

2021-12-02

# Late Ordovician climate change and extinctions driven by elevated volcanic nutrient supply

Longman, J

<http://hdl.handle.net/10026.1/18128>

---

10.1038/s41561-021-00855-5

Nature Geoscience

Nature Research

---

*All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.*

1 **Late Ordovician climate change and extinctions driven by elevated volcanic nutrient**  
2 **supply**

3  
4 Jack Longman<sup>1,2,\*</sup>, Benjamin J. W. Mills<sup>3</sup>, Hayley R. Manners<sup>4,5</sup>, Thomas M. Gernon<sup>4</sup> and  
5 Martin R. Palmer<sup>4</sup>

6 <sup>1</sup> Marine Isotope Geochemistry, Institute for Chemistry and Biology of the Marine  
7 Environment (ICBM), University of Oldenburg, PO Box 2503, 26111 Oldenburg, Germany.

8 <sup>2</sup> School of Geography and the Environment, University of Oxford, South Parks Road,  
9 Oxford, OX1 3QY, UK.

10 <sup>3</sup> School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK.

11 <sup>4</sup> School of Ocean and Earth Sciences, University of Southampton, Southampton, SO14 3ZH,  
12 UK.

13 <sup>5</sup> School of Geography, Earth and Environmental Sciences, University of Plymouth,  
14 Plymouth, PL4 8AA, UK.

15  
16 \*Corresponding Author: [jack.longman@uni-oldenburg.de](mailto:jack.longman@uni-oldenburg.de)

17  
18 **Abstract**

19 **The Late Ordovician (~459–444 million years ago) was characterised by global cooling,**  
20 **glaciation and severe mass extinction. These events may have been driven by increased**  
21 **delivery of the nutrient phosphorus (P) to the ocean, and associated increases in marine**  
22 **productivity, but it is not clear why this occurred in the two pulses identified in the**  
23 **geological record. We link both cooling phases, and the extinction, to volcanic eruptions**  
24 **through marine deposition of nutrient-rich ash and the weathering of terrestrially**  
25 **emplaced ash and lava. We then reconstruct the influence of Late Ordovician volcanic P**  
26 **delivery on the marine system by coupling an estimate of bioavailable phosphate supply**

27 **(derived from a depletion and weathering model) to a global biogeochemical model. Our**  
28 **model compares volcanic ash P content in marine sediments before and after alteration**  
29 **to determine depletion factors, and we find good agreement with observed carbon isotope**  
30 **and reconstructed temperature shifts. Hence, massive volcanism can drive substantial**  
31 **global cooling on million-year timescales due to P delivery associated with long-term**  
32 **weathering of volcanic deposits, offsetting the transient warming of greenhouse gas**  
33 **emission associated with volcanic eruptions. Such longer-term cooling and potential for**  
34 **marine eutrophication may be important for other volcanism-driven global events.**

### 35 **Main Text**

36 The Late Ordovician mass extinction (LOME) occurred in two phases, and in terms of species  
37 loss was the second greatest extinction event in Earth's history<sup>1-3</sup>. The Late Ordovician is  
38 characterised by a number of carbon isotope excursions (CIEs), with two globally-represented,  
39 the Guttenburg (GICE) at ~454 Ma, and Hirnantian (HICE) at ~ 445 Ma<sup>4</sup>. The GICE coincides  
40 with global cooling, and the beginning of the HICE is associated with widespread glaciation,  
41 with the cooling periods generally implicated in instigating the LOME<sup>1,5-7</sup>.

42 The primary driver behind the CIEs and associated cooling is uncertain. One possibility  
43 is that the emergence of early nonvascular land plants amplified terrestrial weathering and  
44 increased the delivery of the key limiting nutrient phosphorus to the oceans<sup>8</sup>. Greater  
45 availability of phosphorus increases marine productivity and organic carbon burial, driving a  
46 reduction in atmospheric CO<sub>2</sub> and a positive excursion in carbonate  $\delta^{13}\text{C}$  (ref.<sup>9</sup>). Other proposals  
47 include an increasing fraction of eukaryotic marine production strengthening the biological  
48 pump<sup>10</sup>, and increased tropical weathering resulting from orogenesis augmenting the supply of  
49 phosphorus to the oceans<sup>11</sup>.

50 The concept that Late Ordovician cooling was driven by organic carbon burial is  
51 supported by observations<sup>12</sup>, but why this occurred in two distinct pulses during the GICE and

52 HICE is unclear. This pulsing may have arisen from early plants colonising new terranes<sup>8</sup>, but  
53 there is little evidence for this, although poor fossil preservation cannot be ruled out<sup>13</sup>. Further,  
54 the pace of early plant evolution remains highly uncertain<sup>13</sup> and there is no evidence that  
55 eukaryotic evolution, or tropical uplift, occurred in distinct pulses. Existing global  
56 biogeochemical models cannot reliably reproduce the Hirnantian glaciation (or isotope  
57 excursions) associated with the HICE when based on known long-term tectonic cycles of uplift  
58 and degassing, and the positioning of the continents<sup>9</sup>, even though these models can accurately  
59 reproduce the Permo-Carboniferous and late Cenozoic icehouses<sup>9</sup>. This suggests that the  
60 Hirnantian icehouse was driven by some climatic forcing mechanism currently not well-  
61 represented in these models.

62         Given the potential association between volcanism and global climate change<sup>14,15</sup>, we  
63 explore the concept that Late Ordovician marine productivity and cooling episodes were  
64 directly related to subaerial volcanic activity. The Late Ordovician was characterised by  
65 extensive volcanic eruptions, preserved in the sedimentary record as bentonites<sup>16,17</sup>. These  
66 bentonites represent some of the largest volcanic eruptions in Earth's history, with estimates  
67 indicating some of the better studied events (Millbrig, Deicke and Kinnekulle) erupted  $\geq 1000$   
68 km<sup>3</sup> of pyroclastic material<sup>18</sup>. In addition, there are hundreds of spatially extensive bentonites  
69 of Late Ordovician (459 – 444 Ma) age preserved across North America<sup>19</sup>, Northern Europe<sup>20</sup>,  
70 and China<sup>16,21</sup>, prompting suggestions of a causal link between volcanism and global cooling  
71 during this period<sup>3,14,17</sup>. Most recently, several studies have employed the total organic carbon  
72 to mercury ratio (TOC/Hg), to directly link volcanic Hg emission to Late Ordovician climatic  
73 change (e.g. refs.<sup>22,23</sup>). However, it remains uncertain whether cooling was driven by rapid  
74 sulfate emissions, through the immediate weathering of ash and lava, or by longer-term  
75 weathering of volcanic arcs and uplifted terranes<sup>17,23</sup>, a problem compounded by poorly  
76 constrained volcanic fluxes.

77 Volcanism may cool the climate on non-transitory timescales due to enhanced  
78 productivity and organic carbon preservation<sup>24</sup>, with one of the key drivers being enhanced P  
79 supply derived from leaching of volcanic ash<sup>25</sup>. It is not currently clear how much P may have  
80 been supplied from ash during the Late Ordovician, or how input of volcanic P may have  
81 influenced the marine environment. To answer these questions, we compile global data on P  
82 depletion in tephra layers today, as a method of quantifying P release to the ocean during ash  
83 deposition and diagenesis. We couple our estimates of P flux to a global biogeochemical model  
84 to investigate the potential impact of such nutrient supply to the Late Ordovician marine carbon  
85 cycle.

#### 86 **Timing and extent of volcanism during the Late Ordovician**

87 To estimate timing of volcanic activity, we compile 43 Ar-Ar and U-Pb dates from  
88 North American and Scandinavian bentonites (Fig. 1a), and 24 dates from Chinese bentonites  
89 of Late Ordovician age (Fig. 1b). Our reconstruction indicates that bentonite deposition  
90 occurred in two discrete pulses (Fig. 1c), corresponding to the eruption of two geographically  
91 distinct volcanic provinces (Figure 2). The first pulse represents North American/Scandinavian  
92 volcanism and is well-constrained, with the greatest depositional intensity occurring between  
93 454.5 – 453 Ma, peaking at 453.5 Ma (Fig. 1c). This peak primarily represents highly-precise  
94 measurements of the North American “big” bentonites, the Deicke and Millbrig<sup>5,26</sup>, and the  
95 Grimstorp bentonite<sup>26</sup>. A slightly earlier peak is also apparent (c. 456.5 Ma), representing  
96 potentially uncertain estimates of the Kinnekulle bentonite age<sup>27</sup>, and other unnamed bentonites  
97 from Oslo<sup>20</sup> (see Supplementary Table 4). Chinese bentonite ages exhibit more spread, with  
98 fewer highly precise dates (Fig. 1c). Our compilation suggests the most intense volcanism in  
99 the China region occurred between 445.25 – 442.5 Ma, with a peak at about 444 Ma (Fig. 1c),  
100 corresponding to some of the most accurate dates from outcrop in the south-western Yunnan  
101 province<sup>28</sup>, and central Hubei province<sup>29</sup>. These two volcanic pulses correspond well to the two

102 primary carbon isotope excursions of the Late Ordovician, the GICE and HICE, and may thus  
103 support a link between volcanism and climate change.

#### 104 **P release during ash deposition, diagenesis and weathering**

105 To investigate this hypothesis, we estimate the amount of P which may have been  
106 supplied by the two main pulses of volcanism. To estimate the percentage of P released during  
107 ash deposition and diagenesis, altered ash compositions are compared to unaltered protolith  
108 compositions to estimate metal mobility<sup>30,31</sup>, using protolith data from the GEOROC database  
109 (<http://georoc.mpch-mainz.gwdg.de>) and our data from altered tephra (see Methods).  
110 Specifically, marine sediment-hosted tephra from the Lesser Antilles and the Aleutian arcs  
111 have been analysed and compared to similar data from eight additional modern volcanic  
112 provinces (Fig. 1). In addition to direct input of P from volcanic ash deposition, the  
113 emplacement and subsequent terrestrial weathering of extensive ash beds would have led to a  
114 secondary source of P to the oceans. The scale of this P flux has been estimated from a Monte  
115 Carlo simulation of inputs using published variables including the number, and scale of  
116 eruptions (Methods, Extended Data Figures 1, 2).

117 Depletion factors indicate between 31% (mean) and 48% (median) of the P originally  
118 hosted in tephra is lost during early diagenesis (Fig. 3). The potential scale of this process is  
119 calculated in the modern oceans, using an average of  $1.14 \pm 0.6 \text{ km}^3$  ash deposited per year,  
120 with  $70 \pm 7.5 \%$  falling into the ocean<sup>31</sup>, an ash density of  $1400 \pm 130 \text{ kg/m}^3$  (ref.<sup>32</sup>), and an  
121 original P content in tephra of  $0.41 \pm 0.19 \text{ wt}\%$  (ref.<sup>33</sup>). For each variable, a Monte Carlo-based  
122 approach is applied, using the average and standard deviation to develop 10,000 possible  
123 iterations of each variable. From this calculation, the most likely annual P flux from ash  
124 deposition and diagenesis is estimated to be approximately  $3 \times 10^{10} \text{ mol P yr}^{-1}$ . This is similar  
125 to estimates of global dust input to the P cycle today ( $3.2 \times 10^{10} \text{ mol P yr}^{-1}$ ), and exceeds the  
126 dissolved riverine input ( $0.6 - 1.1 \times 10^{10} \text{ mol P yr}^{-1}$ ; ref.<sup>34</sup>). Present-day volcanism is thought

127 to be far smaller in scale than in periods such as the Ordovician<sup>35,36</sup>. Therefore, enhanced P  
128 supply tied to volcanism likely played an even more important role in biogeochemical cycles  
129 of P during the Ordovician.

### 130 **Impact of volcanic ash supply on Late Ordovician climate**

131 The depletion factors and estimates of ash supply during the Late Ordovician can be  
132 used to quantify the scale of P supply during the two studied events. For the GICE, our  
133 simulations indicate a mean of  $2.29 \times 10^{15}$  mol P (Fig. 4), which increases to  $6.49 \times 10^{15}$  mol P  
134 in the upper estimates of the simulations (95<sup>th</sup> percentile). For the volcanic episode covering the  
135 HICE, our simulations suggest a mean supply of  $2.89 \times 10^{15}$  mol P, with an upper estimate of  
136  $8.24 \times 10^{15}$  mol P (95<sup>th</sup> percentile) (Fig. 4). In addition to ash falling into the ocean, the impact  
137 of erosion of terrestrially emplaced ash and lava on the P cycle is considered by estimating  
138 weathering fluxes of P (Methods). Newly emplaced ashes and basaltic rocks weather  
139 rapidly<sup>37,38</sup>, such that in Earth's modern configuration, despite representing only 3 – 5% of land  
140 area, chemical weathering of basalt contributes ~30% of the total CO<sub>2</sub> consumption by silicate  
141 weathering<sup>37,38</sup>. Our approach to quantifying the impact of this process results in a mean  
142 additional (riverine) P flux from weathering of  $7.51 \times 10^{14}$  mol P Myr<sup>-1</sup> in the millennia after  
143 emplacement (Fig. 4c), with an upper estimate of  $1.23 \times 10^{15}$  mol P Myr<sup>-1</sup> (95<sup>th</sup> percentile),  
144 providing another source of bioavailable P to the ocean system.

145 The impact of this level of volcanic nutrient supply on Ordovician climate is estimated  
146 using the COPSE global biogeochemical model<sup>39</sup>. The GICE and HICE P inputs are represented  
147 by Gaussian functions with their maxima at the times of highest depositional intensity noted  
148 above (i.e., 453.5 and 444 Ma) and with a width of 2 Myrs, constrained in part by the duration  
149 of the carbon isotope excursions. The total P input is calculated for both the means and 95<sup>th</sup>  
150 percentiles and is summed from the P depletion model and weathering inputs. A further factor  
151 is also added into the P delivery calculation to represent the recycling of P from sediments,

152 because P loading and eutrophication in marginal settings leads to a substantial recycling flux  
153 of P from the sediments<sup>40</sup>, due to the increase in anaerobic processing of organic matter and the  
154 scarcity of Fe(III) phases that scavenge P. The COPSE model does not represent these  
155 feedbacks well, because it has a well-mixed global ocean and no consideration of continental  
156 margins, with substantial recycling of P relying on eutrophication of the global ocean rather  
157 than productive shelves and slope environments alone<sup>39</sup>. This is relevant to the Ordovician, a  
158 time when sea level was perhaps 300 m higher than present<sup>41</sup>, with extensive shelf  
159 environments<sup>42</sup>. Hence, parallel experiments were run to determine the degree to which P  
160 recycling is dampened in COPSE versus a published P cycle model in which the shelves are  
161 considered separately (see Methods, ref.<sup>43</sup>). We conclude that a 5-fold larger P input is required  
162 in COPSE to produce the same spike in marine P concentration observed in the multi-box model  
163 (Extended Data Figure 3). Thus, P inputs in the additional COPSE simulations are increased 5-  
164 fold to represent both the initial input and the additional recycling of P. The large size of this  
165 factor is related to the relatively small size of the ocean shelves (as a fraction of the whole  
166 ocean) compared to their disproportionately large contribution to organic matter burial.

167 An important parameter in COPSE is the degree to which land plants amplify  
168 continental weathering rates. This value is poorly constrained and is typically varied in  
169 sensitivity analyses between around 2- and 7-fold, giving a wide range of possible background  
170 CO<sub>2</sub> concentrations for the early Palaeozoic<sup>44</sup>. We choose a factor 2 enhancement for the model  
171 runs in this work, which gives a relatively low background Ordovician CO<sub>2</sub> concentration of  
172 around 1000 ppm, consistent with more recent proxy data<sup>45</sup>. Other than the new P inputs and  
173 choice of biotic weathering parameter, the model remains identical to the long-term baseline  
174 shown in ref.<sup>39</sup>. Figure 5 shows the model outputs for atmospheric CO<sub>2</sub>, average surface  
175 temperature, marine anoxia, and the  $\delta^{13}\text{C}$  of new sedimentary carbonates. The model outputs  
176 show that the P release from volcanic ash deposition and weathering, combined with the  
177 recycling of P from sediments, is sufficient to cause large-scale changes in climate and



178 biogeochemistry as observed in the geological record<sup>10,14</sup>. In the “95<sup>th</sup> percentile + recycling”  
179 input scenario, carbon isotope excursions of ~3‰ and ~4‰ are predicted, which are  
180 synchronous with the GICE and HICE, respectively, and are of similar magnitude. In this  
181 scenario, maximum global cooling at the HICE is around 3°C, and a global average surface  
182 temperature of below 15°C is reached at the nadir. These temperature predictions are in line  
183 with clumped isotope thermometry which suggests the Hirnantian icehouse was relatively short  
184 lived and represented a similar global average temperature to recent Pleistocene glaciation<sup>6,46</sup>.

185         The extent of marine anoxia increases during the P input events in the model, although  
186 given the global well-mixed ocean in the model, shelf anoxia would be expected to increase by  
187 a larger fraction than the global ocean. This is against a backdrop of marine oxygenation  
188 through the Ordovician and Silurian predicted by COPSE<sup>39</sup>. One of the major features of the  
189 HICE in the geological record is the widespread formation of organic-rich shales, in particular  
190 in China<sup>47,48</sup>, potentially linked to widespread ocean anoxia<sup>10,49</sup>. In COPSE, the relative increase  
191 in anoxia is much larger during the HICE – close to a doubling in the “95<sup>th</sup> percentile +  
192 recycling” scenario.

### 193 **Implications for the LOME**

194         Our model results suggest that volcanic ash diagenesis and weathering of erupted  
195 products likely played a key role in the Late Ordovician Earth system. In order to reproduce the  
196 magnitude of Earth system change, we require that these inputs are at the 95<sup>th</sup> percentile of our  
197 analysis. However, given the relatively sparse nature of the geological record of the Palaeozoic,  
198 and the conservative approach utilised here to derive estimates of P supply from ash (Methods),  
199 we stress that our analysis likely underestimates the number of volcanic events. This is  
200 supported by the close comparison between the model output of the “95<sup>th</sup> percentile +  
201 recycling” input scenario and proxy data (Fig. 5, ref.<sup>50</sup>). Our results may explain several features  
202 of the LOME, which do not follow trends associated with other mass extinctions, in particular

203 their link to cooling, rather than warming. Volcanic activity has been invoked as the driver  
204 behind a number of short-term climatic upheavals and mass extinctions<sup>51</sup>, including those at the  
205 end of the Permian<sup>52</sup> and in the Triassic periods<sup>53</sup>, resulting in the rapid fluctuations between  
206 icehouse and greenhouse conditions known to stress faunas and drive biodiversity loss<sup>3,52</sup>.

207 For the Late Ordovician, it appears that the long-term nature of nutrient supply from  
208 weathering of eruptive products such as volcanic ash plays a more dominant role than the  
209 medium-term warming associated with CO<sub>2</sub> injection. When comparing to climatic change, it  
210 is clear that the first stepped decrease in faunal diversity occurred soon after the GICE, with  
211 two further decreases occurring temporally close to the HICE<sup>3,54</sup>. Our approach considers many  
212 eruptions to estimate nutrient supply on a coarse scale. The super-eruptions represented by  
213 bentonites would likely have led to initial cooling (due to injection of stratospheric aerosols),  
214 followed by warming (from CO<sub>2</sub> injection), before cooling because of increases in nutrient  
215 supply and associated productivity levels. The warming/cooling cycles this scenario represents  
216 are purportedly dangerous for organisms, with biodiversity loss occurring when temperatures  
217 fall outside the optimal window<sup>3</sup>, potentially explaining the LOME initiation. Due to their  
218 global nature, we focus on the HICE and GICE, and only model two P pulses. However,  
219 bentonite ages suggest that multiple eruptions occurred between the two largest volcanic  
220 episodes and CIEs (Fig. 1), which may have led to transient local CIEs, such as those reported  
221 in the Scandinavian sections<sup>7</sup>.

222 In addition to releasing nutrients, it is possible that other toxic metals are also released  
223 during ash alteration and diagenesis<sup>25</sup>. During the Hirnantian glaciation and the HICE, there is  
224 evidence for metal-induced malformations in fossil plankton assemblages<sup>55</sup>. Further, volcanic  
225 ash may lead to the formation of large-scale anoxic conditions below deposited blankets<sup>24</sup>,  
226 which may have further enhanced redox-based recycling of toxic metals<sup>55</sup> and led to the  
227 deposition of widespread black shales<sup>47</sup>. Using the evidence presented here, we conclude that

228 the pulsed nature of global cooling at this time appears to be a result of the eruption of two  
229 distinct volcanic provinces, one in what is now North America and the Baltic, and one in what  
230 is now Southern China. Further, our models suggest that the deposition of extensive ash  
231 blankets and weathering of lavas emplaced during Late Ordovician volcanism, supplied  
232 sufficient P to drive global cooling, glaciation, and the LOME.

### 233 **Acknowledgements**

234 This work was funded by NERC grant NE/K00543X/1, “The role of marine diagenesis of tephra  
235 in the carbon cycle”. B.J.W.M. acknowledges support from NERC grant NE/S009663/1.  
236 T.M.G. acknowledges support of NERC grant NE/R004978/1, and funding from the Alan  
237 Turing Institute (EP/N510129/1). We are grateful for comments from Christian Rasmussen and  
238 the anonymous reviewer(s), which helped to improve the manuscript. We are grateful to staff  
239 of the IODP Gulf Coast Repository and IODP Kochi Core Repository for their assistance during  
240 sampling of cores U1396C and U1339D, respectively.

### 241 **Author Contributions**

242 J.L., T.M.G. and M.R.P. conceived this research. J.L. and H.R.M. completed the laboratory  
243 analyses. B.J.W.M. completing the modelling and J.L. compiled and analysed the data. J.L. and  
244 B.J.W.M. created the figures. J.L. and B.J.W.M. wrote the manuscript, with input from T.M.G.,  
245 H.R.M. and M.R.P.

### 246 **Competing Interests**

247 The authors declare no competing interests.

### 248 **Corresponding Author**

249 All correspondence and request for materials should be addressed to Jack Longman  
250 ([jack.longman@uni-oldenburg.de](mailto:jack.longman@uni-oldenburg.de))

251 **Figure Captions**

252 **Figure 1: Compilation of Late Ordovician bentonite ages from North America and China.**

253 Bentonites ages in North America/Scandinavia (**a**), and China (**b**). Each age is represented by  
254 a probability density curve derived from published mean and standard deviation, from which  
255 10,000 Monte Carlo simulations were completed and binned at 0.25 Myr intervals to attain  
256 probability densities of the eruption occurring in each bin. Colours correspond to the studies  
257 from which each age is obtained. **c**, Average probability densities for each 0.25 Myr bin, for  
258 the North American (blue) and Chinese bentonites (red). Vertical lines indicate the bin in which  
259 bentonite deposition is most likely. (See Supplementary Tables 4 and 5 for references).

260 **Figure 2: Paleogeographic reconstruction for the Late Ordovician at c. 450 Ma (Katian).**

261 Marked with ellipses are the two volcanic provinces investigated in this study, with blue ellipses  
262 representing the North American and Scandinavian province, and a green ellipse to represent  
263 the Chinese province. The base map was constructed using the plate tectonic reconstructions  
264 from ref.<sup>56</sup> and is based partly on ref<sup>57</sup>.

264 **Figure 3: Box and whisker diagrams of phosphorus**

265 **depletion, an indicator of the amount of phosphorus lost to the ocean, from ten present-**

266 **day representative volcanic provinces (a).** Boxes are defined between the first and third

267 quartile (the interquartile range, IQR), with minimum and maximum whiskers representative of

268 1.5 times the IQR. Also shown is a map of each volcanic province used for this reconstruction

269 (**b**), with the provinces identified by numbers given in panel (a).

269 **Figure 4: Monte Carlo**

270 **simulations of phosphorus supply from volcanic weathering during the Late Ordovician,**

271 **with variable distributions defined by our ash depletion and weathering model. (a) and (b)**

272 represent P supply from ash deposition and diagenesis. In both panels, the total ash volume is

273 presented along the x-axis, with total phosphorus supply on the y-axis. Each Monte Carlo

274 simulation is indicated by a circle, with the colour indicating the depletion factor. (**c**) Estimate

275 of P flux resulting from weathering of terrestrial volcanic matter (y-axis), plotted against the

276 area covered by this ash and lava. Again, each simulation is indicated by a filled circle, with  
277 the colour denoting the rate of phosphorus supply.

278 **Figure 5. Biogeochemical model outputs for impacts of volcanism during the GICE and**  
279 **HICE.** COPSE model baseline runs<sup>39</sup> plus P supply from ash. **a**, Grey lines show the P input  
280 Gaussian functions (see text). The P input magnitude follows the mean or 95<sup>th</sup> percentiles of  
281 the values derived for ash supply and weathering combined, with or without recycling of P from  
282 sediments (see main text). **b**, Modelled  $\delta^{13}\text{C}$  of carbonates (with colours defined in panel e)  
283 compared to data<sup>50</sup> (yellow circles). **c**, Modelled atmospheric  $\text{CO}_2$ . **d**, Modelled global average  
284 surface temperature. **e**, Degree of marine anoxia (represented as the modelled proportion of  
285 anoxic seafloor). Solid lines show the same simulations as the dashed lines, but with additional  
286 P input to represent sedimentary recycling of P (see text).

## 287 **References**

- 288 1. Harper, D. A. T., Hammarlund, E. U. & Rasmussen, C. M. Ø. End Ordovician extinctions: A  
289 coincidence of causes. *Gondwana Res.* 25, 1294–1307 (2014).
- 290 2. Bambach, R. K., Knoll, A. H. & Wang, S. C. Origination, extinction, and mass depletions of  
291 marine diversity. *Paleobiology* 30, 522–542 (2004).
- 292 3. Rasmussen, C. M. Ø., Kröger, B., Nielsen, M. L. & Colmenar, J. Cascading trend of Early  
293 Paleozoic marine radiations paused by Late Ordovician extinctions. *Proc. Natl. Acad. Sci. U. S. A.* 116,  
294 7207–7213 (2019).
- 295 4. Bergström, S. M., Schmitz, B., Saltzman, M. R. & Huff, W. D. The Upper Ordovician  
296 Guttenberg  $\delta^{13}\text{C}$  excursion (GICE) in North America and Baltoscandia: Occurrence,  
297 chronostratigraphic significance, and paleoenvironmental relationships. *Geol. Soc. Am. Spec. Pap.* 466,  
298 37–67 (2010).

- 299 5. Metzger, J. G., Ramezani, J., Bowring, S. A. & Fike, D. A. New age constraints on the duration  
300 and origin of the Late Ordovician Guttenberg  $\delta^{13}\text{C}_{\text{carb}}$  excursion from high-precision U-Pb  
301 geochronology of K-bentonites. *GSA Bull.* (2020) doi:10.1130/B35688.1.
- 302 6. Finnegan, S. et al. The magnitude and duration of late Ordovician-early Silurian glaciation.  
303 *Science*. 331, 903–906 (2011).
- 304 7. Ainsaar, L. et al. Middle and Upper Ordovician carbon isotope chemostratigraphy in  
305 Baltoscandia: A correlation standard and clues to environmental history. *Palaeogeogr. Palaeoclimatol.*  
306 *Palaeoecol.* 294, 189–201 (2010).
- 307 8. Lenton, T. M., Crouch, M., Johnson, M., Pires, N. & Dolan, L. First plants cooled the  
308 Ordovician. *Nat. Geosci.* 5, 86–89 (2012).
- 309 9. Mills, B. J. W. et al. Modelling the long-term carbon cycle, atmospheric CO<sub>2</sub>, and Earth surface  
310 temperature from late Neoproterozoic to present day. *Gondwana Research* vol. 67 172–186 (2019).
- 311 10. Shen, J. et al. Improved efficiency of the biological pump as a trigger for the Late Ordovician  
312 glaciation. *Nat. Geosci.* 11, 510–514 (2018).
- 313 11. Swanson-Hysell, N. L. & Macdonald, F. A. Tropical weathering of the Taconic orogeny as a  
314 driver for Ordovician cooling. *Geology* 45, 719–722 (2017).
- 315 12. Bartlett, R. et al. Abrupt global-ocean anoxia during the Late Ordovician–early Silurian detected  
316 using uranium isotopes of marine carbonates. *Proc. Natl. Acad. Sci. U. S. A.* 115, 5896–5901 (2018).
- 317 13. Morris, J. L. et al. The timescale of early land plant evolution. *Proc. Natl. Acad. Sci. U. S. A.*  
318 115, E2274–E2283 (2018).
- 319 14. Buggisch, W. et al. Did intense volcanism trigger the first Late Ordovician icehouse? *Geology*  
320 38, 327–330 (2010).
- 321 15. Herrmann, A. D., Leslie, S. A. & MacLeod, K. G. Did intense volcanism trigger the first Late  
322 Ordovician icehouse?: COMMENT. *Geology* 39, e237–e237 (2011).

- 323 16. Huff, W. D., Bergström, S. M. & Kolata, D. R. Ordovician explosive volcanism. *Geol. Soc.*  
324 *Am. Spec. Pap.* 466, 13–28 (2010).
- 325 17. Tao, H., Qiu, Z., Lu, B., Liu, Y. & Qiu, J. Volcanic activities triggered the first global cooling  
326 event in the Phanerozoic. *J. Asian Earth Sci.* 104074 (2019) doi:10.1016/j.jseaes.2019.104074.
- 327 18. Huff, W. D., Kolata, D. R., Bergström, S. M. & Zhang, Y. S. Large-magnitude Middle  
328 Ordovician volcanic ash falls in North America and Europe: Dimensions, emplacement and post-  
329 emplacement characteristics. *J. Volcanol. Geotherm. Res.* 73, 285–301 (1996).
- 330 19. Sell, B. K. et al. Stratigraphic correlations using trace elements in apatite from late Ordovician  
331 (Sandbian-Katian) K-bentonites of eastern North America. *Bull. Geol. Soc. Am.* 127, 1259–1274  
332 (2015).
- 333 20. Ballo, E. G., Augland, L. E., Hammer, Ø. & Svensen, H. H. A new age model for the Ordovician  
334 (Sandbian) K-bentonites in Oslo, Norway. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 520, 203–213  
335 (2019).
- 336 21. Liu, W. et al. K-bentonites in Ordovician-Silurian transition from South China: Implications for  
337 tectonic evolution in the northern margin of Gondwana. *J. Geol. Soc. London.* jgs2020-049 (2020)  
338 doi:10.1144/jgs2020-049.
- 339 22. Smolarek-Lach, J., Marynowski, L., Trela, W. & Wignall, P. B. Mercury Spikes Indicate a  
340 Volcanic Trigger for the Late Ordovician Mass Extinction Event: An Example from a Deep Shelf of the  
341 Peri-Baltic Region. *Sci. Rep.* 9, 1–11 (2019).
- 342 23. Jones, D. S., Martini, A. M., Fike, D. A. & Kaiho, K. A volcanic trigger for the late Ordovician  
343 mass extinction? Mercury data from south China and Laurentia. *Geology* 45, 631–634 (2017).
- 344 24. Longman, J., Palmer, M. R., Gernon, T. M. & Manners, H. R. The role of tephra in enhancing  
345 organic carbon preservation in marine sediments. *Earth-Science Rev.* 192, 480–490 (2019).

- 346 25. Jones, M. T. & Gislason, S. R. Rapid releases of metal salts and nutrients following the  
347 deposition of volcanic ash into aqueous environments. *Geochim. Cosmochim. Acta* 72, 3661–3680  
348 (2008).
- 349 26. Sell, B., Ainsaar, L. & Leslie, S. Precise timing of the Late Ordovician (Sandbian) super-  
350 eruptions and associated environmental, biological, and climatological events. *J. Geol. Soc. London*.  
351 170, 711–714 (2013).
- 352 27. Tucker, R. D. & McKerrow, W. S. Early Paleozoic chronology: a review in light of new U-Pb  
353 zircon ages from Newfoundland and Britain. *Can. J. Earth Sci.* 32, 368–379 (1995).
- 354 28. Ling, M. X. et al. An extremely brief end Ordovician mass extinction linked to abrupt onset of  
355 glaciation. *Solid Earth Sci.* 4, 190–198 (2019).
- 356 29. Du, X. et al. Was volcanic activity during the Ordovician-Silurian transition in South China part  
357 of a global phenomenon? Constraints from zircon U–Pb dating of volcanic ash beds in black shales.  
358 *Mar. Pet. Geol.* 114, 104209 (2020).
- 359 30. Lee, C.-T. A. et al. Volcanic ash as a driver of enhanced organic carbon burial in the Cretaceous.  
360 *Sci. Rep.* 8, 4197 (2018).
- 361 31. Longman, J., Palmer, M. R., Gernon, T. M. & Manners, H. R. Subaerial volcanism is a major  
362 contributor to oceanic iron and manganese cycles. In Review.
- 363 32. Gudmundsson, M. T. et al. Ash generation and distribution from the April-May 2010 eruption  
364 of Eyjafjallajökull, Iceland. *Sci. Rep.* 2, 572 (2012).
- 365 33. Laeger, K. et al. High-resolution geochemistry of volcanic ash highlights complex magma  
366 dynamics during the Eyjafjallajökull 2010 eruption. *Am. Mineral.* 102, 1173–1186 (2017).
- 367 34. Paytan, A. & McLaughlin, K. The oceanic phosphorus cycle. *Chem. Rev.* 107, 563–576 (2007).
- 368 35. Cao, W., Lee, C. T. A. & Lackey, J. S. Episodic nature of continental arc activity since 750 Ma:  
369 A global compilation. *Earth Planet. Sci. Lett.* 461, 85–95 (2017).



- 370 36. Mills, B. J. W., Scotese, C. R., Walding, N. G., Shields, G. A. & Lenton, T. M. Elevated CO<sub>2</sub>  
371 degassing rates prevented the return of Snowball Earth during the Phanerozoic. *Nat. Commun.* 8, 1–7  
372 (2017).
- 373 37. Dessert, C., Dupré, B., Gaillardet, J., François, L. M. & Allègre, C. J. Basalt weathering laws  
374 and the impact of basalt weathering on the global carbon cycle. *Chem. Geol.* 202, 257–273 (2003).
- 375 38. Dessert, C. et al. Erosion of Deccan Traps determined by river geochemistry: impact on the  
376 global climate and the <sup>87</sup>Sr/<sup>86</sup>Sr ratio of seawater. *Earth Planet. Sci. Lett.* 188, 459–474 (2001).
- 377 39. Tostevin, R. & Mills, B. J. W. Reconciling proxy records and models of Earth’s oxygenation  
378 during the Neoproterozoic and Palaeozoic. *Interface Focus* 10, 20190137 (2020).
- 379 40. Slomp, C. P. & Van Cappellen, P. The global marine phosphorus cycle: sensitivity to oceanic  
380 circulation. *Biogeosciences* 4, 155–171 (2007).
- 381 41. Hallam, A. *Phanerozoic sea-level changes*. (Columbia Univeristy Press, 1992).
- 382 42. Walker, L. J., Wilkinson, B. H. & Ivany, L. C. Continental drift and phanerozoic carbonate  
383 accumulation in shallow-shelf and deep-marine settings. *J. Geol.* 110, 75–87 (2002).
- 384 43. Alcott, L. J., Mills, B. J. W. & Poulton, S. W. Stepwise Earth oxygenation is an inherent property  
385 of global biogeochemical cycling. *Science.* 366, 1333–1337 (2019).
- 386 44. Berner, R. A. A model for atmospheric CO<sub>2</sub> over Phanerozoic time. *Am. J. Sci.* 291, 339–376  
387 (1991).
- 388 45. Witkowski, C. R., Weijers, J. W. H., Blais, B., Schouten, S. & Sinninghe Damsté, J. S.  
389 Molecular fossils from phytoplankton reveal secular PCO<sub>2</sub> trend over the phanerozoic. *Sci. Adv.* 4,  
390 eaat4556 (2018).
- 391 46. Goldberg, S. L., Present, T. M., Finnegan, S. & Bergmann, K. D. A high-resolution record of  
392 early Paleozoic climate. *Proc. Natl. Acad. Sci.* 118, (2021).
- 393 47. Zou, C. et al. Organic-matter-rich shales of China. *Earth-Science Reviews* vol. 189 51–78  
394 (2019).

- 395 48. Su, W. et al. K-bentonite, black-shale and flysch successions at the Ordovician-Silurian  
396 transition, South China: Possible sedimentary responses to the accretion of Cathaysia to the Yangtze  
397 Block and its implications for the evolution of Gondwana. *Gondwana Res.* 15, 111–130 (2009).
- 398 49. LaPorte, D. F. et al. Local and global perspectives on carbon and nitrogen cycling during the  
399 Hirnantian glaciation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 276, 182–195 (2009).
- 400 50. Saltzman, M. R. & Thomas, E. Carbon isotope stratigraphy. in *The Geologic Time Scale 2012*  
401 (eds. Gradstein, F. M., Ogg, J., Schmitz, M. D. & Ogg, G, M.) 207–232 (Elsevier, 2012).  
402 doi:10.1016/B978-0-444-59425-9.00011-1.
- 403 51. Sobolev, S. V. et al. Linking mantle plumes, large igneous provinces and environmental  
404 catastrophes. *Nature* 477, 312–316 (2011).
- 405 52. Black, B. A. et al. Systemic swings in end-Permian climate from Siberian Traps carbon and  
406 sulfur outgassing. *Nat. Geosci.* 11, 949–954 (2018).
- 407 53. Schoene, B., Guex, J., Bartolini, A., Schaltegger, U. & Blackburn, T. J. Correlating the end-  
408 Triassic mass extinction and flood basalt volcanism at the 100 ka level. *Geology* 38, 387–390 (2010).
- 409 54. Fan, J. X. et al. A high-resolution summary of Cambrian to early Triassic marine invertebrate  
410 biodiversity. *Science* . 367, 272–277 (2020).
- 411 55. Vandenbroucke, T. R. A. et al. Metal-induced malformations in early Palaeozoic plankton are  
412 harbingers of mass extinction. *Nat. Commun.* 6, (2015).
- 413 56. Merdith, A. S. et al. Extending full-plate tectonic models into deep time: Linking the  
414 Neoproterozoic and the Phanerozoic. *Earth-Science Rev.* 214, 103477 (2021).
- 415 57. Cocks, L. R. M. & Torsvik, T. H. Ordovician palaeogeography and climate change. *Gondwana*  
416 *Res.* (2020) doi:10.1016/j.gr.2020.09.008.

## 418 **Methods**

### 419 **Major and trace element geochemistry**

420 Tephra layers from IODP cores 1396C (Lesser Antilles) and U1339D (Bering Sea) were  
421 analysed for their phosphorus content. Tephras were identified visually, and microscopically,  
422 in core 1339D and through their low CaCO<sub>3</sub> content in U1396C. P was analysed in tephra layers  
423 after mixed acid (HNO<sub>3</sub>-HCl-HF) bench-top digestion. Samples were then analysed on a Perkin  
424 Elmer 2000B at the University of Oxford. Analysis was completed in both standard mode (m/z  
425 31) and in reaction mode, with O<sub>2</sub> as reaction gas and analysis on m/z 47. In all cases, data were  
426 more accurate and detection limits were sufficient from standard mode analysis and so we  
427 present these results here. Blanks and standards (BHVO2 basalt) were prepared and analysed  
428 in the same manner (Supplementary Table 1). For cores U1396C and U1339D, Al and Zr were  
429 determined after digestion using the same procedure as above, again alongside standard  
430 BHVO2 and blanks. Concentrations of these elements were determined using a Thermo X-  
431 Series ICP-MS at the University of Southampton (Supplementary Table 1).

### 432 **P depletion factors and P release**

433 We used the GEOROC database to estimate the protolith composition of volcanic  
434 material from each of the source regions. These data were filtered to remove any data related  
435 to non-outcrop samples, xenoliths and any mineral-specific analyses. This database was used  
436 to estimate the composition of tephra prior to dissolution and diagenetic alteration. By  
437 normalising P to Zr and plotting this ratio against Ti/Zr (elements which are largely immobile  
438 during diagenesis), the empirical relationship between the two ratios can be used to estimate  
439 the original protolith composition following the method of ref.<sup>30</sup>, developed to estimate metal  
440 mobility in Cretaceous tephras (Supplementary Table 2). The linear regression representing this  
441 relationship is then used back-calculate the original composition of altered tephra

442 (Supplementary Tables 2, 3, refs.<sup>58-64</sup>). These compositions, along with compositions of altered  
443 tephra, are then used to calculate depletion factors using the following equation (Equation 1):

$$444 \quad P_D = \frac{M_P^L}{M_P^O} = 1 - \frac{\left(\frac{C_P^{re}}{C_{Zr}^{re}}\right)}{\left(\frac{C_P^O}{C_{Zr}^O}\right)} \text{ (Eq. 1)}$$

445 The left side of the equation is the depletion factor, where  $M_P^O$  original P mass in the protolith,  
446  $M_P^L$  is the loss of P.  $C_P^{re}$  and  $C_{Zr}^{re}$  are the mass of P and Zr in tephra, and  $C_P^O/C_{Zr}^O$  represents the  
447 ratio of P to Zr in the protolith, back-calculated from the linear regression of GEOROC data  
448 (Fig. 3, Extended Data Figures 1, 2).

#### 449 **Estimating the extent and timing of volcanism during the Late Ordovician**

450 We use Monte Carlo simulations of variables associated with bentonite deposition  
451 during the Late Ordovician to estimate the size of the volcanic eruptions and associated ash  
452 deposition<sup>57</sup>. For the GICE period, we use values from published compilations of North  
453 American bentonites<sup>5,19</sup> (Supplementary Table 4), and for the HICE we collate ages from  
454 published bentonites from China (Supplementary Table 5). For the period 455 – 450 Ma  
455 (corresponding to period covering the GICE), we take the number of ash layers to be 100 based  
456 on observations<sup>19</sup>. We assume these ash layers represent eruptions of VEI 8 due to the location  
457 and characteristics of these bentonites, which constitute discrete centimetre-thick horizons  
458 thousands of kilometres from any proposed source<sup>16,19</sup>. We assume each eruption contained on  
459 average 1000 km<sup>3</sup> erupted material<sup>18</sup>. To estimate how much erupted material was ash, we use  
460 a value of 50%, representing the likely proportions in Ultraplinian eruptions<sup>18,21</sup>. Since we are  
461 only interested, in the first instance, in the ash which may directly supply P to the ocean, we  
462 use an estimate of 50% ashfall in the ocean basins. This number is based upon estimates of  
463 ashfall which has been subducted since the Ordovician, using isopachs constructed from North  
464 American outcrops<sup>18</sup>, and paleogeographic reconstructions which indicate volcanism was

465 linked to the opening of the Iapetus Ocean (Figure 2). For all variables used in equation 2, we  
466 apply standard deviations of all variables set at 25% of the variable mean, unless stated  
467 (Supplementary Table 6). 10,000 simulations of all variables were performed using the r  
468 package *rtrucnorm*, and outputs were used to reconstruct likely ash volumes (in km<sup>3</sup>).

469 For the period 450 – 440 Ma (corresponding to period covering the HICE), a similar set  
470 of likely values for variables was constructed using published data on Chinese bentonite  
471 deposits<sup>21</sup>. In this case, we use 88 ash layers as our mean, derived from the subtraction of 16  
472 Silurian ashes from a compilation of Late Ordovician–early Silurian Chinese bentonites<sup>21,65</sup>.  
473 We use 75% as the oceanic fraction because this volcanism was linked with subduction of the  
474 Zhenge-Dapu Ocean (Figure 2), and so a high proportion will be deposited in this  
475 environment<sup>21</sup>. Again, we apply standard deviations of 25% to each of these variables to  
476 consider the uncertainty.

477 In both cases, to estimate ash density, and the amount of P contained in the original  
478 ashes, we use measured values from Icelandic ashfall<sup>32,33</sup>, with standard deviations derived from  
479 the measurements. Using the ash volume estimates derived from these variables, and our  
480 depletion factors, we simulate 10,000 iterations for total P supply for each period (in mole P),  
481 using the following equation (Eq. 2):

$$482 \quad P \text{ release (mole)} = \left( \frac{V_{Ash} \times \rho_{Ash} \times P_{Ash} \times P_D}{30.97} \right) \times P_{ocean} \text{ (Equation 2)}$$

483 where  $V_{Ash}$ ,  $\rho_{Ash}$  and  $P_{Ash}$  are the volume of ash (in km<sup>3</sup>), density of ash (in kg/m<sup>3</sup>) and  
484 phosphorus content in ash (in wt %).  $P_D$  is the depletion factor of phosphorus,  $P_{ocean}$  is the  
485 proportion falling into the ocean and 30.97 is the molecular weight of P, to convert from grams  
486 to moles. Such an exercise provides an absolute amount of P released for each period, but for  
487 modelling purposes, we must convert our total P supply values into flux (in mol P myr<sup>-1</sup>).

488 To do this, we develop a dataset of all reliably dated (i.e., excluding K-Ar or fission  
489 track dates) bentonites of Late Ordovician age from across the two primary volcanic provinces,  
490 China and North America/Baltica (Figure 2, refs. <sup>5,20,21,26–29,65–80</sup>). For each of the dates, we use  
491 a Monte Carlo based approach to generate 10,000 possible ages, constrained by published age  
492 and error values. We group the outputs of this exercise into 0.25 Myr bins and produce  
493 probability density estimates for each bin (Fig. 1a, b). For each of the two volcanic provinces,  
494 we average across each bin to result in a probability density of each 0.25 Myr period (Fig. 1c).  
495 This exercise results in two distinct peaks, representing the most likely period of volcanism for  
496 both provinces. For North America/Scandinavia, this peak is centred on 453.5 Ma. For China,  
497 the volcanic peak occurs 444.0 Ma. To represent these events in the model we then use a  
498 standard Gaussian curve with  $\sigma=0.4$ , giving an event duration of around 2 Myrs. This width is  
499 informed by the duration of the carbon isotope excursions.

#### 500 **Estimating P flux from weathering**

501 We estimate the spatial extent of erupted material during the Late Ordovician using an  
502 averaged value from a modelling study of Ordovician volcanism ( $1.56 \times 10^6 \text{ km}^2$ ; ref.<sup>60</sup>). We  
503 then use P release value of  $29.77 \text{ kg P km}^{-2} \text{ yr}^{-1}$  as measured from basalts<sup>82</sup>. We estimate that  
504 50% of the ash and lava was terrestrially emplaced based on the observations of ash deposition  
505 considered previously<sup>18,21</sup>. By applying 20% errors to all of these values, we then carried out  
506 10,000 Monte Carlo simulations of each variable, before calculating the final flux (in mol P  
507  $\text{myr}^{-1}$ ) by multiplying each iteration of each variable.

#### 508 **Biogeochemical modelling**

509 We use the latest COPSE biogeochemical model<sup>39</sup>. We run the model baseline and add  
510  $P_{force}$  to the global bioavailable phosphorus weathering flux (Equation 3). This adds additional  
511 phosphorus input during the Late Ordovician to the baseline model run.

512 
$$P_{force} = 10^{-6} P_{GICE} \frac{norm(t, -453.45, 0.4)}{norm(-453.45, -453.45, 0.4)} + 10^{-6} P_{HICE} \frac{norm(t, -444, 0.4)}{norm(-444, -444, 0.4)} \text{ (Eq. 3)}$$

513 Here  $P_{GICE}$  and  $P_{HICE}$  are the total P inputs from ash, weathering, and recycling in moles. Here  
514  $norm$  is a normal function defined as  $norm(time, midpoint, \sigma)$ .  $P_{force}$  is multiplied by 5 in some  
515 simulations to represent the additional recycling of P which is not captured in the COPSE  
516 model. This factor is determined by running a P-C cycling model which has an explicit  
517 representation of the shelf<sup>43</sup> and comparing the ratio between P input from weathering and  
518 overall marine P concentration versus the same metric in COPSE. The reader is referred to  
519 Extended Data Figure 3 for the model comparison plots.

## 520 **Data Availability**

521 The authors declare that data supporting the findings of this study are available within the article  
522 and Supplementary Information and Extended Data. All data have also been uploaded to  
523 Figshare, at the following DOI addresses: <http://dx.doi.org/10.6084/m9.figshare.14914893>,  
524 <http://dx.doi.org/10.6084/m9.figshare.14914911>,  
525 <http://dx.doi.org/10.6084/m9.figshare.14914896> and  
526 <http://dx.doi.org/10.6084/m9.figshare.14914890>.

## 527 **Code availability**

528 COPSE model code can be downloaded at <https://github.com/bjwmills>

## 529 **Methods-only References**

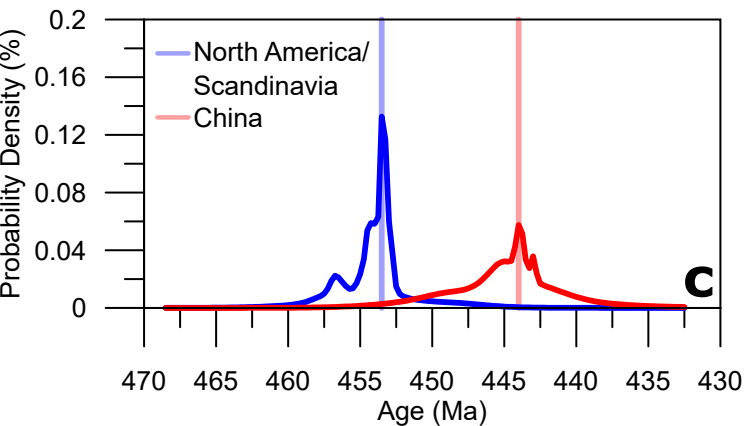
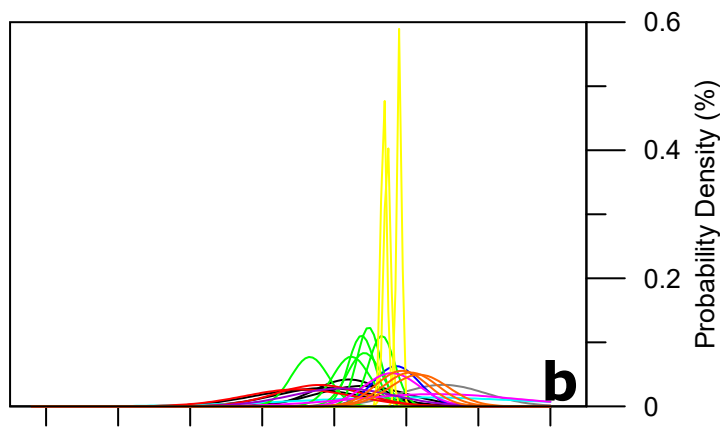
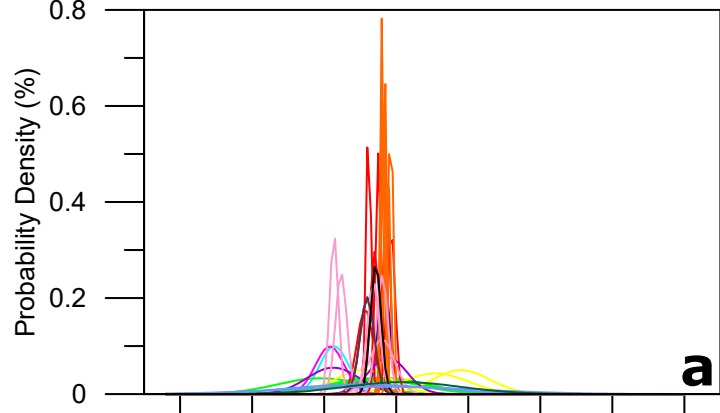
- 530 58. Bitschene, P. R., Mehl, K. W. & Schmincke, H.-U. Composition and origin of marine ash layers  
531 and epiclastic rocks from the Kerguelen Plateau, southern Indian Ocean (Legs 119 and 120). Proc. Ocean  
532 Drill. Program, 120 Sci. Results 120, 135–149 (1992).
- 533 59. Schindlbeck, J. C. et al. One Million Years tephra record at IODP Sites U1436 and U1437:  
534 Insights into explosive volcanism from the Japan and Izu arcs. Isl. Arc 27, e12244 (2018).

- 535 60. Rodehorst, U., Schmincke, H.-U. & Sumita, M. Geochemistry and petrology of Pleistocene ash  
536 layers erupted at Las Cañadas Edifice (Tenerife),. *Scientific Results* vol. 157 (1998).
- 537 61. Salisbury, M. J. et al. Deep-sea ash layers reveal evidence for large, late Pleistocene and  
538 Holocene explosive activity from Sumatra, Indonesia. *J. Volcanol. Geotherm. Res.* 231–232, 61–71  
539 (2012).
- 540 62. Derkachev, A. N. et al. Tephra layers of in the quaternary deposits of the Sea of Okhotsk:  
541 Distribution, composition, age and volcanic sources. *Quat. Int.* 425, 248–272 (2016).
- 542 63. Schindlbeck, J. C. et al. Late Cenozoic tephrostratigraphy offshore the southern Central  
543 American Volcanic Arc: 1. Tephra ages and provenance. *Geochemistry, Geophys. Geosystems* 17,  
544 4641–4668 (2016).
- 545 64. Allan, A. S. R., Baker, J. A., Carter, L. & Wysoczanski, R. J. Reconstructing the Quaternary  
546 evolution of the world's most active silicic volcanic system: insights from an ~1.65 Ma deep ocean  
547 tephra record sourced from Taupo Volcanic Zone, New Zealand. *Quat. Sci. Rev.* 27, 2341–2360 (2008).
- 548 65. Yang, S. et al. Duration, evolution, and implications of volcanic activity across the Ordovician–  
549 Silurian transition in the Lower Yangtze region, South China. *Earth Planet. Sci. Lett.* 518, 13–25 (2019).
- 550 66. Tucker, R. D. U-Pb dating of Plinian-eruption ashfalls by the isotopic dilution method: a reliable  
551 and precise tool for time-scale calibration and biostratigraphic correlation. *Geol. Soc. Amer. Abs. w/  
552 Prog.* 24, A192 (1992).
- 553 67. Oruche, N. E., Dix, G. R. & Kamo, S. L. Lithostratigraphy of the upper Turinian – Lower  
554 Chatfieldian (upper Ordovician) foreland succession, and a U–Pb ID–TIMS date for the Millbrig  
555 volcanic ash bed in the Ottawa embayment. *Can. J. Earth Sci.* 55, 1079–1102 (2018).
- 556 68. Min, K., Renne, P. R. & Huff, W. D. Ar/Ar dating of Ordovician K-bentonites in Laurentia and  
557 Baltoscandia. *Earth Planet. Sci. Lett.* 185, 121–134 (2001).



- 558 69. Samson, S. D., Patchett, P. J., Roddick, J. C. & Parrish, R. R. Origin and tectonic setting of  
559 Ordovician bentonites in North America: isotopic and age constraints. *Geol. Soc. Am. Bull.* 101, 1175–  
560 1181 (1989).
- 561 70. Svensen, H. H., Hammer, Ø. & Corfu, F. Astronomically forced cyclicity in the Upper  
562 Ordovician and U-Pb ages of interlayered tephra, Oslo Region, Norway. *Palaeogeogr. Palaeoclimatol.*  
563 *Palaeoecol.* 418, 150–159 (2015).
- 564 71. Bauert, H. et al. New U-Pb zircon ages of the Sandbian (Upper Ordovician) ‘Big K-bentonite’  
565 in Baltoscandia (Estonia and Sweden) by LA-ICPMS. *GFF* 136, 30–33 (2014).
- 566 72. Compston, W. & Williams, I. S. Ion probe ages for the British Ordovician and Silurian  
567 stratotypes. in *Global perspectives on Ordovician geology* (eds. Webby, B. D. & Laurie, J. R.) 59–67  
568 (1992).
- 569 73. Li, Y., Zhang, T., Shao, D. & Shen, B. New U-Pb zircon age and carbon isotope records from  
570 the Lower Silurian Longmaxi Formation on the Yangtze Platform, South China: Implications for  
571 stratigraphic correlation and environmental change. *Chem. Geol.* 509, 249–260 (2019).
- 572 74. Hu, Y. H., Zhou, J. Bin, Song, B., Li, W. & Sun, W. D. SHRIMP zircon U-Pb dating from K-  
573 bentonite in the top of Ordovician of Wangjiawan section, Yichang, Hubei, China. *Sci. China, Ser. D*  
574 *Earth Sci.* 51, 493–498 (2008).
- 575 75. Xie, S., Wang, Z., Wang, J. & Zhuo, J. LA-ICP-MS zircon U-Pb dating of the bentonites from  
576 the uppermost part of the Ordovician Wufeng Formation in the Haoping section, Taoyuan, Hunan.  
577 *Sediment. Tethyan Geol.* 4, 597 (2012).
- 578 76. Yang, S. et al. Constraints on the accumulation of organic matter in Upper Ordovician-lower  
579 Silurian black shales from the Lower Yangtze region, South China. *Mar. Pet. Geol.* 120, 104544 (2020).
- 580 77. Ge, X. et al. Mineralogical and geochemical characteristics of K-bentonites from the Late  
581 Ordovician to the Early Silurian in South China and their geological significance. *Geol. J.* 54, 514–528  
582 (2019).

- 583 78. Zheng, B. et al. Nature of the Late Ordovician-Early Silurian Xiaohe section, Hunan-Hubei area,  
584 South China: implications for the Kwangsi Orogeny. *Int. Geol. Rev.* 62, 1262–1272 (2020).
- 585 79. Kunk, M. J., Sutter, J., Obradovich, J. D. & Lanphere, M. A. Age of biostratigraphic horizons  
586 within the Ordovician and Silurian systems. *Geol. Soc. Mem.* 10, 89–92 (1985).
- 587 80. Tucker, R. D., Krogh, T. E., Ross, R. J. & Williams, S. H. Time-scale calibration by high-  
588 precision UPb zircon dating of interstratified volcanic ashes in the Ordovician and Lower Silurian  
589 stratotypes of Britain. *Earth Planet. Sci. Lett.* 100, 51–58 (1990).
- 590 81. Lefebvre, V., Servais, T., François, L. & Averbuch, O. Did a Katian large igneous province  
591 trigger the Late Ordovician glaciation?. A hypothesis tested with a carbon cycle model. *Palaeogeogr.*  
592 *Palaeoclimatol. Palaeoecol.* 296, 310–319 (2010).
- 593 82. Hartmann, J., Moosdorf, N., Lauerwald, R., Hinderer, M. & West, A. J. Global chemical  
594 weathering and associated p-release - the role of lithology, temperature and soil properties. *Chem. Geol.*  
595 363, 145–163 (2014).



450 Ma

