Reconstructing Past Ocean pH-Depth Profiles

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Measurement of boron isotope compositions in species of planktonic foraminifera that calcified their tests at different depths in the water column are used to reconstruct the pH profile of the upper water column of the tropical ocean. Results for five time windows from the middle Miocene to the late Pleistocene indicate pH-depth profiles similar to that of the modern ocean in this area, which suggests that this method may greatly aid in our understanding of the global carbon cycle.

The pH of seawater plays an important role in the ocean-atmosphere carbon budget by controlling the speciation of dissolved carbonate species, affecting the depth of the carbonate compensation depth (CCD), and determining the partitioning of gaseous carbon dioxide between the oceans and the atmosphere. As these parameters have varied in the past, the ability to determine the pH of the paleoceans would be of considerable interest to oceanographers as well as climatologists.

Boron dissolved in seawater occurs mainly as $B(OH)_4^-$ and $B(OH)_3$; the relative proportions are largely a function of pH (1). Boron isotopes are fractionated between the species so that ¹⁰B is preferentially partitioned into $B(OH)_4^-$ (2). Boron uptake into foraminiferal calcite takes place by $B(OH)_4^$ incorporation, with little or no boron isotope fractionation (3), so the $\delta^{11}B$ of foraminifera tests potentially record the $\delta^{11}B$ of the $B(OH)_4^-$ in seawater and, hence, the pH of that water (3).

This hypothesis has been used to test whether there have been changes in seawater pH with time. Spivack et al. (4) measured the δ^{11} B of bulk for minifera from the equatorial Pacific and observed an increase from 10.5 per mil 21 million years ago (Ma) to 17.0 per mil 6 Ma, with a fall to a present day value of 16.2 per mil. Hence, they suggested that the pH of surface seawater had increased from 7.4 at 21 Ma to close to its present day value of 8.2 by 6 Ma because of a decrease in atmospheric CO₂. Subsequently, Sanyal et al. (5), measuring benthic and planktonic foraminifera, calculated that the pH of surface water from the tropical Atlantic and Pacific was 0.2 ± 0.1 higher during glacial periods, and the pH of the deep tropical waters was 0.3 ± 0.1 pH unit higher. A comparable study (6) of transitions across the oxygen isotope stage 5-6 boundary, confirmed the glacialinterglacial changes in deep water but did not observe a change in the pH of surface water. Both studies (5, 6) concluded that the changes in deep-water pH resulted from enhanced respiration CO_2 -driven calcite dissolution during glacial maxima due to increased sedimentation of organic carbon. However, the pH changes in surface waters were less readily explained and were interpreted in terms of lower glacial atmospheric CO_2 levels (5), increased calcite production, or decreased nutrient utilization efficiency (6).

We have taken a different approach. Instead of determining variations in the pH of surface water (to be more precise, mixed layer), we have tested whether the $\delta^{11}B$ of different foraminifera species record the depth profile of seawater pH. This approach recognizes that planktonic foraminifera precipitate their shells over a range of depths (7)and that the largest vertical changes in seawater pH occur in the upper water column rather than between surface and bottom waters (8, 9). The pH gradient of the upper ocean depends on the carbonate chemistry of seawater, which largely reflects primary productivity rates (10) and is important in defining ocean-atmosphere interaction (11).

We analyzed individual species of planktonic foraminifera and mixed benthic foraminifera from the sediments of Leg 144, Hole 871A (6°N, 172°E) of the Ocean Drilling Program (12). This site was selected because it is characterized by a pronounced stable thermocline and contains abundant well-preserved planktonic foraminifera that are wellcharacterized in terms of their calcification depth in the water column (13, 14).

We selected five sediment samples for analysis: 1H/1, 124 to 126 cm (upper Pleistocene; about 85 thousand years ago); 3H/2, 123 to 125 cm (middle Pliocene; 2.5 Ma); 3H/5, 123 to 125 cm (late Miocene; 5.8 to 7.1 Ma); 4H/5, 59 to 61 cm (middle-Miocene; 11.5 to 12.6 Ma); and 8H/2, 59 to 61 cm (middle Miocene; 15.2 to 16.2 Ma). Monospecific samples of 30 to 300 pristine tests were picked from washed and sieved sediment and analyzed by a method similar to that of Sanyal et al. (5, 15) (Table 1). Our results are consistent with their studies (5, 6) $(\delta^{11}B \text{ of planktonic and benthic for a minif-}$ era = 17.6 to 25.3 per mil) but are higher than those of Spivack et al. (4) (10.5 to 17.0 per mil).

Individual mixed layer species from 1H/1 show the widest δ^{11} B variation. The wellpreserved nature of all foraminifera analyzed in this study (13) argues against diagenetic alteration of primary δ^{11} B values. We cannot dismiss the possibility that nonstatistical sampling contributes to this wider variation, but this group was treated exactly the same as the other samples. However, the mixed layer species from 1H/1 were the first to be analyzed in our study, so the narrower variation shown by subsequent groups likely reflects an improved understanding of optimum mass spectrometer analytical conditions (15).

The boric acid dissociation constant (pK_b) is temperature and pressure dependent (1, 16), so the calcification depth and temperature of individual species are required before pH values can be calculated from δ^{11} B. The calcification depths were estimated from the



boric acid in seawater are from Dickson (1) and Gieskes (16). Temperature dependences of the boron isotope fractionation factors are from Kakihana *et al.* (2).

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literature (7, 14) and, as a first approximation, we assume that the water column temperature-depth profile at site 871 has been constant over the time period covered by our study (0 to 16 Ma). We recognize that this assumption is simplistic and discuss its implications below.

Each species was assigned to a calcification depth interval—mixed layer (0 to 100 m; 29° to 26.5°C), intermediate (50 to 150 m; 28.4° to 18.5°C), thermocline (100 to 250 m; 26.5° to 10.0°C), deep planktonic (200 to 600 m; 12.8° to 7.5°C), and benthic (1000 to 1250 m; 5° to 4°C) (Table 1)-and the pH was calculated and compared with the pHdepth profile directly measured on seawater from this area of the Pacific (8) (Fig. 1). The relation between the $\delta^{11}B$ of foraminifera and the pH of seawater is such (6) that at 20° C an analytical uncertainty of ± 0.3 per mil at a δ^{11} B of 21.0 per mil yields a calculated pH of 7.21 to 7.50, whereas the same uncertainty and a δ^{11} B of 25.0 per mil yields a pH range of only 8.14 to 8.21. Hence, the minimum pH that can realistically be recorded by the calcite is about 7. The temperature dependence of pK_b also means that the error bars are asymmetric as higher pH values are calculated for the same $\delta^{11}B$ at lower temperatures.

All five samples record surface seawater pH values that are within the range observed in the oceans today, and they all show a decrease in the calculated pH with depth that is similar to that observed in the present-day equatorial Pacific (8) (Fig. 1).

The major discrepancy between the calculated and modern pH-depth profiles is for the deepest samples from sections 4H/5 and 8H/ 2, where low pH values (\leq 7) are calculated, compared with modern seawater (7.5 to 7.3)at 200 to 600 m (8). We do not know anywhere in the modern oceans where pH values are \leq 7, so the calculated pH values are likely too low. This could arise from several causes. Postdepositional alteration of the primary $\delta^{11}B$ (by partial dissolution or growth of surface coatings) cannot be dismissed, but these samples are very well preserved, as are all other samples from this site (13). These samples were treated in exactly the same manner as the others in this study, so there is no reason to suspect that the calcite signal of these samples might be contaminated by adhering clay minerals. The low calculated pH is based on $\delta^{11}B$ measured in a single species (Globoquadrina venezuelana) that is extinct, so it is possible that this species was subject to unknown vital effects during incorporation of boron isotopes. No other planktonic foraminifera species analyzed in this study appear to indicate such vital effects, but we cannot dismiss this hypothesis. The pH was calculated on the basis that this species calcified its test at 12.8° to 7.5°C (the modern water temperature range at 200 to 600 m). A temTable 1. Boron isoope data. Depth assignments are according to (7).

Species	Size (µm)	Mean $\delta^{11}B$
	144-871A-1H/1, 124 to 126 cm	
Clabicariacidas rubar	Mixed layer, 0 to 100 m	22.2
Clobigerinoides ruber	500 to 600	25.2
Clobigerinoides sacculifer	425 to 500	27.7
Globigerinoides sacculifer	355 to 425	24.0
Globigerinoides conglobatus	500 to 600	26.5
Globigerinoides conglobatus	425 to 500	20.5
Globigerinella sinhonifera	500 to 600	23.3
Globigerinella siphonifera	425 to 500	24.6
Globigerinella siphonifera	355 to 425	24.6
Stobigermetta sipitomjera	Intermediate 50 to 150 m	E 110
Sphaeroidenella dehsicens	500 to 600	25.4
Pulleniatina obliquiloculata	500 to 600	22.3
Pulleniatina obliquiloculata	425 to 500	23.4
Pulleniatina obliquiloculata	355 to 425	243
Fullematina Obliganoculata	Thermocline 100 to 250 m	27.5
Claboratalia menardii	500 to 600	21.1
Cloborotalia menardi	ic crust) 500 to 600	21.1
Cloboquadrina condomorata	500 to 600	23.4
Globoquadima conglomerata	Deep >200 m	23.4
Claboratalia tumida (gamataganic a	E_{E} EOO to EOO	10 7
Globorotalia crassaformis	250 to 355	213
Globorolalia Crassajornis	230 to 333	21.5
Nived benthizs	3ea 11001, 1230 111	24.4
Mixed Denthics	230 to 000	24.4
	144-8/1A-3H/2, 123 10 123 CM	
Chaling and a side of a second life of	Mixed layer, 0 to 100 m	27.1
Globigerinoides sacculifer	425 to 500	27.1
Globigerinella siphonifera	425 to 600	25.2
Globigerinoides fistulosis	500 to 600	25.3
	Intermediate, 50 to 150 m	
Pulleniatina praecursor	500 to 600	22.9
	Thermocline, 100 to 250 m	
Globorotalia menardii	500 to 710	20.3
	Deep, >200 m	
Globorotalia tumida (gametogenic c	rust) 500 to 600	20.6
	Sea floor, 1200 m	
Mixed benthics	355 to 850	21.6
	144-871A-3H/5, 123 to 125 cm	
	Mixed layer, 0 to 100 m	
Globigerinoides sacculifer	425 to 600	25.0
Globigerinoides trilobus	355 to 500	23.9
•	Thermocline, 100 to 250 m	
Dentoglobigerina altispira	425 to 600	21.1
Globorotalia menardii	425 to 600	20.1
Globorotalia pleisotumida	250 to 300	20.3
	Sea floor, 1000 m	
Mixed benthics	355 to 850	20.9
	144-871A-4H/5, 59 to 61 cm	
	Mixed layer, 0 to 100 m	
Globigerinoides ruber	250 to 300	23.1
Globigerinoides obliquus	250 to 300	24.5
Globigerinoides trilobus	300 to 425	24.6
	Intermediate, 50 to 150 m	
Paragloborotalia mayeri	300 to 425	21.3
Fohsella fohsi	355 to 425	20.0
	Thermocline, 100 to 250 m	
Dentoglobigerina altispira	500 to 600	22.6
5 5 1	Deep, >200 m	
Globoquadrina venezuelana	425 to 600	19.4
,	144-871A-8H/2, 59 to 63 cm	
	Mixed layer, 0 to 100 m	
Globiaerinoides obliauus	250 to 300	23.1
Globiaerinoides trilobus	300 to 425	24.3
	Intermediate, 50 to 150 m	
Fohsella peripheroronda	250 to 355	23.6
Paradoborotalia maveri	250 to 300	22.0
, alagiobolotalia mayeri	Thermocline 100 to 250 m	
Dentoalobiaerina altispira	500 to 600	22.0
	Deep >200 m	LL.V
Globoquadrina venezuelana	425 to 500	19.4
Stoboquadinia venezuelaria		12.7

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perature of about 2°C would be required to yield a pH of 7.1 for the measured δ^{11} B of 19.4 per mil in G. venezuelana in sections 4H/5 and 8H/2. As middle Miocene oceans are thought to have been warmer than modern oceans (17), this scenario is unlikely. Finally, it is possible that the $\delta^{11}B$ of the oceans has changed. A decrease in the $\delta^{11}B$ of the oceans of 1 per mil would yield a rise in the calculated pH from \leq 7.0 to 7.5, for a for a miniferal $\delta^{11}B$ of 19.4 per mil at a temperature of 7.5°C. The temperature dependence of pK_{b} and the nature of the pH- δ^{11} B relation means that this fall in seawater δ^{11} B would only increase the calculated pH of the mixed layer recorded in section 8H/2 from between 7.80 and 7.90 to between 7.95 and 8.03. Although the residence time of boron in the oceans is long [about 20 million years (18)], a change of 1 per mil in the $\delta^{11}B$ of the oceans is not unreasonable in view of the well-documented variations in seawater ⁸⁷Sr/⁸⁶Sr over the past ~ 16 million years (19). This observation has implications for our ability



Fig. 2. (A) Variation in calculated mixed-layer seawater pH. (B) Variation in calculated mixed-layer temperature. (C) Variation in calculated seawater $\delta^{11}B$ (see text for details).

to reconstruct the pH of the ancient oceans unless an independent monitor of seawater $\delta^{11}B$ can be found.

Measurements from benthic foraminifera consistently indicate that pH was higher than modern seawater from the same depth (8). This may be related to paleoceanographic variations (5, 6); alternatively, benthic foraminifera may record pore water, rather than seawater, pH (20). Benthic foraminifera are rare in sediments from site 871 (13), so we used a mixed assemblage that includes infaunal species. CaCO₃ dissolution in the sediment would consume protons and increase the pH of pore waters. Site 871 has remained above the CCD over the time interval covered in this study and there are no signs of dissolution of foraminifera tests (13); but the modern aragonite lysocline in this area of the Pacific lies close to the paleodepth of site 871 during the late Pleistocene-late Miocene (10, 13), so that dissolution of pteropods in the sediments may account for the high pH recorded by benthic foraminifera. Alternatively, the water temperature at 1000 to 1250 m would have to have been similar to that of surface water (about 28°C) or the $\delta^{11}B$ of seawater would have to have been 4 per mil higher in the late Pleistocene than today in order to reproduce modern seawater pH values at this depth; neither scenario is probable. A further possibility is that the measured deep seawater pH values (8) are in error, as direct determination of seawater pH is a difficult analytical problem that becomes more complex in deeper samples.

If temperature and seawater $\delta^{11}B$ were constant over the past 16 million years, the foraminiferal data can be used to calculate variations in the mixed layer pH (Fig. 2A). The maximum range in calculated pH (7.8 to 8.4) from this study is less than that previously proposed (7.5 to 8.4) over a similar time period (4), but the discrepancy in $\delta^{11}B$ values measured by Spivack et al. (4) compared with those of Sanyal et al. (5, 6) and ourselves makes comparisons of the data sets difficult. If pH and seawater $\delta^{11}B$ were constant the implied temperature variations can be calculated (Fig. 2B). The implied cooler temperatures in the Miocene are contrary to generally accepted climatic variations at this time (17); hence, we do not believe that temperature variations are the cause of the variations in foraminiferal $\delta^{11}B$ values. Similarly, the implied change in seawater $\delta^{11}B$ can be calculated (Fig. 2C) if temperature and pH are fixed. The long oceanic residence time of boron (18) makes it unlikely that short-term variations in for aminiferal $\delta^{11}B$ result from changes in the $\delta^{11}B$ of seawater, but (as noted above) we cannot exclude the possibility that a small change in seawater $\delta^{11}B$ may explain the change in foraminiferal δ^{11} B values between the middle Miocene and late Pleistocene sample.

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- 7. Planktonic foraminifera have complex life cycles and different species calcify at different depths in the water column [C. Hemleben, M. Spindler, O. R. Anderson, Modern Planktonic Foraminifera (Springer-Verlag, Berlin, 1989). Tropical areas, like site 871, with a strong thermocline and thick mixed layer tend to have the most diverse and wellstratified assemblages. Many species (such as in the genus Globigerinoides) that spend their entire life cycle in the mixed layer (upper 100 m) possess obligate photosymbionts and are omnivorous. Other species stratify through intermediate, thermocline, and deep planktonic habitats (such as Globorotalia species) and feed on algae and sinking phytodetritus. Calcification depths for modern and extinct plankton species were estimated based on previous plankton tow and oxygen isotope studies [N. J. Shackleton and E. Vincent, Mar. Micropalaeontol. 3, 1 (1978); J. Erez and S. Honjo, Palaeogeogr. Palaeoclimatol. Palaeoecol. 33, 193 (1981); R. G. Fairbanks, N. Sverdlove, R. Free, P. H. Wiebe, A. W. H. Be, Nature 298, 841 (1982); G. Keller, Geol. Soc. Am. Mem. 163, 177 (1985); W. G. Deuser, J. Foraminiferal Res. 17, 14 (1987); J. T. Gasperi and J. P. Kennett, Mar. Micropalaeontol. 22, 235 (1993); P. N. Pearson and N. J. Shackleton, Proc. Ocean Drilling Program, Scientific Results, 144, 401 (1995); J. M. Watkins, A. C. Mix, J. Wilson, Mar. Micropalaeontol. 33, 157 (1998)]. Specimens of G. tumida with and without a thick gametogenic crust were picked separately and are interpreted as representing thermocline and deep planktonic habitats, respectively. Designation of Dentoglobigerina altispira as a thermocline calcifier differs from some earlier suggestions but follows Pearson and Shackleton, as well as B. N. Opdyke and P. N. Pearson [Proc. Ocean Drilling Program, Scientific Results 144, 993 (1995)].
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project. A standard solution of NBS SRM 951 prepared in a CaCO₃ matrix yielded an average ¹¹B/¹⁰B ratio of 3.9873 (±0.3 per mil; n = 30) compared with a value of 4.0527 (±0.2 per mil; n = 105) obtained for this standard by the Cs₂BO₂⁺ method [J. K. Aggarwal and M. R. Palmer, *Analyst* **120**, 1301 (1995)]. All data in Table 1 are reported as δ^{11} B, where

$$\delta^{11}B = \left[\frac{({}^{11}B/{}^{10}B)_{sample}}{({}^{11}B/{}^{10}B)_{standard}} - 1\right] \times 1000 \text{ and } {}^{11}B/{}^{10}B_{standard}$$

= 3.9873. Seventeen analyses of 2 μ l of open ocean water yielded a $\delta^{11}B$ value of $+39.7\pm0.3$ per mil. No results have been excluded and the average $\delta^{11}B$ values for each sample include all the data for that sample (Table 1).

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Low-Field Electron Emission from Undoped Nanostructured Diamond

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Strong and sustained electron emission at low electric fields was observed in undoped, nanostructured diamond. Electron emission of 10 milliamperes per square centimeter was observed at applied fields of 3 to 5 volts per micrometer. These are the lowest fields ever reported for any field-emitting material at technologically useful current densities. The emitter consists of a layer of nanometer-size diamond particulates, which is heat-treated in a hydrogen plasma. These emission characteristics are attributed to the particles' high defect density and the low electron affinity of the diamond surface. Such emitters are technologically useful, because they can be easily and economically fabricated on large substrates.

Cold-cathode electron field emitters are potentially useful for field emission displays and other vacuum microelectronic devices (1). Although typical metal (such as molybdenum) or semiconductor (such as silicon) emitters have high work functions, diamond can possess a negative electron affinity (NEA) surface (2, 3) that, in principle, allows its surface to emit electrons under low electric fields (4-10). This eliminates the complicated and costly process of fabricating sharp microtips to provide geometric field enhancement. The excellent mechanical and chemical stability of diamond also yields highly durable and reliable emitters, even under extreme conditions.

It is generally thought that undoped diamond is unable to produce sustained electron emission due to its insulating nature. Electron emission from surface states in diamond can occur (11), but there are no obvious mechanisms by which electrons can be transported through the undoped bulk to the surface states. Either the bulk or the surface of diamond must be made conductive. Additional-

*To whom correspondence should be addressed. Email: wzhu@lucent.com ly, the Fermi level must be near the conduction band to allow effective emission, which can be accomplished either by *n*-type doping as reported by Koizumi *et al.* (12) or by introducing defects into the diamond, as we have done here. Although *p*-type diamond can readily be made by boron doping, it does not emit well because the electrons reside deep (>5 eV) below the vacuum level.

We report that strong and sustained electron emission at low applied fields is obtained from undoped diamond using ultrafine, nanoand 1 μ A/cm² at 1 to 2 V/ μ m. Such low field electron emission has been achieved at current densities that are of interest to major technological applications, such as field emission displays. We attribute this emission behavior to the inherently defective structure of nanostructured diamond and the low electron affinity of the diamond surface. As has been pointed out (7, 13), structural defects play an important role in lowering the required emission field for undoped or *p*-type doped diamond, because they form energy bands within the bulk band gap, thus elevating the Fermi level and reducing the energy

structured particulates. The emitters produce

10 mA/cm² at applied fields of 3 to 5 V/ μ m,

be emitted. We used commercially available, 10- to 100-nm micropolycrystalline diamond particles produced by explosive synthesis, which are available as dispersed aqueous suspension. X-ray diffraction patterns show broadened diamond peaks, and each of the particles actually consists of many 1- to 20-nm crystallites and associated grain boundaries. The material is defective because of the presumed rapid growth rate and the incomplete structural evolution limited by the size (14). These particles are smaller than the diamond grit used by Geis et al. (10) in their nickel/cesium-coated emitter experiments. We used no metals in our emitters.

barrier that electrons must tunnel through to

The dispersed diamond was attached to an n-type silicon substrate as a thin, uniform layer by a simple spraying or brushing technique. The layer was dried at ambient temperature, then subjected to a hydrogen plasma treatment at a temperature of 650°C and a pressure of 20 torr for 1 hour. Neither the as-deposited layer nor the structure that was heat treated in a high-purity hydrogen or argon gas atmosphere gave any measurable emission at reasonable fields. A thin and



Fig. 1. (A) SEM taken at an angle to show both the top and the cross-section of the emitter and (B) TEM of the nanostructured diamond.



Fig. 2. Emission *I-V* curves from the nanostructured diamond emitters. This is a collection of many sets of data obtained over an anodecathode distance range between 372.9 μ m and 171.6 μ m at a step size of 3.3 μ m.

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