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Anomalous > 2000-Year-Old Surface Ocean Radiocarbon Age as Evidence for Deglacial Geologic Carbon Release

Patrick A. Rafter[1], José D. Carriquiry[2], Juan-Carlos Herguera[3], Mathis P. Hain[4], Evan A. Solomon[5], and John R. Southon[1]

[1]Department of Earth System Science, University of California, Irvine, CA, USA, [2]Instituto de Investigaciones Oceanológicas, Universidad Autónoma Baja California, Ensenada, Mexico, [3]Departmento de Ecology Marina, Centro de Investigación Cientifica y Educación Superior de Ensenada, Ensenada, Mexico, [4]Department of Earth and Planetary Sciences, University of California, Santa Cruz, CA, USA, [5]School of Oceanography, University of Washington, Seattle, WA, USA

Key Points:
- Recent work suggests increased carbon flux from seafloor volcanism during deglaciation
- We identify increased carbon flux with a unique application of microfossil radiocarbon content in the volcanically active Gulf of California
- This geologic carbon may arrive via sediment pyrolysis and anaerobic oxidation of methane, with a minimal influence on seawater pH

Supporting Information:
- Supporting Information S1

Correspondence to:
P. A. Rafter,
prafter@uci.edu

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Abstract Geologic carbon from seafloor volcanism may influence late Pleistocene glacial terminations by increasing the global inventory of the greenhouse gas CO_2. However, the evidence for geologic carbon flux associated with deep sea volcanism has been, so far, equivocal. Here, we construct a regional, glacial-deglacial carbon budget of the volcanically active Gulf of California using microfossil ^{14}C measurements and find results consistent with an increased addition of geologic carbon related to local seafloor volcanism during the deglaciation. Our estimates point to enhanced geologic carbon flux both before and during the last deglaciation that generally occur alongside carbonate preservation. This leads us to suggest that the carbon was added in the form of partially neutralized, ^{14}C-free bicarbonate associated with known Gulf sedimentary processes—a carbon source that would have a minimal effect on atmospheric CO_2.

Plain Language Summary We account for the carbon entering and leaving the waters of the Gulf of California since the last ice age. Our results argue for increased supply of geologic carbon alongside enhanced volcanic activity after the last ice age. We argue that this delivery of geologic carbon to Gulf seawater was in the form of bicarbonate, not CO_2, which would have a minimal impact on seawater acidity and is consistent with global sedimentary records.

1. Introduction

Given modern carbon cycle perturbations, the rise in atmospheric carbon dioxide (CO_2) that occurs at the end of each late Pleistocene ice age (Marcott et al., 2014; Petit et al., 1999) provides an excellent framework for examining natural perturbations to the global CO_2 inventory. The leading hypothesis for the deglacial rise in CO_2 involves biological carbon sequestration into the deep ocean and subsequent deglacial release of that carbon back to the atmosphere (Sigman et al., 2010), but recent work suggests that volcanism—a primary source of CO_2—may augment atmospheric CO_2 variability because it is sensitive to changes in ice sheets (Huybers & Langmuir, 2009), sea level (Lund & Asimow, 2011), and/or Earth's orbit (Tolstoy, 2015). The possibility of a connection between deglacial volcanism and atmospheric CO_2 rise has been invoked previously (Lund et al., 2016; Ronge et al., 2016), but we have yet to find unambiguous evidence for enhanced volcanic carbon release with a deglacial timing and to constrain the magnitude of that carbon input in order to establish a robust link. Furthermore, the potential lowering of seawater pH from this proposed addition of CO_2 is inconsistent with (in some cases) enhanced preservation of sedimentary carbonate during the deglaciation (Lindsay et al., 2016; Stott & Timmermann, 2011), not to mention the increase in carbonate preservation throughout the equatorial Pacific (Farrell & Prell, 1989). Here, using radiocarbon (^{14}C) measurements of sedimentary microfossils (foraminifera), we exploit the geology and estuarine circulation of the Gulf of California (Figure 1) to create a glacial-interglacial carbon budget for this volcanically active region.

Radiocarbon is a useful tool for identifying the input of geologic carbon (sedimentary or mantle-derived) to the ocean because carbon in sediments older than 50,000 years and in the Earth's mantle contains no detectable ^{14}C. The introduction of geologic carbon to the ocean therefore dilutes the ^{14}C of seawater carbon reducing the ratio of ^{14}C to total C ($^{14}C/C$), corresponding to an older conventional ^{14}C age and a lower

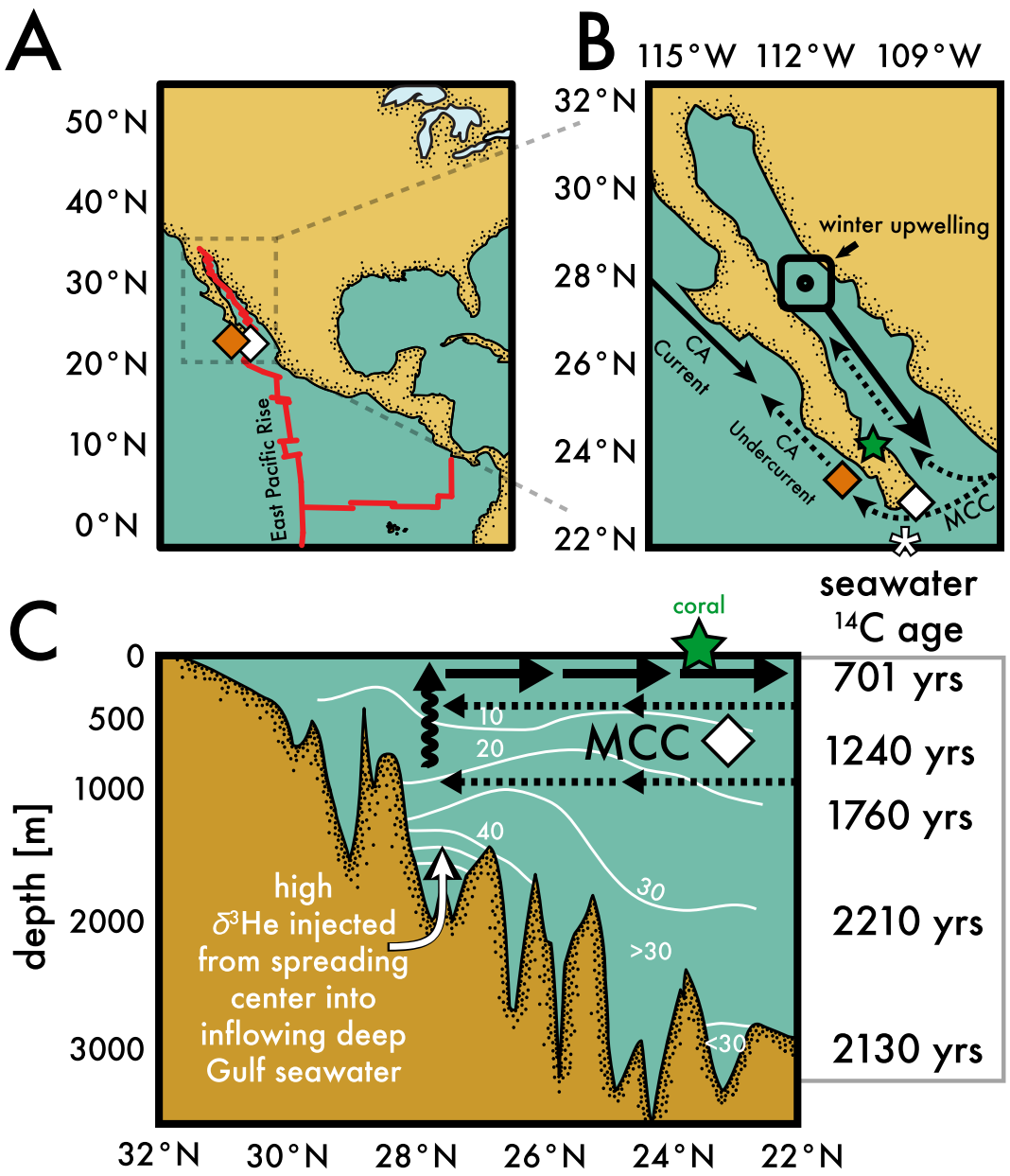

Figure 1. Subtropical North Pacific seafloor spreading, circulation, and sediment core sites. Seafloor spreading along the East Pacific Rise and Gulf of California (red lines in (A)) influence seawater characteristics both at depth and at the surface (B and C). The influence of mantle-derived gases elevates modern Gulf of California seawater δ^3He (white lines in (C); in units of percent (Lupton, 1979)). Mean Gulf circulation is: in at depth (dashed arrows) and out at the surface (solid arrows) (Lavín & Marinone, 2003). Subsurface seawater DIC ^{14}C ages (C, right; see asterisk in (B) for location) are minimally influenced by mid-twentieth-century thermonuclear weapon testing (Key et al., 2004), but the surface ^{14}C age was estimated using "pre-bomb" *Porites* coral (green star; see SI). Diamonds indicate the location of California Undercurrent (red) and Gulf of California (white) site LPAZ-21P. Note that the subsurface (200 to ≈700 m) Mexican Coastal Current (MCC) feeds into the deep Gulf and California Undercurrent (Gómez-Valdivia et al., 2015), bathing both the Gulf and Undercurrent core sites (Lindsay et al., 2015; Marchitto et al., 2007).

reconstructed Δ^{14}C (see Supplementary Materials (SM)). Proxy measurements from sediments on the East Pacific Rise suggest enhanced seafloor volcanic activity between ≈25,000 and ≈10,000 years BP (25- to 10-kyr, where BP is before 1950) (Lund et al., 2016, 2019), such that the associated volcanic carbon release plausibly contributed to deglacial carbon cycle change. While some records of glacial-interglacial seawater ^{14}C/C from foraminifera and deep sea corals display old ^{14}C ages/lower Δ^{14}C values during this interval

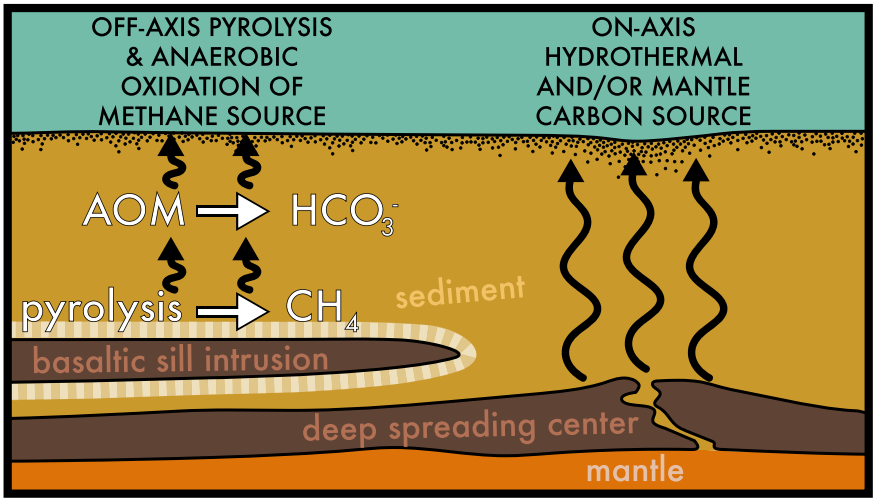

Figure 2. Geologic sources of carbon associated with Gulf of California volcanism. These sources include (left) sedimentary carbon pyrolyzed via basaltic sill intrusion and oxidized to bicarbonate (HCO_3^-) by the anaerobic oxidation of methane (AOM) (Davis & Yarbrough, 1966; Einsele et al., 1980) and (right) CO_2 emitted alongside other mantle-derived gases (such as ^{3}He; see Figure 1C).

(Bryan et al., 2010; Burke & Robinson, 2012; Lindsay et al., 2016; Marchitto et al., 2007; Ronge et al., 2016; Sikes et al., 2000; Skinner et al., 2010; Stott et al., 2009; Thornalley et al., 2011), several others do not (Cléroux et al., 2011; De Pol-Holz et al., 2010), and the natural "aging" of seawater ^{14}C/C (time since equilibration with the atmosphere) leads to ambiguities in interpretation. Hence a widespread interpretation of these anomalously old ^{14}C ages/low Δ^{14}C values is that they originate from the deglacial release of carbon sequestered in the deep sea during the last glaciation (Burke & Robinson, 2012; Marchitto et al., 2007; Rae et al., 2018), rather than from addition of geologic carbon.

The geology and hydrography of the Gulf of California mitigate some of the difficulties in identifying the input of geologic carbon to the ocean. First, the Gulf represents the northward extension of the East Pacific Rise, a seafloor spreading center separating the Pacific Plate from the Cocos, Nazca, and Antarctic Plates and a major part of the global mid-ocean ridge system. Second, activity associated with seafloor volcanism is known to introduce geologic carbon to the water column, either via the direct introduction of mantle-derived gases (e.g., the elevated δ^3He values in modern Gulf seawater shown in Figure 1C) or from the effects of volcanic sill intrusion into marine sediments (Einsele et al., 1980; Lizarralde et al., 2011). This latter source (detailed in Figure 2) involves the thermogenic production of methane via the pyrolysis of sedimentary organic carbon, which can be anaerobically oxidized (AOM) to bicarbonate (HCO_3^-) (Figure 2; Davis & Yarbrough, 1966) resulting in the flux of a partly neutralized form of CO_2 that has only minor effects on seawater pH, carbonate saturation state, and CO_2 concentration. The existence of a flux of geologic carbon to modern Gulf seawater is supported by in situ hydrothermal fluid measurements indicating high concentrations of dissolved inorganic carbon (DIC) and methane containing almost no ^{14}C (Pearson et al., 2005).

Mean circulation in the Gulf of California is estuarine: waters inflowing at depth are upwelled to the surface and flow out in the upper ≈200 m (Figures 1B and 1C) (Lavín & Marinone, 2003), with surface water taking about 1 year to leave the basin (see SM). With respect to the flux of geologic carbon, we expect that the addition of geologic/^{14}C-free carbon from the Gulf seafloor will be entrained in inflowing deep waters to upwell near the Guaymas Basin and flow out along the surface (Figures 1B and 1C). We estimate the modern (pre-1950s) difference between 600 m and surface seawater ^{14}C near the mouth of the Gulf of California to be 539 ± 43 years BP based on observed seawater DIC ^{14}C at 600 m (1240 ± 40 years BP (Key et al., 2004)) and new measurements of coral ^{14}C (701 ± 15 years BP) from before the thermonuclear weapons tests (see SM). Given that ^{14}C-free geologic carbon is being added to inflowing seawater in the modern Gulf (see above and Pearson et al., 2005), this younger ^{14}C age (higher ^{14}C/C) of modern, "pre-bomb" outflowing waters highlights the importance of air-sea equilibration via CO_2 exchange in establishing the modern

surface-to-deep $^{14}C/C$ gradient. Air-sea gas exchange will raise the $^{14}C/C$ of the outflowing surface water, and therefore the estimated magnitude of geologic carbon added en route should be considered a conservative lower bound.

Here we reconstruct the glacial-interglacial $^{14}C/C$ of inflowing (deep) and outflowing (surface) Gulf seawater using ^{14}C measurements of single-species epifaunal benthic foraminifera (*Planulina ariminensis*) and planktic foraminifera (*Globigerina bulloides*) from a sediment core at 624 m near the mouth of the Gulf (sediment core LPAZ-21P; white diamond in Figure 1). Importantly, since our benthic and planktic forams are picked from the same sediment intervals, the ^{14}C age *differences* do not depend on the actual calendar ages: hence, this approach is independent of any age model errors. Nevertheless, we have excellent age model control using calibrated ^{14}C dates of terrestrial material (microscopic wood fragments) recovered from the core (see Rafter et al., 2018, for a detailed discussion).

2. Materials and Methods

2.1. Preparation and Measurement of Foraminifera, Wood, and Coral ^{14}C

Sediment from Gulf of California sites LPAZ-21P (Figure 1) was washed using deionized water in a 63 μm sieve, and foraminifera species were selected from the >250 μm fraction. Each foraminifera sample was sonicated in methanol (≈1 minute) to release detrital carbonates trapped within open microfossil chambers, and at least 10% of each sample was dissolved using HCl to remove potential secondary calcite (precipitated postdeposition). Wood fragments from the >250 μm fraction were prepared using standard acid-base-acid treatments. *Porites* spp. coral was subsampled using a diamond-tipped, handheld Dremel tool at 1 mm intervals following the central axis of growth (see Rafter et al., 2017).

Samples were graphitized following Santos et al. (2007) and analyzed at the Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at University of California, Irvine (Southon et al., 2004). We report radiocarbon as $\Delta^{14}C$ in units of per mil (‰), which is corrected for ^{14}C decay based on its age before 1950, according to convention (Stuiver & Polach, 1977). Analysis of an in-house sedimentary standard (FIRI-C) alongside measurements indicates a combined sample preparation and measurement ^{14}C age error ranging from ±50 years for a full size sample (≈0.7 mg of C) to ±500 years for very small samples (<0.1 mg of C).

2.2. Stable Carbon and Oxygen Isotopic Composition of Foraminifera

The $^{13}C/^{12}C$ and $^{18}O/^{16}O$ of planktic species *G. bulloides* was measured using a Kiel IV Carbonate Device coupled to a Delta XP isotope ratio mass spectrometer at the University of California, Irvine. This isotopic ratio is reported in delta notation, where $\delta^{13}C = (^{13}C/^{12}C_{sample}/^{13}C/^{12}C_{standard} - 1)$ and $\delta^{18}O = (^{18}O/^{16}O_{sample}/^{18}O/^{16}O_{standard} - 1)$, multiplied by 1000 to give "per mil." The standards are IAEA-CO1 and NBS-19 expressed relative to VPDB with standard deviation of 0.04 per mil for $\delta^{13}C$ and 0.07 per mil for $\delta^{18}O$.

3. Foraminifera Record Inflowing and Outflowing Gulf of California Seawater ^{14}C

The Gulf of California core site is bathed in the subsurface, northward-flowing Mexican Coastal Current (MCC in Figure 1). The MCC is also the source of the California Undercurrent (Gómez-Valdivia et al., 2015) that overlies sediment core sites along the Pacific margin of Baja California with comparable ^{14}C records from benthic forams (orange diamonds in Figure 1A) (Lindsay et al., 2015; Marchitto et al., 2007; Rafter et al., 2018). The similarity in the benthic ^{14}C measurements from these geographically distinct "Gulf" and "Undercurrent" sites over the past 30-kyr (shown as both ^{14}C ages and $\Delta^{14}C$ in Figure 3) is striking and provides strong evidence for the persistence of modern circulation pathways (including the estuarine Gulf circulation) over the past 30-kyr (Rafter et al., 2018). Since the same pronounced trend to low ^{14}C values between ≈18- and 10-kyr BP is observed at two widely separated sites with very different sedimentation rates, it cannot be explained by species-biases, microfossil bioturbation, or diagenetic processes (Rafter et al., 2018) and thus validates a lowering of intermediate-depth seawater $^{14}C/C$ during the deglaciation observed at other locations (Bryan et al., 2010; Lund et al., 2011; Ronge et al., 2016; Stott et al., 2009).

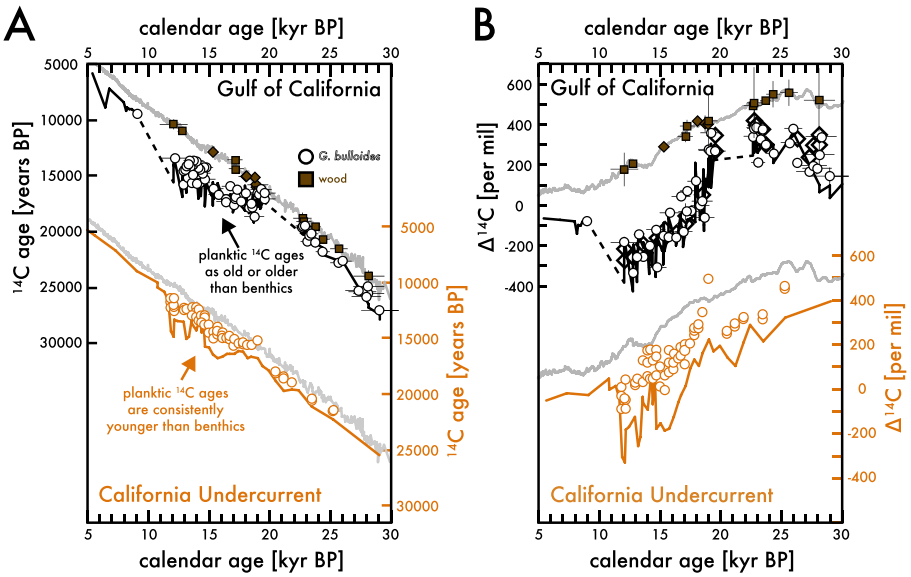

Figure 3. Surface and subsurface ^{14}C/C in the subtropical North Pacific since the last glacial period. The ^{14}C/C of atmospheric CO_2 (gray; (Reimer et al., 2013)), benthic forams (lines; (Lindsay et al., 2016; Marchitto et al., 2007; Rafter et al., 2018)), and planktic forams (symbols) are shown in two ways: (A) As a ^{14}C age and (B) as Δ^{14}C. Measurements from the Gulf of California sediment (black; this study) are compared with those from the California Undercurrent site (orange (Lindsay et al., 2015; Marchitto et al., 2007)) (see Figure 1 for locations). The Gulf sediment core age model is constrained by wood ^{14}C ages (brown symbols) calibrated to atmosphere ^{14}C/C.

3.1. Benthic-Planktic ^{14}C Differencing Points to Anomalously Old Surface Waters

On their own, the benthic foram records are not useful in distinguishing between the competing hypotheses for the lower seawater ^{14}C/C during the deglaciation: the addition of geologic carbon from seafloor volcanism (Ronge et al., 2016; Stott et al., 2009) or carbon release of a previously isolated deep water mass via the Southern Ocean (Marchitto et al., 2007). However, despite the close similarity in Gulf and Undercurrent benthic foraminifera ^{14}C, there are large differences in planktic foraminifera ^{14}C (Figure 3). While Undercurrent planktic foraminifera ^{14}C ages are slightly older relative to the atmosphere during the deglaciation, they are (for the most part) younger than the benthic foraminifera; observations consistent with essentially the entire catalog of published foraminifera ^{14}C measurements (Zhao et al., 2018). This contrasts with the Gulf of California planktic foraminifera, which have ^{14}C ages that are *as old or older than the benthics*, producing several benthic-planktic ^{14}C age reversals. The most extreme planktic foraminifera ^{14}C/C measurement during the deglaciation equates to a surface water radiocarbon age (a.k.a. "reservoir age") of more than 3300 years old, and reservoir ages average > 2000 years for the five deglacial samples with benthic-planktic ^{14}C age reversals. A reversed vertical seawater ^{14}C gradient is unknown in the modern ocean, and isolated anomalous benthic-planktic ^{14}C ages are usually assumed to be disturbed or geochemically altered; two examples include benthic-planktic ^{14}C measurements from the Guaymas Basin (north of our site (Keigwin, 2002)) and one of the sediment core sites underneath the California Undercurrent (Lindsay et al., 2016).

We present the differencing of these benthic-planktic ^{14}C ages alongside atmospheric CO_2 concentrations and the δ^{18}O and δ^{13}C values of *G. bulloides* in Figure 4. White diamonds represent foraminifera abundance maxima in both the benthic and planktic species (from Rafter et al., 2018), and blue circles represent samples where bioturbation biases the benthic-planktic ^{14}C age difference toward high values (down in Figure 4B). In other words, the symbols in Figure 4 represent measurements minimally influenced by bioturbation or where bioturbation would work against the observed benthic-planktic age reversals. Given that the modern deep-surface seawater ^{14}C age difference near our core site of +539 ± 43 years (Figure 1C) includes some known (but not quantified) flux of geologic carbon and partial equilibration of surface water with the atmosphere, the benthic-planktic ^{14}C age differences in Figure 4B suggest significantly larger geologic carbon flux

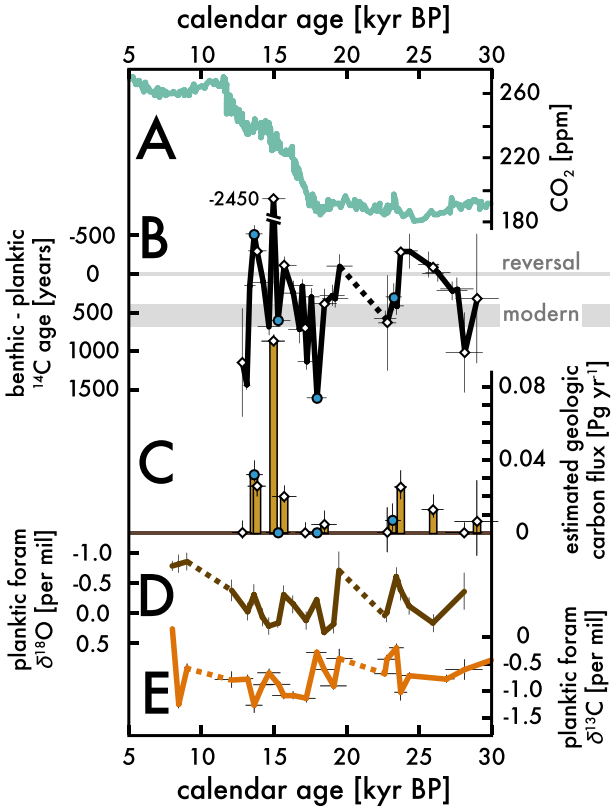

Figure 4. Glacial-interglacial changes in Gulf of California geologic carbon flux. Atmospheric CO_2 concentrations (A) (Marcott et al., 2014) are compared with (B) the benthic-planktic (*P. ariminensis-G. bulloides*) foraminifera ^{14}C age difference at site LPAZ-21P (on a reversed Y-axis). Diamonds signify values minimally influenced by bioturbation and circles indicate values where bioturbation would bias values to a larger difference (benthic to older and planktic to younger ^{14}C ages). The carbon flux necessary to explain deep-surface ^{14}C age differences in (B)—for values less than modern deep-minus-the-surface (+539 years)—is shown in (C). This calculation assumes modern Gulf overturning rate; slower overturning predicts lower estimated carbon flux estimation and vice versa. Symbols are the same as in (B). (D) and (E) show the planktic foraminifera (*G. bulloides*) $\delta^{18}O$ and $\delta^{13}C$, respectively.

than today beginning about 25-kyr BP. Furthermore, the deep-surface proxy seawater ^{14}C differences given by the benthic-planktic ^{14}C measurements are a lower limit measure for geologic carbon added en route because the influence of gas exchange on surface water $^{14}C/C$ increases with the air-to-sea $^{14}C/C$ difference, which was particularly high at the time (see SM).

These extremely low planktic foraminifera $^{14}C/C$ values are not seen at the open ocean/Undercurrent sediment core sites, which lie under the southward flowing surface waters (and presumably better equilibrated) of the California Current, waters that—in contrast with the Gulf of California—do not transit over known regions of geologic carbon flux. The glacial-interglacial trend in Gulf of California benthic-planktic ^{14}C ages are therefore consistent with an increased flux of geologic carbon during the last glacial termination, as predicted by several studies (Lund et al., 2016; Lund & Asimow, 2011; Ronge et al., 2016; Tolstoy, 2015). The timing of the benthic-planktic ^{14}C age reversals suggests an increased flux of ^{14}C-free geologic carbon into the Gulf of California as early as 25-kyr BP (Figure 4)—predating the rise in atmospheric pCO_2 but within the ≈25- to 10-kyr BP time window for increased seafloor hydrothermal (and presumably volcanic) activity on Pacific mid-ocean ridges (Costa et al., 2018; Lund et al., 2011, 2019). The occurrence of the foraminifera ^{14}C age reversals is also consistent with work, suggesting that "high temperature thermogenic reactions [...] released large amounts of carbon" in the northern Gulf of California seafloor between 28- and 7-kyr BP (Geilert et al., 2018) (discussed in more details below).

3.2. Estimating Geologic Carbon Flux to Gulf of California Waters

The marginal and semi-enclosed geometry of the Gulf allows us to use our benthic and planktic ^{14}C data to monitor the $^{14}C/C$ of deep, inflowing Gulf water and the $^{14}C/C$ of near-surface outflowing Gulf water. Even though this simple inventory of Gulf radiocarbon ignores air-sea gas exchange and $^{14}C/C$ equilibration at the surface, it still offers a useful framework to estimate the order of magnitude of geologic carbon addition. For this purpose, we first assume that, in this closed system, inflowing and outflowing Gulf circulation is equal. Therefore, if outflowing Gulf surface water is ≈200 m deep and moves at 1.5 cm s^{-1} ($v_{outflow}$) across a 150 km-wide span of the mouth, the conservative mean in- and outflow is 0.3 sverdrups (1 Sv = 106 m^3 s^{-1}). We then estimate the inflow of carbon at depth (Q_{inflow}) as the product of seawater density (rho; averaged between 200 and 800 m near our site), the outflow of surface water (0.3 Sv; see above), as well as the carbon concentration of inflowing water (DIC_{inflow}):

$$Q_{inflow} \approx \rho * width * depth * v_{outflow} * DIC_{inflow} \approx 1026.8\ \frac{kg}{m^3} * 150\ km * 200\ m * 1.5\ \frac{cm}{s} * 2\ \frac{mmol}{kg} \quad (1)$$

Assuming a typical seawater DIC of 2 mmol kg^{-1} (similar to the modern open ocean; Key et al., 2004), this inflowing Gulf water (Q_{inflow}) would be carrying about 19 Tmol C yr^{-1}. (The faster flow of 0.4 Sv estimated by Bray (1988) gives an even larger Q_{inflow}.) Further, if we assume that the addition of ^{14}C-free (added $^{14}C/C = 0$) geologic carbon is the only significant process within the Gulf (i.e., ignoring gas exchange), we can write the ^{14}C mass balance and solve for the implied flux of added carbon (Q_{added}) and substitute our benthic and planktic data for the $^{14}C/C$ of inflowing and outflowing carbon, respectively:

$$(Q_{inflow} + Q_{added}) * \left(\frac{^{14}C}{C}\right)_{outflow} = Q_{inflow} * \left(\frac{^{14}C}{C}\right)_{inflow} + Q_{added} * \left(\frac{^{14}C}{C}\right)_{added} \quad (2)$$

$$Q_{added} = Q_{inflow} * \frac{\left(\frac{^{14}C}{C}\right)_{deep} - \left(\frac{^{14}C}{C}\right)_{surface}}{\left(\frac{^{14}C}{C}\right)_{surface}} \quad (3)$$

Before performing this calculation, we should note once again that gas exchange at the surface acts to elevate surface (planktic) $^{14}C/C$ relative to the $^{14}C/C$ upwelled from below (benthic), and ignoring gas exchange altogether leads to an underestimate of added carbon flux. As a case in point, if we use our coral $^{14}C/C$ data to constrain $^{14}C/C_{surface}$ before nuclear testing (see SM) and take $^{14}C/C_{deep}$ from modern open ocean hydrographic data (Key et al., 2004), we estimate (using equations 2 and 3) the modern geologic carbon flux to be negative (-0.002 Tmol C yr^{-1}). This is less than the nominal geologic carbon flux that is known to occur in the Gulf today (e.g., Lizarralde et al., 2011) because gas exchange has raised the surface $^{14}C/C$ relative to the deep. This modern deep-surface $^{14}C/C$ contrasts with the anomalous lowering of surface (planktic) $^{14}C/C$ relative to the deep (benthic) $^{14}C/C$ reconstructed in Figure 3, which implies very large geologic carbon flux added en route as water is circulating through the Gulf.

Similar to the benthic-planktic ^{14}C age differencing in Figure 4B, we minimize possible artifacts from bioturbation in our estimated geologic carbon flux (Q_{added}; Figure 4C) by taking advantage of foraminifera abundance maxima (same symbol interpretation as Figure 4B) (Keigwin & Guilderson, 2009). For these data, the benthic-planktic ^{14}C age differences (Figure 4D) point to increased geologic carbon flux for an interval during the glacial period (from 28- to 23-kyr BP) and again during the deglaciation (from 17- to 12.8-kyr BP). We are unable to estimate the flux during the Holocene because planktic foraminifera microfossils are not preserved after ≈12.1-kyr BP, but our coral $^{14}C/C$ data demonstrates that anomalous lowering of surface relative to deep $^{14}C/C$ is not the modern (pre-bomb) state of the Gulf.

The estimated average Q_{added} within the Gulf during the deglacial interval is 1.56 Tmol C yr^{-1} (0.02 Pg C yr^{-1}; Figure 4C) relative to an assumed Q_{inflow} of 19 Tmol C yr^{-1} (equation 1) giving an 8% increase of carbon to the Q_{inflow}, but we note that this result is subject to large uncertainties. For example, if we arbitrarily remove the benthic/planktic pair with the largest ^{14}C age reversal (i.e., at 15-kyr BP), the estimated deglacial Q_{added} drops to 0.76 Tmol C yr^{-1} (0.01 Pg C yr^{-1}). However, our mass balance calculation (equations 2 and 3) underestimates Q_{added} because it ignores air-sea gas exchange as well as the potentially elevated DIC levels in the inflowing water (equation 1) that are implied by the interpretation of low $^{14}C/C$ benthic observations in the region (Lindsay et al., 2015; Marchitto et al., 2007; Rafter et al., 2018).

Our estimate of deglacial geologic carbon flux (Q_{added}) in the Gulf is 2–3 orders of magnitude larger than estimates of the modern geologic carbon flux along the Gulf (Lizarralde et al., 2011) and is of the same order as the estimated modern global carbon flux from seafloor volcanism (1.7 Tmol C yr^{-1}) (Resing et al., 2004). It is important to note that the modern estimates of global geologic carbon flux do not include geologic carbon from sedimentary sources and would therefore be skewed to low values (Lizarralde et al., 2011). We want to also note that our estimated geologic carbon flux is closely tied to the assumed deglacial Gulf circulation, where a 50% slower circulation lowers Q_{added} to 0.78 Tmol C yr^{-1} (46% of the modern global carbon flux) and a 90% slower circulation lowers the Q_{added} to 0.16 Tmol C yr^{-1} (5% of the modern global value). Regardless of these large uncertainties, we argue that the addition of a high (relative to today) flux of geologic carbon along the length of the Gulf of California is the most likely mechanism to explain our benthic-planktic $^{14}C/C$ data.

3.3. Constraining the Geologic Carbon Composition

The paired benthic-planktic ^{14}C measurements in Figure 3 and Figure 4 point to an increased flux of ^{14}C-free carbon, but there are several potential sources of ^{14}C-free geologic carbon in the Gulf of California. These include microbially produced methane, thermogenic methane formed during sill intrusion at the mid-ocean ridge followed by bicarbonate production via anaerobic oxidation of methane (AOM), as well as mantle CO_2. AOM and mantle CO_2 emissions are both plausibly enhanced by increases in seafloor volcanism (see Figure 2).

Because the stable carbon isotopic ratio ($\delta^{13}C$) of the potential geologic carbon sources (Figure 2) are more negative than inflowing deep waters (see SM), the $\delta^{13}C$ of planktic foraminifera (Figure 4E) seemingly offers a useful test for clarifying the geologic carbon sources to the Gulf deep and ultimately surface waters. However, the relatively small rate of carbon addition (about 8% of the inflowing carbon pool; see above) may be partially masked by several factors. These include upper ocean carbon assimilation by phytoplankton (elevating seawater DIC $\delta^{13}C$) and foraminifera "vital effects" (in response to temperature, foraminifera size, and primary production)—masking processes that are likely to respond independently of changing geologic carbon flux. This is not the case for a reduction in carbonate ion concentration (as might be expected from carbon release), which would link an increased addition of geologic carbon directly to known biasing of planktic $\delta^{13}C$ measurements to higher values (Bemis et al., 2000; Spero et al., 1997). We calculate the influence of each potential geologic carbon source on surface DIC $\delta^{13}C$ (see SM) and find that only the very low $\delta^{13}C$ of a microbial methane source would rise above these potential masking effects, allowing us to dismiss microbial methane as the primary source of ^{14}C-free geologic carbon during the deglaciation.

The presence of well-preserved deglacial sedimentary carbonates in these cores offers a another test for the composition of the geologic carbon flux in Figure 4 because the $^{14}C/C$ lowering shown in Figure 3 and Figure 4—measurements of deglacial sedimentary carbonates—is quantitatively inconsistent with mantle CO_2 as the primary source. Given the introduction of ^{14}C-free mantle CO_2 (with a $\Delta^{14}C$ of -1000‰), the drop in planktic foraminifera $\Delta^{14}C$ by ≈400‰ relative to the atmosphere during deglaciation (Figure 3) would require a > 50% increase in DIC concentrations within the Gulf (see SM for more details). If the carbon were added as CO_2, it would form enough carbonic acid to effectively titrate all ambient carbonate ion, acidify the seawater, and thereby drive extensive calcite dissolution in the water column and at the seafloor. A slowdown in sedimentation rates at our site during the deglaciation (dashed lines in Figure 3 and Figure 4) is qualitatively consistent with periods of modest dissolution, but the presence of the pelagic microfossils recording the anomalous $\Delta^{14}C$ declines shown in Figure 3 categorically rules out mantle CO_2 as the major geologic carbon source.

Instead, our results may be best explained by a geologic carbon source in the form of bicarbonate associated with the anaerobic oxidation of thermogenic methane produced during sill intrusion (Figure 2). First, the emplacement of volcanic sills (magmatic intrusion) into organic-rich sediments (Einsele et al., 1980) pyrolyzes sedimentary organic carbon to methane (Galimov & Simoneit, 1982). Because this can occur up to 50 km away from the active spreading center (Lizarralde et al., 2011), this thermogenic generation of geologic methane greatly increases the potential source area for the geologic carbon flux while also linking this flux with increased seafloor volcanism. Second, the anaerobic oxidation of methane at the sulfate-methane transition below the seafloor (by sulfate reducing microbes) produces excess bicarbonate (Davis & Yarbrough, 1966; Presley & Kaplan, 1968) in anaerobic Gulf of California sediments (Goldhaber & Kaplan, 1980). Third, bicarbonate addition has only minor effects on seawater pH, carbonate ion concentration, and calcite saturation state, which is consistent with continued calcification in the water column and burial of carbonates on the seafloor. There are also clear signs of increased thermogenic methane production reaching the Gulf of California seafloor between 28- and 7-kyr ago (Geilert et al., 2018). These independent results are consistent with increased pyrolysis of Gulf of California sediments introducing geologic carbon in the form of bicarbonate to the Gulf of California water column, during a time period that includes the deglaciation (Geilert et al., 2018).

4. Conclusions

We document a substantial decline in seawater $^{14}C/C$ as it passed through the Gulf of California during the last deglacial period. Unlike deglacial ^{14}C anomalies reconstructed for other parts of the (open) ocean, upwelling from the deep ocean is ruled out as the source of that isotopic signature by the semi-enclosed geography of the Gulf. Instead, we take these observations as evidence for the addition of carbon from local volcanism-related sources. Our radiocarbon mass balance-based estimate of this geologic carbon flux is large compared with modern regional and even global fluxes. The simplicity of our calculation allows for future adjustments, especially as we improve our understanding of modern carbon cycling and develop new proxy records. Regardless of the caveats to our estimated geologic carbon flux, our results suggest that glacial and deglacial $^{14}C/C$ anomalies recorded in benthic foraminifera from open ocean sites (Bryan et al.,

2010; Lindsay et al., 2016; Marchitto et al., 2007; Ronge et al., 2016; Stott et al., 2009), and our own benthic Gulf of California record (Rafter et al., 2018) may also reflect geologic carbon addition.

It is less clear how our record of geologic carbon flux in the Gulf of California applies to the hypothesis linking seafloor volcanism and atmospheric CO_2 (e.g., (Huybers & Langmuir, 2009; Lund & Asimow, 2011)). For example, the enhanced geologic carbon flux in the Gulf of California began prior to the rise of atmospheric CO_2 (Figure 4), similar to proxy records of East Pacific Rise hydrothermal activity, which have peak activity ranging from 25- to 11-kyr BP (Lund et al., 2019). These results suggest that, if the proposed feedback mechanism between sea level/seafloor volcanism exists, the reconstructed timing of enhanced volcanism did not occur simultaneously along the length of mid-ocean ridge systems—a finding that would not support a principal role of geologic carbon in the deglacial atmospheric CO_2 rise (Figure 4). This inconsistent timing is to be expected if—as suggested by Lund and Asimow (2011)—the sensitivity of mid-ocean ridge systems to sea level is regulated by features with high spatial variability, such as magma migration and seafloor spreading rates.

Another important and unresolved question of our work and the seafloor volcanism/atmospheric CO_2 hypothesis is the form of the geologic carbon released. The apparent absence of severe, localized acidification over the period of our study effectively requires that the added carbon was already "neutralized." This is consistent with our proposal that much of the carbon was released as ^{14}C-free bicarbonate (HCO_3^-), which would have had a much smaller influence on atmospheric CO_2 than if the geologic carbon source was CO_2. While we cannot easily extrapolate this finding to global seafloor volcanic systems, we note that evidence for severe acidification is also lacking from open ocean sites with distinct deglacial $^{14}C/C$ anomalies.

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Rafter and Southon made all measurements. All authors contributed to writing the manuscript.

Competing Interests

The authors have no competing interests.

Data and Materials Availability

All data is available online (ncdc.noaa.gov and pangaea.de).

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Supporting Information for

Anomalous >2000 year old surface ocean radiocarbon age as evidence for deglacial geologic carbon release

Patrick A. Rafter[1], José D. Carriquiry[2], Juan-Carlos Herguera[3], Mathis P. Hain[4], Evan A. Solomon[5], and John R. Southon[1]

[1]Department of Earth System Science, University of California, Irvine, CA, USA

[2]Universidad Autónoma Baja California, Ensenada, BC, MX

[3]Centro de Investigación Cientifica y Educación Superior de Ensenda, BC, MX

[4]Earth and Planetary Sciences, University of California, Santa Cruz, CA, USA

[5]University of Washington, School of Oceanography, Seattle, WA, USA

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Introduction

This supporting information discusses our new coral ^{14}C results (Text S1), changes in seawater carbon chemistry (Text S2), the influence of various sources on seawater DIC $\delta^{13}C$ (Text S3), the influence of air-sea equilibration on lowering Gulf of California surface seawater DIC 14C (Text S4), and the unlikely influence of riverine DIC on our record (Text S5).

Text S1.

Identifying the "pre-bomb" Gulf of California surface DIC ^{14}C age

The ^{14}C age of Gulf of California waters below 500 m (Fig. 1C) is based on ^{14}C measurements of seawater Dissolved Inorganic Carbon (DIC) at 22°N, 110°W in April 1994 (Key et al., 2004). Modern surface seawater DIC ^{14}C is contaminated with high ^{14}C produced from the mid-20th

century thermonuclear weapons tests (Graven et al., 2012), but we estimate pre-"bomb" surface seawater DIC ^{14}C age using surface-dwelling *Porites* spp. coral collected alive from El Cardonal (23.8°N, 109.7°W) in June 1997 (see green star in Fig. 1). Coral aragonite from 1944-1945 was identified by counting annual growth bands (based on x-ray images). Samples analyzed for ^{14}C using the methods above indicate that the pre-bomb surface seawater DIC ^{14}C age averaged 701±47 years BP (fraction modern (Fm) = 0.9165±0.0053).

Text S2.

Calculating changes in Gulf of California seawater carbon chemistry

We estimated changes in seawater carbon chemistry using the CO2sys_v2.3 program (Pierrot et al., 2006). The initial, inflowing, subsurface seawater carbon chemistry was estimated from average CLIVAR observations between 500 and 700 m (station location at asterisk in Fig. 1B) with salinity of 34.51, temperature of 7.2 °C, total alkalinity of 2329.1 μmol kg^{-1}, and DIC of 2317 μmol kg^{-1} at a depth of 600 m (depth is average of observations between 500-700 m) (Key et al., 2004). This gives a pH of 7.571, a $[CO_3^{2-}]$ of 46.5 μmol kg^{-1}, and an omega calcite (the ratio of $[CO_3^{2-}]$ to $[CO_3^{2-}]$ at calcite saturation) of 0.99. This undersaturated $[CO_3^{2-}]$ of modern waters entering the Gulf of California is consistent with the poor preservation of calcite microfossils in nearby Holocene-aged sediments (Rafter et al., 2018). Increasing DIC by 50% (as put forward in the main text) without parallel increase in alkalinity lowers the pH to 6.422, $[CO_3^{2-}]$ to 2.5 μmol kg^{-1}, and omega calcite to 0.06. Given this estimate of a large undersaturation of seawater $[CO_3^{2-}]$, it is unlikely that sedimentary calcite microfossils such as foraminifera would be preserved under these conditions. Conversely, if the added carbon was neutralized before release (i.e., release as bicarbonate instead of CO_2, with carbon-to-alkalinity ratio of 1:1) the effects on carbonate chemistry are largely mitigated, yielding pH= 7.719, $[CO_3^{2-}]$ = 70.4 μmol kg^{-1}, and Ω = 1.69.

Text S3.

Sources of seawater DIC $\delta^{13}C$ variability and the influence of geologic carbon

The $\delta^{13}C$ of potential geologic carbon sources to Gulf of California seawater range from -6‰ for mantle CO_2 (Deines, 2002) to -9‰ (Pearson et al., 2005) for hydrothermal fluid DIC (here assumed to be representative of the mixed sources and processes linking sill emplacement pyrolysis of sedimentary carbon and AOM to produce HCO_3^-) and -44‰ for microbial methane (Pearson et al., 2005). We chose the DIC and methane $\delta^{13}C$ values from Pearson et al.,

(2005) because they are direct measurements of geologic carbon introduced to the Gulf of California seawater and therefore encompass the various processes influencing pore fluid measurements (e.g., mixing with seawater and partial methane oxidation). Note that -44‰ is an upper bound for microbial methane as noted by (Pearson et al., 2005).

Given an inflowing deep Gulf seawater DIC $\delta^{13}C$ of ≈1‰ (see deglacial age benthic foraminifera $\delta^{13}C$ in (Rafter et al., 2018)) it is logical to presume that the addition of geologic carbon with these lower $\delta^{13}C$ characteristics will be observed by planktic foraminifera. However, several factors make it difficult to observe this presumed lowering of seawater DIC $\delta^{13}C$ by geologic carbon addition using the planktic foraminifera archive. Here we outline the maximum potential $\delta^{13}C$ signal associated with each geological carbon source and then discuss how this is likely overshadowed by other sources of foraminifera $\delta^{13}C$ variability.

Assuming the added geological carbon has $\delta^{13}C$ values described above and inflowing seawater DIC is 2 mmol kg^{-1} (modern values) with a $\delta^{13}C$ of +1‰ (based on deglacial benthic foraminifera $\delta^{13}C$ (Rafter et al., 2018) predicts that seawater DIC $\delta^{13}C$ will lower to: (i) -1.2‰ for the addition of HCO_3^-, (ii) -2.2‰ for mantle CO_2, and (iii) -11.5‰ for methane. These changes are well outside the range of analytical errors (see Methods above), but there are several reasons why planktic foraminifera might not accurately reconstruct seawater DIC $\delta^{13}C$. For example, our ability to reconstruct seawater DIC $\delta^{13}C$ using planktic foraminifera is known to be confounded by temperature-, light level-, size-, and carbonate ion concentration-related affects (Bemis et al., 2000; Spero et al., 1997). We cannot correct for the entire range of these so-called 'vital effects' because many of the necessary parameters are unavailable, but *G. bulloides* $\delta^{13}C$ is known to be highly sensitive to carbonate ion concentration (Spero et al., 1997). As such, a local lowering of carbonate ion concentration during the deglaciation (as part of enhanced geologic carbon flux) would be recorded as an increase in *G. bulloides* $\delta^{13}C$ because of this sensitivity. It is therefore possible that a rise in *G. bulloides* $\delta^{13}C$ by this vital effect could offset the lowering of seawater DIC $\delta^{13}C$ via geologic carbon.

Another potential complication for observing the geologic carbon $\delta^{13}C$ signal involves the elevation of seawater DIC $\delta^{13}C$ by phytoplankton during carbon fixation in the surface Gulf of California. Changes in carbon fixation could operate independently of our proposed influx of

geologic carbon where it would bias the planktic foraminifera $\delta^{13}C$ record. Alternatively, it is possible that an increase in the flux and availability of the major nutrients from increased deglacial upwelling (Chang et al., 2015) and/or the trace metal iron alongside seafloor volcanism (Muñoz-Barbosa et al., 2017) could increase phytoplankton carbon fixation and therefore seawater DIC $\delta^{13}C$ at the Gulf surface—a change in seawater $\delta^{13}C$ that would work in opposition to the geologic carbon $\delta^{13}C$. This increase in phytoplankton carbon fixation is consistent with increased opal accumulation in Guaymas Basin during the deglaciation (Chang et al., 2015). We estimate how much phytoplankton carbon fixation elevates surface seawater DIC $\delta^{13}C$ by looking at the modern northeast Pacific, where there is an elevation of ≈2.5‰ from 100 m to the surface (from 45°N to 10°N and 220°E to 260°E using the data in (Key et al., 2004)).

In summary, planktic foraminifera vital effects and phytoplankton carbon fixation likely work against our ability to accurately reconstruct the influence of geologic carbon on surface water $\delta^{13}C$. It is important to note that this is not the case for $\Delta^{14}C$, which is much lower in geologic carbon (-1000‰) and therefore has a stronger influence on seawater DIC. It is because of this much larger 'end-member' value for ^{14}C that the signal of geologic carbon can be carried to the surface and along the surface of the Gulf of California. We detail additional complications to accurately reconstructing seawater DIC ^{14}C below, although in this instance they work to strengthen our conclusions.

Text S4.

Deep, lower seawater DIC $^{14}C/C$ is elevated at surface by air-sea equilibration

Surface seawater DIC $^{14}C/C$ is increased and ^{14}C age is older by equilibration with the ^{14}C-rich atmosphere. As such, surface seawater DIC $^{14}C/C$ and ^{14}C age is consistently higher than subsurface seawater values in the modern ocean (Key et al., 2004). Combining our 'pre-bomb' seawater ^{14}C measurements (via *Porites* spp. coral; see above) demonstrate that this surface-to-deep seawater DIC $^{14}C/C$ gradient (higher at the surface) persists in the modern Gulf of California, even as DIC with very low $^{14}C/C$ is introduced at depth (Pearson et al., 2005) (Fig. 1C), where it is entrained in the Gulf's overturning circulation (Fig. 1C).

In other words, even partial equilibration with the atmosphere will elevate seawater DIC $^{14}C/C$ above its upwelled value. Given this necessary elevation of surface seawater DIC $^{14}C/C$, we argue that planktic foraminifera ^{14}C ages (reflecting outflowing Gulf of California seawater DIC) that are lower than benthic foraminifera ^{14}C ages (reflecting inflowing Gulf of California seawater DIC) are conservative estimates of the change in Gulf seawater DIC ^{14}C as it transits through the Gulf of California. We estimate a >1 year time of transit based on a surface circulation of 1.5 cm s^{-1} (based on modern observations (Lavín & Marinone, 2003)) and 550 km distance from waters upwelled in Guaymas Basin to advect to the mouth of the Gulf of California (near our core sites; Fig. 1). Seawater equilibration with the atmosphere follows a power law, so that a 1 year equilibration over a 10-year equilibration e-folding timescale of DIC (common for the low latitude Pacific (Galbraith et al., 2015)) means that seawater DIC in the mixed layer is about 10% of its way to equilibration with the atmosphere. Increased upwelling during the deglaciation (Chang et al., 2015) is consistent with windier conditions and a likely increased equilibration with the atmosphere. Although higher concentrations of seawater DIC will slow the ^{14}C equilibration with the atmosphere (Galbraith et al., 2015).

Regardless of ocean-atmospheric conditions during the deglaciation, the presence of planktic foraminifera $\Delta^{14}C$ that is equivalent or more lower than the benthic foraminifera $\Delta^{14}C$ cannot be explained by the transport of lower $\Delta^{14}C$ from the deep to the surface of the Gulf of California.

Text S5.

Changes in riverine geologic carbon supply cannot explain lower surface $^{14}C/C$

Another possible source of ^{14}C-free DIC is the Colorado River, which drains into the northern end of the Gulf of California. Based on a freshwater shell measurement, the pre-bomb $\Delta^{14}C$ value for Lower Colorado River water prior to large scale agricultural diversion of river flow was -156‰ (Goodfriend & Flessa, 1997), and the measured DIC concentration was ≈2700 µmol kg^{-1} in 1971, comparable with that of seawater (McDonald & Loeltz, 1971). However, mean flow over the past 500 years is estimated at ≈600 $m^3 s^{-1}$ (0.0006 Sv) (Stockton & Jacoby, 1976), which is several orders of magnitude lower than mean Gulf of California flow of 0.3 Sv (calculated above) or 0.4 Sv (from (Navarro et al., 2016)). Hence, even allowing for possible changes in DIC concentration prior to the building of Hoover Dam in the 1930s and large-scale

increases in river flow for the late Pleistocene, Colorado River input could not have significantly impacted surface $\Delta^{14}C$ values for the Gulf of California.

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