

# Possible links between extreme oxygen perturbations and the Cambrian radiation of animals

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**The role of oxygen as a driver for early animal evolution is widely debated. During the Cambrian explosion, episodic radiations of major animal phyla occurred coincident with repeated carbon isotope fluctuations. However, the driver of these isotope fluctuations and potential links to environmental oxygenation are unclear. Here, we report high-resolution carbon and sulphur isotope data for marine carbonates from the southeastern Siberian Platform that document the canonical explosive phase of the Cambrian radiation from ~524 to ~514 Myr ago. These analyses demonstrate a strong positive covariation between carbonate  $\delta^{13}\text{C}$  and carbonate-associated sulphate  $\delta^{34}\text{S}$  through five isotope cycles. Biogeochemical modelling suggests that this isotopic coupling reflects periodic oscillations in atmospheric  $\text{O}_2$  and the extent of shallow ocean oxygenation. Episodic maxima in the biodiversity of animal phyla directly coincided with these extreme oxygen perturbations. Conversely, the subsequent Botoman–Toyonian animal extinction events (~514 to ~512 Myr ago) coincided with decoupled isotope records that suggest a shrinking marine**

34 **sulphate reservoir and expanded shallow marine anoxia. We suggest that fluctuations in**  
35 **oxygen availability in the shallow marine realm exerted a primary control on the timing and**  
36 **tempo of biodiversity radiations at a crucial phase in the early history of animal life.**

37

38 The early Cambrian witnessed a dramatic diversification of animal body plans and  
39 behaviours<sup>1</sup>, as well as between-species interactions and palaeocommunity innovations<sup>2,3</sup>,  
40 ultimately leading to modern animal ecosystems. Ocean oxygenation is a commonly invoked  
41 environmental pre-requisite<sup>4-6</sup>. However, some recent studies suggest that despite probable  
42 low-oxygen conditions, the oceans exceeded requisite oxygen thresholds for simple animals,  
43 such as sponges, well before the Cambrian Period<sup>7,8</sup>. Many of the new animal body plans and  
44 lifestyles that appeared during the early Cambrian were associated with considerably higher  
45 oxygen demands<sup>9,10</sup>. Fluctuations in the maximum dissolved oxygen content of surface  
46 waters, or the extent of shallow ocean oxygenation, could therefore have played an important  
47 role in regulating the pattern of Cambrian radiations. This brings into question the role of  
48 oxygen in early animal evolution, which is exacerbated by a lack of convincing evidence for a  
49 direct link between Earth's oxygenation history and early Cambrian bio-radiations and  
50 extinctions<sup>11</sup>.

51

52 High-resolution records of the sulphur and carbon cycles, when considered in the context of  
53 the fossil record may, however, afford an opportunity to resolve potential environmental  
54 controls on early animal evolution. The marine biogeochemical sulphur and carbon cycles  
55 interconnect via their respective redox-sensitive reservoirs and fluxes. Both elements have a  
56 single, large oxidised oceanic reservoir (dissolved sulphate and inorganic carbon), the isotopic  
57 composition of which is governed by isotope fractionation during microbially-mediated  
58 reduction to sulphide (ultimately preserved as pyrite) and organic carbon. Burial of these  
59 reduced species represents the two main net sources of oxygen to the surface environment<sup>12-</sup>  
60 <sup>14</sup>, and also imprints on both the seawater sulphate sulphur isotope ( $\delta^{34}\text{S}$ , as recorded by  
61 carbonate-associated sulphate) and carbon isotope ( $\delta^{13}\text{C}$ , as recorded in carbonate) records,  
62 allowing redox changes in the surface environment to be traced through geologic time.

63

64 Here we present paired carbon and sulphur isotope data from lower Cambrian marine  
65 carbonates from the southeastern Siberian Platform. These data provide a continuous, high-

66 resolution record from Cambrian Stage 2 through to Stage 4 (~524–512 Myr ago; Fig. 1), and  
67 allow a direct assessment of potential links between ocean redox variability, atmospheric  
68 oxygenation, and the major biological events of the early Cambrian.

69

### 70 **Carbon and sulphur isotope systematics**

71 Carbonate  $\delta^{13}\text{C}$  and carbonate-associated sulphate  $\delta^{34}\text{S}$  analyses (see Methods) were  
72 primarily performed on well-preserved micritic limestone samples collected from sections  
73 along the Aldan and Lena rivers in Siberia. These sections archive a continuous and highly  
74 fossiliferous sedimentary record from a shallow, open ocean carbonate platform, and  
75 preserve over half of all fossil diversity currently known from the Cambrian radiation interval  
76 worldwide, thus providing a unique window into early Cambrian shallow marine ecosystems  
77 (see Supplementary Information for geological and palaeontological context, sample details,  
78 diagenesis evaluation and all data).

79

80 Our carbon isotope data record five cycles through Stage 2 and Stage 3 of the lower Cambrian.  
81 Positive excursions are labelled here as III to VII (Fig. 1), consistent with previous studies of  
82 the Siberian Platform<sup>15,16</sup>, but these excursions are also found elsewhere<sup>17,18</sup>. The new sulphur  
83 isotope data range from +16‰ to +36‰, demonstrating that seawater sulphate  $\delta^{34}\text{S}$  values  
84 fell from a peak (~40–45‰) during the late Ediacaran<sup>19,20</sup> to lower values by the early  
85 Cambrian. Significantly, these data also demonstrate for the first time that oceanic sulphate  
86  $\delta^{34}\text{S}$  values varied across five cycles that directly correlate with excursions in seawater  $\delta^{13}\text{C}$   
87 (Fig. 1; see Supplementary Table S1 for statistical correlation parameters). In sharp contrast  
88 to the coupled  $\delta^{13}\text{C}$ - $\delta^{34}\text{S}$  trends during the Cambrian stages 2-3, the  $\delta^{34}\text{S}$  trend across the  
89 early Cambrian Stage 4 Botoman–Toyonian extinctions (BTE; the first animal mass extinction  
90 of the Phanerozoic Eon)<sup>21,22</sup> is characterised by rapid fluctuations of large magnitude that are  
91 decoupled from the carbon isotope record (Fig. 1).

92

93 Over long timescales the excess oxidant generated by increased organic carbon burial (as  
94 indicated by higher carbonate  $\delta^{13}\text{C}$ ) may be balanced by reduced rates of pyrite burial (lower  
95 seawater sulphate  $\delta^{34}\text{S}$ ), and vice-versa, which results in relatively stable atmospheric oxygen  
96 levels and an inverse relationship between the first-order global seawater  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$

97 records<sup>23,24</sup>. However, the positive correlations we observe between  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  in  
98 Cambrian stages 2–3 likely reflect higher rates of both organic carbon and pyrite sulphur  
99 burial, which may have been associated with large distinct pulses in atmospheric oxygenation,  
100 as previously suggested for the late Cambrian SPICE (Steptoean Positive C-isotope Excursion)  
101 event<sup>14</sup>.

102

103 The rate of change of seawater sulphate sulphur isotope ratios allows us to estimate marine  
104 sulphate concentrations through this interval. Using the ‘rate method’ model<sup>25,26</sup> (see  
105 Methods for model details), and taking the average values of the lower end of the data  
106 envelopes shown in Supplementary Fig. S2, an upper estimate can be obtained for marine  
107 sulphate of ~1.0–6.6 mM for the interval from ~524 to ~514 Myr ago, followed by ~0.4–1.4  
108 mM for ~514 to 512 Myr ago. Estimates for the earlier interval are broadly consistent with  
109 previously modelled estimates of ~5–10 mM<sup>25</sup> and with fluid inclusion-based estimates of  
110 ~4.5–11 mM for the early Cambrian<sup>27</sup>, but trend toward lower values. Thus, the early  
111 Cambrian ocean was characterized by a relative paucity of sulphate, when compared with the  
112 modern ocean (~28–29 mM). Our data document a significant drawdown of more than half  
113 of the sulphate pool during early Cambrian Stage 4 (~514–512 Myr ago), coincident with the  
114 BTE.

115

### 116 **Environmental oxygenation and animal radiations**

117 The covariant behaviour of the carbon and sulphur isotope systems during Cambrian Stage 2  
118 to late Stage 3 can be explained by coupled burial of pyrite and organic carbon in marine  
119 sediments under highly productive, anoxic conditions<sup>23,28,29</sup>. Such conditions result in  
120 enhanced preservation and burial of organic carbon, and simultaneously enhance microbial  
121 sulphate reduction (MSR), leading to a high pyrite burial flux. Since pyrite and organic carbon  
122 are enriched in the lighter isotopes ( $^{32}\text{S}$  and  $^{12}\text{C}$  respectively), elevated burial fluxes on a global  
123 scale would drive the positive excursions in seawater sulphate  $\delta^{34}\text{S}$  and inorganic  $\delta^{13}\text{C}$ .

124

125 A biogeochemical box model<sup>12,30,31</sup> (see Methods for model details) was applied to test  
126 whether measured trends in S isotopes can be reproduced from the coupled burial of sulphur  
127 (as pyrite) and carbon (as organic carbon). The model infers the rate of organic carbon burial  
128 using the  $\delta^{13}\text{C}$  record and an isotopic mass balance, while the rate of pyrite burial is calculated

129 by assuming a linear relationship with organic carbon burial, allowing prediction of  $\delta^{34}\text{S}$   
130 values. Results (Fig. 2c) show that both the amplitude of positive sulphur isotope excursions  
131 and their long-term trend from ~524–514 Ma can be replicated in this way. The model  
132 assumes that the isotopic composition of carbon and sulphur inputs ( $\delta^{13}\text{C}_{\text{in}}$ ,  $\delta^{34}\text{S}_{\text{in}}$ ), and the  
133 background carbon and sulphur cycle input fluxes through weathering and metamorphism  
134 remained constant. Variations in these processes may help to explain the slight drift of the  
135 baseline  $\delta^{34}\text{S}$  in model average predictions when compared to the observed  $\delta^{34}\text{S}$  data. The  
136 shaded areas in Fig. 2 show the result of varying  $\delta^{13}\text{C}_{\text{in}}$  between -5‰ and -8‰, allowing the  
137 model to encompass most of the data. Our model requires a low concentration of sulphate in  
138 seawater (best-fit shown is 1 mM), in order to match the rate and amplitude of  $\delta^{34}\text{S}$  variations,  
139 consistent with the lower end of maximum estimates derived from the ‘rate method’ model.

140

141 The coupled carbon and sulphur isotope swings show repeated cycles of approximately 0.5–  
142 2 Myrs duration that reflect cyclical changes in the burial rates of organic carbon and pyrite,  
143 which may have been induced by episodic expansion of bottom-water anoxia/euxinia on the  
144 deeper portions of continental shelves and slopes. Ultimately, coupled burial of both reduced  
145 species in marine sediments results in the release of oxygen and other marine oxidants<sup>14</sup>.  
146 Each rising limb and the peak of the positive isotope swing thus represents enhanced net  
147 oxygen production and a pulse of atmospheric oxygen, which initially increased the extent of  
148 oxygenated waters and/or the maximum dissolved  $\text{O}_2$  in the shallower realm. Subsequently,  
149 increased ventilation of the deep ocean would have resulted in a reduced flux of reductant  
150 (organic carbon and pyrite) to seafloor sediments<sup>32</sup>. This acted to decrease the net oxidant  
151 flux, which ultimately buffered against further oxygenation. Furthermore, positive feedbacks  
152 between ocean ventilation and phosphorus retention in sediments<sup>33</sup> may have driven rapid  
153 bottom-water oxygenation, and in this case the decrease in the net oxidant flux may be  
154 substantial, leading to a re-establishment of anoxia, and potentially giving rise to the  
155 repetitive isotope cycles<sup>33</sup>.

156

157 Alternatively, isotope cyclicity might be driven by orbital forcing via climatic impacts on  
158 weathering, similar to the ~1–2 Ma “third-order” eustatic sequences of the Mesozoic and  
159 Cenozoic Eras<sup>34</sup>. However, neither the timing, duration and frequency of early Cambrian third-  
160 order sea-level fluctuations<sup>18,35</sup>, nor regional sequence stratigraphy data from Siberia<sup>36</sup>

161 (Supplementary Table S3), appear to match the isotope cycles identified in this study.  
162 Similarly, an erosional driver<sup>37</sup> for the observed isotope cycles is incompatible with their  
163 combined high amplitude and frequency, which would require very large (~3-5 fold<sup>37</sup>) changes  
164 in global erosion over geologically-short timescales. Furthermore, an erosional driver is not  
165 supported by contemporaneous changes in seawater  $^{87}\text{Sr}/^{86}\text{Sr}$ <sup>38</sup>. Fluctuations in oxygen  
166 minimum zone depth<sup>39,40</sup>, alongside biological feedbacks such as enhanced diurnal vertical  
167 migration via increased expansion of metazoan mobility<sup>41</sup>, may also have contributed to the  
168 perturbations in shallow ocean oxygenation.

169

170 To summarize, our model indicates the potential for large variations in the net atmospheric  
171 oxygen production flux ( $\pm 50\%$  around the baseline value; Fig. 2d). We propose that periods  
172 of rising  $\delta^{13}\text{C}$  represent enhanced burial of reductants under anoxic bottom-water conditions  
173 and atmospheric oxygenations, whereas the falling limbs record the decrease of reductant  
174 burial under a more widely oxygenated deep ocean. A more direct estimate of oxygen  
175 production rates can be made within our model by treating both  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  as input  
176 parameters, thus inferring rates of organic carbon and pyrite burial, respectively, for the time  
177 points where we have input information for  $\delta^{34}\text{S}$ . These estimates are shown in Fig. 3 and are  
178 similar in magnitude to those of the carbon-only model, which is to be expected as the  
179 carbon-only model produced a reasonable fit to the  $\delta^{34}\text{S}$  data.

180

181 One direct impact of pulses in atmospheric oxygenation during the early Cambrian was  
182 episodic oxygenation of marginal shallow marine environments. Shallow carbonate  
183 platforms, such as the Aldan-Lena rivers region, evidence relatively high animal origination  
184 rates and biodiversity<sup>42,43</sup>. Within shallow ocean ecosystems, biogenic reefs serve as critical  
185 evolutionary cradles and net sources of marine biodiversity<sup>44</sup>. Comparing the isotopic cycles  
186 and estimated oxygen production curves with species diversity curves for the Siberian  
187 Platform (see Supplementary information for full palaeontological data), oxygenation pulses  
188 (III, IV, V, VI, VII) generally coincided with regional biodiversity highs in either reef-building  
189 archaeocyathan or total animal species (Fig. 3). Although no significant total animal  
190 biodiversity high was associated with oxygenation pulse IV, the number of archaeocyathan  
191 species increased dramatically by ~60%. Moreover, the rising limb of isotope excursion IV  
192 coincided with the first emergence of trilobites, bivalved arthropods, and stenothecoids

193 possessing relatively thick biomineralised skeletons, as well as a geographic expansion of  
194 possible burrowing filter-feeding arthropods over the Siberian Platform, as recorded by the  
195 appearance of *Thalassinoides*-type trace fossils<sup>36</sup>. A significant increase in the inter-habitat  
196 (beta)-diversity of reefal palaeocommunities was also restricted to the IV interval in the  
197 Aldan-Lena rivers region<sup>2</sup>, reflecting a differentiation of species between assemblages, and  
198 thus ecological diversification within the shallow marine environment.

199

200 On a global scale, positive isotope excursion V appears to coincide with major radiations of  
201 large predatory arthropods and radiodonts, increased durophagy, and the first appearance of  
202 pelagic motile deuterostomes, evidenced by the Chengjiang biota and similar faunas<sup>11,45</sup>.  
203 Similarly, excursion VII coincided with a global radiation of echinoderms and archaeocyaths.  
204 The latter is revealed by the inter-regional (gamma)-diversity peak reflecting formation of  
205 numerous isolated faunal provinces<sup>2</sup>. By contrast, minor extinction events here and  
206 elsewhere appear to be associated with the negative excursions<sup>11,18,46</sup>. In the deeper ocean  
207 setting of northern Siberia and South China, multi-proxy analyses reveal broadly similar  
208 oceanic redox fluctuations<sup>4,47-49</sup>, which coincide with the positive carbon isotope excursions  
209 in the early Cambrian<sup>16,46,50</sup>. These episodic redox oscillations, evident from the  $\delta^{13}\text{C}$  record  
210 and, in places, as  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  covariance<sup>16</sup> (also see Supplementary Fig. S6 for  $\delta^{13}\text{C}$ - $\delta^{34}\text{S}$   
211 covariance from the Cambrian Stage 2 ZHUJiaqing Carbon isotope Excursion (ZHUCE) in the  
212 Xiaotan section, South China), suggest that these coupled isotope excursions record a global  
213 phenomenon. We therefore propose that perturbations to shallow ocean oxygen budgets  
214 were driven by fluctuations in atmospheric oxygen. High oxygen levels would have suited  
215 various newly evolved animal body plans and lifestyles, and so oxygen fluctuations likely  
216 resulted in episodic expansions/contractions of the habitable zone within shallow ocean  
217 ecosystems. This shallow ocean oxygen control is likely reflected in contemporaneous  
218 fluctuations of animal origination and speciation rates, and thus possibly regulated the global  
219 radiation patterns of early Cambrian animals.

220

### 221 **Expanded shallow ocean anoxia and sulphate reduction across the BTE**

222 In contrast to the coupling of carbon and sulphur isotopes during Cambrian stages 2-3, the  
223 decoupled  $\delta^{13}\text{C}$ - $\delta^{34}\text{S}$  records and unsystematic temporal fluctuations in  $\delta^{34}\text{S}$  values observed  
224 across the BTE (Fig. 1) appear to reflect a significant and persistent decline in oceanic sulphate

225 concentration (Supplementary Fig. S2). At reduced marine residence times,  $\delta^{34}\text{S}$  is more  
226 responsive to perturbations to the sulphur cycle. A fall in seawater sulphate concentration is  
227 generally attributed to enhanced evaporite deposition or widespread anoxia, and indeed,  
228 there are a number of thick evaporite deposits in the global rock record during this  
229 interval<sup>51,52</sup>. However, these evaporites are restricted to the innermost isolated basins of the  
230 Siberian Platform and the Australian part of Eastern Gondwana, and their stratigraphic  
231 distribution does not correlate with the interval of low sulphate inferred for the BTE. This  
232 suggests that anoxic/euxinic conditions likely prevailed in the shallow marine realm at this  
233 time. The expansion of shallow ocean anoxia is consistent with an observed accumulation of  
234 over  $\sim 750,000 \text{ km}^2$  of black organic-rich carbonate-rich sediments (comprising bituminous  
235 limestone, chert and argillaceous calcareous sapropelic shale) in the Sinsk Formation across  
236 the Siberian Platform, as well as enrichments in pyrite, V, As, Cr, Cu and Ni, and the presence  
237 of abundant biomarkers indicative of anaerobic bacteria as a major source of organic  
238 matter<sup>21,53</sup>. Such phenomena have previously been linked to shoaling of oxygen-depleted  
239 waters during a major marine transgression<sup>21,36</sup>, which has been suggested as the cause of  
240 the major extinction pulse of the BTE (Sinsk event; Fig. 1). Thus, while bottom-water anoxia  
241 on the deeper portions of continental shelves and slopes may have contributed to the  
242 episodic burial of reductant and oxygenation of the atmosphere and shallow oceans in  
243 Cambrian stages 2-3, shoaling of anoxic waters in Cambrian Stage 4 may have driven a mass  
244 extinction, and therefore a reduction in primary productivity and overall reductant burial.

245

#### 246 **Implications for early animal diversification**

247 Oxygenation of the early Cambrian shallow marine environment can be inferred from the  
248 coupled behaviour of the carbon and sulphur cycles. Episodic shallow ocean oxygenation  
249 corresponded to pulses of animal diversification, and so provides a plausible environmental  
250 explanation for the step-wise nature of the Cambrian radiation of animals. In the modern and  
251 ancient oceans, well-oxygenated waters are generally associated with larger body sizes,  
252 higher diversity, advanced skeletal biomineralization, and increased motility and  
253 carnivory<sup>9,10,54,55</sup>. Pulses of shallow ocean oxygenation in the early Cambrian likely expanded  
254 the global proportion of habitable marginal ocean to provide new ecological opportunities  
255 and biodiversity cradles. Similarly, the extended radiation of the Great Ordovician  
256 Biodiversification Event ( $\sim 490\text{--}450 \text{ Ma}$ ) also appears to have been facilitated by pulses in



257 atmospheric oxygenation<sup>56</sup>. A prolonged pause in biological diversification, which lasted over  
258 20 million years and was associated with recurring extinctions (BTE, SPICE-trilobite  
259 extinctions<sup>18</sup>), occurred between these two major diversification events. Environmental  
260 stress caused by the persistent development of oxygen-deficient conditions in shallow marine  
261 realms due to low net atmospheric oxygen production<sup>57</sup> is likely to have been a major  
262 contributing factor. Thus, the global extent of well-oxygenated shallow ocean habitats during  
263 the early Paleozoic, as well as the maximum dissolved oxygen content of surface waters,  
264 played a vital role in regulating the emergence and radiation of early animal life.

265

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404

405 **Acknowledgements**

406 This work was supported by the National Natural Science Foundation of China (41661134048)  
407 and Strategic Priority Research Program (B) of the Chinese Academy of Sciences  
408 (XDB18000000) to M.Z., NERC (NE/1005978/1 and NE/P013643/1) to G.A.S., University of  
409 Leeds Academic Fellowship to B.J.W.M., ERC Consolidator grant 682760 (CONTROLPASTCO2)  
410 to P.A.E.PvS, NERC (NE/N018559/1) to S.W.P., T.H. was supported by University College  
411 London Overseas Research Scholarship and the National Natural Science Foundation of China  
412 (41888101). We acknowledge G. Tarbuck and D. Hughes for assistance in the geochemical  
413 analysis. We thank T. W. Dahl, B. S. Wade, R. Newton, C. Yang and L. Yao for valuable  
414 discussions. We thank T. Algeo, B. Gill and M. Gomes for constructive comments.

415

416 **Author contributions**

417 T.H., M.Z., and G.A.S. conceived the project. G.A.S., P.A.E.PvS., B.J.W.M. and M.Z. supervised  
418 the project. M.Z., A.Y. and A.Yu.Z. collected the samples. T.H. and P.M.W. analysed the  
419 samples. A.Yu.Z. provided the fossil data. B.J.W.M. and T.H. created the models. All authors  
420 contributed to data interpretation and the writing of the manuscript.

421

422 **Competing interests**

423 The authors declare no competing interests.

424

425 **Additional information**

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427

428 **Figure captions**

429 **Fig. 1. Carbonate carbon and carbonate-associated sulphate sulphur isotope records from**  
430 **Cambrian Stage 2 to Stage 4 of Siberian Aldan-Lena rivers sections.** Regional stage  
431 subdivisions are shown next to the global subdivision plan for comparison<sup>15</sup> (F.: Fortunian  
432 Stage; N.–D.: Nemakit–Daldynian Stage; TST: Transgressive System Tract<sup>36</sup>; Fm.: Formation;  
433 A.: archaeocyaths; SSFs: small shelly fossils). Names for the positive  $\delta^{13}\text{C}$  peaks (III, IV, V, VI,  
434 VII) are consistent with those of previously suggested  $\delta^{13}\text{C}$  curves<sup>15</sup>. FAD: first appearance  
435 datum.

436

437

438 **Fig. 2. Carbon and sulphur cycle model output. a.** This model takes measured  $\delta^{13}\text{C}$  values as  
439 an input parameter. **b.** Burial rates of organic carbon ( $C_{\text{org}}$ ) are inferred from isotope mass  
440 balance and  $\delta^{13}\text{C}$  record, and burial rates of pyrite are assumed to be controlled by  
441 modelled organic matter availability. **c.** Comparison between analysed  $\delta^{34}\text{S}$  data (green  
442 curve) and simulated seawater sulphate  $\delta^{34}\text{S}$  values (pink); Dashed part of the green curve  
443 shows the sampling gap. **d.** Variations in modelled net oxygen production. For all plots, the  
444 uncertainty window represents an alteration of the  $\delta^{13}\text{C}$  values of carbon inputs between -  
445 5‰ and -8‰.

446

447

448 **Fig. 3. Animal diversity, biological events and their correlation to the isotope records and**  
449 **oxygenation pattern across Cambrian stages 2-4.** Global oxygen production is inferred from  
450 isotope mass balance modelling, using inputs of  $\delta^{13}\text{C}$  only (light shade), or  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$   
451 (dark shade). Archaeocyathan species (blue line) and total animal species (green line)  
452 diversity records are expressed as the mean number of species per sampling unit (grey box)  
453 in Siberia; OP: oxygenation pulse; BH: biodiversity high; F.: Fortunian Stage; N.–D.: Nemakit–  
454 Daldynian Stage. FAD: first appearance datum.

455

## 456 **Methods**

457 **Carbonate-associated sulphate (CAS) extraction and  $\delta^{34}\text{S}$  analysis.** Well preserved carbonate  
458 samples composed primarily of micrite were targeted for CAS extraction. Where that was not  
459 possible, few samples were selected with sparitic or dolomitic textures. Large blocks (>200 g)  
460 of carbonate rocks were cut and polished under running water to trim weathered surfaces  
461 prior to powdering. Blocks were then cut into small chips using a water-cooled, diamond  
462 tipped bench circular saw. Rock chips were ground to a fine powder (flour-like consistency,  
463 <10  $\mu\text{m}$ ) using a *Retsch*<sup>®</sup> Agate Mortar grinder. We applied a high-fidelity miniaturized CAS  
464 extraction protocol, which is an extension of two published approaches<sup>58,59</sup>. The protocol was  
465 established following tests involving twelve consecutive leaching steps on five carbonate  
466 samples from different stratigraphic horizons of the Aldan-Lena river sections and three  
467 samples from the Ediacaran Nama Group<sup>19</sup>. Approximately 10 g of the fine powder for each  
468 sample was leached in 40 ml of 10% NaCl solution for 24 hours to remove the non-CAS  
469 sulphur-bearing compounds and easily soluble sulphate. During leaching, samples were  
470 constantly agitated using a roller shaker at room temperature. Residues were rinsed in  
471 ultrapure water three times between each leach and five times after the final leach. After  
472 each leach, the leachate was retained, and the presence of sulphate was tested by adding  
473 saturated barium chloride solution and allowing three days to precipitate barite. As illustrated  
474 in Supplementary Fig. S3, the amount of sulphur removed during sequential NaCl leaching of  
475 test samples exhibited a sharp decline through multiple NaCl leaches and reached blank levels  
476 in the 3<sup>rd</sup> or 4<sup>th</sup> leachates, suggesting five leaches is sufficient for complete removal of all  
477 soluble sulphur-bearing constituents from ~10 g of carbonate powder. All five-times pre-  
478 leached carbonate samples were treated with 6 M HCl, which was added in calculated aliquots  
479 based on total HCl-leachable carbonate content. This step was completed within 30 minutes  
480 to minimise the potential for pyrite oxidation during dissolution. The insoluble residue was  
481 separated from the solution by centrifugation in 50 ml tubes followed by filtration through  
482 *VWR*<sup>®</sup> 0.2  $\mu\text{m}$  Polypropylene membrane syringe filters. Saturated barium chloride solution  
483 was then added to the filtered solution and left to precipitate within the housing of a sealed  
484 tube over three days at room temperature. Where no visible precipitate was observed after  
485 24 h, 2 mg isotopic-grade sulphur-free quartz powder was added, which served as an inert  
486 medium onto which barium sulphate could precipitate<sup>59</sup>. Each sample was centrifuged, and



487 the supernatant replaced with ultrapure water repeatedly until the pH attained neutral  
488 values. Washed samples were then dried prior to isotope analysis.  $^{34}\text{S}/^{32}\text{S}$  analysis of barium  
489 sulphate precipitates was undertaken using an *Elementar*<sup>®</sup> Pyrocube elemental analyzer  
490 linked to an *Isoprime*<sup>®</sup> 100 mass spectrometer operated in continuous flow mode at the  
491 Lancaster Environment Centre, Lancaster University. Pellets of  $\text{BaSO}_4$ , resulting from sulphate  
492 extraction with or without the addition of quartz powder, were combusted in tin capsules in  
493 the presence of excess vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) at  $1030^\circ\text{C}$  to yield  $\text{SO}_2$  for the  
494 determination of  $\delta^{34}\text{S}$ . All samples and standards were matrix matched, and values were  
495 corrected against VCDT using within-run analyses of international standards NBS-127 and SO5  
496 (assuming  $\delta^{34}\text{S}$  values of  $+20.3\text{‰}$  and  $+0.49\text{‰}$ , respectively). Within-run standard replication  
497 was below  $0.3\text{‰}$  (1sd). Procedural standard solutions of calcium sulphate precipitated as  
498 barium sulphate were used to test the integrity of the method<sup>59</sup>. These yielded  $\delta^{34}\text{S}$  values of  
499  $+2.7\text{‰}$  ( $\pm 0.3\text{‰}$ , 1sd,  $n=12$ ) compared to values of  $+3.0\text{‰}$  ( $\pm 0.3\text{‰}$ , 1sd,  $n=13$ ) for analysis of  
500 the raw calcium sulphate powder. Blank contamination associated with  $\delta^{34}\text{S}$  determination  
501 was zero.

502

#### 503 **CAS concentrations and sulphur content in NaCl leached solution.**

504 The concentration of CAS and sulphur content in each leaching step was measured in aliquots  
505 of filtered solution using a *Varian*<sup>®</sup> 720 Inductively Coupled Plasma Optical Emission  
506 Spectrometer (ICP-OES) at the London Geochemistry and Isotope Centre (LOGIC), University  
507 College London. Wavelength  $182.5\text{ nm}$  was selected to minimise interference with calcium  
508 ions, and analysis was conducted using the  $\text{N}_2$ -purging polyboost function to avoid oxygen  
509 interference in the system.

510

511 **Carbonate carbon and oxygen isotopes.** Micritic limestone was targeted for  $\delta^{13}\text{C}$  analysis.  
512 Where that was not possible, we selected a few sparitic or dolomitised samples and  
513 fossiliferous samples with skeletal components known to secrete low-Mg calcite. About 20  
514 mg of powder drilled from a rock chip was analyzed for stable C and O isotopes. Limestone  
515 samples were reacted with 100%  $\text{H}_3\text{PO}_4$  at  $25^\circ\text{C}$  for more than 12 h, and dolostone samples  
516 were reacted with 100%  $\text{H}_3\text{PO}_4$  at  $50^\circ\text{C}$  for more than 24 h. Prepared gas samples were  
517 analysed for  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  using the Chinese national standard, an Ordovician  
518 carbonate from a site near Beijing (reference number GBW04405:  $\delta^{13}\text{C} = 0.57 \pm 0.03\text{‰}$  VPDB;

519  $\delta^{18}\text{O} = -8.49 \pm 0.13\text{‰}$  VPDB). The analyses were performed using the *Finnigan*<sup>®</sup> MAT 253 mass  
520 spectrometers at the Nanjing Institute of Geology and Palaeontology, Chinese Academy of  
521 Sciences.

522

523 **Elemental analysis.** For concentrations of diagenesis-diagnostic elements, including Ca, Mg,  
524 Mn, and Sr, an aliquot of approximately 50 mg of powder was micro-drilled from a rock chip  
525 and dissolved with excess 6 M hydrochloric acid at room temperature for 12 h. The  
526 concentration of acid used here is identical to the concentration used during CAS extraction.  
527 The reaction was facilitated using an ultrasonic bath and roller shaker. After centrifugation,  
528 aliquots of the supernatant were analysed for elemental concentration using a *Varian*<sup>®</sup> 720  
529 ICP-OES at University College London. Solution standards of certified reference materials,  
530 SRM1c (argillaceous limestone) and SRM120b (Florida phosphate rock), were run at the start  
531 of the analyses along with a blank to monitor the accuracy of the bulk elemental analysis.  
532 Laboratory control solution standards were also run after every batch of 20 samples to  
533 monitor drift and precision. Analytical precision for elemental concentrations was generally  
534 better than 5%.

535

536 **'Rate method' model.** Maximum seawater sulphate concentrations are calculated using the  
537 modified 'rate method'<sup>25,26</sup>. The model was constructed based on the observed rate of change  
538 in seawater sulphate (carbonate-associated sulphate)  $\delta^{34}\text{S}$ , fractionation between oxidized  
539 (sulphate) and reduced sulphur (pyrite) reservoirs and equation (1) that connects the two  
540 parameters, where  $F_x$  represents the input and output fluxes,  $\Delta^{34}\text{S}_x$  represents isotopic  
541 difference of  $\delta^{34}\text{S}$  values between fluxes ( $Q$  = total input flux of sulphur,  $\text{SUL}$  = seawater  
542 sulphate,  $\text{PY}$  = pyrite burial,  $\text{SW}$  = seawater/sulphate deposition) and  $M_{\text{SW}}$  represents the mass  
543 of sulphate in the ocean.

$$544 \frac{d\delta^{34}\text{S}}{dt} = \frac{\left( (F_Q \times \Delta^{34}\text{S}_{Q-\text{SW}}) - (F_{\text{PY}} \times \Delta^{34}\text{S}_{\text{SUL}-\text{PY}}) \right)}{M_{\text{SW}}} \quad (1)$$

545 The maximum rates of  $\delta^{34}\text{S}$  change are attained when sulphur input flux to the ocean  
546 approaches zero ( $F_Q = 0$ ), and the standing oceanic sulphate reservoir is removed as pyrite.  
547 Equation (1) is then transformed to equation (2) to calculate the size of seawater sulphate  
548 reservoir.

$$M_{SW} = \frac{F_{PY} \times \Delta^{34}S_{SUL-PY}}{\frac{d\delta^{34}S}{dt}} \quad (2)$$

550 Because the observed rates of seawater sulphate  $\delta^{34}S$  change in a normal marine  
 551 environment should never exceed the theoretical maximum rates of change ( $d\delta^{34}S/dt$ ), the  
 552 calculation of  $M_{SW}$  using equation (2) should provide the maximum estimate of seawater  
 553 sulphate concentration. The definition of  $F_{PY}$ ,  $\Delta^{34}S_{SUL-PY}$ , and unit-conversion constants (gram  
 554 to mM) are consistent with the values applied for the long-term secular variation of seawater  
 555 sulphate concentration<sup>25</sup>.  $F_{PY} = 4 \times 10^{13} \text{ g yr}^{-1}$  is suggested for a normal marine environment.  
 556  $\Delta^{34}S_{SUL-PY} = 35\text{‰}$  is suggested for the fractionation during MSR. The variation of seawater  
 557 sulphate concentration ( $[SO_4^{2-}]$ ) between  $\sim 524$  Myr ago and  $\sim 512$  Myr ago is represented  
 558 based on a point-to-point calculation (Supplementary Fig. S2). Because the sampling density  
 559 between  $\delta^{34}S$  values is generally below 0.1 Myr (Supplementary Table S3), this study uses a  
 560 0.1 Myr gridded data smoothing curve (red line in Supplementary Fig. S2) to represent the  
 561 best estimate of seawater  $[SO_4^{2-}]$ . Besides, the maximum concentration for an individual point  
 562 could be under or overestimated due to fluctuations and anomalies in the rate of  $\delta^{34}S$   
 563 changes. To overcome this bias, the resulting  $[SO_4^{2-}]$  data are binned into 0.5 Myr bands. The  
 564 lower envelope (black dotted line in Supplementary Fig. S2) of the  $[SO_4^{2-}]$  red curve, which  
 565 links the lowest value for each band, is expected to represent the maximum rates of  $\delta^{34}S$   
 566 change and thus the theoretical estimate of maximum seawater sulphate concentration  
 567 through time.

568

569 **Coupled carbon and sulphur cycle model.** A simple model of the global carbon and sulphur  
 570 cycles was applied to explore the proposed mechanisms for isotopic variations in the system.  
 571 This follows the work of Garrels and Lerman<sup>30</sup>, Berner<sup>12</sup> and Bergman *et al.*<sup>31</sup>. The model  
 572 calculates the global rate of organic carbon burial using isotope mass balance, and then  
 573 attempts to predict the operation of the sulphur system based on the supply of organic  
 574 matter. Supplementary Fig. S4 shows the model processes as a diagram; Supplementary Table  
 575 S2 shows the model flux and parameter values. The model estimates long-term fluxes  
 576 between the ocean and sediments for both carbon and sulphur. Carbon is modelled as  $CO_2$  in  
 577 the atmosphere and ocean (A), and will be buried either as organic carbon (G) or carbonate  
 578 (C). Similarly, sulphur can exist as oceanic sulphate (S), and will be buried as pyrite (PYR) or

579 gypsum (GYP). Weathering (and metamorphism) constitutes the return flux from the  
 580 sediments to the ocean and atmosphere. We set the weathering inputs to constant values in  
 581 line with previous models<sup>12,31</sup>. We allow for around half of present total organic carbon burial  
 582 (and weathering) due to the absence of land plants, and an enhanced burial flux of pyrite  
 583 sulphur due to anoxia. The weathering rate of gypsum is held constant, but the burial rate is  
 584 adjusted so that the model maintains a constant sulphate concentration. Due to the relatively  
 585 short model timeframe relative to the residence times of the vast sedimentary reservoirs,  
 586 these reservoirs are assumed to have a fixed isotopic composition and are assumed not to  
 587 vary in size. The ocean and atmosphere reservoirs are allowed to vary in size and isotopic  
 588 composition. Organic carbon burial is calculated via isotope mass balance<sup>12,30</sup>, which uses the  
 589 total carbon input fluxes and isotopic composition of seawater ( $\delta A$ ) to calculate the required  
 590 burial rate of isotopically depleted organic carbon (equation (3)):

$$591 \quad B(G) = \frac{1}{\Delta B} \{ W(G)(\delta A - \delta G) + W(C)(\delta A - \delta C) \} \quad (3)$$

592 It is assumed that pyrite burial is governed by the supply rate of organic carbon to microbial  
 593 sulphate reducers, and therefore scales with the burial rate of organic carbon (equation (4)).  
 594 The proportionality constant (0.5) is chosen to balance pyrite weathering.

$$595 \quad B(PYR) = 0.5 B(G) \quad (4)$$

596 Variation in the ocean and atmosphere carbon is calculated as:

$$597 \quad \frac{dA}{dt} = W(G) + W(C) - B(G) - B(C) \quad (5)$$

598 Variation in ocean sulphate is calculated as:

$$599 \quad \frac{dS}{dt} = W(PYR) + W(GYP) - B(PYR) - B(GYP) \quad (6)$$

600 Variation in the isotopic composition of ocean sulphate is calculated as:

$$601 \quad \frac{d(S \times \delta S)}{dt} = W(PYR)\delta PYR + W(GYP)\delta GYP - B(PYR)(\delta S - \Delta S) \\ 602 \quad \quad \quad - B(GYP)\delta S \quad (7)$$

603 Net oxygen production flux is calculated from the burial rate of organic carbon and pyrite:

$$604 \quad FO_2 = B(G) + 2 \cdot B(PYR) \quad (8)$$

605

606 The model is solved in MATLAB using the ODE (Ordinary Differential Equation) suite. The  
 607 model broadly reproduces the duration and magnitude of fluctuations in  $\delta^{34}S$  (Fig. 2c). It also

608 predicts similar fluctuations in oxygen production (Fig. 2d). The model does not calculate the  
609 concentration of oxygen in the atmosphere and ocean, and all fluxes are assumed to be  
610 oxygen-independent. More detailed modelling, which takes into account the variation in  
611 oxygen sinks, is required to analyse the overall long-term trends in atmospheric oxygen levels.

612

613 An alternative version of the model is run in Fig. 3 that estimates pyrite burial rates directly  
614 from the  $\delta^{34}\text{S}$  record. In this version, equation (4) is replaced by equation (9), and equation  
615 (7) is not required.

$$616 \quad B(\text{PYR}) = \frac{1}{\Delta S} \{ W(\text{PYR})(\delta S - \delta \text{PYR}) + W(\text{GYP})(\delta S - \delta \text{GYP}) \} \quad (9)$$

617

618 **Total marine animal species diversity.** Supplementary Table S4 shows the distribution and  
619 diversity of total and individual animal species of Cambrian stages 2-4 of the Siberian  
620 Platform. This dataset is an upgrade of a previously published version<sup>21</sup> (see supplementary  
621 information for detailed description and source of data). Siberian biozones  
622 (archaeocyathids/trilobite) are selected as the sampling units for diversity data collection. The  
623 finalised animal diversity record is generated by plotting total species diversity against  
624 sampling units (grey boxes in Fig. 3).

625

#### 626 **Code availability.**

627 The code used to generate the Coupled carbon and sulphur cycle model results is available  
628 from the corresponding author ([T.He@leeds.ac.uk](mailto:T.He@leeds.ac.uk)) on request.

629

#### 630 **Data availability.**

631 The authors declare that data supporting the findings of this study are available within the  
632 article and Supplementary Tables S1–S5.

633

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635

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637 **References**

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