

Empirical relationship between pH and the boron isotopic composition of *Globigerinoides sacculifer*: Implications for the boron isotope paleo-pH proxy

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Abstract. Culture experiments were carried out with the planktonic foraminifera *Globigerinoides sacculifer* at three different pH values (7.6 ± 0.05 , 8.20 ± 0.05 , and 8.60 ± 0.05) in order to establish the pH dependence of the boron isotopic fractionation between the calcitic tests of *G. sacculifer* and seawater. Additional objectives were to compare the pH dependences of boron isotopic composition of *G. sacculifer* with that of *Orbulina universa* and inorganic calcite in order to evaluate the robustness of the boron isotope paleo-pH proxy. The relationship between the boron isotopic composition of *G. sacculifer* and the culture water pH shows heavier boron isotopic values at higher pH. This empirical relationship is similar but offset (by $\sim 3\%$) from that of *O. universa*, indicating the presence of biogenic influence ("vital effect") on the boron isotopic composition of foraminifera. However, comparison of the boron isotopic composition of *O. universa* and *G. sacculifer* with that of inorganic calcite grown over a common pH range shows that inorganic processes are the dominant control on the boron isotopic composition of foraminifera and the "vital effects" play a small but not insignificant role. The results imply that in spite of a small biogenic influence the variation in boron isotopic composition of foraminiferal shells with pH (at least for *O. universa* and *G. sacculifer*) is consistent with that for inorganic calcite, demonstrating the potential of this isotopic signature in foraminifera as a reliable paleo pH proxy.

1. Introduction

In the last few years, several studies have attempted to reconstruct past oceanic pH across different timescales using the boron isotopic composition ($\delta^{11}\text{B}$) of foraminifera [Sanyal et al., 1995, 1997; Spivack et al., 1993; Palmer et al., 1998; Pearson and Palmer, 1999; Sanyal and Bijma, 1999]. To evaluate the robustness of this paleo-pH proxy, both biogenic (planktonic foraminifera *O. universa*) and nonbiogenic (synthetic calcite) calcification experiments have been carried out under controlled pH conditions in the laboratory [Hemming et al., 1995; Sanyal et al., 1996, 2000]. The results of these studies provide strong evidence that the boron isotopic composition of the planktonic foraminifera *O. universa* is controlled primarily by seawater pH. As with other geochemical proxies (e.g., carbon and oxygen isotopes) in foraminifera, a biogenic effect on the boron isotopic composition of this species has also been identified. However, since it is a small component of the total seawater-calcite isotopic fractionation and is constant over the modern seawater pH range, the offset does not mask the influence of seawater pH on *O. universa* $\delta^{11}\text{B}$.

It has been suggested that if the boron isotope systematics of *O. universa* are representative of other foraminifera species, then the pH-boron isotope relationships would be parallel to each other with variable species-dependent offsets [Sanyal et al., 1996]. If so, one could estimate pH based on a common empirical $\delta^{11}\text{B}$ versus pH trend after correcting for the species-dependent offsets determined from natural samples. That would simplify the application of this paleo-pH tool significantly and preclude the need to conduct elaborate culture experiments for different species of interest.

To validate this theory, it is necessary to determine the $\delta^{11}\text{B}$ versus pH relationship of another planktonic foraminiferal species that is known to have a different biogenic influence on its $\delta^{11}\text{B}$ compared to *O. universa*. In this regard, *G. sacculifer* was identified as a suitable candidate as it has an offset of $\sim 3\%$ from *O. universa* [Sanyal et al., 1996, 1997]. In this paper we present the results of culture experiments conducted on *G. sacculifer* at three different pH values to verify if there is a common $\delta^{11}\text{B}$ versus pH trend preserved in foraminiferal calcite despite variable biogenic effect. The added importance of studying *G. sacculifer* is that it is widely used for tropical geochemical reconstructions, and an empirical $\delta^{11}\text{B}$ versus pH curve would enable a direct comparison of reconstructed ocean pH with other geochemical parameters such as $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Mg/Ca ratios.

2. Background

Boron exists in seawater primarily as $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$. The relative abundance of these two species is pH dependent. Because there is an isotopic fractionation between the two species, the boron isotopic composition ($\delta^{11}\text{B}$) of each aqueous species must also be pH dependent. The pattern of variation of $\delta^{11}\text{B}$ with pH for the two aqueous species is related to the

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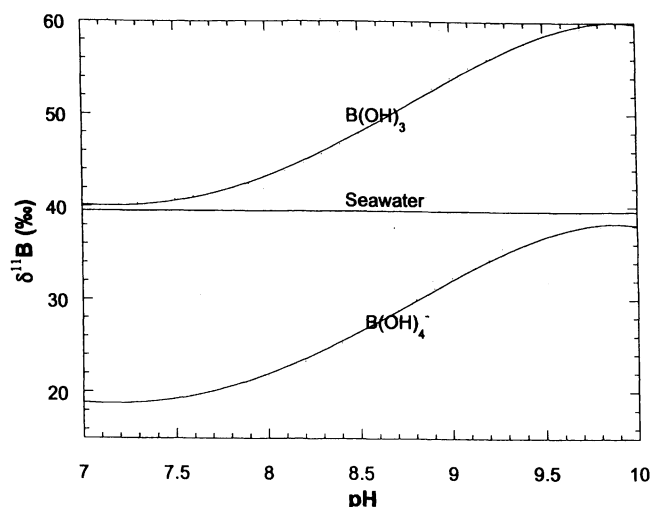


Figure 1. Calculated relationship between pH and $\delta^{11}\text{B}$ of the two dominant aqueous species of boron ($\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$).

magnitude of isotopic fractionation between the two species. *Kakihana et al.* [1977] calculated this fractionation for a temperature range of $0^\circ\text{--}60^\circ\text{C}$ and determined the value corresponding to 25°C as 0.981. Figure 1 shows the relationship between pH and $\delta^{11}\text{B}$ of the two species based on this fractionation factor.

It has been hypothesized in previous studies that $\text{B}(\text{OH})_4^-$ is the sole species being incorporated into carbonates [*Hemming and Hanson*, 1992]. If so, the boron isotopic composition of this species would mainly control the $\delta^{11}\text{B}$ of carbonates. However, there is inadequate knowledge about the exact $\delta^{11}\text{B}$ of the two aqueous species and the mode of incorporation of boron in marine carbonates [*Sen et al.*, 1994]. Thus it is difficult to theoretically determine the exact pH dependence of $\delta^{11}\text{B}$ of marine carbonates. This in turn makes it necessary to rely on empirical $\delta^{11}\text{B}$ versus pH relationships for paleo-pH estimations. As noted earlier, *Sanyal et al.* [2000, 1996] established empirical $\delta^{11}\text{B}$ versus pH relationships for *O. universa* and inorganic calcite. These studies show a parallel $\delta^{11}\text{B}$ versus pH relationship between *O. universa* and nonbiogenic carbonates with an offset of $\sim 1\text{--}2\%$ between the two. Also, the *O. universa* collected from modern sediments yield values identical to *O. universa* cultured under modern conditions, supporting the validity of the empirical $\delta^{11}\text{B}$ versus pH trend to the natural system [*Sanyal et al.*, 1996].

In this study we have determined the empirical $\delta^{11}\text{B}$ versus pH relationship of *G. sacculifer* through culture experiments and compared it with that for inorganic calcite and *O. universa*. The purpose is to better understand the boron isotope systematics in foraminifera and its potential as a reliable paleo-pH proxy.

3. Methods

3.1. Collection and Culturing

G. sacculifer were collected by scuba divers between end of March to early April from surface waters ~ 11.3 km south off La Parguera (Puerto Rico) and maintained in laboratory cultures at the University of Puerto Rico Isla Magueyes Marine Laboratory. We used established procedures for maintaining planktonic foraminifera in laboratory culture [*Bemis and Spero*, 1998; *Bijma et al.*, 1998; *Spero and Lea*, 1993]. Briefly, specimens were identified, measured with an inverted microscope, and transferred to $0.8\ \mu\text{m}$ filtered seawater, whose carbonate chemistry was accurately determined and subsequently modified. Specimens were maintained individually in air-tight 115 mL acid-cleaned jars that were sealed without an air space and placed into thermostated water tanks maintained at a temperature of 27°C ($\pm 0.2^\circ\text{C}$).

Illumination was provided by F24T12/CW/HO fluorescent bulbs on a 12:12 hour light:dark cycle. The average light intensity in the culture jars was $\sim 380\ \mu\text{mol photons m}^{-2}\ \text{s}^{-1}$, providing a sufficient photon flux for maximum photosynthetic rates (P_{max}) of the symbionts [*Spero and Parker*, 1985].

The foraminifers were fed a 1 day old brine shrimp (*Artemia*) nauplius (San Francisco Bay strain, Artemia Reference Center 1157) every third day until gametogenesis (generally after 6–8 days of culture). The brine shrimps were hatched in modified seawater from the same batch as used for culturing the foraminifera. Just prior to feeding, hatched nauplii were transferred once again to fresh medium from the same batch. After feeding, we did not refill the culture jars to avoid the possibility of contamination of water with that of slightly different carbonate chemistry. The CO_2 concentration in the head space is small compared to the total dissolved inorganic carbon (TCO₂) in the culture water and hence has little effect on the carbonate chemistry of the culture water.

Empty shells were collected within 24 hours after successful gametogenesis, rinsed in purified water, and archived in

Table 1. Carbonate Chemistry of Seawater used for Culture Experiments^a

pH	Total Alkalinity, $\mu\text{eq kg}^{-1}$	Total CO_2 , $\mu\text{mol kg}^{-1}$	CO_3^{2-} , $\mu\text{mol kg}^{-1}$	$p\text{CO}_2$, μatm	Total Boron, ppm
7.60 ± 0.05	2446	2069	69	1675	50.8
8.20 ± 0.05	3333	2045	232	423	50.8
8.60 ± 0.05	4769	2061	571	117	50.4

^aBoron concentration increased to ~ 10 times that of natural seawater. Approximately 75 shells were cultured at each pH.

covered slides for later analysis. We grew ~75 shells for each experimental pH. Culture water samples were collected at the start and end of the experiments to verify the boron concentration, its isotopic composition, and the carbon system parameters.

3.2. Artificial Seawater Chemistry

To establish an empirical relationship between pH and the boron isotopic composition ($\delta^{11}\text{B}$) of *G. sacculifer* tests, we modified seawater carbonate chemistry by keeping total CO_2 (TCO_2), temperature, salinity, and nutrient content nearly constant and letting pH and total alkalinity (TALK) vary (Table 1). We have used the carbonic acid dissociation constants of Mehrbach *et al.* [1973] and boric acid dissociation constant of Lyman [1956] so as to maintain a consistency with the carbonate chemistry estimations of Geochemical Ocean Sections Study (GEOSECS).

To reduce the number of specimens needed for isotopic analyses [see Sanyal *et al.*, 1996], we increased the boron concentration to ~10 times the concentration of natural seawater by adding boric acid to the seawater. The pH and TALK were then modified via titration with boron-free NaOH/HCl to bring the experimental pH to desired levels of 7.60 ± 0.05 , 8.20 ± 0.05 , and 8.60 ± 0.05 , respectively (Table 1). For comparison, pH in the surface waters was 8.2 ± 0.05 during our field campaign. Culture water samples collected at the start and at the end of each experiment showed that pH remained nearly constant throughout each experiment. Seawater pH was determined potentiometrically (on the NBS scale) whereas TALK and TCO_2 were determined by titration and coulometry, respectively. In this regard, it is noteworthy that while the boron alkalinity in artificial seawater was significantly higher (due to higher boron concentration) than that in natural seawater, the $\text{B}(\text{OH})_4^-/\text{B}(\text{OH})_3$ ratio is same in both at common pH values.

3.3 Stable Boron Isotope Analysis

The number of chambers built in the laboratory was determined by measuring the shells after gametogenesis and comparing it with its initial size. Chambers secreted during the experiments were amputated from the shell whorl and pooled, independent of chamber position, to provide enough material for boron isotope analyses (one to four chambers depending on size). The pooled chambers and the remaining amputated shells were crushed and soaked in 10% sodium hypochlorite solution for at least 24 hours. They were then washed thoroughly with quartz-distilled water and dissolved in ~15–20 μL

2 N HCl for complete dissolution. The dissolved sample was then loaded directly on a Re filament using a 1 μL pipette and dried under an infrared lamp in a laminar flow hood.

Boron isotopic compositions were determined by negative thermal ionization mass spectrometry (NTIMS) following the procedure outlined by Sanyal *et al.* [1996, 1997]. To check the reproducibility of our procedure and decrease our analytical uncertainty, we ran each sample a minimum of three times. The boron isotopic compositions of cultured *G. sacculifer* and modified seawater are listed in Table 2. The errors are expressed as $2\sigma_{\text{mean}}$.

4. Results and Discussion

The results of these experiments clearly show the dependence of *G. sacculifer* $\delta^{11}\text{B}$ on the pH of seawater. The boron isotopic fractionation between *G. sacculifer* and seawater decreases systematically as pH increases, from 19.9‰ at pH 7.6 to 12.1‰ at pH 8.6 (Table 2). The *G. sacculifer* $\delta^{11}\text{B}$ versus pH trend is also similar to that established for *O. universa* in laboratory experiments [Sanyal *et al.*, 1996] (Figure 2). The culture result at ambient pH (8.20 ± 0.05) is consistent with previous measurements made on Holocene *G. sacculifer* [Sanyal *et al.*, 1995]. This indicates that the experimental $\delta^{11}\text{B}$ values have not been significantly affected by higher boron alkalinity in artificial seawater (due to higher boron concentration) or by any other culture artifact in the laboratory. Hence the results from these two species support the fundamental assumption that the boron isotopic fractionation between seawater and foraminifera decreases with increasing pH.

In order to better understand the boron isotope systematics in foraminifera the empirical $\delta^{11}\text{B}$ versus pH relationship of *G. sacculifer* has been compared with previously determined $\delta^{11}\text{B}$ versus pH relationships of inorganic carbonates [Sanyal *et al.*, 2000] and *O. universa* [Sanyal *et al.*, 1996, Figure 2]. The parallel trend of $\delta^{11}\text{B}$ versus pH relationship of both biogenic and nonbiogenic carbonates shows that as in the case of inorganic calcite, it is seawater pH that has dominant control on $\delta^{11}\text{B}$ of foraminifera.

However, offsets exist between the $\delta^{11}\text{B}$ of inorganic calcite and that of both *O. universa* and *G. sacculifer* at any common pH value. Furthermore, the *O. universa* offset is different from that of *G. sacculifer*. It is important to note that the $\delta^{11}\text{B}$ offset between *O. universa* and *G. sacculifer* is consistent with results from fossil record [Sanyal *et al.*, 1996, 1997] and hence not due to any artifact associated with culture experiments. This suggests the existence of a species-dependent biogenic

Table 2. Boron Isotopic Composition of *G. sacculifer* and Culture Solutions

pH	<i>G. sacculifer</i> $\delta^{11}\text{B}^a$, ‰	Seawater $\delta^{11}\text{B}^a$, ‰	Seawater- <i>G.sac</i> Fractionation $\Delta\delta^{11}\text{B}$, ‰
7.6	-26.8±0.2	-6.9±0.8	19.9±0.8
8.2	-23.9±0.4	-6.9±0.6	17.0±0.7
8.6	-18.4±0.2	-6.3±0.5	12.1±0.5

^aErrors are expressed as $2\sigma_{\text{mean}}$. $\delta^{11}\text{B}$ (‰) = $(R_s/R_{\text{std}} - 1) \times 1000$, $R_s = {}^{11}\text{B}/{}^{10}\text{B}$ of sample, $R_{\text{std}} = {}^{11}\text{B}/{}^{10}\text{B}$ of SRM 951 boric acid standard. Seawater standard = 39.6 ± 0.4 ‰.

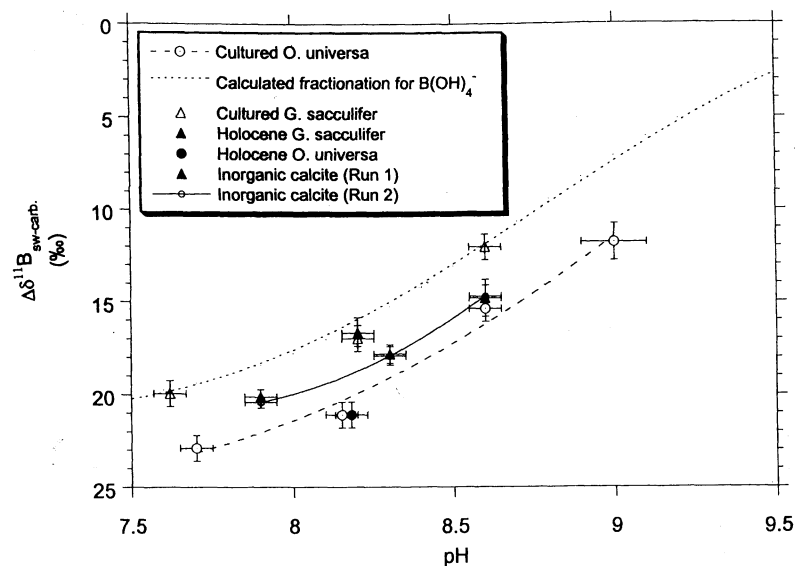


Figure 2. Plot comparing the boron isotopic fractionation ($\Delta\delta^{11}\text{B}$) between seawater and inorganic calcite, *O. universa* (cultured and Holocene [Sanyal et al., 1996]), and *G. sacculifer* (cultured and Holocene) at different pH values. Also shown are the theoretically calculated boron isotopic fractionation between seawater and the aqueous species $\text{B}(\text{OH})_4^-$ over a range of pH.

control on foraminiferal calcite $\delta^{11}\text{B}$ offset. It is known that the pH in the calcifying microenvironment of symbiotic foraminifera species has a significant diurnal variation, with higher pH during day and lower during night [Rink et al., 1998; Jorgensen et al., 1985]. In this regard, it could be speculated that the $\delta^{11}\text{B}$ offset between species could be due to different pH in the microenvironment and/or due to difference in the relative proportion of calcite precipitated during day and night [Lea et al., 1995; P. von Langen, University of California, Santa Barbara, unpublished data, 1998]. Additionally, in order to understand the $\delta^{11}\text{B}$ offsets it is important to estimate any kinetic effect associated with inorganic and/or foraminiferal calcite precipitation [Sanyal et al., 2000].

Pearson and Palmer [1999] suggested that the $\delta^{11}\text{B}$ offset of cultured *O. universa* could be a cultural artifact due to resorption of its juvenile trochospiral shell which formed under natural conditions. However, it is unlikely that it would have a significant contribution to the $\delta^{11}\text{B}$ offset as the resorbed chamber is lightly calcified and constitutes a small proportion of the total weight of the *O. universa* shell. Sanyal et al. [1996] estimated that even if 10% by weight of the *O. universa* shell came from the juvenile chambers, the error introduced would be much less than the errors of the analyses. This is further confirmed by the similarity between Holocene *O. universa* from natural environments and those cultured under ambient conditions [Sanyal et al., 1996].

As far as boron isotope paleo-pH proxy is concerned, the results of laboratory experiments with *G. sacculifer*, *O. universa*, and inorganic calcite [Sanyal et al., 1996, 2000] demonstrate that despite variable biogenic effect, $\delta^{11}\text{B}$ of foraminiferal calcite is controlled by seawater pH. The parallel $\delta^{11}\text{B}$ versus pH trend between the biogenic and nonbiogenic carbonates suggests that the existence of local pH variation in the calcifying microenvironment does not conceal the effect of a change in the bulk seawater pH. Furthermore, as is evident from Figure 2, the foraminifera-inorganic calcite offset (1-2‰) is a small component of the total $\delta^{11}\text{B}$ fractionation be-

tween seawater and calcite (~ 12-20‰) and is constant over seawater pH range, thus preserving the $\delta^{11}\text{B}$ versus pH relationship imposed by seawater pH.

It is noteworthy that empirical $\delta^{11}\text{B}$ versus pH curves for both biogenic and inorganic calcite plot close to the calculated $\text{B}(\text{OH})_4^-$ curve, indicating that the charged species is preferentially incorporated into the carbonates (Figure 2). A parallel offset, however, was identified between the theoretical $\text{B}(\text{OH})_4^-$ curve and the empirical $\delta^{11}\text{B}$ versus pH curve of both *O. universa* and inorganic carbonates. This suggests that the calculated $\text{B}(\text{OH})_4^-$ curve cannot be directly applied to estimate paleo-pH from the $\delta^{11}\text{B}$ of all carbonates. It is difficult to explain the offset between the theoretical $\text{B}(\text{OH})_4^-$ curve and the $\delta^{11}\text{B}$ of these carbonates due to a lack of knowledge about the exact dissociation constant of boric acid in natural seawater [Dickson, 1990; Lyman, 1956]. Furthermore, it is not certain how applicable the calculated isotopic fractionation between the two aqueous species of boron [Kakihana et al., 1977] is to the natural system. In this regard, it is noteworthy that the parallel trend between theoretical trend and the empirical curves suggests that the paleo-pH estimations in previous studies [Sanyal et al., 1995, 1997] based on the slope of the theoretical curves are consistent with that based on the empirical curves.

5. Conclusions

The results presented here convincingly show the dependence of $\delta^{11}\text{B}$ of *G. sacculifer* on the pH of seawater, making this species of foraminifera a reliable pH recorder. They also support the hypothesis that $\text{B}(\text{OH})_4^-$ species is the one preferred for incorporation into foraminiferal calcite. There is a clear biogenic influence on the $\delta^{11}\text{B}$ of *G. sacculifer*, but it does not mask the seawater-pH control on $\delta^{11}\text{B}$ of this species. All these findings are consistent with that for *O. universa* [Sanyal et al., 1996].

The findings of this study together with that of *O. universa* and inorganic calcite demonstrate the strong potential of $\delta^{11}\text{B}$ of foraminifera as paleo-pH indicators. Furthermore, if the boron isotope systematics of *G. sacculifer* and *O. universa* are representative of that of foraminifera in general, then the common empirical $\delta^{11}\text{B}$ versus pH trend of *O. universa* and *G. sacculifer* could also be used to estimate paleo-pH from $\delta^{11}\text{B}$ of other species after correcting for species-dependent offsets. Such offsets could be determined from coexisting species in sediments. It is critical to establish that the offset between species of interest is constant through time, and for that purpose, it would be necessary to analyze sediment samples from different time slices.

References

- Bemis, B. E., and H. J. Spero, Reevaluation of the oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations, *Paleoceanography*, 13(2), 150-160, 1998.
- Bijma J., C. Hemleben, B. T. Huber, H. Erlenkeuser, and D. Kroon, Experimental determination of the ontogenetic stable isotope variability in two morphotypes of *Globigerinella siphonifera* (d'Orbigny), *Mar. Micropaleontol.*, 35, 141-160, 1998.
- Dickson, A. G., Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K, *Deep Sea Res.*, 37(5), 755-766, 1990.
- Hemming, N. G., and G. N. Hanson, Boron isotopic composition and concentration in modern marine carbonates, *Geochim. Cosmochim. Acta*, 56, 537-543, 1992.
- Hemming, N. G., R. J. Reeder, and G. N. Hanson, Mineral-fluid partitioning and isotopic fractionation of boron in synthetic calcium carbonate, *Geochim. Cosmochim. Acta*, 59, 371-379, 1995.
- Jorgensen, B. B., J. Erez, N. P. Revsbech, and Y. Cohen, Symbiotic photosynthesis in a planktonic foraminiferan *Globigerinoides sacculifer* (Brady), studied with microelectrodes, *Limnol. Oceanogr.*, 30, 1253-1267, 1985.
- Kakihana, H., M. Kotaka, S. Satoh, M. Nomura, and M. Okamoto, Fundamental studies on the ion-exchange separation of boron isotopes, *Bull. Chem. Soc. Jpn.*, 50, 158-163, 1977.
- Lea D. W., P. A. Martin, D. A. Chan, H. J. Spero, Calcium-uptake and calcification rate in the planktonic foraminifer *Orbulina-universa*, *J. Foraminiferal Res.*, 25, 14-23, 1995.
- Lyman, J., Buffer mechanisms of seawater, Ph.D. thesis, Univ. of Calif., Los Angeles, 1956.
- Mehrbach, C., C. H. Culbertson, J. E. Hawley, and R. M. Pytkowicz, Measurement of apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, 18, 897-907, 1973.
- Palmer, M. R., P. N. Pearson, and S. J. Cobb, Reconstructing past ocean pH-Depth profiles, *Science*, 282, 1468-1471, 1998.
- Pearson, P. N., and M. R. Palmer, Middle Eocene seawater pH and atmospheric carbon dioxide concentrations, *Science*, 284, 1824-1826, 1999.
- Rink, S., M. Kuhl, J. Bijma, and H. J. Spero, Microsensor studies of photosynthesis and respiration in the symbiotic foraminifer *Orbulina universa*, *Mar. Biol.*, 131, 583-595, 1998.
- Sanyal, A. and J. Bijma, A comparative study of the northwest Africa and eastern equatorial Pacific upwelling zones as sources of CO₂ during glacial periods based on boron isotope paleo-pH estimation, *Paleoceanography*, 14, 753-759, 1999.
- Sanyal, A., N. G. Hemming, G. N. Hanson, and W. S. Broecker, Evidence for a higher pH in the glacial ocean from boron isopes in foraminifera, *Nature*, 373, 234-236, 1995.
- Sanyal, A., N. G. Hemming, W. S. Broecker, and G. N. Hanson, Changes in pH in the eastern equatorial Pacific across stage 5-6 boundary based on boron isotopes in foraminifera, *Global Biogeochem. Cycles*, 11, 125-133, 1997.
- Sanyal, A., N. G. Hemming, W. S. Broecker, D. W. Lea, H. J. Spero, and G. N. Hanson, Oceanic pH control on the boron isotopic composition of foraminifera: Evidence from culture experiments, *Paleoceanography*, 11, 513-517, 1996.
- Sanyal, A., M. Nugent, R. Reeder, and J. Bijma, Seawater pH control on the boron isotopic composition of calcite: Evidence from inorganic calcite precipitation experiments, *Geochim. Cosmochim. Acta*, 64, 1551-1555, 2000.
- Sen, S., J. F. Stebbins, N. G. Hemming, and B. Ghosh, Coordination environments of boron impurities in calcite and aragonite polymorphs: A ¹¹B MAS NMR study, *Am. Mineral.*, 79, 819-825, 1994.
- Spero, H. J., and D. W. Lea, Intraspecific stable isotope variability in the planktic foraminifera *Globigerinoides sacculifer*: Results from laboratory experiments, *Mar. Micropaleontol.*, 22, 221-234, 1993.
- Spero, H. J., and S. L. Parker, Photosynthesis in the symbiotic planktonic foraminifera *Orbulina universa*, and its potential contribution to oceanic primary productivity, *J. Foraminiferal Res.*, 15, 273-281, 1985.
- Spivack, A. J., C. F. You, and H. J. Smith, Foraminifera boron isotope ratios as a proxy for surface ocean pH over the past 21 Myr, *Nature*, 363, 149-151, 1993.

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