PHILOSOPHICAL TRANSACTIONS A

Ocean deoxygenation, the global phosphorus cycle, and the possibility of human-caused large-scale ocean anoxia

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1　Ocean de-oxygenation, the global phosphorus cycle, and the possibility of human-

2　caused large-scale ocean anoxia.

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12　<u>Abstract</u>

13　The major biogeochemical cycles which keep the present-day Earth habitable are

14　linked by a network of feedbacks which has led to a broadly stable chemical

15　composition of the oceans and atmosphere over hundreds of millions of years[1-3].

16　This includes the processes which control both the atmospheric and oceanic

17　concentrations of oxygen. However, one notable exception to the generally well-

18　behaved dynamics of this system is the propensity for episodes of ocean anoxia to

19　occur and to persist for $10^5 - 10^6$ years, these OAEs (Ocean Anoxic Events) being

20　particularly associated with warm "greenhouse" climates[4]. A powerful mechanism

21　responsible for past OAEs was an increase in phosphorus supply to the oceans leading

22　to higher ocean productivity and oxygen demand in subsurface water. This can be

23　amplified by positive feedbacks on the nutrient content of the ocean, with low oxygen

24　promoting further release of phosphorus from ocean sediments, leading to a

25　potentially self-sustaining condition of deoxygenation. We use a simple model for

26   phosphorus in the ocean to explore this feedback, and to evaluate the potential for

27   humans to bring on global-scale anoxia by enhancing P supply to the oceans. While

28   this is not an immediate global change concern, it is a future possibility on millennial

29   and longer time scales, when considering both phosphate rock mining and increased

30   chemical weathering due to climate change. Ocean de-oxygenation, once begun, may

31   be self-sustaining and eventually could result in long-lasting and unpleasant

32   consequences for the Earth's biosphere.

33

34

35   <u>Introduction</u>

36   The oxygen content of the ocean today is finely balanced. In the oxygen minimum

37   zones (OMZs), to be found in the pycnocline of every ocean basin, O_2 is depleted by

38   respiring organisms feeding on sinking biological material originating from

39   photosynthesis at the surface. In a few regions such as the Eastern Pacific and the

40   Northern Indian Ocean, which are far from deep water formation regions and where

41   surface productivity is high, the depletion is sufficient to completely or almost

42   completely de-oxygenate the water [5]. Over most of the ocean, the depletion is

43   substantial but not complete.

44

45   Both models [6-9] and simple calculations (see below) suggest that a modest (e.g.

46   ~2x) increase in the new production of the global ocean, or decrease by a similar

47   factor in atmospheric oxygen, would be sufficient to drive much larger volumes of

48   water towards anoxia. Once dissolved O_2 falls to a small percentage of surface values,

49   denitrification -- bacterial reduction of nitrate -- begins to occur, as is seen today in a

50   number of OMZs such as that of the Arabian Sea [10]. When the small reservoir of

51 nitrate is exhausted, microbial reduction of sulphate may begin and the waters become

52 euxinic, with production of hydrogen sulphide. Though there are no regions of the

53 open ocean today that exhibit permanently euxinic conditions, they are found in the

54 Black Sea below 100m, and in restricted basins such as some fjords, where most of

55 the sulphate reduction actually occurs in underlying sediments rather than the water

56 column. There is good evidence for much more widespread euxinic conditions at

57 intervals in the past [11].

58

59 As first pointed out by Alfred Redfield [12], a simple calculation implies a close

60 balance between nutrients and oxygen in the oceans. Table I summarizes Redfield's

61 argument, updated to use more recent values of stoichiometric ratios. We start from

62 the average deep ocean concentration of phosphate (which we take to be the ultimate

63 limiting nutrient [13]) in the global ocean, of 2.2 μmol kg^{-1} [14]. P is supplied to the

64 surface ocean by the upwelling of deeper water. By mass conservation, an equivalent

65 volume of water must be subducted from the surface mixed layer into the interior,

66 carrying oxygen dissolved from the atmosphere, such that the supply of O_2 to the

67 interior ocean is set by the solubility of oxygen and the atmospheric concentration [5].

68 Redfield assumed that all the nutrients at the surface are used in photosynthesis to fix

69 organic carbon, and this then sinks into the deep sea and is respired and remineralized,

70 consuming the dissolved oxygen. He used the known concentrations of PO_4 in deep

71 water and the stoichiometric ratios which now bear his name, to calculate the oxygen

72 demand. We use the "best guess" value given by Anderson [15] of $-O_2/P = 150$. The

73 computed oxygen demand and the oxygen supply are almost equal to one another,

74 suggesting that essentially all the oxygen carried into the interior of the ocean would

75 be used in respiration.

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76

77 If the assumptions of this calculation were correct, it would imply that the entire deep

78 ocean today should be hypoxic, but it is not. Oxygen demand is set not only by the

79 concentration of the limiting nutrient phosphate in the deep ocean , but also by the

80 efficiency with which the nutrient is used by the biota when the water is upwelled to

81 the surface. The Redfield calculation of Table I assumes that this efficiency is 100%,

82 but globally averaged, it is now believed that only 30-40% of the phosphate in the

83 deep ocean has arrived there via the biological pump: the remainder is "preformed",

84 meaning that it was present in the water, unused by the biota, when it subducted from

85 the surface [16]. Thus the calculation over-estimates oxygen demand by a factor of

86 two or three, and most of the deep sea is well oxygenated, with hypoxia restricted to

87 regions far from deep water formation sites, and underlying zones of high

88 productivity. Nevertheless, models and simple calculations are in agreement that the

89 ocean biogeochemical system responds such that small changes in oxygenation or net

90 primary production substantially affect the volume of hynoxic water, and the area of

91 sediments overlain by hypoxic waters. In this sense, the ocean could be described as

92 being on the "edge of anoxia" [17]. Is there a deeper reason why the ocean globally,

93 should behave in this way, or is this just chance?

94

95 We suspect it is not chance, but is ultimately dictated by the network of feedbacks

96 which link the phosphorus cycle with the redox state of the ocean and atmosphere.

97 These feedbacks are important for the regulation of atmospheric oxygen concentration

98 at levels not too far from the present day, concentrations that have been maintained

99 for the past several hundred million years [2, 17, 18]. Figure 1 illustrates in symbol-

100 and-arrow form a number of possible feedbacks that link atmospheric and ocean

101 oxygen concentrations and ocean nutrients. On geological time scales, the source of

102 bio-available phosphorus to the oceans is the weathering of continental rocks, with the

103 products delivered via rivers. This weathering is strongly accelerated by the terrestrial

104 biota, with land plants, animals, fungi and the soil microflora all playing important

105 roles [19]. Trees and forests are particularly important, since vascular plants with

106 extensive root systems promote weathering of rock, soil formation and bio-

107 availability of phosphorus, though even the earliest land plants are thought to have

108 accelerated P weathering [20-23]. Maintaining relatively stable concentrations over

109 million-year timescales requires the source of phosphorus from continental

110 weathering to balance the sink flux out of the oceans, which is burial in marine

111 sediments. Phosphorus is transported to the sediments alongside organic carbon [24],

112 and this burial of organic carbon is the ultimate source of free oxygen in the

113 atmosphere [2, 25]. The rise of land plants therefore forced up atmospheric oxygen by

114 accelerating carbon burial at the same time as it increased phosphorus weathering.

115 Land plants are however, limited by atmospheric O_2 concentrations: in particular, if

116 O_2 rises too high, there is an increased prevalence of wildfire, which then reduces tree

117 and forest cover, and therefore the extent to which land plants accelerate P

118 weathering. Models of this network of feedbacks [2] suggest that, at steady state,

119 oxygen concentrations are controlled in a "fire window" similar to present levels,

120 while marine phosphate concentrations adjust so that the oceans are not far from

121 Redfield stoichiometric ratio with respect to oxygen.

122

123 Though the original Redfield calculation overstates the closeness of the balance

124 between biological oxygen demand and O_2 supply, the size and intensity of the major

125 de-oxygenated zones are still sensitive to quite small changes in ocean physics or

126   geochemistry. Thus many models suggest that if the concentration of phosphate in the

127   deep sea were to increase significantly, (or equivalently, if changes in ocean

128   circulation were to increase the efficiency of the existing biological utilization of

129   PO_4), a substantially greater volume of ocean water would be depleted in oxygen [6-9,

130   26]. This sensitivity of the low oxygen regions to relatively small changes in

131   circulation or oxygen supply, may in part help to explain observed changes occurring

132   today in the OMZs, under the influence of ongoing climate change [27]. It may also

133   help to explain the frequent occurrence in the geological record of major "oceanic

134   anoxic events" (OAEs) [4], to which we now turn.

135

136   Ocean Anoxic Events

137   While the deep sea today is well-oxygenated, there is evidence for numerous OAEs in

138   the past [4], especially in the Mesozoic Era. OAEs, first recognized in the 1970s [28],

139   are identified by discrete layers of black shales having high organic carbon content,

140   with co-eval deposits often widely separated in space, indicating global as well as

141   local causes. They are often accompanied by excursions in $\delta^{13}C$ (both positive and

142   negative in sign) that indicate major upheaval in the global carbon cycle, with the

143   ocean anoxia implied being over substantial basins, but not global in extent [4]. Some,

144   but by no means all, of these events accompany well-known environmental crisis

145   points and mass extinctions, for example the Permian-Triassic boundary [29]. OAEs

146   typically last for periods $\sim 10^5 - 10^6$ years.

147

148   OAEs seem to occur exclusively during past warm "Greenhouse" periods of Earth's

149   climate, and the expansion of anoxia has been considered one of the defining features

150   of extreme "Hothouse" episodes occurring within these warm greenhouse periods [30,

151   31]. Several factors induced by warm climates might contribute to the spread of

152   anoxia. Oxygen solubility decreases with increasing temperature[32], being about

153   30% less at 20°C than at 2°C for example, so that less O_2 will be dissolved in warmer

154   ocean water[33]. Furthermore, warm climates, at least those induced by increased

155   CO_2 concentrations in the atmosphere such as during the Cretaceous, have smaller

156   equator-to-pole differences in temperature, with the Jurassic and Cretaceous Earth in

157   particular being free of ice caps. To the extent that density differences between

158   warmer and colder waters enhance the meridional overturning circulation, we might

159   expect that such climates would have less vigorous deep water formation, and oceans

160   therefore less well-ventilated, than cold periods [33]. (However, meridional density

161   differences are only one determinant of the overturning circulation [34].)

162

163   A more compelling reason why OAEs may be associated with warm periods, and

164   especially hothouse episodes within them, is that a global warming event, especially if

165   abruptly triggered, is expected to increase the rate of weathering of continental rocks

166   – both through increased humidity and runoff, and the direct effect of temperature on

167   reaction kinetics. Increasing the supply of nutrients to the ocean thereby increases

168   global marine productivity and oxygen demand in subsurface water. An increase in

169   nutrient supply leading to eutrophication of the oceans is indicated by model studies

170   to be the most likely cause for past OAEs [6, 8, 26, 35] and is also indicated by

171   interpretation of geological evidence [11, 36]. It is more powerful in promoting low

172   oxygen than the direct effects of temperature on solubility or circulation, since the

173   effect of increased temperatures on solubility of oxygen is relatively modest, while

174   one effect of reduction in ventilation is to decrease productivity since it implies a

175   reduction in overturning, and hence of the upwelling of nutrient-rich water to the

176   surface.

177

178   The massive volcanic and magmatic events that emplace Large Igneous Provinces

179   (LIPs) have now been implicated in the genesis of several OAEs [30, 31, 37, 38].

180   LIPs are expected to increase the supply of nutrients to the oceans, not only because

181   they might trigger a global warming episode as a result of CO_2 and other greenhouse

182   gases released to the atmosphere, but also because the large volumes of rapidly

183   weathering basalt rocks emplaced by the eruption would be an extra source of

184   phosphorus and potentially also trace element nutrients.

185

186   <u>Phosphorus cycling and ocean anoxia</u>

187   As discussed above, we have cause to believe that there is a negative feedback

188   involving atmospheric oxygen and the long-term source of phosphorus to the ocean,

189   which ties these variables together and regulates them over multi-million year time

190   scales. Figure 1 also highlights a positive feedback between ocean anoxia and oceanic

191   P concentrations, that may play a role in promoting OAEs on somewhat shorter

192   timescales. The sink for marine phosphorus is incorporation in marine sediments,

193   transported there mostly in organically-derived detritus, though much of it is

194   subsequently transformed to authigenic minerals [39, 40]. It is well established that

195   sediments in contact with oxygen-depleted water normally have lower concentrations

196   of reactive P relative to organic carbon, with much of the P being regenerated to the

197   water column under anoxic conditions [41-43]. The P thus released back into the

198   water can act to further boost marine productivity, leading to increased eutrophication

199   and more anoxia. This mechanism is well established to occur in the largest modern

200   coastal hypoxic zone, the Baltic Sea, where the variation in phosphate content of the

201   low oxygen water indicates that most of it is regenerated from low-oxygen sediments

202   rather than input from the land [44]. It is also believed to be significant in the second

203   largest such zone, in the Gulf of Mexico [45]. It would be expected that this

204   mechanism would also be important for the global ocean in generating and sustaining

205   past OAEs, and models suggest this is the case [6, 8, 26, 35].

206

207   The time scale for onset of eutrophication-driven global anoxia will be set by the

208   residence time of bio-available P in the global ocean. Even for the modern ocean there

209   is uncertainty about this number, mirroring the complexity of the phosphorus cycle,

210   but it probably lies in the range $15-35 \times 10^4$ years [24, 46]. Major changes in the total

211   ocean concentration of P are therefore unlikely to occur on time scales shorter than

212   thousands of years, so we may conclude that a global-scale nutrient-induced OAE is

213   not an immediate global change concern. It is nevertheless of interest to explore in a

214   semi-quantitative way the consequences for marine oxygen of our changing the

215   phosphorus cycle on these longer time scales. Specifically, we can ask (1) how fast

216   might oxygen concentrations decrease as a result of human –caused acceleration of

217   the P cycle, (2) what role might the positive feedback on P concentrations play and (3)

218   whether known phosphatic rock reserves sufficient that, if all were fully utilized,

219   major ocean de-oxygenation would occur? As an aid to this we introduce a simple

220   model which captures some aspects of the positive feedback on ocean anoxia in a

221   semi-quantitative manner. Our model is not spatially resolved, unlike those of

222   Palastanga et al. [7], or Niemeyer et al. [47] both of whom have recently published

223   studies using 3-D and intermediate complexity models of the ocean biogeochemistry,

224   focusing on the long-term implications of anthropogenic change on the P cycle.

225   However, P recycling is likely to be very non-linear, dependent in particular on the

226   degree to which low-oxygen waters encroach onto the continental shelves and slopes

227   where the organic and P-rich sediments are laid down. To be accurately represented,

228   this requires high spatial resolution, but to date the spatial resolution of the models

229   employed is quite coarse. Our model represents this non-linearity by an analytical

230   function (described below), which, while obviously an oversimplifcation, is at least

231   transparent in its operation and readily manipulated.

232

233   Model description:

234   The model we describe here is inspired by earlier published studies [26, 48, 49]. The

235   master variable is the ocean P reservoir, the rate of change of which is given by:

236

237    $dP/dt = F_{pw} - F_{sed}$

238

239   where F_{pw} is input of phosphorus from weathering and F_{sed} is the flux that is lost to

240   sediments. The sedimentation term is:

241

242    $F_{sed} = F_{OrgP} + F_{FeP} + F_{CaP}$

243

244   where the three terms are the forms of P removal to sediments that are commonly

245   modelled: F_{OrgP} is burial associated with organic matter, F_{FeP} is burial adsorbed to

246   iron oxides, and F_{CaP} is burial associated with authigenic carbonate minerals. For (pre-

247   industrial) present day fluxes (in GmolP yr^{-1}) we follow Slomp and Van Cappellen

248   [49] with $F_{pw} = 92$, $F_{OrgP} = 23$, $F_{FeP} = k_{FeP} = 23$, $F_{CaP} = k_{CaP} = 46$. For a present

249   reservoir of $P_0 = 3.1 \times 10^{15}$ mol this gives an oceanic residence time of P of ~34 kyr.

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250 We vary the input of phosphorus to the ocean with a weathering control parameter,

251 W:

252

253 $F_{pw} = 92*W$ Gmol P yr^{-1}

254

255 So that W = 1 corresponds to the Slomp and Van Cappellen steady state. The supply

256 of phosphorus and organic carbon to the sediments in sinking organic matter is

257 assumed proportional to the P reservoir size (i.e. $[PO_4]$), which governs export

258 production (assuming fixed circulation). This phosphorus input to sediments can then

259 be buried in its original form (Org-P), or subject to diagenesis, following which much

260 of it can be incorporated into the sediment as authigenic carbonate minerals (Ca-P)

261 and some by adsorption to iron oxides (Fe-P), or else it may be released back to the

262 water column.

263

264 Organic phosphorus burial is sensitive to the fraction of the seafloor overlain by

265 anoxic waters, f_{anoxic}, given very different $(C/P)_{organic}$ burial ratios under anoxic

266 (CP_{anoxic}) and oxic (CP_{oxic}) bottom waters:

267

268 $F_{OrgP} = k_{OrgC}*(P/P_0)*((f_{anoxic}/CP_{anoxic})+((1-f_{anoxic})/CP_{oxic}))$

269

270 Here we take CP_{anoxic}=4000 and CP_{oxic}=250 following earlier work [50]. Given a very

271 small f_{anoxic} at present (see below), the overall $(C/P)_{organic}$ burial ratio is ~250 and an

272 organic carbon burial flux of $k_{OrgC} = 5.75$ TmolC yr^{-1} corresponds to $F_{OrgP} = 23$

273 GmolP yr^{-1}.

274

275   Phosphorus is desorbed from the surface of iron oxides under anoxic bottom waters

276   hence iron-sorbed phosphorus burial scales with the oxic fraction of seafloor:

277

278   $F_{FeP} = k_{FeP}*(P/P_0)*(1-f_{anoxic})$

279

280   Calcium-bound phosphorus burial is assumed to simply scale with the P input to

281   sediments from sinking organic matter, although other work considers a redox

282   sensitivity of this flux (Slomp and Van Cappellen 2007):

283

284   $F_{CaP} = k_{CaP}*(P/P_0)$

285

286   The fraction of seafloor overlain by anoxic waters, f_{anoxic}, is assumed to follow a

287   logistic functional form dependent on the balance between normalised oxygen

288   demand $k_U*(P/P_0)$ and oxygen supply (O_2/O_{20}):

289

290   $f_{anoxic} = 1/(1+e^{-kanox*(ku*(P/P0)-(O2/O20))})$

291

292   Here k_U represents the (in)efficiency of nutrient utilisation in upwelling regions. We

293   choose $k_U = 0.5$ based on the estimates of pre-formed nutrient efficiency [4] and also

294   agreement across a range of models that a transition from an oxic to an anoxic deep

295   ocean occurs at O_2/O_{20} ~0.5 for present nutrient levels, or at P/P_0 ~2 for present O_2

296   levels (Lenton and Daines 2017,[51-53]. $k_{anox} = 12$ is chosen based on observations

297   that ~0.2-0.3% of the seafloor is overlain by anoxic bottom waters at present [54]),

298   and agreement among models that the transition from oxic to anoxic conditions is

299   abrupt, occurring typically as O_2/O_{20} drops from ~0.6 to ~0.4 (Lenton and Daines

300   2017,[52, 53]). Here we treat atmospheric O_2 as a constant i.e. $O_2/O_{20} = 1$, because it

301   varies on a much longer timescale than ocean P and we wish to focus on the

302   conditions required to trigger ocean anoxia.

303

304   Such a simple model of the anoxic fraction fails to capture the effects of ocean

305   hypsometry and in particular the disproportionate contribution of shallow shelf seas to

306   phosphorus removal and recycling. When anoxia impinges on the bottom of the shelf

307   seas we may expect a stronger positive feedback from benthic phosphorus recycling,

308   as seen in the results of Ozaki and co-workers. Such a non-linearity is hard to capture

309   in coarse resolution global ocean models, including GENIE and HAMOCC, because

310   they barely resolve shelf seas and their particular dynamics.

311

312   Results

313   The simple model outlined above encapsulates a strong sensitivity of ocean anoxia

314   (f_{anoxic}) to phosphorus input to the ocean, controlled by the weathering parameter W

315   where W=1 represents the pre-industrial input. Figure 2 shows the behaviour of the

316   steady state solutions as a function of P input. As P input and oxygen consumption

317   increases, expanding anoxia increases P regeneration from sediments until a tipping

318   point is reached, beyond which the ocean abruptly shifts to a largely anoxic state.

319   Decreasing the P input, the steady states eventually shift back to a largely oxic state,

320   but this occurs at a different and lower P input. These dynamics result in a region of

321   bi-stability, where either steady state is possible for a given value of W. For our

322   choice of parameters this bi-stable region is between about W= 1.75 and W=1.95. In

323   this region therefore, a full OAE, once established, is sustained by the additional

324   positive feedback effect on the P cycle. According to the model, the present-day

325   increase of order 2 times in the P input to the ocean due to anthropogenic factors[55],

326   would eventually cause such a shift if it were to be kept up for long enough.

327

328   In terms of the P content of the ocean, as W is increased and the tipping point is

329   reached, ocean P is roughly doubled. Either side of the region of bi-stability ocean P

330   responds approximately linearly to P input (W), but the constant of proportionality

331   increases from the oxic to the anoxic ocean solution because the $(C/P)_{organic}$ burial

332   ratio switches from 250 to 4000 and the Fe-P burial flux is removed.

333

334   Figure 3 shows transient runs starting from the preindustrial steady state, with

335   constant increased inputs of P: for W=2.5 the transition to a fully anoxic ocean is

336   established in a period of about 10^5 years. For a value of W=2, close to the tipping

337   point, the transition occurs only after a long –quasi-static intermediate period, while

338   for lower values it does not occur.

339

340   We can use the model to give semi-quantitative answers to questions about

341   anthropogenic influence on global ocean deoxygenation via the phosphorus cycle:

342   1) *Could the mining of phosphate ore materially influence global ocean anoxia?*

343   The USGS estimates worldwide known reserves of phosphate rock, which

344   generally has a P content of order 20%, as 69 Pg [56], suggesting a content of

345   about 4.5×10^{14} mol P. This is about 15% of the present ocean inventory.

346   Were we to mine all this phosphorus and in due course it were to be washed to

347   the ocean, this is certainly enough to increase the prevalence of anoxia

348   worldwide, (there is however controversy over the USGS estimate of P

349   reserves, with some arguing that it overstates the amount of known and proven

350   ores [57]).

351   However, worldwide *resources* (a broader classification than reserves,

352   covering known phosphorus-containing deposits that might be exploited in the

353   future) are estimated by the USGS at > 300 Pg rock, or perhaps 2×10^{15} mol

354   P. If humanity were desperate enough for phosphorus in the future, additional

355   resources may be discovered, while poorer quality source rock with lesser P

356   content might eventually be exploited. Such a quantity of P would, if it were

357   all to end in the ocean in a bioavailable form, have a very substantial effect on

358   global ocean anoxia – in our model, releasing 2×10^{15} mol P over 1000 years

359   causes the fraction of ocean sediment overlain by anoxic waters (f_{anoxic}), to

360   increase more than 10- fold, from 0.25% to peak at 2.7% (Figure 4 a, b, "1 x

361   mining resource" curve). Releasing twice this quantity causes the anoxic

362   fraction to increase to ~20%. These scenarios represent upper bounda on the

363   potential future delivery of phosphorus to the ocean. Projections by Filippelli

364   [58] suggest total inputs may eventually be an order of magnitude lower than

365   the mining input: Phosphorus undergoes complex processes in the

366   environment, and fertilizer phosphate may be retained for substantial periods

367   in soils, river and lake sediments. Our upper bound assumes that this

368   accumulated phosphorus will eventually be released to the ocean, such that a

369   steady state is reached wherein terrestrial inputs and outputs balance [59].A

370   more conservative scenario is also shown in figure 4 (dashed lines) in which

371   terrestrial P accumulation continues indefinitely and only 10% of the mining

372   resource enters the ocean, in which case the effect on anoxia is quite minor.,

373   2) *Is it feasible that humans might bring about a full scale ocean anoxic event?*

374   From the above discussion, we can conclude that mining of currently known

375   phosphate rock could have a huge impact on ocean anoxia, but would fall

376   short of bringing on a full-scale OAE. However, just as past OAEs are thought

377   to have been caused by increased weathering rates due to global warming

378   events, human-caused warming might have a large additional impact on the

379   oceans by increasing rates of nutrients released by rock and soil weathering.

380   Anthropogenic warming from the spike of fossil fuel-released CO_2 which we

381   are currently creating, will likely be appreciable for at least 10,000 years and

382   perhaps up to 50,000 years into the future, as a result of the slow timescales on

383   which CO_2 is ultimately removed from the ocean-atmosphere system [60].

384   These periods are sufficiently long that comparatively modest increases in

385   phosphate rock weathering due to the warming would have a substantial effect

386   on the ocean inventory.

387   Figure 4 c,d, show model results for an increase in P from weathering of soils and

388   rocks due to global warming by a factor of 2 lasting 50,000 years, and this

389   weathering source combined with the two mining scenarios. All these possible

390   futures predict orders of magnitude enhancement of the fraction of the global

391   ocean affected by anoxia. The most severe scenario tips the ocean into a full scale

392   OAE within 2000 years, from which it does not recover for nearly 100,000 years.

393   Our results appear broadly consistent with those of Palastanga et al [7] and other

394   models e.g. [6]. Palastanga et al, [7] do not show any model runs where whole-

395   ocean anoxia occurs, but they do not consider the large factor of increase in P

396   fluxes that our "mining" scenarios imply. Such a large increase might cause

397   anoxic waters to impinge on the sediments of shelf seas where most sedimentary P

398   is contained, and could conceivably therefore trigger a non-linear switch to global

399   ocean anoxia as seen in our model and others [6].

400

401   <u>Conclusion</u>

402   It is generally believed that, to the extent to which deoxygenation observed to be

403   occurring in the modern ocean is linked with anthropogenic global change, it is

404   probably due to the direct effects of warming in slowing the ventilation of deep waters

405   and decreasing the solubility of O_2 in surface waters. The long-term effect of these

406   mechanisms has been modelled by Shaffer et al. [61] and found to be considerable.

407   However, for the case of the major ocean anoxic events in the past, which are often

408   associated with warming episodes, the most powerful causal mechanism does not

409   seem to have been these effects, but has been due to the global input of nutrient into

410   the oceans [6, 7, 47]. Our very simple model suggests that under unrestricted

411   mobilization of P, this could be important in the future as a result of human activity.

412   Both the deliberate mobilization of phosphorus for agriculture, and the incidental

413   effects of global warming and anthropogenic increases in erosion rates in accelerating

414   the natural weathering of phosphorus, could be important. Conceivably, if our

415   descendants are heedless of the consequences and generate major increases in the flux

416   of phosphorus to the oceans lasting for hundreds or thousands of years, large-scale

417   and long lasting global anoxia might result.

418

419   We might assume that the scenarios modelled here are more extreme than will ever be

420   realized, even if our industrial civilization lasts thousands of years, because our

421   increasing understanding of the Earth System will enable us to foresee the

422   consequences: such sustained mobilization of P would be seen to be irresponsible and

423 dangerous to the health of the whole Earth system, and action would be taken to

424 ensure it did not occur. Let us hope we, and our descendants, are wise enough to take

425 that course.

426 Data accessibility:

427 The code of the model described in the text and used to generate figures 2, 3, and 4 is

428 written in MATLAB, and be obtained from the authors.

429 Competing interests

430 The authors have no competing interests.

431 Authors Contributions

432 This paper was the result of intellectual contributions by all the authors. AJW wrote

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440 [1] Arvidson, R. S., Mackenzie, F. T. & Guidry, M. 2006 MAGic: A Phanerozoic

441 model for the geochemical cycling of major rock-forming components. Am J Sci 306,

442 135-190. (DOI:DOI 10.2475/ajs.306.3.135).

443 [2] Bergman, N. M., Lenton, T. M. & Watson, A. J. 2004 COPSE: A new model of

444 biogeochemical cycling over Phanerozoic time. Am J Sci 304, 397-437. (DOI:DOI

445 10.2475/ajs.304.5.397).

446   [3] Hansen, K. W. & Wallman, K. 2003 Cretaceous and Cenozoic evolution of

447   seawater composition, atmospheric O2 and CO2: a model perspective. Am J Sci 303,

448   94-108. (DOI:10 .2475 /ajs .303 .2 .94.).

449   [4] Jenkyns, H. C. 2010 Geochemistry of oceanic anoxic events. Geochemistry,

450   Geophysics, Geosystems 11. (DOI:10.1029/2009gc002788).

451   [5] Sarmiento, J. L. & Gruber, N. 2006 Ocean Biogeochemical Cycles. Princeton, NJ,

452   Princeton University Press.

453   [6] Ozaki, K., Tajima, S. & Tajika, E. 2011 Conditions required for oceanic

454   anoxia/euxinia: Constraints from a one-dimensional ocean biogeochemical cycle

455   model. Earth and Planetary Science Letters 304, 270-279.

456   (DOI:10.1016/j.epsl.2011.02.011).

457   [7] Palastanga, V., Slomp, C. P. & Heinze, C. 2011 Long-term controls on ocean

458   phosphorus and oxygen in a global biogeochemical model. Global Biogeochem Cy

459   25. (DOI:Artn Gb3024

460   10.1029/2010gb003827).

461   [8] Tsandev, I. & Slomp, C. P. 2009 Modeling phosphorus cycling and carbon burial

462   during Cretaceous Oceanic Anoxic Events. Earth and Planetary Science Letters 286,

463   71-79. (DOI:10.1016/j.epsl.2009.06.016).

464   [9] Van Cappellen, P. & Ingall, E. D. 1996 Redox stabilization of the atmosphere and

465   oceans by phosphorus-limited marine productivity. Science 271, 493-496.

466   [10] Law, C. S. & Owens, N. J. P. 1990 Significant flux of atmospheric nitrous oxide

467   from the northwest Indian Ocean. Nature 346, 826-828.

468   [11] Meyer, K. M. & Kump, L. R. 2008 Oceanic euxinia in Earth history: Causes and

469   consequences. Annu Rev Earth Pl Sc 36, 251-288.

470   (DOI:10.1146/annurev.earth.36.031207.124256).

471   [12] Redfield, A. C. 1958 The biological control of chemical factors in the

472   environment. Am. Sci. 46, 205-222.

473   [13] Holland, H. D. 1978 The chemistry of the atmosphere and oceans, John Wiley

474   and sons; 369 p.

475   [14] Anderson, L. A. & Sarmiento, J. L. 1995 Global ocean phosphate and oxygen

476   simulations. Global Biogeochem Cy 9, 621-636. (DOI:10.1029/95gb01902).

477   [15] Anderson, L. A. 1995 On the hydrogen and oxygen content of marine

478   phytoplankton. Deep-Sea Research Part I 42, 1675-1680. (DOI:10.1016/0967-

479   0637(95)00072-e).

480   [16] Ito, T. & Follows, M. J. 2005 Preformed phosphate, soft tissue pump and

481   atmospheric CO2. Journal of Marine Research 63, 813-839.

482   (DOI:10.1357/0022240054663231).

483   [17] Watson, A. J. 2016 Oceans on the edge of anoxia: Environmental crises can tip

484   the ocean into O2 depletion. Science 354, 1529-1530. (DOI:10.1126/science.aaj2321).

485   [18] Mills, B. J. W., Belcher, C. M., Lenton, T. M. & Newton, R. J. 2016 A modeling

486   case for high atmospheric oxygen concentrations during the Mesozoic and Cenozoic.

487   Geology. (DOI:10.1130/G38231.1).

488   [19] Lovelock, J. E. & Watson, A. J. 1982 The regulation of carbon dioxide and

489   climate: Gaia or geochemistry. Planetary and Space Science 30, 795-802.

490   (DOI:10.1016/0032-0633(82)90112-x).

491   [20] Berner, R. A. 2001 Modeling atmospheric O2 over Phanerozoic time. Geochim

492   Cosmochim Ac 65, 685-694. (DOI:10.1016/s0016-7037(00)00572-x).

493   [21] Lenton, T. M., Dahl, T. W., Daines, S. J., Mills, B. J. W., Ozaki, K., Saltzman,

494   M. R. & Porada, P. 2016 Earliest land plants created modern levels of atmospheric

495   oxygen. P Natl Acad Sci USA 113, 9704-9709. (DOI:10.1073/pnas.1604787113).

Page 21 of 33

Submitted to Phil. Trans. R. Soc. A - Issue

496 [22] Lenton, T. M. & Watson, A. J. 2004 Biotic enhancement of weathering,

497 atmospheric oxygen and carbon dioxide in the Neoproterozoic. Geophys Res Lett 31.

498 (DOI:Artn L05202

499 10.1029/2003gl018802).

500 [23] Lenton, T. M., Crouch, M., Johnson, M., Pires, N. & Dolan, L. 2012 First plants

501 cooled the Ordovician. Nature Geosci 5, 86-89.

502 [24] Ruttenberg, K. C. 2003 The Global Phosphorus Cycle. Treatise on Geochemistry

503 8, 585-643.

504 [25] Berner, R. A. & Canfield, D. E. 1989 A new model for atmospheric oxygen over

505 Phanerozoic time. Am J Sci 289, 333-361.

506 [26] Handoh, I. C. & Lenton, T. M. 2003 Periodic mid-Cretaceous oceanic anoxic

507 events linked by oscillations of the phosphorus and oxygen biogeochemical cycles.

508 Global Biogeochem Cy 17. (DOI:Artn 1092

509 10.1029/2003gb002039).

510 [27] Stramma, L., Johnson, G. C., Sprintall, J. & Mohrholz, V. 2008 Expanding

511 oxygen-minimum zones in the tropical oceans. Science 320, 655-658.

512 (DOI:10.1126/science.1153847).

513 [28] Schlanger, S. O. & Jenkyns, H. C. 1976 CRETACEOUS OCEANIC ANOXIC

514 EVENTS: CAUSES AND CONSEQUENCES. Geologie en Mijnbouw 55, 179-184.

515 [29] Wignall, P. B. & Twitchett, R. J. 1996 Oceanic anoxia and the end permian mass

516 extinction. Science 272, 1155-1158.

517 [30] Kidder, D. L. & Worsley, T. R. 2010 Phanerozoic Large Igneous Provinces

518 (LIPs), HEATT (Haline Euxinic Acidic Thermal Transgression) episodes, and mass

519 extinctions. Palaeogeography, Palaeoclimatology, Palaeoecology 295, 162-191.

520   [31] Kidder, D. L. & Worsley, T. R. 2012 A human-induced hothouse climate? GSA

521   Today 22, 4-11. (DOI:10.1130/G131A.1).

522   [32] Weiss, R. F. 1970 The solubility of nitrogen, oxygen and argon in water and

523   seawater. Deep-Sea Research and Oceanographic Abstracts 17, 721-735.

524   (DOI:10.1016/0011-7471(70)90037-9).

525   [33] Hotinski, R. M., Bice, K. L., Kump, L. R., Najjar, R. G. & Arthur, M. A. 2001

526   Ocean stagnation and end-Permian anoxia. Geology 29, 7-10.

527   [34] Munk, W. & Wunsch, C. 1998 Abyssal recipes II: Energetics of tidal and wind

528   mixing. Deep-Sea Research Part I: Oceanographic Research Papers 45, 1977-2010.

529   (DOI:10.1016/s0967-0637(98)00070-3).

530   [35] Ruvalcaba Baroni, I., Topper, R. P. M., M. Van Helmond, N. A. G., Brinkhuis,

531   H. & Slomp, C. P. 2014 Biogeochemistry of the North Atlantic during oceanic anoxic

532   event 2: Role of changes in ocean circulation and phosphorus input. Biogeosciences

533   11, 977-993. (DOI:10.5194/bg-11-977-2014).

534   [36] Kuypers, M. M. M., Pancost, R. D., Nijenhuis, I. A. & Sinninghe Damsté, J. S.

535   2002 Enhanced productivity led to increased organic carbon burial in the euxinic

536   North Atlantic basin during the late Cenomanian oceanic anoxic event.

537   Paleoceanography 17, 3-1.

538   [37] Sell, B., Ovtcharova, M., Guex, J., Bartolini, A., Jourdan, F., Spangenberg, J. E.,

539   Vicente, J. C. & Schaltegger, U. 2014 Evaluating the temporal link between the Karoo

540   LIP and climatic-biologic events of the Toarcian Stage with high-precision U-Pb

541   geochronology. Earth and Planetary Science Letters 408, 48-56.

542   (DOI:10.1016/j.epsl.2014.10.008).

543   [38] Turgeon, S. C. & Creaser, R. A. 2008 Cretaceous oceanic anoxic event 2

544   triggered by a massive magmatic episode. Nature 454, 323-326.

545   (DOI:10.1038/nature07076).

546   [39] Ruttenberg, K. C. & Berner, R. A. 1993 Authigenic apatite formation and burial

547   in sediments from non-upwelling, continental margin environments. Geochim

548   Cosmochim Ac 57, 991-1007. (DOI:10.1016/0016-7037(93)90035-u).

549   [40] Anderson, L. D., Delaney, M. L. & Faul, K. L. 2001 Carbon to phosphorus ratios

550   in sediments: Implications for nutrient cycling. Global Biogeochem Cy 15, 65-79.

551   (DOI:10.1029/2000gb001270).

552   [41] Ingall, E. & Jahnke, R. 1994 Evidence for enhanced phosphorus regeneration

553   from marine sediments overlain by oxygen depleted waters. Geochim Cosmochim Ac

554   58, 2571-2575. (DOI:10.1016/0016-7037(94)90033-7).

555   [42] Ingall, E. & Jahnke, R. 1997 Influence of water-column anoxia on the elemental

556   fractionation of carbon and phosphorus during sediment diagenesis. Marine Geology

557   139, 219-229. (DOI:10.1016/s0025-3227(96)00112-0).

558   [43] Ingall, E. D., Bustin, R. M. & Van Cappellen, P. 1993 Influence of water column

559   anoxia on the burial and preservation of carbon and phosphorus in marine shales.

560   Geochim Cosmochim Ac 57, 303-316. (DOI:10.1016/0016-7037(93)90433-w).

561   [44] Conley, D. J., Humborg, C., Rahm, L., Savchuk, O. P. & Wulff, F. 2002 Hypoxia

562   in the baltic sea and basin-scale changes in phosphorus biogeochemistry.

563   Environmental Science and Technology 36, 5315-5320. (DOI:10.1021/es025763w).

564   [45] Adhikari, P. L., White, J. R., Maiti, K. & Nguyen, N. 2015 Phosphorus

565   speciation and sedimentary phosphorus release from the Gulf of Mexico sediments:

566   Implication for hypoxia. Estuarine, Coastal and Shelf Science 164, 77-85.

567   (DOI:10.1016/j.ecss.2015.07.016).

568   [46] Filippelli, G. M. 2002 The global phosphorus cycle. In Reviews in Mineralogy

569   and Geochemistry (

570   [47] Niemeyer, D., Kemena, T. P., Meissner, K. J. & Oschlies, A. 2017 A model

571   study of warming-induced phosphorus-oxygen feedbacks in open-ocean oxygen

572   minimum zones on millennial timescales. Earth System Dynamics 8, 357-367.

573   (DOI:10.5194/esd-8-357-2017).

574   [48] Lenton, T. M. & Watson, A. J. 2000 Redfield revisited 2. What regulates the

575   oxygen content of the atmosphere? Global Biogeochem Cy 14, 249-268. (DOI:Doi

576   10.1029/1999gb900076).

577   [49] Slomp, C. P. & Van Cappellen, P. 2007 The global marine phosphorus cycle:

578   Sensitivity to oceanic circulation. Biogeosciences 4, 155-171.

579   [50] Van Cappellen, P. & Ingall, E. D. 1994 Benthic phosphorus regeneration, net

580   primary production, and ocean anoxia: A model of the coupled marine

581   biogeochemical cycles of carbon and phosphorus. Paleoceanography 9, 677-692.

582   (DOI:10.1029/94pa01455).

583   [51] Canfield, D. E. 1998 A new model for Proterozoic ocean chemistry. Nature 396,

584   450-453. (DOI:10.1038/24839).

585   [52] Monteiro, F. M., Pancost, R. D., Ridgwell, A. & Donnadieu, Y. 2012 Nutrients

586   as the dominant control on the spread of anoxia and euxinia across the Cenomanian-

587   Turonian oceanic anoxic event (OAE2): Model-data comparison. Paleoceanography

588   27. (DOI:10.1029/2012pa002351).

589   [53] Ozaki, K. & Tajika, E. 2013 Biogeochemical effects of atmospheric oxygen

590   concentration, phosphorus weathering, and sea-level stand on oceanic redox

591   chemistry: Implications for greenhouse climates. Earth and Planetary Science Letters

592   373, 129-139. (DOI:10.1016/j.epsl.2013.04.029).

593   [54] Helly, J. J. & Levin, L. A. 2004 Global distribution of naturally occurring marine

594   hypoxia on continental margins. Deep-Sea Research Part I: Oceanographic Research

595   Papers 51, 1159-1168. (DOI:10.1016/j.dsr.2004.03.009).

596   [55] Mackenzie, F. T., Ver, L. M. & Lerman, A. 2002 Century-scale nitrogen and

597   phosphorus controls of the carbon cycle. Chemical Geology 190, 13-32.

598   (DOI:10.1016/s0009-2541(02)00108-0).

599   [56] Survey, U. S. G. 2016 U.S. Geological Survey mineral Commodity Summaries.

600   (pp. 124-125.

601   [57] Edixhoven, J. D., Gupta, J. & Savenije, H. H. G. 2014 Recent revisions of

602   phosphate rock reserves and resources: A critique. Earth System Dynamics 5, 491-

603   507. (DOI:10.5194/esd-5-491-2014).

604   [58] Filippelli, G. M. 2008 The global phosphorus cycle: Past, present, and future.

605   Elements 4, 89-95. (DOI:10.2113/gselements.4.2.89).

606   [59] Powers, S. M., Bruulsema, T. W., Burt, T. P., Chan, N. I., Elser, J. J., Haygarth,

607   P. M., Howden, N. J. K., Jarvie, H. P., Lyu, Y., Peterson, H. M., et al. 2016 Long-

608   term accumulation and transport of anthropogenic phosphorus in three river basins.

609   Nat Geosci 9, 353-356. (DOI:10.1038/ngeo2693).

610   [60] Archer, D., Eby, M., Brovkin, V., Ridgwell, A., Cao, L., Mikolajewicz, U.,

611   Caldeira, K., Matsumoto, K., Munhoven, G., Montenegro, A., et al. 2009

612   Atmospheric lifetime of fossil fuel carbon dioxide. In Annu Rev Earth Pl Sc (pp. 117-

613   134.

614   [61] Shaffer, G., Olsen, S. M. & Pedersen, J. O. P. 2009 Long-term ocean oxygen

615   depletion in response to carbon dioxide emissions from fossil fuels. Nat Geosci 2,

616   105-109. (DOI:10.1038/ngeo420).

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618

619   Table I: representative calculation of the approximate oxygen demand per litre of

620   upwelled water, and oxygen supply per litre of subducted water. Concentratiosn are in

621   μmol kg^{-1}.

PO$_4$ concentration in deep water	carbon fixed (= 106 x PO$_4$)	O$_2$ demand (150 x PO$_4$[15])	Saturated [O$_2$] in equilibrium with atmosphere at 5°C and S=35
2.2	106 x 2.2 =233	2.2 * 150= **330**	**320**

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623 <u>Figure Legends</u>

624 Figure 1: Symbol and arrow representation of some Earth system interactions linking

625 atmospheric oxygen and ocean nutrients. Direct relations are shown by solid lines

626 with a plus sign, and inverse relations shown by dashed lines and a minus sign – so

627 for example an increase in C and P burial causes an increase in atmospheric O_2, but an

628 increase in atmospheric O_2 causes a decrease in land vegetation. Where arrows

629 describe a closed circuit, this indicates a feedback loop, which is negative, i.e.

630 stabilizing, where there is one dashed arrow in the loop, and positive if there are none.

631 Thick grey lines highlight two feedback loops. Upper loop: a negative feedback

632 stabilizes atmospheric O_2 and ocean P concentrations via the influence of the

633 atmosphere on land vegetation (principally by wildfire), land vegetation influence on

634 marine P via continental weathering, and marine P influence on atmospheric O2 by

635 stimulating marine production and carbon burial. Lower loop: positive feedback that

636 may be important in sustaining OAEs. ocean anoxia releases P from sediments thus

637 increasing P concentrations, enhancing marine production which further increases

638 anoxia.

639

640 Figure 2: Steady-state solutions for oceanic P inventory and "anoxic fraction"

641 (fraction of ocean sediment overlain by anoxic water), for the simple model described

642 in the text, as a function of the flux of P to the ocean. Arrows show the directions in

643 which two stable solutions are found.

644

645 Figure 3: Evolution of modelled oceanic P inventory and anoxic fraction with time,

646 for constant inputs of P to the oceans of 1.5, 2 and 2.5 x the pre-industrial steady

647 state.

648

649   Figure 4: Evolution of modelled P inventory (a, c) and anoxic fraction (b, d) for future

650   scenarios of enhanced P release into the oceans. The model runs are,

651   a,b: release at a uniform rate over 1 kyr of of multiples of the minimum phosphate-

652   bearing rock resource (the known amount that might be extracted in the future , ~2 x

653 10^{15} mol P) as estimated by USGS[56]. Blue: 1 x the resource, brown: 2x the

654   resource; solid lines show 100% delivered to the ocean, dashed lines show 10%
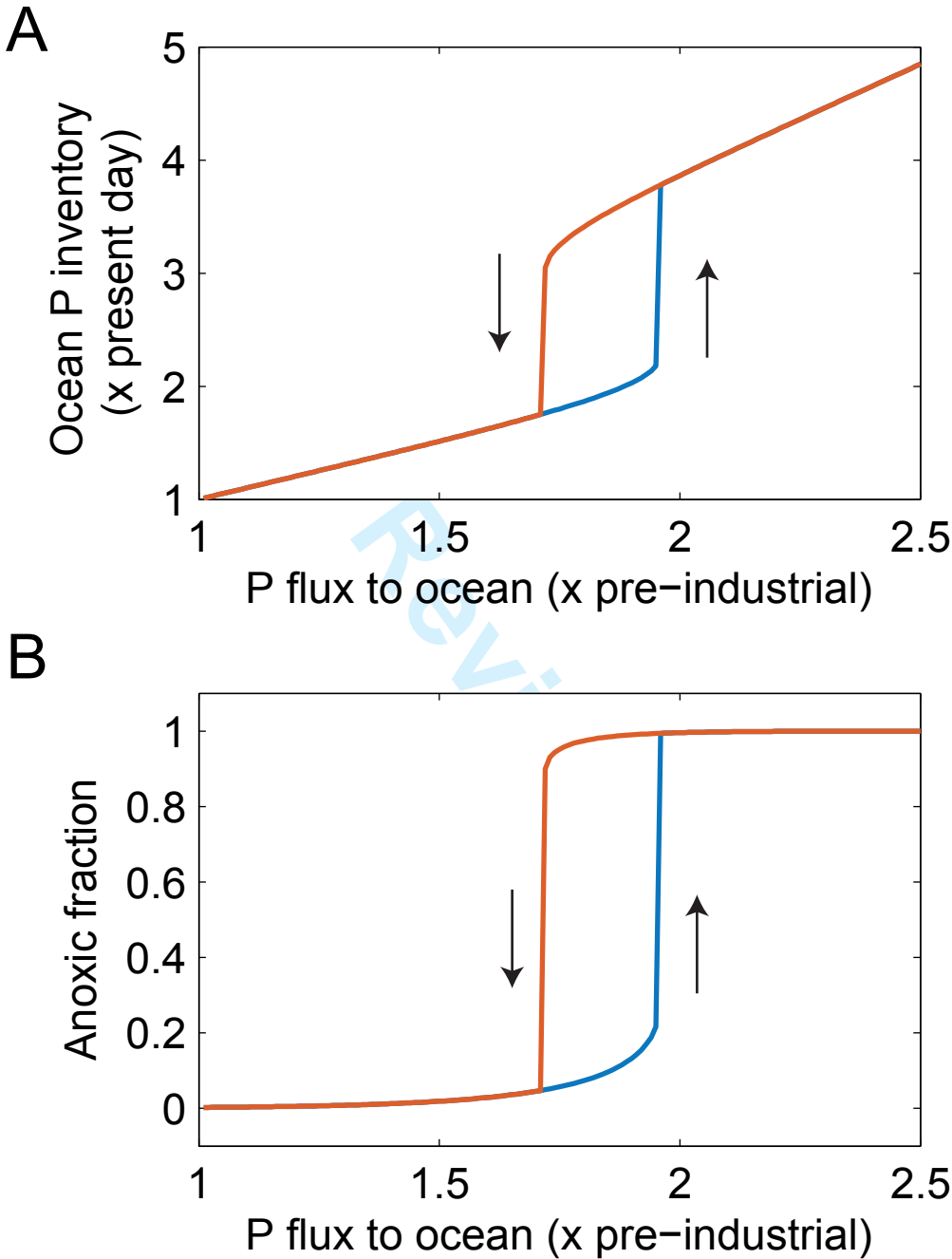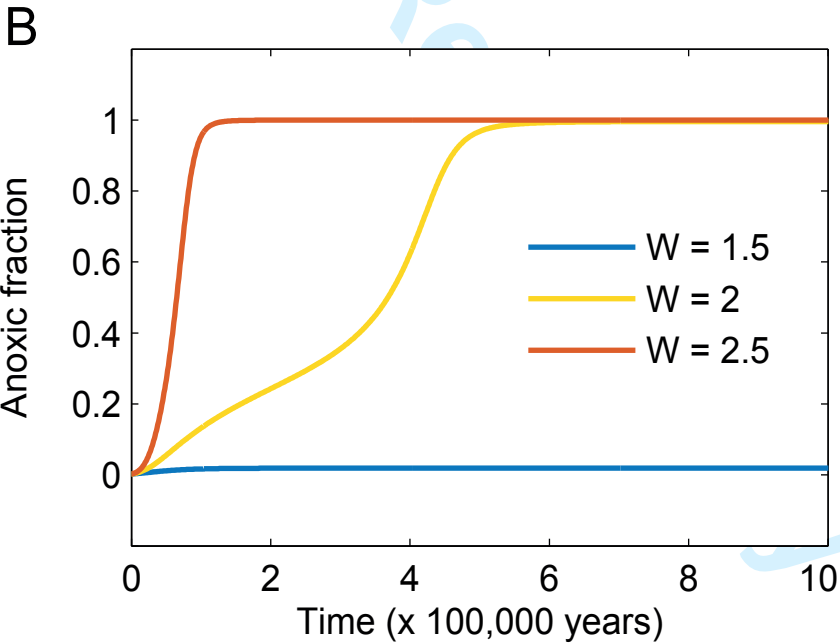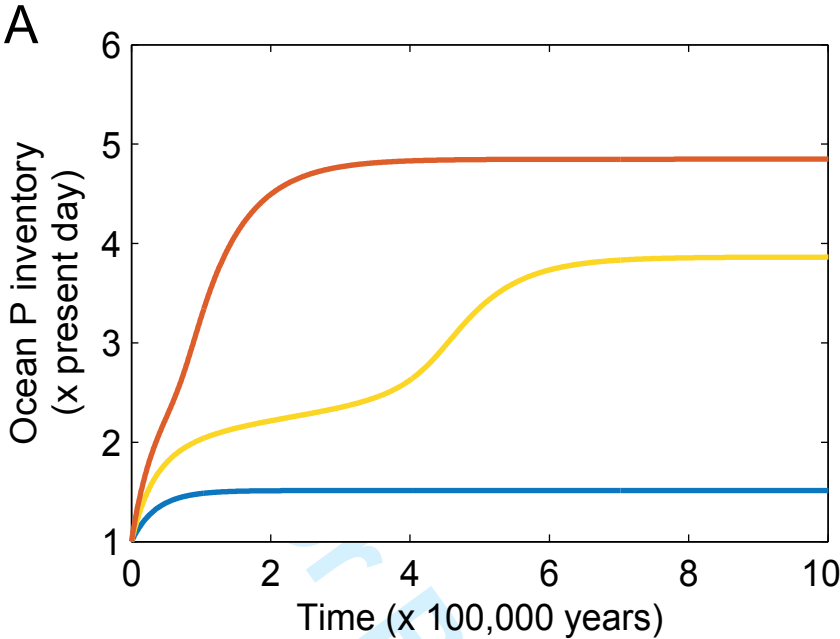
655   delivered to the ocean.

656   c, d; the four scenarios in a,b are combined with increased flux of P from 2 x

657   enhanced weathering of continental rocks extending over 5 x 10^4 years.

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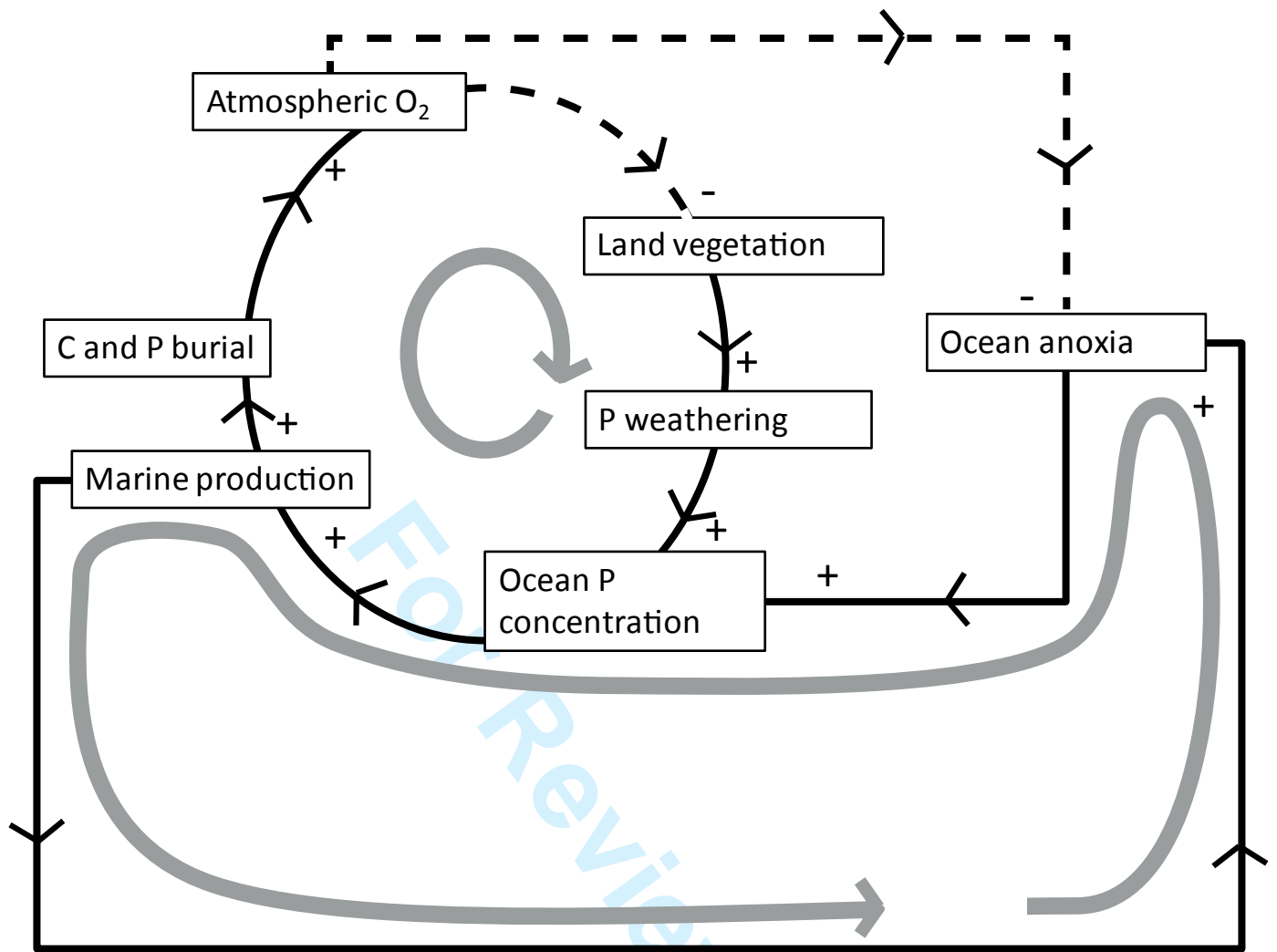
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