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Seawater pH control on the boron isotopic composition of calcite: Evidence from inorganic calcite precipitation experiments

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Abstract—Experiments involving boron co-precipitation with calcite have been carried out inorganically under controlled pH conditions (7.9 ± 0.05, 8.3 ± 0.05 and 8.6 ± 0.05) to determine the dependence of the boron isotopic composition ($\delta^{11}B$) of calcite on the pH of seawater. Another purpose of these experiments was to estimate the magnitude of the biogenic influence on the $\delta^{11}B$ value of foraminifera by comparing their boron isotopic composition with that of the inorganic calcite over a common pH range. The results show a clear relationship between $\delta^{11}B$ of inorganic calcite and the pH of artificial seawater. The variation of boron isotopic fractionation between seawater and calcite with pH, estimated from these experiments, is similar to that estimated for cultured *O. universa* and the theoretically predicted trend. The results also support the hypothesis that $B(OH)_4^-$ is the dominant species incorporated into the calcite structure. However, the boron isotopic fractionation between seawater and inorganic calcite is lower than that estimated for *O. universa* indicating the presence of a biogenic effect on the boron isotopic composition at least of this species of foraminifera. Most importantly, the results imply that in spite of a small biogenic influence on the boron isotopic composition of foraminifera, the variation in $\delta^{11}B$ of foraminiferal shells with pH (at least for *O. universa*) is comparable to that for inorganic calcite, supporting the potential of this isotopic signature in foraminifera as a reliable paleo pH proxy. *Copyright © 2000 Elsevier Science Ltd*

1. INTRODUCTION

Several studies have attempted to reconstruct past oceanic pH using the boron isotopic composition ($\delta^{11}B$) of foraminifera (Pearson and Palmer, 1999; Palmer et al., 1998; Sanyal et al., 1995; Sanyal et al., 1997; Spivack et al., 1993). These studies have clearly shown that, if indeed the underlying assumptions of the boron isotope paleo-pH proxies are true, then the variations in ocean pH, as measured by this technique, indicate significant changes in the global carbon cycle, on both short and long time scales.

The application of boron isotopes to paleo-pH determination relies on a large predicted isotopic fractionation between the two aqueous species of boron in seawater, $B(OH)_3$ and $B(OH)_4^-$, and the pH dependence of their relative abundance. As the relative proportion of these species changes with pH, so also must their respective isotopic compositions (Fig. 1). It has been assumed by most workers that a 20‰ fractionation between the two aqueous boron species, calculated by Kakihana et al. (1977), is valid for the natural system and that only the charged species $(B(OH)_4^-)$ is incorporated into carbonate minerals with insignificant fractionation during uptake (Hemming et al., 1995; Hemming and Hanson, 1992). Furthermore it has generally been assumed that there is no significant biogenic effect on the boron isotopic composition of foraminifera. Based on these assumptions, the calculated $\delta^{11}B$ vs. pH relationship

for the $B(OH)_4^-$ species has been commonly used to directly estimate the ocean pH from $\delta^{11}B$ of foraminifera and other marine calcite (Pearson and Palmer, 1999; Palmer et al., 1998; Hemming et al., 1998; Sanyal et al., 1995; Sanyal et al. 1997).

Recent interest in implementation of this tool highlights the need to test the underlying assumptions of this proxy. For example, even in the absence of a biogenic effect, there is no certainty that the $B(OH)_4^-$ vs. pH theoretical relationship accurately depicts the boron isotope systematics for calcite. This relationship can be tested by determining the fractionation between seawater and inorganic calcite. In addition, laboratory culture experiments indicate that biogenic carbonates precipitate from a microenvironment that has significantly different chemical and isotopic characteristics from that of bulk ocean water (Spero and Lea, 1996; Spero and Lea, 1993; McConnaughey, 1989a,b). Sanyal et al. (1996) conducted a culture study of the species *O. universa* and demonstrated a strong control by ocean pH on the boron isotopic composition of this species of foraminifera. However, biogenic effect on boron isotopic composition cannot be ruled out for all species of foraminifera. To accurately extract a paleo-pH signature from foraminifera, the biogenic effect for any species of interest must be quantified.

Here, we present results that assess the validity of the assumptions underlying the boron isotope paleo-pH proxy. Our calcite-boron coprecipitation experiments quantify the pH vs. $\delta^{11}B$ relationship of inorganic calcite over a pH range covering a significant portion of that seen in the modern and, probably, ancient ocean pH (7.9–8.6). In addition, the results now allow us to quantify the biogenic influence on $\delta^{11}B$ for the species *O.*

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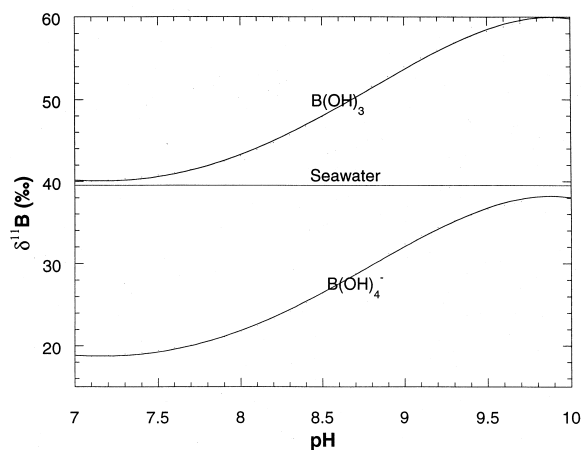
Fig. 1. Calculated relationship between pH and $\delta^{11}B$ of the two dominant aqueous species of boron ($B(OH)_3$ and $B(OH)_4^-$)

Table 1. Boron isotopic composition and concentration of inorganic calcite.

pH	Duration of expt. (hrs)	$\delta^{11}B^a$ (‰)	$[B]^b$ (ppm)
7.9	~24		
Run 1		-19.3 ± 0.3	33.9 (~102)
Run 2		-19.2 ± 0.3	35.2 (~105)
8.3	~12		
Run 1		-16.8 ± 0.3	49.1 (~147)
Run 2		-16.9 ± 0.5	46.4 (~138)
8.6	~3		
Run 1		-13.8 ± 0.7	86.6 (~261)
Run 2		-13.7 ± 0.5	82.6 (~246)

[a] Errors are expressed at $2\sigma_{mean}$.
[b] Boron concentration in composite calcite (seeds + overgrowth). Numbers in parentheses represent boron concentration in overgrowth estimated based on the boron concentration in seeds (~0.4 ppm) and amount of calcite overgrowth (~33%). Since the boron concentration in the seeds is very low, the boron concentration in the overgrowth is approximately three times that of composite calcite. Precision of isotopic dilution abundance measurements is ±5%.
$\delta^{11}B$ (‰) = $(R_s/R_{std} - 1)*1000$, $R_s = {}^{11}B/{}^{10}B$ of sample, $R_{std} = {}^{11}B/{}^{10}B$ of SRM 951 boric acid std.
Artificial Seawater = 1.02 ± 0.4‰.

universa, and we provide a reference curve against which the biogenic influence of other species may be evaluated.

2. EXPERIMENTAL METHODS

Steady state calcite precipitation onto calcite seeds was carried out in a pH-stat system using Mg free artificial seawater with an ionic strength similar to that of natural seawater (I = 0.7). The boron concentration (74 ppm) in the artificial seawater was approximately 17 times that of natural seawater (~4.5 ppm) in order to have adequate quantities of boron in the samples for mass spectrometric analyses (approximately 2–3 ng of B is needed for each run).

The experiments were carried out at ambient laboratory temperature in a 1L glass beaker that was sealed to prevent CO_2 gas exchange and stirred at a constant rate using a floating stir-bar to prevent seed damage. The temperature fluctuations during the course of the experiments (typically a few degrees or less) are thought to have minimal effect compared to pH on isotopic fractionation between the two aqueous species of boron as well as between the dissolved and adsorbed species of boron (<0.5‰; Palmer et al., 1987; Kakihana et al., 1977). The experiments were conducted at pH values of 7.9 ± 0.05, 8.3 ± 0.05 and 8.6 ± 0.05, and duplicate experiments were carried out at each pH value. The pH electrode was calibrated before every run with NBS buffers for pH values of 4, 7 and 10. The reported errors are based on the variation in the measured pH of standard buffers at the start and end of the longest precipitation run (pH = 7.9; ~24 h). Before the start of each run, the pH of the artificial seawater was adjusted to the desired level by adding acid/base (HCl/NaOH). The Ca concentration was also adjusted but nevertheless differences in saturation state with respect to calcite resulted for the different pH solutions. However, the supersaturation was never high enough to cause spontaneous precipitation in these metastable solutions during the experiments, and calcite precipitation was triggered by adding calcite seeds (~200 mg, B conc. ~ 0.4 ppm) to the artificial seawater. The pH of the system was monitored continuously throughout the experiment and maintained at a constant value throughout the experiment by adding 12.5 mM Na_2CO_3 as a titrant via a computer controlled pH stat system. The amount of calcite precipitated was estimated from the total amount of titrant added. The experiment was terminated after precipitation of approximately 100 mg of calcite. The solution was filtered and the calcite crystals were washed thoroughly in deionized water and dried. X-ray diffraction analyses performed on the final seed material confirmed that the overgrowth was calcite; no aragonite was detected. SEM images of the product showed no evidence of secondary nucleation.

The $\delta^{11}B$ value of the inorganic calcite was determined by negative thermal ionization mass spectrometry (NTIMS) following the procedure developed by Hemming and Hanson (1994). Boron concentrations

in the calcite and that in the solution were determined by isotopic dilution.

3. RESULTS AND DISCUSSION

3.1. Boron Isotopic Composition

The $\delta^{11}B$ values of the inorganic calcite precipitated at pH 7.9, 8.3, and 8.6 from artificial seawater are reported in Table 1 and shown in Figure 2a. The $\delta^{11}B$ of artificial seawater is 1.02 ± 0.4‰ and is assumed to be constant during each run as the amount of boron removed is too small to have any measurable effect. The $\delta^{11}B$ values of precipitated inorganic calcite increases systematically as pH increases, from ≈ -19.2‰ at pH 7.9 to ≈ -13.7‰ at pH 8.6. Hence, these results strongly support the fundamental assumption of using boron isotopes as a paleo pH proxy, i.e., the boron isotopic fractionation between calcite and seawater decreases with increasing pH.

The $\delta^{11}B$ vs. pH trend of inorganic calcite parallels the isotopic curves of the two aqueous species calculated based on ~20‰ fractionation between $B(OH)_3$ and $B(OH)_4^-$ (Kakihana et al., 1977). Also, the $\delta^{11}B$ vs. pH curve of inorganic calcite lies much closer to that of $B(OH)_4^-$, but slightly below it by 2–3‰ (Fig. 2b). The similarity between the $\delta^{11}B$ values of the calcite and the $B(OH)_4^-$ curve (just a 2–3‰ difference in comparison to the ~20‰ difference between the $B(OH)_3$ and $B(OH)_4^-$ curves) suggests that $B(OH)_4^-$ is the dominant species incorporated into calcite. This supports the conclusion of Hemming and Hanson (1992) and Hemming et al. (1995), who found that the boron isotopic compositions of biogenic marine calcite and that of synthetic calcite coincide almost exactly with the calculated $B(OH)_4^-$ isotopic curve at pH 8. However, the offset between the $\delta^{11}B$ vs. pH curve calculated for $B(OH)_4^-$ species and that determined for inorganic calcite indicate that, contrary to assumptions in most paleo-pH reconstructions, the calculated $B(OH)_4^-$ curve is not applicable to seawater-inor-
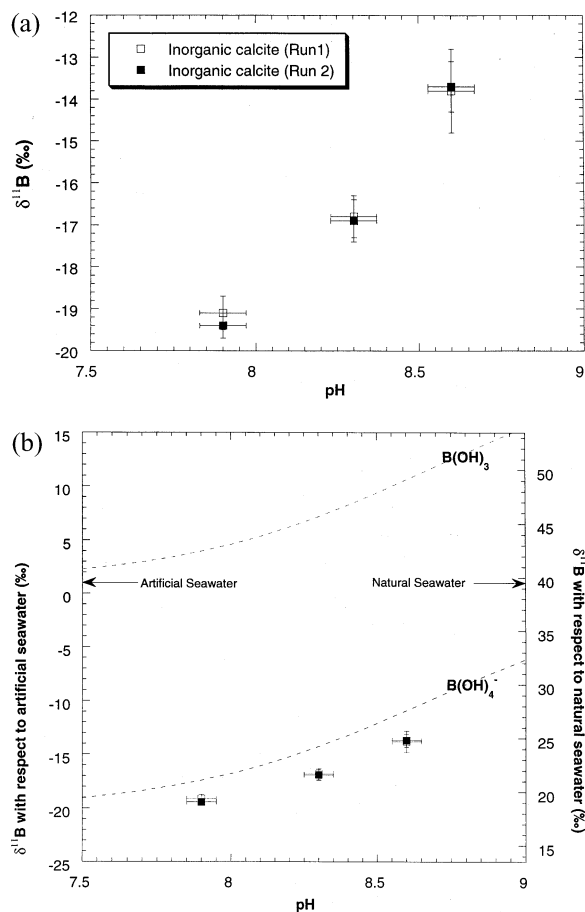
Fig. 2. (a) $\delta^{11}B$ of inorganic calcite precipitated under controlled lab conditions at pH values of 7.9 ± 0.05, 8.3 ± 0.05, 8.6 ± 0.05. Data are plotted for two runs carried out at each pH value. Fig. 2b. Plot showing the boron isotopic composition of inorganic calcite and the two aqueous species of boron with respect to boron isotopic composition of both natural (39.5‰) and artificial seawater (1.02‰). A fractionation of 20‰ has been assumed between the two aqueous species based on calculations by Kakihana et al. (1977).

is difficult to accurately evaluate this aspect due to uncertainty about the $B(OH)_4^-$ curve that is applicable to seawater. This is because the exact dissociation constant of boric acid in natural seawater is not well known (Dickson, 1990; Lyman 1956). Furthermore, it is not certain how applicable the calculated isotopic fractionation between the two aqueous species of boron is to the natural system (Kakihana et al., 1977).

The difference between our curve for inorganic calcite and the value determined by Hemming et al. (1995) at pH 8 is less easily explained. As we noted, the $\delta^{11}B$ value of their inorganically precipitated calcite ($\sim -16.7‰$) lies almost exactly on the calculated $B(OH)_4^-$ isotopic curve of Kakihana et al. (1977) at pH 8. The $\delta^{11}B$ curve for our inorganic calcites parallels this calculated $B(OH)_4^-$ isotopic curve but lies 2–3‰ below it. A possible explanation for this difference may lie in the experimental methods used in each study. Hemming et al. (1995) synthesized their calcite using a batch reactor based on the modified free-drift method described by Gruzensky (1967), in which the solution was not stirred. The pH was measured periodically over the growth period of $\sim$2 weeks. Vertical pH gradients have been noted in similarly designed systems (e.g., Paquette and Reeder, 1995). Although the experimental system used by Hemming et al. (1995) was not identical to that of Paquette and Reeder (1995), it is possible that pH gradients may have existed in the former study and could account for the difference in boron isotopic compositions between the inorganic calcites. In the present work, we used a pH-stat system in which pH was monitored continuously throughout the experiment. We believe pH gradients were unlikely in our rapidly stirred, steady-state reactor.

3.2. Implications for $\delta^{11}B$ of Carbonates a pH Recorders

The usefulness and simplicity of the boron isotopic composition of foraminifera as a paleo pH tool depend on the relative importance of biogenic and inorganic control on the $\delta^{11}B$ value of foraminifera, yet there is not a clear understanding of the biogenic influence on the boron isotope systematics in the calcifying microenvironment. To estimate the magnitude of the biogenic role in controlling the $\delta^{11}B$ of foraminifera we have compared the seawater–O. universa fractionation (determined from culture experiments, Sanyal et al., 1996) with the seawater–inorganic calcite fractionation. Figure 3 shows that there is a constant offset of about 1‰ between these curves, with O. universa isotopically lighter. This offset suggests the existence of a minor biogenic influence on the boron isotopic composition of this species of foraminifera. Even with a biological effect, however, there are two reasons to conclude that the $\delta^{11}B$ values of foraminiferal carbonate are clearly related to seawater pH. Firstly, the biologically induced contribution appears to be a small component of the total fractionation between seawater and calcite, about 1‰ out of a total fractionation of 16–20‰ over the pH range of our study. Secondly, the pH vs. $\delta^{11}B$ curves are closely parallel for both inorganic calcite and biogenic calcite, suggesting that the existence of a minor biological effect does not mask the effect induced by changing the seawater pH. Any biological influence on the $\delta^{11}B$ value, such as a change in the local pH due to a foram microenvironment, does not conceal the effect of a change in the bulk seawater pH,

ganic calcite fractionation and hence cannot be directly applied to determine pH from $\delta^{11}B$ of all marine calcite.

In trying to understand the boron isotope systematics in calcite, it is also important to consider the influence of growth rate on the boron isotopic fractionation between calcite and seawater. In our experiments, it required approximately 24, 12, and 3 h to precipitate 100 mg of calcite on 200 mg of seed at pHs 7.9, 8.3, and 8.6, respectively, resulting in roughly a factor of eight increase in growth rate from pH 7.9 to 8.6. Rapid reactions involving isotope exchange, including crystallization, may be susceptible to kinetic effects by preferentially fractionating the lighter isotope into the reaction product (Turner, 1982). If any such kinetic fractionation affected our results for inorganic calcite growth, it would be expected that, with increasing growth rate and therefore increasing pH, the $\delta^{11}B$ values would deviate increasingly from the trend parallel to the $B(OH)_4^-$ curve. As shown in Figure 2b, our values closely parallel the calculated curve suggesting that the difference in growth rates for our experiments had no discernible effect on the isotope systematics. However, it is important to note that it
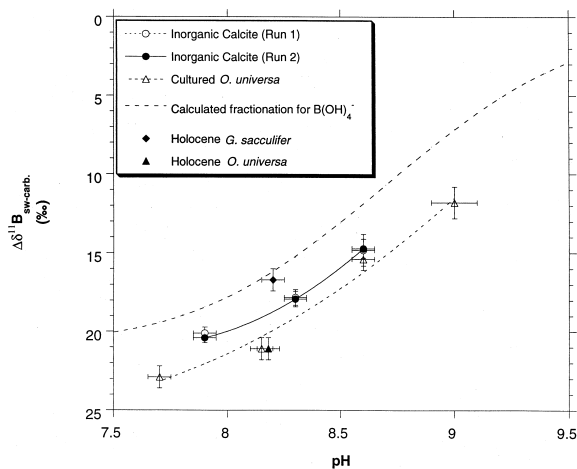
Fig. 3. Plot comparing the boron isotopic fractionation between seawater and inorganic calcite, cultured and Holocene *O. universa*, and Holocene *G. sacculifer* (Sanyal et al., 1996) at different pH values. Also shown are the theoretically calculated boron isotopic fractionation between seawater and the aqueous species $B(OH)_4^-$ over a range of pH.
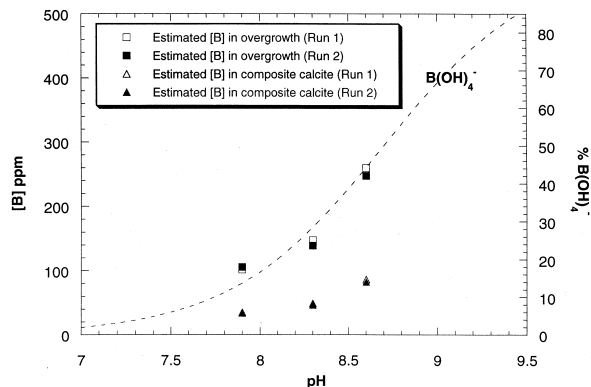

Fig. 4. Boron concentration in composite calcite consisting of both seed material and overgrowth formed by precipitation (triangles). Also shown are boron concentrations in the overgrowth estimated based on the boron concentration in seeds (~0.4 ppm) and amount of calcite overgrowth (~33%) during the course of the experiments (squares). Since the boron concentration in seeds is very low, the boron concentration in the overgrowth is approximately three times that of composite calcite.

making the foraminifera shells (or, at least *O. universa*) potential paleo-pH recorders.

A similar biogenic effect on the boron isotopic composition of foraminiferal shells has been identified in other species of planktonic foraminifera, e.g., *G. sacculifer* (Sanyal et. al., 1996). As for *O. universa*, the biologically induced isotopic fractionation for *G. sacculifer* is a small component of the total fractionation (~2‰; Fig. 3). However, comparative studies based on culture experiments, similar to that carried out for *O. universa*, are needed to confirm the robustness of this and other potential species. In this regard it is also important to check for any cultural artifact by comparing the boron isotopic composition of foraminifera cultured under ambient conditions with that of coretop foraminifera of the same species.

3.2. Boron Co-precipitation Behavior

Although the boron coprecipitation behavior was not the primary focus of our work, we comment briefly on the observed trend. The concentration of boron coprecipitated in the calcite overgrowths increased with solution pH, from ~100 ppm at pH 7.9 to ~250 ppm at pH 8.6 (Fig. 4). This observation is consistent with that of Hobbs and Reardon (1999) in which they estimated boron uptake in calcite over a pH range of 8.5–10.5. A rough comparison with the boron concentration of *O. universa* (Sanyal et al., 1996) is possible if we adopt a simplified distribution relation, $K_d^* = [B]_{cc}/[B]_{sw}$, where $[B]_{cc}$ and $[B]_{sw}$ are boron concentrations (in ppm) in calcium carbonate and seawater respectively. The K_d^* values for *O. universa* over the pH range 7.7–8.6 (1.4–1.5) fall within the range of values for inorganic calcite determined in the present work (1.4–3.4).

As suggested by Hobbs and Reardon (1999), the cause for the increased incorporation of boron at higher pH values could be related to the change in boron speciation (Fig. 4). At pH 7.9, the relative percentages of the species $B(OH)_3$ and $B(OH)_4^-$ are 91 and 9%, respectively; at pH 8.6 they are 68 and 32%. If

$B(OH)_4^-$ is the dominant boron species incorporated into calcite, as Hemming and Hanson (1992) suggested, this change in speciation toward greater $B(OH)_4^-$ at higher pH could explain the greater amount of boron incorporated into calcite. This is supported by the roughly parallel trends of boron concentration in the overgrowths and the relative abundance curve for the $B(OH)_4^-$ species in Figure 4.

Although we believe that the increase in incorporated boron with increasing pH can be explained largely by the change in speciation, we cannot rule out the possibility that other factors, including growth rate effects and surface charge of calcite (Hobbs and Reardon 1999; Morse and Bender, 1990), may play a role. Clearly, additional experiments would be necessary to evaluate the coprecipitation behavior more fully.

4. CONCLUSIONS

Inorganic calcite co-precipitation experiments clearly show that there is a strong control of pH on the $\delta^{11}B$ value of calcite. Using this trend as a baseline for comparison with biogenic calcite (*O. universa*), it can be inferred that the biogenic influence accounts for a small component of the entire fractionation between seawater and foraminiferal calcite. Also the similar $\delta^{11}B$ vs. pH trends for both inorganic and biogenic calcite clearly show that the calcifying microenvironment, though under biogenic influence, responds to changes in pH in the ambient seawater, making the foraminiferal $\delta^{11}B$ value (of at least the species *O. universa*) a seawater pH recorder. There is also a clear dependence of boron concentration in calcite on the pH of seawater.

REFERENCES

Dickson A. G. (1990) Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep Sea Res.* **37(5),** 755–766.

Gruzensky P. M. (1967) Growth of calcite crystals. In *Crystal Growth* (ed. H. S. Peiser), pp. 365–367. Pergamon.

Hobbs M. Y. and Reardon E. J. (1999) Effect of pH on boon coprecipitation by calcite: Further evidence for nonequilibrium partitioning of trace elements. *Geochimica. Cosmochim. Acta.* **63,** 1013–1021.

Hemming N. G., Guilderson T. P., and Fairbanks R. G. (1998) Seasonal variations in the boron isotopic composition of coral: A productivity signal? *Glob. Biogeochem. Cycles* **12,** 581–586.

Hemming N. G. and Hanson G. N. (1992) Boron isotopic composition and concentration in modern marine carbonates. *Geochim. Cosmichim. Acta* **56,** 537–543.

Hemming N. G. and Hanson G. N. (1994) A procedure for the isotopic analysis of boron by negative thermal ionization mass spectrometry. *Chem. Geolog.* **114,** 147–156.

Hemming N. G., Reeder R. J., and Hanson G. N. (1995) Mineral-fluid partitioning and isotopic fractionation of boron in synthetic calcium carbonate. *Geochim. Cosmochim. Acta* **59,** 371–379.

Kakihana H., Kotake M., Satoh S, Nomura M., and Okamoto M. (1977) Fundamental studies on the ion-exchange separation of boron isotopes. *Bull. Chem. Soc. Jap.* **50,** 158–163.

Lyman J. (1956) Buffer mechanisms of seawater. Ph.D. Thesis, University of California, Los Angeles.

McConnaughey T. (1989a) ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns. *Geochim. Cosmochim. Acta* **53,** 151–162.

McConnaughey T. (1989b) ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: II. In vitro simulation of kinetic isotope effects. *Geochim. Cosmochim. Acta* **53,** 163–171.

Morse J. W. and Bender M. L. (1990) Partition-coefficients in calcite-examination of factors influencing the validity of experimental results and their application to natural systems. *Chem. Geol.* **82,** 265–277.

Palmer M. R., Pearson P. N., and Cobb S. J. (1998) Reconstructing past ocean pH-Depth profiles. *Science* **282,** 1468–1471.

Palmer M. R., Spivack A. J., and Edmond J. M. (1987) Temperature and pH controls over isotopic fractionation during adsorption of boron on marine clay. *Geochim. Cosmochim. Acta* **51,** 2319–2323.

Paquette J. and Reeder R. J. (1995) Relationship between surface structure, growth mechanism, and trace element incorporation in calcite. *Geochim. Cosmochim. Acta* **59,** 735–749.

Pearson P. N. and Palmer M. R. (1999) Middle Eocene seawater pH and atmospheric carbon dioxide concentrations. *Science* **284,** 1824–1826.

Sanyal A., Hemming N. G., Hanson G. N., and Broecker W. S. (1995) Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature* **373,** 234–236.

Sanyal A., Hemming N. G., Broecker W. G., and Hanson G. N. (1997) Changes in pH in the eastern equatorial Pacific across stage 5–6 boundary based on boron isotopes in foraminifera. *Glob. Biogeochem. Cycles* **11,** 125–133.

Sanyal A., Hemming N. G., Broecker W. S., Lea D. W., Spero H. J., and Hanson G. N. (1996) Oceanic pH control on the boron isotopic composition of foraminifera: Evidence from culture experiments. *Paleoceanog.* **11,** 513–517.

Spero H. J. and Lea D. W. (1996) Experimental determination of stable isotopic variability in *Globigerina bulloides*: Implications for paleoceanograhic constructions. *Mar. Micropaleo.* **28,** 231–246.

Spero H. J. and Lea D. W. (1993) Intraspecific stable isotope variability in the planktic foraminifera Globigerinoides sacculifer: Results from laboratory experiments. *Mar. Micropaleo.* **22,** 221–234.

Spivack A. J., You C. F., and Smith H. J. (1993) Foraminifera boron isotope ratios as a proxy for surface ocean pH over the past 21 Myr. *Nature* **363,** 149–151.

Turner J. V. (1982) Kinetic fractionation of carbon-13 during calcium carbonate precipitation. *Geochim. Cosmochim. Acta* **46,** 1183–1191.