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Supporting Online Material for

Coupling of CO_2 and Ice Sheet Stability Over Major Climate Transitions of the Last 20 Million Years

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Materials and Methods

A. Samples, analyses, and analytical uncertainty

We used the surface-dwelling species *Globigerinoides ruber* (white, 250-300 μm size fraction) and *G. sacculifer* (without sac, 300-355 μm size fraction). Between 50-60 individuals of each species were picked for each sample and cleaned using a standard 'oxidative' treatment protocol(*S1*-*S3*) and analysed for B/Ca, Mg/Ca, and other metal/calcium ratios on a Perkin-Elmer Elan DRC II quadrupole ICP-MS using a published method described elsewhere(*S2, S3*). Samples were analyzed at a calcium concentration of 100 ppm (±5 ppm). Long-term precision of a consistency standard with a similar B/Ca ratio to our samples is 2.7%.

The uncertainty in B/Ca and Mg/Ca ratios of separately cleaned and analyzed samples was better than 3.5% (% relative standard deviation; 2σ; Table S3). The average 1σ error calculated based on 20 separately cleaned replicates is 0.004 mol/mol for seawater $B(OH)_4^-$/HCO_3, 0.3°C for temperature, and 0.2 psu for salinity. This uncertainty is equivalent to a relative standard deviation of better than 4% (primarily reflecting measurement uncertainty in B/Ca analyses), 1%, and 1%, respectively (Table S8).

The average 1σ error calculated based on 78 paired measurements of *G. ruber* and *G. sacculifer* is 0.004 mol/mol for seawater $B(OH)_4^-/HCO_3$, 0.4°C for temperature, and 0.5 psu for salinity. This uncertainty is equivalent to a relative standard deviation of better than 4%, 1%, and 2%, respectively (Table S9). These differences reflect cleaning reproducibility, measurement reproducibility, and calibration uncertainty. This (mainly analytical) uncertainty in seawater $B(OH)_4^-/HCO_3$ ratios is what is represented by error bars in Fig. 1-2.

We use seawater $B(OH)_4^-/HCO_3$ ratios and estimates of alkalinity or carbonate ion concentration to determine pCO_2 and pH. If a 4% uncertainty in seawater $B(OH)_4^-/HCO_3$ ratios (1σ) is propagated through to calculate pCO_2, the resultant pCO_2value has an uncertainty of 10-20 ppmv (1σ) and pH value has an uncertainty of ~0.02 ppmv (1σ). This (mainly analytical) uncertainty in pCO_2 and pH is what is reflected in the error bars shown on Fig. 1 and 2.

Stable isotope measurements were made on 10-20 individuals using a Micromass Prism. Stable isotope values are reported as delta values (δ) in per mil (parts per thousand) notation (‰) relative to a Vienna Pee Dee Belemnite (V-PDB) standard. Long-term precision of an in-house standard (which was run repeatedly during every sample run) is ±0.08‰ for $\delta^{13}C$ and $\delta^{18}O$.

Sources of age models are listed in Table S11.

B. Equations used for T, S, $\delta^{18}O_w$, and Alk

Mg/Ca ratios were converted to temperature using the following equations for *G. ruber* and *G. sacculifer(S4, S5)*, respectively:

$$SST(°C) = 0.09 \bullet \ln \frac{Mg/Ca}{0.32}$$

$$SST(°C) = 0.09 \bullet \ln \frac{Mg/Ca}{0.30}$$

Water $\delta^{18}O$ values were calculated using a published low-light relationship determined for *Orbulina universa(S6)*. When applied to coretop measurements of calcite $\delta^{18}O$, this equation yields accurate values of surface seawater $\delta^{18}O$(*S4, S7*).

Salinity was determined using the following equation that was derived by regressing paired measurements of salinity and seawater $\delta^{18}O$ (n = 77; R^2 = 0.874) in the modern ocean that were compiled and published for the region 0-10°N, 100-170°E, 0-100 meters water depth(*S7*):

$$S = \frac{\delta^{18}O_w + 12.101}{0.3597}$$

Regional relationships between total surface alkalinity and sea surface salinity (Fig. S6) were determined using published data(*8*). These relationships were calculated using data for 5.5°N-5.5°S, 154.5-165.5°E, (Site 806), and 20.5-31.5°S, 154.5-165.5°E (Site 588).

C. Equilibrium constants and carbonate system definitions used

Equilibrium constants were calculated from empirically derived relationships as a function of temperature and salinity (Table S10). For all of our calculations, we use a consistent set of constants, and where necessary, convert them to the total pH scale. Partial pressures of CO_2 are converted into fugacities and dry mole fractions using published relationships(*S9, S10*).

D. Estimation of seawater $B(OH)_4^-/HCO_3^-$ ratios from foraminiferal B/Ca

The B/Ca ratio of surface-dwelling planktic foraminifera has been shown to be sensitive to pH and temperature(*S2*), although the exact controls on boron uptake into carbonates is not well-understood, and is an area of active research. In seawater, dissolved boron occurs as borate ($B(OH)_4^-$) and boric acid ($B(OH)_3$). The relative abundance of these two species is a function of pH, and it is thought that only borate ions are incorporated into marine carbonates(*S11*). For this reason, the B/Ca ratio of planktic foraminifera is thought to record the abundance of seawater borate(*S2*), which depends on ambient pH as well as the total concentration of dissolved boron. The partitioning of boron into planktic foraminifera also appears to be temperature-dependant(*S2, S12, S13*), consistent with observations in coral(*S14-S16*).

The seawater carbonate system is defined by six variables (pCO_2, pH, alkalinity, total dissolved inorganic carbon, and the concentrations of carbonate and bicarbonate) but has only two degrees of freedom. If two variables can be constrained, as well as temperature, pressure, and salinity, then all the remaining variables can be calculated. To estimate surface water pCO_2 and pH over the past two glacial-interglacial cycles, a previous study used foraminiferal B/Ca ratios to estimate the $B(OH)_4^-/HCO_3^-$ ratio of seawater, and assumed that alkalinity scaled either with surface water salinity or whole ocean salinity (*S2*).

B/Ca ratios were converted to seawater $B(OH)_4^-/HCO_3^-$ ratios using a species-specific K_D-temperature calibration and Mg/Ca-temperatures, as previously described by Yu and colleagues(*S2*).

E. Species-specific K_D-temperature calibration

Using an analogous method to Yu et al.(*S2*), we developed calibrations for *G. ruber* and *G. sacculifer* using coretop and downcore B/Ca and Mg/Ca measurements at Pacific Site 806 (Fig. S3a, Tables S5-S7). K_D was estimated using our measurements of B/Ca ratios for coretop samples and downcore samples from the past 200,000 years and estimated seawater $B(OH)_4^-/HCO_3^-$ ratios. $B(OH)_4^-/HCO_3^-$ ratios were calculated using the program CO_2sys(*S17*), using ice core CO_2 values(*S18*-*S20*), temperature, salinity, and alkalinity estimated from salinity (Fig. S5-S6).

Our K_D-temperature calibrations for *G. ruber* and *G. sacculifer* display a similar sensitivity but different intercept to the published coretop calibrations for *G. inflata* and *G. bulloides*. This trend suggests that the basic mechanism for co-precipitation of boron is the same, but that the starting pool is different, likely because the calcification environment is modified by physiological processes. A similar pattern is also observed in Mg/Ca ratios for these four species(*S5, S21, S22*) (i.e., the K_D-temperature calibrations have similar sensitivities but different intercepts).

We note that in our dataset, calculated $B(OH)_4^-/HCO_3^-$ ratios (and pCO_2 values) for 78 paired measurements of *G. ruber* and *G. sacculifer* from the same sample agreed to within 3%, on average (Table S9). Importantly, the application of a constant K_D does not substantially change calculated pCO_2 values or impact our conclusions (Fig. S4). The average difference between pCO_2 estimated using the constant vs. temperature-dependent K_D values are 13 ± 11 ppmv (1 std. dev.) for *G. ruber* and 14 ± 11 ppmv for *G. sacculifer*. The lack of a significant correlation between measurements of B/Ca and Mg/Ca in the same sample (Fig. S3b) is consistent with the idea that seawater $B(OH)_4^-/HCO_3^-$ (and not temperature) is the primary control on foraminiferal B/Ca ratios(*S2*).

F. Estimation of seawater carbonate system parameters from $B(OH)_4^-/HCO_3^-$ ratios

In order to estimate pCO_2 (and pH) from $B(OH)_4^-/HCO_3^-$ ratios, a further assumption is required to fully constrain the carbonate system. We use seawater $B(OH)_4^-/HCO_3$ ratios and estimates of alkalinity or carbonate ion concentration to determine pH and pCO_2. To test the sensitivity of our calculations to this assumption, we used 28 sets of "reasonable-guess" models for alkalinity, carbonate ion concentration, temperature, and salinity.

These models are shown in Fig. S5-S10, and listed in Table S12. These models include: 1) alkalinity scaled with salinity (blue circles in Fig. 1-4); 2) constant carbonate ion concentration (green circles in Fig. 1); and 3) variable carbonate ion concentration, based on estimates of seawater calcium concentrations, magnesium concentrations and the carbonate compensation depth. Seawater Ca concentrations were constrained using published fluid inclusions and calcium isotope data(*S23, S24*). Seawater magnesium concentrations were estimated using fluid inclusion data(*S24, S25*). The history of the carbonate compensation depth published by Sime et al. (2007) was used(*S26*).

G. Equations used to calculate pH and pCO$_2$ from $B(OH)_4^-/HCO_3^-$ and alkalinity

In order to calculate the remaining carbonate system parameters from $B(OH)_4^-/HCO_3^-$ and alkalinity, we formed a polynomial equation where the only unknowns were $B(OH)_4^-/HCO_3^-$, alkalinity, and H^+. We used 'practical alkalinity' as an approximation for total alkalinity in seawater(*S27*). This term is defined as:

$$[ALK] = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$

We substituted the following terms into the equation above:

$$[CO_3^{2-}] = \frac{[HCO_3^-].k_2}{[H^+]}$$

$$[B(OH)_4^-] = \frac{[B_{tot}].k_B}{([H^+] + k_B)}$$

$$[OH^-] = \frac{k_W}{[H^+]}$$

$$[HCO_3^-] = k_B.B_{tot}.([H^+] + k_B).\left(\frac{B(OH)_4^-}{HCO_3^-}\right)^{-1}$$

Algebraic manipulation of the resultant equation yields a third order polynomial of the form, $a.[H^+]^3 + b.[H^+]^2 + c.[H^+]^1 + d$, with the following expansion coefficients:

$$a) \quad a = 1$$

$$b) \quad b = ALK + k_b$$

$$c) \quad c = (ALK \cdot k_b - B_{tot} \cdot k_b - B_{tot} \cdot k_b \cdot \left(\frac{B(OH)_4^-}{HCO_3^-} \right)^{-1} - k_W)$$

$$d) \quad d = -k_W \cdot k_B - 2 \cdot k_2 \cdot B_{tot} \cdot k_B \cdot \left(\frac{B(OH)_4^-}{HCO_3^-} \right)^{-1}$$

The maximum real root of this equation gives the concentration of H^+. We then calculated $p$$CO_2$ and the remaining carbonate system parameters using published equations(*S27*).

H. Equations used to calculate pH and pCO_2 from $B(OH)_4^-/HCO_3^-$ and CO_3^{2-}

To solve the carbonate system using $B(OH)_4^-/HCO_3^-$ and CO_3^{2-}, we used the following published equation(*S27*):

$$[HCO_3^-] \cdot \left(1 + \frac{[H^+]}{k_1} + \frac{k_2}{[H^+]} \right) = [CO_3^{2-}] \cdot \left(1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1 \cdot k_2} \right)$$

We then divide this equation by $[B(OH)_4^-]$ and, on the right hand side, substitute $[B(OH)_4^-]$ for the following equation:

$$[B(OH)_4^-] = \frac{[B_{tot}] k_B}{([H^+] + k_B)}$$

Algebraic manipulation of the resultant equation yields a fourth order polynomial of the form, $a \cdot [H^+]^4 + b \cdot [H^+]^3 + c \cdot [H^+]^2 + d \cdot [H^+]^1 + e$, with the following expansion coefficients:

$$a)\quad a = -\left(\frac{[CO_3^{2-}]}{k_b \cdot [B_{tot}]}\right)\cdot (k_1 \cdot k_2)^{-1}$$

$$b)\quad b = -k_b \cdot \left(\frac{[CO_3^{2-}]}{k_b \cdot [B_{tot}]}\right)\cdot (k_1 \cdot k_2)^{-1} - \left(\frac{[CO_3^{2-}]}{k_b \cdot [B_{tot}]}\right)\cdot k_2^{-1}$$

$$c)\quad c = k_1^{-1} \cdot \left(\frac{B(OH)_4^-}{HCO_3^-}\right)^{-1} - k_b \cdot \left(\frac{[CO_3^{2-}]}{k_b \cdot [B_{tot}]}\right)\cdot k_2^{-1} - \left(\frac{[CO_3^{2-}]}{k_b \cdot [B_{tot}]}\right)$$

$$d)\quad d = \left(\frac{B(OH)_4^-}{HCO_3^-}\right)^{-1} - k_b \cdot \left(\frac{[CO_3^{2-}]}{k_b \cdot [B_{tot}]}\right)$$

$$e)\quad e = k_2 \cdot \left(\frac{B(OH)_4^-}{HCO_3^-}\right)^{-1}$$

The maximum real root of this equation gives the concentration of H^+. We then calculated $p$$CO_2$ and the remaining carbonate system parameters using published equations(*S27*).

I. Calculating CO_3^{2-} from records of Ca^{2+}

Using the method of Tyrrell and Zeebe(*S28*), we calculate records of CO_3^{2-} from different records of Ca^{2+} using the following relationship,

$$\Omega = \frac{[Ca^{2+}]\cdot[CO_3^{2-}]}{K_{sp}}$$

where Ω is the calcite saturation state of the surface ocean and K_{sp} is the solubility product of calcite. We estimated Ω by assuming it has scaled linearly with the carbonate compensation depth (CCD) over the last 20 Ma. We calculated K_{sp} as a function of salinity and pressure using the published relationship of Mucci and Morse(*S29*). The impact on K_{sp} of changes in the Mg and Ca concentration of seawater is also estimated using the method of Tyrrell and Zeebe(*S28*).

J. Reconstruction of $p$$CO_2$ and other carbonate system parameters over the past 20 Ma

In total, we used 28 different sets of assumptions (listed in Table S12) to calculate $p$$CO_2$ (and other carbonate system parameters) from $B(OH)_4^-/HCO_3^-$ ratios and this range of uncertainty defines the grey shaded region in Figs. 2-4. The pCO_2 values calculated using the 28 models generally agree to within 40 ppmv over the last 800 ka, and the range of uncertainty increases farther back in time (50 ppmv from 5-0 Ma, 60 ppmv from 10-5 Ma, and 100 ppmv from 20-10 Ma), primarily reflecting the uncertainty in seawater B and Ca concentrations (Fig. S11).

Supplemental Figure captions

Fig. S1: Maps showing location of sites used in study and surface-water air-sea pCO_2 difference from a published climatology for February and August of 2000(*S30*). The annual average difference (seawater-air) reported for the grid cells nearest to Site 806 is +28 μatm, and near Site 588 is -16 μatm.

Fig. S2: Comparison of $B(OH)_4^-/HCO_3^-$ and pCO_2 reconstructed using different values for K_D. 1:1 line is also shown. **A)** Average $B(OH)_4^-/HCO_3^-$ values calculated using T-dependent K_D (x-axis) against values calculated using constant K_D (y-axis). **B)** pCO_2 values calculated using individual *G. ruber* B/Ca ratios and T-dependent K_D (x-axis) against values calculated using constant K_D (y-axis). **C)** Same as Panel B but for *G. sacculifer*.

Fig. S3: Different models of seawater alkalinity and carbonate ion concentration used in this study for calculation of pCO_2 and other carbonate system parameters. **A)** Alkalinity calculated by applying modern alkalinity-salinity relationship (Fig. S4) to reconstructed value of sea surface salinity (Fig. S8) for 0-1.4 Ma. Error bars assume a 1 psu uncertainty in salinity. **B)** Same as Panel A but for 5-20 Ma. **C)** Different values for $[CO_3^{2-}]$ for 0-1.4 Ma, including: black line assumes constant value; circles assume modern $\Omega = 6.51$, Ca^{2+} from Fig. S5 (Model A), other data from Fig. S8; diamonds assume modern $\Omega = 6.51$, Ca^{2+} from Fig. S5 (Model B), other data from Fig. S8; triangles assume modern $\Omega = 6.51$, Ca^{2+} from Fig. S5 (Model C), other data from Fig. S8. **D)** Same as Panel C but for 5-20 Ma.

Fig. S4: Relationship between total surface alkalinity and sea surface salinity used in this study for (A) Site 806 and (B) Site 588. Monthly mean data are from Lee et al.(*S8*).

Fig. S5: Different reconstructions of seawater calcium concentrations used in this study for calculations of carbonate ion concentration. Model A (dashed line) is interpolated from three data points constrained by fluid inclusions in halites(*S24*) and modern value. Models B (solid line) and C (dotted line) are based on calculations by Griffith et al. that use calcium isotope measurements from barite, and fluid inclusion data, to constrain the oceanic calcium cycle(*S23*). Models are for 0-1.4 Ma, 2.4-3.4 Ma, and 5-20 Ma.

Fig. S6: Published reconstructions of seawater magnesium concentrations (dashed line) from fluid inclusions(*S24, S25*) as interpolated in another publication(*S28*), and global average carbonate compensation depth (solid line) from Sime et al.(*S26*) used in this study for calculations of carbonate ion concentrations. Reconstructions are for 0-1.4 Ma, 2.4-3.4 Ma, and 5-20 Ma.

Fig. S7: Different reconstructions of seawater boron concentration used in this study. For Model A (open circles), total boron concentration is calculated using reconstructed values of surface water salinity from this study, and a published relationship between boron concentation and salinity(*S2, S31, S32*). Error bars assume a 1 psu uncertainty in salinity. Models B (dotted line) and C (dashed line) are based on calculations by Lemarchand et al.(*S33*) that consider changes in input and output fluxes of boron into the ocean through time. Model B assumes a constant riverine input of boron, and Model C assumes a variable riverine input. Models are for 0-1.4 Ma, 2.4-3.4 Ma, and 5-20 Ma.

Fig. S8: Reconstructed values of sea surface temperature and sea surface salinity used in this study. Values agree well with published records(*S4, S34*). **A)** Temperatures from 0-1.4 Ma;

B) Same as Panel A but from 0-20 Ma; **C)** Salinities from 0-1.4 Ma; **D)** Same as Panel C but from 0-20 Ma.

Fig. S9: Comparison of foraminiferal B/Ca-based estimates of pCO_2 from this study (blue circles from Fig. 1 in main text) to values from ice cores(*S22*). Light blue triangles are for data from 0-0.2 Ma and dark blue circles are data for 0.2-0.8 Ma. There is an uncertainty in foraminiferal sample ages(*S19, S31*), and therefore the horizontal bars for each sample represent the range of possible ice core pCO_2 values corresponding to the range of possible ages for each foraminiferal sample. Vertical error bars reflect reproducibility of measurements. Grey shaded regions show 1:1 line ±10, 20, and 30 ppmv. For the whole population of pCO_2 estimates from 0-0.8 Ma (n = 39), the root mean square error of the residuals is 13 ppmv.

Fig. S1

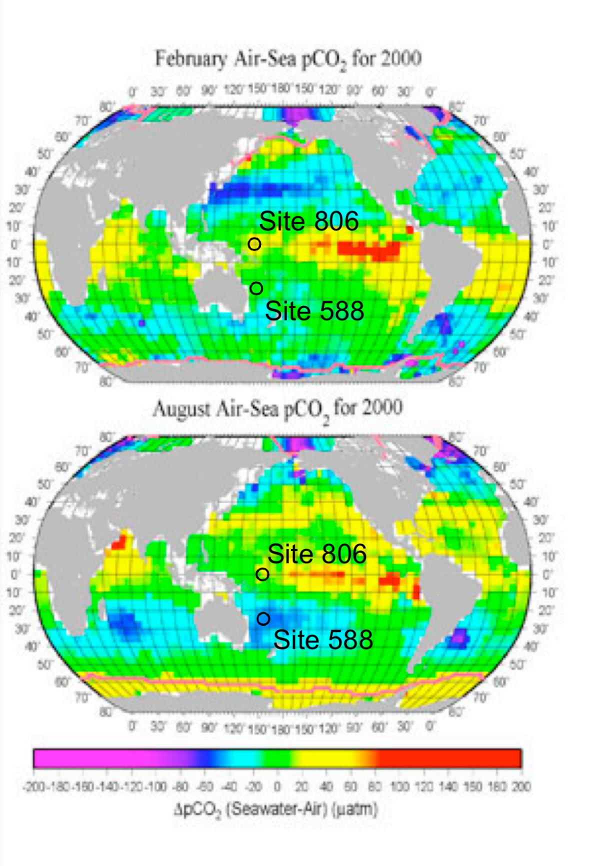

February Air-Sea pCO2 for 2000
Site 806
Site 588
August Air-Sea pCO2 for 2000
Site 806
Site 588
-200 -180 -160 -140 -120 -100 -80 -60 -40 -20 0 20 40 60 80 100 120 140 160 180 200
ΔpCO2 (Seawater-Air) (μatm)

Fig. S2

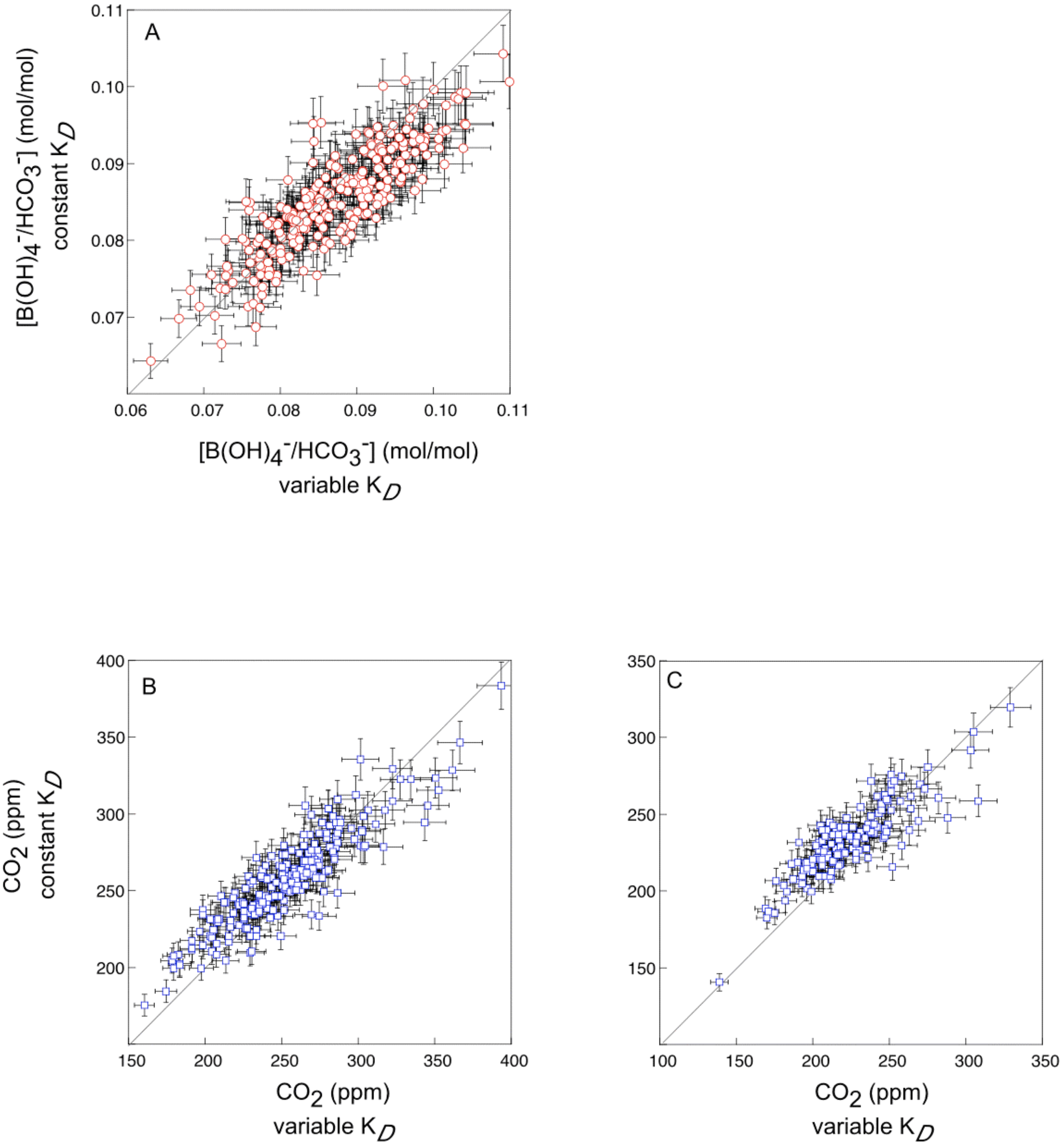

A
[B(OH)4-/HCO3-] (mol/mol)
constant KD
0.11
0.10
0.09
0.08
0.07
0.06
0.07
0.08
0.09
0.10
0.11
[B(OH)4-/HCO3-] (mol/mol)
variable KD
B
CO2 (ppm)
constant KD
400
350
300
250
200
150
200
250
300
350
400
CO2 (ppm)
variable KD
C
350
300
250
200
150
100
150
200
250
300
350
CO2 (ppm)
variable KD

Fig. S3

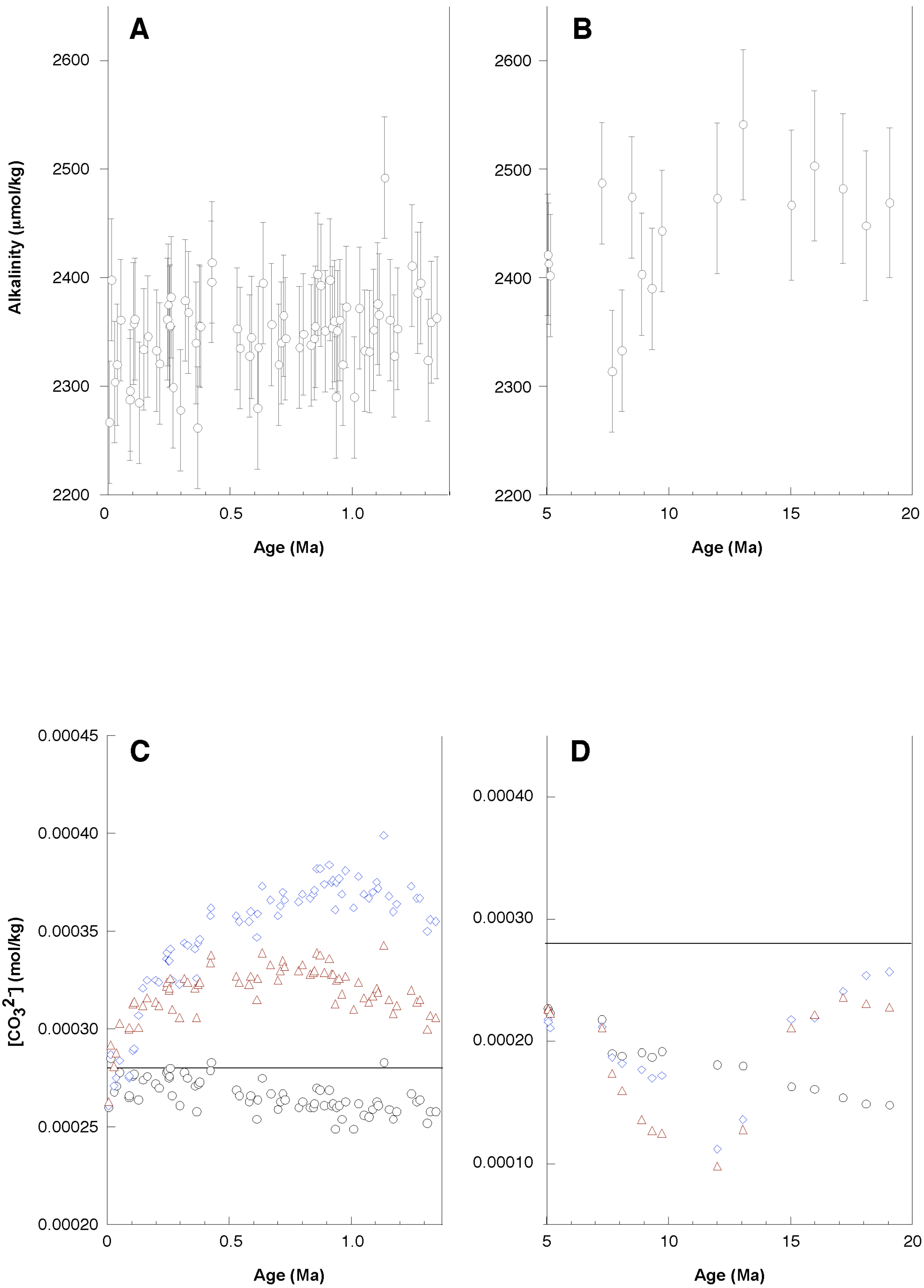

A
B
C
D
Alkalinity (µmol/kg)
[CO3 2-] (mol/kg)
Age (Ma)
2600
2500
2400
2300
2200
0.00045
0.00040
0.00035
0.00030
0.00025
0.00020
0.00010
0
0.5
1.0
5
10
15
20

Fig. S4

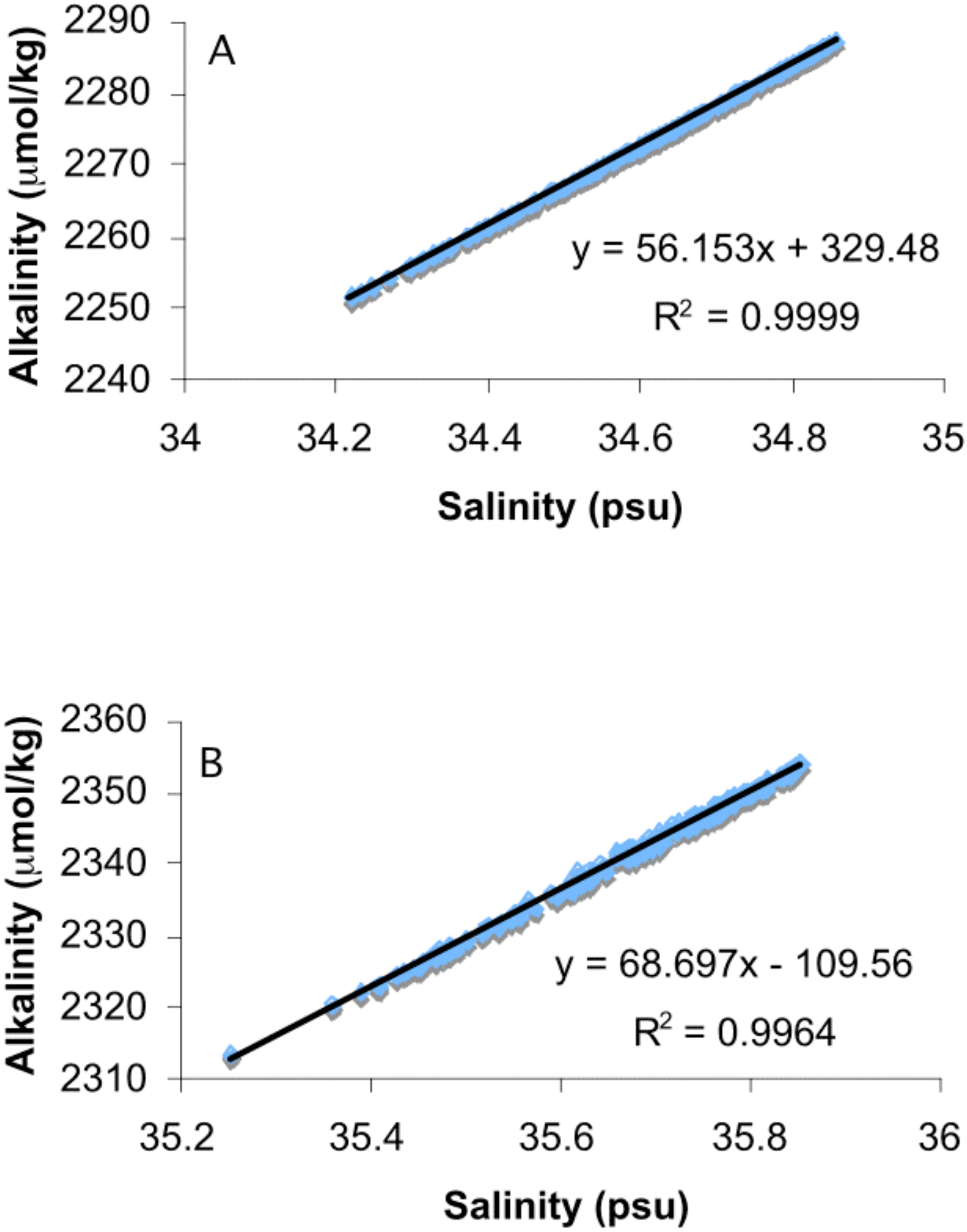

A
Alkalinity (μmol/kg)
2240
2250
2260
2270
2280
2290
34
34.2
34.4
34.6
34.8
35
Salinity (psu)
y = 56.153x + 329.48
R2 = 0.9999
B
Alkalinity (μmol/kg)
2310
2320
2330
2340
2350
2360
35.2
35.4
35.6
35.8
36
Salinity (psu)
y = 68.697x - 109.56
R2 = 0.9964

Fig. S5

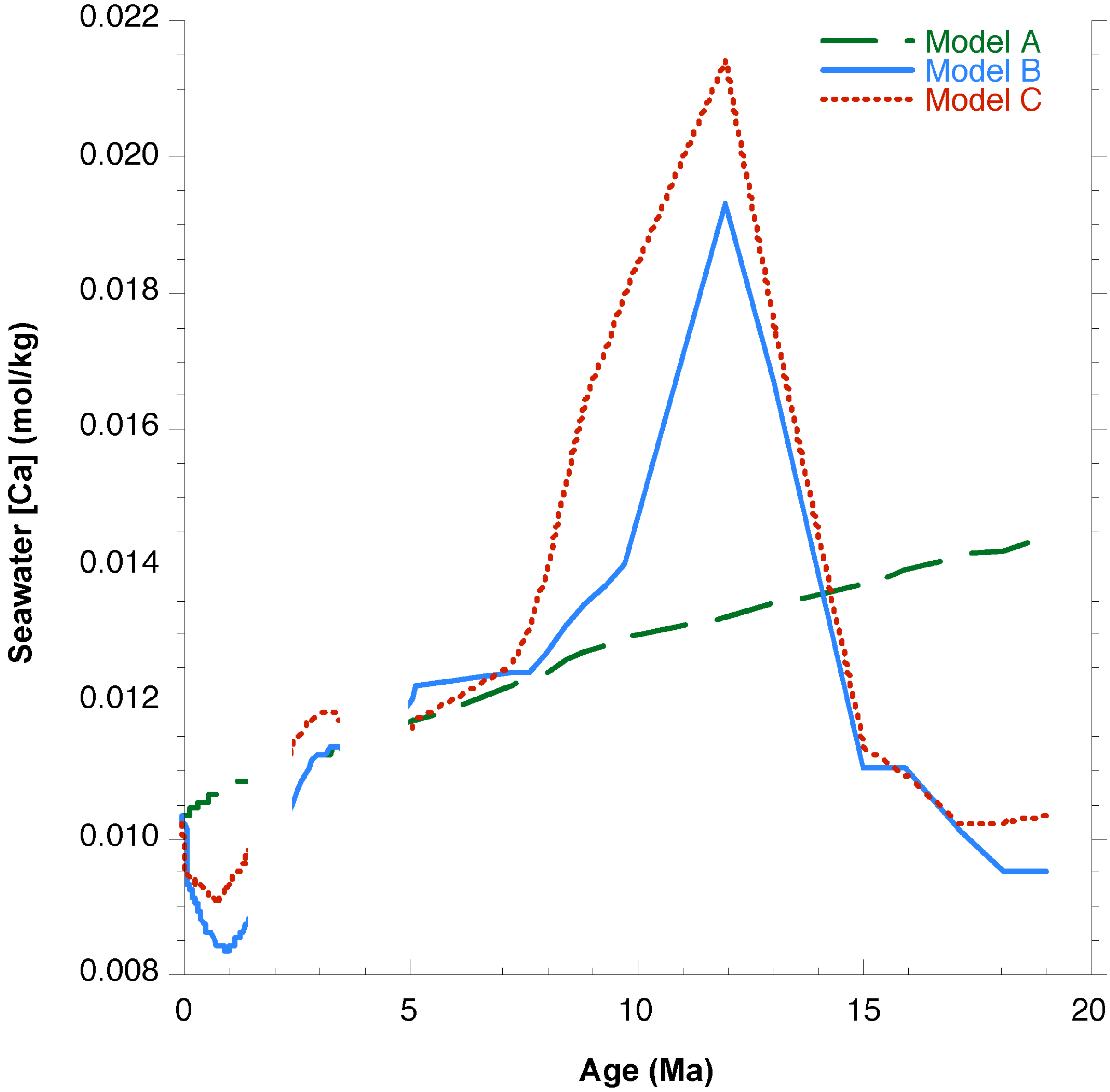
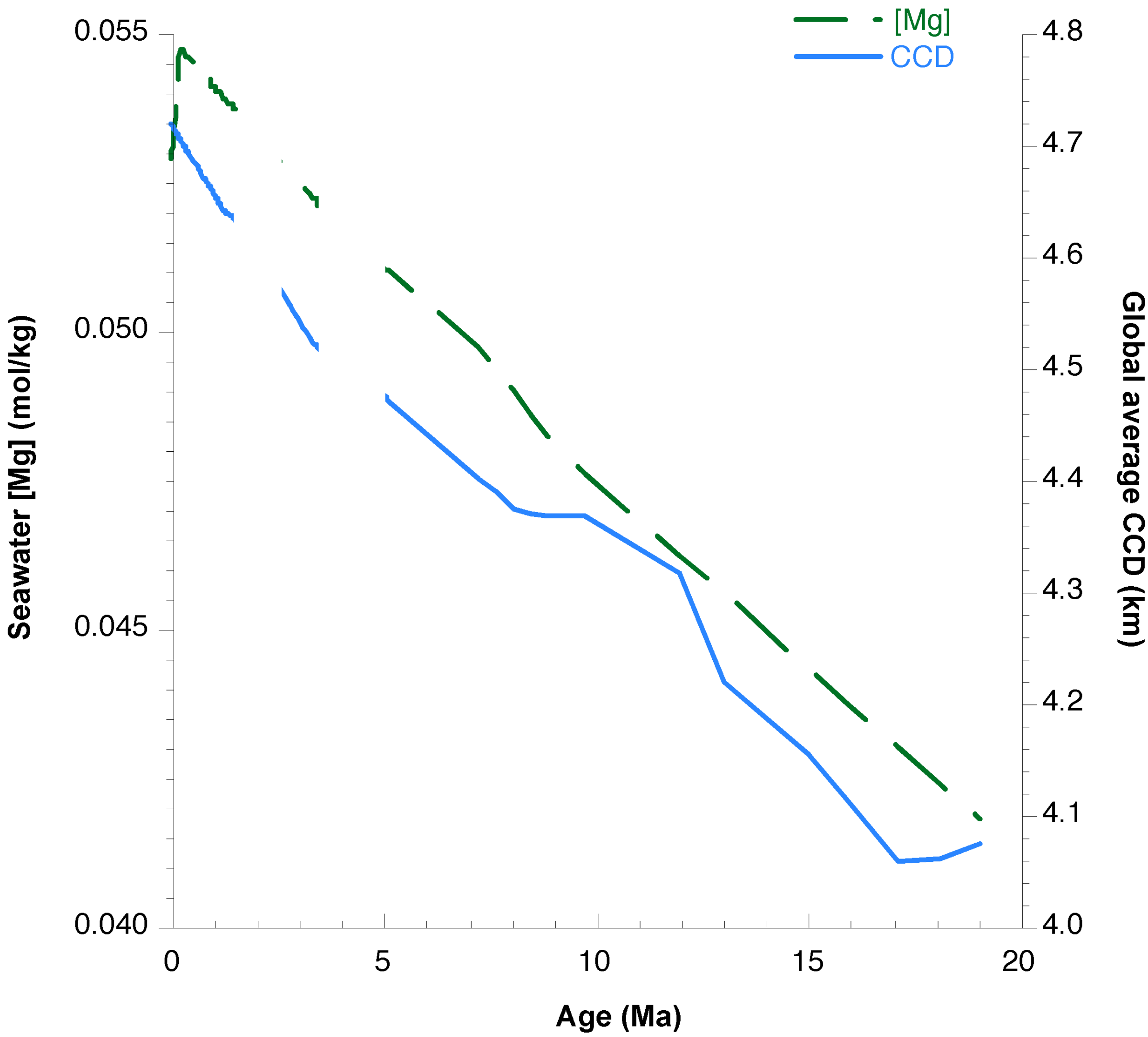
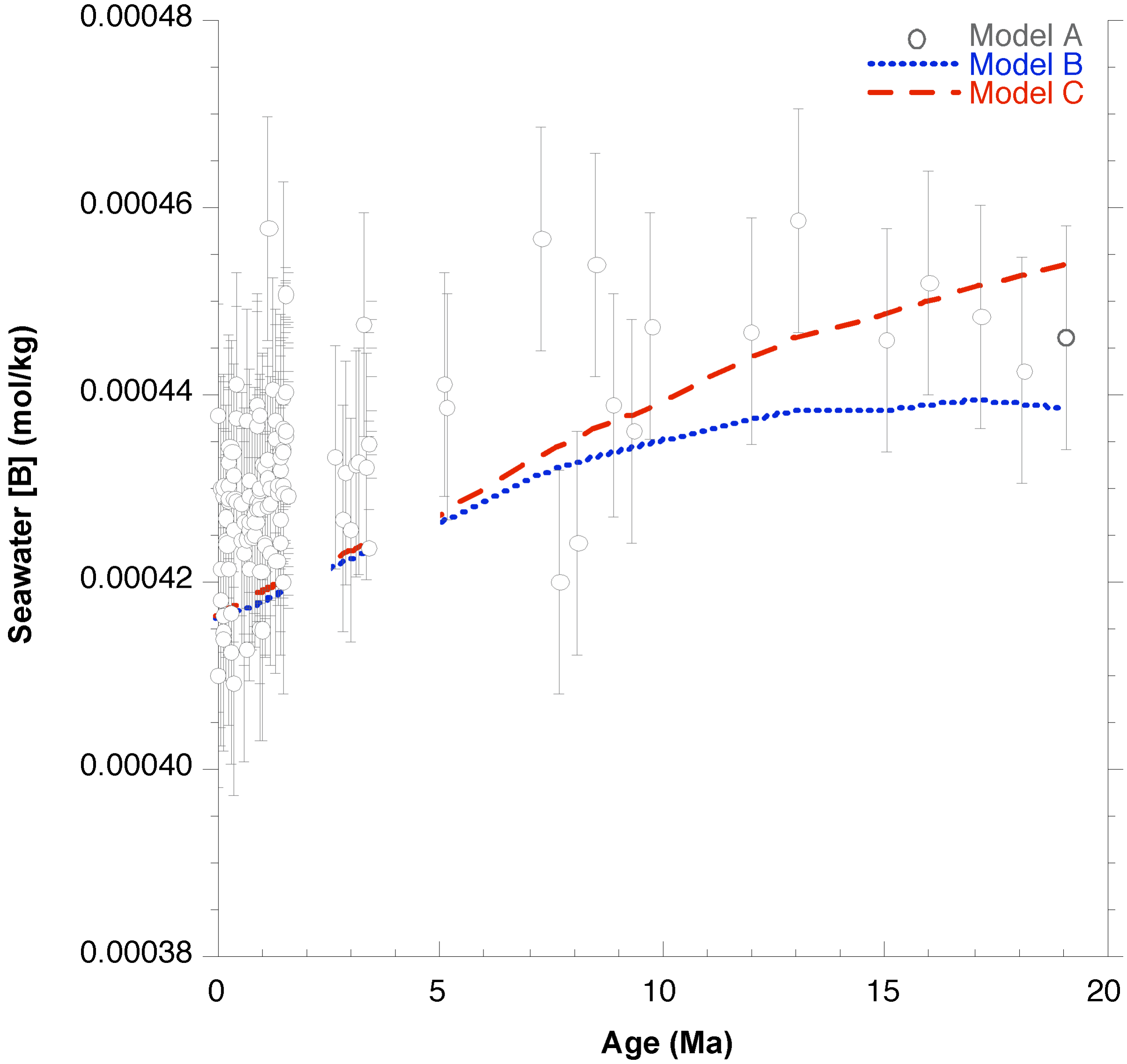

Model A
Model B
Model C
Seawater [Ca] (mol/kg)
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0
5
10
15
20
Age (Ma)

Fig. S6



[Mg]
CCD
0.055
0.050
0.045
0.040
Seawater [Mg] (mol/kg)
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
Global average CCD (km)
0
5
10
15
20
Age (Ma)

Fig. S7



Model A
Model B
Model C
0.00048
0.00046
0.00044
0.00042
0.00040
0.00038
Seawater [B] (mol/kg)
0
5
10
15
20
Age (Ma)

Fig. S8

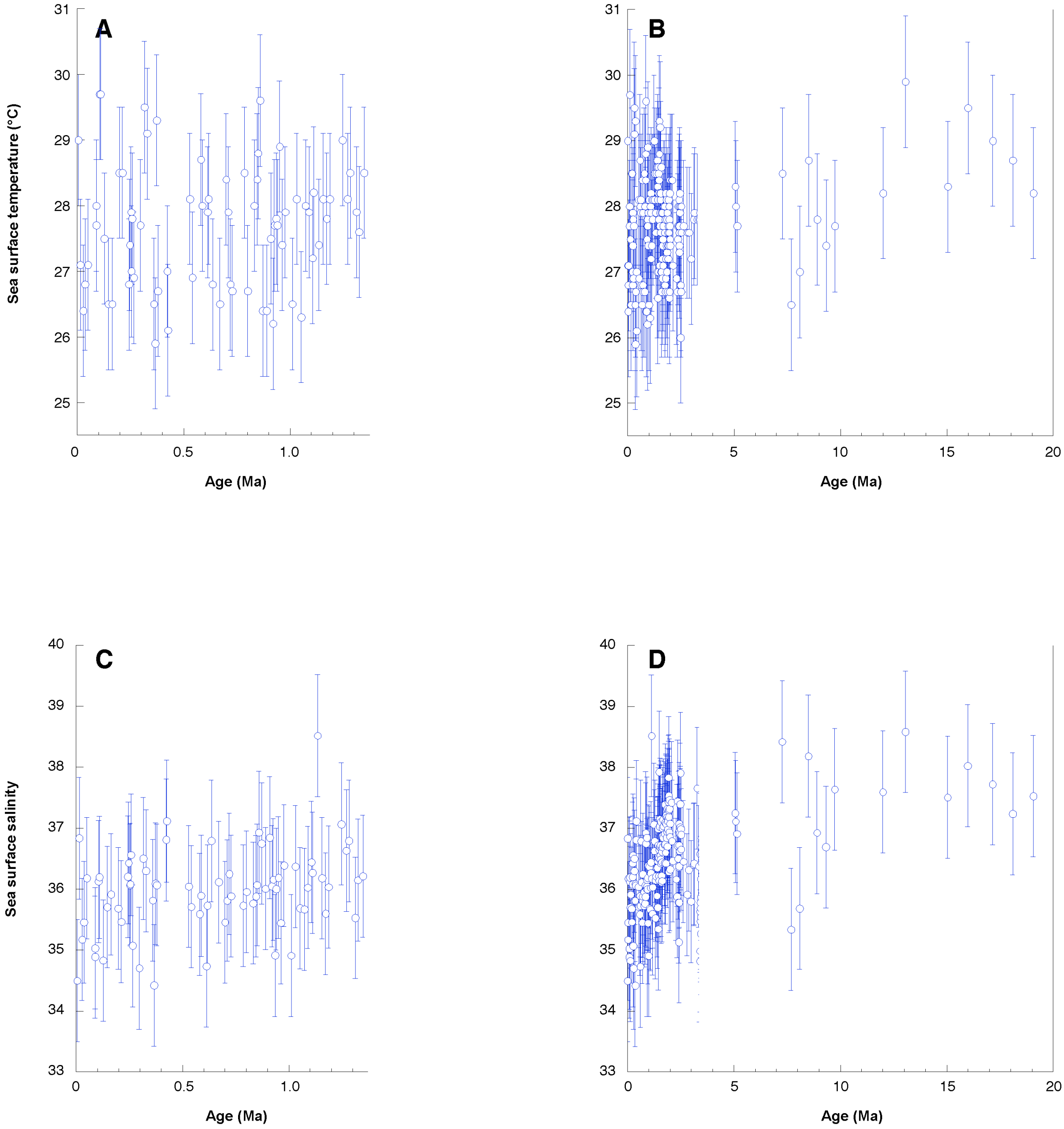
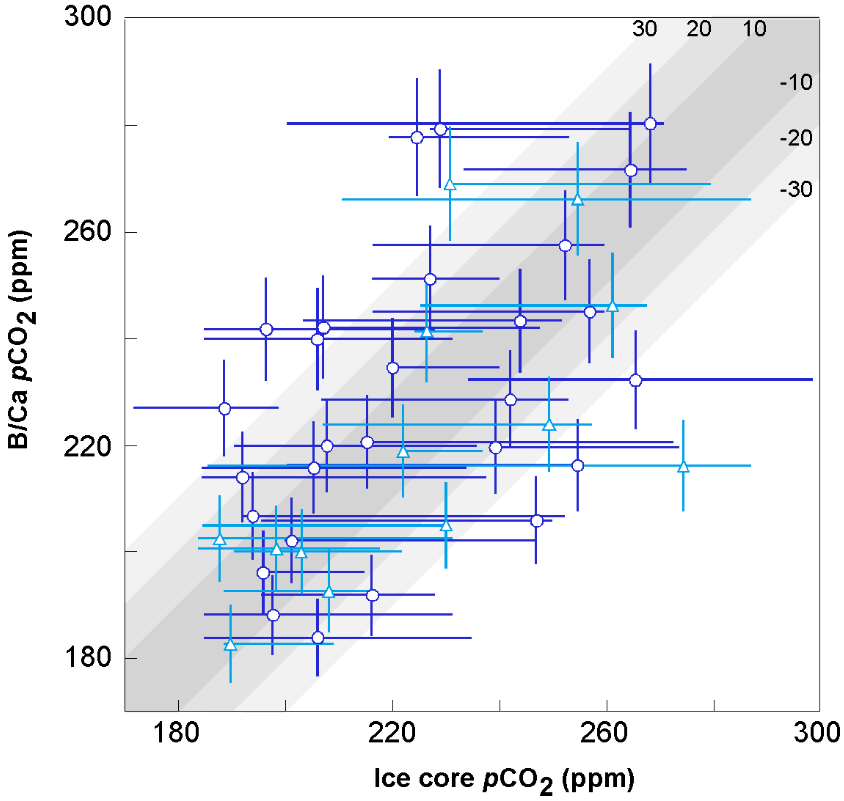

A
B
C
D
Sea surface temperature (°C)
Sea surface salinity
Age (Ma)
Age (Ma)
Age (Ma)
Age (Ma)

Fig. S9



300
260
220
180
30
20
10
-10
-20
-30
B/Ca pCO_2 (ppm)
180
220
260
300
Ice core pCO_2 (ppm)

Table S1: Location of sites used in study.

Site	Latitude	Longitude	Water Depth	Age
806	0°N	159°E	2521 m	0-8 Ma
588	26°S	161°E	1548 m	8-20 Ma

Table S2: Modern air-sea ΔpCO_2 from climatology(*S30*) for two sites used in this study.

Site 588 - 26°S, 161°E
Site 806 - 0°N, 159°E

	Seawater-air ΔpCO_2 (ppmv) at locations closest to 588 and 806					
Month	***24°S 157.5°E***	***24°S 162.5°E***	***28°S 157.5°E***	***28°S 162.5°E***	***0°N 157.5°E***	***0°N 162.5°E***
1	-38.4	-36.6	-52.9	-48.2	34.0	43.5
2	-34.5	-44.8	-49.4	-53.9	35.5	41.8
3	-42.6	-43.4	-52.6	-54.4	37.1	41.3
4	-38.2	-37.7	-51.3	-45.6	25.2	24.0
5	-23.4	-24.1	-24.6	-29.4	14.0	21.1
6	0.7	2.4	15.6	-0.9	8.4	30.7
7	15.9	23.4	20.0	31.4	4.6	26.8
8	13.1	14.8	15.9	22.3	1.1	9.6
9	8.9	4.8	25.7	11.6	16.7	18.1
10	1.0	-0.1	0.9	-0.9	39.1	43.1
11	-10.3	-12.5	-20.0	-16.5	44.4	28.6
12	-24.2	-31.1	-38.4	-37.5	31.4	48.8

	Seawater-air ΔpCO2 (ppmv) at 588 and 806 (mean of closest sites)				
Month	***Site 588***	***Site 806***			
1	-44.0	38.8			
2	-45.6	38.6			
3	-48.2	39.2			
4	-43.2	24.6			
5	-25.4	17.5			
6	4.5	19.6			
7	22.7	15.7			
8	16.5	5.4			
9	12.8	17.4			
10	0.2	41.1			
11	-14.8	36.5			
12	-32.8	40.1			
Annual mean	**-16**	**27.9**		**Difference between 2 sites**	**44 ppmv**

Table S3: B/Ca and Mg/Ca ratios measured in this study.

Depth (mbsf)	Species	B/Ca (μmol/mol)	Mg/Ca (mmol/mol)
0.09	*G. ruber*	119.1	4.4
0.09	*G. sacculifer*	70.5	4.1
0.40	*G. ruber*	119.8	3.7
0.40	*G. ruber*	114.7	3.8
0.40	*G. sacculifer*	77.2	3.4
0.80	*G. ruber*	114.4	3.5
0.80	*G. sacculifer*	76.6	3.3
0.95	*G. ruber*	119.5	3.6
0.95	*G. sacculifer*	74.5	3.5
1.20	*G. ruber*	114.5	3.7
1.20	*G. sacculifer*	78.1	3.4
1.90	*G. ruber*	109.9	3.9
1.90	*G. sacculifer*	73.3	3.6
1.92	*G. ruber*	104.5	4.0
1.92	*G. sacculifer*	70.5	3.7
2.30	*G. ruber*	117.1	4.6
2.30	*G. sacculifer*	76.3	4.2
2.40	*G. ruber*	112.1	4.6
2.40	*G. sacculifer*	83.6	4.4
2.70	*G. ruber*	109.3	3.8
2.70	*G. sacculifer*	72.1	3.6
3.00	*G. ruber*	108.1	3.5
3.00	*G. sacculifer*	73.5	3.3
3.37	*G. ruber*	111.7	3.5
3.37	*G. ruber*	109.7	3.7
3.37	*G. sacculifer*	71.7	3.3
4.20	*G. ruber*	124.8	4.1
4.20	*G. sacculifer*	71.0	3.6
4.50	*G. ruber*	112.6	4.2
4.50	*G. ruber*	113.4	4.2
4.90	*G. sacculifer*	74.1	3.4
5.16	*G. ruber*	122.6	3.6
5.16	*G. ruber*	113.4	3.6
5.16	*G. sacculifer*	73.0	3.6
5.30	*G. ruber*	133.2	3.8
5.30	*G. sacculifer*	76.2	3.5
5.60	*G. ruber*	111.2	3.9
5.60	*G. ruber*	108.9	3.9
5.60	*G. sacculifer*	72.0	3.8
5.70	*G. ruber*	134.9	3.6
5.70	*G. sacculifer*	74.1	3.7
5.85	*G. sacculifer*	72.1	3.7
6.00	*G. ruber*	118.4	3.6
6.42	*G. ruber*	115.5	3.9
6.42	*G. ruber*	109.6	3.7
6.42	*G. sacculifer*	70.0	3.7
6.66	*G. ruber*	123.5	4.7
6.66	*G. ruber*	121.1	4.5
6.66	*G. sacculifer*	75.0	4.3
6.80	*G. ruber*	125.8	4.4

7.35	*G. ruber*	113.9	3.4
7.35	*G. ruber*	118.2	3.5
7.35	*G. sacculifer*	74.1	3.6
7.57	*G. ruber*	99.5	3.4
7.57	*G. ruber*	112.3	3.3
7.57	*G. sacculifer*	68.2	3.6
7.70	*G. ruber*	110.5	4.5
7.79	*G. ruber*	109.2	3.5
7.79	*G. ruber*	96.9	3.7
7.79	*G. sacculifer*	74.0	3.5
8.90	*G. ruber*	91.7	3.6
8.97	*G. ruber*	106.1	3.4
8.97	*G. sacculifer*	71.8	3.5
11.03	*G. ruber*	106.3	4.0
11.03	*G. sacculifer*	77.6	3.9
11.34	*G. ruber*	105.6	3.6
11.34	*G. sacculifer*	72.9	3.6
12.39	*G. ruber*	103.7	4.2
12.63	*G. ruber*	106.5	4.0
12.63	*G. sacculifer*	77.0	3.6
13.28	*G. ruber*	103.3	3.9
13.38	*G. ruber*	107.5	4.2
13.38	*G. ruber*	104.9	4.0
13.84	*G. ruber*	112.0	3.6
13.84	*G. sacculifer*	79.6	3.6
14.58	*G. ruber*	104.6	3.5
14.58	*G. ruber*	101.0	3.7
15.18	*G. ruber*	108.4	4.1
15.38	*G. ruber*	110.8	4.0
15.58	*G. ruber*	102.2	3.6
15.58	*G. sacculifer*	79.2	3.6
15.74	*G. ruber*	102.7	3.6
15.74	*G. sacculifer*	74.0	3.5
16.03	*G. ruber*	118.3	4.1
16.43	*G. ruber*	99.2	3.5
17.08	*G. ruber*	99.2	4.0
17.34	*G. ruber*	104.4	4.1
17.43	*G. ruber*	106.1	4.3
17.61	*G. ruber*	105.5	4.6
17.88	*G. ruber*	101.5	3.5
18.24	*G. ruber*	104.0	3.5
18.24	*G. sacculifer*	88.6	3.3
18.63	*G. ruber*	103.4	3.8
18.83	*G. ruber*	94.9	3.4
19.03	*G. ruber*	101.3	3.9
19.24	*G. ruber*	99.3	3.9
19.36	*G. ruber*	110.0	3.9
19.64	*G. ruber*	100.4	4.3
19.93	*G. ruber*	97.9	3.8
20.29	*G. ruber*	102.0	3.9
21.14	*G. ruber*	99.3	3.5
21.14	*G. sacculifer*	78.1	3.7
21.64	*G. ruber*	97.5	4.0

22.23	*G. ruber*	86.4	3.4
22.73	*G. ruber*	103.6	4.0
23.03	*G. ruber*	98.5	3.9
23.33	*G. ruber*	94.9	3.7
23.43	*G. ruber*	106.8	4.1
23.89	*G. ruber*	95.4	3.8
24.28	*G. ruber*	108.1	4.0
24.28	*G. sacculifer*	77.2	4.1
24.58	*G. ruber*	101.3	3.9
24.83	*G. ruber*	104.3	4.0
25.58	*G. ruber*	104.4	4.4
25.93	*G. ruber*	104.6	4.0
26.17	*G. ruber*	103.5	4.2
26.94	*G. ruber*	103.9	3.9
26.94	*G. sacculifer*	74.3	3.8
27.25	*G. ruber*	104.8	3.8
27.81	*G. ruber*	108.3	4.2
28.34	*G. ruber*	101.6	3.6
28.34	*G. sacculifer*	75.6	3.7
28.50	*G. ruber*	114.4	4.2
49.83	*G. ruber*	100.7	3.9
49.83	*G. sacculifer*	63.7	3.4
50.54	*G. ruber*	107.6	3.9
50.54	*G. sacculifer*	77.2	3.7
50.73	*G. ruber*	104.3	4.0
50.73	*G. sacculifer*	82.1	3.6
50.94	*G. ruber*	112.8	4.0
50.94	*G. ruber*	115.0	4.1
50.94	*G. sacculifer*	73.9	3.7
51.34	*G. ruber*	109.3	3.9
51.34	*G. sacculifer*	73.7	3.2
51.74	*G. ruber*	108.4	4.1
51.74	*G. ruber*	112.5	3.8
51.74	*G. sacculifer*	67.7	3.5
51.94	*G. ruber*	113.1	3.8
51.94	*G. sacculifer*	79.5	3.6
52.04	*G. ruber*	111.3	4.1
52.04	*G. sacculifer*	83.5	3.8
52.18	*G. ruber*	112.3	3.7
52.18	*G. sacculifer*	74.1	3.6
52.64	*G. ruber*	107.1	4.1
52.64	*G. sacculifer*	64.2	3.5
52.78	*G. ruber*	120.6	3.9
52.78	*G. sacculifer*	67.5	3.6
53.38	*G. ruber*	107.0	4.0
53.38	*G. sacculifer*	66.1	3.5
53.54	*G. ruber*	109.6	3.3
53.54	*G. sacculifer*	70.7	3.2
53.74	*G. ruber*	99.9	3.6
53.74	*G. sacculifer*	72.2	3.3
54.15	*G. ruber*	112.8	3.6
54.15	*G. sacculifer*	69.1	3.4
54.35	*G. ruber*	105.9	3.8

54.35	*G. sacculifer*	75.2	3.4
54.59	*G. ruber*	103.3	4.0
54.59	*G. sacculifer*	81.4	3.4
57.98	*G. ruber*	113.4	3.9
57.98	*G. sacculifer*	86.5	3.5
62.55	*G. ruber*	111.8	3.9
62.55	*G. sacculifer*	79.6	3.5
64.75	*G. ruber*	118.6	3.8
64.75	*G. sacculifer*	84.3	3.4
68.49	*G. ruber*	107.1	3.7
68.49	*G. ruber*	109.1	3.9
68.49	*G. sacculifer*	107.1	3.7
72.92	*G. ruber*	117.8	3.9
72.92	*G. sacculifer*	83.9	3.7
73.78	*G. ruber*	112.5	4.0
73.78	*G. sacculifer*	79.0	3.8
78.90	*G. ruber*	115.3	3.9
78.90	*G. sacculifer*	76.6	3.8
80.70	*G. ruber*	126.8	3.9
80.70	*G. sacculifer*	81.1	3.8
82.53	*G. ruber*	103.7	3.9
155.59	*G. sacculifer*	60.8	3.8
156.38	*G. sacculifer*	62.4	3.7
158.80	*G. sacculifer*	74.6	3.6
168.39	*G. sacculifer*	67.6	3.9
177.89	*G. sacculifer*	70.5	3.3
187.35	*G. sacculifer*	73.3	3.4
196.82	*G. sacculifer*	83.1	4.0
206.25	*G. sacculifer*	75.8	3.7
215.87	*G. sacculifer*	73.6	3.5
225.37	*G. sacculifer*	75.4	3.6
251.50	*G. ruber*	98.3	4.0
269.29	*G. ruber*	106.9	4.7
297.72	*G. ruber*	80.8	4.1
307.35	*G. ruber*	100.7	4.6
310.72	*G. ruber*	95.0	4.3
319.18	*G. ruber*	87.8	4.2
327.76	*G. ruber*	92.6	4.0

Table S4: Stable isotope ratios measured in this study, in units of per mil, reported relative to the Pee Dee Belemnite standard.

Hole	Core	Section	Top (cm)	Bottom (cm)	Species	$\delta^{18}O$	$\delta^{13}C$
806A	1	1	9	11	*G. ruber*	-2.31	1.58
806A	1	1	40	42	*G. ruber*	-1.05	1.62
806A	1	1	80	82	*G. ruber*	-1.52	1.48
806A	1	1	95	97	*G. ruber*	-1.50	1.68
806A	1	1	120	122	*G. ruber*	-1.29	1.42
806A	1	2	40	42	*G. ruber*	-1.90	1.90
806A	1	2	42	44	*G. sacculifer*	-1.28	2.14
806A	1	2	80	82	*G. sacculifer*	-1.97	1.91
806A	1	2	90	92	*G. sacculifer*	-1.64	1.75
806A	1	2	120	122	*G. sacculifer*	-0.65	1.66
806A	1	3	37	39	*G. ruber*	-1.26	1.37
806A	1	3	0	2	*G. sacculifer*	-0.78	1.93
806A	1	3	72	74	*G. sacculifer*	-1.39	1.86
806A	1	3	120	122	*G. sacculifer*	-1.15	1.82
806A	1	4	0	2	*G. ruber*	-1.84	1.64
806A	1	4	15	17	*G. ruber*	-1.74	1.55
806A	1	4	40	42	*G. ruber*	-1.16	1.22
806A	1	4	66	68	*G. ruber*	-1.22	1.08
806A	1	4	110	112	*G. ruber*	-1.49	1.90
806A	1	4	135	137	*G. ruber*	-1.31	1.57
806A	1	4	80	82	*G. sacculifer*	-1.06	1.96
806A	1	4	120	122	*G. sacculifer*	-1.15	2.06
806A	1	5	42	44	*G. ruber*	-1.94	1.47
806A	1	5	66	68	*G. ruber*	-1.67	1.40
806A	1	5	0	2	*G. sacculifer*	-1.21	1.86
806A	1	5	80	82	*G. sacculifer*	-0.76	1.36
806A	1	5	135	137	*G. sacculifer*	-1.14	1.75
806A	1	6	7	9	*G. ruber*	-1.67	2.33
806A	2	1	0	2	*G. ruber*	-1.78	1.47
806A	2	1	9	11	*G. ruber*	-1.26	1.60
806A	2	1	40	42	*G. ruber*	-1.46	1.81
806A	2	1	120	122	*G. ruber*	-1.06	1.52
806A	2	1	66	68	*G. sacculifer*	-0.42	2.18
806A	2	1	77	79	*G. sacculifer*	-0.37	2.14
806A	2	1	127	129	*G. sacculifer*	-0.40	2.19
806B	2	4	3	5	*G. sacculifer*	-1.20	1.79
806B	2	4	34	36	*G. sacculifer*	-0.74	1.84
806B	2	4	139	141	*G. sacculifer*	-1.21	2.02
806B	2	5	88	90	*G. ruber*	-1.67	1.48
806B	2	5	13	15	*G. sacculifer*	-0.96	1.97
806B	2	5	78	80	*G. sacculifer*	-1.14	1.72
806B	2	5	134	136	*G. sacculifer*	-0.74	1.92

806B	2	6	58	60	*G. ruber*	-1.19	1.66
806B	2	6	118	120	*G. sacculifer*	-1.33	1.70
806B	2	6	138	140	*G. sacculifer*	-0.95	1.52
806B	2	7	8	10	*G. sacculifer*	-0.75	1.68
806B	2	7	24	26	*G. sacculifer*	-0.71	1.67
806B	3	1	3	5	*G. ruber*	-1.74	1.60
806B	3	1	43	45	*G. ruber*	-4.96	-0.56
806B	3	1	108	110	*G. ruber*	-1.63	1.37
806B	3	1	134	136	*G. ruber*	-1.68	1.42
806B	3	1	143	145	*G. ruber*	-1.70	1.40
806B	3	2	11	13	*G. ruber*	-1.54	1.42
806B	3	2	38	40	*G. ruber*	-0.95	0.64
806B	3	2	113	115	*G. ruber*	-1.14	0.73
806B	3	2	133	135	*G. ruber*	-1.15	1.23
806B	3	2	74	76	*G. sacculifer*	-0.67	1.69
806B	3	3	3	5	*G. ruber*	-1.43	1.55
806B	3	3	24	26	*G. ruber*	-1.90	1.01
806B	3	3	129	131	*G. ruber*	-1.38	1.48
806B	3	4	114	116	*G. ruber*	-1.43	1.64
806B	3	4	64	66	*G. sacculifer*	-1.11	1.95
806B	3	5	23	25	*G. ruber*	-1.30	1.17
806B	3	5	73	75	*G. ruber*	-1.67	1.53
806B	3	5	103	105	*G. ruber*	-1.51	1.74
806B	3	5	133	135	*G. ruber*	-1.22	1.68
806B	3	5	143	145	*G. ruber*	-1.50	1.63
806B	3	6	39	41	*G. ruber*	-0.53	1.90
806B	3	6	108	110	*G. ruber*	-1.66	1.88
806B	3	6	133	135	*G. ruber*	-1.56	1.66
806B	3	6	78	80	*G. sacculifer*	-1.03	1.63
806B	4	1	8	10	*G. ruber*	-1.38	1.42
806B	4	1	43	45	*G. ruber*	-1.34	1.85
806B	4	1	67	69	*G. ruber*	-1.36	1.41
806B	4	1	144	146	*G. ruber*	-1.32	1.45
806B	4	2	25	27	*G. ruber*	-1.41	1.86
806B	4	2	81	83	*G. ruber*	-1.59	1.53
806B	4	2	134	136	*G. sacculifer*	-1.18	1.87
806B	4	3	0	2	*G. ruber*	-1.51	1.85
806B	4	3	19	21	*G. ruber*	-1.55	1.52
806B	4	3	38	40	*G. ruber*	-1.44	1.59
806B	4	3	60	62	*G. ruber*	-1.37	1.60
806B	4	3	98	100	*G. ruber*	-1.41	2.06
806B	4	3	123	125	*G. ruber*	-1.30	1.47
806B	4	3	139	141	*G. ruber*	-1.40	1.33
806B	4	4	3	5	*G. ruber*	-1.57	1.29
806B	4	4	19	21	*G. ruber*	-1.42	1.84
806B	4	4	41	43	*G. ruber*	-1.45	1.51

806B	4	4	60	62	*G. ruber*	-1.66	1.77
806B	6	5	44	46	*G. ruber*	-1.88	1.68
806B	6	5	124	126	*G. ruber*	-1.53	2.26
806B	6	5	4	6	*G. sacculifer*	-1.55	2.40
806B	6	5	23	25	*G. sacculifer*	-1.32	2.04
806B	6	5	86	88	*G. sacculifer*	-1.22	2.08
806B	6	5	144	146	*G. sacculifer*	-1.07	2.13
806B	6	6	4	6	*G. sacculifer*	-1.24	1.97
806B	6	6	18	20	*G. sacculifer*	-1.26	2.21
806B	6	6	64	66	*G. sacculifer*	-1.27	2.13
806B	6	6	78	80	*G. sacculifer*	-1.30	2.17
806B	6	6	138	140	*G. sacculifer*	-1.04	1.76
806B	6	7	4	6	*G. sacculifer*	-0.77	2.08
806B	6	7	24	26	*G. sacculifer*	-0.60	2.07
806B	6	7	65	67	*G. sacculifer*	-0.93	1.96
806B	6	7	85	87	*G. sacculifer*	-1.23	2.20
806B	7	1	59	61	*G. sacculifer*	-1.22	2.09
806B	7	3	98	100	*G. sacculifer*	-1.32	2.20
806B	7	6	105	107	*G. sacculifer*	-1.50	2.30
806B	8	1	125	127	*G. sacculifer*	-1.34	2.05
806B	8	4	49	51	*G. sacculifer*	-1.45	1.98
806B	8	7	42	44	*G. sacculifer*	-1.35	1.71
806B	9	1	78	80	*G. sacculifer*	-1.38	2.29
806B	9	4	140	142	*G. sacculifer*	-0.92	1.66
806B	9	6	20	22	*G. sacculifer*	-1.38	2.05
806B	10	1	3	5	*G. ruber*	-1.94	1.69
806B	10	1	22	24	*G. ruber*	-1.67	1.72
806B	10	1	79	81	*G. ruber*	-1.87	2.04
806B	10	1	99	101	*G. ruber*	-1.71	1.93
806B	10	1	117	119	*G. ruber*	-1.69	1.85
806B	10	1	138	140	*G. ruber*	-1.88	2.17
806B	10	1	30	32	*G. sacculifer*	-1.49	2.10
806B	10	2	20	22	*G. ruber*	-1.72	1.77
806B	10	2	39	41	*G. ruber*	-1.88	1.95
806B	10	2	59	61	*G. ruber*	-1.87	2.40
806B	10	2	98	100	*G. ruber*	-1.71	1.95
806B	10	3	40	42	*G. ruber*	-1.33	1.72
806B	10	4	58	60	*G. ruber*	-1.43	1.64
806B	17	5	59	61	*G. sacculifer*	-1.17	1.97
806B	17	5	138	140	*G. sacculifer*	-1.16	1.86
806B	17	CC	9	11	*G. sacculifer*	-1.15	2.02
806B	18	CC	3	5	*G. sacculifer*	-0.77	2.32
806B	19	CC	4	6	*G. sacculifer*	-1.48	2.24
806B	20	CC	4	6	*G. sacculifer*	-1.46	2.16
806B	21	CC	5	7	*G. sacculifer*	-0.91	2.18
806B	22	CC	7	9	*G. sacculifer*	-1.17	2.20

806B	23	CC	7	9	*G. sacculifer*	-1.18	1.99
806B	24	CC	14	16	*G. sacculifer*	-0.90	2.21

Table S5: Calibration dataset for *G. ruber* (white; 250-300 μm) used in this study.

Age (ka)	B/Ca (μmol/mol)	Mg/Ca (mmol/mol)	T (°C)	K_D x 1000	$B(OH)_4^-/HCO_3^-$ (mol/mol)
6.2	119.1	4.4	29.0	1.47	0.08126
14.3	119.8	3.7	27.1	1.26	0.09476
14.3	114.7	3.8	27.6	1.21	0.09476
27.9	114.4	3.5	26.4	1.13	0.10088
36.8	119.5	3.6	26.8	1.27	0.09379
51.5	114.5	3.7	27.1	1.22	0.09414
90.0	109.9	3.9	27.7	1.18	0.09286
90.9	104.5	4.0	28.0	1.15	0.09080
105.7	117.1	4.6	29.7	1.32	0.08852
111.1	112.1	4.6	29.7	1.34	0.08361
128.2	109.3	3.8	27.5	1.31	0.08331
146.2	108.1	3.5	26.5	1.05	0.10263
163.9	111.7	3.5	26.5	1.09	0.10255
163.9	109.7	3.7	27.1	1.07	0.10255
198.5	124.8	4.1	28.5	1.43	0.08718

Table S6: Calibration dataset for *G. sacculifer* (without sac; 300-355 μm) used in this study.

Age (ka)	**B/Ca (μmol/mol)**	**Mg/Ca (mmol/mol)**	**T (°C)**	**K_D x 1000**	**$B(OH)_4^-/HCO_3^-$ (mol/mol)**
6.2	70.5	4.1	29.0	0.87	0.08126
14.3	77.2	3.4	27.0	0.81	0.09476
27.9	76.6	3.3	26.8	0.76	0.10088
36.8	74.5	3.5	27.3	0.79	0.09379
51.5	78.1	3.4	27.1	0.83	0.09414
90.0	73.3	3.6	27.6	0.79	0.09286
90.9	70.5	3.7	27.9	0.78	0.09080
105.7	76.3	4.2	29.3	0.86	0.08852
111.1	83.6	4.4	29.7	1.00	0.08361
128.2	72.1	3.6	27.5	0.86	0.08331
146.2	73.5	3.3	26.8	0.72	0.10263
163.9	71.7	3.3	26.6	0.70	0.10255
178.3	72.9	4.0	28.7	0.79	0.09270
198.5	71.0	3.6	27.5	0.81	0.08718

Table S7: Non-linear least squares regression between K_D and seawater temperature data for last 200,000 years for site in the western tropical Pacific Ocean (Site 806). Data are plotted in Fig. S2. Equation used is K_D (x1000) = a * exp (b*Temperature). *G. ruber* (white) are from 250-300 μm size fraction, and *G. sacculifer* (without sac) are from 300-355 μm size fraction.

Species	*a*	*b*	Correlation coefficient	R^2	RMS Error
G. ruber	0.211 ± 0.102 p = 0.0579	0.064 ± 0.017 p = 0.0027	0.711	0.505	0.092
G. sacculifer	0.126 ± 0.056 p = 0.0445	0.067 ± 0.016 p = 0.0012	0.763	0.582	0.050

Table S8: Reconstructed values of $B(OH)_4^-/HCO_3^-$, sea surface temperature and salinity for replicates of 20 samples.

Age (Ma)	Species	$B(OH)_4^-/HCO_3^-$ (mol/mol)	T (°C)	S (psu)
0.014	*G. ruber*	0.10115	27.1	36.8
0.014	*G. ruber*	0.09348	27.6	37.2
0.164	*G. ruber*	0.09799	26.5	35.9
0.164	*G. ruber*	0.09238	27.1	36.3
0.212	*G. ruber*	0.08677	28.5	35.5
0.212	*G. ruber*	0.08626	28.7	35.6
0.244	*G. ruber*	0.10554	26.8	36.2
0.244	*G. ruber*	0.09638	27.0	36.3
0.253	*G. ruber*	0.08929	27.9	36.1
0.253	*G. ruber*	0.08714	27.9	36.1
0.297	*G. ruber*	0.09393	27.7	34.7
0.297	*G. ruber*	0.09173	27.2	34.4
0.316	*G. ruber*	0.08778	29.5	36.5
0.316	*G. ruber*	0.08688	29.9	36.8
0.360	*G. ruber*	0.10353	26.5	35.8
0.360	*G. ruber*	0.10067	26.3	35.7
0.367	*G. ruber*	0.10237	25.9	34.4
0.367	*G. ruber*	0.08816	26.3	34.7
0.379	*G. ruber*	0.09424	26.7	36.1
0.379	*G. ruber*	0.08159	27.1	36.3
0.617	*G. ruber*	0.08291	28.1	35.7
0.617	*G. ruber*	0.08224	28.6	36.0
0.670	*G. ruber*	0.09180	26.5	36.1
0.670	*G. ruber*	0.08455	27.2	36.5
1.364	*G. ruber*	0.08560	27.0	35.3
1.364	*G. ruber*	0.07801	28.2	36.1
2.017	*G. ruber*	0.08762	28.4	37.4
2.017	*G. ruber*	0.08043	28.6	37.5
2.264	*G. ruber*	0.08922	28.1	35.1
2.264	*G. ruber*	0.08882	28.5	35.3
2.284	*G. ruber*	0.09198	27.6	35.8
2.284	*G. ruber*	0.08427	28.4	36.2

2.291	*G. ruber*	0.09240	27.6	37.1
2.291	*G. ruber*	0.08682	28.3	37.0
2.857	*G. ruber*	0.08971	27.2	35.8
2.857	*G. ruber*	0.08826	27.7	36.1
4.266	*G. sacculifer*	0.09424	26.5	35.9
4.266	*G. sacculifer*	0.09099	26.8	36.0
4.269	*G. sacculifer*	0.09843	27.2	36.3
4.269	*G. sacculifer*	0.09294	27.0	36.2

Table S9: Reconstructed values of $B(OH)_4^-/HCO_3^-$, sea surface temperature and salinity for paired measurements of *G. ruber* and *G. sacculifer* from 78 samples.

Age (Ma)	Species	$B(OH)_4^-/HCO_3^-$ (mol/mol)	T (°C)	S (psu)
0.006	*G. ruber*	0.08864	29.0	34.5
0.006	*G. sacculifer*	0.07988	29.0	34.5
0.014	*G. ruber*	0.09731	27.1	36.8
0.014	*G. sacculifer*	0.10045	27.0	36.8
0.028	*G. ruber*	0.10054	26.4	35.2
0.028	*G. sacculifer*	0.10086	26.8	35.4
0.037	*G. ruber*	0.10244	26.8	35.5
0.037	*G. sacculifer*	0.09482	27.3	35.7
0.052	*G. ruber*	0.09676	27.1	36.2
0.052	*G. sacculifer*	0.10086	27.1	36.2
0.090	*G. ruber*	0.08885	27.7	34.9
0.090	*G. sacculifer*	0.09145	27.6	36.5
0.091	*G. ruber*	0.08319	28.0	35.0
0.091	*G. sacculifer*	0.08620	27.9	36.7
0.106	*G. ruber*	0.08370	29.7	36.1
0.106	*G. sacculifer*	0.08505	29.3	35.6
0.111	*G. ruber*	0.08017	29.7	36.2
0.111	*G. sacculifer*	0.09042	29.7	36.7
0.128	*G. ruber*	0.08995	27.5	34.8
0.128	*G. sacculifer*	0.09070	27.5	38.2
0.146	*G. ruber*	0.09463	26.5	35.7
0.146	*G. sacculifer*	0.09676	26.8	37.4
0.164	*G. ruber*	0.09519	26.5	35.9
0.164	*G. sacculifer*	0.09589	26.6	36.0
0.198	*G. ruber*	0.09639	28.5	35.7
0.198	*G. sacculifer*	0.08919	27.5	36.8
0.244	*G. ruber*	0.10096	26.8	36.2
0.244	*G. sacculifer*	0.09105	27.6	36.7
0.247	*G. ruber*	0.11043	27.4	36.4
0.247	*G. sacculifer*	0.09662	27.4	37.0
0.253	*G. ruber*	0.08822	27.9	36.1
0.253	*G. sacculifer*	0.08615	28.2	36.3

0.255	*G. ruber*	0.11460	27.0	36.1
0.255	*G. sacculifer*	0.09099	27.8	37.0
0.297	*G. ruber*	0.09283	27.7	34.7
0.297	*G. sacculifer*	0.08537	27.9	34.9
0.316	*G. ruber*	0.08733	29.5	36.5
0.316	*G. sacculifer*	0.08123	29.7	36.6
0.360	*G. ruber*	0.10210	26.5	35.8
0.360	*G. sacculifer*	0.09309	27.5	36.8
0.367	*G. ruber*	0.09526	25.9	34.4
0.367	*G. sacculifer*	0.08476	27.7	35.5
0.379	*G. ruber*	0.08791	26.7	36.1
0.379	*G. sacculifer*	0.09375	27.4	36.4
0.426	*G. ruber*	0.09516	26.1	37.1
0.426	*G. sacculifer*	0.09149	27.3	38.8
0.529	*G. ruber*	0.08412	28.1	36.0
0.529	*G. sacculifer*	0.09086	28.5	37.3
0.541	*G. ruber*	0.08997	26.9	35.7
0.541	*G. sacculifer*	0.09055	27.7	38.0
0.588	*G. ruber*	0.08463	28.0	35.9
0.588	*G. sacculifer*	0.09687	27.5	37.3
0.636	*G. ruber*	0.09616	26.8	36.8
0.636	*G. sacculifer*	0.09852	27.7	38.1
0.720	*G. ruber*	0.08788	26.8	36.2
0.720	*G. sacculifer*	0.09891	27.6	38.0
0.728	*G. ruber*	0.08849	26.7	35.9
0.728	*G. sacculifer*	0.09460	27.2	37.9
0.904	*G. ruber*	0.09145	26.4	36.0
0.904	*G. sacculifer*	0.11664	26.8	37.7
1.012	*G. ruber*	0.08693	26.5	34.9
1.012	*G. sacculifer*	0.09611	27.8	37.1
1.158	*G. ruber*	0.08551	28.1	36.2
1.158	*G. sacculifer*	0.08748	29.0	38.0
1.283	*G. ruber*	0.08334	27.9	35.5
1.283	*G. sacculifer*	0.08969	28.1	36.7
1.295	*G. ruber*	0.08591	27.0	35.9
1.295	*G. sacculifer*	0.09215	27.9	37.0

1.364	*G. ruber*	0.08181	27.0	35.3
1.364	*G. sacculifer*	0.09042	28.1	36.0
1.401	*G. ruber*	0.07125	29.3	37.9
1.401	*G. sacculifer*	0.08075	30.0	38.0
1.426	*G. ruber*	0.08420	28.2	37.0
1.426	*G. sacculifer*	0.09078	28.5	37.3
1.430	*G. ruber*	0.09960	27.9	36.7
1.430	*G. sacculifer*	0.08363	28.9	37.6
1.574	*G. ruber*	0.09277	27.1	36.8
1.574	*G. sacculifer*	0.09852	27.2	36.9
1.665	*G. ruber*	0.08370	26.9	36.6
1.665	*G. sacculifer*	0.09322	26.1	35.6
1.670	*G. ruber*	0.08584	27.2	36.4
1.670	*G. sacculifer*	0.09334	26.4	35.8
1.790	*G. ruber*	0.08775	27.7	37.5
1.790	*G. sacculifer*	0.08610	27.5	36.8
1.800	*G. ruber*	0.08360	27.4	37.4
1.800	*G. sacculifer*	0.08612	27.1	36.5
2.017	*G. ruber*	0.08402	28.4	37.4
2.017	*G. sacculifer*	0.07912	27.7	36.3
2.055	*G. ruber*	0.09092	27.1	36.5
2.055	*G. sacculifer*	0.08456	26.5	35.8
2.161	*G. ruber*	0.09444	26.9	36.2
2.161	*G. sacculifer*	0.09611	27.3	36.3
2.192	*G. ruber*	0.10059	26.7	35.9
2.192	*G. sacculifer*	0.09648	25.8	35.3
2.199	*G. ruber*	0.09016	27.7	36.7
2.199	*G. sacculifer*	0.08247	27.1	35.7
2.218	*G. ruber*	0.09475	27.5	37.4
2.218	*G. sacculifer*	0.09279	26.3	35.5
2.234	*G. ruber*	0.08534	28.0	36.5
2.234	*G. sacculifer*	0.09848	27.8	36.4
2.252	*G. ruber*	0.08167	27.7	36.9
2.252	*G. sacculifer*	0.08336	26.9	36.5
2.256	*G. ruber*	0.08752	27.7	35.8

2.256	*G. sacculifer*	0.09374	28.0	36.0
2.260	*G. ruber*	0.08276	28.0	36.4
2.260	*G. sacculifer*	0.10223	27.6	36.4
2.264	*G. ruber*	0.08902	28.1	35.1
2.264	*G. sacculifer*	0.08976	28.0	36.9
2.269	*G. ruber*	0.08881	27.7	36.7
2.269	*G. sacculifer*	0.09953	26.4	36.0
2.284	*G. ruber*	0.08812	27.6	35.8
2.284	*G. sacculifer*	0.09861	27.7	37.1
2.291	*G. ruber*	0.08961	27.6	37.1
2.291	*G. sacculifer*	0.09983	28.2	37.0
2.300	*G. ruber*	0.09369	27.3	36.4
2.300	*G. sacculifer*	0.09229	27.6	36.6
2.317	*G. ruber*	0.08401	28.2	36.9
2.317	*G. sacculifer*	0.08193	27.3	36.4
2.322	*G. ruber*	0.09649	27.9	36.6
2.322	*G. sacculifer*	0.08493	27.5	36.4
2.346	*G. ruber*	0.08533	28.0	37.4
2.346	*G. sacculifer*	0.08477	27.2	36.9
2.351	*G. ruber*	0.09899	26.0	37.0
2.351	*G. sacculifer*	0.09609	26.3	37.2
2.358	*G. ruber*	0.08602	26.8	37.9
2.358	*G. sacculifer*	0.09673	26.5	37.8
2.373	*G. ruber*	0.09720	26.7	37.0
2.373	*G. sacculifer*	0.09057	26.9	37.0
2.380	*G. ruber*	0.08640	27.6	36.7
2.380	*G. sacculifer*	0.09749	27.0	36.3
2.381	*G. ruber*	0.08235	28.0	36.9
2.381	*G. sacculifer*	0.10557	27.0	36.3
2.504	*G. ruber*	0.09208	27.7	36.5
2.504	*G. sacculifer*	0.11108	27.2	36.2
2.674	*G. ruber*	0.09099	27.6	35.9
2.674	*G. sacculifer*	0.10119	27.3	35.7
2.746	*G. ruber*	0.09707	27.6	36.3
2.746	*G. sacculifer*	0.10939	27.0	36.0

2.857	*G. ruber*	0.08898	27.2	35.8
2.857	*G. sacculifer*	0.13083	27.9	36.2
3.008	*G. ruber*	0.09515	27.8	36.4
3.008	*G. sacculifer*	0.10209	28.0	36.5
3.034	*G. ruber*	0.08990	27.9	36.4
3.034	*G. sacculifer*	0.09367	28.3	36.7
3.194	*G. ruber*	0.09265	27.8	37.7
3.194	*G. sacculifer*	0.09120	28.3	37.9
3.266	*G. ruber*	0.10192	27.8	36.4
3.266	*G. sacculifer*	0.09809	28.1	36.5
3.327	*G. ruber*	0.09093	27.9	36.6
3.327	*G. sacculifer*	0.09784	28.0	36.6
3.406	*G. ruber*	0.09021	28.0	36.6
3.406	*G. sacculifer*	0.08014	28.0	36.1
3.447	*G. ruber*	0.08391	27.7	36.2
3.447	*G. sacculifer*	0.08097	28.3	36.5

Table S10: Sources of relationships used to calculate equilibrium constants.

Constant	Notation	Reference
Acidity constants of carbonic acid	k_1, k_2	(*S35, S36*)
Solubility of CO_2 in seawater	k_0	(*S37*)
Ionic product of water	k_W	(*S38*)
Bisulfate equilibrium constant	k_S	(*S38, S39*)
Hydrogen fluoride equilibrium constant	k_F	(*S38, S40*)
Boric acid equilibrium constant	k_B	(*S38, S41*)
Solubility product of calcite	K_{sp}	(*S29*)

Table S11: Sources of age models used in this study

Interval	Reference
0 to 0.8 Ma	(*S4*)
0.8 to 4 Ma	(*S42*)
4 to 8 Ma	(*S43*)
8 to 20 Ma	(*S44, S45*)

Table S12: Models used to calculated pCO_2 and pH from seawater $B(OH)_4^-/HCO_3^-$.

Model	Description
A	Alkalinity and boron vary with salinity; T & S from Mg/Ca and $\delta^{18}o$
B	Same as Model A; T + 1 deg. C
C	Same as Model A; T - 1 deg. C
D	Same as Model A; S + 1 unit
E	Same as Model A; S - 1 unit
F	Same as Model A; B + 13 to 18 umol/kg (larger further back in time; Fig. S7)
G	Same as Model A; B - 13 to 18 umol/kg (larger further back in time; Fig. S7)
H	Same as Model A; A +50 to 70 umol/kg (larger further back in time)
I	Same as Model A; A - 50 to 70 umol/kg
J	Same as Model A; T + 1 deg., S + 1 unit; B + 1 psu; A +50 to 70 umol/kg
K	Same as Model A; T - 1 deg., S - 1 unit; B - 1 psu; A - 50 to 70 umol/kg
L	Same as Model A; boron follows history 1
M	Same as Model A; boron follows history 2
N	Constant carbonate ion; boron vary with salinity
O	Same as Model N; boron follows history 1
P	Same as Model N; boron follows history 2
Q	Variable carbonate ion; calcium follows history 1; boron varies with salinity
R	Same as Model Q; T + 1 deg. C, S + 1 unit; B + 1 psu
S	Same as Model Q; boron follows history 1
T	Same as Model Q; boron follows history 2
U	Same as Model Q; T + 1 deg. C, S + 1 unit
V	Variable carbonate ion; calcium follows history 2; boron varies with salinity
W	Same as Model V; T + 1 deg. C, S + 1 unit; B + 1 psu
X	Same as Model V; boron follows history 1
Y	Same as Model V; boron follows history 2
Z	Variable carbonate ion; calcium follows history 3; boron varies with salinity
AA	Same as Model Z; boron follows history 1
AB	Same as Model Z; boron follows history 2

References

S1. S. Barker, M. Greaves, H. Elderfield, *Geochemistry, Geophysics, Geosystems*, (2003).

S2. J. Yu, H. Elderfield, B. Hoenisch, *Paleoceanography* **22**, doi:10.1029/2006PA001347 (2007).

S3. J. Yu, J. Day, M. Greaves, H. Elderfield, *Geochem. Geophys. Geosyst.* **6**, doi:10.1029/2005GC000964 (2005).

S4. M. Medina-Elizalde, D. W. Lea, *Science*, doi:10.1126/science.1115933 (2005).

S5. P. Anand, H. Elderfield, M. H. Conte, *Paleoceanography* **18**, 15 (2003).

S6. B. E. Bemis, Spero, H., Bijma, J., Lea, D. W., *Paleoceanography* **13**, 150 (1998).

S7. A. N. LeGrande, G. A. Schmidt, *Geophys. Res. Lett.* **33**, doi:10.1029/2006GL026011 (2006).

S8. K. Lee *et al.*, *Geophysical Research Letters* **33**, doi:10.1029/2006GL027207 (2006).

S9. A. Kortzinger, in *Methods of seawater analysis,* K. Grasshoff, M. Ehrhardt, K. Kremling, Eds. (1999), pp. 149-158.

S10. R. F. Weiss, B. A. Price, *Marine Chemistry* **8**, 347 (1980).

S11. N. G. Hemming, G. N. Hanson, **56**, 537 (1992).

S12. M. W. Wara, M. L. Delaney, T. D. Bullen, A. C. Ravelo, *Paleoceanography* **18**, doi:10.1029/2002PA000797 (2003).

S13. K.-F. Huang, Y. Rosenthal, C.-F. You, H.-L. Lin, Y.-T. Shieh, paper presented at the Fall Meeting of American Geophysical Union, San Francisco, 2008.

S14. D. Sinclair, *Geochimica et Cosmochemica Acta* **69**, 3265 (2005).

S15. D. Sinclair, L. Kinsley, M. McCulloch, *Geochimica et Cosmochemica Acta* **212**, 1889 (1998).

S16. S. J. Fallon, M. McCulloch, R. Woesik, D. Sinclair, *Earth and Planetary Science Letters* **172**, 221 (1999).

S17. E. Lewis, D. W. R. Wallace, in *ORNL/CDIAC-105.* (Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, 1998).

S18. J. R. Petit, e. al., *Nature* **399**, 429 (1999).

S19. U. Siegenthahaler, E. M. Thomas F. Stocker, Dieter Lüthi, Jakob Schwander, Bernhard Stauffer, Dominique Raynaud, Jean-Marc Barnola, Hubertus Fischer, Valérie Masson-Delmotte, Jean Jouzel, *Science* **310**, 1313 (2005).

S20. D. Luthi *et al.*, *Nature* **453**, 379 (2008).

S21. D. W. Lea, T. Mashiotta, H. Spero, *Geochimica et Cosmochimica Acta* **63**, 2369 (1999).

S22. T. Mashiotta, D. W. Lea, H. Spero, *Earth and Planetary Science Letters* **170**, 417 (1999).

S23. E. M. Griffith, A. Paytan, K. Caldeira, T. D. Bullen, E. Thomas, *Science* **322**, 1671 (2008).

S24. J. Horita, H. Zimmerman, H. D. Holland, *Geochim. Cosmochem. Acta* **66**, 3733 (2002).

S25. T. Lowenstein, M. Timofeeff, S. Brennan, L. Hardie, R. Demicco, *Science* **294**, 1086 (2001).

S26. N. Sime *et al.*, *Geochimica et Cosmochemica Acta* **71**, 3979 (2007).

S27. R. E. Zeebe, Wolf-Gladrow, *CO2 in seawater: equilibrium, kinetics, isotopes*. Elsevier Oceanography Series (2001), vol. 65, pp. 346.

S28. T. Tyrrell, R. E. Zeebe, *Geochim. Cosmochem. Acta* **68**, 3521 (2004).

S29. A. Mucci, J. W. Morse, **47**, 217 (1983).

S30. T. Takahashi, S. C. Sutherland, R. Wanninkhof, C. Sweeney, R. A. Feely, D. W. Chipman, B. Hales, G. Friederich, F. Chavez, A. Watson, D. C. E. Bakker, U. Schuster, N. Metzl, H. Yoshikawa-Inoue, M. Ishii, T. Midorikawa, Y. Nojiri, C. Sabine, J. Olafsson, Th. S. Arnarson, B. Tilbrook, T. Johannessen, A. Olsen, Richard Bellerby, A. Körtzinger, T. Steinhoff, M. Hoppema, H. J. W. de Baar, C. S. Wong, Bruno Delille and N. R. Bates, *Deep Sea Research II*, (in press (2008)).
S31. L. R. Uppstrom, *Deep-Sea Res.* **21**, 161 (1974).
S32. B. Hoenisch, N. G. Hemming, *Earth and Planetary Science Letters* **236**, 305 (2005).
S33. D. Lemarchand, J. Gaillardet, E. Lewin, C. Allegre, *Chemical Geology* **190**, 123 (2002).
S34. S. A. Nathan, R. M. Leckie, *Palaeogeography, Palaeoclimatology, Palaeocecology*, (in press (2009)).
S35. A. G. Dickson, F. J. Millero, *Deep-Sea Research* **34**, 1733 (1987).
S36. C. Mehrbach, C. H. Culberson, J. E. Hawley, R. M. Pytkowicz, *Limnol. Oceanogr.* **18**, 897 (1973).
S37. R. F. Weiss, *Marine Chemistry* **2**, 203 (1974).
S38. DOE, *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in seawater.* A. G. Dickson, C. Goyet, Eds., ORNL/CDIAC-74 (1994), vol. 2.
S39. A. G. Dickson, *Journal of Chemical Thermodynamics* **22**, 113 (1990).
S40. A. G. Dickson, J. P. Riley, *Marine Chemistry* **7**, 88 (1979).
S41. A. G. Dickson, *Deep Sea Research* **37**, (1990).
S42. L. E. a. R. Lisiecki, M.E., *Paleoceanography* **20**, doi:10.1029/2004PA001071 (2005).
S43. W. H. Berger, T. Bickert, H. Schmidt, G. Wefer, *Proceedings of the Ocean Drilling Program, Scientific Results* **130**, 381 (1993).
S44. M. Pagani, J. Zachos, K. H. Freeman, B. Tipple, S. Bohaty, *Science* **309**, 600 (2005).
S45. B. P. Flower, J. P. Kennett, *Paleoceanography* **8**, 811 (1993).