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## Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera

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RECORDS of past changes in the pH of the oceans should provide insights into how the carbonate chemistry of the oceans has changed over time. The latter is related to changes in the atmospheric CO<sub>2</sub> content, such as that which occurred during the last glacial–interglacial transition<sup>1</sup>. Previous studies<sup>2,3</sup> have shown that the fractionation of boron isotopes between sea water and precipitated carbonate minerals is pH-dependent. This finding has been used to reconstruct the evolution of ocean pH over the past 20 million years by analyses of boron isotopes in the carbonate shells of foraminifera<sup>4</sup>. Here we use the same approach to estimate changes in ocean pH between the last glacial and the Holocene period. We estimate that the deep Atlantic and Pacific oceans had a pH 0.3 ± 0.1 units higher during the last glaciation. The accompanying change in carbonate ion concentration is sufficient to account for the decrease in atmospheric pCO<sub>2</sub> during the glacial period<sup>1</sup>. These results are consistent with the hypothesis<sup>5</sup> that the low CO<sub>2</sub> content of the glacial atmosphere was caused by an increased ratio of organic carbon to carbonate in the ‘rain’ to the sea floor, which led to an increase in carbonate ion concentration (and thus in pH) of deep water without a corresponding increase in the lysocline depth.

The basis for the boron-isotope palaeoacidity indicator is that the uncharged species B(OH)<sub>3</sub> is enriched<sup>6</sup> in <sup>11</sup>B by ~20‰ over the charged borate species, B(OH)<sub>4</sub><sup>-</sup>. As the fraction of the boron present as these species changes with pH, so also must their respective isotopic compositions. It is assumed that only the charged borate species is incorporated into carbonate minerals and that this incorporation occurs with a small and nearly constant isotopic fractionation. Thus the isotopic composition of

the borate incorporated into marine carbonate should serve as an indicator of the palaeoacidity. As the residence time of boron in sea water is many millions of years<sup>4</sup>, the boron isotope composition of sea water cannot have changed significantly over the past several glacial cycles. Thus the only mechanism by which the isotopic composition of the charged borate species in sea water can have varied is by changes in seawater pH.

We tested the validity of the boron isotope ratio as a pH indicator by plotting the δ<sup>11</sup>B (defined in Table 1) of the modern planktonic and benthic foraminifera from both the Atlantic and Pacific oceans against the pH calculated from GEOSECS data<sup>7</sup> at the sites of the cores from which they were obtained (Fig. 1). If we assume a small but constant fractionation (0.8‰) during the course of incorporation of B(OH)<sub>4</sub><sup>-</sup> into the foraminiferal calcite, then it can be seen that the data is within analytical errors of the calculated curves. Within a particular pH range, the slope of the calculated curves is almost the same for both surface and deep water. Hence the difference in pH between two water masses of interest (ΔpH) calculated from Δδ<sup>11</sup>B within this range of pH is similar for both the curves. (Δδ<sup>11</sup>B = δ<sup>11</sup>B<sub>SAMPLE a</sub> - δ<sup>11</sup>B<sub>SAMPLE b</sub>.)

To exploit this potential, we analysed foraminiferal shells hand-picked from the coarse fraction of marine sediment. The shells were cleaned in hydrogen peroxide and then dissolved in hydrochloric acid; the solution was loaded directly onto a rhenium filament and analysed by negative-ion mass spectrometry<sup>3</sup> at SUNY, Stony Brook. All sample solutions were analysed a number of times because this technique is subject to variable fractionation and isobaric interference<sup>8</sup>. Criteria for accepting an analysis include no indication of an isobaric interference on mass 42 (<sup>10</sup>BO<sub>2</sub><sup>-</sup>) from CNO (determined by monitoring mass 26, CN), and no variable fractionation during the analysis (mini-

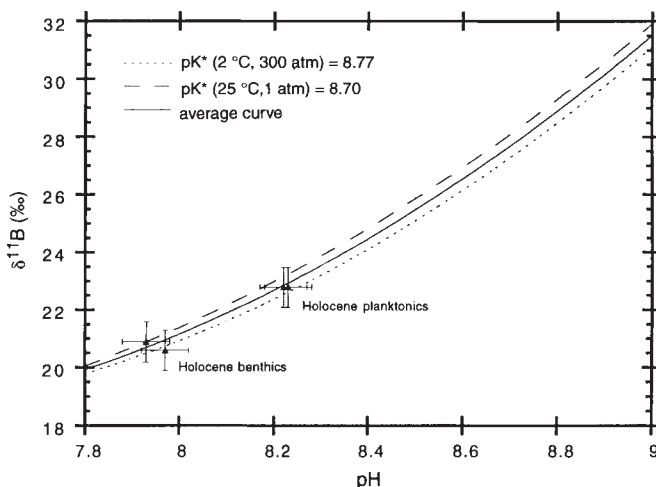


FIG. 1 Relationship between the boron isotope ratio of foraminifera and pH of sea water. The relationship was calculated by using an isotopic fractionation of 20‰ between the two aqueous species of boron<sup>6</sup> and pressure-corrected pK\* (where pK\* is the apparent dissociation constant of boric acid in sea water) of the surface and deep sea water (Lyman<sup>16</sup>; Culberson and Pytkowicz<sup>17</sup>). It is assumed that B(OH)<sub>4</sub><sup>-</sup> is the sole species being incorporated and that this incorporation takes place with a constant fractionation of 0.8‰. Based on this, the boron isotope composition of Holocene foraminifera would be expected to fall, within errors, on the two curves corresponding to the pH of sea water in which they grew. The Holocene planktonics and the benthics have been plotted against the GEOSECS-calculated<sup>7</sup> pH of surface and deep water (3,000 m), respectively, at the sites of the cores from which the samples were obtained. To simplify calculations we adopt an average curve, drawn between the two curves. Based on this average curve, ΔpH has been calculated from Δδ<sup>11</sup>B (ΔpH = 0.29(Δδ<sup>11</sup>B) - 0.0037(Δδ<sup>11</sup>B)(δ<sup>11</sup>B<sub>a</sub> + δ<sup>11</sup>B<sub>b</sub>), where subscripts a and b represent two different samples).

TABLE 1 Boron isotope composition of foraminifera

	Holocene* $\delta^{11}\text{B}_\text{H}(\text{‰})$	Glacial* $\delta^{11}\text{B}_\text{G}(\text{‰})$	$\delta^{11}\text{B}_\text{G}-\delta^{11}\text{B}_\text{H}$ (‰)	$\Delta\text{pH}\S$
Pacific Ocean Planktonics†	22.5 (A) 23.0 (A)	24.4 (B) 25.3 (B) 24.2 (B) 24.4 (B)		
Mean	$22.8 \pm 0.5$	$24.6 \pm 0.5$	$1.8 \pm 1.0$	$0.20 \pm 0.11\parallel$
Benthics‡	20.7 (A) 21.4 (A) 20.7 (A)	23.7 (B) 22.9 (B) 23.6 (B)		
Mean	$20.9 \pm 0.5$	$23.4 \pm 0.5$	$2.5 \pm 1.0$	$0.31 \pm 0.12$
Atlantic Ocean Planktonics†	22.0 (C) 23.3 (C) 23.2 (C)	25.3 (D) 24.3 (D) 24.2 (D)		
Mean	$22.8 \pm 0.7$	$24.6 \pm 0.7$	$1.8 \pm 1.0$	$0.20 \pm 0.11$
Benthics‡	20.7 (E) 20.7 (E) 20.5 (E)	24.2 (D) 22.7 (D) 23.2 (D) 22.9 (D)		
Mean	$20.6 \pm 0.1$	$23.3 \pm 0.7$	$2.7 \pm 1.0$	$0.34 \pm 0.12$

$$\delta^{11}\text{B} = \left\{ \left( \frac{^{11}\text{B}/^{10}\text{B}}{\text{sample}} / \frac{^{11}\text{B}/^{10}\text{B}}{\text{standard}} \right) - 1 \right\} \times 1,000 \text{ per mil.}$$

\* The letters refer to the cores from which the samples were taken: A, V35-16 (1° N, 159° 14' E, 2,674 m); B, V28-238 (1° 01' N, 160° 29' E, 3,120 m); C, Knorr 110 82GGC (4° 20.2' N, 43° 29.2' W, 2,816 m); D, V25-59 (1° 22.4' N, 33° 28.9' W, 3,824 m); E, V29-179 (44° 00.6' N, 24° 32.4' W, 3,331 m).

† *Globigerinoides sacculifer*.

‡ Mixed benthics.

§ Calculated from  $\Delta\text{pH} = 0.29(\Delta\delta^{11}\text{B}) - 0.0037(\Delta\delta^{11}\text{B})(\delta^{11}\text{B}_\text{a} + \delta^{11}\text{B}_\text{b})$ ; see also Fig. 1.

|| The uncertainties are  $2\sigma$  of mean.

imum of 50 ratios). As a result ~50% of the analyses were discarded. We estimate the difference in pH of both the surface ocean and the deep ocean between the last glacial and the Holocene period from the difference in the boron isotope composition of glacial and Holocene planktonic and benthic samples, respectively. This is necessary because at present we are unable to obtain accurate absolute boron isotope results. The reason is that matrix effects require that the foraminifera be analysed at higher filament temperatures than for NBS standards of sea water. As the modern planktonic and benthic foraminifera yield  $\delta^{11}\text{B}$  values consistent with the pH values calculated using GEOSECS data, we consider this an indication that the higher temperature of ionization required for foraminiferal samples does not introduce a large bias.

The results as calculated from the boron isotope data are (Table 1): the pH of surface water of glacial age in the tropical Atlantic and Pacific oceans was  $0.2 \pm 0.1$  pH units higher than that during the Holocene, and the pH of deep water of glacial age in the equatorial Atlantic and equatorial Pacific oceans was  $0.3 \pm 0.1$  pH units higher than during the Holocene. The concentration of boron in foraminifera ranges from 10 to 15 p.p.m. with no apparent correlation with boron isotope composition.

As shown in Table 2, the pH change for deep Pacific Ocean water associated with both the 3% increase in salinity resulting from the growth of the ice caps and the 700-m deepening of the lysocline<sup>9</sup> are so small that they would lie within the uncertainty of pH reconstructions based on boron isotopes. If the glacial to Holocene drop in pH (0.3 units) suggested by the boron isotope measurements on benthic foraminifera was mainly accomplished by excess  $\text{CaCO}_3$  accumulation, then the alkalinity of deep Pacific water must have been ~10% higher during glacial time. As a result, the carbonate ion concentration of deep Pacific water during glacial time would have been  $\sim 100 \mu\text{mol kg}^{-1}$  higher than

the present-day value, deepening the calcite saturation horizon by several kilometres.

In the case of tropical surface water, estimates of the glacial temperature and  $\text{CO}_2$  partial pressure are available. As can be seen in Fig. 2, if the  $\text{CaCO}_3$  addition required to explain the deep-ocean pH change is applied to the entire ocean, it would produce the atmospheric  $\text{CO}_2$  drop recorded in ice cores (that is, from an interglacial value of  $280 \mu\text{atm}$  to a glacial value of  $200 \mu\text{atm}$ ). The associated pH change would be 0.15 units (compared to the boron-isotope-based estimate of  $0.20 \pm 0.11$  pH units). The reason why identical  $\text{CaCO}_3$  additions result in only half as large a pH change in surface water than in deep water is that the former has twice the  $\text{CO}_3^{2-}$  content of the latter.

Although it is not well established where calcite dissolution takes place, there is evidence suggesting that much of the dissolution occurs within the sediment<sup>10</sup>. Some of this dissolution is driven by  $\text{CO}_2$  released into the pore waters of the sediment as a result of respiration. As shown by Archer and co-workers<sup>11,12</sup>, this  $\text{CO}_2$  produces a minimum of  $\text{CO}_3^{2-}$  concentration at a depth of a few centimetres in the sediment, permitting dissolution to occur despite calcite supersaturation in the overlying bottom water. This produces a separation in the depth of the water-column saturation horizon and the depth of the sedimentary lysocline<sup>13</sup> (the depth at which calcite dissolution commences).

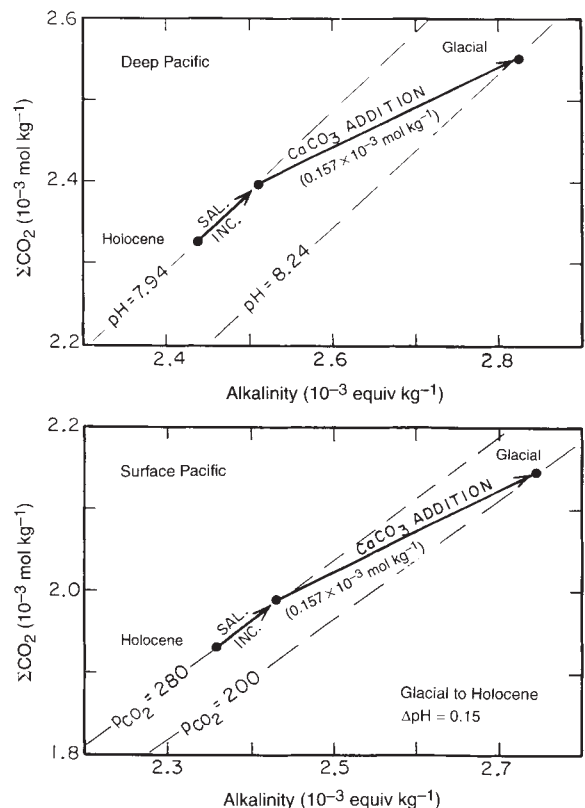


FIG. 2 Top, diagrammatic representation of the differences in carbon chemistry between Holocene and glacial deep Pacific water. As the result of ice-cap growth, glacial water had 3% higher salinity, alkalinity and total  $\text{CO}_2$  ( $\Sigma\text{CO}_2$ ) content. If the observed higher glacial pH ( $+0.3 \pm 0.1$ ) was the result of excess calcite dissolution, then  $0.157 \times 10^{-3}$  moles of  $\text{CaCO}_3$  must have been added to each kilogram of sea water. Bottom, a similar diagram representing the difference for tropical surface water. As can be seen, adding the same  $\text{CaCO}_3$  amount as required for deep water drops the  $\text{CO}_2$  partial pressure ( $p\text{CO}_2$ ) to a value very close to that observed in ice cores (that is, from 280 to  $200 \mu\text{atm}$ ). The corresponding pH change is 0.15 pH units, a value lying within the error of the boron-isotope-based value of  $0.2 \pm 0.1$  pH units.

TABLE 2 Changes in deep Pacific Ocean pH

	T (°C)	S (p.p.t.)	ALK ( $\mu\text{eq kg}^{-1}$ )	$\Sigma\text{CO}_2$ ( $\mu\text{mol kg}^{-1}$ )	$\text{CO}_3^{2-}$ ( $\mu\text{mol kg}^{-1}$ )	pH	$\Delta\text{pH}$ (Glacial-modern)
Modern ocean GEOSECS Stn 251, 4.5° S 179° E, 3.5 km	1.5	34.7	2,438	2,325	86	7.94	—
Glacial ocean							
Step 1: 3% salinity increase due to 115 m drop in sea level	1.5	35.7	+73 2,511	+70 2,395	89	7.93	-0.01
Step 2: $\text{CaCO}_3$ addition due to lysocline deepening of ~700 m (ref. 9)	1.5	35.7	+26 2,537	+13 2,408	96	7.96	+0.02
Step 3: $\text{CaCO}_3$ addition required to match boron-isotope-based pH	1.5	35.7	+288 2,825	+144 2,552	187	8.24	+0.30

These changes in pH are associated with higher glacial salinity, deepened glacial lysocline and higher glacial organic rain rate. The final target is the 0.30 unit rise in pH suggested by boron isotope measurements on glacial age benthic foraminifera shells. Symbols used: T, temperature; S, salinity; ALK, total alkalinity;  $\Sigma\text{CO}_2$ , total  $\text{CO}_2$ ;  $\text{CO}_3^{2-}$ , carbonate ion concentration.

It is important to mention that a recent study by Jahnke *et al.*<sup>14</sup> found no evidence of respiration-driven carbonate dissolution in sediments located above the saturation horizon.

Archer and Maier-Reimer<sup>5</sup> attempt to explain the lowered  $\text{CO}_2$  content of the glacial atmosphere by postulating that the ratio of organic carbon ( $C_{\text{org}}$ ) to carbonate in the 'rain' to the sea floor was higher during glacial time. If this had been brought about by an increase in organic-carbon rain rate (without a change in the absolute rate of carbonate rain), it would have brought about a larger respiration-induced reduction in the carbonate-ion concentration of pore water due to  $\text{CO}_2$  released by degradation in pore water of the increased organic carbon rain, and an increase in the concentration of that ion in the bottom water<sup>5</sup> (and thus deepening of the saturation horizon). An increase in the carbonate ion concentration of the deep ocean would lead to an increase in the concentration of that ion in the surface ocean (over a glacial-interglacial timescale) which in turn would lead to a drawdown of atmospheric  $\text{CO}_2$ . There need not, however, be a significant change in the depth of the lysocline corresponding to the deepening of the saturation horizon. Our boron isotope results seem to lend support to this hypothesis because even though these results suggest about a twofold increase in the  $\text{CO}_3^{2-}$  concentration of the bottom water (which would lead to a deepening of the saturation horizon by several kilometres), sedimentary records indicate that the lysocline deepened by only ~700 m in the glacial Pacific Ocean. Model calculations show that a 40% increase in the  $C_{\text{org}}$ /carbonate rain rate ratio to the sea floor is required in order to bring about an increase of ~60  $\mu\text{mol kg}^{-1}$  in the carbonate ion concentration of the bottom water (D. Archer, personal communication).

Although consistent with the hypothesis of Archer and Maier-Reimer<sup>5</sup> our results point up two difficulties associated with this scenario. The first problem is that if, as Archer and Maier-Reimer<sup>5</sup> suggested, a higher  $C_{\text{org}}$ /carbonate rain rate ratio during glacial time produced an increase of several kilometres in the offset between the saturation horizon and the lysocline, then one would expect there to be a substantial offset associated with today's organic rain. Yet, taken at face value, the evidence in hand does not suggest that the saturation horizon is displaced below the lysocline by several kilometres. It is hard to understand how the proposed glacial increase in the rain of organic material could lead to a several-fold increase in the separation between these horizons.

The second problem has to do with the enormous preservation event which would have been triggered if the glacial excess organic flux were turned off on a timescale short with respect to the adjustment time for the deep ocean's  $\text{CO}_3^{2-}$  content (that is, several thousand years). If, as our boron-isotope-derived pH

changes suggest, the deep ocean had about 100  $\mu\text{mol kg}^{-1}$  higher  $\text{CO}_3^{2-}$  content than today's, then in the absence of the excess glacial organic rain the lysocline would drop well beneath the ocean's abyssal plains. Calcite would have accumulated everywhere on the sea floor. In order to bring the abyssal waters in the Pacific and Indian oceans back to the saturation  $\text{CO}_3^{2-}$  concentration, ~1–2  $\text{g cm}^{-2} \text{kyr}^{-1}$  of excess calcite would have had to accumulate across the entire sea floor. This would require<sup>15</sup> several thousand years. Then, as the lysocline reached the elevation of the abyssal plains, the  $\text{CaCO}_3$  deposited during the preservation event would begin to redissolve leading to a pause in the lysocline rise, during which dissolution of calcite from the abyssal plain would temporarily balance the deposition of excess calcite elsewhere on the ocean floor. Only when this abyssal-plain calcite had largely dissolved would the lysocline and saturation horizons continue their rise.

In an attempt to confirm these preliminary results, we are currently analysing a set of Barbados corals, spanning the entire transition from full glacial to Holocene conditions. We also plan to analyse both benthic and planktonic foraminifera from marine stages 6 (the penultimate glaciation) and 5e (last interglacial) to see whether a repeat of the last glacial to Holocene pH change is found. Although the present results may suggest an explanation for the reduction of atmospheric  $\text{CO}_2$  during glacial time, we freely admit that this explanation has implications that are difficult to accept. □

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