

1 Unique Neoproterozoic carbon isotope excursions sustained
2 by coupled evaporite dissolution and pyrite burial

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4 Graham A. Shields¹, Benjamin J.W. Mills², Maoyan Zhu^{3,4}, Timothy D. Raub⁵ Stuart
5 Daines⁶ & Timothy M. Lenton⁶

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7 ¹*Department of Earth Sciences, University College London, Gower Place, London, WC1E*
8 *6BT, UK*

9 ²*School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK*

10 ³*State Key Laboratory of Palaeobiology and Stratigraphy & Center for Excellence in Life*
11 *and Palaeoenvironment, Nanjing Institute of Geology and Palaeontology, Chinese Academy of*
12 *Sciences, Nanjing, 210008, China*

13 ⁴*College of Earth [and Planetary](#) Sciences, University of Chinese Academy of Sciences,*
14 *Beijing, 100049, China*

15 ⁵*School of Earth and Environmental Sciences, University of St. Andrews, KY16 9AL, UK*

16 ⁶*Global Systems Institute, University of Exeter, Exeter, EX4 4QE, UK*

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18 Correspondence and requests for materials should be addressed to G.S.

19 (g.shields@ucl.ac.uk), B.M (b.mills@leeds.ac.uk) or M.Z. (myzhu@nigpas.ac.cn)

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23 **The Neoproterozoic Era witnessed a succession of biological innovations that culminated**
24 **in diverse animal body plans and behaviours during the Ediacaran-Cambrian radiations.**
25 **Intriguingly, this interval is also marked by perturbations to the global carbon cycle, as**
26 **evidenced by extreme fluctuations in climate and carbon isotopes. The Neoproterozoic**
27 **isotope record has defied parsimonious explanation because sustained ^{12}C -enrichment**
28 **(low $\delta^{13}\text{C}$) in seawater seems to imply that substantially more oxygen was consumed by**
29 **organic carbon oxidation than could possibly have been available. We propose a solution**
30 **to this problem, in which carbon and oxygen cycles can maintain dynamic equilibrium**
31 **during negative $\delta^{13}\text{C}$ excursions when surplus oxidant is generated through bacterial**
32 **reduction of sulfate that originates from evaporite weathering. Coupling of evaporite**
33 **dissolution with pyrite burial drives a positive feedback loop whereby net oxidation of**
34 **marine organic carbon can sustain greenhouse forcing of chemical weathering, nutrient**
35 **input and ocean margin euxinia. Our proposed framework is particularly applicable to**
36 **the late Ediacaran ‘Shuram’ isotope excursion that directly preceded the emergence of**
37 **energetic metazoan metabolisms during the Ediacaran-Cambrian transition. Here we**
38 **show that non-steady state sulfate dynamics contributed to climate change, episodic ocean**
39 **oxygenation and opportunistic radiations of aerobic life during the Neoproterozoic Era.**

40

41 The Neoproterozoic Era (1000 – c.540 Ma) marks a turning point in Earth history when groups
42 of morphologically complex multicellular eukaryotes, including algae and animals, attained
43 ecological dominance, irrevocably changing Earth System dynamics¹. These biological
44 radiations took place amid fluctuating climate, including two prolonged episodes of global
45 glaciation during the Cryogenian Period (c.715 – c.660 and c.650 – c.635 Ma) and short-lived,
46 regional ice ages during the Ediacaran Period (e.g. c.580 Ma), interspersed with warmer
47 intervals. The world’s oceans also became episodically more oxygenated during the

48 Neoproterozoic with the extent of oxygenated seafloor reaching near-modern levels at times
49 during the early Cambrian². Both climate and oxygenation are regulated by Earth's long-term
50 carbon cycle, and this interval is characterised by extreme carbon isotope instability³ (Fig. 1).
51 For over 30 years⁴⁻⁷, the uniquely high amplitudes of Neoproterozoic $\delta^{13}\text{C}$ excursions have
52 defied conventional interpretation^{3,8-10}. Here we relate the largest of these anomalies to the
53 transfer of oxidant from the evaporite rock reservoir to the surface environment by coupling
54 sulfate weathering, enhanced by the tectonic amalgamation of Gondwanaland¹¹, and pyrite
55 burial.

56

57 **The negative carbon isotope anomaly problem**

58 Conventional carbon isotope mass balance is based on the principle that the isotopic
59 composition of carbon input via outgassing and weathering, and that of sedimentary carbon
60 outputs are equal on time scales of $>10^5$ years. This $\delta^{13}\text{C}$ value is considered to be unchanging
61 at -5‰, which is taken to be the average composition of crustal carbon. Because organic matter
62 is depleted in ^{13}C , and carbonate rocks precipitate in isotopic equilibrium with ambient
63 dissolved inorganic carbon (DIC), the mean $\delta^{13}\text{C}$ value of carbonate rocks and fossils can be
64 used to determine the proportion that sedimentary organic matter makes up of the total
65 sedimentary carbon sink. This proportion is generally referred to as f_{org} , which has varied over
66 Earth history between 0.1 and 0.3¹². During the Neoproterozoic Era, globally correlative
67 marine carbonate rocks from at least three intervals (~720 Ma Garvellach¹³, ~650 Ma
68 Trezona^{14,15}, ~560 Ma Shuram^{5,16}/Wonoka⁷/DOUNCE¹⁷ anomalies) are characterised by $\delta^{13}\text{C}$
69 values below -5‰ (Fig. 1), which can, using a conventional mass balance approach, only be
70 explained by negative rates of organic burial. This is particularly true of the late Ediacaran
71 Shuram excursion, during which $\delta^{13}\text{C}$ remained below -8‰ for at least ~10 Myr^{18,19}. In order
72 to address this quandary, it was proposed that the pool of dissolved organic matter (DOM) in

73 the Proterozoic ocean was much larger than today, and that negative excursions represent non-
74 steady-state remineralisation of that pool³. However, later numerical treatments of this
75 model^{20,21} pointed out that the Earth system cannot remain out of oxygen (and carbon) balance
76 for such a long period of time. In other words, there is insufficient oxidant even in the modern
77 atmosphere and oceans to remineralise enough organic matter to drive a -8‰ $\delta^{13}\text{C}$ excursion
78 for several million years. As a result, many authors have interpreted extreme negative
79 anomalies as diagenetic alteration²², authigenic cements¹⁰ or as regional phenomena²³.
80 However, such arguments appeal to an inexplicable sampling bias, whereby globally
81 correlative isotopic signatures are presumed to be unrepresentative of the global carbonate sink.
82 Here we take a different approach to the problem of negative $\delta^{13}\text{C}$ excursions by viewing them
83 in terms of a linked carbon-sulfur-oxygen system, whereby changes in oxidant dynamics
84 caused an excess of organic carbon oxidation over burial, resulting in a smaller DOM reservoir.
85 For steady state to be maintained throughout a negative $\delta^{13}\text{C}$ excursion, shrinkage of the DOM
86 pool would need to match surplus oxidant production for the duration of the anomaly. If we
87 consider plausible $\delta^{13}\text{C}$ values of -10‰¹⁷ and -35‰ for deposited carbonates and kerogen
88 (globally averaged carbon sinks), respectively, and -30‰²⁴ and -5‰ for the DOM reservoir
89 and crustal carbon (globally averaged carbon sources), respectively, then organic carbon
90 oxidation would need to increase over the background rate by approximately a factor of three
91 (Methods 1). This oxidant imbalance then requires three times as much oxygen as could have
92 been supplied by organic burial alone. Therefore, it can only plausibly be sustained via the
93 other major net source of oxygen to the Earth system: pyrite burial.

94

95 **A coupled sulfate dissolution and pyrite burial solution**

96 Although bacterial sulfate reduction coupled with pyrite burial releases on a mole-for-mole
97 basis almost twice as much oxygen as organic burial²⁵, it is generally assumed that the oxygen
98 released by pyrite burial is approximately matched by the oxygen consumed during pyrite
99 weathering. However, most riverine sulfate derives from the weathering of evaporites²⁶, rates
100 of which due to the sporadic and regional nature of evaporite deposits, will vary considerably
101 over time²⁷. During parts of the Proterozoic, when oceans were both iron-rich and anoxic²⁸,
102 and so prone to sulfate reducing conditions (euxinia) at productive margins, one might
103 realistically suppose that the amount of oxidising power transferred from rock sulfate to the
104 surface environment would also have varied considerably, particularly during times when no
105 basin-scale evaporite deposits were forming.

106 By writing a simple steady state mass-balance for the surface carbon cycle (Methods 1) we can
107 map the broad relationship between the evaporite sulfate input rate, net DOM oxidation and
108 $\delta^{13}\text{C}$ composition of the ocean-atmosphere system (Fig. 2). These calculations show that an
109 evaporite weathering flux of around 1.1×10^{13} mol S yr⁻¹ (around 10 times the modern flux,
110 as proposed for the dissolution event during the early Cenozoic²⁷) could sustain a carbon
111 isotope excursion of between -10‰ and -15‰, depending on the proportion of the riverine
112 sulfate flux that is eventually buried as pyrite. Thus, the amount of oxidant required to achieve
113 a deep negative carbon isotope excursion through net organic carbon oxidation may reasonably
114 result from basin-scale evaporite dissolution.

115 Although plausible, we acknowledge that the above steady-state approximation is highly
116 idealised and does not capture the true dynamics of the expected events, which include both
117 positive and negative feedbacks (Fig. 3). For a negative $\delta^{13}\text{C}$ excursion to be generated, oxidant
118 input needs to be coupled to shrinkage of a marine DOM reservoir, rather than accumulating
119 as an atmospheric oxygen increase. The rate of DOM oxidation is controlled by the deep ocean
120 redox state, which itself is largely controlled by the abundance of atmospheric oxygen.

121 Therefore, the process of DOM oxidation must be self-limiting and it should not be possible to
122 deplete the surface oxygen reservoir beyond the level that causes the deep ocean to become
123 entirely anoxic. Net oxidation of organic carbon should cause a substantial rise in atmospheric
124 CO₂ concentration and hence additional climate feedbacks. Rising CO₂ and temperature would
125 support enhanced continental weathering, with the potential to drive further evaporite
126 dissolution and therefore sustain oxidant delivery.

127

128 **Biogeochemical modelling results**

129 The network of long-term biogeochemical feedbacks between the sulfur, carbon and oxygen
130 cycles is adequately represented by the COPSE biogeochemical box model²⁹, and in order to
131 explore how changes in the evaporite sulfate weathering flux might affect the oxidant balance
132 in a Proterozoic marine environment, we modify COPSE to include a dynamic reservoir of
133 deep-ocean DOM (modelled as DOC) and an extra input flux of sulfate from weathering
134 (Methods 2 and SI). The model is first set up for an ‘Ediacaran like’ steady state ($pO_2 = 0.05$
135 PAL, $pCO_2 = 13$ PAL, $SO_4 = 0.1$ of present ocean level and a mostly anoxic deep ocean). This
136 is achieved by fixing background tectonic parameters (uplift, degassing) at assumed values for
137 600 Ma, while lowering the phosphorus input rate by 50%³⁰.

138 We then perturb the system by adding a weathering pulse of sulfate from evaporite dissolution,
139 and a smaller pulse of sulfate from pyrite oxidation, assuming that pyrite-bearing sediments
140 would also be exposed during uplift. These pulses follow simple stepwise increases and
141 decreases²⁷, but also include a dependence on climate through runoff as summarized in figure
142 3 (see methods for details). Figure 4a shows the overall amount of S delivery from evaporite
143 dissolution ($\sim 50 - \sim 100 \times 10^{18}$ mol), which is chosen to be similar to that proposed for
144 basin-scale evaporite dissolution in the Cenozoic ($\sim 1.1 \times 10^{13}$ mol S yr⁻¹ for ~ 5 Myrs)²⁷,

145 although we use a longer timeframe to compare to the long duration of the Shuram excursion.
146 The control model run with no DOC reservoir is shown in grey in figure 4. As shown
147 previously²⁷, this level of sulfate input raises ocean sulfate concentration considerably.
148 Increased burial of pyrite leads to a substantial increase in pO_2 and less prevalence of anoxia
149 (shown as fraction of anoxic seafloor). Oxidative weathering of fossil organic carbon increases
150 as O_2 rises, causing a small reduction in $\delta^{13}C$ and increase in pCO_2 . Seawater $\delta^{34}S$ decreases
151 during the evaporite dissolution event as the combined $\delta^{34}S$ value of inputted evaporite and
152 pyrite sulfur is lower than the initial seawater value (we set $\delta^{34}S_{pyr} = 0\text{‰}$ and $\delta^{34}S_{evap} = 15\text{‰}$
153 for the weathered material cf.³¹). The increase in pyrite burial buffers against this change by
154 driving $\delta^{34}S$ to more positive values (manifest as a ‘hump’ in the model $\delta^{34}S$ curve), but is
155 insufficient to reverse the overall trend.

156 We view net oxidation of deep ocean DOC as a feedback process driven by other model
157 variables, and model it accordingly. Model runs include a DOC reservoir of size 20 times (light
158 blue) and 30 times (dark blue) the modern DIC reservoir, respectively. The reservoir is assumed
159 to have a carbon isotopic composition of -30‰ and is allowed to be oxidized when the degree
160 of anoxia (*ANOX*) is reduced below a threshold value (see Methods 2). In both runs, oxidation
161 of DOC begins as the deep ocean becomes more widely oxygenated, however, as DOC
162 oxidation is an oxygen sink, *ANOX* remains at the threshold value until the DOC reservoir
163 nears depletion. In this period, the model is in a quasi-steady state wherein the transition to an
164 oxygenated deep ocean is prevented by the net oxidation of DOC. During this state, ocean $\delta^{13}C$
165 is around -9‰ , close to the value suggested by the simple calculations shown in Figure 2 for
166 this level of sulfate input. Persistent anoxia, nutrient delivery, and the related increase in pyrite
167 burial rates drive $\delta^{34}S$ values higher than the control run, but the model still produces a negative
168 excursion in $\delta^{34}S$, consistent with available observations^{16,32}. On depletion of the DOC

169 reservoir, the deep ocean can be oxygenated, and the model gradually returns to follow the
170 control experiment.

171 The duration of the carbon isotope anomaly in our COPSE model reconstruction depends on
172 the size of the DOM pool and on being able to maintain high rates of pyrite burial, but crucially
173 does not depend on (or deplete) the atmospheric O₂ pool, which is predicted to increase during
174 the course of the excursion. A high rate of pyrite burial would be maintained in part due to the
175 effect of organic remineralisation on raising *p*CO₂ and global temperatures, which produces a
176 positive feedback loop (Fig. 3), whereby high chemical weathering rates and nutrient input can
177 sustain euxinic ocean margins until either the DOM pool or the evaporite weathering flux
178 decreases below a certain threshold value. Our treatment of these aspects is necessarily simple:
179 we assume in the model run shown that 80% of the inputted sulfate is buried as pyrite by a
180 near-shore biota that is sensitive to river inputs³³. We also assume that gypsum, pyrite and
181 organic carbon weathering fluxes are related to the model global rate of runoff (in addition to
182 following a prescribed stepwise increase and decrease for pyrite and gypsum). We show further
183 model runs in the SI in which the climate-weathering effect is not considered, and in which
184 only evaporite inputs are considered, without any weathering of pyrite. We also show runs
185 where differing amounts of P release from DOM oxidation fuels additional primary
186 productivity. Sustained, highly-negative δ¹³C excursions remain possible in all of these cases,
187 but a closely corresponding negative δ³⁴S excursion can only be achieved when a smaller pulse
188 of pyrite weathering accompanies the evaporite weathering pulse. While pyrite weathering is
189 important in setting seawater δ³⁴S values, pyrite weathering and deposition form an O₂-neutral
190 cycle over long timescales so other model processes are relatively unaffected.

191

192 **Implications for climate and oxygen regulation at other times**

193 This evaporite dissolution / DOM oxidation scenario appears to be the most parsimonious
194 solution to the Shuram C-isotope conundrum in that it predicts the extent of oxic seafloor to
195 increase towards the end of the excursion, while maintaining high sulfate concentrations, which
196 is in line with geochemical studies^{34,35}. Furthermore, the Shuram anomaly coincided with
197 orogenic uplift relating to the formation of Gondwanaland³⁶, and in particular the tectonic
198 inversion of all major basin-scale evaporite sulfate deposits of Tonian age (see SI 4). Although
199 our model fits best the late Ediacaran Shuram anomaly, coupled evaporite dissolution and
200 pyrite burial may have also played a role in other extreme negative carbon isotope excursions
201 of the Neoproterozoic, which all occurred after one of the largest evaporite depositional events
202 in Earth history between c.830 Ma and c.770 Ma³⁷. The succeeding interval of major carbon
203 cycle disruption from c.770 Ma until c.550 Ma was a time of little or no basin-scale evaporite
204 deposition, suggesting that, as in the Cenozoic⁵, the sulfate weathering-deposition cycle was
205 not in steady-state. However, unlike the Cenozoic, the low atmospheric oxygen and anoxic
206 deep ocean of the Neoproterozoic allowed evaporite-derived oxidizing power to be effectively
207 transmitted into a negative $\delta^{13}\text{C}$ signal.

208 The existence of a series of negative carbon isotope excursions during much of the
209 Neoproterozoic Era indicates that the DOM pool underwent dynamic size changes throughout
210 this time, and served as a buffer against oxygenation and climate change, but only when the
211 pool was sufficiently large. Exhaustion of the DOM pool may have occurred during the Shuram
212 anomaly, suggesting that the expansion of aerobic Ediacaran fauna at that time was an
213 opportunistic radiation in response to a transient oxidant surplus. We conclude that a greatly-
214 reduced DOM pool continued to wax and wane well into the Cambrian Period, during which
215 seafloor redox conditions episodically reached modern proportions for the first time².

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327

328 **Author contributions**

329 G.A.S. and B.J.W.M. conceived the project. B.J.W.M. created the model, which was revised
330 from previous versions created by T.M.L., B.J.W.M. and S.D. All authors contributed to data
331 interpretation and the writing of the manuscript.

332

333 **Correspondence and requests for materials** should be addressed to G.A.S

334 (g.shields@ucl.ac.uk), B.J.W.M. (b.mills@leeds.ac.uk) or M.Z. (myzhu@nigpas.ac.cn).

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337 **Figure 1. Carbonate carbon isotope record (reproduced from ³⁸).** Grey area indicates values
338 below the average continental crust and mantle value of between -5‰ and -6‰ with three
339 major excursions at ~720 (Garvellach anomaly¹³), ~650 (Trezona anomaly¹⁴) and ~560 Ma
340 (Shuram anomaly^{5,16}). Smaller post-glacial excursions occur after Cryogenian (Sturtian and
341 Marinoan) low latitude glacial events (blue bars). Black dashed line indicates progressive
342 deep ocean oxygenation between ~580 and ~520 Ma^{2, 39-40}. Note that excursions to below the
343 mantle value occur before and during deep-ocean oxygenation and climate events.

344

345 **Figure 2. Negative $\delta^{13}\text{C}$ excursion driven by net oxidation of a dissolved organic carbon**
346 **reservoir via coupled evaporite weathering and pyrite burial.** The magnitude of the $\delta^{13}\text{C}$
347 anomaly depends on the O_2 production rate from pyrite burial, which results from the
348 evaporite weathering flux and the fraction of this flux that is buried as pyrite.

349

350 **Figure 3. Feedback diagram illustrating the effects of evaporite weathering on ocean**
351 **oxygenation and $\delta^{13}\text{C}$.** Boxes show quantities, ovals show processes, solid arrows show
352 positive effects and dashed arrows show negative effects in sulfur cycle (yellow) and carbon
353 cycle (red). Increased sulfate dissolution results in more pyrite burial, which increases
354 atmospheric and ocean O_2 . Resultant depletion of the dissolved organic carbon (DOC)
355 reservoir represents a negative feedback on ocean oxygenation, driving ocean $\delta^{13}\text{C}$ lower.
356 Red arrows show potential for positive feedback: DOC oxidation increases atmospheric CO_2 ,
357 surface temperature, precipitation and runoff, fuelling further evaporite dissolution and
358 nutrient delivery.

359

360

361 **Figure 4. COPSE Model forced with sulfate input and including differently sized DOC**
362 **reservoirs. A. Input rates of sulfate from gypsum and pyrite weathering. B. Size of DOC**
363 **reservoir in moles of carbon. C. A. Relative atmospheric oxygen concentration. D. Degree of**
364 **ocean anoxia. E. Relative atmospheric carbon dioxide concentration. F. Relative ocean sulfate**
365 **concentration. G. Calculated $\delta^{13}\text{C}$ of new carbonate. H. Calculated seawater $\delta^{34}\text{S}$.**

366

367

368 **Methods**

369 **1. Steady state mass balance calculations**

370 In order to estimate the surplus oxygen flux needed to sustain the late Ediacaran Shuram
371 anomaly, we apply standard isotope mass balance, and assume $\delta^{13}\text{C}$ values of -10‰^{17} and -
372 35‰ for deposited carbonates ($\delta^{13}\text{C}_{\text{carb}}$) and kerogen ($\delta^{13}\text{C}_{\text{org}}$), respectively, and -30‰^{24} and -
373 5‰ for the integrated carbon sources ($\delta^{13}\text{C}_{\text{input}}$) of DOM oxidation and crustal carbon,
374 respectively. Following standard C-isotope mass balance, $\delta^{13}\text{C}_{\text{carb}} = (\Delta^{13}\text{C}_{\text{carb-org}}) \cdot f_{\text{org}} +$
375 $\delta^{13}\text{C}_{\text{input}}$ at steady state, and so during the excursion when $f_{\text{org}} = 0.1^{12}$, then $\delta^{13}\text{C}_{\text{input}} = -12.5\text{‰}$.
376 The proportion that DOM oxidation contributed to the global carbon cycle, i.e. $f_{\text{DOM}} = 0.3$,
377 whereby $\delta^{13}\text{C}_{\text{excursion input}} = -12.5\text{‰} = \delta^{13}\text{C}_{\text{pre-excursion input}} (1-f_{\text{DOM}}) + \delta^{13}\text{C}_{\text{DOM}} \cdot f_{\text{DOM}}$. A
378 conservative estimate for the requisite surplus oxygen flux (f_{DOM}) would therefore be about
379 three times greater than that supplied by organic burial (f_{org}) alone, thus requiring a
380 contribution from other sources, most likely pyrite burial.

381 In order to explore the potential for evaporite dissolution to drive surface system
382 oxygenation and negative carbon isotope excursions, we first solve a simple isotope mass
383 balance calculation for the $\delta^{13}\text{C}$ composition of the total combined atmosphere and ocean
384 carbon pool (A). Variations in A over time follow the formulation:

$$385 \quad \frac{dA}{dt} = F_{\text{oxidw}} + F_{\text{ocdeg}} + F_{\text{carbw}} + F_{\text{ccdeg}} - F_{\text{ocb}} - F_{\text{mccb}} - F_{\text{sffw}} + F_{\text{DOCox}} \quad (1)$$

386 Where F_{oxidw} is oxidative weathering, F_{ocdeg} is organic carbon metamorphism and
387 degassing, F_{carbw} is carbonate weathering, F_{ccdeg} is carbonate degassing, F_{ocb} is organic
388 carbon burial, F_{mccb} is marine carbonate burial and F_{sffw} is seafloor weathering
389 (following^{29,21}). We add F_{DOCox} to represent the oxidation of a deep ocean reservoir of
390 dissolved organic carbon. As a general approximation to the expected Ediacaran carbon cycle
391 we take $F_{\text{oxidw}} = 2.5 \times 10^{12} \text{ mol yr}^{-1}$, $F_{\text{ocdeg}} = 0.5 \times 10^{12} \text{ mol yr}^{-1}$, $F_{\text{carbw}} = 8 \times 10^{12} \text{ mol}$

392 yr^{-1} , $F_{ccdeg} = 6 \times 10^{12} \text{ mol yr}^{-1}$, $F_{ocb} = 3 \times 10^{12} \text{ mol yr}^{-1}$, $F_{mccb} = 12 \times 10^{12} \text{ mol yr}^{-1}$, and
 393 $F_{sfw} = 2 \times 10^{12} \text{ mol yr}^{-1}$. Here $\frac{dA}{dt} = 0$, thus the carbon cycle is in steady state, and the
 394 fraction of carbon buried in organic form (f_{org}) is 0.2.

395 We assume that the sulfur cycle begins at steady state, and allow an addition of sulfate
 396 from evaporite dissolution, F_{evap} (in moles S). To maintain long-term steady state this
 397 evaporite must leave the system in oxidised (e.g. gypsum) or reduced (e.g. pyrite) forms. We
 398 denote f_{py} as the fraction of the evaporite input that exits the system as pyrite and experiment
 399 with values of 0.5 and 1. Assuming that DOC oxidation is driven solely by excess oxygen
 400 produced by burial of pyrite, we set the flux of DOC oxidation as $F_{DOCox} = 2 \times f_{py} F_{evap}$. To
 401 maintain long term steady state in the carbon cycle, the flux of additional CO_2 from DOC
 402 oxidation must be balanced by burial of carbonates and organic carbon. We assume this
 403 occurs at the initial ratio of 4:1 in favour of carbonates (e.g. $f_{org} = 0.2$). Thus the equation
 404 for long term carbon isotopic mass balance is:

$$\begin{aligned}
 405 \quad & F_{oxidw} \delta_G + F_{ocdeg} \delta_G + F_{carbw} \delta_C + F_{ccdeg} \delta_C - F_{ocb} (\delta_A - \Delta B) - F_{mccb} \delta_A - F_{sfw} \delta_A + \\
 406 \quad & F_{DOCox} \delta_{DOC} - 0.2 F_{DOCox} (\delta_A - \Delta B) - 0.8 F_{DOCox} \delta_A = 0 \quad (2)
 \end{aligned}$$

407 where δ_A is the isotopic composition of atmosphere and ocean carbon, δ_C is the compositions
 408 of buried carbonates, δ_G is the composition of buried organic carbon and δ_{DOC} is the
 409 composition of the oceanic DOC reservoir. We take $\delta_C = 0\%$, $\delta_G = -25\%$, $\Delta B = 25\%$,
 410 $\delta_{DOC} = -30\%$, and solve for δ_A under varying values for F_{evap} . Results are shown in figure
 411 2.

412

413 2. COPSE model reconstructions

414 We run the COPSE model²¹ to steady state under assumed Ediacaran forcings, add a
415 deep ocean reservoir of dissolved organic carbon that responds to the degree of ocean anoxia,
416 then impose an evaporite dissolution and pyrite burial event.

417 *Ediacaran steady state*

418 The ‘Ediacaran’ steady state is achieved by fixing all model parameters at the assumed
419 values for 600 Ma. In all but two cases, these values are assumed to be the same as at the
420 beginning of the Phanerozoic, but we lower the rate of phosphorus input by 50% to reduce
421 atmospheric oxygen (e.g. as in Daines et al. 2017²²) and use a static gypsum burial rate of
422 50% of the present day to reduce ocean sulfate. The steady state has $pO_2 = \sim 0.05$ PAL, pCO_2
423 $= \sim 13$ PAL, $SO_4 = \sim 0.1$ of present ocean level and a mostly anoxic deep ocean ($ANOX \approx 0.9$).

424 *Dissolved organic carbon reservoir*

425 The size of the model DOC reservoir is set at the beginning of the model run. The
426 reservoir has a single output flux via DOC oxidation, which depends on the degree of ocean
427 anoxia ($ANOX$):

$$428 \quad \frac{dDOC}{dt} = \begin{cases} 0, & DOC < 1 \times 10^{12} \text{ mol} \\ -\frac{k}{1+e^{-a(1-ANOX-c)}} \left(\frac{DOC}{DOC_0} \right), & DOC \geq 1 \times 10^{12} \text{ mol} \end{cases} \quad (3)$$

429 here $a = 300$, $c = 0.35$ and $k = 1 \times 10^{14} \text{ mol yr}^{-1}$ are scaling parameters for the sigmoid
430 function, which define the anoxia level at which DOC oxidation begins and the rapidity of the
431 transition. In practice, this function allows for geologically-rapid oxidation of DOC when
432 $ANOX < 0.7$. The threshold here is chosen to be slightly below the model steady state so that
433 the DOC reservoir is stable under the COPSE Ediacaran setup. DOC oxidation is terminated
434 when the reservoir becomes smaller than 10^{12} moles, rather than zero, to prevent system
435 instability. The rate of DOC oxidation is controlled by O_2 supply and never reaches the value

436 of k . This is shown in the SI for different values of c . We assume that DOC is oxidised
437 directly by O_2 , although oxidation via microbial sulfate reduction is also possible.

438 ***Sulfate input***

439 An uplift and evaporite dissolution event is prescribed in the model using a simple
440 step-forcing that follows previous work on evaporite dissolution⁵. The time-dependent
441 forcing function for sulfate input is:

$$442 \quad S_{input} = [0 \ 1 \ 10 \ 16], [0 \ 7 \ 7 \ 0] \quad (4)$$

443 where the first bracket is time in million years and the second bracket is the additional sulfate
444 input in terms of the background weathering fluxes. For the model run in the manuscript,
445 steady state ‘background’ and additional ‘pulse’ inputs of both pyrite and gypsum are
446 considered:

$$447 \quad gypw_{background} = k_{gypw} \cdot g_{runoff} \quad (5)$$

$$448 \quad gypw_{pulse} = k_{gypw} \cdot g_{runoff} \cdot S_{input} \quad (6)$$

$$449 \quad pyrw_{background} = k_{pyrw} \cdot g_{runoff} \quad (7)$$

$$450 \quad pyrw_{pulse} = k_{pyrw} \cdot g_{runoff} \cdot S_{input} \quad (8)$$

451 here k_{gyp} and k_{pyr} are the present day weathering rates of gypsum and pyrite, and g_{runoff} is a
452 climate-dependence representing the effect of global runoff on weathering fluxes, e.g. Berner
453 (1994)⁴¹:

$$454 \quad g_{runoff} = 1 + 0.087(T - T_0) \quad (9)$$

455 where T is global average surface temperature and T_0 is the present day value.

456 ***Sulfate burial***

457 The COPSE model assumes that sulfate burial fluxes are linearly proportional to the
458 total oceanic sulfate concentration, which means that concentration would have to rise to
459 many times the present day level in order to bury large amounts of pyrite. We add an
460 additional flux of pyrite burial ($mps_{b_{additional}}$) that is directly related to the pulsed weathering
461 input of sulfate, so pyrite burial is more clearly related to the sulfate supply to high-
462 productivity near-shore environments. A partitioning constant f_{py} is used to determine what
463 fraction of the pulsed sulfate input is buried as pyrite. This is set at 0.8 in the plot shown in
464 the ms. Additional sulfate that is not buried as pyrite is assumed to be buried as gypsum:

$$465 \quad mps_{b_{additional}} = f_{py} \cdot (pyr_{pw_{pulse}} + gyp_{pw_{pulse}}) \quad (10)$$

$$466 \quad mgs_{b_{additional}} = (1 - f_{py}) \cdot (pyr_{pw_{pulse}} + gyp_{pw_{pulse}}) \quad (11)$$

467

468 ***Other model alterations***

469 The following alterations are made to COPSE to make the model more applicable to
470 the scenario being tested:

471

- 472 1. COPSE uses a sigmoid function to calculate the degree of ocean anoxia, *ANOX*. A
473 modified version of the function was previously presented³⁰, based on the anoxia
474 response of 3D ocean models. Whilst the functions are similar and the choice
475 makes little difference in the Phanerozoic version of COPSE, the Watson et al.
476 version of the function has a more gradual transition to anoxia and allows the
477 model to more easily assume an ‘Ediacaran-like’ steady state under minimal
478 alteration of other parameters and is therefore used here.
- 479 2. COPSE predicts low $\delta^{13}\text{C}$ values for the Ediacaran steady state ($\sim -2\text{‰}$). In order
480 to clearly test the size of the evaporite-induced excursion, we set the overall
481 crustal carbonate reservoir $\delta^{13}\text{C}$ value to 2‰ , which raises the $\delta^{13}\text{C}$ value of

482 carbon inputs and makes newly formed $\delta^{13}\text{C}_{\text{carb}}$ is $\sim 0\%$. This alteration merely
483 shifts the baseline of $\delta^{13}\text{C}$.

484 3. We take crustal values of $\delta^{34}\text{S}_{\text{pyrite}} = 0\%$ and $\delta^{34}\text{S}_{\text{gypsum}} = 30\%$ to reproduce
485 Ediacaran pre-excursion baseline values¹⁶, and assume that the pulse of evaporite
486 weathering has $\delta^{34}\text{S}_{\text{gypsum}} = 15\%$.

487 4. COPSE has a relatively high rate of gypsum weathering and burial at present day,
488 we alter the present day reference rate of gypsum weathering to $1 \times 10^{12} \text{ mol S yr}^{-1}$,
489 to better represent the background rate used in ref 5, for which our evaporite
490 dissolution scenario is based.

491 **3. Additional model experiments**

492 See supplementary information 1 for additional model runs where we assume no
493 climate dependence for sulfur weathering fluxes, and consider the role of pyrite versus
494 gypsum weathering, and test uncertainty in the DOC oxidation function.

495 **4. Full model description**

496 See supplementary information 2 for full modified COPSE model equations and
497 description.

498

499 **Data availability statement**

500 The authors declare that data supporting the findings of this study are available within the
501 article and supplementary material.

502

503 **Code availability statement**

504 MATLAB code for COPSE is freely available at <https://github.com/sjdaines/COPSE/releases>

505

506 **References in Methods only**

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