

1 **Deglacial Pulse of Neutralized Carbon from the Pacific Seafloor: Constraints from**  
2 **the Radiocarbon Budget**

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8 **Key Points:**

- 9
- 10 • Observed deglacial changes in atmospheric CO<sub>2</sub> and <sup>14</sup>C/C allow for up to 2397 Pg of neutralized geologic carbon (i.e., bicarbonate) release
  - 11 • Inverse modeling yields two bicarbonate pulses that are insufficient to drive basin-scale <sup>14</sup>C anomalies and have limited CO<sub>2</sub> effect
  - 12
  - 13 • The global carbon cycle is essentially “blind” to neutralized carbon release and only
  - 14 constrained by <sup>14</sup>C budget
  - 15

## 16 Abstract

17 In the intermediate depth Eastern Tropical Pacific Ocean, multiple deglacial radiocarbon ( $^{14}\text{C}$ )  
18 records show anomalously low  $^{14}\text{C}/\text{C}$  values that appear to be best explained by the addition of  
19  $^{14}\text{C}$ -free geologic carbon. We use inverse carbon cycle modeling and data assimilation of  
20 reconstructed atmospheric  $\text{CO}_2$  and  $\Delta^{14}\text{C}$  to develop an upper bound constraint on this speculated  
21 deglacial geologic carbon release. Our analysis suggests two primary opportunities where large  
22 bicarbonate pulses (up to  $1.3 \text{ PgC yr}^{-1}$ ) could occur with little effect on atmospheric  $\text{CO}_2$  and  
23 without upsetting  $^{14}\text{C}$  mass-balance constraints. Including the release of  $^{14}\text{C}$ -free permafrost  
24 carbon and regrowth of the terrestrial biosphere, we obtain a set of permissible scenarios for  
25 ocean geologic carbon release that ranges from 900-2400 PgC. Based on these results, we  
26 conclude that geologic carbon release is a plausible interpretation for the spatio-temporal cluster  
27 of anomalous  $^{14}\text{C}$  data near the East Pacific Rise.

## 28 Plain language summary

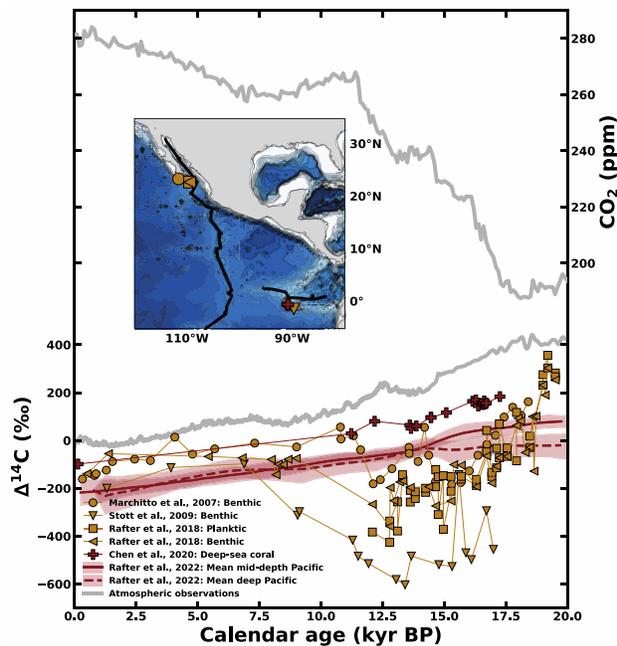
29 Oceanic records indicate that the Eastern Pacific Ocean contained pockets of extremely old water  
30 after the last ice age. The cause of this phenomenon has been puzzling because the water is too  
31 old to have been caused by a slowdown of ocean circulation. It was proposed that the old water  
32 may have instead been caused by geologic carbon addition since the records are located near  
33 volcanically active spreading centers on the seafloor. However, the scale of possible geologic  
34 carbon addition is unclear. To help constrain this, we modeled different geologic carbon release  
35 scenarios and compared the results with observed atmospheric and ocean data. Our findings  
36 indicate that if the geologic carbon were neutralized with equal amounts of alkalinity, then large  
37 quantities (up to 6% of the total carbon inventory) could be added to the ocean without causing  
38 significant changes to the atmosphere or surrounding ocean regions. Based on these findings, it is  
39 possible that large-scale neutralized carbon release occurred since the last ice age and may  
40 explain the exceptionally old water in the Eastern North Pacific. This neutralized carbon would  
41 unlikely cause significant changes to the atmosphere or greater ocean regions.

## 42 1 Introduction

43 Due to the tight coupling of the carbon cycle and climate (Marcott et al., 2014), we must  
44 understand how the natural carbon cycle has changed in the past. An unexplained feature of the  
45 natural carbon cycle is the presence of anomalously low radiocarbon ( $^{14}\text{C}/\text{C}$ ) content—relative to  
46 the contemporaneous atmosphere and most parts of the global ocean—within marine foraminifera  
47 between 18,000 and 11,500 years before 1950 (18-11.5 thousand years before present or kyr BP,  
48 Fig. 1). These deglacial records of  $^{14}\text{C}$  depletion (decay-corrected  $^{14}\text{C}:^{12}\text{C}$  ratio, expressed as  
49  $\Delta^{14}\text{C}$ ; Stuiver & Polach, 1977) have been uncovered throughout the intermediate-depth  
50 (<1000m) Pacific Ocean (Lindsay et al., 2016; Marchitto et al., 2007; Rafter et al., 2018, 2019;  
51 Stott et al., 2009). Occurring roughly at the same time as the deglacial rise in atmospheric  $\text{CO}_2$   
52 and near the weakly ventilated Pacific shadow zone (Gehrie et al., 2006; Holzer et al., 2021),  
53 these depletions in seawater  $\Delta^{14}\text{C}$  were initially attributed to a release of dissolved inorganic  
54 carbon (DIC) that had been sequestered for thousands of years in the abyssal ocean, hinting at  
55 deglacial changes in ocean circulation (Bova et al., 2018; Broecker, 2009; Broecker & Barker,  
56 2007; Marchitto et al., 2007). However, this ocean release interpretation has two main  
57 shortcomings (Hain et al., 2011): (a) the LGM deep ocean was not sufficiently  $^{14}\text{C}$ -depleted (Fig.  
58 1) to be the source of the mid-depth anomalies, and (b) once the isotopic signature of

59 anomalously  $^{14}\text{C}$ -depleted carbon is transported to the mid-depth Pacific it would rapidly  
 60 dissipate into the global carbon cycle via ocean circulation and air/sea gas exchange. This view is  
 61 further supported by a new compilation showing no appreciable  $^{14}\text{C}$ -depletion at any depth for  
 62 the basin-scale Pacific during the deglaciation (Fig. 1; Rafter et al., 2022). Additionally, deep-sea  
 63 coral  $^{14}\text{C}$  records from the Galápagos with excellent age model controls (Fig. 1; Chen et al.,  
 64 2020) and South Pacific  $^{14}\text{C}$  records bathed in modern Antarctic Intermediate Water (De Pol-  
 65 Holz et al., 2010; Rose et al., 2010; Siani et al., 2013; Zhao & Keigwin, 2018) show no  
 66 significant  $^{14}\text{C}$ -depletion. This lack of basin-wide mid-depth  $\Delta^{14}\text{C}$  depletion is an important  
 67 observational constraint we will consider below.

68 An alternative set of proposals suggest these anomalously low  $\Delta^{14}\text{C}$  values reflect an addition of  
 69  $^{14}\text{C}$ -free carbon from a geologic source (Rafter et al., 2018, 2019; Ronge et al., 2016; Skinner &  
 70 Bard, 2022; Stott et al., 2009; Stott & Timmermann, 2011). A common objection to this  
 71 hypothesis is the potential for ocean acidification, which would contradict the evidence  
 72 supporting enhanced carbonate preservation during the last deglacial (Allen et al., 2015, 2020;  
 73 Cartapanis et al., 2018; Marchitto et al., 2005; Yu et al., 2013). However, if the geologic carbon  
 74 addition was neutralized by a commensurate influx of alkalinity (e.g., carbon added as  
 75 bicarbonate ion instead of  $\text{CO}_2$ )—there would be muted effects on seawater pH,  $\text{CaCO}_3$  burial,  
 76 and atmospheric  $\text{CO}_2$  (Rafter et al., 2019).



**Figure 1. Deglacial intermediate-depth (< 1000m)  $\Delta^{14}\text{C}$  records (red and yellow) compared to atmospheric  $\Delta^{14}\text{C}$  and  $\text{CO}_2$  (gray). Yellow records (foraminifera) show anomalously low  $\Delta^{14}\text{C}$  values, while red records (foraminifera and coral) broadly track atmospheric  $\Delta^{14}\text{C}$ . The solid red line shows the mean mid-depth  $\Delta^{14}\text{C}$ , and the dashed red line shows the mean deep Pacific  $\Delta^{14}\text{C}$  for all Pacific sites from Rafter et al. (2022). The red shading indicates the 95% confidence interval error envelope. Locations of individual  $\Delta^{14}\text{C}$  records are shown in the map, with ocean bathymetry and the East Pacific Rise spreading center (black lines).**

This neutralized  $^{14}\text{C}$ -free carbon—likely produced within marine sediments (Rafter et al., 2019; Skinner & Bard, 2022)—would

95 eventually be transported to the upper water column and atmosphere, diluting the atmospheric  
 96  $^{14}\text{C}$  reservoir and lowering atmospheric  $\Delta^{14}\text{C}$ . Although there was a rapid decline in atmospheric  
 97  $\Delta^{14}\text{C}$  during the last deglaciation, also known as the ‘mystery interval’ (Broecker, 2009;  
 98 Broecker & Barker, 2007), this  $\Delta^{14}\text{C}$  decline can mostly be explained by Southern Ocean  $\text{CO}_2$   
 99 release, Atlantic circulation changes, and the cosmogenic decline in  $^{14}\text{C}$  production (Hain et al.,  
 100 2014), leaving limited opportunities in the planetary  $^{14}\text{C}$  budget for the addition of  $^{14}\text{C}$ -free  
 101 geologic carbon.

102 Moreover, terrestrial carbon cycle changes, such as permafrost destabilization (release of  $^{14}\text{C}$ -  
103 depleted  $\text{CO}_2$ ) and regrowth of the land biosphere (uptake of  $^{14}\text{C}$ -enriched  $\text{CO}_2$ ), are thought to  
104 have occurred during the last deglaciation (Adams et al., 1990; Behling, 2002; Ciais et al., 2012;  
105 Crichton et al., 2016; Köhler et al., 2014; Lindgren et al., 2018), and would further influence the  
106 opportunity for  $^{14}\text{C}$ -free geologic carbon addition. With multiple established mechanisms  
107 lowering deglacial atmospheric  $\Delta^{14}\text{C}$ , is there room in the  $^{14}\text{C}$  budget for geologic carbon  
108 release?

109 In this study, we incorporate these terrestrial processes alongside submarine geologic carbon  
110 release into the deglacial model scenario from Hain et al. (2014) to simulate their combined  
111 effect on atmospheric  $\text{CO}_2$  and the planetary  $^{14}\text{C}$  budget. We use a stepwise numerical model  
112 optimization method that assimilates observed atmospheric  $\text{CO}_2$  and  $\Delta^{14}\text{C}$  data into the model to  
113 find the optimal rate of geologic carbon and alkalinity release. This optimization yields an upper  
114 bound limit on the amount of geologic carbon that could have been added since the LGM and  
115 characterizes the chemical speciation (i.e.,  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , or  $\text{CO}_3^{2-}$ ) of that geologic carbon  
116 release. These results provide valuable insight into the sensitivity of the global carbon cycle after  
117 various open-system carbon perturbations, ultimately allowing us to show that geologic carbon  
118 addition remains a viable explanation for the deglacial  $\Delta^{14}\text{C}$  anomalies.

## 119 **2 Materials and Methods**

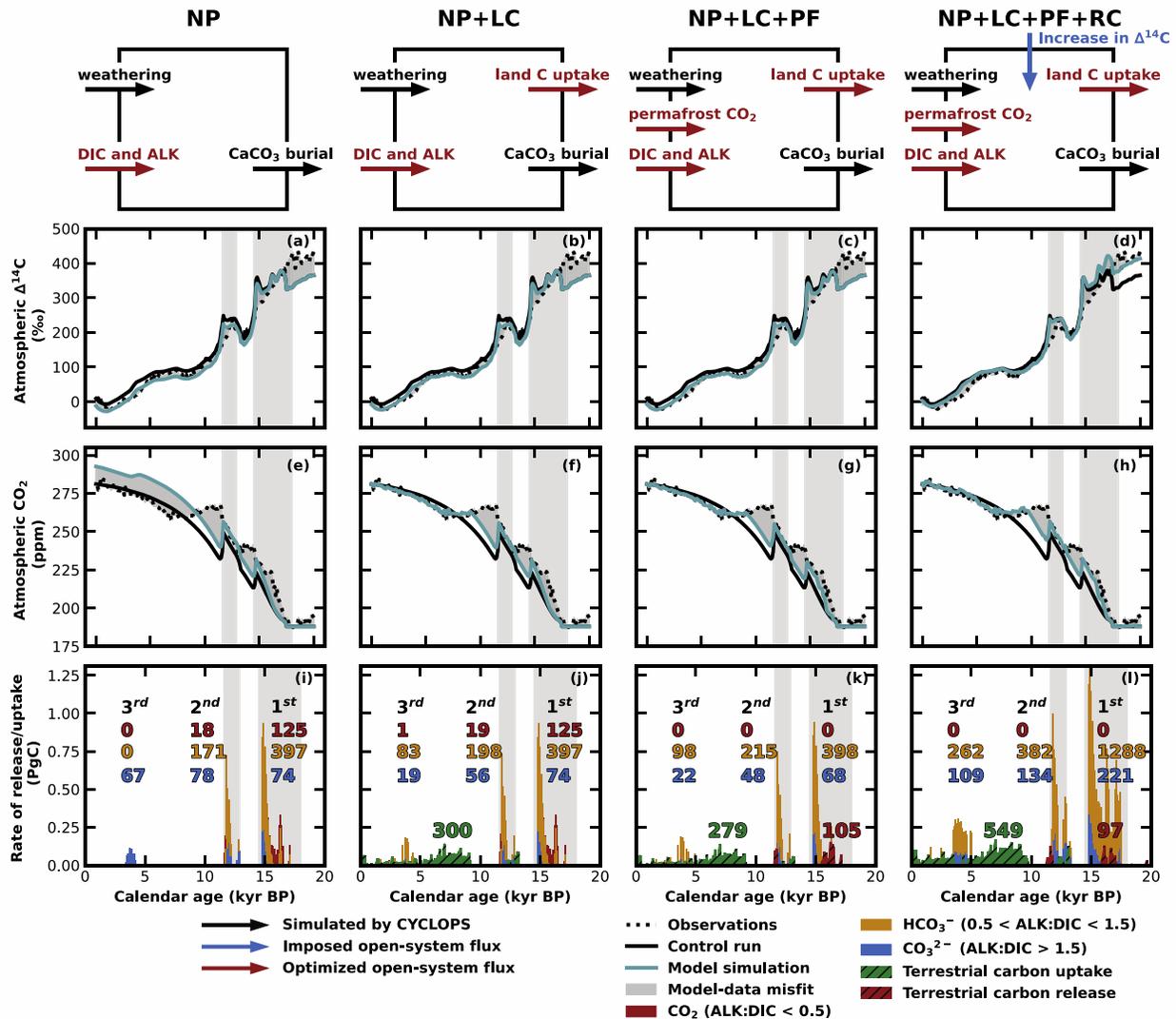
120 We use the CYCLOPS global carbon cycle model (Hain et al., 2010, 2011, 2014; Keir, 1988;  
121 model configuration described in supplementary material) to simulate four experiments,  
122 progressively adding optimized and imposed open-system carbon and alkalinity fluxes (Fig. 2):  
123 (1) we invert for the optimal rates of carbon and alkalinity release to the mid-depth North Pacific  
124 region of the model (experiment NP), (2) we add the possibility of land carbon uptake to the  
125 optimization (experiment NP+LC), (3) we include the release of  $^{14}\text{C}$ -free permafrost carbon  
126 (experiment NP+LC+PF), and (4) we adjust the initial LGM  $^{14}\text{C}$  inventory by +3.5%  
127 (experiment NP+LC+PF+RC). All experiments include the identical background forcings of the  
128 control run, based on the deglacial carbon cycle scenario from Hain et al. (2014). More in-depth  
129 descriptions of the experiments can be found in the supplementary material (SM). The optimized  
130 fluxes are determined by a numerical algorithm that minimizes the deviation between simulated  
131 atmospheric  $\text{CO}_2$  ( $\text{CO}_2^{\text{model}}$ ) and  $\Delta^{14}\text{C}$  ( $\Delta^{14}\text{C}^{\text{model}}$ ) compared to reconstructed atmospheric  $\text{CO}_2$   
132 ( $\text{CO}_2^{\text{obs}}$ ) from the most recent compilation of Antarctic ice core  $\text{CO}_2$  data (Bereiter et al., 2015)  
133 and  $\Delta^{14}\text{C}$  ( $\Delta^{14}\text{C}^{\text{obs}}$ ) from IntCal20 (Reimer et al., 2020). Details of the algorithm can be found in  
134 the SM.

## 135 **3 Results**

### 136 **3.1 Atmospheric constraints on geologic carbon addition**

137 All four simulations improve the overall  $\text{CO}_2$  and  $\Delta^{14}\text{C}$  model-data misfit compared to the  
138 control run (blue vs. black line, Fig. 2). This model-data misfit is progressively minimized as  
139 more open-system carbon and alkalinity fluxes are added to the model, with the NP+LC+PF+RC  
140 simulating the smallest model-data misfit. Each simulation has two main pulses of geologic  
141 carbon during the deglaciation and one smaller pulse during the Holocene. These geologic pulses  
142 occur when  $\Delta^{14}\text{C}^{\text{model}}$  rises above  $\Delta^{14}\text{C}^{\text{obs}}$ , which we call  $^{14}\text{C}$  opportunities. Majority of the  
143 geologic carbon is added as bicarbonate ion (61-84%, Table S1), with net ALK-to-DIC ratios

144 between 1.08 and 1.19 (Table S1) across all four simulations. We note there is a small carbonate  
 145 ion pulse that occurs only during the Holocene of the NP simulation (Fig. 2i). The algorithm  
 146 adds carbonate to counteract a CO<sub>2</sub> misfit of ~20 ppm during the Holocene (Fig. 2e) that  
 147 emerged due to simulated alkalinity loss from ongoing carbonate compensation (raising  
 148 atmospheric CO<sub>2</sub>) in conjunction with the underlying CO<sub>2</sub> rise from Holocene Southern Ocean  
 149 changes found in our control run (Hain et al., 2014). Only the NP simulation simulates this  
 150 carbonate pulse because the other models include terrestrial regrowth, thus minimizing the  
 151 Holocene CO<sub>2</sub> misfit with land carbon uptake instead (Fig. 2j-l).



152

153 **Figure 2. Visual representation of each experiment and the simulation results .** Cartoons in  
 154 the top row show the progressive addition of optimized and imposed open-system fluxes (colored  
 155 arrows) for each experimental simulation. The other rows show atmospheric  $\Delta^{14}\text{C}$  (a-d),  
 156 atmospheric CO<sub>2</sub> (e-h), and the rate of carbon release or uptake (i-l). In panels i-l, the colored  
 157 numbers show the amount of CO<sub>2</sub> (red), HCO<sub>3</sub><sup>-</sup> (yellow), and CO<sub>3</sub><sup>2-</sup> (blue) for each pulse of  
 158 geologic carbon release. Similarly, the amount of terrestrial carbon uptake is shown in green,

159 *and the amount of terrestrial carbon release is shown in red. All colored numbers are in units of*  
 160 *PgC.*

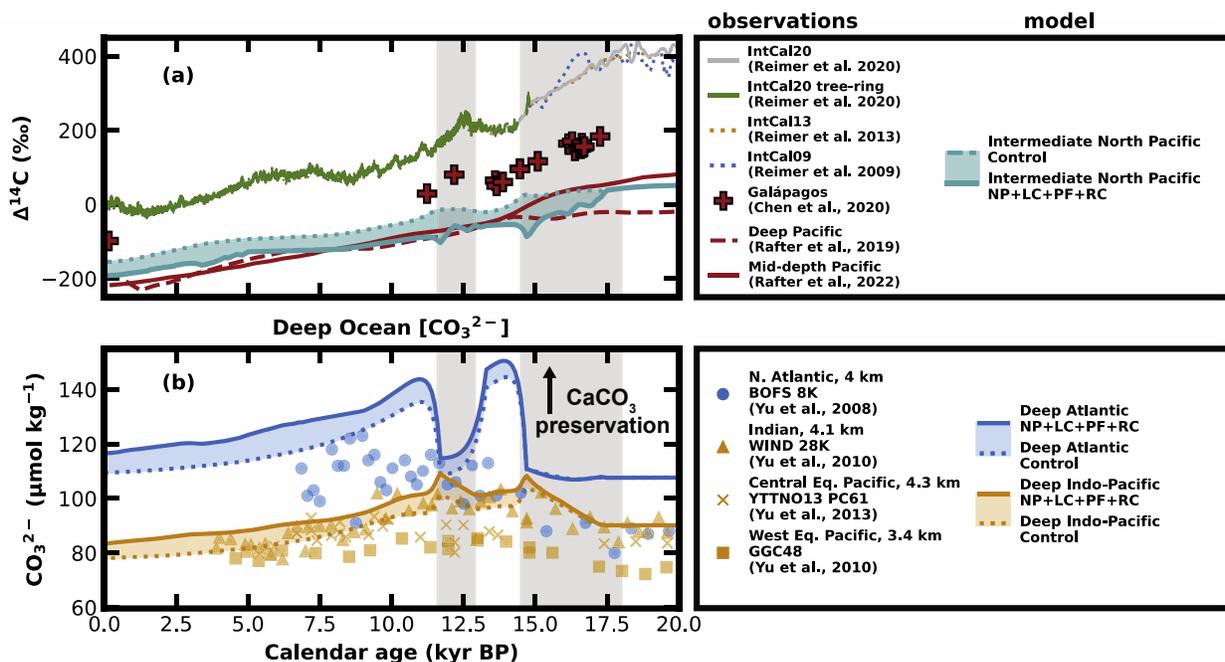
161 For our first three experiments (NP, NP+LC, NP+LC+PF)—which include no change to the  $^{14}\text{C}$   
 162 inventory—geologic carbon was added at rates as large as  $0.93 \text{ PgC yr}^{-1}$  (Fig 2i-k), totaling  
 163 between 846-929 PgC over the 20-kyr experiment (Table S1). Of those that included terrestrial  
 164 regrowth (NP+LC, NP+LC+PF), between 279-300 PgC (Table S1) of simulated carbon uptake  
 165 occurs, mainly during the Holocene. When we include terrestrial carbon release from permafrost  
 166 thaw (NP+LC+PF), 105 PgC (Fig 2k, Table S1) is released around 16-kyr BP and during the first  
 167 pulse of carbon addition. Our fourth experiment, NP+LC+PF+RC, includes an adjusted  $^{14}\text{C}$   
 168 inventory at the LGM initial state alongside all the above open-system fluxes. The higher initial  
 169 model  $\Delta^{14}\text{C}$  increases the opportunity for the subsequent addition of  $^{14}\text{C}$ -free carbon, leading to  
 170 higher rates of carbon addition (up to  $1.3 \text{ PgC yr}^{-1}$ , Fig. 2l) and a greater amount of total carbon  
 171 added (2396 PgC, Table S1). Consequently, land carbon uptake increases to 550 PgC (Table S1).  
 172 NP+LC+PF+RC simulates the release of 97 PgC from permafrost thaw around 16-kyr BP.

### 173 **3.2 Additional constraints on geologic carbon addition**

174 We also consider local effects—regional  $\Delta^{14}\text{C}$ ,  $\text{CaCO}_3$  burial, and regional  $\delta^{13}\text{C}$ —to further  
 175 constrain the geologic carbon release hypothesis. For NP+LC+PF+RC (the largest geologic  
 176 carbon addition scenario), only minor  $\Delta^{14}\text{C}$  anomalies are simulated in the intermediate depth  
 177 North Pacific box where the carbon is released (solid turquoise line, Fig. 3a). The  $\Delta^{14}\text{C}$  deviation  
 178 from the control run (dotted turquoise line, Fig. 3a) is shown with turquoise shading (Fig. 3a).  
 179 Although NP+LC+PF+RC is our most extreme geologic carbon addition simulation, the  
 180 simulated intermediate depth North Pacific  $\Delta^{14}\text{C}$  (solid turquoise line) is in broad agreement with  
 181 the mean  $\Delta^{14}\text{C}$  from the mid-depth (neutral density of  $27.5\text{--}28 \text{ kg m}^{-3}$ ) Pacific, calculated from a  
 182 new proxy  $^{14}\text{C}/\text{C}$  compilation (red line—Fig. 3a, Rafter et al., 2022). Furthermore, the lack of  
 183 severe  $\Delta^{14}\text{C}$  depletion found in the NP+LC+PF+RC simulation is supported by a deep-sea coral  
 184 record considered representative of the  $^{14}\text{C}$  content of intermediate waters near the Galápagos  
 185 islands (Chen et al., 2020).

186 Figure 3b shows the Atlantic (blue) and Indo-Pacific (yellow) deep ocean  $[\text{CO}_3^{2-}]$  from the  
 187 NP+LC+PF+RC and control simulation. An increase in deep-ocean  $[\text{CO}_3^{2-}]$  would promote the  
 188 preservation and burial of  $\text{CaCO}_3$  in sediments. Both simulations show two transient increases in  
 189  $[\text{CO}_3^{2-}]$ , during and after HS1 and YD in the Indo-Pacific and in the Atlantic (gray shaded areas,  
 190 Fig. 3b), as well as simulating an overall increase in Atlantic  $[\text{CO}_3^{2-}]$  from the LGM to the  
 191 Holocene. After 1509 PgC is added during the first pulse (Skinner & Bard, 2022)e of geologic  
 192 carbon addition (Fig. 2l), NP+LC+PF+RC simulates a  $\sim 10 \mu\text{mol kg}^{-1}$  in Atlantic  $[\text{CO}_3^{2-}]$  and a  
 193  $\sim 5 \mu\text{mol kg}^{-1}$  increase in Indo-Pacific  $\text{CO}_3^{2-}$  for the remainder of the simulation compared to the  
 194 control run (shaded blue and yellow). The simulated increase in Atlantic  $[\text{CO}_3^{2-}]$  since the LGM

195 and the transient increase in the Indo-Pacific  $[\text{CO}_3^{2-}]$  between 11 and 15-kyr BP is supported by  
 196 the observations shown in Figure 3b (Yu et al., 2008, 2010).



197

198 **Figure 3. Comparing the NP+LC+PF+RC simulation to observations.** Panel a shows  
 199 NP+LC+PF+RC driving only mild  $\Delta^{14}\text{C}$  depletion from the control run (shaded turquoise area),  
 200 in broad agreement with other datasets that show no noticeable  $\Delta^{14}\text{C}$  depletion, i.e.,  $\Delta^{14}\text{C}$  from  
 201 deep-sea coral near the Galápagos (red plus sign), the mean  $\Delta^{14}\text{C}$  from mid-depth and deep  
 202 Pacific (solid and dashed red line), and atmospheric  $\Delta^{14}\text{C}$  (solid gray and green, dotted yellow  
 203 and blue). We note the atmospheric  $\Delta^{14}\text{C}$  disagreement near the LGM across the last three  
 204 iterations of IntCal, before converging as tree-ring data becomes available (solid green line).  
 205 Panel b shows NP+LC+PF+RC driving an increase  $[\text{CO}_3^{2-}]$ , indicative of a  $\text{CaCO}_3$   
 206 preservation event, in the Atlantic (blue) and Indo-Pacific deep ocean basins (yellow) compared  
 207 to the control run (shaded blue and yellow). These simulated deep ocean  $[\text{CO}_3^{2-}]$  are in broad  
 208 agreement with observations from the North Atlantic (blue circle), Indian (yellow triangle), and  
 209 Equatorial Pacific (yellow square and X). The gray bars show Heinrich Stadial 1 and Younger  
 210 Dryas.

211 We have focused on  $\Delta^{14}\text{C}$  rather than  $\delta^{13}\text{C}$  for two reasons. First,  $\Delta^{14}\text{C}$  is corrected for mass and  
 212 temperature-dependent isotopic fractionation (Stuiver & Polach, 1977). Thus, isotopic gradients  
 213 in the  $\Delta^{14}\text{C}$  record can be attributed directly to changes in production, transport, and/or decay of  
 214  $^{14}\text{C}$ . Second, we know the  $\Delta^{14}\text{C}$  of geologic carbon ( $^{14}\text{C}$ -free) but not the  $\delta^{13}\text{C}$  value, which  
 215 varies depending on the geologic source. To constrain which geologic sources are plausible, we  
 216 run an additional set of experiments by calculating the bulk ocean  $\delta^{13}\text{C}$  change for two possible  
 217 neutralized geologic sources (described in SM): bicarbonate from anaerobic oxidation of  
 218 thermogenic methane (AOM, see Rafter et al. 2019;  $\delta^{13}\text{C} = -25\text{‰}$ ), and geologic  $\text{CO}_2$  neutralized  
 219 by carbonate dissolution (Skinner & Bard, 2022;  $\delta^{13}\text{C} = -2.5\text{‰}$ ). While  $\delta^{13}\text{C}$  values could vary  
 220 within the range of -25 to -2.5‰, the test cases utilized in this study are treated as endmember  
 221 scenarios. When 2400 PgC (as suggested by our NP+LC+PF+RC experiment) is added, we

222 observe bulk  $\delta^{13}\text{C}$  ocean changes of -1.5‰ for AOM and -0.2‰ for carbonate dissolution. Given  
223 that observed oceanic  $\delta^{13}\text{C}$  values have not fluctuated more than ~1‰ over the last 800-kyrs  
224 (Hodell et al., 2003), our simulations suggest geologic carbon from a methane source ( $\delta^{13}\text{C} \leq -$   
225 25‰) is unlikely for our extreme carbon addition scenario of 2400 PgC.

## 226 **4 Discussion**

227 Our results indicate that the atmospheric  $\text{CO}_2$  and  $\text{CaCO}_3$  burial constraints are effectively blind  
228 to carbon release neutralized by alkalinity (i.e., carbon added as bicarbonate,  $\text{HCO}_3^-$ ). This  
229 allows for large-scale geologic carbon addition scenarios constrained by only the planetary  
230 radiocarbon budget. Additionally, these large-scale carbon addition scenarios did not drive  
231 significant  $\Delta^{14}\text{C}$  depletion across the North Pacific, in agreement with observations  
232 representative of the North Pacific and Pacific basins. This supports the idea that these enigmatic  
233  $\Delta^{14}\text{C}$  anomalies are likely regional or localized phenomena that may still be explained by  
234 geologic carbon addition.

### 235 **4.1 Large amounts of bicarbonate allowable**

236 We optimized our carbon cycle modeling simulations, which include different open-system  
237 fluxes and changes to the  $^{14}\text{C}$  inventory, with the addition of geologic carbon. The simulations  
238 show that up to 2397 Pg of geologic carbon, mainly as bicarbonate ion, can be consistent with  
239 the observed deglacial changes in atmospheric  $\text{CO}_2$  and  $\Delta^{14}\text{C}$ . Due to the alkalinity  
240 accompanying DIC during bicarbonate addition, geologic carbon in this form can be added at  
241 rates as large as  $1.3 \text{ PgC yr}^{-1}$  (Fig. 2l) with limited impacts on atmospheric  $\text{CO}_2$  and deep-sea  
242  $[\text{CO}_3^{2-}]$ .

243 Prior work has estimated that deglacial geologic  $\text{CO}_2$  emissions from mantle decompression  
244 could have reached up to  $0.2 \text{ PgC yr}^{-1}$  (Cartapanis et al., 2018; Roth & Joos, 2012), much smaller  
245 than our maximum yearly rates. However, these lower rates were derived assuming the geologic  
246 carbon came only as  $\text{CO}_2$  rather than as bicarbonate ion. When carbon is added without alkalinity  
247 (i.e.,  $\text{CO}_2$ ), atmospheric  $\text{CO}_2$  and  $\text{CaCO}_3$  burial constraints are highly sensitive to any carbon  
248 added to the system. However, when adding neutralized carbon (bicarbonate), atmospheric  $\text{CO}_2$   
249 and  $\text{CaCO}_3$  burial constraints become effectively blind to the carbon release, no longer  
250 constraining the carbon release rate or total. During bicarbonate addition, the constraining factor  
251 shifts to the planetary  $^{14}\text{C}$  mass balance and its reflection in the atmospheric  $\Delta^{14}\text{C}$  record (via  
252 IntCal20, Reimer et al., 2020), which can indirectly record the dilution of  $^{14}\text{C}$ -enriched  
253 environmental carbon by  $^{14}\text{C}$ -free geologic carbon. This  $\Delta^{14}\text{C}^{\text{obs}}$  constraint on bicarbonate release  
254 leads to an upper bound of 800-1000 PgC in all our open-system simulations (NP, NP+LC,  
255 NP+LC+PF)—a 2-2.5% increase of total ocean carbon inventory. Furthermore, if we take into  
256 consideration the uncertainty in the planetary  $^{14}\text{C}$  mass balance (Dinauer et al., 2020; Roth &  
257 Joos, 2013) by increasing the initial LGM  $^{14}\text{C}$  inventory by 3.5%, the opportunity for subsequent  
258 geologic carbon release increases to ~2500 PgC (6.5% increase of total ocean carbon inventory).  
259 In other words, a higher initial LGM  $^{14}\text{C}/\text{C}$  can substantially increase the opportunity for  $^{14}\text{C}$ -free  
260 geologic carbon release since the LGM.

261 Considering the idealized nature of our experiments and because of biases inherited from our  
262 control run (Hain et al., 2014), our optimization results should not be taken as estimates of

263 geologic carbon release or of other simulated open-system carbon fluxes (e.g., LC, PF). Instead,  
264 we argue that geologic carbon release greater than 800 -1000 PgC is rendered unlikely, and  
265 release of greater than 2400 PgC is implausible in the face of the  $\Delta^{14}\text{C}^{\text{obs}}$ . Further, if indeed there  
266 was substantial geologic carbon release since the LGM, it must have been in the neutralized form  
267 of bicarbonate ion with a net ALK-to-DIC ratio near 1, as proposed by Rafter et al. (2019), to  
268 avoid violating constraints from atmospheric  $\text{CO}_2$  and  $\text{CaCO}_3$  burial. Therefore, we argue that  
269 geologic carbon release played only a minor role in raising  $\text{CO}_2$  at the end of the last ice age,  
270 even if the total amount of carbon release was substantial. This contrasts with prior deglacial  
271 geologic carbon addition research, which attributes glacial/interglacial  $\text{CO}_2$  variability to liquid  
272  $\text{CO}_2$  release (Stott et al., 2019; Stott & Timmermann, 2011).

#### 273 **4.2 Geologic carbon as an explanation for $\Delta^{14}\text{C}$ anomalies?**

274 When first discovered, the  $\Delta^{14}\text{C}$  anomalies in the ETNP were taken to be the signature of carbon  
275 release from the deep ocean to the atmosphere (Marchitto et al., 2007). This earlier view of the  
276  $\Delta^{14}\text{C}$  anomalies buttresses the longstanding notion that stagnation of deep ocean circulation  
277 during the LGM created an isolated  $^{14}\text{C}$ -deplete reservoir for the sequestration of atmospheric  
278  $\text{CO}_2$  (Broecker & Barker, 2007; Skinner et al., 2010)—and this view remains prevalent (e.g.,  
279 Bova et al., 2018). However, deep ocean carbon storage and its effect on atmospheric  $\text{CO}_2$  is  
280 more closely tied to the degree of nutrient consumption in the polar ocean regions that form new  
281 deep water (Hain et al., 2010, 2014; Ito & Follows, 2005; Marinov et al., 2008a, 2008b; Sigman  
282 et al., 2010, 2021; Sigman & Haug, 2003) rather than being a simple function of the rate of deep  
283 ocean overturning. Further, a new compilation of global ocean  $\Delta^{14}\text{C}$  records reveals that the  
284 LGM  $^{14}\text{C}$  age of the global deep ocean was about  $\sim 1000$  years greater than today (Rafter et al.,  
285 2022), sufficient to explain a large portion of the observed  $\Delta^{14}\text{C}^{\text{obs}}$  decline during the deglacial  
286 period (Broecker & Barker, 2007; Hain et al., 2014), but not nearly  $^{14}\text{C}$ -deplete enough to  
287 produce the ETNP  $\Delta^{14}\text{C}$  anomalies (Fig. 3a). Rather than becoming a plank in our evolving  
288 understanding of coupled glacial/interglacial changes in ocean circulation and the global carbon  
289 cycle, the existence of these  $\Delta^{14}\text{C}$  anomalies has become its own vexing problem, defying  
290 conventional explanations based on ocean circulation.

291  
292 There are numerous reasons why a given sample would yield an anomalously low reconstructed  
293  $^{14}\text{C}/\text{C}$ , but the spatial-temporal clustering of  $^{14}\text{C}$  anomalies in the upper 1 km of the ETNP water  
294 column is remarkable (e.g., Bova et al., 2018; Lindsay et al., 2015; Marchitto et al., 2007; Rafter  
295 et al., 2018, 2019; Stott et al., 2019), especially when contrasted with nearby records that broadly  
296 track atmospheric  $^{14}\text{C}$  change without discernible  $^{14}\text{C}$  anomalies (e.g., Bova et al., 2018; Chen et  
297 al., 2020; De Pol-Holz et al., 2010; Rose et al., 2010; Siani et al., 2013; Zhao & Keigwin, 2018).  
298 Previous modeling of the problem suggests that any  $^{14}\text{C}$  anomaly in the upper ocean would  
299 rapidly dissipate by ocean circulation and air/sea gas exchange (Hain et al., 2011) such that  
300 upper ocean  $\Delta^{14}\text{C}$  is expected to track atmospheric  $\Delta^{14}\text{C}$  change since the LGM (Hain et al.,  
301 2014), as is observed in independently dated coral  $^{14}\text{C}$  records from the Atlantic and Pacific (e.g.,  
302 Chen et al., 2020) and other records outside the anomalous ETNP cluster. Our new results  
303 advance the argument by demonstrating that even the release of  $>2000$  PgC is insufficient to  
304 generate a significant  $^{14}\text{C}$  anomaly on the basin scale resolved in the model (Fig. 3a). That is, the  
305 absence of anomalies in most upper ocean  $^{14}\text{C}$  reconstructions are normal and expected even in  
306 the case of substantial simulated carbon release. The caveat to the argument is that a small  $\Delta^{14}\text{C}$

307 reduction simulated at the basin scale would be consistent with a severe  $^{14}\text{C}$  anomaly  
308 concentrated in a small sub-region, such as observed in the ETNP.

309  
310 If not continuously sourced from a persistently  $^{14}\text{C}$ -depleted upstream water mass signature (e.g.,  
311 Hain et al., 2011), the  $^{14}\text{C}$  anomalies of the ETNP may instead record carbon release associated  
312 with processes linked to spreading centers separating the Cocos, Nazca, and Pacific plates and  
313 the very high regional geothermal heat flux ( $>0.1 \text{ W m}^{-2}$  throughout the region; Pollack et al.,  
314 1993). While we cannot usefully comment on whether these geologic systems are dynamic  
315 enough to yield defined pulses of carbon release, our results highlight that only a neutralized  
316 form of carbon release would be consistent with the atmospheric  $\text{CO}_2$  constraint and  
317 observations of good (sometimes improved) seafloor carbonate preservation (Fig. 3b; Yu et al.,  
318 2008, 2010, 2013) during the main purported geologic carbon pulses. Indeed, the temporal  
319 coincidence of the  $^{14}\text{C}$  anomalies with stadial/interstadial climate change, deglacial ocean heat  
320 uptake (Poggemann et al., 2018), and circulation change (e.g., McManus et al., 2004; Rafter et  
321 al., 2022) may point to a climatic or environmental trigger of carbon release, rather than a being  
322 a purely volcanogenic phenomenon.

323  
324 However, why would severe  $^{14}\text{C}$  anomalies persist for millennia in the ETNP upper ocean water  
325 column if ocean circulation and air/sea gas exchange act to rapidly dissipate the anomalous  
326 carbon globally (Hain et al., 2011)? We propose two alternative resolutions that we cannot  
327 distinguish based on our current model and existing data: Either the anomalies are localized and  
328 reflect geologic carbon diffusion out of the underlying sediment stack rather than bottom water  
329  $\Delta^{14}\text{C}$ , or the anomalies are regional and reflect the accumulation of geologic carbon in the ETNP  
330 shadow zone of ocean circulation with a sharp and persistent chemical gradient to the open ocean  
331 mid-depth Pacific.

332  
333 If the anomalies are localized, we might expect each anomalous record to differ in magnitude  
334 and timing. Finding individual mid-depth sites in the ETNP where  $^{14}\text{C}$  anomalies are missing  
335 (e.g., Bova et al., 2018; Chen et al., 2020) alongside records with  $^{14}\text{C}$  anomalies that are only  
336 broadly similar, would tend to support the localized explanation. Conversely, if geologic carbon  
337 were added to a dynamically isolated region, such as the upper ocean ETNP (Margolskee et al.,  
338 2019), then seawater  $\Delta^{14}\text{C}$  might diverge substantially from the  $\Delta^{14}\text{C}$  of the open Pacific and  
339 atmosphere. However, that regional signal would still need to be shared by all radiocarbon  
340 records in the hydrodynamic region (cf. Chen et al., 2020). If the anomalies did reflect the  
341 restricted regional ocean circulation of the ETNP, it would seem plausible that the carbon release  
342 mechanism also operated in regions outside the ETNP but without producing characteristic  
343 seawater  $\Delta^{14}\text{C}$  anomalies.

## 344 **5 Conclusion**

345 We document a set of carbon cycle model scenarios since the LGM that include substantial (800-  
346 2400 PgC) release of geologic carbon that appear broadly consistent with reconstructed  
347 atmospheric  $\text{CO}_2$  rise,  $\Delta^{14}\text{C}$  decline, and deep-sea  $\text{CaCO}_3$  burial patterns. In all simulations,  
348 geologic carbon release is primarily bicarbonate ion, with minimal effect on simulated ocean pH  
349 and atmospheric  $\text{CO}_2$ . That is, the global carbon cycle is effectively blind to geologic carbon  
350 release if neutralized by an equivalent release of alkalinity (ALK-to-DIC ratio near 1). Hence,  
351 reconstructed  $\text{CO}_2$  change does not require geologic carbon release nor constrain how much

352 bicarbonate may have been released into the environment. One key outcome of our study is that  
353 large-scale geologic bicarbonate release since the LGM is possible.

354 Geologic carbon release dilutes the planetary inventory of cosmogenic radiocarbon ( $^{14}\text{C}$ ), with  
355 2400 Pg of  $^{14}\text{C}$ -free carbon release reducing the average  $\Delta^{14}\text{C}$  of environmental carbon by about  
356  $\sim 50\%$ . Therefore, the planetary  $^{14}\text{C}$  budget can be used to rule out the most extreme scenarios  
357 for geologic carbon release, offering an upper-bound constraint for carbon transfers from  
358 geologic and terrestrial carbon reservoirs to the ocean/atmosphere carbon cycle. That is, our  
359 model scenarios are designed to explore the limit of what appears to be possible in the context of  
360 global constraints from  $\text{CO}_2$  and  $^{14}\text{C}$  reconstructions. We find that bicarbonate release was likely  
361 limited to less than 1000 PgC. When considering uncertainty in the history of cosmogenic  $^{14}\text{C}$   
362 production, the limit for bicarbonate release may be as high as 2400 PgC.

363 The spatial cluster of severe negative deglacial  $\Delta^{14}\text{C}$  anomalies in the upper water column of the  
364 ETNP may be evidence for geologic carbon release associated with the seafloor spreading center  
365 defining the East Pacific Rise (Fig. 1; (Lindsay et al., 2015; Marchitto et al., 2007; Rafter et al.,  
366 2018, 2019; Stott et al., 2009). Confirming or rejecting this hypothesis would have several  
367 implications: Without large-scale carbon release, we lack an adequate explanation for the ETNP  
368  $\Delta^{14}\text{C}$  anomalies, suggesting an open gap in our understanding of the  $^{14}\text{C}$ -proxy system used to  
369 reconstruct ocean circulation changes in response to deglacial climate change. Alternatively,  
370 with large pulses of geologic carbon release in the ETNP, we lack an adequate explanation for  
371 how bicarbonate is derived from geologic carbon sources during the deglaciation, suggesting a  
372 gap in our understanding of glacial/interglacial changes in seafloor spreading and its role in the  
373 global carbon cycle. Further, if 1000 PgC or more of bicarbonate were released without causing  
374 ocean acidification or substantial  $\text{CO}_2$  effects, the ETNP radiocarbon anomalies may hold lessons  
375 for mitigating and neutralizing anthropogenic carbon emissions via artificial Ocean Alkalinity  
376 Enhancement deployments.

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## 380 **Open Research**

381 Detailed model description and configuration are available in the Supporting Information. The  
382 plotting code and simulation results are found on GitHub  
383 (<https://github.com/RyanAGreen/Deglacial-Neutralized-Carbon-14C>) and Zenodo  
384 (<https://zenodo.org/badge/latestdoi/627637425>).

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