3   On the use of models in understanding

4   the rise of complex life

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7   Abstract

8   Recently several seemingly irreconcilably different models have been proposed for relationships

9   between Earth system processes and the rise of complex life. These models provide very different

10   scenarios of Proterozoic atmospheric oxygen and ocean nutrient levels, whether they constrained

11   complex life, and of how the rise of complex life affected biogeochemical conditions. For non-

12   modellers it can be hard to evaluate which – if any – of the models and their results have more

13   credence – hence this article. I briefly review relevant hypotheses, how models are being used to

14   incarnate and sometimes test those hypotheses, and key principles of biogeochemical cycling

15   models should embody. Then I critically review the use of biogeochemical models in: inferring key

16   variables from proxies; reconstructing ancient biogeochemical cycling; and examining how complex

17   life affected biogeochemical cycling. Problems are found in published model results purporting to

18   demonstrate long-term stable states of very low Proterozoic atmospheric pO_2 and ocean P levels. I

19   explain what they stem from and highlight key empirical uncertainties that need to be resolved.

20   Then I suggest how models and data can be better combined to advance our scientific understanding

21   of the relationship between Earth system processes and the rise of complex life.

Keywords

Earth system; biogeochemical cycling; complex life; modelling; oxygen; phosphorus

Introduction

As complex and self-aware organisms, some of us are fascinated by the origin and rise of complex life – because it is a key part of our origins. As well as establishing when those origins were, and in what order things evolved, as scientists we are drawn to questions of causality: Were those origins determined by intrinsic controls on biological evolution, by abiotic factors, or by a more complex interplay between living and non-living parts of the Earth system? How did the rise of complex life in turn alter the Earth system? And how can we gain knowledge about any causal relationships, given the hundreds of millions of years that have passed since?

At the Discussion meeting behind this Special Issue, Jochen Brocks asked: What is the role of models in understanding the rise of complex life? And how should non-modellers view their results? This review is an attempt to answer those queries. For non-modellers, models can be 'black boxes' playing an opaque role in gaining scientific knowledge. This can insulate models and modellers from critical scrutiny. Hence this paper aims to expose and explore the ways in which models are being used to address the relationships between biogeochemical processes and the rise of complex life.

The broad time correlation between the rise of complex life and huge changes in the Earth system – including the carbon cycle and climate – during the Neoproterozoic Era, has led many researchers to assume there is a causal connection between them. However, there are currently very different perspectives on the direction(s) of causality. One perspective argues that environmental constraints held back the evolution [1] – or rise to ecological prominence [2] – of complex life. An opposing perspective argues that complex life evolved and then it altered ecological and environmental conditions [3]. A co-evolutionary feedback perspective combines elements of these two positions, arguing that complex life transformed ecology and biogeochemical cycling, feeding back into its

46   subsequent evolution [4]. Other important perspectives recognise the challenging evolutionary-

47   developmental aspects of animal origins [5], and consider how unusual environmental conditions

48   may have triggered (rather than suppressed) their origin [6].

49   Modelling has been used to varying degrees to represent and sometimes to test different

50   hypotheses for the relationship between complex life and Earth system processes. Predominantly

51   this has been biogeochemical modelling. Modelling of the ecological changes associated with the

52   rise of complex life is less common. Modelling the physiology of early complex life is even rarer, and

53   modelling the evolutionary dynamics of the rise of complex life has only been attempted in the

54   generic spirit of evolutionary theory. Hence this review focuses predominantly on biogeochemical

55   modelling – but the forward look considers other approaches.

56   First, I briefly review relevant hypotheses concerning the relationships between the rise of complex

57   life and Earth system processes, the different roles that models can play in understanding deep time,

58   and the key biogeochemical principles models should embody. Then I critically review published

59   model approaches to inferring key environmental conditions from proxies; understanding

60   Proterozoic biogeochemical cycling; and modelling how complex life altered biogeochemical

61   conditions. I consider what all the current biogeochemical models may be missing. Then I suggest

62   ways forward for modelling to help improve our understanding of the rise of complex life.

63   Relevant hypotheses

64   Complex life means more here than just animals (Metazoa). Currently there is much interest in

65   whether the late rise of algae to ecological prominence, detected in the biomarker record in the

66   Cryogenian Period, was due to chronically limiting nutrient levels beforehand [7]. More prominently,

67   it has long been argued [8] that a lack of oxygen held back the evolution – or at least the radiation –

68   of animal life. Recently it became apparent that oxygen levels would have to have been very low to

69   have constrained the evolution or ecological expansion of sponges (the basal animals) [9] and

70 several other (subsequently evolved) types of animal life [2]. One response to this has been to argue

71 that Proterozoic atmospheric oxygen levels were in fact much lower than previously thought [1].

72 Another response has been to argue that oxygen constrained particular eco-physiological traits of

73 animal life, if not its origin [10]. Yet another response has been to reject the role of oxygen as a

74 constraint altogether [3]. Other candidate environmental constraints have occasionally been

75 considered, for example, too much toxic hydrogen sulphide suppressing eukaryotes [11].

76 A different view is that the evolution of complex life was just intrinsically difficult and slow and its

77 timing had nothing to do with environmental conditions or constraints. However, given natural

78 selection occurs, and given evidence of changes in environmental variables known to affect the

79 physiology and ecology of animals, it seems odd to rule out some role for the environment in the

80 evolution of complex life – even if the pertinent 'environment' is a localised and ecological context

81 selecting some traits over others. Furthermore, highly differentiated animals with apoptosis

82 (programmed cell death) pose their own evolutionary puzzle, as they represent a major evolutionary

83 transition to a new level of selection [12]. Explaining such transitions remains a major subject of

84 evolutionary enquiry. It generally needs special conditions in which between-group variation and

85 selection outweighs within-group variation and selection [13]. One hypothesis is that extreme

86 environmental conditions – in particular the 'snowball Earth' events – could have altered the

87 selective environment in a way that favoured animal evolution [6].

88 Once they had evolved, complex life forms could affect ecology and biogeochemical cycling [3, 4, 14-

89 16]. Several hypotheses have been proposed: By grazing on the smallest (cyanobacterial)

90 phytoplankton cells, the first predatory protists (using phagocytosis) could have created a niche for

91 larger (algal) phytoplankton cells, which in turn created a niche for larger predators, and so on – thus

92 starting to create a size-structured community [16]. The advent of larger phytoplankton cells could

93 have increased the efficiency of the biological pump (sinking of organic matter through the water

94 column) [4]. The evolution of filter-feeding sponges, which filter out the smallest phytoplankton

95 cells, could also have selected for larger (eukaryotic) algae and strengthened the biological pump [4].

96 When planktonic animals with through-guts and faecal pellets evolved this could have further added

97 to the efficiency of the biological pump [14]. Sessile benthic animals including sponges and

98 'rangeomorph' fronds could have concentrated resources where they were located on the

99 sediments [17]. When mobile, burrowing, bioturbating animals evolved they could have oxygenated

100 the upper sediments altering the cycling of phosphorus, carbon and sulphur and ultimately the

101 oxygen content of the atmosphere [18, 19].

Uses of models

103 Models are currently being used in several ways to probe potential causal relationships between

104 Earth system processes and the rise of complex life. Biogeochemical models, in particular, are being

105 used: to interpret proxy data; to explore how the ancient world could have worked; and to try to

106 establish how it did work by testing hypotheses against data. There are two principal scientific

107 targets for this modelling: to establish Proterozoic biogeochemical conditions; and to quantify the

108 potential effects of complex life on those conditions.

General considerations

110 A model should be as simple as possible but not too simple, following Einstein's advice. Hence users

111 of model results should always look critically at whether the underlying model is too simple or

112 unnecessarily complex to address the question at hand. All models must obey some basic principles

113 of consistency with well-established constraints – such as conservation of matter. In our focal

114 context, a model may need to capture some of the spatial heterogeneity of biogeochemical

115 conditions – but no more than necessary to accurately capture key process controls. Models should

116 also be grounded in sound process representations, ideally ones that have empirical support, which

117 in this context, usually means from studies of contemporary or more recent Earth system processes.

118 If a model contains ad hoc process representations, or representations that are clearly at odds with

119 current scientific understanding, then its results should be questioned. We should ask how those

120   results are sensitive to changing the process representations that we have doubts about. (This

121   means performing a 'structural' sensitivity analysis where functional forms are varied, not just a

122   more typical parameter sensitivity analysis where only parameter values are varied.) If the modellers

123   do not provide an answer we should suspend judgement on whether their model is telling us

124   anything meaningful or useful about the ancient world.

Inferring key variables from proxies

126   In almost all deep time cases, a model is necessary to convert a proxy measurement into an Earth

127   system property (environmental parameter) of interest. For hypotheses surrounding the rise of

128   complex life, key Earth system properties that we would like to know include: the oxygen content of

129   the atmosphere, the redox state of the ocean, the levels of limiting nutrients in the ocean, and the

130   productivity of the biosphere. Sometimes the role of models in proxy interpretation is well hidden –

131   the presence of a model may not be mentioned at all – but there is always some model involved

132   (however simple) whenever we are dealing with a 'proxy' – i.e. we do not have a direct

133   measurement of our variable of interest. Sometimes the absence of some proxy is used, via a model,

134   to infer a constraint on a variable of interest – adding the familiar complication that "absence of

135   evidence is not evidence of absence".

Exploring how the world could have worked

137   Models are also used, more ambitiously, to help us think in a qualitatively and quantitatively

138   consistent way about how the world *could* work – in this case how the Earth system and its

139   relationship with complex life could work. The 'Earth system' modelling challenge here is generally

140   greater than the interpretation of proxy data, because it demands making an internally-consistent

141   model of the whole world, or at least pertinent aspects of it. The exercise can be insightful, in

142   particular in limiting what may otherwise seem like a very large 'possibility space', because the act of

143   building an internally-consistent model usually significantly limits the range of behaviours and results

144   it can exhibit. Making the model obey well-established constraints – such as closure of

145   biogeochemical cycles and conservation of Earth's surface redox balance – can be critical in this (and

146   in the next section I outline some of these key principles). Nevertheless, exploring how the ancient

147   world *could* have worked is not the same as establishing how it *did* work.

Testing hypotheses to establish how the world did work

149   To help to establish how the ancient world actually *did* work, we need to be able to test and falsify

150   hypotheses for causal relationships. That means we need to use data from the time(s) in question to

151   test our models against. Thus we need to combine models of how the Earth could have worked with

152   proxy data. This means modelling the link between variables of interest and available proxies, as well

153   as modelling the controls on the variables of interest. Here the role of the model is to incarnate

154   (represent) mechanistic hypotheses, and make quantitative predictions from those hypotheses of

155   variables that are detectable in the geologic record. That 'testbed' data needs to be independent

156   from any data that is used to drive the model (to avoid circular reasoning), and for the comparison of

157   model with data to be possible, the model has to predict observable proxy variable(s). There are

158   numerous caveats here, not least that there are always a multitude of wrong models that can

159   successfully fit any given data. However, if the model cannot fit the data it pertains to predict, and

160   we think the data are reliable, then clearly there is something wrong with the model and it can be

161   said to be *falsified* (at least in some part). Increasing the number of independent data targets we try

162   to get the model to predict generally increases the chances of falsifying the model (lowers the

163   success rate). However, here we must be wary of modellers making a model more complex as that

164   just increases the potential field of successful but wrong models.

Key principles of biogeochemical cycling

166   To help readers evaluate models of Proterozoic conditions, and the potential effects of complex life

167   on those conditions, it is important to review some basic principles of biogeochemical cycling.

Timescale separation and material balances

169 Different key Earth system variables have different natural timescales (Figure 1), and those

170 timescales are separated in a way that can help us to understand Earth system functioning and

171 simplify our modelling. For material variables like the oxygen content of the atmosphere-ocean or

172 the phosphorus content of the ocean it is standard to define a mean residence time for an atom or

173 molecule in the reservoir – that is the size of the reservoir divided by its input/output flux [20].

174 Response timescales in the presence of feedback can also be defined [20]. Over timescales

175 comparable to or longer than the residence time, the inputs to and outputs from the reservoir must

176 be in close balance, otherwise the constituent would build up indefinitely or disappear [20]. The

177 timescale(s) we are interested in determine what processes we need to include in our models.

178 Things that change much slower than our timescale(s) of interest can be treated as approximately

179 constant (and excluded from our model). Things that change much faster than our timescale(s) of

180 interest can be assumed to be close to 'steady state' – i.e. with inputs and outputs in balance (which

181 does not mean they are constant). However, we must consider the processes setting that steady

182 state and whether and how they (and the resulting steady state) change with the slower variables.

183 The origin and rise of complex life played out over hundreds of millions of years, after a preceding

184 Proterozoic state that persisted for a billion years. Over these timescales, there could have been

185 significant material exchanges between the crust and the mantle [21], which most models neglect,

186 as well as ~500 Myr supercontinent (Wilson) cycles. Crucially, models must include the exchange of

187 matter (including electrons/redox equivalents) with sedimentary rock reservoirs that are recycled by

188 plate tectonics over ~100 Myr timescales. As Bob Garrels and colleagues first showed in the 1970s,

189 enforcing the conservation of key elements and electrons across sedimentary reservoirs and the

190 ocean-atmosphere system provides a powerful constraint on models, enabling reconstruction of key

191 variables such as CO_2 and O_2 consistent with major (C, S) isotope records [22-24].

192 The surface, fluid aspects of the Earth system – the oceans and atmosphere (including the

193 biosphere) and different reservoirs of matter within them – generally have shorter timescales than

194 sedimentary rocks. Today, sulphate in the ocean has a residence time of ~12 million years, oxygen in

195 the atmosphere(-ocean-biosphere) ~6 million years (with respect to exchange with the crust),

196 carbon dioxide and dissolved inorganic carbon (DIC) in the ocean-atmosphere ~500,000 years,

197 phosphorus in the ocean ~20,000 years, and nitrogen in the ocean ~5,000 years. The timescale

198 separation between variables means, for example, that today we can consider oxygen to be

199 approximately constant over the timescales over which phosphorus varies, or conversely when

200 considering timescales of variation in atmospheric oxygen, phosphorus must be close to steady

201 state. However, in the Proterozoic we should consider whether residence times were quite different,

202 including whether some constituents had a shorter timescale than the ~1,000 year ocean mixing

203 timescale and therefore would have heterogeneous distributions in the ocean [25].

204 ## Linking nutrients, carbon and oxygen

205 Nutrients are linked to oxygen via the limitation of primary production and the associated

206 production and eventual burial of organic carbon, which represents the net source of oxygen – i.e.

207 the net of oxygen production and consumption in respiration and other oxidative pathways. Today

208 plants on land make a major contribution to organic carbon burial and net oxygen production [26],

209 but in the Proterozoic, although there were photosynthetic microbial mats on land [27], they are

210 generally assumed not to have contributed significantly to organic carbon burial. Hence the focus

211 has been on the controls on marine production of organic carbon, its sinking through the water

212 column (the 'biological pump'), and its preservation and burial in sediments.

213 A crucial notion is that the availability of one nutrient in the ocean ultimately limits the export

214 (sinking) flux of new photosynthetic matter from the surface ocean. Today that nutrient is

215 phosphorus, even though nitrogen may be proximately limiting (i.e. run out first) – because nitrogen

216 levels adjust (on a shorter timescale) to variations in phosphorus levels through the stimulation or

217   suppression of nitrogen fixation (and the action of denitrification) [28, 29]. In the more anoxic

218   Proterozoic-early Paleozoic ocean, we need to consider whether elevated levels of denitrification

219   made nitrogen more proximately limiting (i.e. phosphorus levels in the ocean could considerably

220   exceed organisms' requirement for phosphorus) [25, 30], and whether trace metals limited nitrogen

221   fixation and thus primary production [31].

222   How much of the organic matter created in primary production sinks and reaches the sediments –

223   i.e. the efficiency of the 'biological pump' – plays a crucial role in determining ocean redox state and

224   in setting ocean nutrient levels [4, 16, 25]. On the ~10^3 yr timescale of ocean mixing, the amount and

225   location of organic matter remineralisation in the water column, together with the supply of oxygen

226   from above, jointly determine the redox state of deeper waters. On the ~10^4 yr timescale of

227   balancing the phosphorus cycle, the phosphorus (and coupled nitrogen) concentration in the ocean

228   must adjust until output to sediments matches input from rivers. For example, if without complex

229   life the biological pump was less efficient (i.e. it was more difficult to get organic material to the

230   bottom of the shelf seas and ocean and bury it), then (all else being equal) nutrient and productivity

231   levels would need to have been higher to balance the phosphorus cycle [4, 16]. Alternatively, if in a

232   more anoxic ocean there were another efficient way of transferring phosphorus to the sediments –

233   e.g. removal with iron minerals of mixed redox state such as vivianite – then a lower phosphorus

234   concentration could have balanced the phosphorus cycle [32, 33]. Either way, phosphorus

235   concentration can be decoupled from phosphorus input/output.

236   The burial efficiency of organic matter in sediments and the C:P stoichiometry of what is buried also

237   affect phosphorus and atmospheric oxygen levels [34-36]. Today most of the organic material that

238   reaches the sediments is recycled (remineralised) back to the water column. There is a long-running

239   debate about whether organic carbon is more efficiently remineralised under oxic versus anoxic

240   bottom water conditions. Any difference is unclear under the high sedimentation rates of shallow

241   ocean margins where >80% of organic carbon is buried today, but preservation could be markedly

242 more effective under anoxic conditions at the low sedimentation rates in the deep ocean [37]. Under

243 today's oxic ocean conditions, phosphorus is more efficiently recycled than carbon leaving buried

244 organic matter with a higher $(C:P)_{org}$ ratio than primary production, but phosphorus is often trapped

245 in other forms in sediments – especially in authigenic calcium minerals (e.g. apatite), or adsorbed to

246 the surface of iron oxide minerals, meaning the total sedimentary ratio of organic carbon to reactive

247 phosphorus $(C_{org}:P_{react})$ can be lower than in primary production. The recycling of phosphorus from

248 organic matter markedly increases under anoxic conditions, increasing $(C:P)_{org}$ burial ratios,

249 phosphorus concentration, organic carbon burial and atmospheric oxygen [36]. However, if the

250 evolution of complex life increased the efficiency of phosphorus preservation in sediments then this

251 would have lowered phosphorus concentration, organic carbon production and burial and

252 atmospheric oxygen [19].

Earth surface redox balance

254 If we tally up all the significant reduced and oxidised reservoirs in the ocean-atmosphere and their

255 input and output fluxes these must be near long-term balance – or Earth's surface redox state,

256 including atmospheric oxygen levels, will change [23, 24]. Today, organic carbon burial is balanced

257 both by the oxidative weathering of ancient sedimentary organic carbon exposed on the continents,

258 and by the volcanic outgassing and subsequent oxidation of subducted organic carbon. The sulphur

259 cycle also plays an important role in today's redox balance. In sediments the electrons in organic

260 carbon may be transferred to pyrite (FeS_2) before burial. Ancient pyrite exposed on the continents is

261 rapidly oxidised and some pyrite sulphur is outgassed and oxidised. Carbon and sulphur also have

262 large oxidised sedimentary reservoirs – carbonate and gypsum – which are deposited from the

263 ocean, weathered on continents and the C and S they contain outgassed from volcanoes following

264 subduction. Over geologic time, the fraction of carbon buried in organic (reduced) versus oxidised

265 form may vary, as may the fraction of sulphur buried in pyrite (reduced) versus oxidised form.

266 Changes in both burial fractions have affected Earth's surface redox state over Phanerozoic time [22,

267 30], but (as will see) the situation was different in the Proterozoic. Furthermore, over Proterozoic

268 timescales, net oxidation of iron in the Earth's crust, and hydrogen loss to space, could have

269 significantly affected Earth surface redox balance.

Alternative model interpretations of proxy data

270

271 Currently major debates surround oxygen levels in the Proterozoic atmosphere and phosphorus,

272 nitrogen and productivity levels in the Proterozoic ocean. This is partly because different models give

273 very different inferences of key variables from the same proxy data. Summaries of the proxy data

274 can be found in e.g. [25] (spanning Earth history) and [38] (this volume; spanning Neoproterozoic-

275 Paleozoic).

Atmospheric oxygen levels

276

277 There is currently no widely accepted, direct record of atmospheric oxygen levels prior to the

278 Quaternary ice-core record. Measurements of gas inclusions in halite minerals have been suggested

279 to record the ancient atmosphere [39], but can be contaminated with modern air [40]. Hence

280 attempts to derive a proxy for atmospheric oxygen rely on models. The absence of mass

281 independent fractionation of sulphur isotopes (MIF-S) since the Great Oxidation ~2.3 Ga, indicates

282 the continuous presence of an ozone layer and that the sulphate level in the ocean has remained

283 sufficient to prevent any MIF-S signals being recorded. 1-D atmosphere models suggest the ozone

284 layer starts to form at pO_2 ~10^{-5} PAL, although total column depth of ozone is still an order of

285 magnitude below present at pO_2 ~0.001 PAL [41]. The presence of mass independent fractionation

286 of oxygen ($\Delta^{17}O$) at times in the Proterozoic [42], indicates sufficient oxygen and ozone to initiate the

287 required stratospheric photochemistry, which models suggest requires pO_2 ≥0.001 PAL [41, 43].

288 Other proxies for atmospheric oxygen rely on models of oxidation processes in weathering,

289 transport, or shallow ocean environments, which are complicated by the existence of gradients in

290 oxygen concentration from the atmosphere to depth in weathering profiles or shelf seas, and by any

291 presence of organic matter or other reductants.

292   Traditionally, steady state model interpretations of data indicating oxidised iron retention at the top

293   of rare ancient soil profiles (paleosols) were used to set a lower limit on pO_2, given an assumed pCO_2

294   – e.g. pO_2 >0.01 PAL at 1.85 Ga (Flin Flon paleosol) and at 1.1 Ga (Sturgeon Falls paleosol) [44]. Some

295   subsequent modelling has revised the 1.85 Ga constraint upwards to >0.05 PAL [45]. Other mass

296   balance modelling has given lower pCO_2 estimates requiring lower pO_2 to explain iron retention [46].

297   Iron retention in the 1.1 Ga Sturgeon Falls paleosol has also been questioned, leaving the 1.1 Ga pO_2

298   inference uncertain [43]. The presence of any microbial mats, e.g. secreting organic acids that can

299   cause iron loss, further complicates paleosol interpretation [27]. More recently, kinetic modelling of

300   abiotic or biotic manganese oxidation and associated chromium oxidation and isotope fractionation

301   was used to argue that pO_2 <0.001 PAL is necessary to explain a lack of positively fractionated $\delta^{53}Cr$

302   in marine ironstones and shales [1]. However, the modelling assumed equilibration of soil pore fluids

303   with atmospheric pO_2, whereas more realistic 1D modelling of shale weathering shows that the

304   presence of ancient organic matter (kerogen) can readily drive entire weathering profiles anoxic up

305   to pO_2 ~0.05 PAL [47]. Furthermore, new data has shown evidence of positively fractionated $\delta^{53}Cr$ in

306   mid-Proterozoic shales [48] and carbonates [49] – illustrating that the previous absence of evidence

307   should not have been taken as universal evidence of absence with which to infer pO_2 over >1 Gyr.

308   Instead it seems likely that pO_2 varied over Proterozoic time. What remains unresolved is what

309   minima it reached when positive $\delta^{53}Cr$ is absent, and whether the overall pattern was of oxygenation

310   events against a very low pO_2 baseline [50], or deoxygenation events against a higher pO_2 baseline.

311   Traditionally, the lack of detrital pyrite (or uraninite) in sediments after the Great Oxidation indicates

312   exposure of these grains to sufficient oxygen in weathering or aquatic transport environments to

313   fully oxidise them. Modelling of shale weathering profiles across observed ranges of erosion rates on

314   the land surface, predicts that the oxidation of pyrite in soils would be incomplete at pO_2 <0.1 PAL

315   [47]. Kinetic modelling of the dissolution of detrital pyrite (and uraninite) grains in solution

316   equilibrated with atmospheric oxygen – e.g. during transport down rivers – indicates pO_2 >0.05 PAL

317   would be required to completely dissolve them, especially for short river transport times [51]. This

318   pO_2 limit would go up if the grains spend time in organic-rich riverine sediments – as seems likely for

319   longer river transport times – because they are readily driven anoxic at low pO_2. These models all

320   depend on poorly known pyrite oxidation kinetics at low pO_2, which have recently been revised

321   faster [52], which will tend to shift the pO_2 lower limits downwards.

Deeper ocean redox state

323   Models can indicate how ocean redox state varies with atmospheric pO_2, ocean nutrient levels, and

324   the nature of the biological pump, helping infer ocean redox state from marine sediment proxies.

325   The most established redox proxy – iron speciation of sediments – is a localised proxy usually taken

326   to directly indicate whether overlying waters were oxic, anoxic and sulphate-reducing (euxinic), or

327   anoxic and iron-reducing ('ferruginous'). Models suggest that 'ferruginous' does not imply iron rich,

328   but rather $[Fe^{2+}]$ ~0.1μM [25, 53], and oxygen and nitrate rather than iron may dominate organic

329   carbon remineralisation [53]. A growing range of redox-sensitive trace metals with anoxic or euxinic

330   sinks are also being used to try and get a 'global' proxy of ocean redox state. Different metals with

331   different redox sensitivity can add information – for example molybdenum (Mo) removal is

332   specifically sensitive to euxinic (rather than ferruginous) conditions whereas uranium (U) removal

333   tracks anoxic conditions in general. Models are still required to estimate the global spatial extent of

334   anoxic or euxinic bottom waters, and the results are typically sensitive to assumptions about

335   kinetics, the present extent of anoxic bottom waters, and other uncertain terms in the isotopic mass

336   balance. They show that complete removal of redox sensitive metals need not imply global anoxia or

337   euxinia, with estimates of >30-40% of Proterozoic seafloor anoxic and ~1-10% euxinic [54].

338   Consistent with this, basin transects and broader compilations of iron-speciation data indicate a

339   spatially heterogeneous deeper ocean redox state at several Proterozoic times. This is supported by

340   other redox proxies in very rare samples of the deep ocean, which indicate oxic bottom waters at

341   some places and times [55, 56]. To interpret such spatially heterogeneous redox structure requires a

342   spatially explicit model, and one model in particular has been used.

GENIE

344 'GENIE' is a coarse-resolution 3-D ocean model coupled to a 2-D (single layer) atmosphere and sea-

345 ice, with marine C, P, S, and optional N, biogeochemical cycling, designed to consider controls on

346 ocean redox state, atmospheric pCO_2 and global temperature. GENIE's strengths include that it is

347 fast for a 3-D model and has data-assimilated modern biogeochemistry, which has been tested

348 against multiple events in the geochemical record. It also captures some of the spatial variability in

349 climate and has an optional weathering module. Key limitations include the lack of an open P cycle,

350 limited iron-nutrient relationships, and very limited resolving of shelf seas. Atmospheric pO_2 is

351 prescribed and so, crucially, is ocean P content. GENIE can be run with a closed or open C cycle

352 (Figure 1) – i.e. with prescribed or interactive pCO_2. With an open C cycle, including interactive

353 silicate weathering, GENIE can be integrated for up to a million years to achieve steady state of the

354 inorganic carbon cycle. However, as ocean P content is prescribed this leads to some timescale

355 inconsistency – e.g. organic carbon burial is prescribed, when in reality it responds interactively (and

356 can affect pCO_2) over such timescales. Hence we concentrate on closed O_2, C and P system

357 applications of GENIE to interpret proxy data, and consider open N system responses. Later we

358 consider the inclusion of ecological dynamics, noting throughout that the lack of an open P cycle

359 response limits what we can infer about dynamical responses over timescales $\geq 10^4$ yr.

360 GENIE has been used to explore how ocean redox state depends on prescribed pO_2 [25, 57], PO_4 [25,

361 58], and the nature of the biological pump [25, 59]. This suggests that spatial redox heterogeneity

362 requires a finely-poised global balance between atmospheric oxygen levels and ocean limiting

363 nutrient levels, and is sensitive to the nature of the biological pump. Assuming a modern biological

364 pump, it requires pO_2:nutrient ~0.4 of today's ratio [25], consistent with other models. This can be

365 achieved in very different ways. If Proterozoic pO_2 << PAL then nutrients must have been chronically

366 limiting, but if nutrients were near present ocean levels (POL) then pO_2 ~0.4 PAL is consistent with

367 times of deeper ocean redox heterogeneity. Prototype inclusion of Fe-S cycling in such a mixed

368   redox state ocean predicts $[Fe^{2+}]$ ~$0.1\mu M$ with removal as pyrite in euxinic settings but iron oxide at

369   the oxic-anoxic boundary [25].

370   GENIE further shows that at pO_2:nutrient <0.05 of today – under which deeper waters would be

371   completely anoxic – surface waters of the ocean start to exhibit redox heterogeneity including

372   'oxygen oases' and anoxic areas (i.e. they cease to be equilibrated with the atmosphere) [25, 57].

373   This makes other recent model attempts to infer very low pO_2 ~0.001 PAL from shallow ocean

374   sediment redox proxies e.g. ~1.85 Ga [60] problematic, because conceivably anoxic signatures, e.g.

375   in Ce/Ce* [60] (or iron-speciation), simply indicate anoxic areas caused by excess local reductant

376   input. These may indicate less extreme pO_2 <0.05 PAL or higher nutrient levels, noting that shallow

377   shelf-sea locations are often enriched with nutrient runoff from land.

378   ## Ocean nutrient levels and productivity

379   Modelling was originally used to infer very low ocean $[PO_4]$ from the phosphorus content of iron

380   formations [61]. Subsequently, experiments showed that the results are highly sensitive to

381   assumptions about the concentration of other ions in seawater, notably silica [62, 63]. Using

382   plausible limits on [Si], revised estimates put mid-Proterozoic $[PO_4]$ at or above present ocean levels

383   (POL) and well above them in the Neoproterozoic [64]. A more recent high-profile paper argues from

384   the low bulk phosphorus content of shales that prior to the Neoproterozoic, $[PO_4]$ << 1 POL [33].

385   However, the argument that because phosphorus burial was less, phosphorus concentration in the

386   ocean must have been lower is logically flawed. Phosphorus burial is only directly informative of

387   phosphorus input to the ocean (on timescales longer than the residence time), *not* phosphorus

388   concentration. Instead, the authors construct a model (discussed below) in which a very efficient

389   process of phosphorus removal is assumed to have been going on elsewhere, in unrecorded deep

390   ocean settings, thus maintaining low $[PO_4]$. Without this assumption they predict elevated $[PO_4]$, and

391   if we assume the biological pump was less efficient, much higher $[PO_4]$ could be predicted. Hence

392   huge uncertainty currently surrounds Proterozoic $[PO_4]$ levels. The application of phosphorus

393   speciation to ancient sediments holds great potential to improve knowledge but will also need

394   modelling to interpret it. The first data from ~1 Ga indicates efficient P removal with iron minerals in

395   a low productivity, ferruginous ocean margin setting, but $(C:P)_{org}$ suggests that primary production

396   was no more nutrient limited than today [65].

397   Ancient marine N cycling is hard to constrain even with data and models. The nitrogen isotope

398   composition of shales should provide some information, but unfortunately the same $\delta^{15}N$ signature

399   can be produced in different ways. In GENIE simulations of a mixed redox state Proterozoic ocean,

400   abundant nitrogen fixation comprising ~1/3rd of new production is predicted to balance intense

401   regions of denitrification, and the deep ocean comprises small and rapidly turning over reservoirs of

402   nitrate and ammonium in anoxic and oxic waters respectively [25]. Consequently, [PO_4] is decoupled

403   significantly above the nitrogen levels determining productivity and P burial in a more anoxic ocean

404   – at around double the levels that would make it proximately limiting. Recent GENIE results suggests

405   the decoupling of P above N could be even greater [66]. Extending such a spatial model to predict

406    $\delta^{15}N$ distributions could provide a test of this scenario against available data.

407   Recently a simple model has been used to try and infer gross primary productivity (GPP) from the

408   triple oxygen isotope ($\Delta^{17}O$) composition of sedimentary sulphate at particular times in the

409   Proterozoic [42, 67, 68]. However, the problem is under-constrained, because $\Delta^{17}O$ depends jointly

410   on pO_2, pCO_2 and GPP, with positive correlation between pO_2 and GPP. Hence, e.g. at ~1.4 Ga, both

411   lower pO_2 ~0.001-0.01 PAL and GPP ~6% of today, and higher pO_2 ~0.01-0.1 PAL and GPP ~40% of

412   today, are consistent with the same $\Delta^{17}O$ data [42]. Had the authors considered pO_2 >0.1 PAL their

413   GPP inference would be higher again. The same issue pertains at other times of $\Delta^{17}O$ data, although

414   around ~2 Ga there is $\Delta^{17}O$ evidence that GPP declined [68] or pO_2 increased. Attempts to further

415   constrain the solution space [43], by mechanistically tying the unknown variables together, depend

416   on contestable models (that are discussed next). They risk circular reasoning – taking a model that

417   ties low pO_2 and low nutrients together, taking different model-dependent inferences of low pO_2,

418   and then (unsurprisingly) inferring from $\Delta^{17}O$ a low productivity, low nutrient, low pO_2 world.

Alternative models for global biogeochemical cycling

420   I now consider three recent models of global biogeochemical cycling including oxygen and nutrient

421   levels prior to and during the rise of complex life (Figure 1). I compare and contrast these different

422   models, explain why they come to quite different results, examine what (if any) testable predictions

423   they make, and thus try to establish which (if any) results we should trust. Table 1 summarises and

424   contrasts key process representations in the three models.

CANOPS

426   'CANOPS' is a 1-D ocean-atmosphere box model designed to consider controls on ocean nutrient and

427   redox state [69, 70], that has been used to explore how C, N, P, S cycling could have worked under

428   different prescribed levels of atmospheric pO_2 [33, 71]. CANOPS represents several key input and

429   output fluxes from/to the lithosphere, but it does not represent key sedimentary reservoirs or their

430   tectonic cycling. The modelling approach involves prescribing permissible distributions on a range of

431   model boundary conditions (including pO_2), drawing many different instances of the model from

432   those parameter distributions, and running those model variants to steady state for ocean reservoirs

433   (if possible). Additional data-derived constraints may then be imposed on what is considered a

434   permissible result. In ocean steady state, the input/output fluxes do not necessarily balance with

435   respect to particular sedimentary reservoirs, nor do they necessarily achieve redox balance – instead

436   an ad hoc flux is invoked to achieve that [71].

437   In one high-profile publication [33], CANOPS purportedly supports a "stable low-oxygen world" in

438   the Proterozoic with very low ocean nutrient levels. However, as pO_2 is prescribed (by the modellers)

439   the first claim appears tautological. Several critical assumptions in the model's ocean process

440   representation (Table 1) determine that it produces a low nutrient ocean when low pO_2 is

441   prescribed. Firstly, efficient abiotic removal of phosphorus is prescribed, nominally due to

442   scavenging by iron minerals forming at the redox boundary of a largely anoxic water column

443   (although Fe cycling is not represented). Secondly, the C:P stoichiometry of primary production is

444   assumed to increase ~3-fold under low nutrient levels. Thirdly, organic C preservation is assumed to

445   be more efficient under anoxic conditions [37]. The first assumption directly generates low P and

446   productivity levels. The latter two assumptions dictate that when prescribed low pO_2 inevitably

447   makes the ocean anoxic, in order to match the relatively low organic C content of Proterozoic shales,

448   an anoxic ocean must have low P levels and productivity (because organic carbon creation and

449   preservation are assumed more efficient). Hence the model 'result' is wired into its assumptions. As

450   the authors show [33], if the first assumption is dropped and there is no prescribed efficient

451   scavenging of P, the response to prescribed low pO_2 is completely different, with higher than present

452   P levels in the anoxic ocean supporting greater than present organic carbon burial, which would tend

453   to cause pO_2 to rise.

454   In a subsequent paper [71], CANOPS purportedly manages to "constrain global redox balance",

455   support mid-Proterozoic "severe P biolimitation" and find a role for the sulphur cycle in "regulating

456   atmospheric O_2 levels". Here independent but model-based estimates of $[SO_4]$~0.1-1 mM are used

457   to constrain subsets of permissible model solutions. The modellers show Earth's surface in redox

458   balance by invoking an arbitrary balance term (Φ_{out}[Red] in Figure 5 of [71] – reproduced here as

459   Figure 2a,b with that flux labelled 'redox imbalance'). However, the failure to impose strict Earth

460   surface redox balance within the model violates the assumption that pO_2 is fixed (stable) and the

461   required balancing flux must be critically examined. Similarly, the lack of balanced sedimentary

462   reservoirs should lead readers to question whether the purported model steady states and assumed

463   pO_2 levels are sustainable in the long-term. In the assumed 'low' pO_2 ~0.001 PAL case (Figure 2a,

464   reproducing Figure 5a of [71]), the required redox balance term is a large net removal of oxygen (~-

465   2.1 Tmol O_2 eq yr^{-1}), which exceeds the sum of the resolved reduced matter input terms (~-1.6 Tmol

466   O_2 eq yr^{-1}), or the uncertainty today in unresolved reduced matter input terms (-(0.8-1.4) Tmol O_2 eq

467 yr^{-1}). Without this term (i.e. with the fluxes that are actually modelled), pO$_2$ would tend to rise. With

468 a ~1.1 Tmol O$_2$ eq yr^{-1} input of reduced C gases required to balance the organic carbon cycle in the

469 model (and consistent with today's unresolved reduced matter inputs), a ~1 Tmol O$_2$ eq yr^{-1}

470 imbalance would remain, which can generate today's pO$_2$ reservoir in 37 Myr. This redox imbalance

471 (and the organic carbon cycle imbalance) largely disappears in CANOPS' 'high' pO$_2$ ~0.033 PAL case

472 (Figure 2b, reproducing Figure 5b of [71]).

473 The redox imbalance at pO$_2$ ~0.001 PAL exists because (in electron or oxygen equivalents), pyrite

474 burial greatly exceeds sulphur oxidation, and organic carbon burial far exceeds organic carbon

475 oxidation (plus iron oxidation) requiring a large unresolved input of H$_2$, CO, CH$_4$, Fe^{2+}. Pyrite

476 oxidation is incomplete, at odds with the lack of detrital pyrite. The imbalance in the S cycle involves

477 an excess of gypsum weathering and (implicit) degassing over (minimal) burial, which is

478 unsustainable over Proterozoic timescales. There was gypsum deposition (for the first time) in the

479 aftermath of the Great Oxidation, but the assumed initial model reservoir of (50±25)x10^{18} mol would

480 shrink on a ~100 Myr timescale (based on the modelled input/output imbalance). This would leave a

481 crustal sulphur reservoir dominated by pyrite, invalidating the claim that sulphur cycling and

482 especially pyrite burial played a role in regulating atmospheric O$_2$ over Proterozoic timescales (see

483 below).

484 'LaaSch'

485 Laakso and Schrag have developed a simple box model – which I dub 'LaaSch' – to consider how

486 atmospheric oxygen could have been regulated at different levels over Earth history [72, 73]. LaaSch

487 is an Earth surface model where outputs have to balance inputs for ocean-atmosphere reservoirs of

488 material to be at steady state. Atmospheric pO$_2$ is an interactive variable (unlike in CANOPS) and

489 predicting its stable level(s) is a key target of the model. In an early version of LaaSch, C, P, S and

490 alkalinity cycling are included [72], with a subsequent version adding Fe and H cycling [73]. LaaSch

491 does not include sedimentary reservoirs or their tectonic cycling. However, it does require that

492   atmospheric pO_2 and the redox fluxes to/from the surface system adjust until redox balance is

493   achieved. Again one should look at the predicted fluxes into and out from the sediments and

494   consider whether they imply net transfers of C or S (or Fe) between sedimentary forms and whether

495   those are consistent with observations or could be sustained over Proterozoic timescales >100 Myr.

496   In its process representation (Table 1), LaaSch makes critical assumptions – firstly that phosphorus is

497   increasingly efficiently scavenged by iron minerals in rivers/estuaries as atmospheric pO_2 declines

498   [72]. The shape of the functional response is arbitrarily chosen (and is changed markedly between

499   studies [72, 73]) in a way that generates alternative stable states for atmospheric pO_2 at ~1 PAL and

500   ~0.1 PAL. The authors are explicit that "the parameterization is tuned to give stability [of pO_2] at

501   levels consistent with proxy records". The reason a decline in P input with declining pO_2 is required is

502   that LaaSch also assumes spectacularly efficient organic C transfer to sediments in an anoxic water

503   column and very high preservation efficiency in anoxic sediments, which would otherwise tend to

504   push pO_2 back towards modern levels. In a lower Proterozoic pO_2 steady state, LaaSch simulate only

505   ~0.1% of modern primary production but >70% of it being buried (whereas in today's world only

506   ~0.1% is buried). Virtually no remineralisation occurs in the model anoxic water column because it is

507   assumed to only depend on O_2 (which is predicted absent) or SO_4 (which has a low predicted

508   concentration), ignoring water column methanogenesis (or other oxidants). This is wrong and

509   demonstrably incompatible with the geochemical record – for example, mid-Proterozoic euxinic

510   shales require a productive biosphere and extensive sulphate reduction, and ignoring water column

511   methanogenesis leads to erroneously low atmospheric methane levels, especially in the Late

512   Archean where there is isotopic evidence for extensive marine methane cycling. The increase in

513   organic carbon burial efficiency under anoxic conditions is also erroneously high because the model

514   only considers the deep ocean, failing to recognise that >80% of organic carbon burial occurs in

515   shallow ocean margin sediments today [74], where the much higher sedimentation rates mask any

516   difference between oxic and anoxic remineralisation rates [37].

517   The modelled 'low O_2' state (Figure 2c) is predominantly stabilised by oxygen-sensitive iron oxidation

518   in the water-column, which would be expected to generate iron deposits and net oxidation of iron in

519   the crust, whereas crustal iron oxidation appears to have mostly occurred during the 'Lomagundi'

520   event 2.22-2.06 Ga [75] and Banded Iron Formations (BIFs) disappeared after ~1.8 Ga. This low pO_2

521   model solution also has gypsum dominating sulphur burial despite pyrite oxidation dominating

522   sulphur input (and that is even true of the Archean "anoxic" model solution, because pyrite

523   oxidation is erroneously assumed to be complete at pO_2 ~10^{-7} PAL). This implies a sulphur cycle

524   imbalance with transfer of sulphur from pyrite to gypsum sedimentary reservoirs – and a

525   corresponding carbon cycle imbalance with transfer of electrons from pyrite to the organic carbon

526   sedimentary reservoir. Such a sulphur cycle imbalance is unsustainable over Proterozoic timescales,

527   and is inconsistent with the sporadic nature of gypsum deposition in the Proterozoic and with

528   evidence of widespread anoxic ocean conditions depositing extensive euxinic shales. Furthermore, it

529   is well established from the $\delta^{13}C$ and $\delta^{34}S$ records and from models that do include sedimentary

530   reservoirs that the major transfer of S from pyrite to gypsum (and corresponding transfer of

531   electrons from pyrite to organic carbon) occurred in the Paleozoic [22, 30]. The simulated low pO_2

532   state also has minimal oxidative weathering of organic carbon, because that is wrongly [47] assumed

533   to depend linearly on pO_2 (Table 1). With considerable organic carbon burial this implies massive

534   growth of the sedimentary reservoir of organic carbon over Proterozoic time (Figure 2c). This is a

535   more appropriate scenario for prior to the Great Oxidation than after it [47]. The predicted organic

536   fraction of carbon burial is considerably greater than today, implying higher $\delta^{13}C$ than the 0‰

537   observed (were it to be simulated). To counter this, the authors invoke an (un-simulated) isotopically

538   heavy authigenic carbonate sink, but authigenic carbonate is typically isotopically light not heavy

539   [76].

540 ## COPSE

541 My own efforts with colleagues extend the COPSE (Carbon, Oxygen, Phosphorus, Sulphur and

542 Evolution) model, developed and tested for the Phanerozoic [30, 77], back into Proterozoic time [47,

543 78, 79], to try and understand both how the Earth system could have worked and to test hypotheses

544 to establish how it did work. COPSE is an Earth surface model that includes sedimentary rock

545 reservoirs – following the tradition of Garrels, Berner and others. It has not (yet) included material or

546 redox exchange with the mantle (or H loss to space). It maintains ocean-atmosphere redox balance

547 and conserves matter and redox equivalents (electrons) in the total ocean-atmosphere-sediment

548 system. COPSE includes C, O, P, S and N cycling (although some published work has removed the S

549 cycle [47], for reasons explained below). Atmospheric pO_2 is interactive and predicting its stable

550 level(s) is a key model target. COPSE predicts stable isotope records of carbon ($\delta^{13}C$), sulphur ($\delta^{34}S$),

551 and strontium ($^{87}Sr/^{86}Sr$), to enable model testing against data. COPSE is forced by changing solar

552 luminosity, changing tectonic factors (degassing, uplift/erosion), and changing biological factors.

553 Key process representations include a careful treatment of oxidative weathering (of C and S) based

554 on running a detailed 1-D weathering model over a realistic range of erosion rates [47]. This predicts

555 that pyrite oxidation ceases to be complete below pO_2 ~0.1 PAL, and that organic carbon oxidation

556 ceases at ~0.01 PAL and is particularly sensitive to varying pO_2 around ~0.1 PAL. COPSE includes the

557 major contribution of land plants to organic carbon burial today, which when removed prior to the

558 mid Paleozoic inevitably produces lower pO_2 and lower $\delta^{13}C$ ~0‰ (rather than ~2‰) consistent with

559 data [30]. COPSE does not assume more efficient organic carbon burial under anoxic conditions, but

560 does include more efficient P recycling from organic matter under anoxic conditions, which is well

561 established. It does not invoke more efficient P scavenging under lower pO_2, either in

562 rivers/estuaries or in an anoxic water column. P fluxes are parameterised based on oxic or euxinic

563 conditions with no special distinction of ferruginous P cycling – because like the other models it does

564 not distinguish euxinic from ferruginous conditions. COPSE includes N cycling but has no distinction

565   of ammonium from nitrate reservoirs, and does not predict $\delta^{15}N$. The efficiency of the biological

566   pump is not varied. COPSE simulates a predominantly anoxic ocean in the early Paleozoic and

567   preceding Proterozoic, in which N and productivity levels are comparable to modern, but P levels are

568   roughly double modern levels (required to support abundant N-fixation and a balanced N cycle).

569   Proterozoic COPSE simulations with a mostly anoxic ocean predict that pyrite burial dominates S

570   removal and the pyrite sedimentary reservoir dominates the gypsum reservoir. Pyrite oxidation

571   followed by pyrite burial has no net effect on Earth's redox state or atmospheric pO_2. Hence in one

572   Proterozoic study the S cycle was assumed balanced and removed for simplicity [47]. This contrasts

573   with the (implicitly) unbalanced sulphur cycles of CANOPS (net transfer from gypsum to pyrite) and

574   LaaSch (net transfer from pyrite to gypsum). COPSE predicts stable Proterozoic atmospheric pO_2 ~0.1

575   PAL, with a lower limit of pO_2 ~0.01 PAL below which the Great Oxidation is reversed because

576   organic carbon burial (electron removal) is insufficient to outweigh the input of reduced volcanic

577   gases that are rapidly oxidised [47]. Incomplete oxidative weathering of organic carbon is the key

578   oxygen regulator and it leads to the robust prediction of stable $\delta^{13}C$ ~0‰, consistent with the long-

579   term record. In a Neoproterozoic study [79], driven by increasing degassing inferred from plate

580   tectonic models, COPSE predicts a modest increase in pO_2 from ~0.2 to ~0.3 PAL and can reasonably

581   match the $\delta^{34}S$ and $^{87}Sr/^{86}Sr$ records. Subsequent work with COPSE shows how large and persistent

582   Neoproterozoic negative $\delta^{13}C$ excursions (notably the 'Shuram' event) can be maintained by gypsum

583   evaporite weathering events following earlier sporadic deposition of gypsum [80].

Comparison and evaluation

585   As approaches to understanding how the Proterozoic world could have worked, the three models

586   vary in the timescales they can be applied to (Figure 1). CANOPS (as used thus far) is appropriate for

587   making inferences about shorter timescale variables than pO_2 [33], but inappropriate for considering

588   pO_2 regulation or redox balance over 10+ Myr timescales [71]. LaaSch needs major modifications,

589   after which it may be applied to pO_2 timescales, but not 100+ Myr sedimentary ones [72, 73]. COPSE

590   is applicable to pO_2 and sedimentary timescales but is missing longer timescale exchanges with the

591   mantle. The structural limitations of CANOPS and LaaSch lead them to predict long-term imbalances

592   in redox [71] and/or crucial elemental cycles [71, 73] that are at odds with data. CANOPS overall has

593   better process representation than LaaSch, so if its timescale limitations can be overcome (or more

594   carefully considered in study design), it has greater potential.

595   As approaches to establishing how the Proterozoic world actually did work, COPSE makes testable

596   predictions and has successfully simulated key records, notably $\delta^{13}C$. CANOPS qualitatively captures

597   the low organic C content of shales, and LaaSch discuss the implications of their results for $\delta^{13}C$, but

598   neither CANOPS nor LaaSch quantitatively predict proxy variables. Hence they cannot test

599   hypotheses (in any quantitative sense).

600   All of the models contain contestable process representations – although at least with COPSE these

601   can (in principle) be falsified if the model fails to match proxy data. COPSE recognises, whilst

602   CANOPS and LaaSch ignore, the contribution of plants to today's organic carbon burial and oxygen

603   balance. This necessarily generates lower Proterozoic-early Paleozoic pO_2 in COPSE, whereas

604   CANOPS and LaaSch invoke strong feedbacks to generate bi-stability including an alternative low pO_2

605   steady state. A third option would be that the rise of complex life itself altered pO_2. To achieve

606   stable low pO_2, CANOPS assumes very effective P removal with iron minerals to the (anoxic) deep

607   ocean floor, LaaSch assumes very efficient P removal in rivers/estuaries, but neither of these

608   sedimentary environments tend to be preserved (making these assumptions untestable). COPSE

609   assumes less efficient P removal with iron minerals under anoxic ocean conditions, which warrants

610   revision. CANOPS and LaaSch also assume organic carbon burial efficiency increases markedly under

611   anoxic conditions, whereas COPSE does not, and the empirical data on this has been widely debated

612   [37].

Models linking complex life to biogeochemical cycling

613   There has been less work modelling causal links between complex life and biogeochemical cycling.

615   The hypothesis that the first predatory protists, by grazing on the smallest (cyanobacterial)

616   phytoplankton cells, would have left nutrients underused and thus created a niche for larger (algal)

617   phytoplankton cells [16], is based on adapting a classic model of size-structuring in marine

618   communities [81]. The hypothesis that filter-feeding sponges, by predating the smallest

619   phytoplankton cells, also selected for larger (eukaryotic) algae [4] follows the same logic – although

620   how strong the selective effect of sponges is has yet to be modelled.

621   The same model [81] inspires the hypothesis that putative extreme Proterozoic nutrient limitation

622   could have limited phytoplankton cell size and the expansion of eukaryotic algae [7]. Recent

623   inclusion of a size-structured marine ecosystem in GENIE [82], confirms the original results [81] that

624   prescribed nutrients limit cell size and trophic structure – for example, excluding zooplankton if PO_4

625   <10% of present ocean levels [82]. However, if GENIE had an open phosphorus cycle, the

626   correspondingly weak biological pump and limited P supply to sediments should cause ocean $[PO_4]$

627   to rise and rebalance at a higher concentration. Furthermore, the most abundant algae in today's

628   ocean are 1-3 μm diameter mixotrophs that predate cyanobacteria [83] and would not be excluded

629   even at 1% of present ocean nutrient levels [82]. Hence the hypothesis that lack of nutrients

630   prevented the expansion of marine algae lacks support from current models.

631   Whilst CANOPS assumes the biological pump has got less efficient since the mid-Proterozoic, LaaSch

632   assumes it has got much less efficient, and COPSE assumes no change in efficiency, other models

633   have begun to examine the effects of postulated increases in the efficiency of the biological pump

634   [4, 14]. Effects on ocean redox structure have been considered independently of effects on

635   phosphorus levels, but over >10^4 yr timescales these effects should be consistently combined [4, 16].

636   3D GENIE simulations of effects on redox structure for a prescribed ocean nutrient inventory, show

637   that without an effective biological pump, diffusion concentrates oxygen demand in intermediate

638   waters just below the surface ocean, generating the most intense anoxia there [25]. This could have

639   left the deep ocean oxygenated by ventilation from high latitude surface waters, thanks to little or

640   no oxygen demand from organic matter – assuming pO_2 >0.001 PAL and 20 Sv ventilation sufficient

641   to outweigh abiotic reductant input from mid-ocean ridges [25]. An inefficient biological pump also

642   makes it harder to drive the deeper parts of shelf seas anoxic. As the biological pump becomes more

643   efficient, this shifts oxygen demand to deeper waters and sediments, making it easier to drive deep

644   shelves and the deep ocean anoxic, but making it harder to drive (near) surface waters anoxic.

645   However, the effect of changes in the biological pump on ocean P inventory (over ~10^4 yr timescales)

646   and hence total oxygen demand in the water column works in the opposite direction. Simple

647   calculations suggest going from cyanobacterial to algal cells causes a roughly 10-fold increase in

648   sinking terminal velocity and a 2.5-fold increase in material reaching the sediments [84]. A less

649   efficient biological pump requires higher limiting nutrient levels in order to balance the P cycle, and

650   an increase in pump efficiency tends to lower those nutrient levels, thus lowering total oxygen

651   demand in the water column. Simple modelling of the net effect supports earlier suppositions [4,

652   16] that the change in nutrient inventory dominates – with a weaker pump P levels are higher and

653   therefore deep anoxia more intense. As the pump strengthens this tends to lower ocean P levels and

654   the propensity for anoxia. The (much) longer timescale effects on organic C burial and atmospheric

655   pO_2 may work in the opposite direction again: if C_{org}/P_{react} burial ratios decline with ocean

656   oxygenation this will cause pO_2 to decline, ultimately reinstating anoxia, and creating the potential

657   for long-timescale oscillations [85, 86]. Other modelling predicts that an increase in biological pump

658   efficiency lowered atmospheric pCO_2 and might have contributed to triggering snowball Earth events

659   [87].

660   Models have yet to simulate the impact of sessile benthic animals including sponges and

661   'rangeomorph' fronds concentrating resources where they were located on the sediments [17].

662   However, models have begun to consider proposed impacts of mobile, burrowing, bioturbating

663   animals on biogeochemical cycling [18, 19]. Including in COPSE the idea that by oxygenating the

664   upper sediments, bioturbating animals increase the retention of phosphorus and lower the $(C/P)_{org}$

665   burial ratio, leads to a decline and then stabilisation of atmospheric pO_2, consistent with evidence of

666   ocean deoxygenation in the Late Cambrian-Ordovician [19]. The assumed timing of significant

667   increase in bioturbation depth has been critiqued and argued to be much later in the Paleozoic [88].

668   However, a subsequent version of COPSE showed that an early, non-linear impact of shallow

669   burrowing on C, S and P sediment cycling provides a better fit to $\delta^{13}C$, $\delta^{34}S$ and ocean redox data

670   than a late impact [89]. Alongside this simple box modelling, detailed 1D reaction-transport

671   sediment modelling has provided some support that bioturbation lowers C_{org}/P_{react} burial ratios [90].

672   There is clearly scope for more detailed process modelling of this kind to generate further insight

673   into effects of bioturbation on P-speciation.

674   ## Ways forward

675   There is considerable scope for improved Proterozoic biogeochemical modelling. Better models of

676   weathering, transport and sedimentary environments can improve understanding and interpretation

677   of proxies. Models of global biogeochemical cycling need to be built on well-established principles,

678   incorporating appropriate reservoirs and processes for the timescales they pertain to address –

679   which for considerations of atmospheric oxygen regulation means enforcing Earth's surface redox

680   balance and including sedimentary reservoirs. Biogeochemical models should predict proxy data

681   targets to be testable and adding proxy targets has the potential to constrain model results – for

682   example, COPSE could predict $\Delta^{17}O$ and better predict P-speciation. Once an appropriate model

683   structure and link to data is established, a key unsolved challenge is to establish whether and how

684   atmospheric oxygen could be regulated at pO_2 ~0.001 PAL. Predicting long-term fluctuations in pO_2

685 and nutrient levels is also a key target, which will require reconstruction of tectonic drivers and

686 representation of how they affect climate and weathering.

687 Biogeochemical modelling should also explore a wider 'possibility space' of process assumptions.

688 Most existing models assume phosphorus is the ultimate limiting nutrient, although COPSE and

689 GENIE find nitrogen much more proximately limiting when anoxia is widespread, suggesting that

690 possible trace metal limitation of nitrogen fixation deserves consideration [31]. Current models also

691 assume that marine phytoplankton dominated global primary production in the Proterozoic, but if

692 we take seriously existing predictions of much lower phytoplankton productivity [33, 71, 73, 84, 91],

693 then modelling should consider whether microbial mats at the bottom of shelf-seas, in freshwaters

694 and/or on land [27] could have contributed significantly to global productivity. More complete Earth

695 system modelling, including other potentially important factors for complex life, notably climate and

696 the occurrence of 'snowball Earth' events, would also add insight and constrain results.

697 The possibility of significant feedback between biogeochemical conditions and the rise of complex

698 life invites approaches that go beyond biogeochemical modelling. Trait-based physiological and

699 ecological modelling could capture the environmental constraints on particular types of complex life,

700 and coupling this to biogeochemical modelling could capture resultant feedbacks. For example,

701 models of the physiological constraints on sponge pumping metabolism [92] and its hydrodynamics

702 [93], could be coupled to models of its effects on phytoplankton community size structure and

703 biogeochemical cycling. Size-structured modelling of phytoplankton community dynamics [81, 82]

704 could be extended to model the effects of different cell sizes, faecal pellets, zooplankton vertical

705 migration, etcetera, on the biological pump [94-96], and resultant biogeochemical feedbacks. This

706 more comprehensive approach would offer new opportunities for testing hypotheses against

707 empirical data. For example, the combination of molecular phylogenetics and relaxed molecular

708 clocks calibrated on minimum ages from fossils can provide timing estimates for the origin of

709 particular traits (e.g. animal guts). Models that can map from these traits to their biogeochemical

710   consequences, including observable proxies, then give the potential to test and refine those age

711   estimates.

Summary and implications

713   Some of the disagreements between existing models of atmospheric oxygen and ocean nutrient

714   levels associated with the rise of complex life are the result of applying conceptual frameworks

715   designed for a shorter range of timescales to longer timescales and questions, which demand the

716   consideration of additional processes and balances. Some are due to disagreement over uncertain

717   process representations, and some are due to clear flaws in process representation in some models.

718   Considering these model limitations, I conclude that Proterozoic atmospheric pO_2 varying in the

719   range ~0.01-0.4 PAL is mechanistically plausible and could be consistent with available proxies,

720   depending on the timing of pO_2 variations. No consistent model of biogeochemical cycling yet shows

721   how pO_2 could be regulated at ≤0.001 PAL over long timescales, and it is not clear from model

722   interpretations that any proxy demands such low levels, if we recognise that reductant inputs can

723   create disequilibrium anoxic conditions in near-surface environments. However, this does not rule

724   out that such conditions occurred and it should inspire further modelling to see if and how they

725   could occur. Meanwhile, given current estimates of their minimum oxygen requirements it is unclear

726   that the evolution of stem group animals, sponges, or simple bilaterian animals was prevented by

727   lack of oxygen. However, the same reductant input that can create local anoxia and anoxic proxy

728   signatures would clearly pose a problem for animals in those local environments. Furthermore, it

729   remains possible that insufficient pO_2 and/or unstable redox conditions restricted the later rise of

730   more oxygen-demanding animal traits and modes of life.

731   A very wide range of stable Proterozoic phosphorus levels and associated productivity could be

732   consistent with available phosphorus burial data, depending on contestable and largely untested

733   model assumptions. Furthermore, phosphorus levels could have been several times above Redfield

734   ratio to proximately limiting nitrogen levels in a largely anoxic ocean. The lower atmospheric pO_2,

735   the lower the limiting nutrient level consistent with times of heterogeneous ocean redox structure,

736   but Earth surface redox balance requires a marine organic carbon burial flux of comparable order-of-

737   magnitude to today. This makes it crucial to resolve the efficiency of the biological pump prior to

738   complex life and the efficiency of organic carbon remineralisation in a more anoxic ocean. Until we

739   have more P-speciation data and models tested against it, the jury should remain out on Proterozoic

740   nutrient levels. Currently there is no decisive support for nutrient limitation of algae prior to the

741   Cryogenian, leaving the late rise of algae to ecological prominence as an unsolved puzzle.

742   The effects of complex life on biogeochemical cycling remain wide open for exploration, with current

743   models suggesting that they could be substantial.

Author contributions

745   TML conceived the study, analysed the different models, and wrote the paper.

Acknowledgements

Data accessibility

752   All data discussed were extracted from the cited literature and can be found there.

Funding

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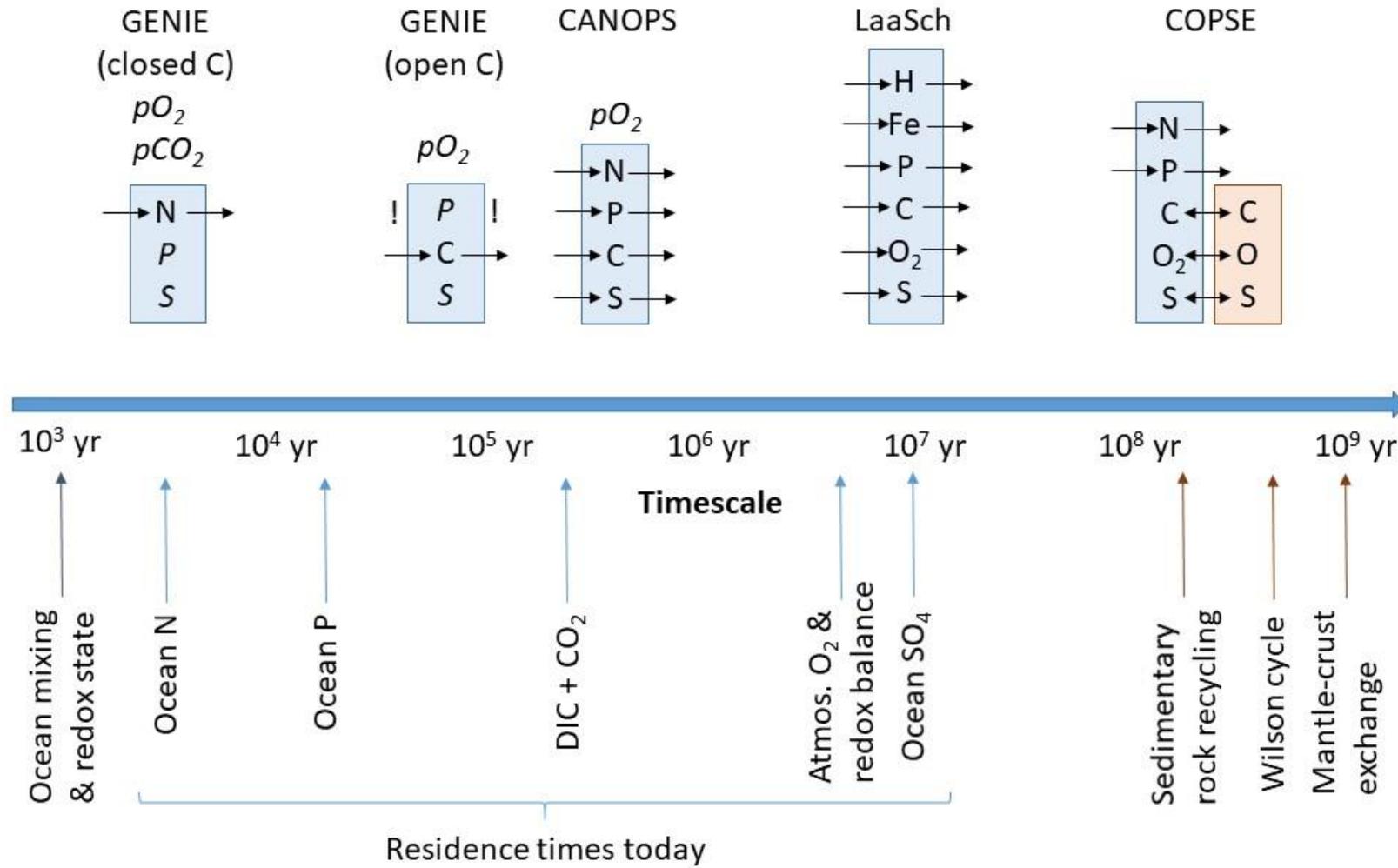
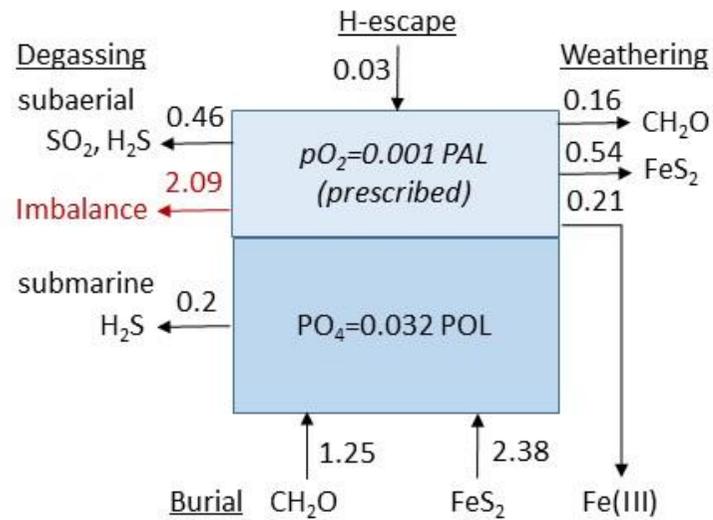1001 **33**, 181-199. (doi:10.1029/2018gb005983).

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1003

Figure captions

Figure 1. Timescales of key Earth system processes and of model applicability. Timescales of key processes (below the line) include residence times of several key variable reservoirs today (DIC = dissolved inorganic carbon), 'redox state' refers to deep ocean redox state, 'redox balance' refers to Earth surface redox balance. Models are positioned above the line according to their approximate (maximum) timescale of applicability, given their assumptions about which reservoirs are treated as constant (in italics). Note that inferences about much longer timescales than indicated have been made in some studies using CANOPS and LaaSch (discussed in text). The major element cycles captured within the ocean-atmosphere of each model are listed inside the blue box, ordered fast to slow (from top to bottom) based on present day residence times. Incoming and outgoing arrows indicate an open system representation for a cycle. Double headed arrows indicate exchange with sedimentary rock elemental reservoirs, which are indicated in a brown box. Two ways of running GENIE are indicated. Exclamation marks indicate a timescale inconsistency (where a fast variable is treated as constant despite a slower variable being treated with an open system).

Figure 2. Earth surface redox (im)balance for proposed Proterozoic states of different models. Arrows indicate fluxes in Tmol O_2 (equivalents) yr^{-1} (electrons flow in the opposite direction), PAL = present atmospheric level, POL = present ocean level, CH_2O = organic carbon, FeS_2 = pyrite (but note the stoichiometry may differ), "from" is used to indicate a source of electrons recognising the gases/fluids will not be in that chemical form. **a)** CANOPS "Low O_2" scenario reproduced from Figure 5a of [71] with unmodelled reductant input (Φ_{out}[Red]) indicated in red as redox "imbalance". **b)** CANOPS "High O_2" scenario reproduced from Figure 5b of [71]. **c)** LaaSch "Low-O_2" scenario reconstructed from [73] (note 'pyrite' burial flux actually has stoichiometry FeS). **d)** COPSE example Proterozoic state from [47] assuming present day marine organic carbon burial flux, and indicative S fluxes assuming sedimentary S reservoir is dominated by pyrite (in brackets because the S cycle can then be excluded from the model and its redox balancing – see text).

a) CANOPS ('low' O₂ case)

H-escape

Degassing   Weathering
subaerial   0.46   0.16
SO₂, H₂S ←   → CH₂O
                    pO₂=0.001 PAL   0.54
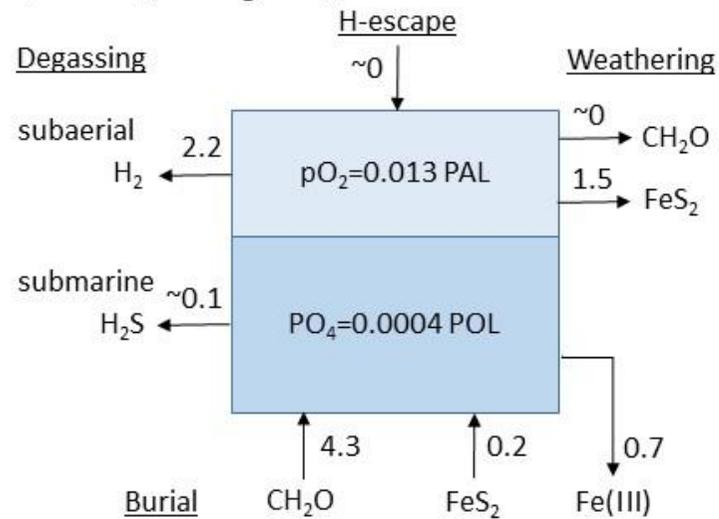   (prescribed)   → FeS₂
        2.09   0.21
Imbalance ←

submarine   0.2
H₂S ←   PO₄=0.032 POL

            1.25   2.38
Burial CH₂O   FeS₂   Fe(III)

0.03

b) CANOPS ('high' O₂ case)

H-escape

Degassing   Weathering
subaerial   0.46   2.22
SO₂, H₂S ←   → CH₂O
                    pO₂=0.033 PAL   0.98
                    (prescribed)   → FeS₂
        0.19   0.29
Imbalance ←

submarine   0.2
H₂S ←   PO₄=0.052 POL

            1.94   2.30
Burial CH₂O   FeS₂   Fe(III)

0.10

c) LaaSch ('low' O₂ state)

H-escape

Degassing   Weathering
subaerial   2.2   ~0
H₂ ←   → CH₂O
                    pO₂=0.013 PAL   1.5
                                        → FeS₂

submarine ~0.1
H₂S ←   PO₄=0.0004 POL

            4.3   0.2   0.7
Burial CH₂O   FeS₂   Fe(III)

~0

d) COPSE (example Proterozoic state)

Degassing   Weathering
            1.25   1.25
from CH₂O ←   → CH₂O
                    pO₂~0.1 PAL   (~2.3)
        (~0.7)   → FeS₂
from FeS₂ ←

                    PO₄~2 POL
                    NO₃~1 POL

            2.5   (~3.0)
Burial CH₂O   FeS₂

1030

1031 Tables

1032 **Table 1: Representation of key biogeochemical fluxes in three Proterozoic models**

Cycle	Model		
Process	**CANOPS**	**LaaSch**	**COPSE**
Nitrogen			
Nitrogen fixation	compensates any N deficit	-	α (P-N/16)^2
Denitrification (water)	f([NO$_3^-$],[O$_2$])	-	f(anoxia,N)
Denitrification (sediment)	f([NO$_3^-$],[O$_2$],C$_{org}$)	-	f(N)
Phosphorus			
P weathering	Fixed flux: 0.18 TmolP yr^{-1}	Apatite (silicate) + oxidative	Silicate + carbonate + oxidative
P bioavailability to ocean	= P weathering	0.33$\rightarrow$1 as pO$_2$ 0.1$\rightarrow$1 PAL (nominally Fe-mineral scavenging in estuaries)	= P weathering – P to land plants
P scavenging in ocean	α P upwelling $*$ σ_{scav} parameter (0-1) (nominally by Fe-minerals)	α P (small flux)	-

Org-P burial	Complex function, $(C_{org}:P_{org})_{burial}$ increases with anoxia	P regeneration α f(O_2, (sedimentary oxic respiration + SO_4 reduction + Fe reduction))	α C_{org} burial, $(C_{org}:P_{org})_{burial}$ increases with anoxia (250→4000)
Ca-P (authigenic) burial	Suppressed by anoxia		Suppressed by anoxia
Fe-P burial	Suppressed by anoxia		Suppressed by anoxia
Organic Carbon			
C_{org} degassing	-	(implicit in H_2 input)	α C_{org} sedimentary reservoir
C_{org} oxidative weathering	α $pO_2^{0.5}$	α pO_2	α $pO_2^{0.5}$, C_{org} sedimentary reservoir
C_{org} burial land plants	-	-	50% of today's total C_{org} burial
Export/new production	P-limited (Michaelis-Menten), C:P increases 106→400 as P decreases	P-limited (linear), C:P=106	N-limited, C:P=106
Biological pump efficiency	Remineralisation=f(O_2,NO_3,SO_4,CH_2O)	Remineralisation= f(O_2,SO_4)	(Constant)
C_{org} burial efficiency	Enhanced by anoxia	Enhanced by anoxia	Optional f(pO_2)
Sulphur			(optional)
S degassing	0.7 TmolS yr^{-1} (SO_2:H_2S=9:1) subaerial + 0.1 TmolS yr^{-1} (H_2S) submarine	0.07 TmolS yr^{-1} (H_2S) submarine, (no subaerial)	Reduced α pyrite reservoir, Oxidised α gypsum reservoir

Pyrite weathering	Biotic≠f(O_2) + Abiotic=f(O_2), complete oxidation pO_2>0.0035 PAL	0.8 TmolS yr^{-1}, complete oxidation pO_2>10^{-7} PAL	α pyrite sedimentary reservoir (complete oxidation)
Pyrite formation and burial	α sediment-water H_2S flux, burial efficiency suppressed by [O_2]	Water-column and sediment formation	α C_{org} burial, [SO_4], (pO_2)$^{-1}$
Gypsum weathering	Constant α assumed initial gypsum reservoir, assumed erosion rate	2.8 TmolS yr^{-1}	α gypsum reservoir
Gypsum deposition	α [SO_4]	α [SO_4]	α [SO_4]
Other O_2 terms			
H_2 input	-	2.2 Tmol O_2 eq yr^{-1}	-
Hydrogen escape	α CH_4	f(H), diffusion limited	-
Seafloor oxidation	-	α [O_2]$_d$	-
Fe^{2+} weathering	f(O_2), buried on land	α silicate weathering, all goes to ocean	-
Fe^{2+} hydrothermal	-	0.4 TmolFe yr^{-1}	-
Fe^{2+} ocean oxidation	-	α [O_2][Fe^{2+}], some buried as siderite	-

1033