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Supporting Information for

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

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Introduction

Here we provide in-depth descriptions of our model configuration, algorithm design, and experimental design. We also include a brief description of the geologic sources of neutralized carbon we considered and their $\delta^{13}C$ values.

Text S1. Model configuration

We use the CYCLOPS global carbon cycle box model and deglacial carbon cycle scenario of Hain et al. (2014) as our baseline control run, but with an initial 2700 Pg terrestrial carbon reservoir and an increased model temperature of 1.1˚ C, to raise the simulated LGM CO_2 to 188 ppm and preindustrial CO_2 to 281 ppm (Figure 2a). The model includes a constant $CaCO_3$ weathering flux of 0.192 Pg C yr^{-1} and saturation state dependent $CaCO_3$ preservation and burial on the deep seafloor, yielding a 113 µmol kg^{-1} net loss of bulk ocean alkalinity throughout the deglacial control run (i.e., 1875 Pg C net $CaCO_3$ burial). The control run deglacial scenario (Hain et al., 2014) includes changes in ocean circulation, nutrient utilization, and productivity intended to mimic LGM Subantarctic iron fertilization, shoaling of the Atlantic Meridional overturning circulation, and Antarctic surface isolation (Hain et al., 2010; Sigman et al., 2020), reverting to the modern reference conditions throughout the simulated deglacial period (Hain et al., 2014). In this scenario, the ocean's biological pump weakens during the deglaciation, causing a deglacial $CaCO_3$ preservation event, with the loss of biological carbon sequestration and ocean alkalinity significantly contributing to the simulated CO_2 rise (Hain et al., 2010). The model also includes time-varying ^{14}C production modulated by the GLOPIS-75 record of Earth's magnetic field (Kovaltsov et al., 2012; Laj et al., 2004; as described in Hain et al. (2014)), yielding a 19% decline in the global ^{14}C inventory since the LGM and simulated atmospheric $\Delta^{14}C$ broadly matching the temporal pattern of the IntCal13 and IntCal20 data products (Reimer et al., 2013, 2020; Figure 2a, d, g, j). The simulations presented in this study include all these background changes of the control run, providing us with a framework to assess other fluxes of the open-system carbon cycle.

Text S2. Numerical algorithm design

We develop a numerical algorithm based on Powell's method (Press et al., 2007) to iteratively minimize the deviation between CO_2^{model} and $\Delta^{14}C^{model}$ compared to CO_2^{obs} (Bereiter et al., 2015) and $\Delta^{14}C^{obs}$ (Reimer et al., 2020). The algorithm is evaluated at 100-year time steps to find the optimized rate of open-system carbon and alkalinity fluxes (terrestrial and submarine) to minimize the mismatch represented by the weighted objective function. The objective function is given approximately equal weight to the two data constraints by scaling the misfit relative to the 90 ppm and the 250‰ magnitude of glacial/interglacial CO_2 and $\Delta^{14}C$ change presumed to be driven by the global carbon cycle:

$$f(CO_2, \Delta^{14}C) = \frac{|CO_2^{EPICA} - CO_2^{model}|}{90\ ppm} + \frac{|\Delta^{14}C^{IntCal} - \Delta^{14}C^{model}|}{250\ ‰}$$

Further, we implement a dampening strategy to introduce a low-pass filter suppressing short-term fluctuations in carbon and alkalinity release while allowing the algorithm to converge on CO_2^{obs} and $\Delta^{14}C^{obs}$ over timescales greater than the minimization time step

of 100 years. Additionally, since the objective function is based on instantaneous atmospheric values (CO_2^{obs} and $\Delta^{14}C^{obs}$), we use a greater dampening effect (smaller dampening term) for optimized submarine fluxes compared to optimized terrestrial carbon cycle fluxes, to account for the residence time of oceanic carbon before ventilation with the atmosphere. As a result, our dampening parameters are 0.016 for optimized submarine carbon cycle fluxes and 0.55 for optimized terrestrial carbon cycle fluxes.

Text S3. Experimental design

We present four experiments, progressively adding optimized and imposed open-system carbon and alkalinity fluxes: (1) we invert for the optimal rates of carbon and alkalinity release to the mid-depth North Pacific region of the model (experiment NP), (2) we add the possibility of land carbon uptake to the optimization (experiment NP+LC), (3) we include the release of ^{14}C-free permafrost carbon (experiment NP+LC+PF), and (4) we adjust the initial LGM ^{14}C inventory by +3.5% (experiment NP+LC+PF+RC). All these scenarios include the identical background forcings of the control run.

The first experiment (NP) allows for the release of ^{14}C-free carbon with a variable proportion of alkalinity to the mid-depth North Pacific model region, but only if the simulated $\Delta^{14}C$ is greater than IntCal20, since geologic carbon will ultimately lower atmospheric $\Delta^{14}C$. Removal of DIC is not permitted, and the alkalinity flux is constrained to ALK-to-DIC ratios in the range 0 to 2, where a ratio of 0 corresponds to CO_2 release, a ratio of 1 corresponds to HCO_3^- (bicarbonate ion) release, and a ratio of 2 corresponds to adding CO_3^{2-} (carbonate ion, likely through the addition of dissolved $CaCO_3$). As discussed further below, the $\Delta^{14}C^{obs}$ constraint tends to determine the optimal carbon release rate, while the CO_2^{obs} constraint mainly affects the optimal ALK-to-DIC ratio.

The second experiment (NP+LC) allows for net land carbon uptake in addition to North Pacific carbon/alkalinity release, but only if CO_2^{model} is greater than CO_2^{obs} and the atmospheric $\Delta^{14}C$ model-data misfit is less than 20 ‰. These conditions were selected to favor land carbon uptake during the Holocene when simulated alkalinity loss from ongoing carbonate compensation in the control run tends to raise atmospheric CO_2. With this deliberate heuristic, our algorithm can determine the optimal instantaneous rate of land carbon uptake and hence the integrated change in land carbon storage through time. The CO_2^{obs} constraint primarily drives the optimization of land carbon uptake with only a minor impact on simulated atmospheric $\Delta^{14}C$ stemming indirectly from the CO_2 dependence of air/sea carbon isotope equilibration (Galbraith et al., 2015).

The third experiment (NP+LC+PF) allows the addition of ^{14}C-free CO_2 into the atmosphere to represent the impact of permafrost destabilization and carbon release. This optimized open-system permafrost flux is only activated when the optimization algorithm would otherwise be adding CO_2 into the mid-depth North Pacific, instead releasing the equivalent amount of CO_2 directly to the atmosphere. The algorithm still optimizes for the geologic addition of bicarbonate and carbonate into the mid-depth

North Pacific as in the previous experiments. This sensitivity experiment intends to assess how early deglacial permafrost carbon release changes the inversion solution relative to the NP+LC experiment, with the expectation that permafrost carbon release will reduce the opportunity for geologic carbon release based on the $\Delta^{14}C^{obs}$ constraint.

The fourth experiment (NP+LC+PF+RC) imposes a 3.5% greater initial ^{14}C inventory as a crude way to assess model bias from the uncertain history of Earth's magnetic field and ^{14}C production (Dinauer et al., 2020; Roth & Joos, 2013), which are used to calculate $\Delta^{14}C^{model}$ (Hain et al., 2014). Additionally, this experiment accounts for uncertainty in $\Delta^{14}C^{obs}$ at the LGM, as there has been disagreement in the last three iterations of IntCal (Fig. 3a). After this change in the initial state, the LGM $\Delta^{14}C^{model}$ increases from 365 ‰ in the control run to 413 ‰, bringing the model's initial LGM $\Delta^{14}C$ into closer agreement with reconstructions (~425 ‰). This speculative sensitivity experiment intends to assess how the model bias of a low LGM ^{14}C inventory may hide a substantial opportunity for geologic carbon release within the $\Delta^{14}C^{obs}$ constraint.

Text S4. Neutralized carbon sources considered and their $\delta^{13}C$ values

We consider two plausible geological carbon sources on the marine sedimentary environment that produce neutralized carbon. The first was suggested by Rafter et al. 2019, combining the two known sedimentary processes of basaltic sill intrusion and anaerobic oxidation of methane (AOM). Basaltic sill intrusion can produce thermogenic methane from sedimentary organic carbon, and that methane can be anaerobically oxidized into bicarbonate. We use a $\delta^{13}C$ value of -25‰ for this pathway due to the $\delta^{13}C$ of marine organic matter ranging from -31 to -19‰ (Mackensen & Schmiedl, 2019). The second geologic source was proposed by (Skinner & Bard, 2022), consisting of subsurface geologic CO_2 (Stott et al., 2019) dissolving carbonates deep in the sediment column. With mantle CO_2 estimated to be around -5‰ and $CaCO_3$ shells around 0‰ (Mackensen & Schmiedl, 2019), we designate a $\delta^{13}C$ of -2.5‰ for the carbonate dissolution pathway.

Table S1. Results from the four experimental simulations. All carbon amounts are in PgC, except "Net ALK-to-DIC ratio" and "% HCO_3^-" are unitless. Values reported are totals at the end of the 20 kyr simulation.

	NP	NP+LC	NP+LC+PF	NP+LC+PF+RC
CO_2	**143**	**145**	**-**	**-**
HCO_3^-	**568**	**678**	**711**	**1933**
CO_3^{2-}	**219**	**149**	**138**	**464**
Geologic carbon added	**929**	**970**	**846**	**2396**
Terrestrial carbon uptake	**-**	**300**	**279**	**550**

Terrestrial carbon release	**-**	**-**	**105**	**97**
Net ALK-to-DIC ratio	**1.08**	**1.00**	**1.16**	**1.19**
% HCO_3^-	**61**	**70**	**84**	**81**

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