

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

3 **R. A. Green¹, M. P. Hain¹, and P. A. Rafter²**

4 ¹ Earth and Planetary Science Department, University of Santa Cruz, Santa Cruz, USA

5 ² Department of Earth System Science, University of California, Irvine, CA, USA

6

7 Corresponding author: Ryan A. Green (rygreen@ucsc.edu)

8 **Key Points:**

- 9
- 10 • Observed deglacial changes in atmospheric CO₂ and ¹⁴C/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 ¹⁴C anomalies and have limited CO₂ effect
 - 12
 - 13 • The global carbon cycle is essentially “blind” to neutralized carbon release and only
 - 14 constrained by ¹⁴C budget
 - 15

16 Abstract

17 In the intermediate depth Eastern Tropical Pacific Ocean, multiple deglacial radiocarbon (^{14}C)
18 records show anomalously low $^{14}\text{C}/\text{C}$ values that appear to be best explained by the addition of
19 ^{14}C -free geologic carbon. We use inverse carbon cycle modeling and data assimilation of
20 reconstructed atmospheric 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 PgC yr^{-1}) could occur with little effect on atmospheric CO_2 and
23 without upsetting ^{14}C mass-balance constraints. Including the release of ^{14}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}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}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 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}C -depleted (Fig.
58 1) to be the source of the mid-depth anomalies, and (b) once the isotopic signature of

59 anomalously ^{14}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}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}C records from the Galápagos with excellent age model controls (Fig. 1; Chen et al.,
 64 2020) and South Pacific ^{14}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}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}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 CO_2)—there would be muted effects on seawater pH, CaCO_3 burial,
 76 and atmospheric CO_2 (Rafter et al., 2019).

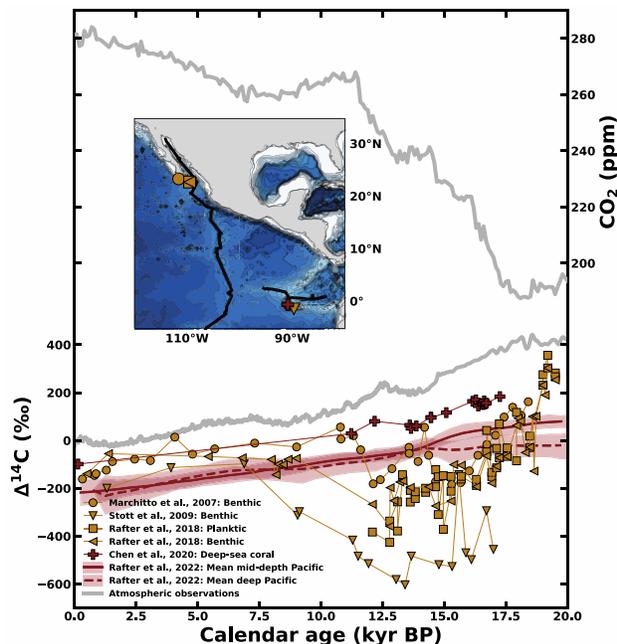


Figure 1. Deglacial intermediate-depth (< 1000m) $\Delta^{14}\text{C}$ records (red and yellow) compared to atmospheric $\Delta^{14}\text{C}$ and CO_2 (gray). Yellow records (foraminifera) show anomalously low $\Delta^{14}\text{C}$ values, while red records (foraminifera and coral) broadly track atmospheric $\Delta^{14}\text{C}$. 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}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}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 CO_2
 99 release, Atlantic circulation changes, and the cosmogenic decline in ^{14}C production (Hain et al.,
 100 2014), leaving limited opportunities in the planetary ^{14}C budget for the addition of ^{14}C -free
 101 geologic carbon.

102 Moreover, terrestrial carbon cycle changes, such as permafrost destabilization (release of ^{14}C -
103 depleted CO_2) and regrowth of the land biosphere (uptake of ^{14}C -enriched 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}C -free geologic carbon addition. With multiple established mechanisms
107 lowering deglacial atmospheric $\Delta^{14}\text{C}$, is there room in the ^{14}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 CO_2 and the planetary ^{14}C budget. We use a stepwise numerical model
112 optimization method that assimilates observed atmospheric 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., CO_2 , HCO_3^- , or 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**

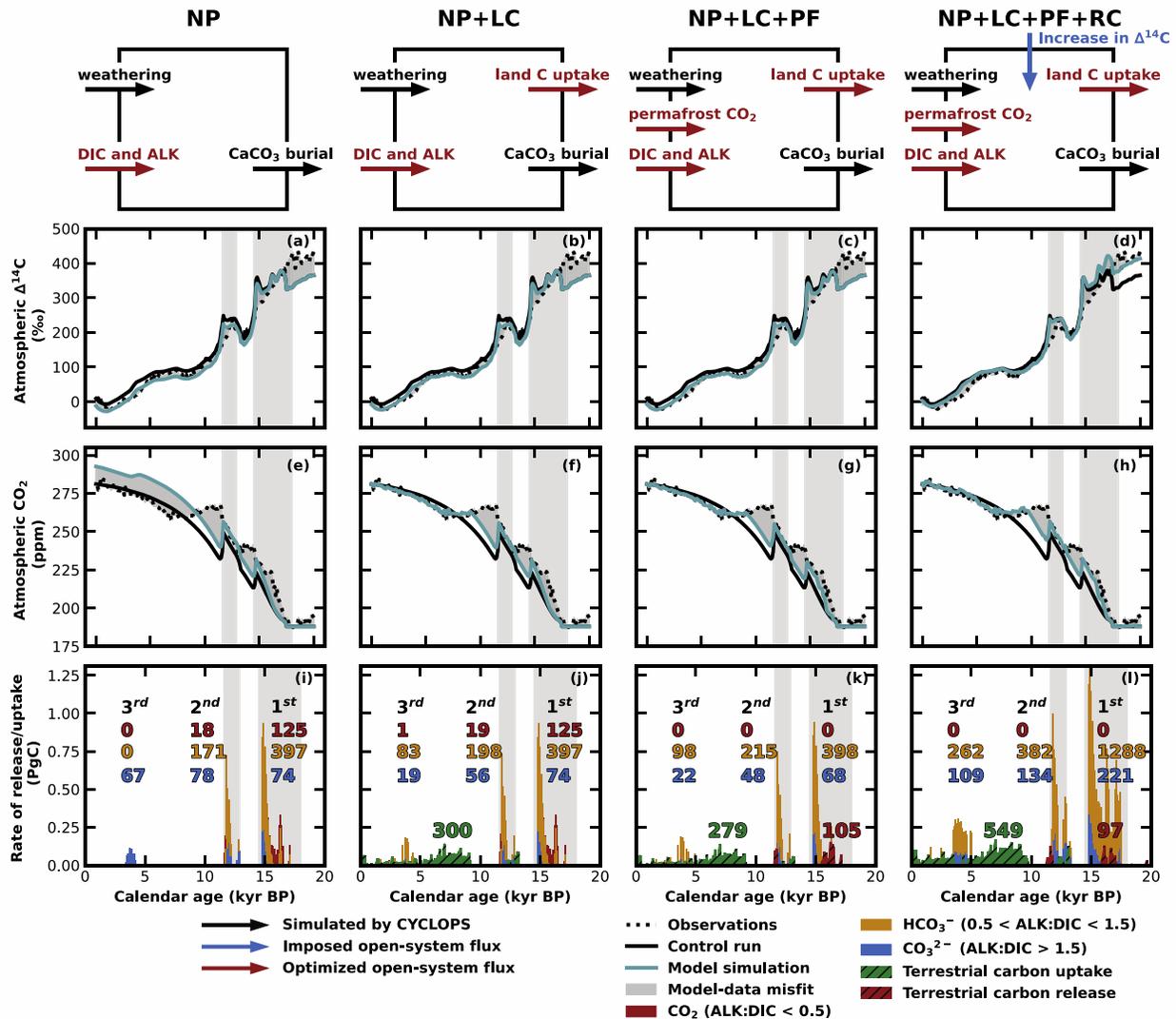
120 We use the CYCLOPS global carbon cycle model (Hain et al., 2010, 2011, 2014; Keir, 1988;
121 model configuration described in supplementary material) to simulate four experiments,
122 progressively adding optimized and imposed open-system carbon and alkalinity fluxes (Fig. 2):
123 (1) we invert for 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}C -free permafrost carbon
126 (experiment NP+LC+PF), and (4) we adjust the initial LGM ^{14}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 CO_2 ($\text{CO}_2^{\text{model}}$) and $\Delta^{14}\text{C}$ ($\Delta^{14}\text{C}^{\text{model}}$) compared to reconstructed atmospheric CO_2
132 (CO_2^{obs}) from the most recent compilation of Antarctic ice core 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 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}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 CO₂ misfit of ~20 ppm during the Holocene (Fig. 2e) that
 147 emerged due to simulated alkalinity loss from ongoing carbonate compensation (raising
 148 atmospheric CO₂) in conjunction with the underlying CO₂ 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 CO₂ 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 Δ¹⁴C (a-d),
 156 atmospheric CO₂ (e-h), and the rate of carbon release or uptake (i-l). In panels i-l, the colored
 157 numbers show the amount of CO₂ (red), HCO₃⁻ (yellow), and CO₃²⁻ (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.*

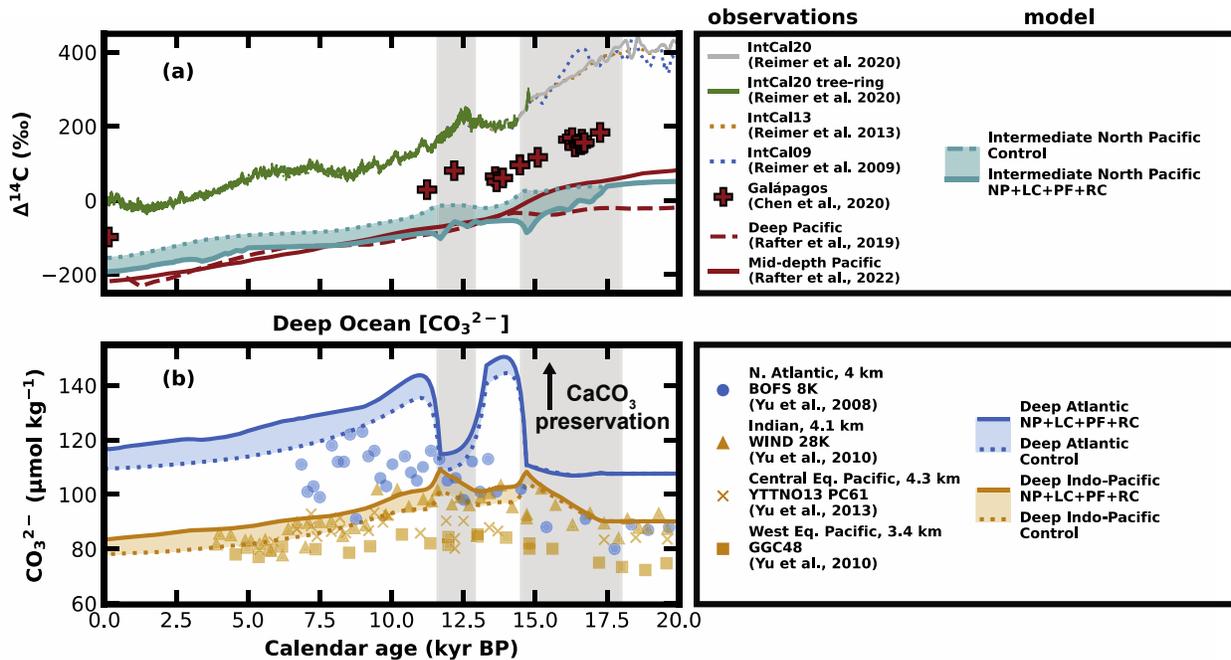
161 For our first three experiments (NP, NP+LC, NP+LC+PF)—which include no change to the ^{14}C
 162 inventory—geologic carbon was added at rates as large as 0.93 PgC yr^{-1} (Fig 2i-k), totaling
 163 between 846-929 PgC over the 20-kyr experiment (Table S1). Of those that included terrestrial
 164 regrowth (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}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}C -free carbon, leading to
 170 higher rates of carbon addition (up to 1.3 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 $\Delta^{14}\text{C}$, 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}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 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 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 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}C . Second, we know the $\Delta^{14}\text{C}$ of geologic carbon (^{14}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 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 CO_2 and CaCO_3 burial constraints are effectively blind
228 to carbon release neutralized by alkalinity (i.e., carbon added as bicarbonate, 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}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 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 PgC yr^{-1} (Fig. 2l) with limited impacts on atmospheric CO_2 and deep-sea
242 $[\text{CO}_3^{2-}]$.

243 Prior work has estimated that deglacial geologic CO_2 emissions from mantle decompression
244 could have reached up to 0.2 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 CO_2 rather than as bicarbonate ion. When carbon is added without alkalinity
247 (i.e., CO_2), atmospheric CO_2 and CaCO_3 burial constraints are highly sensitive to any carbon
248 added to the system. However, when adding neutralized carbon (bicarbonate), atmospheric CO_2
249 and 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}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}C -enriched
253 environmental carbon by ^{14}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}C mass balance (Dinauer et al., 2020; Roth &
257 Joos, 2013) by increasing the initial LGM ^{14}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}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 CO_2 and CaCO_3 burial. Therefore, we argue that
269 geologic carbon release played only a minor role in raising 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 CO_2 variability to liquid
272 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}C -deplete reservoir for the sequestration of atmospheric
278 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 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}C age of the global deep ocean was about ~ 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}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}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}C change without discernible ^{14}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}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}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}C anomaly on the basin scale resolved in the model (Fig. 3a). That is, the
305 absence of anomalies in most upper ocean ^{14}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}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}C -depleted upstream water mass signature (e.g.,
311 Hain et al., 2011), the ^{14}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 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}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}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}C anomalies are missing
335 (e.g., Bova et al., 2018; Chen et al., 2020) alongside records with ^{14}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 CO_2 rise, $\Delta^{14}\text{C}$ decline, and deep-sea 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 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 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}C), with
355 2400 Pg of ^{14}C -free carbon release reducing the average $\Delta^{14}\text{C}$ of environmental carbon by about
356 $\sim 50\%$. Therefore, the planetary ^{14}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 CO_2 and ^{14}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}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}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 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.

377 **Acknowledgments**

378 This research was funded by the National Science Foundation (Collaborative Research Grants
379 OCE-2032340 to MPH and OCE-2032340 to PAR).

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>).

385 **References:**

386 Adams, J. M., Faure, H., Faure-Denard, L., McGlade, J. M., & Woodward, F. I. (1990). Increases in terrestrial
387 carbon storage from the Last Glacial Maximum to the present. *Nature*, *348*(6303), 711–714.
388 <https://doi.org/10.1038/348711a0>

- 389 Allen, K. A., Sikes, E. L., Anderson, R. F., & Rosenthal, Y. (2020). Rapid Loss of CO₂ From the South Pacific
390 Ocean During the Last Glacial Termination. *Paleoceanography and Paleoclimatology*, *35*(2),
391 e2019PA003766. <https://doi.org/10.1029/2019PA003766>
- 392 Allen, K. A., Sikes, E. L., Hönisch, B., Elmore, A. C., Guilderson, T. P., Rosenthal, Y., & Anderson, R. F. (2015).
393 Southwest Pacific deep water carbonate chemistry linked to high southern latitude climate and atmospheric
394 CO₂ during the Last Glacial Termination. *Quaternary Science Reviews*, *122*, 180–191.
395 <https://doi.org/10.1016/j.quascirev.2015.05.007>
- 396 Behling, H. (2002). Carbon storage increases by major forest ecosystems in tropical South America since the Last
397 Glacial Maximum and the early Holocene. *Global and Planetary Change*, *33*(1), 107–116.
398 [https://doi.org/10.1016/S0921-8181\(02\)00065-6](https://doi.org/10.1016/S0921-8181(02)00065-6)
- 399 Bereiter, B., Eggleston, S., Schmitt, J., Nehrbass-Ahles, C., Stocker, T. F., Fischer, H., Kipfstuhl, S., & Chappellaz,
400 J. (2015). Revision of the EPICA Dome C CO₂ record from 800 to 600 kyr before present. *Geophysical
401 Research Letters*, *42*(2), 542–549. <https://doi.org/10.1002/2014GL061957>
- 402 Bova, S. C., Herbert, T. D., & Altabet, M. A. (2018). Ventilation of Northern and Southern Sources of Aged Carbon
403 in the Eastern Equatorial Pacific During the Younger Dryas Rise in Atmospheric CO₂. *Paleoceanography
404 and Paleoclimatology*, *33*(11), 1151–1168. <https://doi.org/10.1029/2018PA003386>
- 405 Broecker, W. (2009). The Mysterious ¹⁴C Decline. *Radiocarbon*, *51*(1), 109–119.
406 <https://doi.org/10.1017/S0033822200033737>
- 407 Broecker, W., & Barker, S. (2007). A 190‰ drop in atmosphere’s Δ14C during the “Mystery Interval” (17.5 to 14.5
408 kyr). *Earth and Planetary Science Letters*, *256*(1–2), 90–99. <https://doi.org/10.1016/j.epsl.2007.01.015>
- 409 Cartapanis, O., Galbraith, E. D., Bianchi, D., & Jaccard, S. L. (2018). Carbon burial in deep-sea sediment and
410 implications for oceanic inventories of carbon and alkalinity over the last glacial cycle. *Climate of the Past*,
411 *14*(11), 1819–1850. <https://doi.org/10.5194/cp-14-1819-2018>
- 412 Chen, T., Robinson, L. F., Burke, A., Claxton, L., Hain, M. P., Li, T., Rae, J. W. B., Stewart, J., Knowles, T. D. J.,
413 Fornari, D. J., & Harpp, K. S. (2020). Persistently well-ventilated intermediate-depth ocean through the last
414 deglaciation. *Nature Geoscience*, *13*(11), Article 11. <https://doi.org/10.1038/s41561-020-0638-6>

- 415 Ciais, P., Tagliabue, A., Cuntz, M., Bopp, L., Scholze, M., Hoffmann, G., Laurantou, A., Harrison, S. P., Prentice, I.
416 C., Kelley, D. I., Koven, C., & Piao, S. L. (2012). Large inert carbon pool in the terrestrial biosphere during
417 the Last Glacial Maximum. *Nature Geoscience*, 5(1), Article 1. <https://doi.org/10.1038/ngeo1324>
- 418 Crichton, K. A., Bouttes, N., Roche, D. M., Chappellaz, J., & Krinner, G. (2016). Permafrost carbon as a missing
419 link to explain CO₂ changes during the last deglaciation. *Nature Geoscience*, 9(9), 683–686.
420 <https://doi.org/10.1038/ngeo2793>
- 421 De Pol-Holz, R., Keigwin, L., Southon, J., Hebbeln, D., & Mohtadi, M. (2010). No signature of abyssal carbon in
422 intermediate waters off Chile during deglaciation. *Nature Geoscience*, 3(3), Article 3.
423 <https://doi.org/10.1038/ngeo745>
- 424 Deutsch, C., Gruber, N., Key, R. M., Sarmiento, J. L., & Ganachaud, A. (2001). Denitrification and N₂ fixation in
425 the Pacific Ocean. *Global Biogeochemical Cycles*, 15(2), 483–506. <https://doi.org/10.1029/2000GB001291>
- 426 Dinauer, A., Adolphi, F., & Joos, F. (2020). Mysteriously high $\Delta^{14}\text{C}$ of the glacial atmosphere: Influence of ¹⁴C
427 production and carbon cycle changes. *Climate of the Past*, 16(4), 1159–1185. [https://doi.org/10.5194/cp-](https://doi.org/10.5194/cp-16-1159-2020)
428 [16-1159-2020](https://doi.org/10.5194/cp-16-1159-2020)
- 429 Fine, R. A., Maillet, K. A., Sullivan, K. F., & Willey, D. (2001). Circulation and ventilation flux of the Pacific
430 Ocean. *Journal of Geophysical Research: Oceans*, 106(C10), 22159–22178.
431 <https://doi.org/10.1029/1999JC000184>
- 432 Gehrie, E., Archer, D., Emerson, S., Stump, C., & Henning, C. (2006). Subsurface ocean argon disequilibrium
433 reveals the equatorial Pacific shadow zone. *Geophysical Research Letters*, 33(18).
434 <https://doi.org/10.1029/2006GL026935>
- 435 Gruber, N., & Sarmiento, J. L. (1997). Global patterns of marine nitrogen fixation and denitrification. *Global*
436 *Biogeochemical Cycles*, 11(2), 235–266. <https://doi.org/10.1029/97GB00077>
- 437 Hain, M. P., Sigman, D. M., & Haug, G. H. (2010). Carbon dioxide effects of Antarctic stratification, North Atlantic
438 Intermediate Water formation, and subantarctic nutrient drawdown during the last ice age: Diagnosis and
439 synthesis in a geochemical box model. *Global Biogeochemical Cycles*, 24(4), n/a-n/a.
440 <https://doi.org/10.1029/2010GB003790>

- 441 Hain, M. P., Sigman, D. M., & Haug, G. H. (2011). Shortcomings of the isolated abyssal reservoir model for
442 deglacial radiocarbon changes in the mid-depth Indo-Pacific Ocean. *Geophysical Research Letters*, 38(4).
443 <https://doi.org/10.1029/2010GL046158>
- 444 Hain, M. P., Sigman, D. M., & Haug, G. H. (2014). Distinct roles of the Southern Ocean and North Atlantic in the
445 deglacial atmospheric radiocarbon decline. *Earth and Planetary Science Letters*, 394, 198–208.
446 <https://doi.org/10.1016/j.epsl.2014.03.020>
- 447 Hodell, D. A., Venz, K. A., Charles, C. D., & Ninnemann, U. S. (2003). Pleistocene vertical carbon isotope and
448 carbonate gradients in the South Atlantic sector of the Southern Ocean. *Geochemistry, Geophysics,*
449 *Geosystems*, 4(1), 1–19. <https://doi.org/10.1029/2002GC000367>
- 450 Holzer, M., DeVries, T., & de Lavergne, C. (2021). Diffusion controls the ventilation of a Pacific Shadow Zone
451 above abyssal overturning. *Nature Communications*, 12(1), Article 1. [https://doi.org/10.1038/s41467-021-](https://doi.org/10.1038/s41467-021-24648-x)
452 [24648-x](https://doi.org/10.1038/s41467-021-24648-x)
- 453 Huybers, P., & Langmuir, C. (2009). Feedback between deglaciation, volcanism, and atmospheric CO₂. *Earth and*
454 *Planetary Science Letters*, 286(3), 479–491. <https://doi.org/10.1016/j.epsl.2009.07.014>
- 455 Ito, T., & Follows, M. J. (2005). Preformed phosphate, soft tissue pump and atmospheric CO₂. *Journal of Marine*
456 *Research*, 63(4), 813–839. <https://doi.org/10.1357/0022240054663231>
- 457 Keir, R. S. (1988). On the Late Pleistocene ocean geochemistry and circulation. *Paleoceanography*, 3(4), 413–445.
458 <https://doi.org/10.1029/PA003i004p00413>
- 459 Köhler, P., Knorr, G., & Bard, E. (2014). Permafrost thawing as a possible source of abrupt carbon release at the
460 onset of the Bølling/Allerød. *Nature Communications*, 5(1), Article 1. <https://doi.org/10.1038/ncomms6520>
- 461 Lindgren, A., Hugelius, G., & Kuhry, P. (2018). Extensive loss of past permafrost carbon but a net accumulation
462 into present-day soils. *Nature*, 560(7717), Article 7717. <https://doi.org/10.1038/s41586-018-0371-0>
- 463 Lindsay, C. M., Lehman, S. J., Marchitto, T. M., Carriquiry, J. D., & Ortiz, J. D. (2016). New constraints on
464 deglacial marine radiocarbon anomalies from a depth transect near Baja California. *Paleoceanography*,
465 31(8), 1103–1116. <https://doi.org/10.1002/2015PA002878>
- 466 Lindsay, C. M., Lehman, S. J., Marchitto, T. M., & Ortiz, J. D. (2015). The surface expression of radiocarbon
467 anomalies near Baja California during deglaciation. *Earth and Planetary Science Letters*, 422, 67–74.
468 <https://doi.org/10.1016/j.epsl.2015.04.012>

- 469 Marchitto, T. M., Lehman, S. J., Ortiz, J. D., Fluckiger, J., & van Geen, A. (2007). Marine Radiocarbon Evidence
470 for the Mechanism of Deglacial Atmospheric CO₂ Rise. *Science*, *316*(5830), 1456–1459.
471 <https://doi.org/10.1126/science.1138679>
- 472 Marchitto, T. M., Lynch-Stieglitz, J., & Hemming, S. R. (2005). Deep Pacific CaCO₃ compensation and glacial–
473 interglacial atmospheric CO₂. *Earth and Planetary Science Letters*, *231*(3), 317–336.
474 <https://doi.org/10.1016/j.epsl.2004.12.024>
- 475 Marcott, S. A., Bauska, T. K., Buizert, C., Steig, E. J., Rosen, J. L., Cuffey, K. M., Fudge, T. J., Severinghaus, J. P.,
476 Ahn, J., Kalk, M. L., McConnell, J. R., Sowers, T., Taylor, K. C., White, J. W. C., & Brook, E. J. (2014).
477 Centennial-scale changes in the global carbon cycle during the last deglaciation. *Nature*, *514*(7524), Article
478 7524. <https://doi.org/10.1038/nature13799>
- 479 Margolskee, A., Frenzel, H., Emerson, S., & Deutsch, C. (2019). Ventilation Pathways for the North Pacific Oxygen
480 Deficient Zone. *Global Biogeochemical Cycles*, *33*(7), 875–890. <https://doi.org/10.1029/2018GB006149>
- 481 Marinov, I., Follows, M., Gnanadesikan, A., Sarmiento, J. L., & Slater, R. D. (2008a). How does ocean biology
482 affect atmospheric pCO₂? Theory and models. *Journal of Geophysical Research: Oceans*, *113*(C7).
483 <https://doi.org/10.1029/2007JC004598>
- 484 Marinov, I., Gnanadesikan, A., Sarmiento, J. L., Toggweiler, J. R., Follows, M., & Mignone, B. K. (2008b). Impact
485 of oceanic circulation on biological carbon storage in the ocean and atmospheric pCO₂. *Global
486 Biogeochemical Cycles*, *22*(3). <https://doi.org/10.1029/2007GB002958>
- 487 McManus, J. F., Francois, R., Gherardi, J.-M., Keigwin, L. D., & Brown-Leger, S. (2004). Collapse and rapid
488 resumption of Atlantic meridional circulation linked to deglacial climate changes. *Nature*, *428*(6985),
489 Article 6985. <https://doi.org/10.1038/nature02494>
- 490 Poggemann, D.-W., Nürnberg, D., Hathorne, E. C., Frank, M., Rath, W., Reißig, S., & Bahr, A. (2018). Deglacial
491 Heat Uptake by the Southern Ocean and Rapid Northward Redistribution Via Antarctic Intermediate
492 Water. *Paleoceanography and Paleoclimatology*, *33*(11), 1292–1305.
493 <https://doi.org/10.1029/2017PA003284>
- 494 Pollack, H. N., Hurter, S. J., & Johnson, J. R. (1993). Heat flow from the Earth's interior: Analysis of the global data
495 set. *Reviews of Geophysics*, *31*(3), 267–280. <https://doi.org/10.1029/93RG01249>

- 496 Rafter, P. A., Carriquiry, J. D., Herguera, J., Hain, M. P., Solomon, E. A., & Southon, J. R. (2019). Anomalous >
497 2000-Year-Old Surface Ocean Radiocarbon Age as Evidence for Deglacial Geologic Carbon Release.
498 *Geophysical Research Letters*, *46*(23), 13950–13960. <https://doi.org/10.1029/2019GL085102>
- 499 Rafter, P. A., Gray, W. R., Hines, S. K. V., Burke, A., Costa, K. M., Gottschalk, J., Hain, M. P., Rae, J. W. B.,
500 Southon, J. R., Walczak, M. H., Yu, J., Adkins, J. F., & DeVries, T. (2022). Global reorganization of deep-
501 sea circulation and carbon storage after the last ice age. *Science Advances*, *8*(46), eabq5434.
502 <https://doi.org/10.1126/sciadv.abq5434>
- 503 Rafter, P. A., Herguera, J.-C., & Southon, J. R. (2018). Extreme lowering of deglacial seawater radiocarbon
504 recorded by both epifaunal and infaunal benthic foraminifera in a wood-dated sediment core. *Climate of the*
505 *Past*, *14*(12), 1977–1989. <https://doi.org/10.5194/cp-14-1977-2018>
- 506 Reimer, P. J., Austin, W. E. N., Bard, E., Bayliss, A., Blackwell, P. G., Ramsey, C. B., Butzin, M., Cheng, H.,
507 Edwards, R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Hajdas, I., Heaton, T. J., Hogg, A. G.,
508 Hughen, K. A., Kromer, B., Manning, S. W., Muscheler, R., ... Talamo, S. (2020). The IntCal20 Northern
509 Hemisphere Radiocarbon Age Calibration Curve (0–55 cal kBP). *Radiocarbon*, *62*(4), 725–757.
510 <https://doi.org/10.1017/RDC.2020.41>
- 511 Reimer, P. J., Baillie, M. G. L., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Ramsey, C. B., Buck, C. E.,
512 Burr, G. S., Edwards, R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Hajdas, I., Heaton, T. J.,
513 Hogg, A. G., Hughen, K. A., Kaiser, K. F., Kromer, B., ... Weyhenmeyer, C. E. (2009). IntCal09 and
514 Marine09 Radiocarbon Age Calibration Curves, 0–50,000 Years cal BP. *Radiocarbon*, *51*(4), 1111–1150.
515 <https://doi.org/10.1017/S0033822200034202>
- 516 Reimer, P. J., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Ramsey, C. B., Buck, C. E., Cheng, H., Edwards,
517 R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Haflidason, H., Hajdas, I., Hatté, C., Heaton, T. J.,
518 Hoffmann, D. L., Hogg, A. G., Hughen, K. A., ... Plicht, J. van der. (2013). IntCal13 and Marine13
519 Radiocarbon Age Calibration Curves 0–50,000 Years cal BP. *Radiocarbon*, *55*(4), 1869–1887.
520 https://doi.org/10.2458/azu_js_rc.55.16947
- 521 Ronge, T. A., Tiedemann, R., Lamy, F., Köhler, P., Alloway, B. V., De Pol-Holz, R., Pahnke, K., Southon, J., &
522 Wacker, L. (2016). Radiocarbon constraints on the extent and evolution of the South Pacific glacial carbon
523 pool. *Nature Communications*, *7*(1), 11487. <https://doi.org/10.1038/ncomms11487>

- 524 Rose, K. A., Sikes, E. L., Guilderson, T. P., Shane, P., Hill, T. M., Zahn, R., & Spero, H. J. (2010). Upper-ocean-to-
525 atmosphere radiocarbon offsets imply fast deglacial carbon dioxide release. *Nature*, *466*(7310), Article
526 7310. <https://doi.org/10.1038/nature09288>
- 527 Roth, R., & Joos, F. (2012). Model limits on the role of volcanic carbon emissions in regulating glacial–interglacial
528 CO₂ variations. *Earth and Planetary Science Letters*, *329–330*, 141–149.
529 <https://doi.org/10.1016/j.epsl.2012.02.019>
- 530 Roth, R., & Joos, F. (2013). A reconstruction of radiocarbon production and total solar irradiance from the Holocene
531 ¹⁴C and CO₂ records: Implications of data and model uncertainties. *Climate of the Past*, *9*(4), 1879–1909.
532 <https://doi.org/10.5194/cp-9-1879-2013>
- 533 *ScienceDirect Snapshot*. (n.d.). Retrieved September 9, 2022, from
534 <https://www.sciencedirect.com/science/article/pii/S0277379113002400>
- 535 Siani, G., Michel, E., De Pol-Holz, R., DeVries, T., Lamy, F., Carel, M., Isguder, G., Dewilde, F., & Lourantou, A.
536 (2013). Carbon isotope records reveal precise timing of enhanced Southern Ocean upwelling during the last
537 deglaciation. *Nature Communications*, *4*(1), Article 1. <https://doi.org/10.1038/ncomms3758>
- 538 Sigman, D. M., Fripiat, F., Studer, A. S., Kemeny, P. C., Martínez-García, A., Hain, M. P., Ai, X., Wang, X., Ren,
539 H., & Haug, G. H. (2021). The Southern Ocean during the ice ages: A review of the Antarctic surface
540 isolation hypothesis, with comparison to the North Pacific. *Quaternary Science Reviews*, *254*, 106732.
541 <https://doi.org/10.1016/j.quascirev.2020.106732>
- 542 Sigman, D. M., Hain, M. P., & Haug, G. H. (2010). The polar ocean and glacial cycles in atmospheric CO₂
543 concentration. *Nature*, *466*(7302), 47–55. <https://doi.org/10.1038/nature09149>
- 544 Sigman, D. M., & Haug, G. H. (2003). *6.18 The Biological Pump in the Past*.
- 545 Skinner, L. C., & Bard, E. (2022). Radiocarbon as a Dating Tool and Tracer in Paleoceanography. *Reviews of*
546 *Geophysics*, *60*(1), e2020RG000720. <https://doi.org/10.1029/2020RG000720>
- 547 Skinner, L. C., Fallon, S., Waelbroeck, C., Michel, E., & Barker, S. (2010). Ventilation of the Deep Southern Ocean
548 and Deglacial CO₂ Rise. *Science*, *328*(5982), 1147–1151. <https://doi.org/10.1126/science.1183627>
- 549 Stott, L. D., Harazin, K. M., & Krupinski, N. B. Q. (2019). Hydrothermal carbon release to the ocean and
550 atmosphere from the eastern equatorial Pacific during the last glacial termination. *Environmental Research*
551 *Letters*, *14*(2), 025007. <https://doi.org/10.1088/1748-9326/aafe28>

- 552 Stott, L., Southon, J., Timmermann, A., & Koutavas, A. (2009). Radiocarbon age anomaly at intermediate water
553 depth in the Pacific Ocean during the last deglaciation. *Paleoceanography*, *24*(2), n/a-n/a.
554 <https://doi.org/10.1029/2008PA001690>
- 555 Stott, L., & Timmermann, A. (2011). Hypothesized Link Between Glacial/Interglacial Atmospheric CO₂ Cycles and
556 Storage/Release of CO₂-Rich Fluids From Deep-Sea Sediments. In H. Rashid, L. Polyak, & E. Mosley-
557 Thompson (Eds.), *Geophysical Monograph Series* (Vol. 193, pp. 123–138). American Geophysical Union.
558 <https://doi.org/10.1029/2010GM001052>
- 559 Stuiver, M., & Polach, H. A. (1977). Discussion Reporting of ¹⁴C Data. *Radiocarbon*, *19*(3), 355–363.
560 <https://doi.org/10.1017/S0033822200003672>
- 561 Yu, J., Anderson, R. F., Jin, Z., Menviel, L., Zhang, F., Ryerson, F. J., & Rohling, E. J. (2014). Deep South Atlantic
562 carbonate chemistry and increased interocean deep water exchange during last deglaciation. *Quaternary*
563 *Science Reviews*, *90*, 80–89. <https://doi.org/10.1016/j.quascirev.2014.02.018>
- 564 Yu, J., Anderson, R. F., Jin, Z., Rae, J. W. B., Opdyke, B. N., & Eggins, S. M. (2013). Responses of the deep ocean
565 carbonate system to carbon reorganization during the Last Glacial–interglacial cycle. *Quaternary Science*
566 *Reviews*, *76*, 39–52. <https://doi.org/10.1016/j.quascirev.2013.06.020>
- 567 Yu, J., Broecker, W. S., Elderfield, H., Jin, Z., McManus, J., & Zhang, F. (2010). Loss of Carbon from the Deep Sea
568 Since the Last Glacial Maximum. *Science*, *330*(6007), 1084–1087. <https://doi.org/10.1126/science.1193221>
- 569 Yu, J., Elderfield, H., & Piotrowski, A. M. (2008). Seawater carbonate ion- $\delta^{13}\text{C}$ systematics and application to
570 glacial–interglacial North Atlantic ocean circulation. *Earth and Planetary Science Letters*, *271*(1), 209–
571 220. <https://doi.org/10.1016/j.epsl.2008.04.010>
- 572 Zhao, N., & Keigwin, L. D. (2018). An atmospheric chronology for the glacial-deglacial Eastern Equatorial Pacific.
573 *Nature Communications*, *9*(1), Article 1. <https://doi.org/10.1038/s41467-018-05574-x>
- 574 **References From the Supporting Information:**
- 575 Bereiter, B., Eggleston, S., Schmitt, J., Nehrbass-Ahles, C., Stocker, T. F., Fischer, H., Kipfstuhl, S., & Chappellaz,
576 J. (2015). Revision of the EPICA Dome C CO₂ record from 800 to 600 kyr before present. *Geophysical*
577 *Research Letters*, *42*(2), 542–549. <https://doi.org/10.1002/2014GL061957>

- 578 Dinauer, A., Adolphi, F., & Joos, F. (2020). Mysteriously high $\Delta^{14}\text{C}$ of the glacial atmosphere: Influence of ^{14}C
 579 production and carbon cycle changes. *Climate of the Past*, 16(4), 1159–1185. [https://doi.org/10.5194/cp-](https://doi.org/10.5194/cp-16-1159-2020)
 580 16-1159-2020
- 581 Galbraith, E. D., Kwon, E. Y., Bianchi, D., Hain, M. P., & Sarmiento, J. L. (2015). The impact of atmospheric pCO₂
 582 on carbon isotope ratios of the atmosphere and ocean. *Global Biogeochemical Cycles*, 29(3), 307–324.
 583 <https://doi.org/10.1002/2014GB004929>
- 584 Hain, M. P., Sigman, D. M., & Haug, G. H. (2010). Carbon dioxide effects of Antarctic stratification, North Atlantic
 585 Intermediate Water formation, and subantarctic nutrient drawdown during the last ice age: Diagnosis and
 586 synthesis in a geochemical box model. *Global Biogeochemical Cycles*, 24(4), n/a-n/a.
 587 <https://doi.org/10.1029/2010GB003790>
- 588 Hain, M. P., Sigman, D. M., & Haug, G. H. (2014). Distinct roles of the Southern Ocean and North Atlantic in the
 589 deglacial atmospheric radiocarbon decline. *Earth and Planetary Science Letters*, 394, 198–208.
 590 <https://doi.org/10.1016/j.epsl.2014.03.020>
- 591 Kovaltsov, G. A., Mishev, A., & Usoskin, I. G. (2012). A new model of cosmogenic production of radiocarbon ^{14}C
 592 in the atmosphere. *Earth and Planetary Science Letters*, 337–338, 114–120.
 593 <https://doi.org/10.1016/j.epsl.2012.05.036>
- 594 Laj, C., Kissel, C., & Beer, J. (2004). High resolution global paleointensity stack since 75 kyr (GLOPIS-75)
 595 calibrated to absolute values. *Washington DC American Geophysical Union Geophysical Monograph*
 596 *Series*, 145, 255–265. <https://doi.org/10.1029/145GM19>
- 597 Mackensen, A., & Schmiedl, G. (2019). Stable carbon isotopes in paleoceanography: Atmosphere, oceans, and
 598 sediments. *Earth-Science Reviews*, 197, 102893. <https://doi.org/10.1016/j.earscirev.2019.102893>
- 599 Reimer, P. J., Austin, W. E. N., Bard, E., Bayliss, A., Blackwell, P. G., Ramsey, C. B., Butzin, M., Cheng, H.,
 600 Edwards, R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Hajdas, I., Heaton, T. J., Hogg, A. G.,
 601 Hughen, K. A., Kromer, B., Manning, S. W., Muscheler, R., ... Talamo, S. (2020). The IntCal20 Northern
 602 Hemisphere Radiocarbon Age Calibration Curve (0–55 cal kBP). *Radiocarbon*, 62(4), 725–757.
 603 <https://doi.org/10.1017/RDC.2020.41>
- 604 Reimer, P. J., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Ramsey, C. B., Buck, C. E., Cheng, H., Edwards,
 605 R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Haflidason, H., Hajdas, I., Hatté, C., Heaton, T. J.,

- 606 Hoffmann, D. L., Hogg, A. G., Hughen, K. A., ... Plicht, J. van der. (2013). IntCal13 and Marine13
607 Radiocarbon Age Calibration Curves 0–50,000 Years cal BP. *Radiocarbon*, 55(4), 1869–1887.
608 https://doi.org/10.2458/azu_js_rc.55.16947
- 609 Roth, R., & Joos, F. (2013). A reconstruction of radiocarbon production and total solar irradiance from the Holocene
610 ^{14}C and CO_2 records: Implications of data and model uncertainties. *Climate of the Past*, 9(4), 1879–1909.
611 <https://doi.org/10.5194/cp-9-1879-2013>
- 612 Sigman, D. M., Fripiat, F., Studer, A. S., Kerneny, P. C., Martínez-García, A., Hain, M. P., Ai, X., Wang, X., Ren,
613 H., & Haug, G. H. (2020). The Southern Ocean during the ice ages: A review of the Antarctic surface
614 isolation hypothesis, with comparison to the North Pacific. *Quaternary Science Reviews*, 106732.
615 <https://doi.org/10.1016/j.quascirev.2020.106732>
- 616 Skinner, L. C., & Bard, E. (2022). Radiocarbon as a Dating Tool and Tracer in Paleoceanography. *Reviews of*
617 *Geophysics*, 60(1), e2020RG000720. <https://doi.org/10.1029/2020RG000720>
- 618 Stott, L., Davy, B., Shao, J., Coffin, R., Pecher, I., Neil, H., Rose, P., & Bialas, J. (2019). CO_2 Release From
619 Pockmarks on the Chatham Rise-Bounty Trough at the Glacial Termination. *Paleoceanography and*
620 *Paleoclimatology*, 34(11), 1726–1743. <https://doi.org/10.1029/2019PA003674>
- 621