} \right) J_{\text{org}}^{\text{r,lnd}}, \tag{90}$$

$$J_{\text{CH}_4}^{\text{lnd}} = \frac{1}{2}(1-\delta) g_{\text{CH}_4} J_{\text{org}}^{\text{r,lnd}}, \tag{91}$$

1163 where g_{O2} and g_{CH4} denote the fraction of organic matter decomposed by aerobic respiration and

1164 methanogenesis, respectively. δ represents the fraction of methane that is consumed by aerobic methanotrophy

1165 that is a function of O_2:

$$\delta = \frac{M_{O_2}^{atm}}{M_{O_2}^{atm} + K_{O_2}^{'}} , \tag{92}$$

1166 with K'_{O2} = 0.273×10^{18} mol (Goldblatt et al., 2006). A fraction of organic matter decomposed by

1167 methanogenesis, g_{CH4}, can be calculated based on Eqs. (89) and (91). Then, g_{O2} is determined from 1-g_{CH4}.

1168 **2.5.3 Weathering**

1169 The oxidative weathering of continental crust is a major oxygen sink on geologic timescales, providing a

1170 fundamental control on atmospheric O_2 levels. The weathering rate in the model is assumed to be proportional

1171 to sedimentary reservoir size and a global erosion factor, f_R, expressing the effect of continental

1172 denudation/erosion on terrestrial weathering:

$$J_{org}^{w} = f_R f_{orgw}^{O_2} \left(\frac{ORG}{ORG^*} \right) J_{org}^{w,*} , \tag{93}$$

$$J_{pyr}^{w} = f_R f_{pyrw}^{O_2} \left(\frac{PYR}{PYR^*} \right) J_{pyr}^{w*} , \tag{94}$$

1173 where J_{org}^{w} and J_{pyr}^{w} denotes the oxidative weathering of organic carbon and pyrite, respectively, and f_{orgw}^{O2}

1174 and f_{pyrw}^{O2} represent the O_2 dependency. For the oxidative weathering of organic matter, previous

1175 biogeochemical models have adapted a $(pO_2^{PAL})^{0.5}$ relationship (Bergman et al., 2004; Lasaga and Ohmoto,

1176 2002). In this study, we employ alternative empirical relationships based on results obtained from a 1-D

1177 weathering model (Bolton et al., 2006; Daines et al., 2017):

$$f_{orgw}^{O_2} = c_{orgw} \frac{pO_2^{PAL}}{pO_2^{PAL} + K_{orgw}} , \tag{95}$$

$$f_{pyrw}^{O_2} = c_{pyrw} \frac{pO_2^{PAL}}{pO_2^{PAL} + K_{pyrw}} , \tag{96}$$

1178 where K_{orgw} and K_{pyrw} denote half-saturation constants (K_{orgw} = 0.334 and K_{pyrw} = 0.017) and c_{orgw} and c_{pyrw}

1179 are normalized constants (c_{orgw} = 1.334 and c_{pyrw} = 1.017), respectively. The Monod-type relationship captures

1180 the fact that the rate of oxidative weathering reaches its maximum as determined by the erosion rate under

1181 highly oxygenated conditions (i.e., transport-limited regime). For example, due to the fast dissolution kinetics

1182 of pyrite, oxidative weathering can be regarded as transport-limited under modern conditions (Bolton et al.,

1183 2006) (Fig. 10). In the CANOPS-GRB model, J_{org}^{w*} is calibrated based on the global redox budget of the

1184 reference run (see Sect. 2.2.5).

1185

1186 It is important to note that above equations ignore the possible importance of microbial activity and

1187 temperature on the rate of oxidative weathering (Petsch et al., 2001; Soulet et al., 2021). Both represent

1188 important topics for future research.

1189
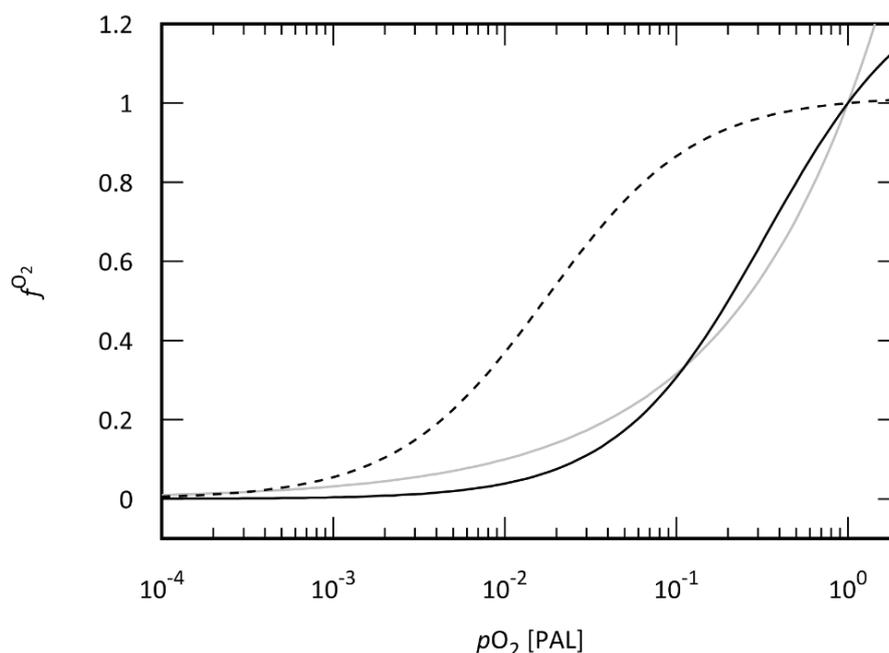
1190

1191 **Figure 10** O$_2$ dependency of the oxidative weathering rate of organic matter and pyrite sulfur. Gray line
1192 denotes the $(pO_2^{PAL})^{0.5}$ relationship assumed in previous biogeochemical models (Daines et al., 2017; Lasaga
1193 and Ohmoto, 2002). Solid and dashed black lines represent the empirical Monod-type relationships for
1194 oxidative weathering of organic matter and pyrite sulfur based on the results obtained from a 1-D weathering
1195 model (Bolton et al., 2006; Daines et al., 2017), which are adopted in the standard model of the CANOPS-
1196 GRB model. PAL = present atmospheric level.

1197

1198 The present riverine flux of sulfur, J_S^{r*}, is estimated at 2.6 Tmol S yr^{-1} (Raiswell and Canfield, 2012),

1199 representing the dominant source to the oceans. Riverine flux is written as the sum of the gypsum weathering

1200 flux J_{gyp}^w and the oxidative weathering of pyrite J_{pyr}^w and depends directly or indirectly on the oxidation state

1201 of the atmosphere:

$$J_S^r = J_{gyp}^w + J_{pyr}^w. \tag{97}$$

1202 Based on previous studies (Bergman et al., 2004; Berner, 2009; Markovic et al., 2015; Wortmann and Paytan,

1203 2012), a 3:1 ratio in modern rivers of SO_4^{2-} from gypsum versus pyrite weathering is assumed. Gypsum

1204 weathering flux is assumed to be proportional to its sedimentary reservoir size, GYP, and f_R:

$$J_{gyp}^w = f_R \left(\frac{GYP}{GYP^*} \right) J_{gyp}^{w*}, \tag{98}$$

1205 where * represents the present value.

1206

1207 In the previous version of the CANOPS (Ozaki et al., 2019a), oxidative weathering of pyrite was divided to

1208 biogenic and abiotic weathering fluxes. In this study, we simplify this (Eq. (94)). Also, oxidative weathering

1209 of Fe(II)-bearing minerals is ignored in this study, which simplifies the framework of the global O_2 budget

1210 (Sect. 2.2.5).

2.5.4 Volcanic degassing

1212 Volcanic outgassing fluxes of carbon and sulfur are assumed to be proportional to their respective crustal

1213 reservoir sizes:

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

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

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

1214 We set the reference value of the volcanic outgassing flux of organic carbon, $J_{org}^{m,*}$, at 1.25 Tmol C yr^{-1}

1215 (Bergman et al., 2004). The estimates of modern volcanic fluxes of sulfur fall within the range of ~0.3−3 Tmol

1216 S yr^{-1} (Catling and Kasting, 2017; Kagoshima et al., 2015; Raiswell and Canfield, 2012; Walker and

1217 Brimblecombe, 1985). We adopted a recent estimate of 0.8 Tmol S yr^{-1} (Kagoshima et al., 2015).

2.5.5 Sedimentary reservoirs

1219 We extend the original model framework to the explicit calculation of the secular evolution of the sedimentary

1220 reservoirs, linking the biogeochemical cycles in the ocean-atmosphere system to the rock cycle. The mass

1221 balance equation for sedimentary organic carbon (*ORG*) can be written as follows:

$$\frac{dORG}{dt} = J_{\text{org}}^{\text{b}} - J_{\text{org}}^{\text{w}} - J_{\text{org}}^{\text{m}}, \tag{102}$$

1222 where $J_{\text{org}}^{\text{b}}$ denotes the sum of the burial rate of marine and terrigenous organic matter ($J_{\text{org}}^{\text{b,ocn}} + J_{\text{org}}^{\text{b,lnd}}$), the

1223 primary source of sedimentary organic carbon. Primary outputs are oxidative weathering, volcanic outgassing

1224 and metamorphism. Previous estimates of the present reservoir size of *ORG* fall in the range of 1000−1300

1225 Emol (1 E =10^{18}) (Berner, 1989; Garrels and Perry, 1974; Mackenzie et al., 1993). We assumed 1250 Emol

1226 for the reference value of *ORG*.

1227

1228 The sedimentary reservoir sizes of pyrite sulfur (*PYR*) and gypsum sulfur (*GYP*) are also written as the balance

1229 between the input (burial) and outputs (weathering and outgassing):

$$\frac{dPYR}{dt} = J_{\text{pyr}}^{\text{b}} - J_{\text{pyr}}^{\text{w}} - J_{\text{pyr}}^{\text{m}}, \tag{103}$$

$$\frac{dGYP}{dt} = J_{\text{gyp}}^{\text{b}} - J_{\text{gyp}}^{\text{w}} - J_{\text{gyp}}^{\text{m}}, \tag{104}$$

1230 where $J_{\text{pyr}}^{\text{b}}$ represents the sum of pyrite precipitation rates in the water column and sediments, $J_{\text{pyr}}^{\text{b,wc}} + J_{\text{pyr}}^{\text{b,sed}}$.

1231 Previous estimates of present reservoir sizes of *GYP* and *PYR* fall in the range of 77−300 Emol and 155−300

1232 Emol (Berner, 2006; Bottrell and Newton, 2006a; Holser et al., 1989; Kump, 1989; Lasaga, 1989; Schlesinger

1233 and Bernhardt, 2013; Sleep, 2005; Yaroshevsky, 2006), respectively. We adopted 200 Emol and 200 Emol for

1234 *GYP** and *PYR**.

2.6 Atmosphere model

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_4 appears to have been the dominant hydrogen-bearing species in the stratosphere, and the flux, J_{Hesc} (mol yr^{-1}), is calculated as

$$J_{Hesc} = sM_{CH_4}^{atm},$$

(105)

where M_{CH4}^{atm} denotes the abundance of CH_4 in the atmosphere (mol) and s (= 3.7×10^{-5} yr^{-1}) is a proportional coefficient (Goldblatt et al., 2006).

2.6.2 Photochemistry

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

$$J_{CH_4ox} = k_{CH_4ox}M_{O_2}^{atm}M_{CH_4}^{atm},$$

(106)

where M_{O2}^{atm} and M_{CH4}^{atm} denote the abundance of O_2 and CH_4 in the atmosphere (mol). The reaction rate k_{CH4ox} (mol^{-1} yr^{-1}) is expressed as a polynomial function of the reservoir sizes of O_2 and CH_4 (Ozaki and Reinhard, 2021):

$$\log k_{CH_4ox} = \alpha_0^j + \alpha_1^j \cdot \varphi_{O_2} + \alpha_2^j \cdot \varphi_{O_2}{}^2 + \alpha_3^j \cdot \varphi_{O_2}{}^3 + \alpha_4^j \cdot \varphi_{O_2}{}^4 + \alpha_5^j \cdot \varphi_{O_2}{}^5 + \alpha_6^j \cdot \varphi_{O_2}{}^6,$$

(107)

where a_i^j are fitting coefficients for given atmospheric CH_4 levels and φ_{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^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 2×10^{-3} bar, and k_{CH4ox} is calculated as a function of pO_2 and pCH_4 with a log-linear interpolation method.

2.6.3 Mass balance

CANOPS-GRB accounts for the atmospheric concentrations of O_2 and CH_4. The atmospheric concentration of O_2 is determined by the biogenic source (from the ocean and terrestrial ecosystems) and the consumption through the series of oxidation reaction (the continental weathering of kerogen and pyrite, volcanic outgassing, and photochemical oxidation of methane):

$$\frac{dM_{O_2}^{atm}}{dt} = J_{O_2\uparrow}^{air\text{-}sea} + J_{O_2\uparrow}^{air\text{-}lnd} - \left(J_{Hesc} + 2J_{CH_4 ox} \right) - \left(J_{org}^{w} + J_{org}^{m} \right) - 2\left(J_{pyr}^{w} + J_{pyr}^{m} \right), \qquad (108)$$

where M_{O2}^{atm} denotes the mass of O_2 in the atmosphere (moles), and the first and second term on the right hand side represents the biogenic flux of O_2 from marine and terrestrial ecosystems. The third term denotes O_2 consumption via photochemistry, and the fourth and fifth terms are the O_2 consumption via organic C and pyrite S sub-cycles.

The abundance of CH_4 in the atmosphere, M_{CH4}^{atm}, is determined by input from the ecosystems and the consumption of CH_4 via photolysis, as well as by the hydrogen escape:

$$\frac{dM_{CH_4}^{atm}}{dt} = J_{CH_4\uparrow}^{air\text{-}sea} + J_{CH_4\uparrow}^{air\text{-}lnd} - \left(J_{Hesc} + J_{CH_4 ox} \right). \qquad (109)$$

No abiotic CH_4 input via hydrothermal systems is included.

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).

3.1 Distribution of circulation tracers

Comparisons of model output with circulation tracers, such as potential temperature (θ) and radiocarbon ($\Delta^{14}C$), permit a test of the physical exchange scheme. Figure 11 depicts the simulated patterns of physical tracers with observational data. The physical circulation in the model generally agrees well with oceanic observations, although we note that model temperatures for low-mid latitudes above 1,000 m water depth tend to be higher than observed because temperature distribution in the real ocean is strongly controlled by vertical structure and advective processes that are not captured in our simple circulation scheme. Despite this model limitation, the modelled temperature distribution generally reproduces the observed distribution. The $\Delta^{14}C$ minimum in the model for the low-mid latitude region corresponds well with observations. The modelled background radiocarbon for young deep waters (about -150±25‰) is closer to the value for the Southern Ocean (approximately -150‰) than for North Atlantic deep waters (approximately -80‰), and old deep waters (-200±15‰) correspond to the South Pacific. We conclude that the simulated circulation tracers generally match well with ocean data.

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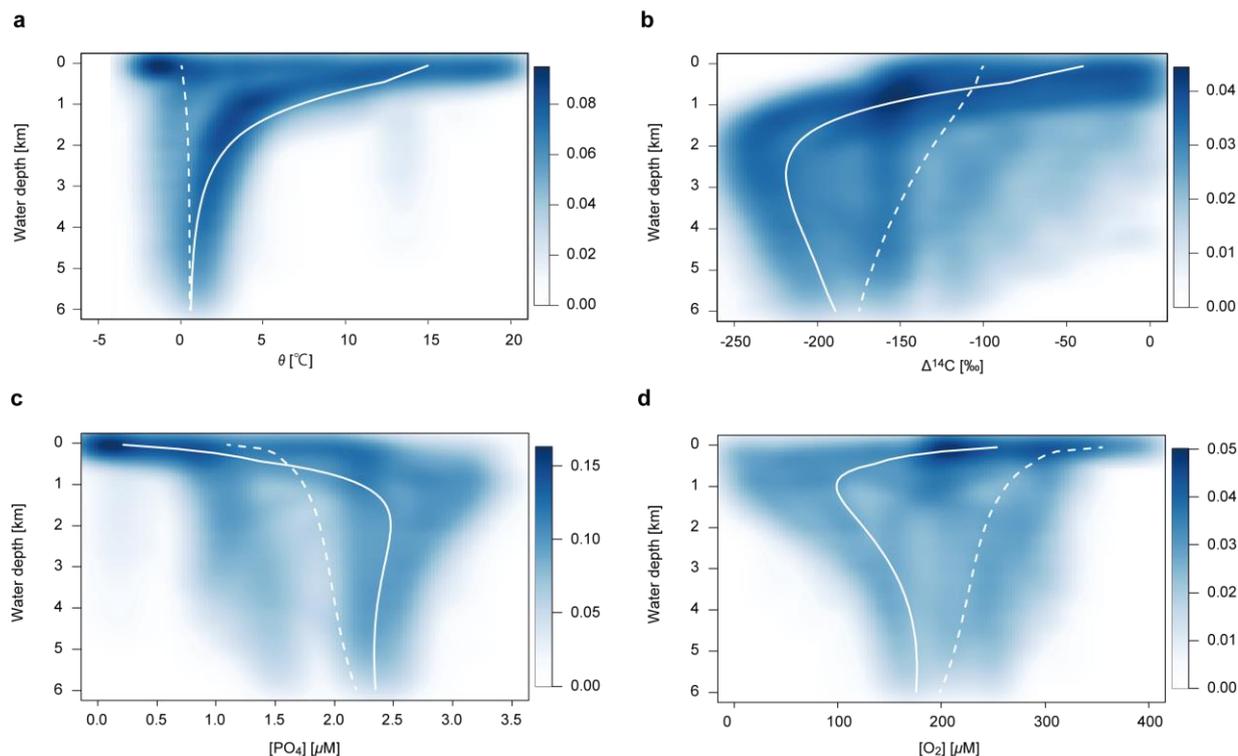
Figure 11 Simulated steady state depth-profiles of (**a**) potential temperature, θ, (**b**) radio carbon, $\Delta^{14}C$, (**c**) DIP (dissolved inorganic phosphorus, PO_4^{3-}), and (**d**) dissolved oxygen, O_2. Solid and dashed white lines denote the simulated profiles for LD and HD region, respectively. 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.

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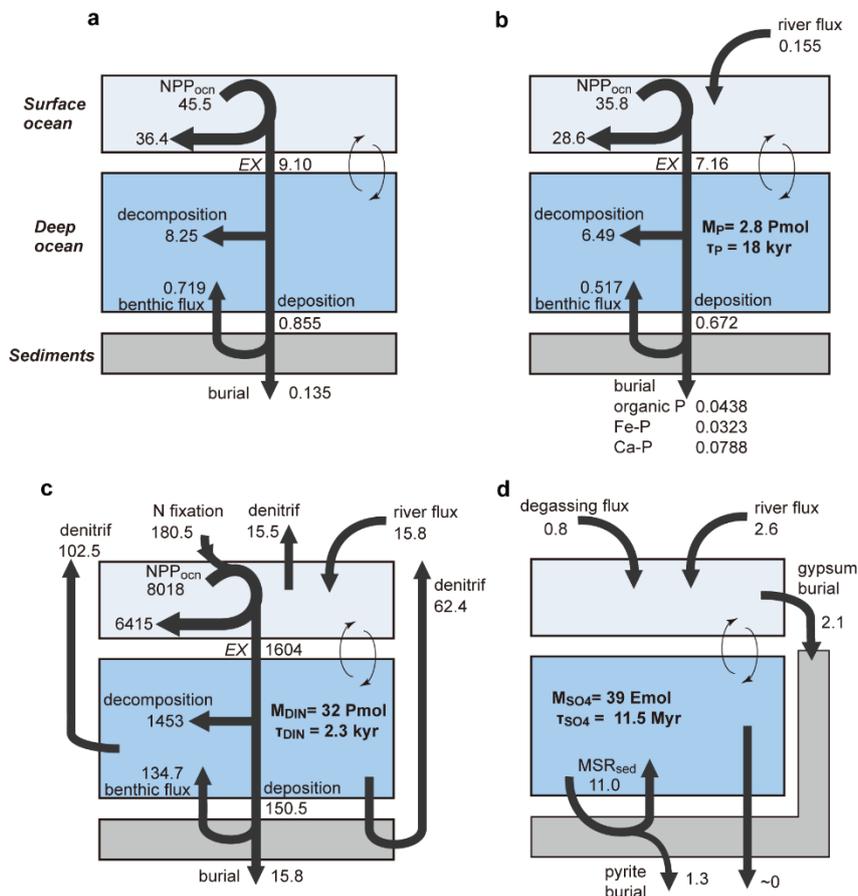
Figure 12 Schematics of the simulated material flow in the ocean for the reference run. (**a**) Organic carbon (in Gt C yr^{-1}), (**b**) phosphorus (in Tmol P yr^{-1}), (**c**) nitrogen (in Tg N yr^{-1}), and (**d**) sulfur (in Tmol S yr^{-1}). NPP$_{ocn}$ = oceanic net primary production. EX = export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

3.2.1 Distribution of nutrients and oxygen

The simulated vertical profile of phosphate captures the characteristic features and values of observational data (Fig. 11c). More specifically, the distribution in the low-mid latitude region is more similar to that in the Pacific and Indian Ocean, and distribution of high-mid latitude region is similar to that in the Southern Ocean. This is a consequence of limiting high-latitude productivity (preformed DIP is 1.1 μM) which results in higher concentrations in the ocean interior. The model dissolved O$_2$ profile for low-mid latitude shows a minimum of approximately 100 μM at water depth of 1,000 m, corresponding to the oxygen minimum zone (Fig. 11d).

67

1313 In contrast, dissolved O_2 for high-mid latitude sector (HD) shows a monotonically decreasing trend. This is
1314 because of oxygen consumption via POM decomposition during downwelling.

3.2.2 Carbon cycling

1316 The marine export/new production in our model is 9.1 Gt C yr^{-1} (8.36 Gt C yr^{-1} at L and 0.74 Gt C yr^{-1} at H).
1317 This is consistent with previously estimated global values of 8.5–12 Gt C yr^{-1} (Dunne et al., 2007a; Heinze et
1318 al., 2009; Laws et al., 2000; Sarmiento and Gruber, 2006). In particular, our estimate is close to the mid-point
1319 of the previously estimated range of 9.6±3.6 Gt C yr^{-1} (Dunne et al., 2007b). This is a marked improvement
1320 from earlier studies with box models which have underestimated marine new production by a factor of 2 or
1321 more (Archer et al., 2000; Shaffer et al., 2008). Simulated global oceanic NPP is 45.5 Gt C yr^{-1}. This is also
1322 consistent with the previous estimated range of 44–65 Gt C yr^{-1} (Berelson et al., 2007; Carr et al., 2006;
1323 Prentice et al., 2001; Woodward, 2007).

1324
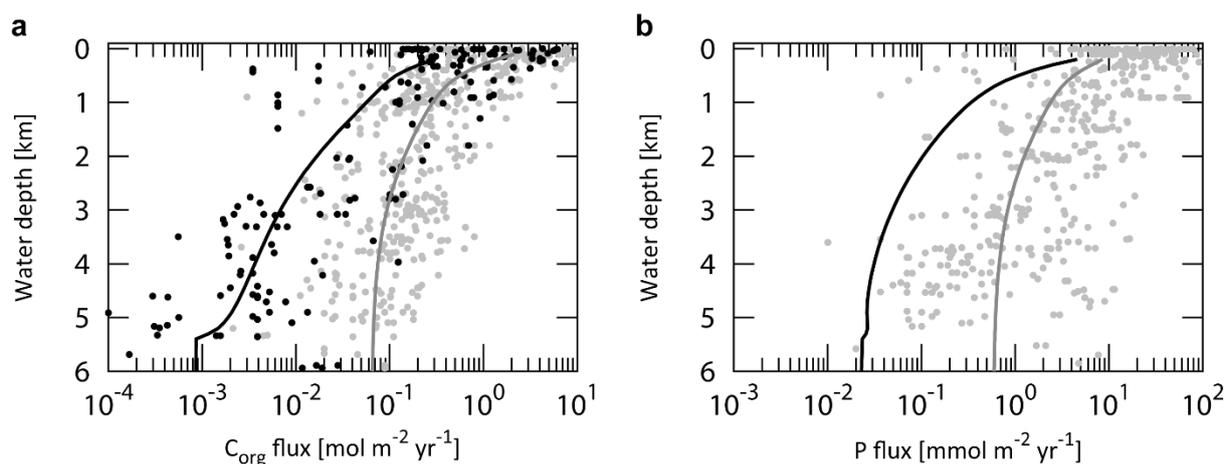
Figure 13 Simulated steady-state depth-profiles of organic C and reactive P flux density for the LD region. In
(**a**), gray dots denote observations of depositional/settling flux density, whereas black dots represent
observations of burial flux density compiled from literature survey (Baturin, 2007; Betts and Holland, 1991;
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 obtained
from literature survey (Colman et al., 2000; Hartnett and Devol, 2003; Hensen et al., 1998; Ingall and Jahnke,
1994, 1997; McManus et al., 1997; 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 P obtained from
the reference run.

1335

1336   The global marine POC flux depends largely on water depth. Model-generated fluxes compare well with

1337   independent estimates of deposition, burial, and regeneration. The gray line in Fig. 13a shows the simulated

1338   sinking flux density of POC in the water column for LD region, compared with observations (Archer et al.,

1339   2002; Baturin, 2007; Betts and Holland, 1991; Lutz et al., 2002). The preferential consumption of labile

1340   compounds (G_1 and G_2) during the settling process leads to a continuous decrease in reactivity and therefore,

1341   remineralization rates from the surface ocean down to the deep. Our estimate lies well within the range of

1342   observations. The model tends to give lower fluxes than observed above 2,000 m water depth, and higher

1343   below 5,000 m water depth. This is probably because of the assumption of homogeneous productivity in the

1344   surface ocean. In the real ocean, oceanic productivity is generally greater at the continental margins than in

1345   the pelagic gyre regions (Lutz et al., 2002). This is a model limitation, but the simulated biological pump is

1346   sufficient to describe the general characteristics of global ocean biogeochemistry.

1347

1348   Of total exported POC, 91% (8.25 Gt C yr^{-1}) is decomposed in the water column and the rest (0.85 Gt C yr^{-1})

1349   sinks to the sediment surface (Fig. 12a). The simulated global POC depositional flux is comparable not only

1350   with observational estimates of 0.93 Gt C yr^{-1} (Muller-Karger et al., 2005) and 0.67±0.48 Gt C yr^{-1} for off-

1351   shore regions (Dunne et al., 2007b), but also with an estimate using EMIC (0.87 Gt C yr^{-1}) (Ridgwell and

1352   Hargreaves, 2007). The depositional fluxes of C_{org} in marginal (<2,000 m) and deep-sea sediments (>2,000

1353   m) are estimated at 0.58 Gt C yr^{-1} and 0.27 Gt C yr^{-1}, respectively. These estimates are slightly lower than

1354   previous estimates of 0.62–1.98 Gt C yr^{-1} and 0.31–0.62 Gt C yr^{-1} (Bohlen et al., 2012; Burdige, 2007; Dunne

1355   et al., 2007a; Muller-Karger et al., 2005).

1356

1357   In our standard run, benthic remineralization removes 7.9% of the exported POC (0.72 Gt C yr^{-1}), equivalent

1358   of 84% of the global POC sedimentation rate. As a result, only 1.5% (0.135 Gt C yr^{-1} or 11.3 Tmol C yr^{-1}) of

1359   the global POC export production is ultimately buried in marine sediments. Our model demonstrates that much

1360   (91%) of the total burial occurs on the continental margins (<2,000 m water depth), where the settling flux

1361   and burial efficiency are relatively high. Previous studies (Dunne et al., 2007b; Muller-Karger et al., 2005)

1362   estimated a C_{org} burial rate of 0.29±0.15 Gt C yr^{-1} and >0.06±0.06 Gt C yr^{-1} at the margin. Our estimate of

1363 0.123 Gt C yr^{-1} lies between these values, whereas our estimate for the deep sea, 0.012 Gt C yr^{-1}, is on the

1364 lower end of previous estimates of 0.012±0.02 Gt C yr^{-1} (Dunne et al., 2007b) and 0.017±0.005 Gt C yr^{-1}

1365 (Hayes et al., 2021). Also, Hayes et al. (2021) and Sarmiento and Gruber (2006) estimated the burial rate

1366 below 1,000 m as 0.02±0.006 Gt C yr^{-1}; our estimate of 0.019 Gt C yr^{-1} is consistent with this. Combined with

1367 the prescribed burial rate of terrigenous C_{org} 0.036 Gt C yr^{-1} (3 Tmol C yr^{-1}), the total burial rate is calculated

1368 to be 0.17 Gt C yr^{-1} (14.3 Tmol C yr^{-1}). This is somewhat higher than previous estimates (Berner, 1982;

1369 Burdige, 2005; Muller-Karger et al., 2005), but given the rather large uncertainty we consider it defensible.

1370

1371 Figure 14 shows OPD as a function of water depth. Although the benthic data could be biased towards highly

1372 specific environments, such as sediments underlying upwelling areas and continental margins, our estimates

1373 capture the general features of modern observations.

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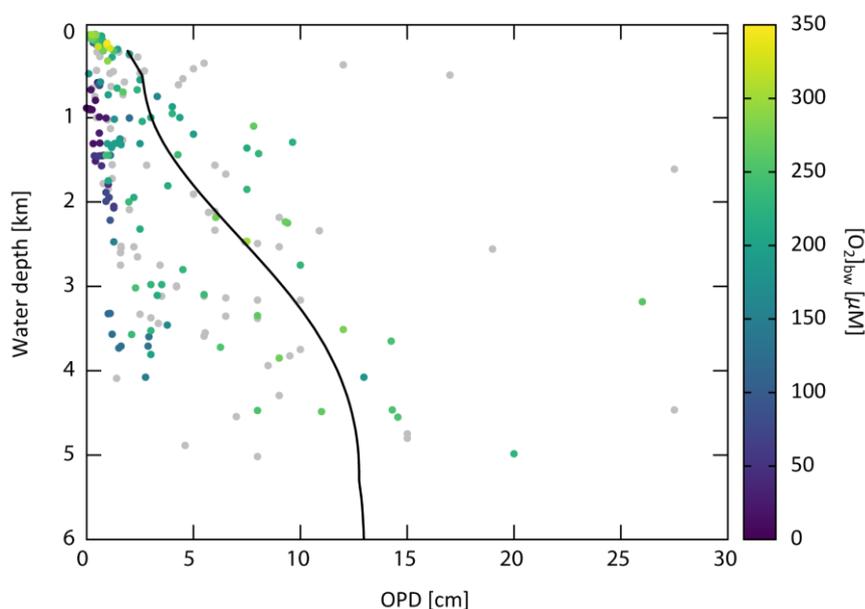
1375

1376 **Figure 14** Oxygen penetration depth (OPD) as a function of water depth. Color dots denote the observational
1377 data obtained from literature survey (Bradley et al., 2020; Devol and Christensen, 1993; Donis et al., 2016;
1378 Gundersen and Jorgensen, 1990; Hartnett et al., 1998; Hedges et al., 1999; Hyacinthe et al., 2001; Martin and
1379 Sayles, 2014; McManus et al., 2005; Morford and Emerson, 1999; Nierop et al., 2017; Pfeifer et al., 2002;
1380 Rowe et al., 2008; Sachs et al., 2009). Colors represent the O_2 concentration of bottom water (Gray dots
1381 represents the unknown dissolved O_2 concentration). The simulated OPD obtained from the reference run is
1382 shown as a black line.

1383

3.2.3 Phosphorus cycling

1385 The removal of phosphate from surface waters occurs through photosynthetic fixation by primary producers

1386 and subsequent export in the form of POP into deeper waters, where it is largely remineralized back into DIP.

1387 Through this process there is a vertical partitioning of DIP within the ocean with reduced surface

1388 concentrations. Phosphorus export production is 7.16 Tmol P yr^{-1}, which is coupled with carbon according to

1389 the POM compositional ratio (C:P = 106:1 for our standard model). The remineralization in the water column

1390 (6.49 Tmol P yr^{-1}) and total sedimentation rate (0.672 Tmol P yr^{-1}) are also proportional to those of POC. In

1391 contrast, the benthic DIP flux is decoupled from the carbon flux. Figure 13b shows modelled DIP benthic

1392 efflux and burial flux together with observed fluxes. Some observational data showing a relatively large

1393 abyssal (4–6 km) benthic flux are from upwelling regions in the South Atlantic (Hensen et al., 1998). The

1394 deviation is therefore not critical for our globally averaged model. Our model gives the total benthic efflux of

1395 DIP as 0.517 Tmol P yr^{-1}, which is roughly three times the riverine reactive P input rate. This is within the

1396 range of previous estimates of 0.05–1.25 Tmol P yr^{-1} (Colman and Holland, 2000; Compton et al., 2000;

1397 Wallmann, 2003b; Wallmann, 2010b).

1398

1399 The preservation efficiency (here defined as burial flux divided by the export flux) of P is 2.1%. This is higher

1400 than that of organic carbon (1.5%), indicating that more P is trapped in marine sediments than might be

1401 expected from Redfield stoichiometry. In oxic marine sediments, a fraction of the DIP released to pore waters

1402 from POM decomposition can be absorbed by iron-oxyhydroxide or precipitated as authigenic fluorapatite

1403 (Fig. 9). Therefore, the global averaged C_{org}/P_{reac} ratio of buried sediments is generally less than the Redfield

1404 of 106 (approximately 65±25 based on observations; Algeo and Ingall, 2007). The modelled global average

1405 C_{org}/P_{reac} ratio of buried sediment is 73, consistent with this. The P burial fluxes of organic P, Fe-bound P and

1406 authigenic P are estimated at 0.044 Tmol P yr^{-1}, 0.032 Tmol P yr^{-1}, and 0.079 Tmol P yr^{-1}, respectively.

1407

1408 The C_{org}/P_{org} ratio of burying organic matter shows a non-linear relationship with respect to sedimentation

1409 rate. The observed C_{org}/P_{org} ratios are generally greater than the Redfield value of 106, especially for sediments

1410   in oxygen minimum zones (OMZs), which are characterized by a high depositional flux of organic matter

1411   (C_{org}/P_{org} ratios up to 600 for the present open ocean) (Ingall and Cappellen, 1990). For example, the averaged

1412 C_{org}/P_{org} molar ratio at the Peru-Chile OMZ and Black Sea are 600, and the estimated burial ratio of sapropel

1413   S1 of Mediterranean Sea is in the range of 400−800 (Slomp et al., 2002). This reflects the preferential

1414   regeneration of P relative to C during microbial remineralization of marine organic matter and reflect the more

1415   labile nature of P-biochemicals relative to most non-phosphorus containing organic carbon compounds.

1416   Additional rationale for this observation is that P is preferentially targeted for remineralization to support

1417   subsequent biological productivity as an essential and potentially limiting nutrient. Our model demonstrates

1418   that we can reproduce the first-order relationship between C_{org}/P_{org} and sediment accumulation rate (Fig. 15).

1419

1420   The modelled marine DIP inventory is 2.75×10^{15} mol, consistent with the observational estimate of around

1421 3×10^{15} mol (e.g., Delaney, 1998; Guidry et al., 2000). Given the riverine reactive P input flux of 0.155 Tmol

1422   P yr^{-1}, the phosphorus residence time is estimated at 18 kyr, which is also consistent with previous estimates

1423   of 20 kyr or shorter (Benitez-Nelson, 2000; Ruttenberg, 2003).

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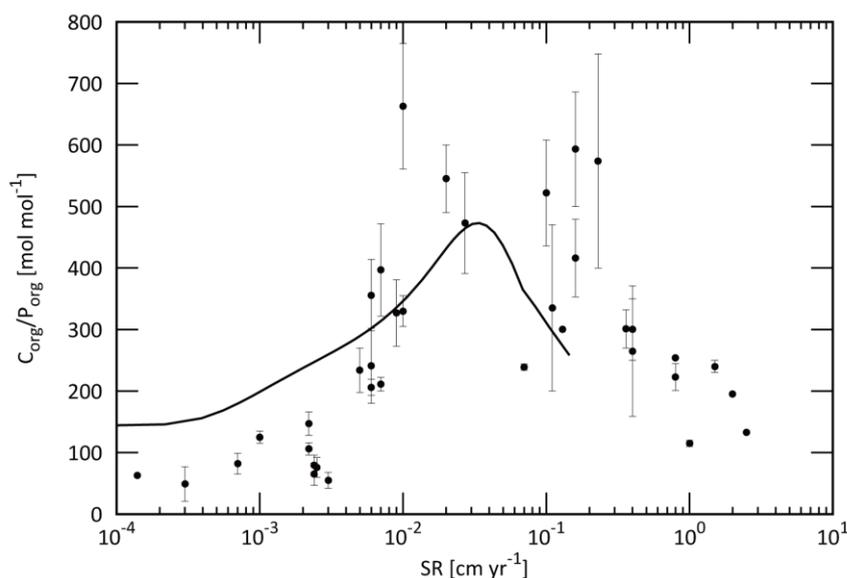
1425

1426   **Figure 15** C_{org}/P_{org} ratios of buried sediments as a function of sedimentation rate. Black dots represent the
1427   observational data (Ingall and Cappellen, 1990). The simulated C_{org}/P_{org} ratios for the LD region obtained
1428   from our reference run is shown as a black line.

1455   The modelled DIN inventory is 4.5×10^5 Tg N. Given the total source flux of 196 Tg N yr^{-1}, the residence time

1456   of DIN is estimated at 2.3 kyr.

3.2.5 Sulfur cycling

1458   MSR is a major early diagenetic pathway of carbon oxidation in organic-rich sediments deposited below

1459   oxygenated waters. For the standard run, aerobic oxidation is a dominant process in the water column, but

1460   MSR contributes 37% of benthic degradation. CANOPS-GRB estimates a global rate of benthic sulfate

1461   reduction at 11 Tmol S yr^{-1}. This is lower than the previously reported value of gross MSR (40–75 Tmol S yr^{-1}

1462   ; Canfield and Farquhar, 2009; Jørgensen and Kasten, 2006) but agrees better with net MSR (Bowles et al.,

1463   2014). Bowles et al. (2014) have estimated global net MSR at 6.2 Tmol S yr^{-1} and 11.3 Tmol S yr^{-1} for $z >$

1464   200 m depth and $z > 0$ m depth, respectively. Our estimate is within this range. MSR is most pronounced on

1465   the shelf where high fluxes of organic matter to the seafloor lead to shallow OPD, high sulfide production,

1466   and consequently high pyrite precipitation (Fig. 16).
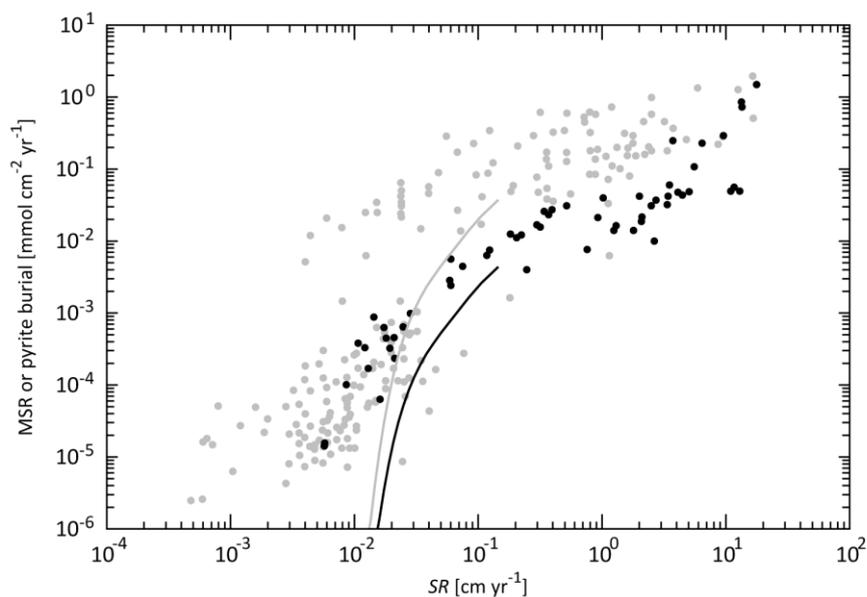
1467

1468   **Figure 16** MSR and pyrite burial flux density as a function of sedimentation rate. Gray and black dots depict
1469   observational data compilation of depth-integrated MSR flux density and pyrite burial flux density for normal
1470   (oxic) marine sediments (Berner and Canfield, 1989; Canfield, 1989; Raiswell and Canfield, 2012). The unit
1471   of sedimentation rate was converted from g cm^{-2} yr^{-1} to cm yr^{-1} with assuming the dry bulk density of 2.5 g
1472   cm^{-3} and porosity of 0.9. Solid lines are the results obtained from the reference run of the CANOPS-GRB
1473   model.

1474   In the CANOPS-GRB model, pyrite burial efficiency e_{pyr} (Sect. 2.3.4) for sediments underlying oxic bottom

1475   waters is set such that simulated seawater [SO$_4^{2-}$] of the reference run is consistent with the modern value of

1476   28.9 mM. The tuned value of 11.7% agrees well with observations suggesting that pyrite precipitation rate is

1477   about 10−20% of the rate of MSR (Fig. 16). Our reference value is also consistent with other estimates of

1478   11−20% (Bottrell and Newton, 2006a; Tarhan et al., 2015; Turchyn and Schrag, 2006b).

1479

1480   The sulfate inventory of our reference state is 39×10^{18} mol. Given the total source flux of 3.4 Tmol S yr^{-1}, the

1481   residence time of sulfate is 11.5 Myr.

1482   3.3 Global oxygen cycling

1483   The global O$_2$ budget for our reference state is shown in Fig. 17. The simulated O$_2$ inventory in the ocean-

1484   atmosphere system is 38×10^{18} mol (atmosphere $= 38 \times 10^{18}$ mol, ocean $= 0.23 \times 10^{18}$ mol). Organic carbon burial

1485   represents a major O$_2$ source flux (marine = 11.3 Tmol O$_2$ equiv. yr^{-1} and terrigenous = 3 Tmol O$_2$ equiv. yr^{-1}

1486   ). Pyrite burial and hydrogen escape to space contribute 2.6 Tmol O$_2$ equiv. yr^{-1} and 0.001 Tmol O$_2$ equiv.

1487   yr^{-1}, respectively. Given the total source/sink flux of 16.9 Tmol O$_2$ yr^{-1}, the residence time of O= in the ocean-

1488   atmosphere system of our reference state is estimated as 2.26 Myr, which is consistent with previous estimates

1489   of 2−4 Myr (Berner, 1989; Berner, 2004b; Garrels and Perry, 1974).
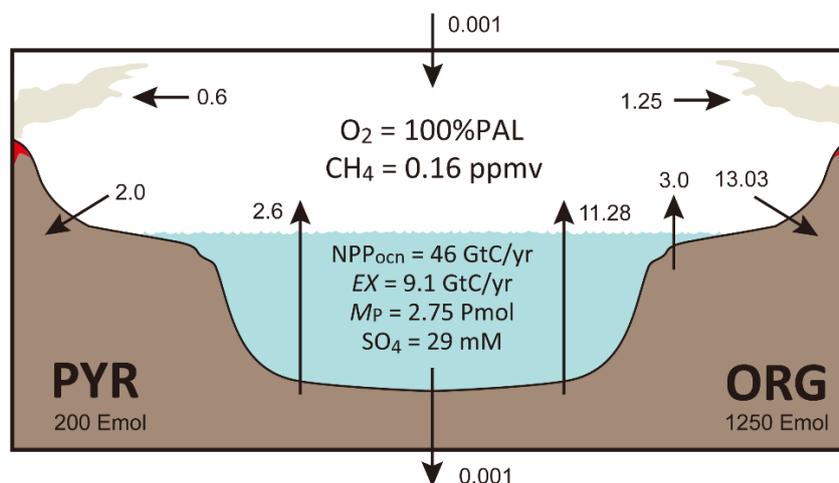
1490

1491   **Figure 17** Schematics of global redox (O$_2$) budget for the reference run. Arrows represent the O$_2$ flux in terms

1492   of 10^{12} mol O$_2$ equiv. yr^{-1}. PAL = present atmospheric level. Pmol $= 10^{15}$ mol. Emol $= 10^{18}$ mol. ORG =

1493   sedimentary organic carbon. PYR = sedimentary pyrite sulfur.

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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.

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.

The simulated transient response is shown in Fig. 18. As expected, lower P availability leads to 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^{-1} and 0.13 Tmol C yr^{-1} at 10^5 yr, respectively (cf. the reference value of 11.3 Tmol C yr^{-1}).

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_{org} 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_2 levels. After atmospheric deoxygenation (>~4

1521 Myr), the system again reaches its quasi-steady state. Specifically, f_P values of 10% and 1% result in

1522 atmospheric O_2 levels of 9% PAL and 0.6% PAL, respectively.
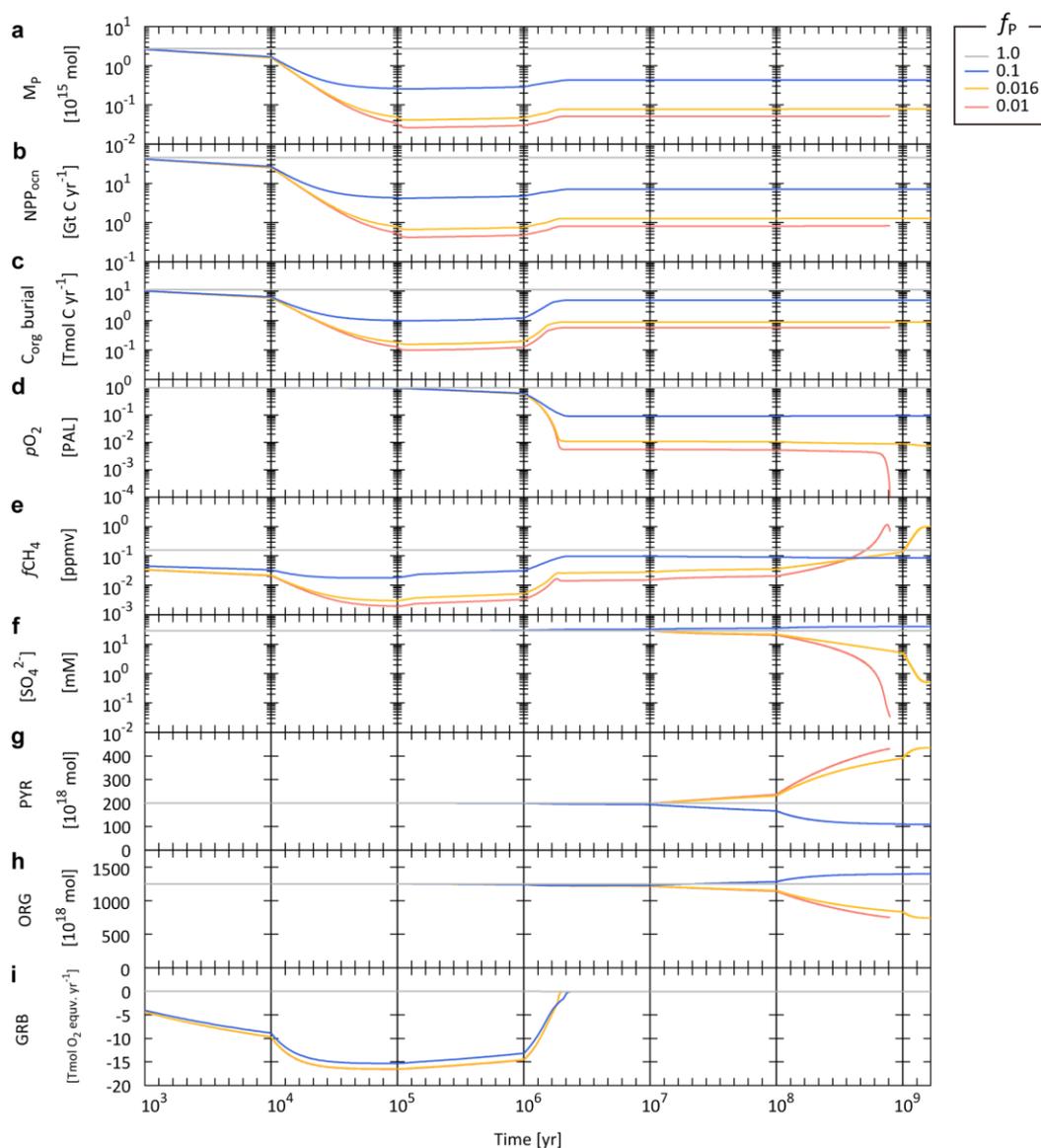
1523

1524 **Figure 18** Biogeochemical responses obtained from the CANOPS-GRB model with different values of P
1525 availability, f_P. (**a**) Oceanic phosphate inventory, M_P. (**b**) Oceanic net primary production (NPP$_{ocn}$). (**c**) Burial
1526 rate of organic carbon (C$_{org}$) in marine sediments. (**d**) Atmospheric partial pressure of O_2. PAL = present
1527 atmospheric level. (**e**) Atmospheric CH$_4$ mixing ratio. (**f**) Sulfate concentration in the surface ocean layer. (**g**)
1528 Sedimentary reservoir size of pyrite sulfur, *PYR*. (**h**) Sedimentary reservoir size of organic carbon, *ORG*. (**i**)
1529 Global redox budget, *GRB*. For the f_P = 1% run (black line), the calculation stopped when the atmospheric O_2
1530 level decreased to ~10^{-5} PAL due to the numerical instability.

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1531

1532 The following change is driven by the response of oceanic S cycle, which is characterized by the long residence

1533 time of 11.5 Myr (see Sect. 3.2.6). Ocean anoxia promotes the MSR and subsequent precipitation of pyrite in

1534 the ocean interior. However, our model demonstrates that the decline of seawater SO_4^{2-} on a timescale of tens

1535 of millions of years is small (Fig. 18f), because the rate of MSR depends not only on the oceanic redox state

1536 but on the availability of organic matter for the MSR. The significant reduction of seawater SO_4^{2-} occurs on

1537 the longer timescales (>100 Myr) for extremely low f_P scenarios (0.016 and 0.01), in which atmospheric O_2

1538 levels decrease to <1% PAL. These scenarios also accompany with a growth of sedimentary S from gypsum

1539 to pyrite (Fig. 18g).

1540

1541 On longer timescales, sedimentary reservoirs affect the redox state of the atmosphere and oceans. The present

1542 result demonstrates that f_P of 1% finally leads to the catastrophic decrease in atmospheric O_2 level at around

1543 0.9 billion years (Fig. 18d). The simulation was stopped at this point due to the numerical instability. For other

1544 scenarios, the system reaches a new steady state after roughly three billion model years.

1545

1546 Biogenic CH_4 production tends to be enhanced in the anoxic oceans. However, the present result demonstrates

1547 that CH_4 degassing to the atmosphere is inhibited by both limited availability of organic matter for

1548 methanogenesis and the anaerobic oxidation of CH_4 by SO_4^{2-}. Once the seawater $[SO_4^{2-}]$ decreases below 1

1549 mM, CH_4 can escape from oceans to the atmosphere, promoting the buildup of CH_4 in the atmosphere.

1550 Nevertheless, because of the limited biological activity, atmospheric CH_4 levels are comparable to the modern

1551 value (~1 ppmv) (Fig. 18e).

1552 **4.2 O_2 budget for the less oxygenated scenario**

1553 Figure 19 shows the O_2 budget of the less oxygenated state ($f_P = 1.6\%$ scenario). Because P availability exerts

1554 a primary control on biospheric O_2 production, the strongly suppressed P delivery to the ocean leads to low

1555 oceanic P levels and commensurately low biological productivity (0.08 Pmol and 1.3 Gt C yr^{-1}, respectively).

1556 As a consequence, the atmospheric O_2 level is low (0.75% PAL). In this scenario the ocean interior is globally

1557 anoxic, and the preservation of organic C in marine sediments is enhanced. However, the suppressed biological

78

1558 productivity results in a low overall burial rate of organic C (0.9 Tmol O_2 equiv. yr^{-1}; ~9% of the reference

1559 value). When combined with the burial rate of terrigenous organic C, total O_2 production by the organic C

1560 sub-cycle is 0.97 Tmol O_2 equiv. yr^{-1}. This O_2 source is balanced by the sum of oxidative weathering and

1561 metamorphism. The role of the pyrite S sub-cycle in the global redox budget is also shown in Fig. 19. Most

1562 of the SO_4^{2-} entering the anoxic ocean is buried as pyrite, representing a major O_2 source (2.64 Tmol O_2 equiv.

1563 yr^{-1}). This O_2 source is balanced by oxidation of sedimentary pyrite S through weathering (1.33 Tmol O_2 equiv.

1564 yr^{-1}) and metamorphism (1.31 Tmol O_2 equiv. yr^{-1}). In other words, the O_2 budget for the weakly-oxygenated

1565 Earth system is largely controlled by the crustal S sub-cycle. This is in marked contrast to the well-oxygenated

1566 Earth system, on which the O_2 budget is mainly controlled by organic C sub-cycle.

1567

1568 The present result demonstrates that low atmospheric O_2 states (~1% PAL) can be achieved in scenarios where

1569 the availability of P is strongly limited. However, a slight decrease of f_P to 1% leads to the destabilization of

1570 global O_2 budget, providing implications for the stability and evolution of atmospheric O_2 levels during the

1571 Proterozoic. This point will be further systematically examined in future work.

1572
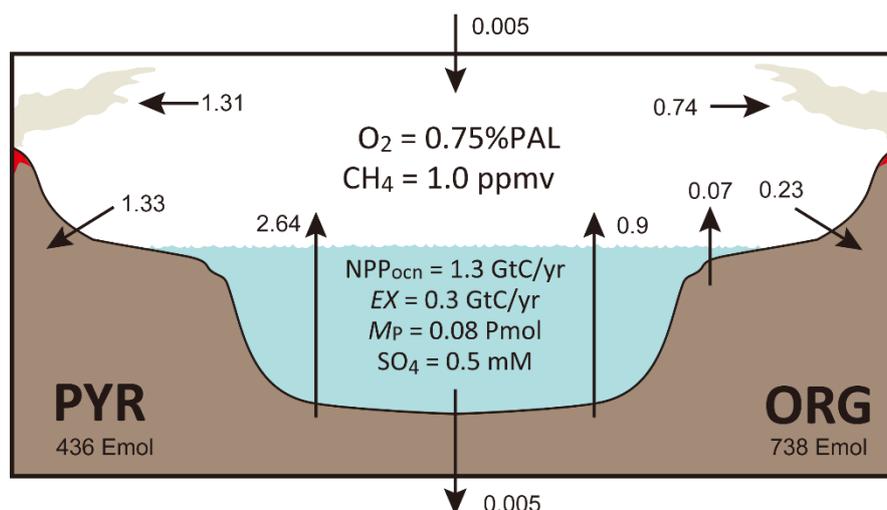
1573

1574 **Figure 19** Schematics of global redox (O_2) budget for the f_P = 1.6% (=$10^{-1.8}$) run. Arrows represent the O_2
1575 flux in terms of 10^{12} mol O_2 equiv. yr^{-1}. PAL = present atmospheric level. Pmol = 10^{15} mol. Emol = 10^{18} mol.
1576 Gt C = 10^{15} g C. ORG = sedimentary organic C. PYR = sedimentary pyrite S.
1577

5 Discussion

1578

1579 The reference run under the present condition demonstrates generally good agreement with modern

1580 observations (Sect. 3). The water circulation scheme provides an adequate representation of general ocean

1581 circulation, resulting in robust and reliable tracer distributions that are comparable to the modern observations.

1582 This provides a mechanistic foundation for simulating generalized ocean biogeochemical cycles. The ocean

1583 biogeochemistry module includes a series of biogeochemical processes in oxic-anoxic-sulfidic environments.

1584 The reference run gives rise to the distributions of nutrients and dissolved O_2 that capture fundamental

1585 properties observed in the modern ocean. Integrated biogeochemical fluxes of the global ocean, such as

1586 biological productivity, material flow in the water column, and burial into sediments are also consistent with

1587 observational data. Some future developments to the N cycle may be needed, especially with regard to

1588 denitrification (e.g., anammox, coastal benthic denitrification). Nevertheless, our ocean biogeochemical

1589 model is adequate for representing the general property of the coupled C-N-P-O_2-S cycles.

1590

1591 A new scheme for oxidative weathering of organic matter and pyrite sulfur, mass balance calculation of O_2 in

1592 the atmosphere, and time evolution of sedimentary reservoirs are explicitly included in the CANOPS-GRB

1593 model. These are a significant improvement from the previous versions of CANOPS (Lenton, 2020). The

1594 simplified framework for the global O_2 budget is also useful to understand the response of complex

1595 biogeochemical systems. The computational efficiency of our CANOPS-GRB model allows us to conduct

1596 simulations over billions of model years with reasonable wall times (on the order of weeks), providing a useful

1597 tool for exploring the wide range of topics about the oxygenation history of Earth's atmosphere.

1598

1599 Sensitivity experiments with respect to the terrestrial weathering rate of P were conducted in order to see how

1600 the redox state of the ocean-atmosphere system responds to varying P availability in the surface system (Sect.

1601 4). The CANOPS-GRB model appears to adequately simulate the biogeochemical dynamics over a wide range

1602 of timescales and is applicable for quantitative assessment of the evolution and stability of Earth's O_2 cycling.

1603 Perhaps even more importantly, our results encourage us to perform further systematic examinations with

1604 Earth system models which have different complexities. Such an 'Earth system model intercomparison' would

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1605 be a critical step towards better mechanistic understanding of the stability and dynamics of atmospheric O_2

1606 levels over Earth's history.

1607

1608 Due to a lack of explicit Fe cycling and anaerobic metabolisms (such as anoxygenic photosynthesis), the

1609 current version of the model cannot be applicable for the simulation under the Archean-like weakly-

1610 oxygenated ($pO_2 < 10^{-5}$ PAL) conditions. These topics are left to future studies, but it would be an achievable

1611 goal (Ozaki et al., 2018; Ozaki et al., 2019b; van de Velde et al., 2021). The model design presented here also

1612 ignores the interaction between the surface system and the mantle (e.g., subduction) except for the degassing

1613 of reducing gases from the mantle. We note, however, that the surface-mantle interaction would have exerted

1614 a primary control on the long-term redox budget of Earth's surface system through the Earth's history

1615 (Canfield, 2004; Eguchi et al., 2020; Hayes and Waldbauer, 2006) and may be important for the discussion

1616 about the distant future (Ozaki and Reinhard, 2021). The importance of mantle and solid Earth controls on

1617 surficial environments is a crucially important topic for future research.

6 Conclusions

A new Earth system box model was developed—CANOPS-GRB. The new code release provides an improved description of the coupled C-N-P-O_2-S biogeochemical cycles in the ocean-atmosphere-crust system, which can be utilized to examine the dynamics and stability of Earth's O_2 cycle over a wide range of timescales. The computational efficiency and simple model design of CANOPS-GRB make it relatively easy to modify existing processes or add entirely new processes and components. CANOPS-GRB is thus a new and uniquely flexible tool capable of providing a coherent mechanistic framework for quantifying the biogeochemical cycles regulating Earth's O_2 cycle. CANOPS-GRB is also a useful tool for the development of more comprehensive, low- to intermediate-complexity Earth system box models of biogeochemistry.

CANOPS-GRB will provide an important step forward when coupled to new and existing geochemical proxy data. The accumulating geological/geochemical records have led to new hypothesis for the evolution of atmospheric O_2 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 cycles and its effect on the redox budget through Earth history. Through the model-data synergy, CANOPS-GRB has a great potential to provide an integrated, quantitative, and statistically informative picture of biogeochemical states, opening new perspectives on a wide range of scientific questions in research seeking to understand the Earth's chemical evolution, and in particular the cause-and-effect relationships with evolving biosphere.

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

1646

1647 **Code availability.** The bulk of CANOPS-GRB is written in Fortran as a stand-alone model. The model code
1648 can be found at GitHub (doi:10.5281/zenodo.5893804). This model is still undergoing regular development
1649 and it is recommended that potential users contact the corresponding author (Kazumi Ozaki;
1650 kazumi.ozaki@sci.toho-u.ac.jp) to obtain the latest version. The CANOPS-GRB code is provided freely but
1651 with the requirement that prospective users contact the corresponding author with their research plans to avoid
1652 parallel projects emerging.

1653

1654 **Author contributions.** KO designed the study, wrote the code, and ran model simulations. DBC and CTR
1655 contributed to code debugging. KO wrote the manuscript, with inputs from DBC, CTR, and ET.

1656

1657 **Competing interests.** The authors declare that they have no conflict of interest.

1658

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