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# 1 Reconciling proxy records and models of Earth's oxygenation during 2 the Neoproterozoic and Palaeozoic

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7

## 8 **Abstract**

9 A hypothesised rise in oxygen levels in the Neoproterozoic, dubbed the Neoproterozoic  
10 oxygenation event (NOE), has been repeatedly linked to the origin and rise of animal life.  
11 However, a new body of work has emerged over the past decade that questions this  
12 narrative. We explore available proxy records of atmospheric and marine oxygenation, and  
13 considering the unique systematics of each geochemical system, attempt to reconcile the  
14 data. We also present new results from a comprehensive COPSE biogeochemical model that  
15 combines several recent additions, to create a continuous model record from 850–250 Ma.  
16 We conclude that oxygen levels were intermediate across the Ediacaran and early  
17 Palaeozoic, and highly dynamic. Stable, modern-like conditions were not reached until the  
18 Late Palaeozoic. We therefore propose that the terms Neoproterozoic Oxygenation Window  
19 (NOW) and Palaeozoic Oxygenation Event (POE) are more appropriate descriptors of the rise  
20 of oxygen in Earth's atmosphere and oceans.

21

## 22 **1. Introduction**

23 Since the Great Oxidation Event, 2.5 – 2.3 billion years ago (Ga), oxygen has been a  
24 persistent feature of Earth’s atmosphere<sup>1</sup>, but has remained at low levels throughout the  
25 Palaeoproterozoic and Mesoproterozoic eras (2.5 – 1.0 Ga). A hypothesised rise towards  
26 modern oxygen levels in the Neoproterozoic (1.0 – 0.54 Ga) was dubbed the  
27 “Neoproterozoic Oxygenation Event” (NOE)<sup>2</sup>. Evidence for the NOE included broad increases  
28 in the average molybdenum and vanadium concentrations in black shales<sup>3</sup>; an increase in  
29 the isotope fractionation between sulfate and pyrite ( $\Delta^{34}\text{S}_{\text{SO}_4\text{-pyr}}$ )<sup>4</sup>; and Fe speciation  
30 evidence for local deep water oxygenation<sup>5</sup>.

31

32 Geochemical data collected over the last decade has disrupted this narrative. Despite an  
33 increase in the breadth and depth of proxy data now available, we appear to be further  
34 from a consensus on the timing and dynamics of oxygenation. Some proxies support a  
35 single, unidirectional step change in oxygen levels, although estimates of the timing span  
36 almost 600 Myrs<sup>6–15</sup>. Other proxy data support a more dynamic system, with large  
37 oscillations in oxygen availability<sup>16–18</sup>.

38

39 How can we reconcile these different proxy records? One possibility is that some of the  
40 geochemical data do not record ancient redox conditions, because they have been  
41 overprinted by diagenesis and metamorphism. While some published data may be need to  
42 be revisited, other geochemical signals are reproducible in samples from different basins  
43 (e.g., Uranium isotopes<sup>18,19</sup>, or redox sensitive trace elements<sup>7,17,20,21</sup>). In addition,  
44 geochemical redox analysis can be paired with petrography or other geochemical data to  
45 screen for potential alteration. Another possibility is that we are misinterpreting primary  
46 geochemical signals. Because today’s oceans are largely well-oxygenated, proxy systems are

47 calibrated in isolated basins and lakes, and these environments may not provide a  
48 reasonable analogue for a globally anoxic deep ocean. Alternatively, each proxy may be  
49 capturing different parts of a complex transition, depending on the proxy systematics,  
50 marine residence time, reduction potential, and sampling density. Here, we critically  
51 evaluate current proxy evidence for Neoproterozoic–Palaeozoic oxygenation, attempt to  
52 reconcile the various records, and compare them to the latest biogeochemical modelling  
53 results.

54

## 55 **2. Evaluation of current geochemical evidence**

### 56 **2.1 Local Marine Geochemical Proxies**

57 Local marine redox proxies record progressive changes within a single basin<sup>5,22</sup>, but if those  
58 changes are driven by local hydrodynamics or changes in productivity, they may not reflect  
59 global changes in oxygen availability. When sufficient local proxy data are collected from  
60 multiple basins, the compiled data may record a statistically significant change in the  
61 average oxidation state of the ocean. However, these proxy records are necessarily biased  
62 towards shelf and slope environments, as Proterozoic sediments from the abyssal plain are  
63 rarely preserved. Proxies preserved in carbonates, such as I/Ca and Ce anomalies, are  
64 further biased towards warm, shallow shelf environments at low latitudes.

65

#### 66 *Iron speciation:*

67 The ratio of highly reactive to total iron preserved in carbonates and shales is indicative of  
68 the redox chemistry in the water column directly above the accumulating sediments<sup>23</sup>.

69 Robust calibrations of the proxy in modern sediments allows the differentiation of oxic

70 ( $Fe_{HR}/Fe_T < 0.22$ ) and anoxic water masses ( $Fe_{HR}/Fe_T > 0.38$ ), although ambiguous ratios may

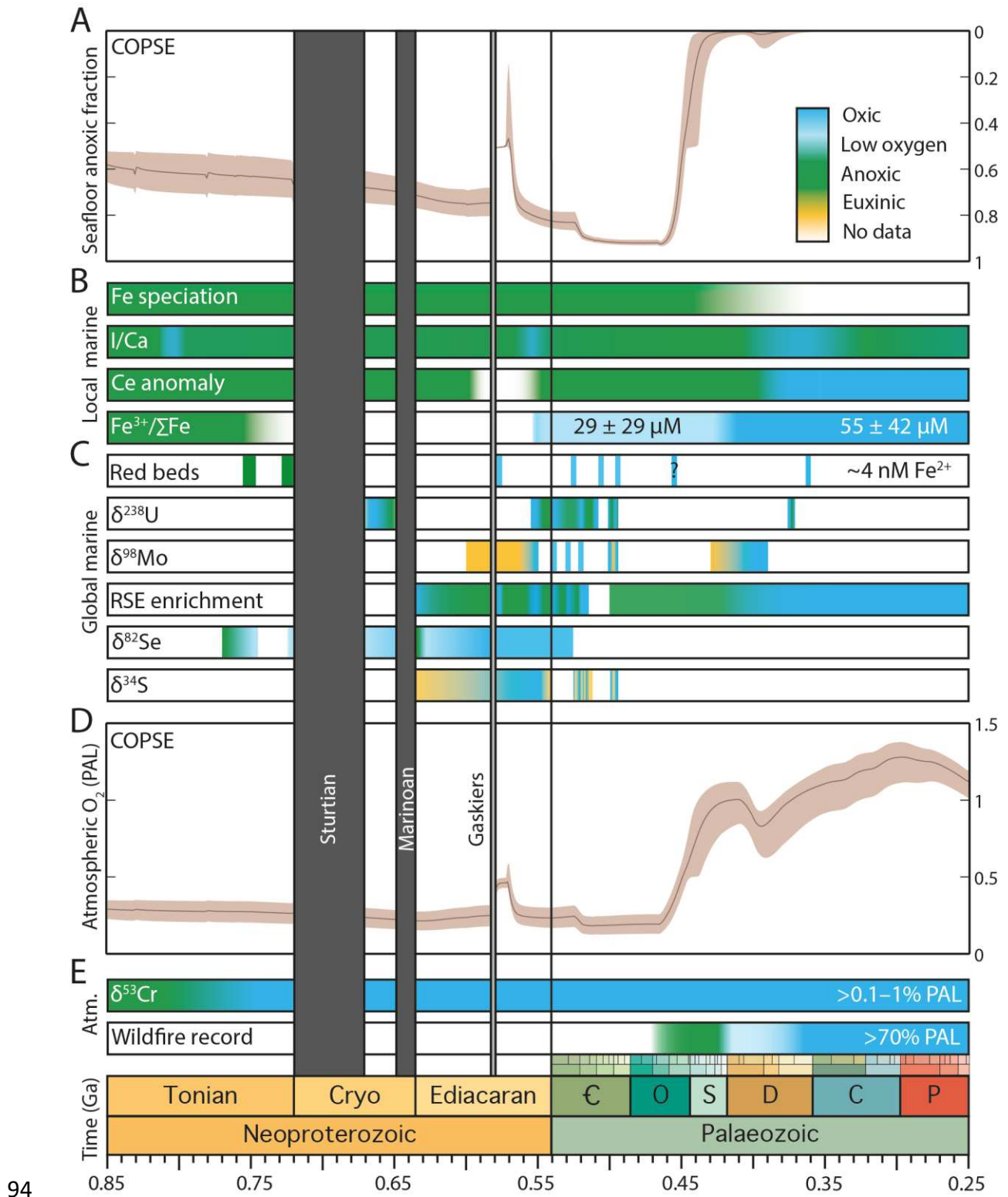
71 be generated under high sedimentation or mixing rates ( $Fe_{HR}/Fe_T$  0.22–0.38). For anoxic  
 72 water masses, the proportion of pyrite in the highly reactive iron phase can distinguish  
 73 between Fe-bearing (ferruginous) and sulfidic (euxinic) anoxia (Table 1). Therefore, “oxic”  
 74 conditions identified by iron speciation could potentially incorporate suboxic and well-  
 75 oxygenated conditions. Systematic diagenetic biases could be introduced to the iron  
 76 speciation record through transformation of unsulfidised highly reactive iron minerals to  
 77 less reactive sheet silicates, producing a false oxic signal.

78  
 79 A transition towards oxic Fe speciation signals ~580 Ma, recorded in shales deposited on a  
 80 continental slope, was thought to pinpoint permanent oxygenation of the deep ocean<sup>5</sup>.  
 81 However, as more data have been collected, an increasingly complex picture of spatial and  
 82 temporal heterogeneity has emerged. For example, data from basins of the same age in the  
 83 Canadian cordillera show no such oxygenation<sup>21,24</sup>, and younger basins record anoxic waters  
 84 impinging onto the shelf<sup>25</sup>. A recent statistical analysis of 4,700 Fe speciation measurements  
 85 from deep water settings across a range of ages and locations has revealed no significant  
 86 long term (i.e., 100 Myr) trend towards more oxic conditions across the Neoproterozoic and  
 87 early Palaeozoic (Figure 1 and 2)<sup>14</sup>. This study has good spatial and temporal coverage from  
 88 ~2.1 Ga to 440 Ma, although Silurian–Devonian data come from just two studies and may be  
 89 subject to sampling biases (Figure 2)<sup>7,26</sup>.

90  
 91 **Table 1:** *Summary of proxy systematics*

	<b>Proxy</b>	<b>Responds to</b>	<b>Redox sensitivity</b>	<b>Archives</b>	<b>Systematic bias?</b>
Local/ Regio	Iron speciation	Integrated regional water column redox conditions	Ferruginous anoxia and euxinia	Shales, carbonate	Variab le

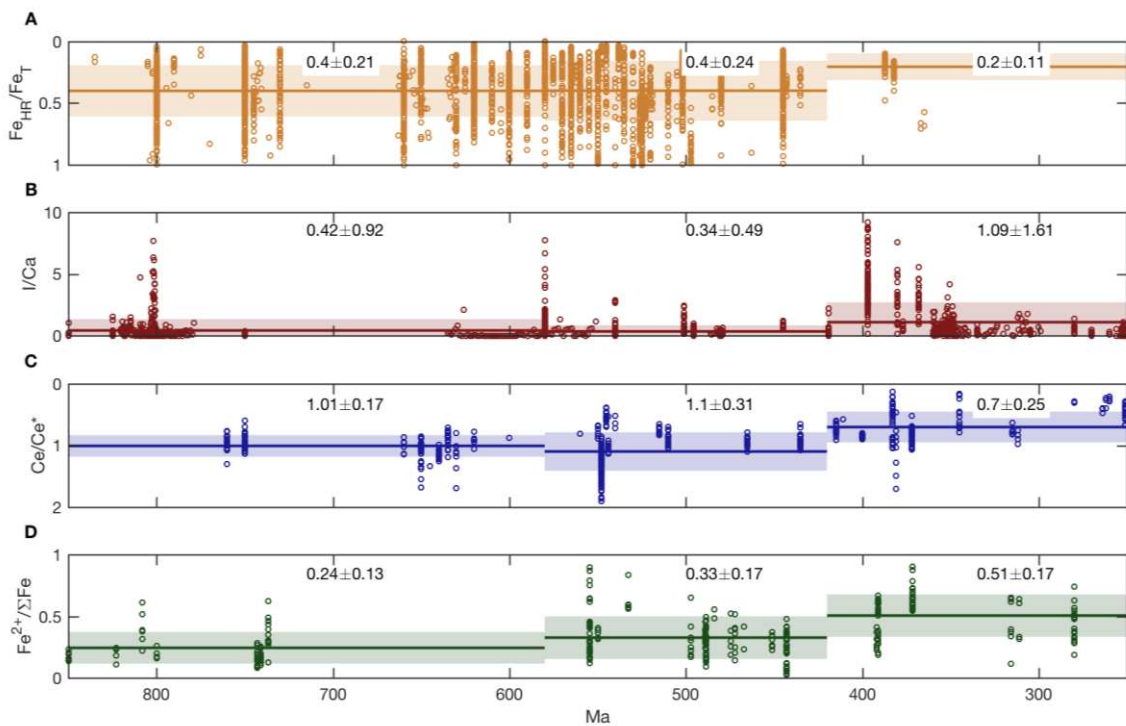
		above accumulating sediments			
	I/Ca ratios	Upper ocean oxygen gradients	Hypoxic (<70 $\mu\text{M O}_2$ ) to suboxic (between manganous and nitrogenous)	Carbonates	False anoxic
	Ce anomalies	Local–regional water column redox at site of carbonate precipitation	Suboxic (manganous)	Carbonates, phosphorites, iron formation	False anoxic
	$\Sigma\text{Fe}^{3+}/\text{Fe}$	Regional deep water oxygen concentrations	Progressive with increasing $\text{O}_2(\text{aq})$	Basalts	False anoxic
	Marine red beds	Regional deep ocean oxygen concentrations following periods of anoxia	Ferruginous anoxia	Marine red beds	
Global marine	$\delta^{238}\text{U}$	Area of global seafloor bathed in anoxic waters	Anoxia	Carbonates, shales	False anoxic
	$\delta^{98}\text{Mo}$	Area of global seafloor bathed in anoxic waters	Euxinia	Shales	False anoxic
	RSE enrichments	Area of global seafloor bathed in anoxic waters	Euxinia (Mo); ferruginous anoxia (Cr, Re, U, V)	Euxinic shales	False anoxic
	$\delta^{82}\text{Se}$	Local redox conditions and size of global–regional oxidised $\text{SeO}_x^{2-}$ reservoir.	Ferruginous anoxia	shales	
	$\delta^{34}\text{S}$	Size of global marine sulfate reservoir and global proportional pyrite burial flux	Euxinia, atmospheric $\text{O}_2$	Carbonates, evaporites	Variable
Atmospheric	$\delta^{53}\text{Cr}$	Atmospheric oxygen	>0.1–1% PAL	Shales, ironstones	
	Wildfire record	Atmospheric oxygen	>70% PAL	Charcoal	



**Figure 1. COPSE model predictions of atmospheric and marine redox and inferred redox conditions based on geochemical proxies through the Neoproterozoic and Paleozoic. A.**

**Modelled sea floor anoxia. Shaded area shows bounds of 10,000 sensitivity analyses. B. Proxy**

98 *inferences for local marine oxygenation, indicating dominantly euxinic (yellow), anoxic*  
 99 *(green), low oxygen (light blue), and oxic (dark blue) conditions. Surface waters have*  
 100 *contained some oxygen since the GOE, but these interpretations represent the dominant*  
 101 *redox conditions. Therefore, a green bar does not imply that the entire ocean was anoxic.*  
 102 *For interpretation of each data set, and relevant references, see discussion in the text. C.*  
 103 *Proxy inferences for global marine oxygenation. D. Modelled atmospheric O<sub>2</sub> (PAL). E. Proxy*  
 104 *inferences for atmospheric O<sub>2</sub>.*



105  
 106 **Figure 2: Geochemical data for local–regional redox proxies from 850–250 Ma.** Data (open  
 107 circles) for Fe speciation from shales<sup>14</sup>, I/Ca ratios in carbonate rocks<sup>10,27–29</sup>, Ce anomalies in  
 108 carbonate rocks<sup>30–32</sup> and Fe<sup>2+</sup>/ΣFe ratios of seafloor basalts<sup>15</sup>. The average (solid line) and an  
 109 error window of 1 standard deviation (shaded region) is shown for time bins 850–580, 580–  
 110 420 and 420–250 Ma.

111

112 *I/Ca ratios:*

113 Iodine to calcium ratios in carbonate rocks reflect local water column redox conditions.

114 Since the reduction of iodate ( $\text{IO}_3^-$ ) to iodide ( $\text{I}^-$ ) has a relatively high reduction potential, the

115 *I/Ca* proxy is sensitive to intermediate redox conditions, from hypoxic ( $<70\text{--}100\ \mu\text{M O}_2$ ) to

116 suboxic (manganous – nitrogenous conditions)<sup>33</sup> (Table 1). Iodate is incorporated into

117 carbonate rocks, and so *I/Ca* ratios reflect the oxidised iodate concentration in the local

118 water column at the depth of carbonate formation, which varies with the concentration of

119 oxygen in surface waters and the depth of the top of the OMZ<sup>10</sup>. Due to the slow kinetics of

120 iodide oxidation, water masses with fluctuating redox conditions, or anoxia nearby, may

121 retain a low iodate signature, biasing primary signatures towards anoxic conditions. In

122 addition, diagenesis can reduce the *I/Ca* ratio, but not increase it, systematically biasing the

123 rock record towards anoxic conditions<sup>27</sup>.

124

125 *I/Ca* data span a large range at any given location, but if there are sufficient data, then an

126 increase in the maximum *I/Ca* may indicate oxygenation. Long term compilations reveal

127 variable but low *I/Ca* across the Neoproterozoic and Early Palaeozoic<sup>27</sup> (Figure 2), with

128 notable peaks during the Bitter Springs ( $\sim 810\text{--}800\ \text{Ma}$ )<sup>29</sup> and the Shuram excursion ( $\sim 560$

129  $\text{Ma}$ )<sup>27,34</sup>. *I/Ca* ratios show a significant peak in the Devonian, between  $\sim 400$  and  $\sim 350\ \text{Ma}$ ,

130 but a return to lower values in the Carboniferous and Permian (Figure 1 and 2)<sup>10</sup>. There is no

131 permanent change towards higher *I/Ca* ratios until the early Mesozoic. The maximum *I/Ca*

132 recorded in any given time window may evolve as more data are collected.

133

134 *Ce anomalies*

135 Negative Ce anomalies in rare earth element patterns are indicative of locally oxic water  
136 column conditions. Under oxidising conditions, Ce(III) is oxidised to Ce(IV) on the surface of  
137 Mn (oxyhydr)oxide minerals, resulting in relative depletion in shale-normalised seawater Ce  
138 concentrations compared with the other rare earth elements. The generation of Ce  
139 anomalies requires oxidation of Mn and Ce, both of which have relatively high reduction  
140 potentials (+1.23 mV and +1.44 mV, respectively). Therefore, Ce anomalies are responsive  
141 to the onset of manganoous conditions, which may overlap with low oxygen concentrations  
142 (<10  $\mu$ M). Ce anomalies can respond to redox changes over meter scales<sup>35</sup>, although in the  
143 open ocean, local signals may be overprinted by basin-wide signals due to slow kinetics<sup>30</sup>  
144 (Table 1). The magnitude of any Ce anomaly may correspond to the concentration of oxygen  
145 or the thickness of the oxic layer, but can also be influenced by other factors such as local  
146 Mn oxide fluxes<sup>36</sup>. Rare earth elements, and associated Ce anomalies, substitute for Ca<sup>2+</sup> in  
147 the carbonate mineral lattice, and as such, can faithfully record seawater REE at the site of  
148 carbonate formation, and are relatively robust to diagenesis and even dolomitisation<sup>31,37</sup>.

149

150 A progressive increase in the magnitude of the Ce anomaly after 551 Ma in carbonate rocks  
151 from South China was interpreted to record an increase in oxygen levels in the shallow  
152 marine environment during the late Ediacaran Period<sup>22</sup>. However, reducing signals have  
153 since been recorded in contemporaneous rocks from the Nama Group, Namibia<sup>32</sup>,  
154 suggesting oxygenation was not a global phenomenon. Further, long term compilations of  
155 Ce anomaly data from eighteen formations show no significant change until the Late  
156 Devonian (~383 Ma; Figures 1 and 2)<sup>30</sup>. However, this broad compilation includes large  
157 sample gaps. For example, there is only one sample between ~600 Ma and ~550 Ma.

158

159 *Fe<sup>3+</sup>/ΣFe ratio of submarine basalts*

160 As oxygenated water circulates through seafloor basalts, reduced iron is oxidised to Fe<sup>3+</sup>.

161 Therefore, the Fe<sup>3+</sup>/ΣFe ratio of submarine basalts varies with the magnitude of

162 hydrothermal fluxes and with the oxygen content of bottom waters. As such, seafloor

163 basalts, preserved as ophiolites, can provide a direct record of deep water oxygen

164 concentrations (Table 1). Metamorphism acts to reduce Fe<sup>3+</sup>, and so could systematically

165 bias the Fe<sup>3+</sup>/ΣFe ratio towards lower values.

166

167 Long term compilations of Fe<sup>3+</sup>/ΣFe data show no significant change across the Archean and

168 Proterozoic (Archean = 0.20 ± 0.04; Palaeo–Mesoproterozoic = 0.26 ± 0.02; Neoproterozoic

169 = 0.26 ± 0.05), but a progressive increase across the Early Palaeozoic (0.34 ± 0.08), Late

170 Palaeozoic (0.47 ± 0.10) and Mesozoic–Cenozoic (0.58 ± 0.11) (Figure 2)<sup>15</sup>. This indicates a

171 progressive increase in oxygen content of the deep ocean from 11 ± 17 μmolkg<sup>-1</sup> in the

172 Neoproterozoic, to 29 ± 29 μmolkg<sup>-1</sup> in the Early Palaeozoic, 55 ± 42 μmolkg<sup>-1</sup> in the Late

173 Palaeozoic, and 80 ± 53 μmolkg<sup>-1</sup> in the Mesozoic–Cenozoic (Figure 1). Due to the

174 distribution of rare ophiolites in the geological record, there are large gaps where no data

175 are available, as well as large uncertainties in the age of some samples. For example, there

176 are no data between 736 ± 1.7 Ma and 554.5 ± 136.5 Ma. In the Stolper and Keller (2018)

177 study, the Neoproterozoic time bin is dominated by samples >700 Ma, but samples between

178 555 and 541 are within range of the Early Palaeozoic average (this is reflected in Figure 1).

179

180 *Red beds:*

181 The distribution of iron rich rocks through the geological record may reflect ocean redox

182 dynamics and Fe<sup>2+</sup> concentrations<sup>13</sup>. Iron formation requires Fe<sup>2+</sup> concentrations >50μM,

183 whereas marine red beds, which are thinner and have lower %Fe, only require >4 nM. Major  
184 periods of marine red bed deposition occurred in the mid-Ediacaran, Cambrian, and Late  
185 Devonian, with a possible event in the late Silurian<sup>13</sup> (blue on Figure 1). These sporadic  
186 events indicate lower deep water Fe concentrations following anoxic events, which could be  
187 consistent with more oxygenated deep oceans. This record is biased towards preserved  
188 shelf sediments, and may evolve if more examples are documented.

189

## 190 **2.2 Global Marine Geochemical Proxies**

### 191 *U isotopes:*

192 The uranium isotope ratio of seawater ( $\delta^{238}\text{U}$ ) is sensitive to the global proportion of  
193 seafloor overlain by anoxic bottom waters. During reduction of soluble U(VI) to insoluble  
194 U(IV) under anoxic conditions, sedimentary U(IV) is enriched in  $^{238}\text{U}$ , leaving seawater  
195 depleted in  $^{238}\text{U}$ . Therefore, when the anoxic sink expands, seawater  $\delta^{238}\text{U}$  decreases, and  
196 this signal can be preserved in carbonates. Organic-rich mudrocks also track changes in  
197 seawater  $\delta^{238}\text{U}$ , but the signal is offset by a variable local fractionation factor<sup>38</sup> (Table 1).  
198  $\delta^{238}\text{U}$  data can be used to calculate the proportion of anoxic seafloor, although these  
199 estimates rely on several calibration factors that were determined in modern lakes (e.g., the  
200 Black Sea<sup>39</sup>). In particular, the calculations are sensitive to the isotope fractionation during U  
201 reduction, but more work is needed to explore how this varies under euxinic and anoxic  
202 ferruginous conditions. Above ~20% seafloor anoxia, the proxy begins to saturate<sup>40</sup>, and  
203 large changes in the proportion of seafloor anoxia only translate into small changes in  $\delta^{238}\text{U}$ .  
204 These small changes are within the error introduced by diagenesis<sup>41</sup>, which can result in  
205 positive  $\delta^{238}\text{U}$  offsets of <0.3%.

206

207 Uranium isotope data are available for parts of the Neoproterozoic–Cambrian record (the  
208 post-Sturtian interval, and ~560 to ~510 Ma). These data show large oscillations between  
209 high, modern-like  $\delta^{238}\text{U}$ , and very low  $\delta^{238}\text{U}$ , suggesting that long term anoxia was  
210 punctuated by ocean oxygenation events at ~660, ~560, ~540 and ~520 Ma (Figure  
211 1)<sup>9,18,19,40,42,43</sup>. Some of these oscillations are confirmed by multiple studies in different  
212 basins<sup>9,18,19</sup>. Short-term switches towards anoxic conditions are recorded ~497 Ma<sup>44</sup> and 372  
213 Ma<sup>45</sup>. Placing  $\delta^{238}\text{U}$  into a quantitative model suggests seafloor anoxia oscillated from >30%  
214 during periods of quiescence, to <1% during oxygenation events<sup>18</sup>.

215

216 *Mo isotopes:*

217 High  $\delta^{98}\text{Mo}$  values preserved in shales indicate globally widespread oxic conditions, under  
218 which large negative isotope fractionations occur during adsorption of Mo onto Mn oxides,  
219 leaving seawater enriched (Table 1). In contrast, under euxinic conditions, Mo is rapidly and  
220 quantitatively removed. Since all known sedimentary Mo sinks have a  $\delta^{98}\text{Mo}$  below  
221 contemporaneous seawater,  $\delta^{98}\text{Mo}$  measurements only provide a minimum constraint on  
222  $\delta^{98}\text{Mo}_{\text{sw}}$ . Further, interpretations of sedimentary  $\delta^{98}\text{Mo}$  rely on independent proxy evidence  
223 for local redox conditions. Changes in  $\delta^{98}\text{Mo}$  could also result from a switch from euxinic to  
224 ferruginous anoxia, with no overall increase in oxygenated waters.

225

226 Pulses in  $\delta^{98}\text{Mo}$  are recorded in between ~550 and ~520 Ma, each one reaching  
227 progressively higher  $\delta^{98}\text{Mo}$  maxima<sup>6</sup>. This was interpreted to indicate progressive marine  
228 oxygenation across the Cambrian, but the data contain a lot of scatter, and could also be  
229 consistent with discrete oxygenation pulses at ~552, ~540, ~530 and ~521 Ma (Figure 1)<sup>6,7,9</sup>.  
230 Distinguishing between these two scenarios is difficult because the rarity of black shales

231 deposited under fully euxinic conditions limits the resolution of the record. The magnitude  
232 of  $\delta^{98}\text{Mo}$  enrichments increases through time, suggesting each oxygenation event was more  
233 significant than the last<sup>6</sup>.  $\delta^{98}\text{Mo}$  reaches stable, modern-like levels between the mid-Silurian  
234 and mid-Devonian (~430–390 Ma)<sup>7</sup>. Modelling calculations suggest that oxygenation events  
235 in the Neoproterozoic were limited (33% oxic seafloor)<sup>6,7</sup>, but reached >97% oxic seafloor by  
236 ~520 Ma, although many of the parameters in these models are poorly constrained.

237

#### 238 *Redox sensitive elements:*

239 Because Mo is scavenged from seawater under euxinic conditions, and V, U, Re and Cr are  
240 scavenged under ferruginous conditions, an increase in the concentration of redox sensitive  
241 elements (RSE) in seawater can indicate the global retreat of anoxic sinks. RSE  
242 concentrations in shales are controlled by the size of the global RSE reservoir and an  
243 enrichment factor, which varies with the local redox conditions. RSE concentrations are  
244 commonly analysed in sediments where there is independent evidence for local euxinia, to  
245 ensure a consistent local enrichment factor, meaning any enrichments in RSE can be  
246 attributed to an expanded global marine RSE reservoir (Table 1). RSE data typically show  
247 large amounts of scatter, but an increase in the average or maximum concentration can be  
248 interpreted as evidence for an increase in the area of oxic seafloor.

249

250 Long term compilations appeared to show an abrupt increase in Mo, V and U concentrations  
251 between 663 and 551 Ma<sup>3,46</sup>, interpreted to mark widespread oxygenation of the oceans<sup>2</sup>. A  
252 recent re-analysis of the U record shows that there is a statistically significant increase in  
253 average U concentrations between the Cambrian–Silurian and Devonian–Permian,  
254 suggesting any step change towards more permanently oxygenated oceans occurred in the

255 Palaeozoic (Figure 1)<sup>14,46</sup>. The precise timing of any change will depend on the positions of  
256 relatively long timescale bins used for data analysis. However, a more complete  
257 stratigraphic record with higher sampling density, from a demonstrably open ocean section  
258 in Wuhe, South China, has revealed pulses of RSE enrichment at regular intervals,  
259 representing ocean oxygenation events at ~635, ~580, ~560, ~540, ~530 and ~522 Ma  
260 (Figure 1)<sup>17</sup>. Similar enrichments are observed in other sections located on different cratons,  
261 suggesting a truly global signal<sup>7,20,21</sup>. In between these oxygenation events, the widespread  
262 anoxia that characterises much of the Proterozoic returns. Modelling efforts suggest that  
263 relatively limited seafloor euxinia (1–10%) and more extensive seafloor anoxia (>30–40%)  
264 are needed to crash the global Mo and Cr reservoirs, respectively<sup>47</sup>.

265

266 *Se isotopes:*

267 Se isotopes ( $\delta^{82}\text{Se}$ ) in marine shales are a novel tracer for ocean–atmosphere oxygenation.  
268 Se has a reduction potential between S(–II)/S(IV) and Fe(III)/Fe(II), and a relatively short  
269 marine residence time (1,100–26,000 years)<sup>48</sup>. During oxyanion ( $\text{SeO}_x^{2-}$ ) reduction under  
270 anoxic conditions, isotopically light Se is sequestered into the sediments, driving surface  
271 waters isotopically heavy. In addition, an increase in the size of the  $\text{SeO}_x^{2-}$  reservoir  
272 correlates with larger fractionations in locally suboxic sediments (Table 1). Sediments  
273 deposited in oxic open oceans, or below well connected OMZs, have lower  $\delta^{82}\text{Se}$  than those  
274 from restricted anoxic basins, due to the larger  $\text{SeO}_x^{2-}$  reservoir.  $\delta^{82}\text{Se}$  yields insight into the  
275 local water column redox conditions, with an additional global control. The signal may be  
276 further complicated by variations in riverine input, locally enhanced productivity, or basin  
277 restriction.

278

279 A progressive decrease in  $\delta^{82}\text{Se}$  is recorded in shales across the Ediacaran, reaching a  
280 minimum around the end of the Ediacaran Period<sup>12</sup>. For the pre-Gaskiers record, the signal  
281 is confirmed in multiple sections, suggesting a global control. This is probably a reflection of  
282 an increasing  $\text{SeO}_x^{2-}$  reservoir, which could reflect ocean oxygenation. Overall, the record is  
283 difficult to interpret, but suggests a slow but steady shift from fully anoxic to fully oxic deep  
284 waters between  $\sim 750$  and  $\sim 540$  Ma.

285

286 *S isotopes:*

287 Under euxinic conditions, microbial sulfate reduction converts sulfate ( $\text{SO}_4^{2-}$ ) into sulfide  
288 ( $\text{HS}^-$ ), which may be buried as pyrite. The  $\delta^{34}\text{S}$  of seawater sulfate is sensitive to the global  
289 pyrite burial flux, and the isotope fractionation associated with that pyrite burial. Both of  
290 these parameters are closely tied to ocean–atmosphere redox (Table 1). The  $\delta^{34}\text{S}$  signature  
291 of seawater is complex<sup>49</sup>, but higher  $\delta^{34}\text{S}_{\text{SO}_4}$  could indicate enhanced pyrite burial, which  
292 may be driven by expanded euxinia. Large offsets between  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{34}\text{S}_{\text{pyr}}$  ( $\Delta^{34}\text{S}_{\text{SO}_4\text{-pyr}}$ )  
293 have been interpreted to result from a larger marine sulfate reservoir, as well as complex  
294 sulfur cycling associated with oxidative side of the S cycle, both of which are associated with  
295 higher oxygen levels. At modern marine sulfate concentrations, the  $\delta^{34}\text{S}$  of seawater should  
296 be globally homogeneous, and is preserved in carbonate rocks and evaporites.

297

298 Sedimentary records shows a progressive increase in  $\Delta^{34}\text{S}_{\text{SO}_4\text{-pyr}}$  across the Ediacaran (635–  
299  $\sim 550$  Ma)<sup>8</sup>, interpreted to represent an increase in the marine sulfate reservoir, and then  
300 the onset of oxidative sulfur cycling. The  $\Delta^{34}\text{S}_{\text{SO}_4\text{-pyr}}$  decreases again in the late Ediacaran  
301 ( $\sim 550$  Ma), along with an increase in  $\delta^{34}\text{S}_{\text{SO}_4}$ , suggesting increased pyrite burial and a return  
302 to anoxia<sup>50</sup>. However, subsequent work has questioned the link between  $\Delta^{34}\text{S}_{\text{SO}_4\text{-pyr}}$  and

303 oxidative sulfur cycling<sup>51</sup>. A series of rapid oscillations in  $\delta^{34}\text{S}_{\text{SO}_4}$  are recorded 524–512 Ma<sup>16</sup>,  
304 coincident with excursions in with  $\delta^{13}\text{C}_{\text{carb}}$ , where the rising limbs are associated with  
305 periods of ocean anoxia and increased pyrite burial. This increase in net pyrite burial would  
306 produce a pulse of atmospheric oxygen, in turn driving anoxia from the shelf. Further  $\delta^{34}\text{S}_{\text{SO}_4}$   
307 oscillation are recorded ~500 Ma<sup>44</sup>. Sulfur isotopes therefore support dynamic redox  
308 conditions into the Cambrian and beyond.

309

### 310 **2.3 Constraints on atmospheric oxygen**

#### 311 *Cr isotopes*

312 The oxidation and reduction of Cr between Cr(III) and Cr(VI) results in large fractionations.  
313 Cr oxidation occurs through dissolution of Cr(III) in soils and reaction with Mn oxides, the  
314 presence of which is linked to free O<sub>2</sub>. This yields dissolved Cr(VI) species ( $\text{CrO}_4^{2-}$  and  $\text{HCrO}_4^-$   
315 ) that are more soluble, and enriched in the heavy isotope, compared with Cr(III). Therefore,  
316 under reducing conditions, the marine Cr record in shales and ironstones will be dominated  
317 by unfractionated crustal Cr(III), whereas under an oxidising atmosphere, the Cr record will  
318 be isotopically enriched.

319

320 The long term  $\delta^{53}\text{Cr}$  record shows a marked enrichment between 800 and 750 Ma<sup>11</sup>,  
321 recorded in both shales and ironstones, and interpreted to indicate a rise in atmospheric O<sub>2</sub>  
322 concentrations. Although the pre-800 record is dominated by low  $\delta^{53}\text{Cr}$ , isolated examples  
323 of  $^{53}\text{Cr}$  enrichments have been recorded<sup>52</sup>. Cr(III) oxidation during weathering is dependent  
324 on Mn oxide availability. Quantitative modelling suggests Mn oxide formation occurs at low  
325 O<sub>2</sub> (>0.1–1% PAL), providing a maximum constraint on pre-800 Ma atmosphere<sup>11</sup>, and  
326 suggesting a modest increase in atmospheric O<sub>2</sub> around 800–750 Ma.

327

328 *Wildfire record*

329 Wildfires can only be sustained when atmospheric oxygen levels are high (>15–17%)<sup>53</sup>.

330 Charcoal, the geological expression of palaeo-wildfires, is present in the geological record

331 from the latest Silurian onwards<sup>54</sup>. Charcoal is low in abundance across the Silurian and

332 Devonian, but increases by 1–2 orders of magnitude in the late Devonian<sup>55</sup>. This suggests

333 oxygen crossed a critical threshold in the Late Silurian (>15%), but rose further in the Late

334 Devonian (>17%). Wildfires are dependent on the presence of land plants, which evolved

335 ~470 Ma, so the charcoal record cannot constrain pre-Ordovician pO<sub>2</sub>.

336

337

338 **3. Reconciling proxy records**

339 Direct proxies for atmospheric oxygen are scarce. Chromium isotopic fractionations indicate

340 that O<sub>2</sub> rose above 0.1–1% of present atmospheric levels (PAL) at around 800 Ma<sup>11</sup>,

341 however earlier evidence for fractionation of chromium has been recorded<sup>52</sup>. More certain

342 is a rise in O<sub>2</sub> to >70% PAL during the Late Silurian, and a final rise towards modern levels in

343 the Devonian (>80% PAL or above)<sup>55,56</sup>. Regardless of atmospheric oxygen concentrations,

344 substantial spatial and temporal variability is expected in marine redox conditions, as water

345 column O<sub>2</sub> is controlled by a balance between the oxygen supply and its utilization during

346 remineralization. Modelling calculations suggest that widespread deep ocean oxygenation

347 requires atmospheric oxygen to exceed 30–40% PAL, but this depends on the availability of

348 the limiting nutrient phosphate<sup>57</sup>, and on the model itself. That said, to first order, deep

349 water oxygenation would be expected to track a substantial rise in atmospheric oxygen

350 levels.

351

352 Some global marine geochemical proxies record a permanent change towards widespread  
353 oxygenation in the late Palaeozoic, including  $\delta^{98}\text{Mo}$  and U enrichments<sup>7,14,46</sup>. Similarly,  
354 compilations of local marine redox proxies don't detect any statistically significant change in  
355 oxygen availability across the Neoproterozoic, and instead pinpoint widespread marine  
356 oxygenation later, in the Late Palaeozoic–Mesozoic: post-Ordovician for Fe speciation<sup>14</sup>,  
357 Late Devonian for Ce anomalies<sup>30</sup>, Late Palaeozoic for  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios<sup>15</sup>, and Early Devonian  
358 for I/Ca<sup>10</sup>. There is some variability in the precise timing recorded by each proxy, which may  
359 be accounted for by their different sensitivity to the spatial extent or location of anoxia, or  
360 to increasing redox state. More importantly, the timing of oxygenation in long term data  
361 compilations is highly sensitive to sampling density as well as the boundaries of data bins.  
362 For example,  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio data are necessarily sparse as they are derived from rare  
363 ophiolites. Therefore, these techniques can only be used to make broad comparisons  
364 between, e.g., the Early Palaeozoic and Late Palaeozoic. Four compilations of local proxy  
365 data, re-analysed using consistent time bins, all show a significant increase in oxygenation in  
366 the period 420–250 Ma compared with 580–420 Ma (Figure 2).

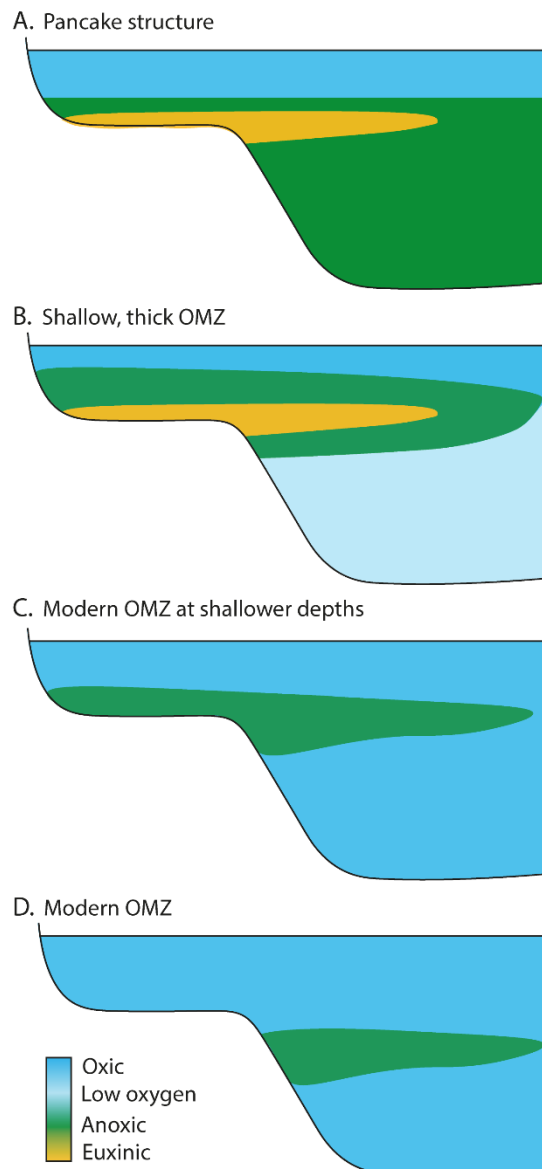
367

368 Broadly anoxic Neoproterozoic–Early Palaeozoic oceans could manifest as oxic surface  
369 waters overlying fully anoxic deep waters in a 'pancake' structure (Figure 3a), or as shallow,  
370 expanded OMZs (Figure 3b and c). A four dimensional transect of local redox conditions  
371 across a shelf suggests that OMZ-like structures were established by the Cambrian Period<sup>58</sup>,  
372 implying that the deep ocean contained low levels of oxygen. This is consistent with  
373  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios<sup>15</sup> and the marine red bed record<sup>13</sup>, which support low levels of oxygen in

374 deep waters from the mid-Ediacaran onwards. A shallower OMZ could be a reflection of  
375 lower atmospheric oxygen levels, but could also result from differences in carbon cycling.  
376

377 If there were indeed mildly oxidising conditions in the deep ocean, then how do we  
378 reconcile this with global redox proxies that suggest widespread marine anoxia? Global  
379 redox proxies tend to record the percentage of seafloor, globally, that is overlain by anoxic  
380 bottom waters, but don't provide insight into the location of those anoxic waters. This is  
381 further complicated by the lack of information available on marine productivity, sinking  
382 fluxes and ocean circulation, which are key controls on OMZ characteristics. Shallowing of  
383 oxygen minimum zones can result in a much larger contact area between anoxic waters and  
384 the continental shelf, translating into a larger area of anoxic seafloor, despite no change in  
385 the thickness of the OMZ<sup>59</sup> (Figure 3c and 3d). If the OMZ also expanded in thickness, the  
386 combined effect could result in the estimated >10–30% seafloor anoxia and >1% seafloor  
387 euxinia required to generate anoxic  $\delta^{98}\text{Mo}$ ,  $\delta^{238}\text{U}$  and U-enrichment signals (Figure 3b).

388 Furthermore, if bottom waters in the deep ocean were oxic, but contained only low levels of  
389 oxygen (<10  $\mu\text{M}$ ), then shallow pore waters would be commonly driven anoxic, which may  
390 further contribute to anoxic draw down of RSE such as Mo and U.



391

392

**Figure 3. Cartoon showing various possible redox structures for early oceans.**

393

394 Although large areas of the seafloor remained anoxic or contained only low levels of oxygen

395 through the Neoproterozoic–Lower Palaeozoic, some proxy systems suggest conditions

396 were dynamic, with brief ocean oxygenation events (OOEs). Some OOEs are recorded

397 independently by multiple proxy systems. For example, the transition back towards anoxic

398 conditions following the ~550 Ma OOE is recorded by  $\delta^{98}\text{Mo}$ ,  $\delta^{238}\text{U}$ , RSE enrichments, I/Ca

399 ratios and  $\delta^{34}\text{S}$  (Figure 1)<sup>8,9,17,18,27,50</sup>. In contrast, OOEs are not detected in any compilations

400 of local proxy data. For I/Ca ratio and Ce anomaly data, this is likely because sample  
401 coverage is too sparse to detect them. For Fe speciation or  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio data, OOE would  
402 not be detected as data are binned into periods orders of magnitude longer than the  
403 duration of OOE, so OOE are averaged out or not sampled. Therefore, global redox  
404 proxies, analysed in continuous, high resolution sections, detect variability that can be  
405 missed by compilations of local redox proxies.

406

#### 407 **4. Modelling the long-term redox transition**

408 Global biogeochemical models can be used to evaluate the processes which have caused  
409 the observed oxygenation pattern. The COPSE model<sup>60</sup> is a non-dimensional system (or 'box  
410 model'), which computes the operation of the global C-O-P-S cycles over geological  
411 timescales, and is based on the pioneering GEOCARB models<sup>61,62</sup>. Like GEOCARB, the key  
412 considerations for COPSE are the global weathering, burial and degassing processes that  
413 control the transfer of key species between the hydrosphere and the crust. The long-term  
414  $\text{O}_2$  sources are burial of either organic carbon or pyrite sulfur in sediments (removal of a  
415 reductant leads to net oxygenation), and the  $\text{O}_2$  sinks are the uplift and weathering, or  
416 subduction and degassing, of these reduced species which consumes  $\text{O}_2$ . Importantly,  
417 COPSE differs from the GEOCARB models in that it is a 'forwards' model, meaning that it  
418 computes all processes via an internally-consistent set of biogeochemical rules<sup>63,64</sup>, rather  
419 than seeking to infer them directly from the geological record. This means that COPSE can  
420 produce estimates of key geochemical proxies such as carbonate  $\delta^{13}\text{C}$ , sulfate  $\delta^{34}\text{S}$  and  
421 strontium  $^{87}\text{Sr}/^{86}\text{Sr}$ , which are then used to test the 'skill' of the model by comparing to  
422 geological data.

423

424 The model is subject to ‘external forcings’: the rate of tectonic CO<sub>2</sub> input, continental  
425 uplift and paleogeography, exposed lithological classes, and a variety of switches that  
426 represent the evolution of different modes of life which affect global biogeochemistry.  
427 Recent reviews are available that describe the latest version of the model<sup>65,66</sup>. Originally  
428 COPSE was built for reconstructing the Phanerozoic Earth system, but in the last decade  
429 there have been many extensions to apply the model to the late Precambrian. These  
430 extensions have tended to focus on single events such as snowball Earth termination<sup>67</sup> or  
431 the (~580 Ma) Shuram negative carbon isotope excursion<sup>68</sup>. We now bring together the key  
432 modifications of the model to produce a complete suite of simulations over the  
433 Neoproterozoic and Paleozoic (see supplementary material for full explanation of model  
434 parameters and differential equations).

435

436 We begin from the model of Mills et al.<sup>66</sup>, which extended the latest major model  
437 release<sup>65</sup> by updating the rates of CO<sub>2</sub> degassing and tectonic uplift with new estimates, as  
438 well as revising the link between global climate and chemical weathering rates, informed by  
439 Phanerozoic temperature and CO<sub>2</sub> proxies. We then add a function for the evolution of  
440 bioturbation during the early Cambrian<sup>69</sup>; a function that represents input of reduced  
441 species from the mantle<sup>70</sup>; a deep ocean reservoir of dissolved organic carbon<sup>68</sup> and an  
442 uplift-weathering event of evaporite sulfate coincident with the Shuram negative carbon  
443 isotope anomaly<sup>68</sup>. Each of these additions has been made to the model previously in  
444 isolation and the reader is referred to the cited work for more details. To summarize:  
445 bioturbating animals are assumed to evolve by 520 Ma and are presumed to increase the  
446 re-oxidation of sedimentary organic matter, and drawdown of the nutrient phosphorus;  
447 reductant input is assumed to scale with the ridge generation rate and consumes O<sub>2</sub>; a deep

448 ocean reservoir of dissolved organic carbon (DOC) is assumed to have built up over the  
449 Precambrian and is rapidly oxidised when the deep ocean becomes oxic – driving a sharp  
450 negative carbon isotope excursion; and a large sulfate input event occurs at 580 Ma due to  
451 the uplift and weathering of Tonian-age evaporite giants. Debate continues about whether  
452 an enlarged marine DOC reservoir is required in order to explain Neoproterozoic C isotope  
453 dynamics<sup>71</sup>, and around the timing of the effects of bioturbation<sup>72</sup>. It is hoped that further  
454 analytical and modelling efforts will help to fully resolve these questions. Incorporating  
455 these mechanisms into a single consistent model is a part of this process.

456

457 Figure 1 shows the combined COPSE model predictions for atmospheric O<sub>2</sub> and seafloor  
458 anoxia over the Neoproterozoic and Paleozoic, and compares them to the proxies discussed  
459 earlier. The brown shaded area represents the boundaries of a suite of 10,000 model  
460 sensitivity analyses in which the major external forcings (uplift, degassing, lithology) are  
461 varied by  $\pm 20\%$ . There is some agreement with the proxies for atmospheric O<sub>2</sub>: COPSE  
462 predicts (far) above 0.1% PAL for the entire Neoproterozoic, a rise to >70% PAL by the  
463 Silurian, and to 100% PAL in the Devonian. This broad pattern is controlled by the evolution  
464 of land plants, which are assumed to increase the weathering delivery of the nutrient  
465 phosphate (which drives marine productivity), and also the burial of terrestrially-derived  
466 organic carbon<sup>55</sup>. Other key features of the atmospheric O<sub>2</sub> predictions are a spike between  
467 580–570 Ma, caused by uplift and weathering of evaporite sulfate which stimulates pyrite  
468 burial<sup>68</sup>, and a drop during the Cambrian coincident with the evolution of significant  
469 bioturbation, which limits organic carbon preservation<sup>69</sup>. The only area of substantial  
470 disagreement with proxies is that COPSE does not produce lower atmospheric O<sub>2</sub> before  
471 ~800 Ma, whereas the lack of fractionation in the Chromium isotope record suggests O<sub>2</sub>

472 might be below 1% PAL<sup>11</sup>. It is not currently clear how strong the constraint from the Cr  
473 isotope record is, given that fractionations have been found in several pre-800 Ma  
474 samples<sup>52</sup>, but it is also possible that a major process is still missing from COPSE, which if  
475 included, would result in lower atmospheric O<sub>2</sub>. There are several candidates here, including  
476 the lack of explicit productivity-remineralization dynamics in the ocean, or a better  
477 representation of Precambrian tectonics. Research is ongoing.

478

479 The seafloor anoxia prediction from COPSE follows the transitions in atmospheric O<sub>2</sub>,  
480 with more than 50% of the seafloor anoxic during the Neoproterozoic, and full ventilation  
481 during the Devonian. In general agreement with the proxies, there is a period of expanded  
482 oxic seafloor immediately post-Gaskiers, which then returns to almost entirely anoxic by the  
483 later Cambrian. But there are three major discrepancies between the model predictions and  
484 the proxies for seafloor anoxia. Firstly, the model does not produce any of the rapid  
485 variability attested to by the proxies (OOEs). Secondly, the model fails to reproduce longer  
486 term oxygenation surrounding the Sturtian and Marinoan glaciations. Finally, the model  
487 predicts very large anoxic seafloor areas during the later Cambrian and Ordovician, which  
488 are not directly supported by any proxies.

489

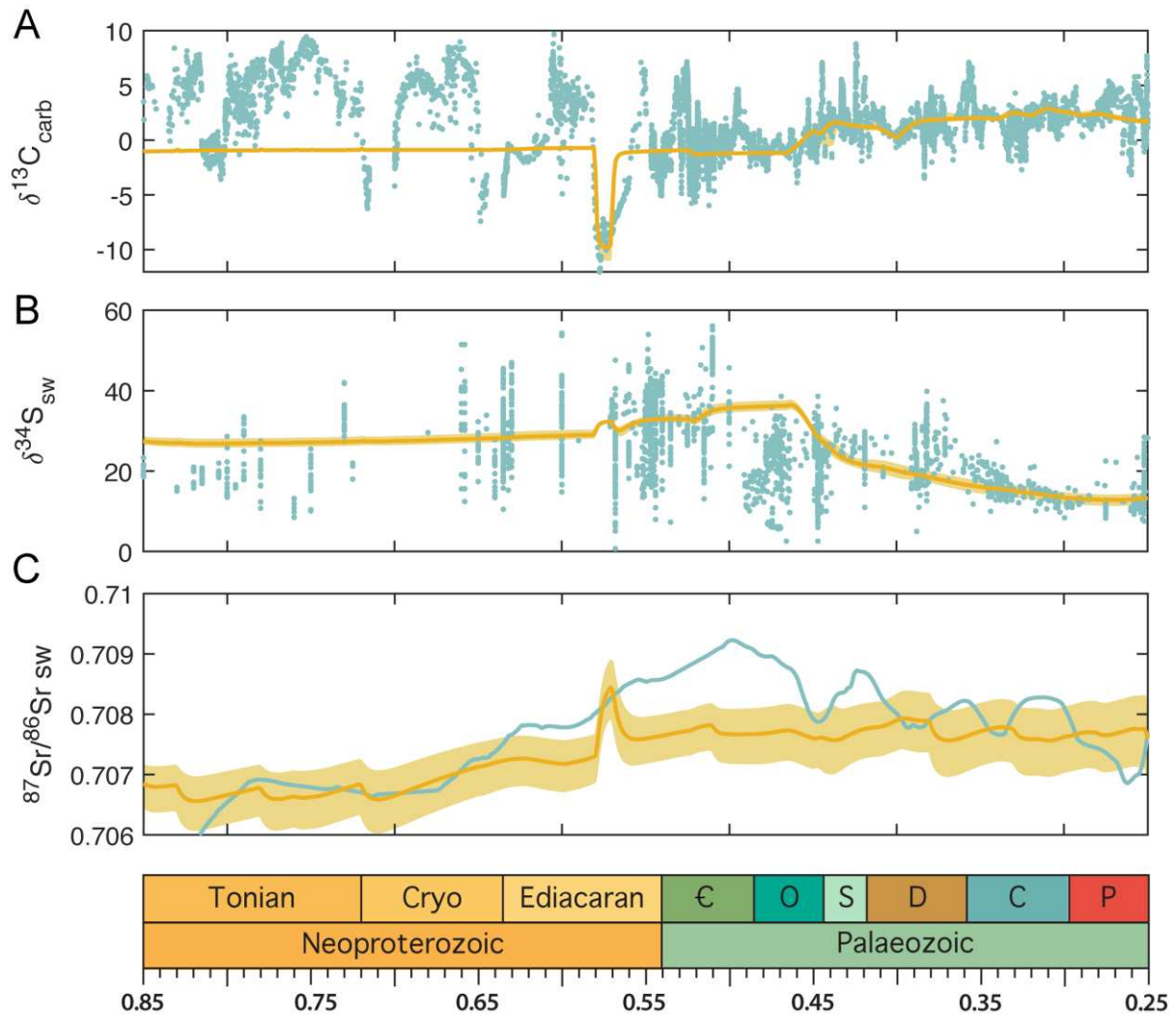
490 The inability of the COPSE model to reproduce the OOEs in the later Ediacaran and  
491 Cambrian is probably due to the model's use of a single-box ocean. In COPSE, the shelf  
492 environments and (much more vast) deeper ocean are considered to be a single system.  
493 This adds a huge amount of buffering capacity, which may not be realistic. A more  
494 sophisticated biogeochemical model<sup>73,74</sup> splits the ocean into multiple boxes representing  
495 areas of the shelf, open ocean and deep ocean. This model shows that OOEs can occur due

496 to feedbacks between the marginal phosphorus and oxygen cycles, and thus the lack of  
497 OOE in COPSE may be a consequence of limited representation of shelf environments.

498

499         The lack of any appreciable oxygen changes around the Sturtian and Marinoan  
500 glaciations is also relatively easily explained, as this version of the COPSE model still does  
501 not incorporate any of the processes associated with either the initiation or termination of  
502 these snowball Earth events. Looking to the model outputs for sedimentary isotope ratios  
503 (Figure 4), it is clear that while the Post-Gaskiers predictions are within reason, the model is  
504 missing major aspects of Earth system function pre-600 Ma, especially in the carbon cycle.  
505 Here, the large and sustained positive carbon isotope excursions that occur before the  
506 Sturtian, and during the aftermath of both glaciations, may represent increased productivity  
507 and oxygen production, which is supported by the O<sub>2</sub> proxies.

508



509

510 **Figure 4. COPSE model isotopic outputs.** *Geochemical constraints are shown in teal, and*

511 *model outputs in yellow. A.  $\delta^{13}\text{C}$  carbonate sediments. B.  $\delta^{34}\text{S}$  seawater sulfate. C.  $^{87}\text{Sr}/^{86}\text{Sr}$*

512 *carbonate sediments.*

513

514 An argument could be made that the break-up of the Rodinia supercontinent was

515 underway by  $\sim 750 \text{ Ma}$ <sup>75</sup> and led to enhanced continental weathering<sup>76</sup>, high rates of organic

516 carbon burial, and high  $\delta^{13}\text{C}$ , before driving the system towards the Sturtian snowball Earth.

517 It is then possible that  $\text{CO}_2$  rose to extremely high levels during the glaciations, meaning that

518 the super-greenhouse period that followed glaciation lasted several 10s of Myrs before  $\text{CO}_2$

519 could be reduced to background levels<sup>67</sup>. Adding these ideas into the COPSE model is

520 possible, but in order to reproduce the timing of isotope excursions, the weathering  
521 response to temperature and the effect of erosion on weathering must be very carefully  
522 chosen. Thus, we defer further investigation of the dynamics and timing of global glaciations  
523 and weathering events in the Cryogenian to spatial models with a better approximation of  
524 continental weathering (e.g., GEOCLIM<sup>77,78</sup>).

525

526         The large areas of anoxic seafloor during the Cambrian–Ordovician coincide with  
527 carbonate  $\delta^{13}\text{C}$  predictions that sit generally below the data, indicating that the model may  
528 be underestimating oxygen production (or incorrectly simulating organic C weathering<sup>79</sup>).  
529 This may be due to an over-estimate of the importance of bioturbation in re-oxidising  
530 sedimentary organic carbon and burying phosphate. New reaction-transport models of the  
531 bioturbation process will hopefully help test this.

532

### 533 **5. Assessing the role of oxygen in early animal evolution**

534 The hypothesised rise in oxygen levels across the Neoproterozoic–Palaeozoic has been  
535 repeatedly linked to the origin and radiation of early animals<sup>5–7,11,16,80</sup>. Given that oxygen is  
536 required by all extant animals, this hypothesis seems intuitive and has proved rather  
537 attractive. But a large body of recent work has shown that the role of oxygen in early animal  
538 ecosystems is more complex than previously thought<sup>18,81,82</sup>. One issue is that not all  
539 geochemical data provide the information needed to address ecologically relevant  
540 questions, such as the precise oxygen levels. Waters containing 100  $\mu\text{M}$  or 1  $\mu\text{M}$   $\text{O}_2$  would  
541 be indistinguishable in many proxy systems, but the first could host a complex ecosystem  
542 containing skeletal animals and motile predators, and the second would be largely  
543 uninhabitable<sup>83,84</sup>. These issues can be partly resolved by considering the systematics of

544 each geochemical proxy, and exactly what information they provide about the redox  
545 structure of ancient environments.  
546  
547 Minimum oxygen levels are necessary, but not sufficient, to explain the appearance of new  
548 species or ecological traits. Simple sponge-grade animals have very low oxygen demands (1–  
549 10  $\mu\text{M}$ )<sup>81</sup>, and these requirements appear to have been met continuously in surface waters  
550 from at least 800 Ma onwards<sup>11</sup>. During the Neoproterozoic, there may have been  
551 progressive increase in the maximum dissolved  $\text{O}_2$ ; enabling the development of more  
552 aerobically demanding traits, such as motility and bioturbation. However, for most of the  
553 Ediacaran, many proxies suggest widespread anoxic deep waters<sup>18,19</sup>. Ecosystem dynamics,  
554 animal distributions, and migration patterns will be influenced by this reduction in habitable  
555 space, but clearly, early animal communities continued to thrive in shallow, well-oxygenated  
556 shelf environments where their oxygen demands were met<sup>25,32</sup>. It is therefore important to  
557 constrain the maximum  $\text{O}_2(aq)$  available in shelf environments, as well as the spatial extent  
558 of inhospitable environments.

559

560 The marine redox landscape in the Cryogenian and Ediacaran appears to have been highly  
561 dynamic. It has been suggested that OOE's could have stimulated evolution, and their  
562 frequency appears to increase in the late Ediacaran and Cambrian, coincident with an  
563 intense period of diversification<sup>17</sup>. Periods of anoxia in between OOE's could even stimulate  
564 the development of genetic diversity<sup>82</sup>. Geochemical data and model results suggest that  
565 although the Neoproterozoic redox landscape was dynamic, there was no permanent  
566 change towards stable, well-oxygenated oceans until at least the Devonian, likely assisted  
567 by the evolution of land plants<sup>7,10,14,15,30,55</sup>.

568

## 569 **6. Conclusions and future directions**

570 The proxy data are best reconciled in the following way: Atmospheric O<sub>2</sub> reached a  
571 concentration of >0.1% PAL by around ~800 Ma, and potentially earlier. Surface waters in  
572 contact with this atmosphere contained low levels of dissolved oxygen, but the deep oceans  
573 remained anoxic. Atmospheric oxygen probably rose in steps or pulses throughout the  
574 Cryogenian and Ediacaran, associated with major events such as the break-up of Rodinia,  
575 and the Sturtian, Marinoan and Gaskiers glaciations. The post-Sturtian is also marked by the  
576 first brief OOE, which continue into the Cambrian. There is some evidence for OOE  
577 magnitude increasing over time<sup>6</sup>, and a gradual rise in oxygen over the Neoproterozoic is  
578 also consistent with selenium isotope data<sup>12</sup>. By the start of the Cambrian, pO<sub>2</sub> surpassed  
579 30–40% PAL, but oxygen concentrations in much of the deep ocean remained low and the  
580 OMZ was thick and shallow. Atmospheric oxygen rose again in the Late Silurian, surpassing  
581 70% PAL, and rose to modern-like levels in the Devonian, pushing the OMZ back off the shelf  
582 and establishing modern, well-oxygenated oceans (Figure 3d). The COPSE model is unable to  
583 reproduce the full complexity revealed by geochemical data, but does capture first order  
584 patterns of atmospheric and marine oxygenation from the Ediacaran onwards, giving  
585 confidence that the behaviour we see in the proxies is reasonable. The hypothesised  
586 Neoproterozoic Oxygenation Event (NOE) would be more accurately described as a  
587 Neoproterozoic Oxygenation Window (NOW), featuring dynamic pulses of oxygenation  
588 against a background of gradually rising oxygen levels, and any step change towards stable,  
589 well-oxygenated conditions appears to have been delayed until the Palaeozoic Oxygenation  
590 Event (POE).

591

592 Moving forward, we need to consider which geochemical data can best capture this  
593 transition. To understand the timing, frequency and duration of OOE's, we need to target  
594 high resolution continuous successions and analyse multiple global redox proxies. To  
595 meaningfully address questions surrounding the role of oxygen in early animal ecosystems,  
596 we need to focus on developing quantitative constraints on maximum  $O_2(aq)$ . These could  
597 include proxies for atmospheric oxygen, such as Cr isotopes, or marine redox proxies that  
598 respond to intermediate redox conditions, such as Ce anomalies and I/Ca. Detailed 4D maps  
599 across shelf ecosystems can reveal the structure of marine anoxia (i.e., pancake vs. OMZ),  
600 and be tied directly to the fossil record.

601

#### 602 **Data accessibility**

603 The geochemical data are all published elsewhere, and discussed in full in the relevant  
604 references. Differential equations and fixed parameters from the model are available in the  
605 supplementary material. All modelling code and outputs can be obtained from BJWM on  
606 request.

607

#### 608 **Author's contributions**

609 R.T. compiled proxy data, and B.J.W.M. modified the COPSE biogeochemical model. R.T. and  
610 B.J.W.M discussed the results and wrote the manuscript together.

611

#### 612 **Competing interests**

613 The authors declare no competing interests

614

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622

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