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1                   Vertical decoupling in Late Ordovician anoxia due to  
2                   reorganization of ocean circulation

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19

20 **ABSTRACT**

21

22 Geochemical redox proxies indicate that seafloor anoxia occurred during the latest Ordovician  
23 glacial maximum, coincident with the second pulse of the Late Ordovician mass extinction.

24 However, expanded anoxia in a glacial climate strikingly contrasts with the warming-associated  
25 Mesozoic anoxic events, and raises questions both as to the causal mechanism of ocean

26 deoxygenation and its relationship with extinction. Here we firstly report iodine to calcium ratio  
27 (I/Ca) data that documents increased upper-ocean oxygenation despite the concurrent expansion

28 of seafloor anoxia. We then resolve these apparently conflicting observations as well as their

29 relationship to global climate, by means of a series of Earth System model simulations. Applying

30 available Late Ordovician (Hirnantian) sea-surface temperature estimates from oxygen isotope

31 studies as constraints, alongside our I/Ca data, leads us to identify a scenario in which Hirnantian

32 glacial conditions permit both the spread of seafloor anoxia and increased upper-ocean

33 oxygenation. Our simulated mechanism – a reorganization of global ocean circulation, with

34 reduced importance of northern-sourced waters and a poorer ventilated and deoxygenated deep

35 ocean – has parallels with Pleistocene state transitions in Atlantic meridional overturning

36 (despite a very different continental configuration), and suggests that no simple and predictable

37 relationship between past climate state and oxygenation may exist.

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42 The Late Ordovician mass extinction (LOME) is the first of the ‘Big Five’ mass extinctions<sup>1</sup> and  
43 was characterized by the disappearance of ~85% of marine species<sup>2</sup>. Extinction clustered in two  
44 apparent pulses<sup>2</sup> (Fig. 1) – at the beginning of the Hirnantian and near the end of the Hirnantian  
45 (‘LOME 1’ and ‘LOME 2’, respectively). LOME 1 may be related to habitat loss associated with  
46 glacioeustatically-driven sea-level changes or potentially volcanism<sup>2-4</sup>, while the drivers  
47 responsible for LOME 2 are more debated. In the traditional time-line interpretation, LOME 2  
48 occurred during deglaciation; extinction was then triggered by the expansion of anoxia onto the  
49 shelves during the associated sea-level rise<sup>5</sup>. However, studies conducted at higher stratigraphic  
50 resolution have recently challenged this model<sup>6,7</sup> and suggest that seafloor anoxia<sup>7</sup> was already  
51 well established during the latest Hirnantian glacial maximum<sup>7,8</sup>.

52 The increased areal extent of seafloor anoxia, indicated by  $\delta^{238}\text{U}$ , coincident with glacial  
53 conditions rather than global warming, presents several apparent conundrums. Firstly, this is  
54 seemingly at odds with the well-established conceptual model for typical Mesozoic Ocean  
55 Anoxic Events which links volcanism with greenhouse-driven warming and hence the  
56 occurrence of global-scale anoxia<sup>9</sup>. Indeed, previous ocean biogeochemical modeling studies of  
57 Hirnantian climate have reported increased oxygenation during glaciation<sup>10</sup> – the expected  
58 corollary of decreased oxygenation during Mesozoic warming episodes<sup>9</sup>. Secondly, despite  
59 uranium isotopic evidence for expanded seafloor anoxia globally<sup>7</sup>, most preserved stratigraphic  
60 sections, deposited at various latitudes in shelf and slope settings, record a shift to more oxic  
61 depositional facies during the Hirnantian<sup>11</sup>. How can deep ocean deoxygenation develop in a  
62 cold climate, and become decoupled from increased shallow marine oxygenation?

63 We resolve this conundrum through a series of Earth System model experiments that reveal  
64 how state transitions in large-scale ocean circulation in response to Ordovician climate change

65 can lead to a dramatic redox restructuring of the marine environment. However, we start by  
66 confirming the existence of surface-to-deep redox decoupling during the latest Ordovician and  
67 report the results of carbonate I/Ca measured in two Laurentian sections spanning the late Katian  
68 to earliest Silurian (Rhuddanian).

### 69 **I/Ca data and upper-ocean oxygenation during LOME 2**

70 Bulk carbonate I/Ca (Methods) reflects changes in dissolved iodate ( $\text{IO}_3^-$ ) concentration, which  
71 decreases in the presence of low-oxygen water masses<sup>12,13</sup>. Lower I/Ca values have been  
72 documented previously during Mesozoic warming events<sup>12</sup>, providing evidence for the ocean  
73 deoxygenation/warming link. Here, results obtained for two Laurentian sections (Extended Data  
74 Fig. 1) show increasing mean I/Ca values from the middle segment of the Hirnantian Isotope  
75 Carbon Excursion (mid HICE) to the late HICE and LOME 2 (Fig. 1, Extended Data Fig. 2). The  
76 higher I/Ca values recorded in the Laurentian epicontinental seas (water depths < ~200 meters)  
77 suggest that latest Ordovician cooling was contemporaneous with increased oxygenation of the  
78 upper ocean, which is independently supported by the Anticosti Island organic biomarker  
79 analysis of Rohrssen et al.<sup>14</sup> and is not easily explained as a diagenetic artifact<sup>15,16</sup>  
80 (Supplementary Discussion and Extended Data Fig. 3). Furthermore, I/Ca values are higher at  
81 Anticosti Island (Canada)<sup>7</sup> than at Copenhagen Canyon (USA)<sup>17</sup> during LOME 2 (Fig. 1). This is  
82 consistent with Copenhagen Canyon being deposited in predominantly poorly oxygenated  
83 offshore waters and closer to the large Laurentian oxygen minimum zone (OMZ; Extended Data  
84 Fig. 1) core as well as with Fe-speciation data from Vinini Creek (Nevada) recording local  
85 anoxic deep waters in an upwelling setting<sup>18</sup> (Fig. 1).

### 86 **Two models for seafloor anoxia in a cold climate**

87 To reconcile the various observations of increased seafloor anoxia from uranium isotopes<sup>7</sup>, but  
88 increased upper-ocean oxygenation from I/Ca, we carry out a gridded parameter ensemble of  
89 simulations using the cGENIE Earth System model of intermediate complexity<sup>19</sup> configured with  
90 Ordovician continental boundary conditions and reduced (3.65 %) Ordovician solar luminosity  
91 value (Methods). We simulate a range of plausible Hirnantian climatic conditions by running the  
92 model multiple times using different atmospheric pCO<sub>2</sub> values (the first parameter axis in the  
93 ensemble), for which we chose a range spanning ×5 through ×24 pre-industrial (280 ppm)  
94 concentrations<sup>20</sup> – equivalent to 1400 to 6720 ppm.

95 In the ocean, it is likely that nutrient inventories were lower than modern as a consequence of  
96 reduced (compared to modern) Ordovician plant cover<sup>21</sup> and high sea level<sup>22</sup>, both tending to  
97 suppress terrestrial weathering and cause lower river-nutrient input than today. We therefore also  
98 simultaneously considered a range of ocean dissolved phosphate inventories, from 0.2 to 1.0  
99 times the present-day mean oceanic concentration ([PO<sub>4</sub>]) of 2.159 μmol kg<sup>-1</sup> (Fig. 2), which  
100 constitutes the 2<sup>nd</sup> parameter axis of our ensemble. We hence explore a total of 30 different  
101 combinations of pCO<sub>2</sub> and ocean phosphate inventory in a regular grid. All simulations were run  
102 to steady state (10,000 years) and the ensemble we focus on assumes a reasonable estimate for  
103 the Ordovician atmospheric oxygen abundance<sup>23–25</sup> of 8.38 % – ×0.4 the modern value of 20.95  
104 %. Changes in the extent of seafloor anoxia simulated in response to changes in both  
105 atmospheric pCO<sub>2</sub> and ocean [PO<sub>4</sub>] are shown in Fig. 2.

106 At ×0.2 [PO<sub>4</sub>], the model Ordovician seafloor is fully oxic, regardless of the value of pCO<sub>2</sub>  
107 and hence climatic state (Fig. 2). As expected, the extent of seafloor anoxia (defined as benthic  
108 [O<sub>2</sub>] ≤ 0 μmol kg<sup>-1</sup> and the presence of free sulphide (H<sub>2</sub>S) in the model) shows a generally  
109 positive saturating relationship with increasing phosphate inventory – a direct response of the

110 changing bacterial oxygen demand as biological primary productivity and carbon export to the  
111 ocean interior (and the strength of the ‘biological pump’) increase. In contrast, we find an  
112 unexpected and highly non-linear relationship between the extent of seafloor anoxia and pCO<sub>2</sub>,  
113 with a prominent maximum in % anoxia reached for intermediate pCO<sub>2</sub> values (between ×6 and  
114 ×10 CO<sub>2</sub>) at ×0.4 [PO<sub>4</sub>].

115 To identify a plausible scenario through climate-productivity space for the cooling climate  
116 leading into the Hirnantian glacial maximum (Fig. 2), we first compare modeled surface ocean  
117 temperatures with estimates from carbonate clumped isotopes<sup>26</sup> and δ<sup>18</sup>O<sub>apatite</sub><sup>7,27</sup> (Supplementary  
118 Results). Hirnantian climate trends are not currently known with sufficient resolution on  
119 Anticosti (or elsewhere) to precisely establish the timing of the onset of cooling leading into the  
120 late HICE glacial maximum and its relationship to the δ<sup>238</sup>U and I/Ca records. We estimate the  
121 magnitude of cooling by comparing paleotemperatures from the Laframboise Member of the  
122 Ellis Bay Formation with those from the lower Ellis Bay Formation (because the Laframboise  
123 Member is interpreted as representing deglacial transgression rather than the glacial maximum<sup>6</sup>,  
124 our estimated temperature changes are best regarded as minimal). Clumped isotopes suggest a  
125 decrease from ca. 33 °C to 29 °C, while δ<sup>18</sup>O<sub>apatite</sub> suggest a decrease from ca. 30 °C to 23 °C.  
126 We use these estimates to posit 2 end-member possibilities for the associated change in  
127 atmospheric pCO<sub>2</sub> within the model ensemble – a drop from ×24 to ×8.5 CO<sub>2</sub><sup>26</sup> (cooling  
128 Scenario #1), or a drop from ×7 to ×5 CO<sub>2</sub><sup>7,27</sup> (cooling Scenario #2).

129 Next, and with these 2 plausible cooling scenarios in mind, we seek to constrain pairs of  
130 simulations that are characterized by an appropriate expansion of seafloor anoxia in the cold  
131 climatic state. Mass balance modeling of the late Hirnantian negative carbonate δ<sup>238</sup>U excursion  
132 at Anticosti Island<sup>7</sup> permits us to refine the estimate of anoxia extent by accounting for the

133 marine uranium budget<sup>28</sup> and indicates a shift from near-modern levels of ocean oxygenation (<  
134 1 % seafloor area anoxic)<sup>7,8</sup>, to anywhere from 3 % to 80 % total anoxic seafloor area<sup>8</sup> (Extended  
135 Data Fig. 4; Supplementary Results). We can hence further refine our choice of model  
136 simulations to pairs in which the extent of seafloor anoxia is initially (in the warm state) close to  
137 modern but is substantially expanded in the cold state.

138 As illustrated in Fig. 2 (and Extended Data Fig. 5), for Scenario #1 (a pCO<sub>2</sub> drop from ×24 to  
139 ×8.5 CO<sub>2</sub>), we identify a pair of model experiments consistent with our criteria for anoxia  
140 expansion (in this case, from ca. 0 % to 45 % of seafloor area) at a constant nutrient inventory of  
141 ×0.4 [PO<sub>4</sub>]. For #2 (pCO<sub>2</sub> decreasing from ×7 to ×5 CO<sub>2</sub>), an increase in ocean phosphate is  
142 required in addition to the cooling in order to trigger deep-ocean deoxygenation. We identify an  
143 increase from ×0.2 to ×0.6 [PO<sub>4</sub>] as consistent with our criteria for seafloor anoxia expansion  
144 (Fig. 2, Extended Data Fig. 5). The possibility of an increase in ocean nutrient inventory is  
145 supported by models and experiments suggesting that colonization of the continents by (non-)<sup>21</sup>  
146 vascular<sup>29</sup> land plants could have driven a substantial increase in phosphorus weathering flux  
147 during the Hirnantian<sup>21,30</sup>. Additional simulations run under alternative assumptions of  
148 atmospheric pO<sub>2</sub> (Extended Data Fig. 6) reveal that these nutrient scenarios are not unique, and  
149 that different combinations of pO<sub>2</sub> and ocean phosphate inventory may produce similar modelled  
150 values of seafloor anoxia. However, the major distinction between the two scenarios remains the  
151 same: cooling alone, triggers the expansion of seafloor anoxia in Scenario #1, while cooling in  
152 Scenario #2 requires a simultaneous increase in ocean nutrient inventory.

### 153 **Reconciling shallow- and deep-marine oxygenation trends**

154 To distinguish between the 2 model scenarios, we now turn to evidence for upper-ocean  
155 oxygenation changes. A key difference between Scenarios #1 and #2 is the change in the oxygen

156 concentrations simulated in the upper ocean (Fig. 3). In Scenario #1, oxygen concentrations in  
157 the upper ocean increase in response to climate cooling because oxygen solubility increases in  
158 colder water<sup>10,31</sup> while the metabolic rates of marine organisms, and thus primary productivity,  
159 decrease<sup>32</sup>. The rate at which particulate organic matter is degraded in the ocean interior also  
160 decreases in response to lower temperatures<sup>32,33</sup>, with less remineralization (and hence demand in  
161 oxygen) occurring in the upper water column, leaving a relatively larger flux to be consumed at  
162 greater depths. A more efficient (deeper penetrating) biological pump also reduces the return  
163 nutrient flux to the ocean surface, further lowering primary productivity (see Methods and  
164 Supplementary Results). In contrast, for Scenario #2, upper-ocean (subsurface) oxygen  
165 concentrations decrease primarily as a consequence of a dominant nutrient inventory-driven  
166 enhancement of the biological pump which overwhelms the effects of cooling (Supplementary  
167 Results). Our I/Ca measurements then distinguish between the two scenarios and identify  
168 Scenario #1 as best capturing the overall Hirnantian ocean redox changes, with the spread of  
169 seafloor anoxia<sup>7</sup> paired with increased oxygenation of the upper ocean (Fig. 1).

170 By applying multiple data constraints to an ensemble of different realizations of Ordovician  
171 climate and marine biogeochemical cycle states, we can reconcile the divergent trends in seafloor  
172 and upper-ocean oxygenation in response to ongoing global cooling. In the model, we account  
173 for the observations as a result of a fundamental reorganization occurring in large-scale ocean  
174 circulation patterns. In the warmest  $\times 24$  CO<sub>2</sub> state, deep-water formation in the model  
175 predominantly occurs at the highest ocean latitudes (which in the Late Ordovician were located  
176 in the Northern Hemisphere) and ventilates much of the Ordovician seafloor with highly  
177 oxygenated waters (Fig. 4i-l). As pCO<sub>2</sub> is lowered through to  $\times 8.5$ , seasonal sea ice appears over  
178 the North Pole (Fig. 4e-h). Seasonal freshwater fluxes associated with retreating sea-ice cover

179 locally stratify and thus stabilize the water column (Supplementary Results). This mechanism,  
180 possibly strengthened by a positive feedback between reduced northwards salinity transport and  
181 deep-water formation and hence overturning, leads to a shutdown of deep-water formation over  
182 the North Pole. Although Southern Hemisphere overturning strengthens, this is restricted to the  
183 West of the low-latitude Laurentia and Baltica continents and leaves much of the ocean floor  
184 (particularly to the East of Laurentia and Baltica) poorly ventilated (Fig. 4f-g). We find support  
185 for such a shift in large-scale ocean circulation occurring in response to cooling, in the higher  
186 resolution MITgcm study of Pohl et al.<sup>10</sup>. Despite using a different continental reconstruction of  
187 the Late Ordovician<sup>34</sup>, they found a shut-down of northern-sourced, deep water in response to a  
188 reduction in the solar constant and cooling, with a similar change in the pattern of global  
189 overturning (Supplementary Results) and a restriction of southern-sourced oxygenation to the  
190 West of Laurentia and Baltica. More idealized basin geometry (and coincidentally also using  
191 MITgcm) modelling also demonstrates the potential for abrupt transitions in meridional  
192 overturning circulation and Rose et al.<sup>35</sup> find this specifically in response to the incipient growth  
193 of a polar sea-ice cover. Regardless, further work using coupled climate models that can account  
194 for the potential role of inter-annual variability and ocean-atmosphere modes in the state-  
195 dependence of large-scale circulation patterns in the Ordovician (that we are unable to address  
196 with the cGENIE model) is important and would help identify which modes of Late Ordovician  
197 ocean circulation are robust (and which might be model-dependent) and how they respond to  
198 climate change.

199 We suggest that a helpful analogy for better visualizing the Ordovician circulation and  
200 oxygenation changes that occur in our model between  $\times 24$  and  $\times 8.5$  pCO<sub>2</sub> (Scenario #1), can be  
201 found during the glacial-interglacial cycles of the late Pleistocene. Specifically, we note how

202 northern-sourced, deep-water production in the Atlantic decreases as climate cools (and is  
203 replaced at depth by deep water sourced from the South)<sup>36</sup>, with the potential for multiple  
204 circulation states with abrupt transitions between them<sup>35,37</sup>. Furthermore, shallowing of the  
205 Atlantic meridional overturning circulation coincides with proxy evidence for reduced  
206 oxygenation at depth, despite glacial deep-ocean temperatures being colder than during  
207 interglacials<sup>38,39</sup>.

208 Finally, an important conclusion we draw from our I/Ca data and simulations is that  
209 increased seafloor anoxia is, by itself, an insufficient explanation for the LOME 2. There is no  
210 evidence of reduced local upper-ocean oxygenation associated with LOME 2 at Anticosti; if  
211 anything there is evidence of increased oxygenation based on I/Ca at this time (Fig. 1). The  
212 majority of Anticosti taxonomic last occurrences also occur above the onset of the negative  
213 uranium isotope excursion<sup>40,41</sup>, and globally many of the taxa that disappear during LOME 2  
214 occurred primarily in shallow-water habitats that would have remained well oxygenated under  
215 almost any reasonable global change scenario. Thus, we suggest that cooling must have  
216 interacted with other factors such as changes in nutrient cycling and primary producer  
217 communities<sup>11,42</sup>, and potentially heavy metal toxicity<sup>43</sup>, to drive the LOME 2 extinction.

218

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223



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#### 234 **AUTHOR CONTRIBUTIONS**

235 A.P., Z.L. S.F. and A.R. designed the study and wrote the manuscript with input from all co-  
236 authors. AP. conducted the FOAM and cGENIE experiments and led the analysis of the model  
237 results. Z.L., W.L., and R.H. carried out the I/Ca analyses. Z.L. led the analysis of the I/Ca  
238 results. R.G.S. conducted the mass balance modeling of the uranium isotope cycle.

#### 239 **COMPETING INTERESTS**

240 The authors declare no competing interests.

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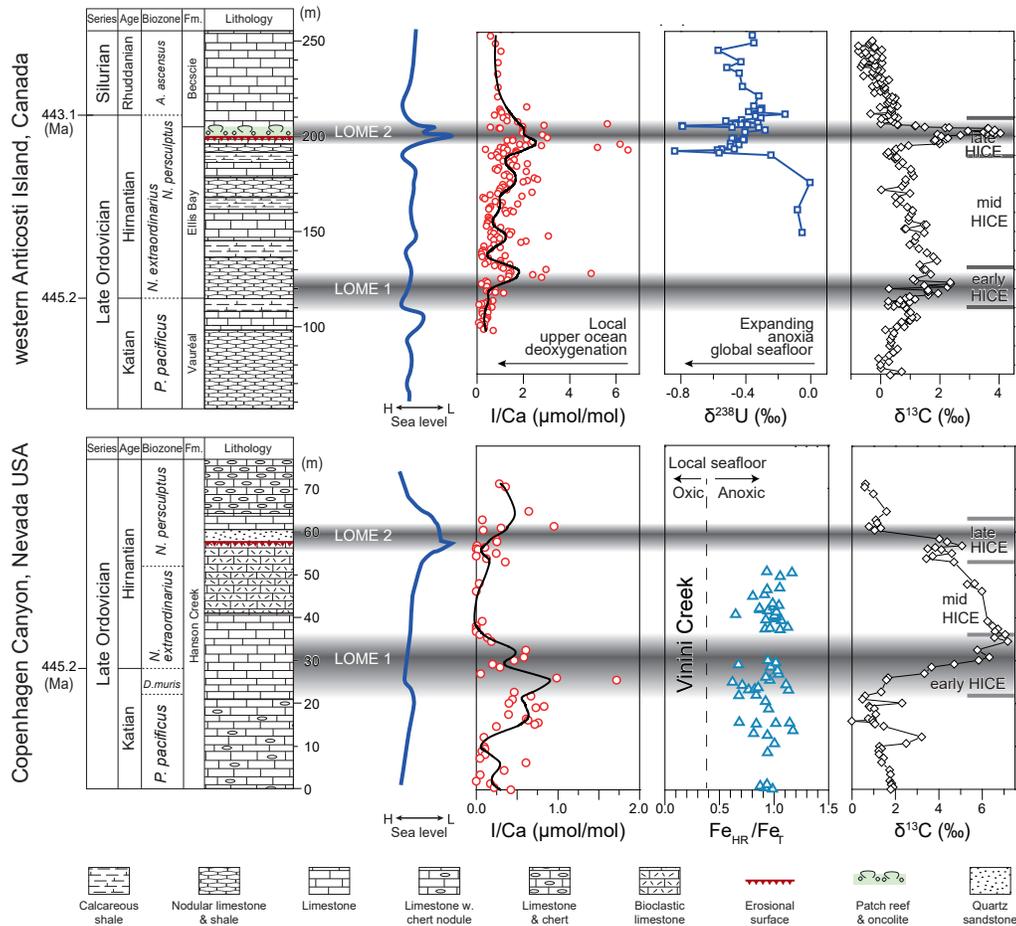
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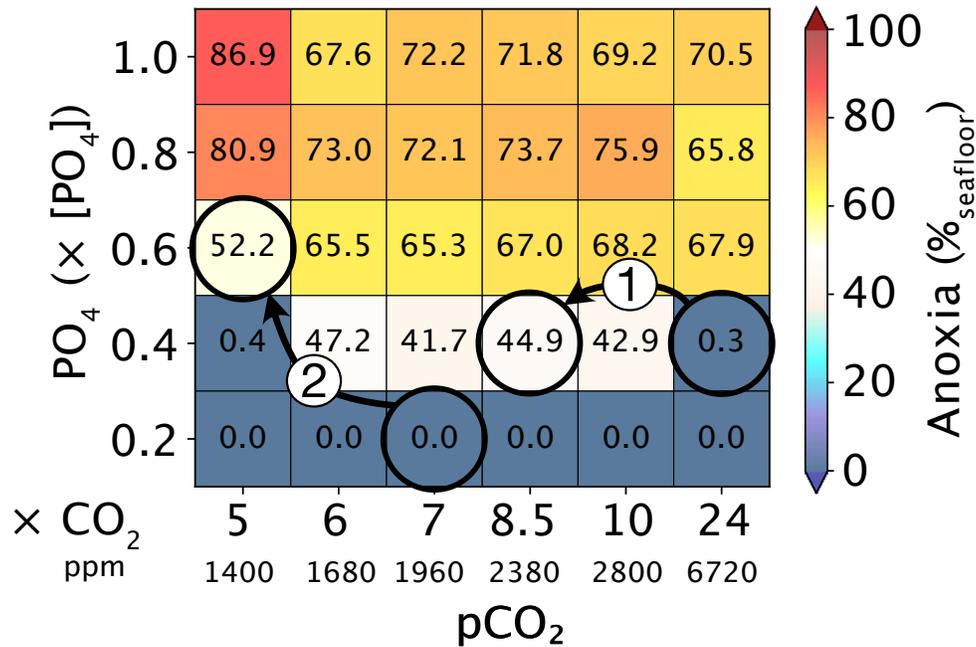
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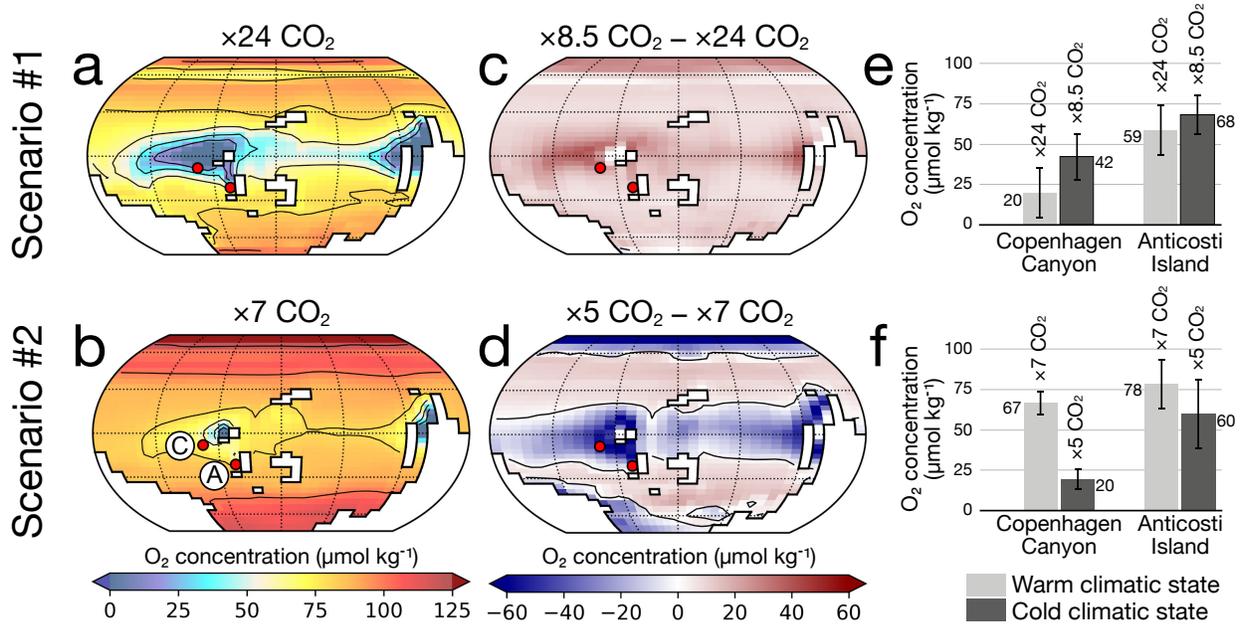
248 Figure 1. Stratigraphic, glacio-eustatic and geochemical records from (a) western Anticosti  
 249 Island (Quebec, Canada) and (b) Copenhagen Canyon (Nevada, USA). The I/Ca curves shown  
 250 with LOESS smoothing are from this study. Note the difference in scale for I/Ca between  
 251 Anticosti and Copenhagen Canyon. For western Anticosti Island, stratigraphic, sea level,  $\delta^{13}\text{C}$ ,  
 252 and  $\delta^{238}\text{U}$  data are from refs<sup>6,7,44</sup>. For Copenhagen Canyon, stratigraphic, sea level, and  $\delta^{13}\text{C}$  data  
 253 are from refs<sup>17,45</sup>; Fe-speciation data<sup>18</sup> are from a nearby section (Vinini Creek, Nevada). Gray  
 254 shaded bands indicate the approximate stratigraphic position of LOME extinctions. Numerical  
 255 ages are from ref<sup>46</sup>. Location of each section is shown in Fig. 3 and Supplementary Fig. 1. *HICE*:  
 256 *Hirnantian Isotope Carbon Excursion*; *LOME 1 and 2*: *Late Ordovician Mass Extinction*  
 257 *apparent pulses #1 and #2*.



259

260 Figure 2. Simulated sensitivity of ocean anoxia to climate and marine productivity. Extent of  
 261 seafloor anoxia (defined as percentage of the total seafloor area characterized by a benthic ocean  
 262  $[\text{O}_2] \leq 0 \mu\text{mol kg}^{-1}$ ) as a function of both  $\text{pCO}_2$  (x-axis) and ocean  $\text{PO}_4$  inventory (y-axis). Values  
 263 and color in each cell represent the extent of anoxia of single simulation. Arrows and labels  
 264 represent Scenarios #1 and #2 discussed in the main text, selected to capture the expansion of  
 265 seafloor anoxia in the latest Hirnantian glacial climate, based on temperature estimates derived  
 266 respectively from clumped isotopes<sup>26</sup> and  $\delta^{18}\text{O}_{\text{apatite}}$ <sup>7,27</sup>. Note that  $\text{pCO}_2$  values (x-axis) are shown  
 267 in two scales: ppm and  $\times \text{CO}_2$  (times the preindustrial atmospheric concentration of 280 ppm).

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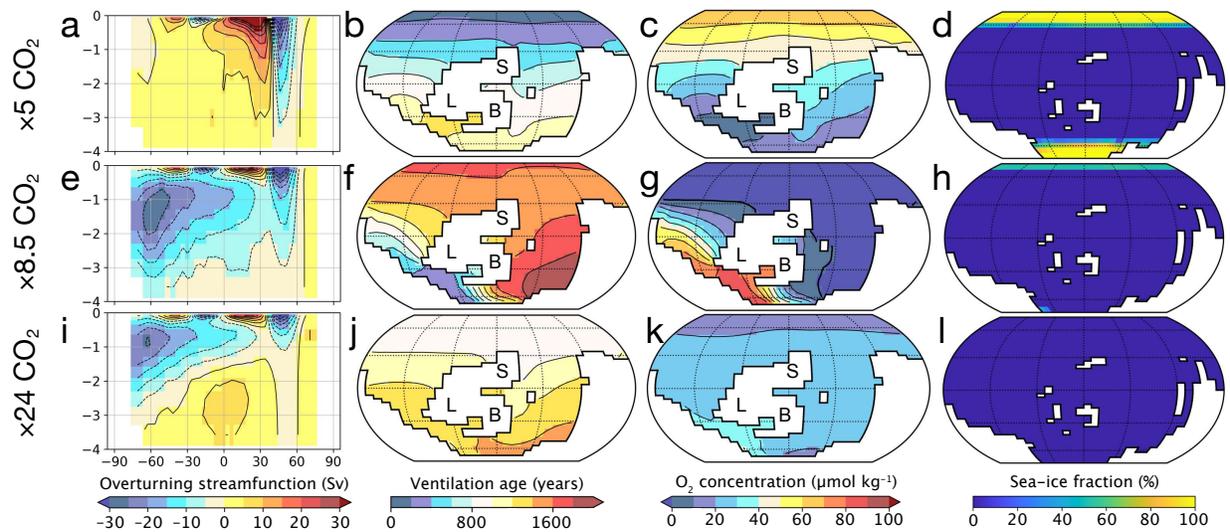
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270 Figure 3. Upper-ocean oxygen concentrations for Scenarios #1 and #2. Upper row (a, c, e)  
 271 corresponds to Scenario #1 (defined in text), bottom row (b, d, f) is Scenario #2. Left column (a,  
 272 b) shows the ocean oxygen concentration simulated between 80 and 175 m water depth (i.e., the  
 273 subsurface grid level in the ocean model) before cooling in Scenarios #1 (a;  $\times 24 \text{ CO}_2$ ;  $\times 1 \text{ CO}_2 =$   
 274 280 ppm) and #2 (b;  $\times 7 \text{ CO}_2$ ). Middle column shows the impact of cooling on ocean oxygenation  
 275 at the same water depth in each scenario. Emerged landmasses are shaded white and contoured  
 276 with a thick black line. Red dots represent the paleo locations of Anticosti Island (A) and  
 277 Copenhagen Canyon (C) (see Fig. 1). Bar plots (e, f) give, for each scenario, the oxygen  
 278 concentration simulated at Anticosti and Copenhagen Canyon before (light grey) and after (dark  
 279 grey) cooling. Error bars are  $\pm 1$  standard deviation, calculated based on all oceanic neighboring  
 280 points in the model.

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285 Figure 4. Ocean circulation response to cooling. Meridional overturning circulation (1<sup>st</sup> column,  
 286 1 Sv = 10<sup>6</sup> m<sup>3</sup> s<sup>-1</sup>), deep-ocean ventilation age (2<sup>nd</sup> column) simulated at ca. 3900 m water depth,  
 287 deep-ocean oxygen concentration (3<sup>rd</sup> column) simulated at ca. 3900 m water depth and mean  
 288 annual sea-ice fraction (4<sup>th</sup> column) simulated using a pCO<sub>2</sub> of (a-d) ×5, (e-h) ×8.5 and (i-l) ×24  
 289 (×1 CO<sub>2</sub> = 280 ppm). Results shown in panels (c), (g) and (k) were obtained at ×0.4 pO<sub>2</sub> and  
 290 ×0.4 [PO<sub>4</sub>]. In panels (a), (e) and (i), positive (negative) values in the meridional overturning  
 291 circulation represent clockwise (anticlockwise) cells. The ventilation age represents the time  
 292 since a parcel of water last reached the ocean surface. *L*: Laurentia; *B*: Baltica; *S*: Siberia.

293

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403

## 404 **METHODS**

### 405 **Description of the model**

406 Simulations were conducted using the Earth System model of intermediate complexity  
407 cGENIE<sup>19</sup> (Supplementary Methods). cGENIE is rooted in a 3D ocean circulation model, but for  
408 speed, includes only a 2D energy-moisture-balance atmospheric component plus sea-ice module.  
409 The model was configured on a 36×36 equal area grid, with 16 unevenly-spaced vertical levels in  
410 the ocean. The cycling of carbon and associated tracers in the ocean is based on a single  
411 (phosphate) nutrient limitation of biological productivity following Reinhard *et al.*<sup>47</sup> but adopts  
412 the Arrhenius-type temperature-dependent scheme for the remineralization of organic matter  
413 exported to the ocean interior of John *et al.*<sup>33</sup>. Compared to recent Earth System models of the  
414 Coupled Model Intercomparison Project phase 6 (CMIP6), the simplified climatic component of  
415 cGENIE offers a rapid model integration time, facilitating the numerous sensitivity tests required

416 to quantify the impact of the uncertainty in the model boundary conditions pervading deep-time  
417 studies, as well as the 10,000-year-long model simulations necessary to ensure deep-ocean  
418 equilibrium (Supplementary Results).

#### 419 **Description of the numerical experiments**

420 We adopted the Hirnantian (445 Ma) continental reconstruction of Scotese and Wright<sup>22</sup>  
421 (Extended Data Fig. 1). In the absence of better constraints, a flat bottom ocean floor was used,  
422 which is not expected to significantly impact simulated global benthic ocean oxygenation  
423 patterns<sup>48</sup> (Supplementary Methods). We calculated solar luminosity at 445 Ma ( $1318.1 \text{ W m}^{-2}$ )  
424 after Gough<sup>49</sup>, and employed a null eccentricity-minimum obliquity orbital configuration, which  
425 provides an equal mean annual insolation to both hemispheres with minimum seasonal contrasts.  
426 For each different atmospheric  $\text{pCO}_2$  assumption, we first ran the FOAM<sup>50</sup> general circulation  
427 model experiment for 2 kyrs using these boundary conditions (Supplementary Methods). We  
428 then derived the 2D wind speed and wind stress, and 1D zonally-averaged albedo forcing fields  
429 required by the cGENIE model, using the ‘muffingen’ open-source software version v0.9.20,  
430 which is assigned a DOI: 10.5281/zenodo.4615664.

431 cGENIE model simulations were initialized with a sea-ice free ocean and homogeneous  
432 temperature and salinity in the ocean ( $5 \text{ }^\circ\text{C}$  and  $34.9 \text{ ‰}$ , respectively). The model was then  
433 integrated for 10,000 years until equilibrium of the deep-ocean oxygen concentration. Results of  
434 the mean of the last simulated year were used for this analysis.

#### 435 **Materials and I/Ca methods**

436 Samples from two Upper Ordovician sections were analyzed for I/Ca: Anticosti Island, Quebec,  
437 Canada and Copenhagen Canyon, Nevada, USA (Supplementary Methods). Rock samples were  
438 crushed and homogenized to fine powder. Around 4 mg of powdered samples were weighed and

439 rinsed with de-ionized water to remove soluble iodine. Nitric acid (3%) was added to dissolve  
440 carbonate. The samples were then diluted to a consistent matrix containing ~50 ppm Ca, 0.5%  
441 tertiary amine (to stabilize iodine), 5 ppb In and Cs (internal standards). The measurements were  
442 performed immediately on a quadrupole ICP-MS (Bruker M90) at Syracuse University. Iodine  
443 calibration standards were prepared daily from KIO<sub>3</sub> powder. The sensitivity of iodine was tuned  
444 to 80-100 kcps for a 1 ppb standard. The reference standard JCp-1 was analyzed repeatedly to  
445 monitor long-term accuracy<sup>12,24</sup>. The detection limit of I/Ca is on the order of 0.1 μmol mol<sup>-1</sup>.

#### 446 **DATA AVAILABILITY**

447 The I/Ca data can be downloaded from Zenodo  
448 (<https://zenodo.org/record/5136966#.YP5vCIMzbu6>).

#### 449 **CODE AVAILABILITY**

450 The code for the version of the ‘muffin’ release of the cGENIE Earth System Model used in this  
451 paper, is tagged as v0.9.20, and is assigned a DOI: 10.5281/zenodo.4618023.

452 Configuration files for the specific experiments presented in the paper can be found in the  
453 directory: genie-userconfigs/MS/ pohletal.NatGeo.2020. Details on the experiments, plus the  
454 command line needed to run each one, are given in the readme.txt file in that directory. All other  
455 configuration files and boundary conditions are provided as part of the code release.

456 A manual detailing code installation, basic model configuration, tutorials covering various  
457 aspects of model configuration and experimental design, plus results output and processing, is  
458 assigned a DOI: 10.5281/zenodo.4615662.

#### 459 **REFERENCES CITED IN METHODS**

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