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

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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,**  
28 **Ga). Ocean redox chemistry exerts a strong control on the biogeochemical**  
29 **cycling of phosphorus (P), a limiting nutrient, and hence on primary production,**  
30 **but the 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), *p*O<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  
48 at relatively constant levels after ~2.0 Ga, until the later Neoproterozoic (~0.8 to  
49 0.542 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  
54 P concentrations in the Precambrian ocean have relied on P contents of black shales  
55 and iron-rich chemical deposits<sup>10-12</sup>. In the latter case, the assumption is that P  
56 contents in iron formations provide a first order estimation of dissolved P in the water  
57 column, with only minimal remobilisation during diagenesis<sup>10</sup>. However, conflicting  
58 experimental determinations of P co-precipitation and adsorption coefficients have led  
59 to widely 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  
62 has led to the suggestion that oceanic phosphate concentrations were extremely low  
63 until ~0.8 Ga<sup>12</sup>, which might support inferences of extremely low atmospheric  $pO_2$   
64 (<0.001 PAL) until the Neoproterozoic rise in atmospheric oxygen<sup>2</sup>. However, bulk  
65 shale P contents are limited in that they do not specifically track bioavailable P. In  
66 addition, bulk shale P contents cannot provide detailed understanding of the extent of  
67 P recycling from the sediment back to the water column, which is highly dependent  
68 on the precise 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  $C_{org}$  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*  
76 partial decomposition of organic matter and the reduction of Fe (oxyhydr)oxides<sup>20–23</sup>.  
77 This process may be compensated by re-adsorption onto Fe minerals at the sediment-  
78 water interface<sup>24</sup>, enhancing sedimentary P fixation in association with crystalline Fe  
79 oxides<sup>25</sup> or Fe phosphates<sup>19,26–28</sup>. By contrast, phosphorus recycling back to the water  
80 column may be particularly intense under euxinic conditions<sup>23,29</sup>, due to the rapid  
81 reduction of P-bearing Fe (oxyhydr)oxides by hydrogen sulphide<sup>30,31</sup>, and the  
82 preferential release of P from decaying organic matter during sulphate  
83 reduction<sup>21,23,29</sup>. As a result, C:P ratios commonly surpass the canonical Redfield ratio  
84 of 106:1 by several orders of magnitude<sup>21</sup>. However, under all redox scenarios, some,  
85 or all, of the recycled phosphorus may be fixed in the sediment *via* the formation of  
86 authigenic phases during ‘sink-switching’, which involves the transfer of P from its  
87 carrier phase to a stable mineral form, such as authigenic apatite<sup>29,32</sup> or Fe phosphates  
88 (e.g., vivianite)<sup>19,26–28</sup>.

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

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

107

### 108 **Geological setting**

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

116

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

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

124 carbonate fluorapatite (CFA) associated-P ( $P_{\text{auth}}$ ), and detrital P ( $P_{\text{det}}$ ) are the two  
125 largest P pools, representing an average of ~29% and ~58% of total P, respectively.

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

135

### 136 **Phosphorus cycling in the sediment**

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

143 The Huainan Basin sediments are characterised by low  $C_{\text{org}}$  (Fig. 2) and low pyrite  
144 concentrations, coupled with significant preservation of Fe (oxyhydr)oxide minerals  
145 (Fig. S4). This suggests that microbial recycling of  $C_{\text{org}}$  during early diagenesis was  
146 likely limited, and pore water chemistry at the sediment-water interface would have  
147 been poised at Fe reduction, rather than sulphate reduction. A lack of sulphide  
148 production close to the sediment-water interface would ultimately result in enhanced

149 sedimentary P fixation, initially in association with Fe minerals and organic matter,  
150 followed by ‘sink-switching’ to other mineral phases such as authigenic apatite<sup>32</sup> or  
151 vivianite<sup>37</sup> deeper in the sediment profile. The speciation of P in our samples is  
152 consistent with these suggestions, whereby the relatively low  $P_{Fe}$  and  $P_{org}$  we observe  
153 relative to  $P_{auth}$  (Fig. 2) suggest significant ‘sink-switching’.

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

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



174 throughout the succession (see SI), which suggests that the measured  $P_{\text{det}}$  dominantly  
175 reflects the actual detrital P input, rather than post-depositional recrystallization. In  
176 support of these observations, we note that modern continental margin sediments  
177 typically have  $P_{\text{det}}$  contents of  $186 \pm 21$  ppm (ref. 32), which is somewhat higher than  
178 the average of  $145 \pm 89$  ppm we observe for the Huainan Basin sediments.  
179 Furthermore, modern oligotrophic settings commonly have  $P_{\text{det}}$  values of 62-310 ppm  
180 ( $78 \pm 41$  ppm, ref. 27), which is similar to the range we observe (30-496 ppm). Hence,  
181 potential recrystallization of authigenic apatite was insignificant in terms of the  
182 dominant phase partitioning of phosphorus.

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

190

### 191 **An early Neoproterozoic oligotrophic ocean**

192 The Huainan Basin sediments provide a case study for the behaviour of the P cycle  
193 under global ferruginous ocean conditions, and suggest that the low P content of these  
194 open ocean sediments reflects a relatively low seawater P reservoir in the early  
195 Neoproterozoic. This would have been a natural consequence of widespread P  
196 drawdown in association with Fe minerals as euxinia retracted and continental shelves  
197 transitioned to a ferruginous state<sup>8</sup>. A prediction of such conditions would be that  
198 sedimentary P should be dominated by detrital phosphorus<sup>12</sup>, with some fixation of

199 primary Fe-bound P as authigenic P, both of which we observe in the Huainan basin  
200 (Fig. 2). The development of a low seawater P reservoir would be expected to act as a  
201 limiting constraint on primary production. Indeed,  $C_{\text{org}}/P_{\text{org}}$  ratios close to the Redfield  
202 ratio, combined with lower  $C_{\text{org}}/P_{\text{reac}}$  ratios, are typical signatures of modern  
203 oligotrophic settings<sup>27</sup>.

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

216 We can, however, provide a further, more direct test of this hypothesis *via*  
217 detailed investigation of euxinic sediments from the preceding mid-Proterozoic. We  
218 thus augment our data with ~1.1 Ga and ~1.8 Ga sediments deposited under euxinic  
219 conditions in the Taoudeni Basin (Mauritania) and the Animikie Basin (North  
220 America), respectively (see SI for sample descriptions and redox interpretations). In  
221 contrast to the ferruginous data, Figure 3B demonstrates extensive recycling of P from  
222 organic matter, in addition to efficient recycling of P back to the water column  
223 ( $C_{\text{org}}/P_{\text{org}}$  and  $C_{\text{org}}/P_{\text{reac}}$  are both significantly greater than the Redfield ratio), as we

224 anticipated<sup>15</sup> under the euxinic conditions that characterised productive mid-  
225 Proterozoic continental margins<sup>34,35</sup>. Thus, when placed in the context of the global  
226 shale record (Fig. 4), the low P content of early Neoproterozoic sediments likely  
227 reflects low seawater P bioavailability under the global ferruginous conditions that  
228 occurred from ~1.0 to 0.8 Ga. This contrasts with the preceding mid-Proterozoic,  
229 where relatively low P contents instead reflect extensive recycling back to the water  
230 column under widespread euxinic conditions, resulting in a positive productivity  
231 feedback and hence increased C<sub>org</sub> burial on a global scale (Fig. 5). However, despite  
232 an early Neoproterozoic drop in global productivity, sedimentary C<sub>org</sub>:P<sub>org</sub> ratios close  
233 to the Redfield ratio (Fig. 3A) suggest P limitation of primary production was not  
234 sufficiently extreme to alter phytoplankton stoichiometry.

235

### 236 **Maintaining an oxidizing atmosphere**

237 A recent model of Proterozoic atmospheric  $pO_2$  regulation predicts a  $pO_2$  of ~0.1 PAL  
238 during the Proterozoic, with a lower limit of  $pO_2 > 0.01$  PAL, below which  $O_2$  is  
239 unstable and the GOE is reversed<sup>45</sup> (see SI for details on model assumptions). The  
240 sulphur cycle is estimated to have been a net sink for oxygen at ~1.0-0.9 Ga due to  
241 widespread gypsum evaporite deposition<sup>8</sup>. Hence, to maintain an oxidising  
242 atmosphere, the C<sub>org</sub> burial flux must have exceeded the input flux of reduced gases  
243 ( $\sim 1.25 \times 10^{12}$  mol  $O_2$  eq yr<sup>-1</sup> in the present day, ref. 45). Comparing this to estimates  
244 of modern total ( $\sim 5 \times 10^{12}$  mol  $O_2$  eq yr<sup>-1</sup>) and marine ( $\sim 2.5 \times 10^{12}$  mol  $O_2$  eq yr<sup>-1</sup>)  
245 organic C burial, it suggests that Proterozoic C<sub>org</sub> burial could not have fallen below  
246 ~25% of today's total value, or ~50% of today's marine value<sup>45</sup>.

247 This constraint requires that reactive phosphorus inputs were at least half of  
248 today's value, and the global average C<sub>org</sub>/P<sub>reac</sub> burial ratio was comparable in

249 magnitude to today. Our maximum total P contents of 0.05 wt% are comparable to the  
250 average value for upper continental crust<sup>46</sup> of 0.065 wt%, and the maximum TOC  
251 content of 0.3 wt% (Fig. 2) is comparable to today's reduced C content of upper  
252 continental crust and sediments of 0.4-0.6 wt%. Assuming our section is globally  
253 representative, a pre-anthropogenic sediment erosion rate of  $\sim 7 \times 10^{15}$  g yr<sup>-1</sup> (ref. 47)  
254 gives a total P burial flux of  $< 1.1 \times 10^{11}$  mol P yr<sup>-1</sup>, and a P<sub>reac</sub> burial flux of  $< 4.6 \times$   
255  $10^{10}$  mol P yr<sup>-1</sup> (using our average reactive P content of 42% total P), which is  
256 comparable to today's P weathering flux, estimated at  $\sim 4$  (2.3-15.5)  $\times 10^{10}$  mol P yr<sup>-1</sup>  
257 (ref. 48). This gives a C<sub>org</sub> burial flux of  $< 1.75 \times 10^{12}$  mol C yr<sup>-1</sup>, which exceeds the  
258  $\sim 1.25 \times 10^{12}$  mol yr<sup>-1</sup> threshold required to maintain an oxidising atmosphere (ref. 45).  
259 Thus, while efficient P removal under global ferruginous conditions drove a negative  
260 productivity feedback, we infer there was just sufficient C<sub>org</sub> burial to maintain an  
261 oxidising atmosphere in the early Neoproterozoic.

262 Furthermore, the observation that the deep ocean was anoxic<sup>49</sup> implies that oxygen  
263 demand exceeded supply in deeper waters. During the early Neoproterozoic, which  
264 plausibly had a much weaker biological carbon pump, it would have been more  
265 difficult to drive deeper waters anoxic, requiring a  $pO_2/[PO_4]$  ratio  $\ll 0.4$  of present  
266 levels<sup>50</sup>. Therefore, if  $pO_2$  was  $> 0.01$  PAL, then  $[PO_4] \gg 0.025$  of present ocean levels  
267 (POL) would be required, corresponding to  $[PO_4] \gg 0.055$   $\mu\text{mol kg}^{-1}$ . Alternatively, if  
268  $pO_2$  was  $\sim 0.1$  PAL, then  $[PO_4]$  at  $\gg 0.25$  POL ( $> 0.55$   $\mu\text{mol kg}^{-1}$ ) would be required to  
269 maintain deep ocean anoxia.

270

271 In summary, we infer that in the ferruginous early Neoproterozoic ocean, P was  
272 effectively removed from the water column and fixed in the sediment as authigenic  
273 phases. The lack of phosphorus regeneration into the water column likely constrained

274 primary production and  $C_{\text{org}}$  burial, limiting the extent of atmospheric oxygen  
275 production. However, whilst the early Neoproterozoic had lower  $[\text{PO}_4]$  and  $p\text{O}_2$  than  
276 the preceding late Paleo-Mesoproterozoic, our data and existing models suggest that  
277 the nature of P cycling supported sufficient  $C_{\text{org}}$  burial to maintain an oxidising  
278 atmosphere, with a stable  $p\text{O}_2$  of  $>0.01$  PAL, and  $[\text{PO}_4] \gg 0.025$  POL. Furthermore,  
279 sedimentary organic matter close to today's  $C_{\text{org}}/P_{\text{org}}$  Redfield ratio of  $\sim 106:1$  argues  
280 against extreme P limitation of productivity. Together, these observations imply  
281 significant potential variability in atmospheric oxygen concentrations across Earth's  
282 'middle age', which were tied to global-scale changes in ocean redox chemistry.

283

#### 284 **Data availability**

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

287

#### 288 **References**

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

- 298 6. Reinhard, C. T., Planavsky, N. J., Olson, S. L., Lyons, T. W. & Erwin, D. H.  
299 Earth's oxygen cycle and the evolution of animal life. *Proceedings of the National*  
300 *Academy of Sciences* **113**, 8933–8938 (2016).
- 301 7. Zhang, K. *et al.* Oxygenation of the Mesoproterozoic ocean and the evolution of  
302 complex eukaryotes. *Nature Geoscience* **11**, 345–350 (2018).
- 303 8. Guilbaud, R., Poulton, S. W., Butterfield, N. J., Zhu, M. & Shields-Zhou, G. A. A  
304 global transition to ferruginous conditions in the early Neoproterozoic oceans.  
305 *Nature Geoscience* **8**, 466–470 (2015).
- 306 9. Sperling, E. A. *et al.* Statistical analysis of iron geochemical data suggests limited  
307 late Proterozoic oxygenation. *Nature* **523**, 451–454 (2015).
- 308 10. Bjerrum, C. J. & Canfield, D. E. Ocean productivity before about 1.9 Gyr ago  
309 limited by phosphorus adsorption onto iron oxides. *Nature* **417**, 159 (2002).
- 310 11. Planavsky, N. J. *et al.* The evolution of the marine phosphate reservoir. *Nature*  
311 **467**, 1088–1090 (2010).
- 312 12. Reinhard, C. T. *et al.* Evolution of the global phosphorus cycle. *Nature* **541**, 386  
313 (2017).
- 314 13. Jones, C., Nomosatryo, S., Crowe, S. A., Bjerrum, C. J. & Canfield, D. E. Iron  
315 oxides, divalent cations, silica, and the early earth phosphorus crisis. *Geology* **43**,  
316 135–138 (2015).
- 317 14. Konhauser, K. O., Lalonde, S. V., Amskold, L. & Holland, H. D. Was there really  
318 an Archean phosphate crisis? *Science* **315**, 1234–1234 (2007).
- 319 15. Poulton, S. W. Biogeochemistry: Early phosphorus redigested. *Nature Geoscience*  
320 **10**, 75 (2017).
- 321 16. Rivas-Lamelo, S. *et al.* Magnetotactic bacteria as a new model for P sequestration  
322 in the ferruginous Lake Pavin. (2017).

- 323 17. Konhauser, K. O. *et al.* Decoupling photochemical Fe (II) oxidation from  
324 shallow-water BIF deposition. *Earth and Planetary Science Letters* **258**, 87–100  
325 (2007).
- 326 18. Zegeye, A. *et al.* Green rust formation controls nutrient availability in a  
327 ferruginous water column. *Geology* **40**, 599–602 (2012).
- 328 19. Cosmidis, J. *et al.* Biomineralization of iron-phosphates in the water column of  
329 Lake Pavin (Massif Central, France). *Geochimica et Cosmochimica Acta* **126**, 78–  
330 96 (2014).
- 331 20. Froelich, P. N. *et al.* Early oxidation of organic matter in pelagic sediments of the  
332 eastern equatorial Atlantic: suboxic diagenesis. *Geochimica et Cosmochimica*  
333 *Acta* **43**, 1075–1090 (1979).
- 334 21. Ingall, E. & Jahnke, R. Influence of water-column anoxia on the elemental  
335 fractionation of carbon and phosphorus during sediment diagenesis. *Marine*  
336 *Geology* **139**, 219–229 (1997).
- 337 22. Krom, M., Kress, N., Brenner, S. & Gordon, L. Phosphorus limitation of primary  
338 productivity in the eastern Mediterranean Sea. *Limnology and Oceanography* **36**,  
339 424–432 (1991).
- 340 23. Slomp, C. P., Thomson, J. & de Lange, G. J. Controls on phosphorus regeneration  
341 and burial during formation of eastern Mediterranean sapropels. *Marine Geology*  
342 **203**, 141–159 (2004).
- 343 24. Dellwig, O. *et al.* A new particulate Mn–Fe–P-shuttle at the redoxcline of anoxic  
344 basins. *Geochimica et Cosmochimica Acta* **74**, 7100–7115 (2010).
- 345 25. Thompson, J. *et al.* Development of a modified SEDEX phosphorus speciation  
346 method for ancient rocks and modern iron-rich sediments. *Chemical Geology* **524**,  
347 383–393 (2019).

- 348 26. Egger, M., Jilbert, T., Behrends, T., Rivard, C. & Slomp, C. P. Vivianite is a  
349 major sink for phosphorus in methanogenic coastal surface sediments.  
350 *Geochimica et Cosmochimica Acta* **169**, 217–235 (2015).
- 351 27. Slomp, C. P. *et al.* Coupled dynamics of iron and phosphorus in sediments of an  
352 oligotrophic coastal basin and the impact of anaerobic oxidation of methane. *PLoS*  
353 *one* **8**, e62386 (2013).
- 354 28. Xiong, Y. *et al.* Phosphorus cycling in Lake Cadagno, Switzerland: A low sulfate  
355 euxinic ocean analogue. *Geochimica et Cosmochimica Acta* **251**, 116–135 (2019).
- 356 29. Van Cappellen, P. & Ingall, E. D. Benthic phosphorus regeneration, net primary  
357 production, and ocean anoxia: A model of the coupled marine biogeochemical  
358 cycles of carbon and phosphorus. *Paleoceanography* **9**, 677–692 (1994).
- 359 30. Canfield, D. E., Raiswell, R. & Bottrell, S. H. The reactivity of sedimentary iron  
360 minerals toward sulfide. *American Journal of Science* **292**, 659–683 (1992).
- 361 31. Dos Santos Afonso, M. & Stumm, W. Reductive dissolution of iron (III)(hydr)  
362 oxides by hydrogen sulfide. *Langmuir* **8**, 1671–1675 (1992).
- 363 32. Ruttenberg, K. C. & Berner, R. A. Authigenic apatite formation and burial in  
364 sediments from non-upwelling, continental margin environments. *Geochimica et*  
365 *cosmochimica acta* **57**, 991–1007 (1993).
- 366 33. Planavsky, N. J. *et al.* Widespread iron-rich conditions in the mid-Proterozoic  
367 ocean. *Nature* **477**, 448–451 (2011).
- 368 34. Poulton, S. W., Fralick, P. W. & Canfield, D. E. Spatial variability in oceanic  
369 redox structure 1.8 billion years ago. *Nature Geosci* **3**, 486–490 (2010).
- 370 35. Poulton, S. W. & Canfield, D. E. Ferruginous Conditions: A Dominant Feature of  
371 the Ocean through Earth's History. *Elements* **7**, 107–112 (2011).



- 372 36. Tang, Q. *et al.* Organic-walled microfossils from the early Neoproterozoic  
373 Liulaobei Formation in the Huainan region of North China and their  
374 biostratigraphic significance. *Precambrian Research* **236**, 157–181 (2013).
- 375 37. März, C. *et al.* Redox sensitivity of P cycling during marine black shale  
376 formation: dynamics of sulfidic and anoxic, non-sulfidic bottom waters.  
377 *Geochimica et Cosmochimica Acta* **72**, 3703–3717 (2008).
- 378 38. Turekian, K. K. & Wedepohl, K. H. Distribution of the Elements in Some Major  
379 Units of the Earth’s Crust. *Geological Society of America Bulletin* **72**, 175–192  
380 (1961).
- 381 39. Teng, Y.-C., Primeau, F. W., Moore, J. K., Lomas, M. W. & Martiny, A. C.  
382 Global-scale variations of the ratios of carbon to phosphorus in exported marine  
383 organic matter. *Nature Geoscience* **7**, 895 (2014).
- 384 40. Ingall, E. D., Bustin, R. & Van Cappellen, P. Influence of water column anoxia on  
385 the burial and preservation of carbon and phosphorus in marine shales.  
386 *Geochimica et Cosmochimica Acta* **57**, 303–316 (1993).
- 387 41. Schrag, D. P., Higgins, J. A., Macdonald, F. A. & Johnston, D. T. Authigenic  
388 carbonate and the history of the global carbon cycle. *science* **339**, 540–543  
389 (2013).
- 390 42. Creveling, J. R. *et al.* Phosphorus sources for phosphatic Cambrian carbonates.  
391 *Geological Society of America Bulletin* **126**, 145–163 (2014).
- 392 43. Kipp, M. A. & Stüeken, E. E. Biomass recycling and Earth’s early phosphorus  
393 cycle. *Science advances* **3**, eaao4795 (2017).
- 394 44. Sperling, E. A. & Stockey, R. G. The Temporal and Environmental Context of  
395 Early Animal Evolution: Considering All the Ingredients of an “Explosion”.  
396 *Integrative and Comparative Biology* **58**, 605–622 (2018).

- 397 45. Daines, S. J., Mills, B. J. & Lenton, T. M. Atmospheric oxygen regulation at low  
398 Proterozoic levels by incomplete oxidative weathering of sedimentary organic  
399 carbon. *Nature communications* **8**, 14379 (2017).
- 400 46. Wedepohl, K. H. The composition of the continental crust. *Geochimica et*  
401 *cosmochimica Acta* **59**, 1217–1232 (1995).
- 402 47. Mackenzie, F., Lerman, A. & Andersson, A. Past and present of sediment and  
403 carbon biogeochemical cycling models. *Biogeosciences Discussions* **1**, 27–85  
404 (2004).
- 405 48. Compton, J. *et al.* Variations in the global phosphorus cycle. (2000).
- 406 49. Stolper, D. A. & Keller, C. B. A record of deep-ocean dissolved O<sub>2</sub> from the  
407 oxidation state of iron in submarine basalts. *Nature* **553**, 323 (2018).
- 408 50. Lenton, T. M. & Daines, S. J. Biogeochemical transformations in the history of  
409 the ocean. *Annual review of marine science* **9**, 31–58 (2017).

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413

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422 **Author contributions**

423 R.G. and S.W.P. devised the research. R.G., S.W.P., G.A.S., Y.Z. and M.Z. collected  
424 the samples. J.T. and K.F.H. analysed the Mesoproterozoic samples. R.G. analyses the  
425 Neoproterozoic samples and interpreted the data. R.G. wrote the manuscript, with  
426 significant contributions from all co-authors.

427

428 **Financial and non-financial competing interests**

429 The authors declare no competing interests.

430

431 **Figure Captions**

432 **Figure 1. Sample locations within the north China craton.**

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

437

438 **Figure 2. Geochemical variations against the main stratigraphy of the Huainan**  
439 **Basin.**

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

446 bond ( $P_{\text{org}}$ ), and Fe oxide-bond ( $P_{\text{Fe}}$ ) phosphorus within the total phosphorus pool.  
447 Errors are included within the data points.

448

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

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

456

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

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

465

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

468 **a**, Prior to ~1 Ga, mid-depth, euxinic (sulphide-rich,  $\text{H}_2\text{S}$ ) continental margins  
469 promoted phosphorous regeneration (as phosphate,  $\text{PO}_4^{3-}$ ) through preferential release  
470 from organic carbon ( $\text{C}_{\text{org}}$ ) and the reduction of Fe (oxyhydr)oxides, resulting in

471 higher productivity and higher C<sub>org</sub>-to-organic P (P<sub>org</sub>) ratio. **b**, After ~1 Ga, under the  
472 globally ferruginous (Fe(II)-rich) early Neoproterozoic ocean, P was effectively  
473 removed from the water column and fixed in the sediment as authigenic phases  
474 through ‘sink-switching’, resulting in oligotrophic continental margins and C<sub>org</sub>/P<sub>org</sub>  
475 close to the Redfield ratio.

476

## 477 **Methods**

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

487

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

494

495 **Elemental analysis.** Bulk sediment digestions were performed on ~50 mg of rock  
496 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  
497 Al contents were measured by ICP-OES, along with Mn and Sr, with a precision of ±  
498 0.4 ppm for P and ± 0.9 ppm for Al, respectively (*n* = 8). Total digests of standard  
499 material (PACS-2, National Research Council of Canada) yielded values within the  
500 certified range for all analyses elements (<3%).

501

502 **P speciation.** We performed the sequential phosphorus SEDEX extraction<sup>51</sup> adapted  
503 for ancient sedimentary rocks<sup>25</sup> (Table S2 and ref. 52) on sediment aliquots of ~150-  
504 200 mg. The method targets five operationally-defined phosphorus sedimentary pools,  
505 including iron bound phosphorus (P<sub>Fe</sub>), authigenic CFA-associated P (P<sub>auth</sub>), detrital  
506 apatite and inorganic P (P<sub>det</sub>), organic bound P (P<sub>org</sub>) and total P (P<sub>tot</sub>). The applied  
507 method was slightly different to the SEDEX scheme, in that the “loosely sorbed P”  
508 step was omitted, and an additional HNO<sub>3</sub>-HF-HClO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub>-HCl extraction step (V)  
509 was performed on the residue in order to achieve near complete P recovery. Using this  
510 approach, an average recovery of 99% of the total P pool (as determined by ICP-OES)  
511 was achieved during the sequential extractions (Fig. S3-A). For each extraction step  
512 and washes, except for extraction step I, P concentrations were determined  
513 spectrophotometrically using the molybdate-blue method on a Spectronic  
514 GENESYS™ 6 at 880 nm. Reagents used in extraction I interfere with the molybdate  
515 complex, and for this step, P contents were measured by ICP-OES. Replicate analysis  
516 of a sample (*n* = 5) gave a RSD of <10% for each step, apart from P<sub>Fe</sub>, where the RSD  
517 was 16%, partly due to the low concentrations of this phase (Table S2).

518

519 **References only in Methods**

520 51. Ruttenberg, K. C. Development of a sequential extraction method for different  
521 forms of phosphorus in marine sediments. *Limnology and Oceanography* **37**,  
522 1460–1482 (1992).

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