



**UNIVERSITY OF LEEDS**

This is a repository copy of *Phosphorus-limited conditions in the early Neoproterozoic ocean maintained low levels of atmospheric oxygen*.

White Rose Research Online URL for this paper:  
<http://eprints.whiterose.ac.uk/156389/>

Version: Accepted Version

---

**Article:**

Guilbaud, R, Poulton, SW [orcid.org/0000-0001-7621-189X](https://orcid.org/0000-0001-7621-189X), Thompson, J et al. (5 more authors) (2020) Phosphorus-limited conditions in the early Neoproterozoic ocean maintained low levels of atmospheric oxygen. *Nature Geoscience*. ISSN 1752-0894

<https://doi.org/10.1038/s41561-020-0548-7>

---

© The Author(s), under exclusive licence to Springer Nature Limited 2020. This is an author produced version of an article published in *Nature Geoscience*. Uploaded in accordance with the publisher's self-archiving policy.

**Reuse**

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.



[eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk)  
<https://eprints.whiterose.ac.uk/>

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24

**Phosphorus-limited conditions in the early Neoproterozoic ocean  
maintained low levels of atmospheric oxygen**

Romain Guilbaud<sup>1\*</sup>, Simon W. Poulton<sup>2</sup>, Jennifer Thompson<sup>2</sup>, Kathryn F. Husband<sup>2</sup>,  
Maoyan Zhu<sup>3,4</sup>, Ying Zhou<sup>5</sup>, Graham A. Shields<sup>5</sup>, Timothy M. Lenton<sup>6</sup>

<sup>1</sup>Géosciences Environnement Toulouse, CNRS, UMR5563, 31400 Toulouse, France

<sup>2</sup>School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

<sup>3</sup>State Key Laboratory of Palaeobiology and Stratigraphy & Center for Excellence in  
Life and Palaeoenvironment, Nanjing Institute of Geology and Palaeontology, Nanjing  
210008, China

<sup>4</sup>College of Earth Sciences, University of Chinese Academy of Sciences, Beijing,  
100049, China

<sup>5</sup>Department of Earth Sciences, University College London, London WC1E 6BT, UK

<sup>6</sup>Global Systems Institute, University of Exeter, Exeter EX4 4QE, UK

\*Corresponding author: [romain.guilbaud@get.omp.eu](mailto:romain.guilbaud@get.omp.eu)

25 **ABSTRACT: The redox chemistry of anoxic continental margin settings evolved**  
26 **from widespread sulphide-containing (euxinic) conditions to a global ferruginous**  
27 **(iron-containing) state in the early Neoproterozoic (1 to ~0.8 billion years ago, Ga).**  
28 **Ocean redox chemistry exerts a strong control on the biogeochemical cycling of**  
29 **phosphorus (P), a limiting nutrient, and hence on primary production, but the**  
30 **response of the P cycle to this major ocean redox transition has not been**  
31 **investigated. Here, we use a P speciation technique to investigate the phase**  
32 **partitioning of phosphorus in an open marine, early Neoproterozoic succession**  
33 **from the Huainan Basin, North China. We find that effective removal of**  
34 **bioavailable P in association with iron (Fe) minerals in a globally ferruginous**  
35 **ocean resulted in oligotrophic (nutrient limited) conditions, and hence a probable**  
36 **global decrease in primary production, organic carbon burial and, subsequently,**  
37 **oxygen production. Nevertheless, P availability and organic carbon burial were**  
38 **just sufficient to maintain an oxidising atmosphere. These data imply significant**  
39 **nutrient-driven variability in atmospheric oxygen levels through the Proterozoic,**  
40 **rather than the stable levels commonly invoked.**

41

42 Phosphorus is generally considered the ultimate limiting nutrient on geological  
43 timescales<sup>1</sup>, and is thus a key element in controlling primary productivity, organic C  
44 (C<sub>org</sub>) burial, and consequently oxygen production. Atmospheric oxygen models  
45 suggest that after the Great Oxidation Event (GOE), pO<sub>2</sub> remained well below the  
46 present atmospheric level (PAL), with estimates ranging from <0.001 to ~0.4 PAL [2–  
47 4]. Furthermore, it is generally inferred that atmospheric oxygen may have remained at  
48 relatively constant levels after ~2.0 Ga, until the later Neoproterozoic (~0.8 to 0.542  
49 Ga; refs 3,5,6). However, evidence for fluctuations in both the extent of ocean

50 oxygenation<sup>4,7</sup> and the global-scale nature of ocean redox conditions<sup>8,9</sup> in the interim,  
51 could suggest variations in atmospheric oxygen concentrations.

52 The role of P bioavailability in controlling atmospheric oxygen between the GOE  
53 and the later Neoproterozoic is poorly constrained. Attempts to reconstruct dissolved P  
54 concentrations in the Precambrian ocean have relied on P contents of black shales and  
55 iron-rich chemical deposits<sup>10-12</sup>. In the latter case, the assumption is that P contents in  
56 iron formations provide a first order estimation of dissolved P in the water column, with  
57 only minimal remobilisation during diagenesis<sup>10</sup>. However, conflicting experimental  
58 determinations of P co-precipitation and adsorption coefficients have led to widely  
59 divergent reconstructions of Precambrian P concentrations<sup>11,13,14</sup>.

60 In contrast to iron-rich chemical sediments, shales P content offers the significant  
61 advantage of a continuous record through the entire geologic timescale. This record has  
62 led to the suggestion that oceanic phosphate concentrations were extremely low until  
63 ~0.8 Ga<sup>12</sup>, which might support inferences of extremely low atmospheric pO<sub>2</sub> (<0.001  
64 PAL) until the Neoproterozoic rise in atmospheric oxygen<sup>2</sup>. However, bulk shale P  
65 contents are limited in that they do not specifically track bioavailable P. In addition,  
66 bulk shale P contents cannot provide detailed understanding of the extent of P recycling  
67 from the sediment back to the water column, which is highly dependent on the precise  
68 redox state of both the water column and sediment pore waters<sup>15</sup>.

69 The flux of P to marine sediment commonly occurs via the transport of detrital  
70 apatite, organic matter and Fe minerals through the water column. During deposition  
71 under oxic conditions, up to 90% of C<sub>org</sub> may be re-mineralised, releasing organic P  
72 back to the water column. However, under ferruginous conditions, bacterial P  
73 accumulation<sup>16</sup> and P uptake by iron minerals such as ferrihydrite<sup>17</sup> and green rust<sup>18,19</sup>  
74 in the water column may be particularly significant sinks for P. Upon settling, P may

75 be released to pore waters and the water column during anaerobic diagenesis, via partial  
76 decomposition of organic matter and the reduction of Fe (oxyhydr)oxides<sup>20–23</sup>. This  
77 process may be compensated by re-adsorption onto Fe minerals at the sediment-water  
78 interface<sup>24</sup>, enhancing sedimentary P fixation in association with crystalline Fe oxides<sup>25</sup>  
79 or Fe phosphates<sup>19,26–28</sup>. By contrast, phosphorus recycling back to the water column  
80 may be particularly intense under euxinic conditions<sup>23,29</sup>, due to the rapid reduction of  
81 P-bearing Fe (oxyhydr)oxides by hydrogen sulphide<sup>30,31</sup>, and the preferential release of  
82 P from decaying organic matter during sulphate reduction<sup>21,23,29</sup>. As a result, C:P ratios  
83 commonly surpass the canonical Redfield ratio of 106:1 by several orders of  
84 magnitude<sup>21</sup>. However, under all redox scenarios, some, or all, of the recycled  
85 phosphorus may be fixed in the sediment via the formation of authigenic phases during  
86 ‘sink-switching’, which involves the transfer of P from its carrier phase to a stable  
87 mineral form, such as authigenic apatite<sup>29,32</sup> or Fe phosphates (e.g., vivianite)<sup>19,26–28</sup>.

88 An understanding of P recycling thus requires detailed analysis of both the phase  
89 partitioning of P, and the redox context in which P was transported to, and preserved  
90 in, ancient sediments. From ~1.8 Ga, oceans were generally characterised by  
91 oxygenated surface waters overlying mid-depth euxinic waters in productive regions,  
92 with ferruginous deeper waters<sup>33–35</sup>. Mid-depth water column euxinia would be  
93 expected to promote extensive P recycling to the water column from slope and shelf  
94 sediments<sup>15</sup>, hence exerting a strong positive feedback on rates of primary production.  
95 Extensive euxinia in the mid-Proterozoic ocean contrasts sharply with the early  
96 Neoproterozoic (~1 to 0.8 Ga), where ferruginous conditions dominated the global  
97 ocean<sup>8</sup>. However, the response of the P cycle to this fundamental change in ocean redox  
98 chemistry has not been investigated.

99 Here, we quantify the speciation of P in ~1 to 0.9 Ga Neoproterozoic sediments  
100 from the Huainan basin (North China craton). We combine these data with C isotope  
101 systematics and existing Fe speciation data<sup>8</sup> to evaluate redox controls on P cycling and  
102 bioavailability. We subsequently incorporate constraints from Earth's surface redox  
103 balance and redox state to provide internally-consistent estimates of P, C<sub>org</sub> and O<sub>2</sub>  
104 cycling under the globally-expansive ferruginous oceanic conditions of the early  
105 Neoproterozoic.

106

### 107 **Geological setting**

108 We focused on the ~1.0 to 0.9 Ga Liulaobei and Jiuliqiao formations (Huainan and  
109 Feishui Groups, Fig. 1), which represent unambiguously open marine continental  
110 margin successions covering a wide range of palaeodepths<sup>8</sup>. The Huainan Basin has  
111 experienced only low grade regional metamorphism<sup>36</sup>, providing an ideal opportunity  
112 to explore the speciation of sedimentary P during the early Neoproterozoic. Full details  
113 of the geological setting are provided in Methods and Supplementary Information (SI).

114

### 115 **Phosphorus drawdown in a ferruginous ocean**

116 Iron speciation data for the succession shows strong evidence for persistent ferruginous  
117 water column conditions in the Huainan Basin<sup>8</sup>, in agreement with the global signal  
118 from continental margin settings at this time<sup>8,9</sup>. Fe-bound phosphorus (P<sub>Fe</sub>) constitutes  
119 the smallest P pool, representing on average ~5% of total P, despite the relatively high  
120 proportion of ferric oxides in our samples (Fig. S4). Organic P (P<sub>org</sub>) is the second  
121 smallest contributor to total P (~9% on average). Authigenic carbonate fluorapatite  
122 (CFA) associated-P (P<sub>auth</sub>), and detrital P (P<sub>det</sub>) are the two largest P pools, representing  
123 an average of ~29% and ~58% of total P, respectively.

124 Under ferruginous conditions, the increased transport of P in association with Fe  
125 minerals can result in significantly higher sedimentary P/Al ratios<sup>37</sup>. Yet, in the  
126 persistently ferruginous Huainan Basin, sediment phosphorus ( $P_{\text{Tot}}$ ) contents are low  
127 throughout the entire succession (Fig. 2). Normalised P/Al ratios are close to the  
128 average shale value of 0.009 (ref. 38), and show no evidence for P. These low P contents  
129 may reflect either a relatively low marine phosphate reservoir, which is faithfully  
130 recorded by the P preserved in the sediment, or a high degree of phosphorus recycling  
131 back to the water column during early diagenesis, which we explore further below.

132

### 133 **Phosphorus cycling in the sediment**

134 The extent to which P is released from organic matter and Fe (oxyhydr)oxides, and  
135 ultimately fixed in the sediment or recycled back to the water column, will likely  
136 depend on the  $C_{\text{org}}$  loading close to the sediment-water interface. This would affect rates  
137 of microbial organic matter degradation and the production of sulphide (and thus  
138 ultimately the release of  $P_{\text{org}}$  and  $P_{\text{Fe}}$ ), at a depth in the sediment column where the P  
139 released could readily diffuse to the overlying water column.

140 The Huainan Basin sediments are characterised by low  $C_{\text{org}}$  (Fig. 2) and low pyrite  
141 concentrations, coupled with significant preservation of Fe (oxyhydr)oxide minerals  
142 (Fig. S4). This suggests that microbial recycling of  $C_{\text{org}}$  during early diagenesis was  
143 likely limited, and pore water chemistry at the sediment-water interface would have  
144 been poised at Fe reduction, rather than sulphate reduction. A lack of sulphide  
145 production close to the sediment-water interface would ultimately result in enhanced  
146 sedimentary P fixation, initially in association with Fe minerals and organic matter,  
147 followed by ‘sink-switching’ to other mineral phases such as authigenic apatite<sup>32</sup> or  
148 vivianite<sup>37</sup> deeper in the sediment profile. The speciation of P in our samples is

149 consistent with these suggestions, whereby the relatively low  $P_{Fe}$  and  $P_{org}$  we observe  
150 relative to  $P_{auth}$  (Fig. 2) suggest significant ‘sink-switching’.

151 To further evaluate controls on P cycling, we consider variations in molar  $C_{org}:P_{org}$   
152 ratios. Today, there is considerable variation between lower  $C_{org}:P_{org}$  ratios in nutrient  
153 replete conditions and higher  $C_{org}:P_{org}$  ratios in the most oligotrophic subtropical gyres  
154 (up to ~600; ref. 39). Consequently, it has been suggested that extreme P limitation in  
155 the mid-Proterozoic may have resulted in molar  $C_{org}:P_{org}$  ratios of up to 400 (ref. 12).  
156 Additionally, during incomplete remineralisation of  $C_{org}$ , preferential regeneration of P  
157 commonly results in higher  $C_{org}/P_{org}$  values<sup>21,23,29</sup>. For example, in laminated sediments  
158 underlying anoxic waters, C/P ratios may approach 600 in modern settings<sup>21</sup>, and  
159 average at 3,900 in the geological record<sup>40</sup> (Table S2).

160 In our samples,  $C_{org}/P_{org}$  values are close to the Redfield ratio (Fig. 3A), reflecting  
161 little preferential loss of P from organic matter during deposition and early diagenesis.  
162 This is also supported by dominantly heavy carbonate-C isotope values (Fig. 2), as  
163 larger amounts of  $C_{org}$  mineralisation during diagenesis would potentially result in a  
164 wider range of (more) negative  $\delta^{13}C_{carb}$  (ref. 41).  $C_{org}/P_{reac}$  ratios (where  $P_{reac}$  represents  
165 potentially mobile P during deposition and early diagenesis; calculated as  $P_{org} + P_{auth} +$   
166  $P_{Fe}$ ) also provide useful insight into controls on P cycling<sup>32</sup>. First, however, we consider  
167 whether our  $P_{det}$  analyses may have been affected by a possible transfer of authigenic  
168 apatite (i.e.  $P_{auth}$ ) to the detrital apatite pool during burial diagenesis and  
169 metamorphism<sup>42</sup>, which would lower primary  $P_{reac}$  values. We find strong linear  
170 relationships between  $P_{det}$  and Al (as a proxy for the detrital input) throughout the  
171 succession (see SI), which suggests that the measured  $P_{det}$  dominantly reflects the actual  
172 detrital P input, rather than post-depositional recrystallization. In support of these  
173 observations, we note that modern continental margin sediments typically have  $P_{det}$



174 contents of  $186 \pm 21$  ppm (ref. 32), which is somewhat higher than the average of  $145$   
175  $\pm 89$  ppm we observe for the Huainan Basin sediments. Furthermore, modern  
176 oligotrophic settings commonly have  $P_{\text{det}}$  values of 62-310 ppm ( $78 \pm 41$  ppm, ref. 27),  
177 which is similar to the range we observe (30-496 ppm). Hence, potential  
178 recrystallization of authigenic apatite was insignificant in terms of the dominant phase  
179 partitioning of phosphorus.

180 The molar ratios of  $C_{\text{org}}/P_{\text{reac}}$  plot below the Redfield ratio (Fig. 3A). Since we see  
181 little evidence for preferential release of P from organic matter, our novel  $C_{\text{org}}/P_{\text{reac}}$   
182 approach therefore implies efficient drawdown of P from the ferruginous water column,  
183 presumably as Fe-bound P. While a small proportion of this original  $P_{\text{Fe}}$  was preserved,  
184 a significant proportion was ultimately fixed in the sediment as  $P_{\text{auth}}$ . This is consistent  
185 with high proportions of  $\text{Fe}_{\text{carb}}$  (Fig. S4), which likely formed during diagenesis  
186 following the dissolution of Fe minerals and release of adsorbed P.

187

### 188 **An early Neoproterozoic oligotrophic ocean**

189 The Huainan Basin sediments provide a case study for the behaviour of the P cycle  
190 under global ferruginous ocean conditions, and suggest that the low P content of these  
191 open ocean sediments reflects a relatively low seawater P reservoir in the early  
192 Neoproterozoic. This would have been a natural consequence of widespread P  
193 drawdown in association with Fe minerals as euxinia retracted and continental shelves  
194 transitioned to a ferruginous state<sup>8</sup>. A prediction of such conditions would be that  
195 sedimentary P should be dominated by detrital phosphorus<sup>12</sup>, with some fixation of  
196 primary Fe-bound P as authigenic P, both of which we observe in the Huainan basin  
197 (Fig. 2). The development of a low seawater P reservoir would be expected to act as a  
198 limiting constraint on primary production. Indeed,  $C_{\text{org}}/P_{\text{org}}$  ratios close to the Redfield

199 ratio, combined with lower  $C_{\text{org}}/P_{\text{reac}}$  ratios, are typical signatures of modern  
200 oligotrophic settings<sup>27</sup>.

201 An alternative view to the ‘Fe-bound phosphorus shuttle’ as a driver for  
202 Precambrian ocean P limitation invokes decreased aerobic  $C_{\text{org}}$  remineralisation due to  
203 widespread ocean anoxia<sup>43</sup>. However, if a lack of aerobic recycling was responsible for  
204 low productivity throughout the Precambrian, then no significant change would be  
205 expected in the TOC loading of sediments as the redox structure of the anoxic ocean  
206 evolved from widespread euxinia to global ferruginous conditions. Although TOC  
207 contents are not a direct metric for the  $C_{\text{org}}$  flux to the sediment, there is, however, an  
208 apparent contrast between lower TOC contents in early Neoproterozoic shales and the  
209 preceding Mesoproterozoic<sup>44</sup> (see SI). This apparent contrast is entirely consistent with  
210 a mechanism invoking diminished  $C_{\text{org}}$  burial driven by a global decrease in  
211 productivity, due to efficient P removal and limited recycling under a global ferruginous  
212 state.

213 We can, however, provide a further, more direct test of this hypothesis via detailed  
214 investigation of euxinic sediments from the preceding mid-Proterozoic. We thus  
215 augment our data with ~1.1 Ga and ~1.8 Ga sediments deposited under euxinic  
216 conditions in the Taoudeni Basin (Mauritania) and the Animikie Basin (North  
217 America), respectively (see SI for sample descriptions and redox interpretations). In  
218 contrast to the ferruginous data, Figure 3B demonstrates extensive recycling of P from  
219 organic matter, in addition to efficient recycling of P back to the water column ( $C_{\text{org}}/P_{\text{org}}$   
220 and  $C_{\text{org}}/P_{\text{reac}}$  are both significantly greater than the Redfield ratio), as we anticipated<sup>15</sup>  
221 under the euxinic conditions that characterised productive mid-Proterozoic continental  
222 margins<sup>34,35</sup>. Thus, when placed in the context of the global shale record (Fig. 4), the  
223 low P content of early Neoproterozoic sediments likely reflects low seawater P

224 bioavailability under the global ferruginous conditions that occurred from ~1.0 to 0.8  
225 Ga. This contrasts with the preceding mid-Proterozoic, where relatively low P contents  
226 instead reflect extensive recycling back to the water column under widespread euxinic  
227 conditions, resulting in a positive productivity feedback and hence increased  $C_{org}$  burial  
228 on a global scale (Fig. 5). However, despite an early Neoproterozoic drop in global  
229 productivity, sedimentary  $C_{org}:P_{org}$  ratios close to the Redfield ratio (Fig. 3A) suggest P  
230 limitation of primary production was not sufficiently extreme to alter phytoplankton  
231 stoichiometry.

232

### 233 **Maintaining an oxidizing atmosphere**

234 A recent model of Proterozoic atmospheric  $pO_2$  regulation predicts a  $pO_2$  of ~0.1 PAL  
235 during the Proterozoic, with a lower limit of  $pO_2 > 0.01$  PAL, below which  $O_2$  is unstable  
236 and the GOE is reversed<sup>45</sup> (see SI for details on model assumptions). The sulphur cycle  
237 is estimated to have been a net sink for oxygen at ~1.0-0.9 Ga due to widespread  
238 gypsum evaporite deposition<sup>8</sup>. Hence, to maintain an oxidising atmosphere, the  $C_{org}$   
239 burial flux must have exceeded the input flux of reduced gases ( $\sim 1.25 \times 10^{12}$  mol  $O_2$  eq  
240  $yr^{-1}$  in the present day, ref. 45). Comparing this to estimates of modern total ( $\sim 5 \times 10^{12}$   
241 mol  $O_2$  eq  $yr^{-1}$ ) and marine ( $\sim 2.5 \times 10^{12}$  mol  $O_2$  eq  $yr^{-1}$ ) organic C burial, it suggests that  
242 Proterozoic  $C_{org}$  burial could not have fallen below ~25% of today's total value, or  
243 ~50% of today's marine value<sup>45</sup>.

244 This constraint requires that reactive phosphorus inputs were at least half of today's  
245 value, and the global average  $C_{org}/P_{reac}$  burial ratio was comparable in magnitude to  
246 today. Our maximum total P contents of 0.05 wt% are comparable to the average value  
247 for upper continental crust<sup>46</sup> of 0.065 wt%, and the maximum TOC content of 0.3 wt%  
248 (Fig. 2) is comparable to today's reduced C content of upper continental crust and

249 sediments of 0.4-0.6 wt%. Assuming our section is globally representative, a pre-  
250 anthropogenic sediment erosion rate of  $\sim 7 \times 10^{15}$  g yr<sup>-1</sup> (ref. 47) gives a total P burial  
251 flux of  $< 1.1 \times 10^{11}$  mol P yr<sup>-1</sup>, and a P<sub>reac</sub> burial flux of  $< 4.6 \times 10^{10}$  mol P yr<sup>-1</sup> (using  
252 our average reactive P content of 42% total P), which is comparable to today's P  
253 weathering flux, estimated at  $\sim 4$  (2.3-15.5)  $\times 10^{10}$  mol P yr<sup>-1</sup> (ref. 48). This gives a C<sub>org</sub>  
254 burial flux of  $< 1.75 \times 10^{12}$  mol C yr<sup>-1</sup>, which exceeds the  $\sim 1.25 \times 10^{12}$  mol yr<sup>-1</sup> threshold  
255 required to maintain an oxidising atmosphere (ref. 45). Thus, while efficient P removal  
256 under global ferruginous conditions drove a negative productivity feedback, we infer  
257 there was just sufficient C<sub>org</sub> burial to maintain an oxidising atmosphere in the early  
258 Neoproterozoic.

259 Furthermore, the observation that the deep ocean was anoxic<sup>49</sup> implies that oxygen  
260 demand exceeded supply in deeper waters. During the early Neoproterozoic, which  
261 plausibly had a much weaker biological carbon pump, it would have been more difficult  
262 to drive deeper waters anoxic, requiring a pO<sub>2</sub>/[PO<sub>4</sub>] ratio  $\ll 0.4$  of present levels<sup>50</sup>.  
263 Therefore, if pO<sub>2</sub> was  $> 0.01$  PAL, then [PO<sub>4</sub>]  $\gg 0.025$  of present ocean levels (POL)  
264 would be required, corresponding to [PO<sub>4</sub>]  $\gg 0.055$   $\mu\text{mol kg}^{-1}$ . Alternatively, if pO<sub>2</sub>  
265 was  $\sim 0.1$  PAL, then [PO<sub>4</sub>] at  $\gg 0.25$  POL ( $> 0.55$   $\mu\text{mol kg}^{-1}$ ) would be required to  
266 maintain deep ocean anoxia.

267

268 In summary, we infer that in the ferruginous early Neoproterozoic ocean, P was  
269 effectively removed from the water column and fixed in the sediment as authigenic  
270 phases. The lack of phosphorus regeneration into the water column likely constrained  
271 primary production and C<sub>org</sub> burial, limiting the extent of atmospheric oxygen  
272 production. However, whilst the early Neoproterozoic had lower [PO<sub>4</sub>] and pO<sub>2</sub> than  
273 the preceding late Paleo-Mesoproterozoic, our data and existing models suggest that

274 the nature of P cycling supported sufficient C<sub>org</sub> burial to maintain an oxidising  
275 atmosphere, with a stable pO<sub>2</sub> of >0.01 PAL, and [PO<sub>4</sub>] >>0.025 POL. Furthermore,  
276 sedimentary organic matter close to today's C<sub>org</sub>/P<sub>org</sub> Redfield ratio of ~106:1 argues  
277 against extreme P limitation of productivity. Together, these observations imply  
278 significant potential variability in atmospheric oxygen concentrations across Earth's  
279 'middle age', which were tied to global-scale changes in ocean redox chemistry.

280

### 281 **Data availability**

282 All data generated and analysed for the current study are attached, and are available  
283 from data repository DOI:10.5285/72c9a48f-4813-4507-9137-a97d7e6bd2d9.

284

### 285 **References**

- 286 1. Tyrrell, T. The relative influences of nitrogen and phosphorus on oceanic primary  
287 production. *Nature* **400**, 525 (1999).
- 288 2. Planavsky, N. J. et al. Low Mid-Proterozoic atmospheric oxygen levels and the  
289 delayed rise of animals. *science* **346**, 635–638 (2014).
- 290 3. Kump, L. R. The rise of atmospheric oxygen. *Nature* **451**, 277 (2008).
- 291 4. Zhang, S. et al. Sufficient oxygen for animal respiration 1,400 million years ago.  
292 *Proceedings of the National Academy of Sciences* **113**, 1731–1736 (2016).
- 293 5. Lyons, T. W., Reinhard, C. T. & Planavsky, N. J. The rise of oxygen in Earth's  
294 early ocean and atmosphere. *Nature* **506**, 307–315 (2014).
- 295 6. Reinhard, C. T., Planavsky, N. J., Olson, S. L., Lyons, T. W. & Erwin, D. H.  
296 Earth's oxygen cycle and the evolution of animal life. *Proceedings of the National*  
297 *Academy of Sciences* **113**, 8933–8938 (2016).

- 298 7. Zhang, K. et al. Oxygenation of the Mesoproterozoic ocean and the evolution of  
299 complex eukaryotes. *Nature Geoscience* **11**, 345–350 (2018).
- 300 8. Guilbaud, R., Poulton, S. W., Butterfield, N. J., Zhu, M. & Shields-Zhou, G. A. A  
301 global transition to ferruginous conditions in the early Neoproterozoic oceans.  
302 *Nature Geoscience* **8**, 466–470 (2015).
- 303 9. Sperling, E. A. et al. Statistical analysis of iron geochemical data suggests limited  
304 late Proterozoic oxygenation. *Nature* **523**, 451–454 (2015).
- 305 10. Bjerrum, C. J. & Canfield, D. E. Ocean productivity before about 1.9 Gyr ago  
306 limited by phosphorus adsorption onto iron oxides. *Nature* **417**, 159 (2002).
- 307 11. Planavsky, N. J. et al. The evolution of the marine phosphate reservoir. *Nature*  
308 **467**, 1088–1090 (2010).
- 309 12. Reinhard, C. T. et al. Evolution of the global phosphorus cycle. *Nature* **541**, 386  
310 (2017).
- 311 13. Jones, C., Nomosatryo, S., Crowe, S. A., Bjerrum, C. J. & Canfield, D. E. Iron  
312 oxides, divalent cations, silica, and the early earth phosphorus crisis. *Geology* **43**,  
313 135–138 (2015).
- 314 14. Konhauser, K. O., Lalonde, S. V., Amskold, L. & Holland, H. D. Was there really  
315 an Archean phosphate crisis? *Science* **315**, 1234–1234 (2007).
- 316 15. Poulton, S. W. Biogeochemistry: Early phosphorus redigested. *Nature Geoscience*  
317 **10**, 75 (2017).
- 318 16. Rivas-Lamelo, S. et al. Magnetotactic bacteria as a new model for P sequestration  
319 in the ferruginous Lake Pavin. (2017).
- 320 17. Konhauser, K. O. et al. Decoupling photochemical Fe (II) oxidation from  
321 shallow-water BIF deposition. *Earth and Planetary Science Letters* **258**, 87–100  
322 (2007).

- 323 18. Zegeye, A. et al. Green rust formation controls nutrient availability in a  
324 ferruginous water column. *Geology* **40**, 599–602 (2012).
- 325 19. Cosmidis, J. et al. Biomineralization of iron-phosphates in the water column of  
326 Lake Pavin (Massif Central, France). *Geochimica et Cosmochimica Acta* **126**, 78–  
327 96 (2014).
- 328 20. Froelich, P. N. et al. Early oxidation of organic matter in pelagic sediments of the  
329 eastern equatorial Atlantic: suboxic diagenesis. *Geochimica et Cosmochimica*  
330 *Acta* **43**, 1075–1090 (1979).
- 331 21. Ingall, E. & Jahnke, R. Influence of water-column anoxia on the elemental  
332 fractionation of carbon and phosphorus during sediment diagenesis. *Marine*  
333 *Geology* **139**, 219–229 (1997).
- 334 22. Krom, M., Kress, N., Brenner, S. & Gordon, L. Phosphorus limitation of primary  
335 productivity in the eastern Mediterranean Sea. *Limnology and Oceanography* **36**,  
336 424–432 (1991).
- 337 23. Slomp, C. P., Thomson, J. & de Lange, G. J. Controls on phosphorus regeneration  
338 and burial during formation of eastern Mediterranean sapropels. *Marine Geology*  
339 **203**, 141–159 (2004).
- 340 24. Dellwig, O. et al. A new particulate Mn–Fe–P-shuttle at the redoxcline of anoxic  
341 basins. *Geochimica et Cosmochimica Acta* **74**, 7100–7115 (2010).
- 342 25. Thompson, J. et al. Development of a modified SEDEX phosphorus speciation  
343 method for ancient rocks and modern iron-rich sediments. *Chemical Geology* **524**,  
344 383–393 (2019).
- 345 26. Egger, M., Jilbert, T., Behrends, T., Rivard, C. & Slomp, C. P. Vivianite is a  
346 major sink for phosphorus in methanogenic coastal surface sediments.  
347 *Geochimica et Cosmochimica Acta* **169**, 217–235 (2015).

- 348 27. Slomp, C. P. et al. Coupled dynamics of iron and phosphorus in sediments of an  
349 oligotrophic coastal basin and the impact of anaerobic oxidation of methane. *PLoS*  
350 *one* **8**, e62386 (2013).
- 351 28. Xiong, Y. et al. Phosphorus cycling in Lake Cadagno, Switzerland: A low sulfate  
352 euxinic ocean analogue. *Geochimica et Cosmochimica Acta* **251**, 116–135 (2019).
- 353 29. Van Cappellen, P. & Ingall, E. D. Benthic phosphorus regeneration, net primary  
354 production, and ocean anoxia: A model of the coupled marine biogeochemical  
355 cycles of carbon and phosphorus. *Paleoceanography* **9**, 677–692 (1994).
- 356 30. Canfield, D. E., Raiswell, R. & Bottrell, S. H. The reactivity of sedimentary iron  
357 minerals toward sulfide. *American Journal of Science* **292**, 659–683 (1992).
- 358 31. Dos Santos Afonso, M. & Stumm, W. Reductive dissolution of iron (III)(hydr)  
359 oxides by hydrogen sulfide. *Langmuir* **8**, 1671–1675 (1992).
- 360 32. Ruttenger, K. C. & Berner, R. A. Authigenic apatite formation and burial in  
361 sediments from non-upwelling, continental margin environments. *Geochimica et*  
362 *cosmochimica acta* **57**, 991–1007 (1993).
- 363 33. Planavsky, N. J. et al. Widespread iron-rich conditions in the mid-Proterozoic  
364 ocean. *Nature* **477**, 448–451 (2011).
- 365 34. Poulton, S. W., Fralick, P. W. & Canfield, D. E. Spatial variability in oceanic  
366 redox structure 1.8 billion years ago. *Nature Geosci* **3**, 486–490 (2010).
- 367 35. Poulton, S. W. & Canfield, D. E. Ferruginous Conditions: A Dominant Feature of  
368 the Ocean through Earth's History. *Elements* **7**, 107–112 (2011).
- 369 36. Tang, Q. et al. Organic-walled microfossils from the early Neoproterozoic  
370 Liulaobei Formation in the Huainan region of North China and their  
371 biostratigraphic significance. *Precambrian Research* **236**, 157–181 (2013).



- 372 37. März, C. et al. Redox sensitivity of P cycling during marine black shale  
373 formation: dynamics of sulfidic and anoxic, non-sulfidic bottom waters.  
374 *Geochimica et Cosmochimica Acta* **72**, 3703–3717 (2008).
- 375 38. Turekian, K. K. & Wedepohl, K. H. Distribution of the Elements in Some Major  
376 Units of the Earth’s Crust. *Geological Society of America Bulletin* **72**, 175–192  
377 (1961).
- 378 39. Teng, Y.-C., Primeau, F. W., Moore, J. K., Lomas, M. W. & Martiny, A. C.  
379 Global-scale variations of the ratios of carbon to phosphorus in exported marine  
380 organic matter. *Nature Geoscience* **7**, 895 (2014).
- 381 40. Ingall, E. D., Bustin, R. & Van Cappellen, P. Influence of water column anoxia on  
382 the burial and preservation of carbon and phosphorus in marine shales.  
383 *Geochimica et Cosmochimica Acta* **57**, 303–316 (1993).
- 384 41. Schrag, D. P., Higgins, J. A., Macdonald, F. A. & Johnston, D. T. Authigenic  
385 carbonate and the history of the global carbon cycle. *science* **339**, 540–543  
386 (2013).
- 387 42. Creveling, J. R. et al. Phosphorus sources for phosphatic Cambrian carbonates.  
388 *Geological Society of America Bulletin* **126**, 145–163 (2014).
- 389 43. Kipp, M. A. & Stüeken, E. E. Biomass recycling and Earth’s early phosphorus  
390 cycle. *Science advances* **3**, eaao4795 (2017).
- 391 44. Sperling, E. A. & Stockey, R. G. The Temporal and Environmental Context of  
392 Early Animal Evolution: Considering All the Ingredients of an “Explosion”.  
393 *Integrative and Comparative Biology* **58**, 605–622 (2018).
- 394 45. Daines, S. J., Mills, B. J. & Lenton, T. M. Atmospheric oxygen regulation at low  
395 Proterozoic levels by incomplete oxidative weathering of sedimentary organic  
396 carbon. *Nature communications* **8**, 14379 (2017).

- 397 46. Wedepohl, K. H. The composition of the continental crust. *Geochimica et*  
398 *cosmochimica Acta* **59**, 1217–1232 (1995).
- 399 47. Mackenzie, F., Lerman, A. & Andersson, A. Past and present of sediment and  
400 carbon biogeochemical cycling models. *Biogeosciences Discussions* **1**, 27–85  
401 (2004).
- 402 48. Compton, J. et al. Variations in the global phosphorus cycle. (2000).
- 403 49. Stolper, D. A. & Keller, C. B. A record of deep-ocean dissolved O<sub>2</sub> from the  
404 oxidation state of iron in submarine basalts. *Nature* **553**, 323 (2018).
- 405 50. Lenton, T. M. & Daines, S. J. Biogeochemical transformations in the history of  
406 the ocean. *Annual review of marine science* **9**, 31–58 (2017).

407

#### 408 **Corresponding author**

409 Correspondence to Romain Guilbaud: [romain.guilbaud@get.omp.eu](mailto:romain.guilbaud@get.omp.eu)

410

#### 411 **Acknowledgements**

412 This work was supported by NERC (NE/I005978/1) and NSFC (41661134048) through  
413 the Co-evolution of Life and the Planet programme, through the Biosphere Evolution,  
414 Transitions and Resilience (NE/P013651) programme, and the Strategic Priority  
415 Research Program (B) of the Chinese Academy of Sciences (XDB18000000). SWP and  
416 TML were supported by Royal Society Wolfson Research Merit Awards and SWP by  
417 a Leverhulme Trust Fellowship.

418

#### 419 **Author contributions**

420 R.G. and S.W.P. devised the research. R.G., S.W.P., G.A.S., Y.Z. and M.Z. collected  
421 the samples. J.T. and K.F.H. analysed the Mesoproterozoic samples. R.G. analyses the

422 Neoproterozoic samples and interpreted the data. R.G. wrote the manuscript, with  
423 significant contributions from all co-authors.

424

#### 425 **Financial and non-financial competing interests**

426 The authors declare no competing interests.

427

#### 428 **Figure Captions**

##### 429 **Figure 1. Sample locations within the north China craton.**

430 **a**, Location of the Huainan Basin within the Rodinia supercontinent during the early  
431 Neoproterozoic. **b**, Huainan region location within modern day China. **c**, Sample  
432 locations (red stars) within the Huainan region in the Anhui province. The figure was  
433 modified after refs. (8,36).

434

##### 435 **Figure 2. Geochemical variations against the main stratigraphy of the Huainan** 436 **Basin.**

437 **a**, Stratigraphy of the Huainan Basin and lithology of the sections studied, modified  
438 after ref. (8). Geochemical variations include: **b**, Total organic carbon (TOC) and total  
439 Fe ( $Fe_T$ ) contents; **c**, Organic carbon and carbonate carbon isotope compositions  
440 ( $\delta^{13}C_{org}$  and  $\delta^{13}C_{carb}$ , respectively); **d**, Total phosphorus ( $P_{tot}$ ) contents and the P to  
441 aluminium ratio (P/Al), the dotted line representing the average shale value<sup>38</sup> (note the  
442 difference in x-axis); **e**, The proportion of detrital ( $P_{det}$ ), authigenic ( $P_{auth}$ ), organic-bond  
443 ( $P_{org}$ ), and Fe oxide-bond ( $P_{Fe}$ ) phosphorus within the total phosphorus pool. Errors are  
444 included within the data points.

445

##### 446 **Figure 3. Organic carbon (C) versus P (P) contents in Proterozoic sediments.**

447 **a**, Molar organic C versus total P ( $P_{\text{tot}}$ ), reactive P ( $P_{\text{reac}}$ ) and organic-bound P ( $P_{\text{org}}$ ) in  
448 the ferruginous Huainan Basin. **b**, Comparison with the ~1.1 Ga Taoudeni Basin,  
449 Mauritania (euxinic setting, represented by triangles) and the ~1.8 Ga Animikie Basin,  
450 North America (euxinic setting, represented by squares). The grey lines represent the  
451 Redfield C/P ratio of 106:1. C and P contents are given in mol per 100 g of sediment.  
452 Errors are included in the datapoints.

453

454 **Figure 4. Phosphorus contents in black shales through time.**

455 Compiled data of P contents in shales, plotted as grey circles, are from ref. 12. Data  
456 from the Huainan Basin (this study) are represented by closed red circles. The green  
457 boxes represent the whisker data for each associated time period. Compiled data were  
458 binned as a function of the time period considered, and the boxes represent the 1<sup>st</sup>  
459 quartile, median and 3<sup>rd</sup> quartile of the binned data. Whiskers mark the Tukey's range  
460 test for the binned data. Arrows indicate high value data in the Phanerozoic and the late  
461 Neoproterozoic that could not be represented on the figure.

462

463 **Figure 5. Biogeochemical evolution of the ocean at the Mesoproterozoic-**  
464 **Neoproterozoic boundary (~1 Ga).**

465 **a**, Prior to ~1 Ga, mid-depth, euxinic (sulphide-rich,  $\text{H}_2\text{S}$ ) continental margins  
466 promoted phosphorous regeneration (as phosphate,  $\text{PO}_4^{3-}$ ) through preferential release  
467 from organic carbon ( $\text{C}_{\text{org}}$ ) and the reduction of Fe (oxyhydr)oxides, resulting in higher  
468 productivity and higher  $\text{C}_{\text{org}}$ -to-organic P ( $P_{\text{org}}$ ) ratio. **b**, After ~1 Ga, under the globally  
469 ferruginous (Fe(II)-rich) early Neoproterozoic ocean, P was effectively removed from  
470 the water column and fixed in the sediment as authigenic phases through 'sink-

471 switching', resulting in oligotrophic continental margins and  $C_{org}/P_{org}$  close to the  
472 Redfield ratio.

473

#### 474 **Methods**

475 **Geological context.** The Huainan basin only witnessed low grade metamorphism, and  
476 hosts exceptionally well preserved, light-coloured acritarchs<sup>36</sup>, as a result of low  
477 temperature gradients since deposition. Samples were collected from freshly exposed  
478 outcrops from an extensive, 700-800 m thick succession of shales, siltstones, mudstones  
479 and carbonates from the ~1-0.9 Ga Liulaobei and Jiuliqiao Formations. Because these  
480 sedimentary successions begin with relatively deep-water continental slope deposits,  
481 and shallow upwards to intertidal stromatolitic dolomites, they present an ideal site for  
482 exploring nutrient provision and cycling across a range of water depths.

483

484 **TOC and C isotopes.** TOC values are from a previously published study<sup>8</sup>. C isotope  
485 analyses were performed on the organic and carbonate fractions of the sediment  
486 samples. For the organic fraction, samples were decarbonated via two 24 h HCl washes  
487 (25% vol/vol), rinsed, centrifuged and dried before analysis. All data are reported with  
488 respect to the Vienna Pee Dee Belemnite standard (V-PDB), with a precision of  $\pm$   
489 0.07‰ (1 $\sigma$  level).

490

491 **Elemental analysis.** Bulk sediment digestions were performed on ~50 mg of rock  
492 powder using HNO<sub>3</sub>-HF-HClO<sub>4</sub> at ~70°C, followed by H<sub>3</sub>BO<sub>3</sub> and HCl. Total P and Al  
493 contents were measured by ICP-OES, along with Mn and Sr, with a precision of  $\pm$  0.4  
494 ppm for P and  $\pm$  0.9 ppm for Al, respectively (n = 8). Total digests of standard material

495 (PACS-2, National Research Council of Canada) yielded values within the certified  
496 range for all analyses elements (<3%).

497

498 **P speciation.** We performed the sequential phosphorus SEDEX extraction<sup>51</sup> adapted  
499 for ancient sedimentary rocks<sup>25</sup> (Table S2 and ref. 52) on sediment aliquots of ~150-  
500 200 mg. The method targets five operationally-defined phosphorus sedimentary pools,  
501 including iron bound phosphorus ( $P_{Fe}$ ), authigenic CFA-associated P ( $P_{auth}$ ), detrital  
502 apatite and inorganic P ( $P_{det}$ ), organic bound P ( $P_{org}$ ) and total P ( $P_{tot}$ ). The applied  
503 method was slightly different to the SEDEX scheme, in that the “loosely sorbed P” step  
504 was omitted, and an additional  $HNO_3$ -HF- $HClO_4$ - $H_3BO_3$ -HCl extraction step (V) was  
505 performed on the residue in order to achieve near complete P recovery. Using this  
506 approach, an average recovery of 99% of the total P pool (as determined by ICP-OES)  
507 was achieved during the sequential extractions (Fig. S3-A). For each extraction step  
508 and washes, except for extraction step I, P concentrations were determined  
509 spectrophotometrically using the molybdate-blue method on a Spectronic GENESYS™  
510 6 at 880 nm. Reagents used in extraction I interfere with the molybdate complex, and  
511 for this step, P contents were measured by ICP-OES. Replicate analysis of a sample (n  
512 = 5) gave a RSD of <10% for each step, apart from  $P_{Fe}$ , where the RSD was 16%, partly  
513 due to the low concentrations of this phase (Table S2).

514

#### 515 **References only in Methods**

516 51. Ruttenberg, K. C. Development of a sequential extraction method for different  
517 forms of phosphorus in marine sediments. *Limnology and Oceanography* **37**,  
518 1460–1482 (1992).

519 52. Full data are available in the repository DOI: 10.0.20.165/72c9a48f-4813-4507-

520 9137-a97d7e6bd2d9.

521