

# Supporting Online Material for

# Marine Radiocarbon Evidence for the Mechanism of Deglacial Atmospheric CO<sub>2</sub> Rise

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# **Supporting Online Material**

### Methods

Bulk sediment samples were washed using a sodium hexametaphosphate solution and picked for benthic foraminifera using the >250 µm size fraction, supplemented with 150-250 µm specimens where necessary. Toward the end of this study, picked foraminifera were also briefly sonicated in methanol (Table S1). Foraminiferal samples were hydrolyzed with H<sub>3</sub>PO<sub>4</sub> and reduced to graphite using an Fe catalyst in the presence of H<sub>2</sub>. The 19 published radiocarbon samples (S1) were graphitized at the National Ocean Sciences AMS Facility in Woods Hole (NOSAMS), while the 31 new samples were graphitized at the INSTAAR Laboratory for AMS Radiocarbon Preparation and Research at the University of Colorado, Boulder (NSRL). All published radiocarbon data (S1) were analyzed at NOSAMS, while all new data were analyzed at the Keck Carbon Cycle AMS Facility at the University of California, Irvine (KCCAMS),  $\delta^{13}$ C corrections were based on off-line measurement for NOSAMS results, and on measurement within the AMS for KCCAMS results. KCCAMS  $\delta^{13}$ C values are not suitable for paleoceanographic interpretation, and are therefore not reported. Age-corrected  $\Delta^{14}$ C calculations were based on the conventions of Stuiver and Polach (S2).  $\Delta^{14}$ C error bars were calculated by compounding radiocarbon age errors with estimated calendar age errors listed in Table S1. Calendar age errors depend solely on the estimated precision of our picks with respect to the GISP2-Hulu chronology, and not on any errors in the GISP2-Hulu chronology itself. The latter would affect both our record and the Cariaco Basin atmospheric  $\Delta^{14}$ C record similarly.

# Hulu Cave adjustments to GISP2 age model

In order to compare PC08 results with the most recent and most consistent atmospheric  $\Delta^{14}$ C reconstructions (S3-S5), the correlation between PC08 reflectance and GISP2  $\delta^{18}$ O (S6) (used to derive calendar ages for calculating PC08  $\Delta^{14}$ C) requires that the GISP2 chronology be consistent with the Hulu Cave chronology (S7), as outlined in the main text. Younger than ~20-25 kyr BP the Hulu Cave and GISP2 chronologies appear to be consistent with each other, so no corrections need to be applied to the more recent parts of the GISP2 age model (Fig. S1). GISP2 also agrees with the latest NGRIP chronology (GICC05) to within 250 yr over this interval (S8). We adjusted the GISP2 chronology older than 23.4 kyr BP (the start of Interstadial 2) by linearly interpolating between three Hulu Cave tie-points corresponding to major interstadial warmings in Greenland. The resulting GISP2 age model appears to agree with Hulu Cave to within a few hundred years throughout the past 50 kyr (Fig. S1). The resulting age-depth relationship for PC08 is shown in Fig. S2A.

#### Methane synchronization of Dome C and GISP2

As outlined above and in the main text, the GISP2, Hulu Cave, and coral chronologies are similar over the last ~20-25 kyr. However, these chronologies differ from the glaciological age model on which the EPICA Dome C CO<sub>2</sub> and  $\delta$ D records of Monnin *et al.* (S9) were originally presented. To obtain a timescale that is consistent with the various  $\Delta^{14}$ C reconstructions, we have used CH<sub>4</sub> records from the Dome C, GISP2, and GRIP ice cores (S9-S11) to derive a GISP2 synchronized gas age scale for Dome C.

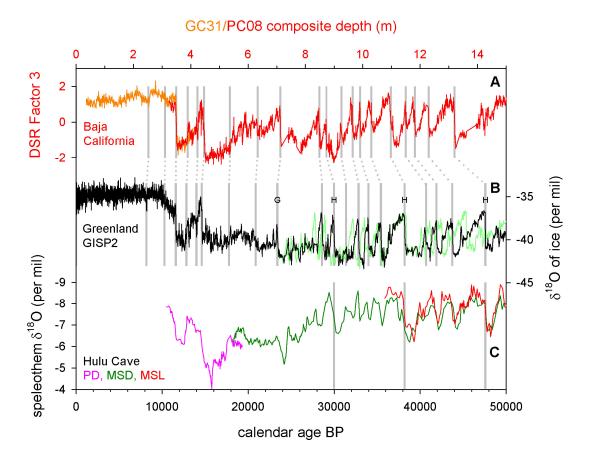
Seven tie-points (Table S2) were defined based on the comparison of the Dome C CH<sub>4</sub> record (on the EDC3 time scale (S12, S13)) and the GISP2 and GRIP CH<sub>4</sub> records (on the GISP2 time scale (S10)). Between the tie-points the EDC3 gas age scale was linearly interpolated to GISP2 ages. The associated ice age scale for Dome C was derived from the synchronized gas age scale described above and the delta ages (gas age to ice age differences in the ice core) taken from the EDC3 time scale (S12, S13).

# **Sedimentary artifacts**

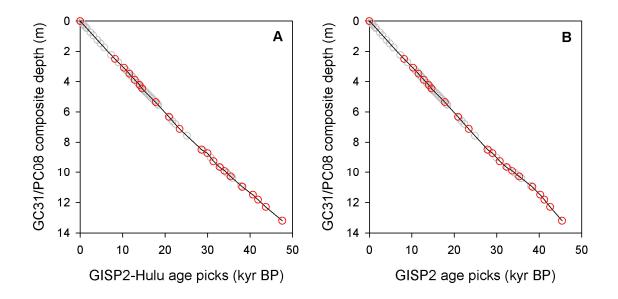
The two deglacial intervals of depleted radiocarbon activity that we report appear, in part, as large age plateaus in the conventional radiocarbon age:depth relationship (Table S1). During the first (earlier) event, radiocarbon age is nearly constant over 90 cm of core depth, and during the second event, radiocarbon age is nearly constant over at least 45 cm. Near-instantaneous massive inputs of sediment, namely slumps, could theoretically produce age plateaus. However, such events would necessarily produce large kinked offsets in the calendar age:depth relationship, which are clearly not observed (Fig. S2). Additionally, slumps are much more likely to produce age reversals than plateaus. Radiocarbon age plateaus could also theoretically be created during intervals of very intense bioturbation, such that age is homogenized over some depth interval. However, it is unreasonable to postulate a complete, simultaneous bioturbational homogenization of the upper 90 cm (or 45 cm) of the sediment column, especially in this low-O<sub>2</sub> environment. The entire MC19/GC31/PC08 record is dominated by low-O<sub>2</sub> benthic foraminiferal taxa (mainly Bolivina and Uvigerina), and sedimentary Mo remains enriched by ~4-8 times crustal values during deglaciation, indicative of shallow pore water sulfide and suboxic bottom waters (S14). Finally, very intense bioturbation would homogenize other paleoclimate proxies in this core. Notably, our second age plateau crosses the Allerød-Younger Dryas boundary in GC31/PC08, which is marked by a sharp reflectance change that is inferred to record a shift in surface ocean productivity (S15). We therefore conclude decisively that the <sup>14</sup>C age-depth patterns in our record reflect changes in intermediate water <sup>14</sup>C activity and not sedimentary processes.

## Alternate PC08 age model

We have also calculated Baja California  $\Delta^{14}$ C based on correlation to GISP2 using the original layer-counted age model of Meese *et al.* (*S16*) (Fig. S3). This record only differs from our preferred GISP2-Hulu age model prior to 23.4 kyr BP. In Fig. S3 we compare this alternate record to the original Cariaco Basin  $\Delta^{14}$ C record based on correlation to GISP2 (*S17*). It is clear that our conclusions are not affected by the choice of age model, though the agreement between Cariaco Basin and coral  $\Delta^{14}$ C is better in Fig. 1 than in Fig. S3 (*S5*). The PC08 age-depth relationship for the alternate age model is shown in Fig. S2B.



**Fig. S1.** Derivation of GISP2-Hulu Cave composite age model. (**A**) Diffuse spectral reflectance factor 3 from Baja California composite sediment core MV99-GC31/PC08, plotted versus depth (*S15*). Gray lines show tie-points to Greenland record used to derive calendar age model. (**B**)  $\delta^{18}$ O of Greenland ice core GISP2 (*S6*) on provisional revised timescale (black). New timescale deviates from original timescale (green) older than 23.4 kyr BP (line labeled G). New timescale is based on linear interpolation between point G and three tie-points whose ages are derived from U-Th-dated Hulu Cave (lines labeled H). (**C**) Hulu Cave  $\delta^{18}$ O from three different stalagmites (*S7*). Gray lines indicate tie-points used to adjust GISP2 chronology.



**Fig. S2.** (A) Age-depth relationship for MV99-MC19/GC31/PC08 based on correlation to GISP2  $\delta^{18}$ O with Hulu Cave age adjustment. Red points are tie-points and gray points represent radiocarbon measurements. The unusually constant sedimentation rate allows for relatively precise calendar age assignments between tie-points. (B) Same as (A) except using alternate age model as in Fig. S3.

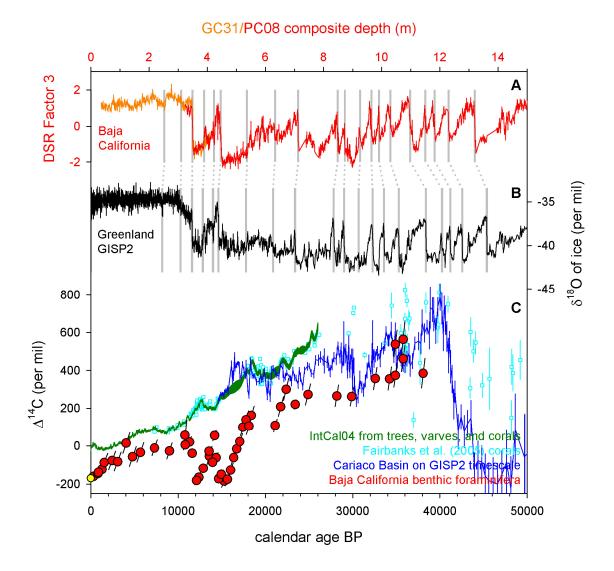


Fig. S3. Baja California  $\Delta^{14}$ C record based on alternate age model. (A) Diffuse spectral reflectance factor 3 from Baja California composite sediment core MV99-GC31/PC08, plotted versus depth (top axis) (S15). Gray lines show tie-points to Greenland record used to derive alternate calendar age model. (B)  $\delta^{18}$ O of Greenland ice core GISP2 on original timescale (bottom axis) (S6, S16). (C) Atmospheric radiocarbon activities based on tree rings, planktonic foraminifera from Cariaco Basin varve-counted sediments, and U-Th-dated corals (dark green) (S3); additional recent coral measurements (cyan) (S4); and planktonic foraminifera from Cariaco Basin using age model derived from reflectance correlation to GISP2 (blue) (S17). Red points show intermediate water activities from benthic foraminifera in MC19/GC31/PC08. Yellow point is estimate for modern bottom waters at this site.

Table S1. Core MC19/GC31/PC08 radiocarbon data.

			3	<sup>14</sup> C age	Calendar	Calendar	$\Delta^{14}{ m C}$	$\delta^{13}$ C			
Sample	Таха	Composite denth (m)	C age (kvr BP)	error (kvr)	age (kvr BP)	age error (kvr)	(per mil)	(per mil)	Accession #	Son?	Reference
MC19-10 cm	mixed benthics	0.100	1.720	0.030	0.32	0.1	-161	-0.61	OS-33198	no	I
MC19-25 cm	mixed benthics	0.250	2.050	0.035	0.81	0.2	-146	69.0-	OS-33199	no	I
GC31-3-2 cm	mixed benthics	0.270	2.050	0.030	0.87	0.3	-139	98.0-	OS-33201	no	I
MC19-40 cm	mixed benthics	0.400	2.320	0.035	1.29	0.4	-124	-0.56	OS-33200	no	I
GC31-3-22.5 cm	mixed benthics	0.475	2.230	0.035	1.54	0.4	-88	-0.91	OS-25612	no	I
GC31-3-50.5 cm	Bolivina spp.	0.755	3.030	0.040	2.44	0.4	-78	nm	OS-22946	no	I
GC31-3-70 cm	mixed benthics	0.950	3.690	0.045	3.08	0.4	-84	-0.60	OS-33202	no	I
GC31-3-100.5 cm	Bolivina spp.	1.255	3.840	0.050	4.07	0.4	14	nm	OS-22947	no	I
GC31-3-123 cm	mixed benthics	1.480	5.130	0.060	4.79	0.4	-57	-0.53	OS-33203	no	I
GC31-2-0.5 cm	Bolivina spp.	1.755	5.810	0.040	5.69	0.4	-35	nm	OS-22948	no	I
GC31-2-50.5 cm	Bolivina spp.	2.255	7.190	0.050	7.31	0.3	-11	nm	OS-22949	no	I
GC31-2-100.5 cm	Bolivina spp.	2.755	8.980	090.0	9.01	0.3	-27	-0.90	OS-22955	no	I
GC31-1-8.5 cm	Bolivina spp.	3.255	10.050	0.410	10.79	0.2	99	-1.15	OS-23513	no	I
PC08-9-45 cm	mixed benthics	3.260	10.460	0.030	10.81	0.2	9		CURL-8750	yes	this study
PC08-9-60 cm	mixed benthics	3.410	10.845	0.030	11.32	0.2	20		CURL-8752	yes	this study
GC31-1-32.5 cm	mixed benthics	3.495	11.600	0.070	11.61	0.1	-39	-1.49	OS-25611	no	I
PC08-9-85 cm	mixed benthics	3.660	13.380	0.035	12.12	0.2	-181		CURL-8751	yes	this study
GC31-1-58.5 cm	Bolivina spp.	3.755	13.500	0.070	12.41	0.2	-164	-1.49	OS-22956	no	I
PC08-9-110 cm	mixed benthics	3.910	13.530	0.030	12.88	0.1	-118		CURL-8444	no	this study
PC08-9-130 cm	mixed benthics	4.110	13.420	0.025	13.57	0.1	-29		CURL-8445	no	this study
GC31-1-94.5 cm	Bolivina spp.	4.115	13.650	0.150	13.58	0.3	-54	-1.43	OS-22957	no	I
PC08-9-141 cm	Uvigerina spp.	4.220	14.285	0.035	13.94	0.1	-88		CURL-8746	yes	this study
PC08-9-150 cm	mixed benthics	4.310	13.370	0.030	14.20	0.2	55		CURL-8446	no	this study
PC08-8-6.5 cm	Uvigerina spp.	4.375	14.485	0.035	14.37	0.2	-62		CURL-8721	yes	this study
PC08-8-16.5 cm	Uvigerina spp.	4.475	15.755	0.040	14.65	0.1	-172		CURL-8726	yes	this study
PC08-8-25.5 cm	Uvigerina spp.	4.565	15.850	0.040	14.96	0.2	-150		CURL-8720	yes	this study
PC08-8-35 cm	mixed benthics	4.660	16.505	0.040	15.30	0.3	-184		CURL-8447	no	this study

this study	this study	this study	this study	this study	I	this study	this study	I	this study	this study	this study	this study	this study	I	this study	this study						
yes	yes	no	yes	yes	no	yes	yes	no	no	no	no	no	no	no	no	no						
CURL-8724	CURL-8729	CURL-8744	CURL-8742	CURL-8743	CURL-8749	CURL-8748	CURL-8745	CURL-8448	CURL-8728	CURL-8722	OS-33204	CURL-8727	CURL-8725	OS-33205	CURL-8449	CURL-8450	CURL-7188	CURL-7189	CURL-7192	OS-33206	CURL-7187	CURL-7193
											-0.81			-0.57						-0.72		
-176	-127	-62	-17	22	86	139	105	162	108	208	299	220	311	396	394	443	407	577	408	582	477	356
0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.3	0.3	0.1	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
15.67	16.02	16.37	16.73	17.08	17.43	17.78	18.12	18.41	21.14	21.77	22.39	23.43	25.15	29.00	30.73	33.11	34.55	35.11	35.11	35.89	35.89	37.92
0.045	0.040	0.045	0.040	0.050	0.045	0.040	0.040	0.040	090.0	090.0	0.080	0.070	0.070	0.170	0.130	0.160	0.170	0.190	0.180	0.280	0.190	0.260
16.785	16.665	16.425	16.390	16.425	16.185	16.235	16.810	16.680	19.720	19.640	19.650	21.170	22.260	25.500	27.200	29.230	30.830	30.460	31.370	31.200	31.750	34.400
4.765	4.865	4.965	5.065	5.165	5.265	5.365	5.470	5.560	6.415	6.615	808.9	7.135	7.585	8.560	9.010	9.710	10.060	10.210	10.210	10.410	10.410	10.910
Uvigerina spp.	Uvigerina spp.	mixed benthics	Uvigerina spp.	Uvigerina spp.	mixed benthics	Uvigerina spp.	Uvigerina spp.	mixed benthics	mixed benthics	mixed benthics	Uvigerina spp.	Uvigerina spp.	Bolivina spp.	mixed benthics	Uvigerina spp.	Bolivina spp.						
PC08-8-45.5 cm	PC08-8-55.5 cm	PC08-8-65.5 cm	PC08-8-75.5 cm	PC08-8-85.5 cm	PC08-8-95.5 cm	PC08-8-105.5 cm	PC08-8-116 cm	PC08-8-125 cm	PC08-7-60.5 cm	PC08-7-80.5 cm	PC08-7-99.75 cm	PC08-7-132.5 cm	PC08-6-20.5 cm	PC08-6-118 cm	PC08-5-25 cm	PC08-5-95 cm	PC08-5-130 cm	PC08-5-145 cm	PC08-5-145 cm	PC08-4-15 cm	PC08-4-15 cm	PC08-4-65 cm

Composite depth is relative to the top of MC19, as in (SI). Calendar age errors are based on estimated precision of tie-points and distance of samples from tie-points.  $\delta^{13}C$  data are only reported for NOSAMS measurements; 'nm' indicates not measured. Column labeled 'Son?' indicates whether or not radiocarbon samples were sonicated in methanol prior to graphitization.

**Table S2.** Tie-points between the EPICA Dome C EDC3 and GISP2 time scales.

EDC3 gas age (yr BP)	GISP2 gas age (yr BP)	estimated uncertainty (yr)	event description
0	0	0	
8200	8200	25	8.2 ka BP event
11400	11620	25	YD termination
12400	12750	100	Onset of YD
14110	14810	150	Onset of B-A
16700	17600	200	First deglacial CH <sub>4</sub> rise
21860	22950	300	CH <sub>4</sub> peak in GRIP and Dome C

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