Vital effects in foraminifera do not compromise the use of $\delta^{11}B$ as a paleo-*p*H indicator: Evidence from modeling

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[1] The stable boron isotope composition ($\delta^{11}B$) of fossil foraminiferal shells is used as a paleo-*p*H recorder and is therefore one of the most promising paleocarbonate chemistry proxies ("paleoacidimetry"). One crucial question regarding this proxy is whether foraminifera record the *p*H of the bulk seawater or the *p*H of the microenvironment (diffusive boundary layer, ~500 μm), which is strongly influenced by life processes. Here we present a novel theoretical approach to address this question by using a diffusion-reaction model. Model results indicate that the $\delta^{11}B$ in planktonic foraminifera is primarily controlled by the *p*H of the microenvironment. We therefore predict that the $\delta^{11}B$ of different species (e.g., symbiont-bearing versus symbiont-barren) or of foraminifera grown in the dark and in the light should be offset from the $\delta^{11}B$ of inorganic calcite. This theoretical prediction was experimentally confirmed while this paper was written [*Hönisch et al.*, 2003]. Most importantly, the model predicts that this offset is constant over a wide *p*H range. Thus the use of $\delta^{11}B$ as a paleo-*p*H indicator is not compromised through vital effects as modeled here. *INDEX TERMS:* 1050 Geochemistry: Marine geochemistry (4835, 4850); 4255 Oceanography: General: Numerical modeling; 4267 Oceanography: General: Paleoceanography; 4806 Oceanography: Biological and Chemical: Carbon cycling; 4870 Oceanography: Biological and Chemical: Stable isotopes; *KEYWORDS:* stable boron isotopes, foraminifera, paleo-pH, vital effects, modeling

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1. Introduction

[2] Proxies for the marine paleocarbonate chemistry are much desired because of the coupling of ocean carbonate chemistry to the pCO_2 of the atmosphere which is a key climate variable. Over the past decade, stable boron isotopes ($\delta^{11}B$) in foraminifera have been established as a tool for reconstructing the *p*H of the paleocean [e.g., *Spivack et al.*, 1993; *Sanyal et al.*, 1995; *Palmer et al.*, 1998; *Pearson and Palmer*, 2000]. Briefly, the stable boron isotope-*p*H proxy works as follows. The stable isotope ^{11}B is enriched in $B(OH)_3$ compared to $B(OH)_4^-$ and the isotopic composition of the dissolved species change with *p*H (Figure 1). At low *p*H, the dominant species is $B(OH)_3$ and its isotopic composition is equal to the isotopic composition of the total dissolved boron, ~39.5‰. In contrast, at high *p*H the dominant species is $B(OH)_4^-$ and its $\delta^{11}B$ is ~39.5‰. In between, the $\delta^{11}B$ of both species change, with $B(OH)_3$ being enriched at equilibrium by ca. 20‰ [*Kakihana et al.*, 1977] with respect to $B(OH)_4^-$ at any *p*H. Based on the assumption that the charged species $B(OH)_4^-$ is incorporated into foraminiferal calcite, the $\delta^{11}B$ of calcite also increases with *p*H and a paleo-*p*H proxy is constructed. We refer to this as "paleoacidimetry."

[3] One of the fundamental assumptions underlying this proxy is that *p*H changes of the seawater in which the foraminifera lived left behind equivalent changes in the $\delta^{11}B$ of their shells. Using culture experiments, Sanyal and coworkers demonstrated that this is the case for the two planktonic species *Orbulina universa Globigerinoides sacculifer* [*Sanyal et al.*, 1996, 2001]. The $\delta^{11}B$ in these foraminifera increased with the *p*H of the culture medium as expected from theoretical considerations (Figure 2). These results corroborated the use of stable boron isotopes in planktonic foraminifera as a paleo-*p*H indicator.

[4] Although encouraging, the culture studies also showed significant offsets between the $\delta^{11}B$ of the two species and offsets from the theoretically expected $\delta^{11}B$, potentially indicating the influence of vital effects. Vital effects such as photosynthesis of the symbiotic algae, respiration of the host-symbiont system, and calcification can drastically alter the *p*H of the seawater in the close vicinity (microenvironment) of the foraminifer [*Wolf-Gladrow et al.*, 1999; *Zeebe et al.*, 1999; *Rink et al.*, 1998]. This may constitute a severe problem if the *p*H of the microenvironment ultimately determines the $\delta^{11}B$ of the calcite because this $\delta^{11}B$ can be very different from that reflecting the *p*H of the bulk seawater. Because the latter *p*H is required in paleoceanographic studies, one crucial issue yet to be addressed is the impact of vital effects on the $\delta^{11}B$ in planktonic foraminifera.

[5] In the current paper we use a diffusion-reaction model to investigate the influence of life processes on the $\delta^{11}B$ in planktonic foraminifera. The model has been shown to adequately calculate *p*H gradients in foraminifera by

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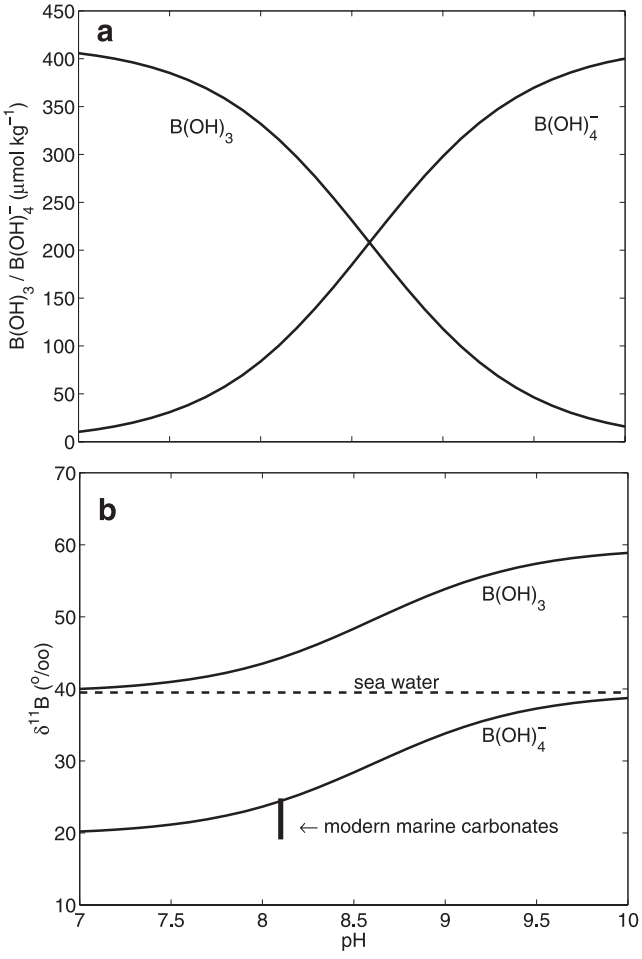

Figure 1. Basics of the boron isotope paleo-*p*H recorder [cf. *Hemming and Hanson*, 1992]. (a) Speciation of the dissolved forms of boron in seawater: boric acid ($B(OH)_3$) and borate ion ($B(OH)_3$), pK_B = 8.60 [*Dickson*, 1990]. (b) Stable boron isotope composition of $B(OH)_3$ and $B(OH)_4^-$. If the charged species $B(OH)_4^-$ is incorporated into foraminiferal calcite, the $\delta^{11}B$ of calcite increases with *p*H and can be used as a paleo-*p*H proxy.

comparison with results from *p*H measurements using microsensors (data kindly provided by B. B. Jørgensen) [cf. *Wolf-Gladrow et al.*, 1999]. Recently published information on the kinetics of the boric acid-borate equilibrium in seawater [*Zeebe et al.*, 2001] enables us to include the dissolved boron species $B(OH)_3$ and $B(OH)_4^-$, and the stable boron isotopes ^{11}B and ^{10}B into the model. In the following, the model is briefly introduced. Then we will show that the $\delta^{11}B$ in planktonic foraminifera is primarily controlled by the *p*H of the microenvironment. It is predicted that the $\delta^{11}B$ of different species (e.g., symbiont-bearing versus symbiont-barren) or of individuals of the same species grown in the dark and in the light should be offset from the $\delta^{11}B$ of inorganic calcite. We present experimental data [*Hönisch et al.*, 2003] which confirms this model prediction. The modeled offset from the inorganic calcite, however, is constant over a wide *p*H range. Finally, we will conclude that the use of $\delta^{11}B$ as a paleo-*p*H indicator is not compromised through vital effects as modeled here.

2. The Model

[6] The diffusion-reaction model is described in detail in *Wolf-Gladrow et al.* [1999]. Briefly, the model calculates the carbonate chemistry including the *p*H within the microenvironment of the foraminifer (diffusive boundary layer ~500 μm, see Figure 3). On this length scale, the concentrations of e.g., CO_2, HCO_3^-, CO_3^{2-}, OH^-, and H^+ are controlled by diffusion and reaction of these chemical species in response to disequilibria brought about by life processes of the foraminifer. For example, during photosynthesis in symbiont-bearing species, inorganic carbon is taken up by the symbiotic algae and the microenvironment becomes more alkaline, i.e., the *p*H increases. As a response, CO_2 diffusion from the bulk medium toward the shell and chemical conversion from HCO_3^- to CO_2 replaces the removed CO_2. After some seconds, a steady state will be established [*Jørgensen et al.*, 1985; *Rink et al.*, 1998].

[7] In the model, a steady state is assumed and the concentration profiles of the various chemical species in response to photosynthesis, respiration, and calcification are calculated. The appropriate diffusion-reaction equation reads:

$$0 = \frac{\partial [c_i(r,t)]}{\partial t} = \text{Diffusion}_i + \text{Reaction}_i + \text{Source/Sink}_i, \quad (1)$$

where $[c_i(r, t)]$ is the concentration of the chemical species c_i, r is the distance to the center of the foraminiferal

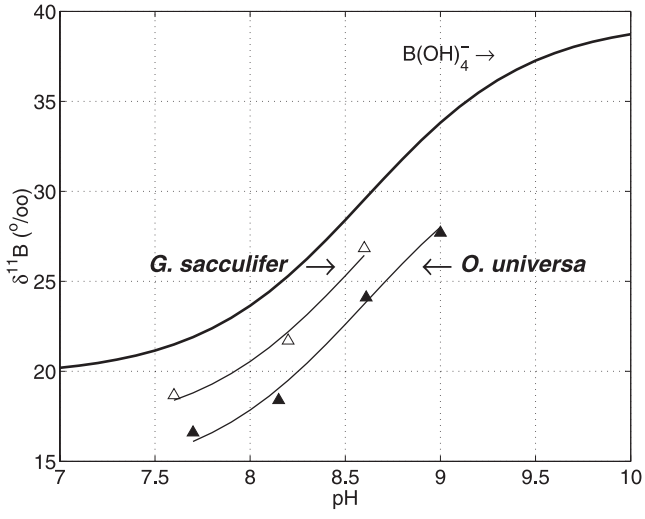

Figure 2. $\delta^{11}B$ of the planktonic foraminifera *G. sacculifer* (open triangles) and *O. universa* (closed triangles) as a function of *p*H determined in culture experiments [*Sanyal et al.*, 1996, 2001].

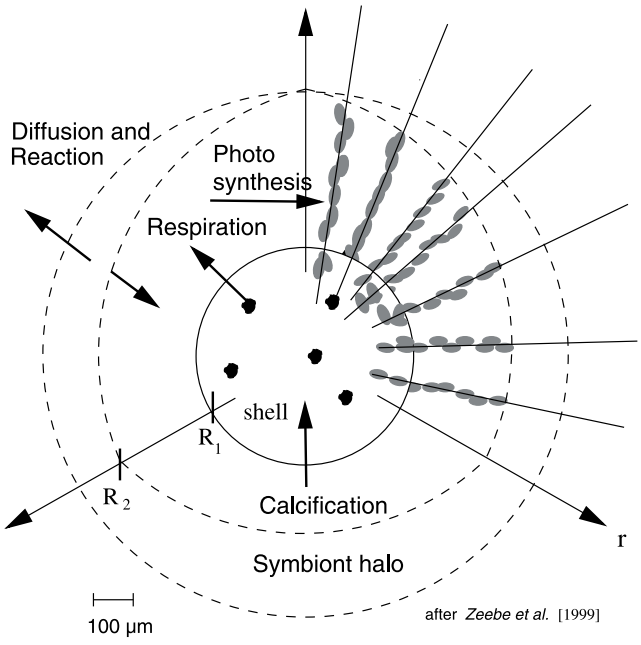

Figure 3. Schematic illustration of the model. The chamber of the foraminifer is assumed as spherical. Diffusion and reaction of chemical species, and life processes of the foraminifer such as photosynthesis, respiration, and calcification are considered in the model [see *Zeebe et al.*, 1999].

shell, and t is time. The chemical reactions considered are:

$$CO_2 + H_2O \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} HCO_3^- + H^+ \tag{2}$$

$$CO_2 + OH^- \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} HCO_3^- \tag{3}$$

$$CO_3^{2-} + H^+ \underset{k_{-5}}{\overset{k_{+5}}{\rightleftharpoons}} HCO_3^- \tag{4}$$

$$H_2O \underset{k_{-6}}{\overset{k_{+6}}{\rightleftharpoons}} H^+ + OH^- \tag{5}$$

$$B(OH)_3 + OH^- \underset{k_{-7}}{\overset{k_{+7}}{\rightleftharpoons}} B(OH)_4^-, \tag{6}$$

where ks are reaction constants and k_2 and k_3 have been omitted as conventionally used for other reactions [*Zeebe et al.*, 2001; *Zeebe and Wolf-Gladrow*, 2001]. For example, the diffusion-reaction equation for $^{11}B(OH)_4^-$ reads

$$0 = \frac{D_{B(OH)_4^-}}{r^2}\frac{d}{dr}\left(r^2\frac{d\left[^{11}B(OH)_4^-\right]}{dr}\right) + k_{+7}\left[^{11}B(OH)_3\right][OH^-] - k_{-7}\left[^{11}B(OH)_4^-\right] \tag{7}$$

where $D_{B(OH)_4^-}$ is the diffusion coefficient of $B(OH)_4^-$ [*Boudreau and Canfield*, 1993], assumed to be the same for $^{11}B(OH)_4^-$ and $^{10}B(OH_4^-$, and $k_{\pm 7}$ are the reaction constants of the reactions involving the heavy isotope ^{11}B [*Zeebe et al.*, 2001].

3. Model Results

[8] In an earlier paper, we have demonstrated that the model adequately describes the carbonate chemistry in the vicinity of foraminifera [*Wolf-Gladrow et al.*, 1999] and the details are not repeated here. In the following, we will rather briefly present a test case that involves *p*H profiles in foraminifera and then put our emphasis on describing model results for stable boron isotopes in foraminifera.

3.1. Test Case: *p*H Profiles in *G. sacculifer*

[9] Figures 4a and 4b show calculated *p*H profiles in the vicinity of the planktonic foraminifer *G. sacculifer* in the dark and in the light, respectively. The input data to the model are rates of photosynthesis, respiration, and calcification taken from O_2-microsensor measurements by *Jørgensen et al.* [1985] and ^{45}Ca uptake studies by *Anderson and Faber* [1984]. From the input data, the model calculates the carbonate chemistry including the *p*H in the microenvironment of the foraminifer which agrees very well with independent *p*H-microsensor data (diamonds in Figure 4) [see also *Wolf-Gladrow et al.*, 1999]. Note that HCO_3^- uptake for calcification is assumed here; CO_3^{2-} uptake is discussed in section 4.1.

[10] Figures 4c and 4d show the corresponding profiles of $\delta^{11}B_{B(OH)_4^-}$ which mirror the decrease and increase of *p*H toward the shell in the dark and in the light, respectively. The deviation of $\delta^{11}B_{B(OH)_4^-}$ at the shell from the bulk value is substantial and amounts up to 3.5‰ in the light. Obviously, the $\delta^{11}B_{B(OH)_4^-}$ at the shell is controlled by the *p*H at this site rather than by the *p*H of the bulk medium. This is an important issue because it determines whether the $\delta^{11}B$ corresponding to the bulk *p*H or to the *p*H of the microenvironment will be recorded in the calcite shells of foraminifera. For paleoceanographic studies the bulk seawater *p*H is, of course, the desired quantity. Because the *p*H of the microenvironment is surely different in different species, one runs into problems if one attempts to reconstruct, for example, absolute bulk *p*H values from mixed species assemblages.

3.2. Which *p*H is Recorded?

[11] Which *p*H is recorded in the calcite shell has to do with the speed of diffusion and chemical reaction between $B(OH)_3$, $B(OH)_4^-$, OH^-, and H^+. If the reaction is much quicker than diffusion, the concentrations of chemical species are in local equilibrium and are thus tightly coupled. Otherwise, they are independent of each other on this length scale. A measure of the relative importance of diffusion and reaction is the reacto-diffusive length scale, $\lambda = \sqrt{(D/k)}$, where D is the diffusion coefficient and k is the reaction constant. One may say that λ is the mean length a molecule diffuses before it reacts.

[12] Earlier we have studied the chemical kinetics of the boric acid-borate equilibrium in seawater [*Zeebe et al.*,

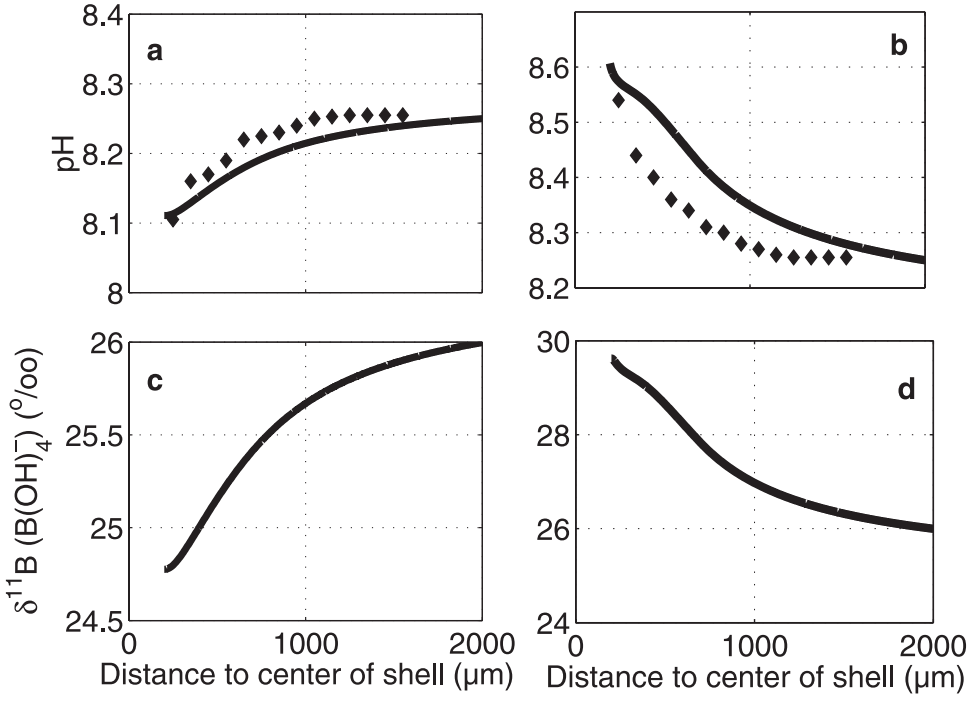

Figure 4. Modeled (solid lines) and measured (diamonds) *p*H profiles in *G. sacculifer* in the dark (a) and in the light (b) and corresponding modeled $\delta^{11}B_{B(OH)_4^-}$ profiles in the dark (c) and in the light (d). Microsensor *p*H transects were measured by B. B. Jørgensen and coworkers [cf. *Wolf-Gladrow et al.*, 1999].

2001]. The reaction constants given in that paper enable us to estimate the reacto-diffusive length scale as $\lambda \simeq 2$ μm (see Appendix A). Because this length is much smaller than the typical diffusive boundary layer, which is of the order of the radius of a foraminifer (∼300 μm), it is safe to say that the boron compounds and the *p*H are tightly coupled within the microenvironment. Thus the $\delta^{11}B$ recorded in the foraminiferal shell should reflect the *p*H of the microenvironment and not that of the bulk *p*H. As a result, symbiont-bearing species should be enriched in ^{11}B over symbiont-barren species because of the elevated *p*H that symbiont-bearing species "see" during photosynthesis in the light. Note that we have derived this conclusion in two different ways, firstly by integrating the full numerical model (Figure 4) and secondly by analytical means using λ.

3.3. Vital Effects in *G. Sacculifer* and *O. Universa*

[13] In our model test case for *G. sacculifer* (Figure 4), the $\delta^{11}B$ incorporated into the shell is about 1‰ lighter than the $\delta^{11}B_{B(OH)_4^-}$ of the bulk medium in the dark, and 3.5‰ heavier in the light. This corresponds to a *p*H of 8.1 and 8.6 at the foraminiferal shell, respectively. Assuming that the ratio of dark:light calcification in *G. sacculifer* is about 1:8 [*Anderson and Faber*, 1984], the final $\delta^{11}B$ of the shell would be ∼3.2‰ heavier than the $\delta^{11}B_{B(OH)_4^-}$ of the bulk seawater. In other words, the stable boron isotope ratio in *G. sacculifer* would reflect a *p*H of 8.55 rather than 8.25, the latter being the true bulk *p*H of the seawater.

[14] Can this offset explain the whole difference of about 3‰ observed between *G. sacculifer* and *O. universa* (Figure 2)? Taking into account that dark:light calcification in *O. universa* is about 1:3 [*Lea et al.*, 1995], and assuming that photosynthetic rates in *O. universa* are only 50 of those in *G. sacculifer* [*Rink et al.*, 1998], the final $\delta^{11}B$ in *O. universa* would be ∼1.6‰ lighter than the $\delta^{11}B$ in *G. sacculifer*. Thus our model explains about half of the observed $\delta^{11}B$ difference between the two species. Currently, we cannot offer an explanation for the other half.

3.4. Dark and Light Calcification: Comparison With Experimental Data

[15] While this paper was written, *Hönisch et al.* [2003] analyzed $\delta^{11}B$ data from culture experiments with *O. universa* grown under low-light and high-light conditions. We will now use these data to check whether model predictions and observations are consistent. In culture experiments, 140 individuals of *O. universa* were grown in otherwise natural seawater but with 10 times enriched boron concentrations, half of them under low-light conditions (∼20 μEin m^{-2} s^{-1}, 12 hours light:12 hours dark), the other half under high-light conditions (∼320 μEin m^{-2} s^{-1}, 12 hours light:12 hours dark). Figure 5 shows the measured $\delta^{11}B$ of the foraminiferal shells from the low-light and high-light experiments (closed and open star, respectively). Note that the offset of the experimental data from the x axis is chosen arbitrarily because the important quantity here is the difference between the low-light and high-light experiment but not the absolute value.

[16] The model was run to simulate conditions similar to those of the culture experiments. The radius of the model foraminifer is 250 μm; photosynthesis, respiration, and

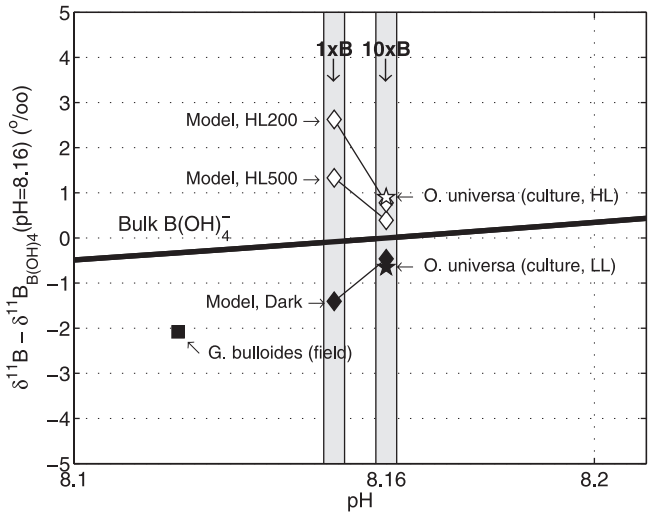

Figure 5. Comparison between results of culture experiments with O. universa under low-light and high-light conditions (closed and open star; *Hönisch et al.* [2003]) and model results (diamonds). The offset of the experimental data from the x axis is chosen arbitrarily (see text). The left column of diamonds on left gray bar are model results for natural seawater boron concentrations (1 × *B*), while the right column refers to 10 times enriched total boron concentrations (10 × B) as in culture experiments. Note that all model runs refer to bulk *p*H = 8.16 but are separated into two columns for clarity. Model results labeled by HL500 and HL200 refer to high-light conditions with an assumed symbiont halo thickness of 500 and 200 μm, respectively. The closed square shows one δ^{11}B measurement of calcite of the symbiont-barren species Globigerina bulloides from plankton tows [*Hönisch et al.*, 2003].

calcification rates are 0, 2, and 1 nmol C h^{-1} in the dark and 10, 2, and 3 nmol C h^{-1} in the light. The bulk *p*H value is 8.16, T = 22°C, S = 33.7. The results are indicated by the closed and open diamonds for the dark and high-light (12 hours light:12 hours dark) simulation, respectively. The δ^{11}B value of the calcite for high light was calculated using a dark:light calcification ratio of 1:3 [*Lea et al.*, 1995].

[17] First of all it is to emphasize that the model results for δ^{11}B for dark and high-light conditions are lighter and heavier than the δ^{11}B of bulk $B(OH)_4^-$, respectively. This follows directly from the elevated and reduced *p*H at the calcite shell during respiration and photosynthesis and is consistent with the experimental data. Now let us look at the details. It turned out that the calculated δ^{11}B of the shell is sensitive to the assumed thickness of the symbiont halo because this largely determines the magnitude of the *p*H elevation at the shell for a given photosynthesis rate. In order to demonstrate this sensitivity, model results for an assumed symbiont halo thickness of 500 and 200 μm under high light are shown in Figure 5 (open diamonds, labeled HL500 and HL200, respectively). The *p*H adjacent to the shell is higher for the denser symbiont halo (200 μm) which results in a δ^{11}B which is up to 1.5 higher than for the less dense symbiont halo.

[18] If the model is run with natural seawater boron concentrations (1 × B, left column of diamonds on left gray bar), the calculated offsets of shell δ^{11}B from the δ^{11}B of $B(OH)_4^-$ are much larger than the observed offsets for both low-light and high-light conditions. However, if the model is run with 10 times enriched total boron concentrations as in culture experiments (10 × B, right column of diamonds on right gray bar), the agreement between model and experiment is quite good. The reason for the smaller offsets at elevated boron concentrations in the model is as follows. The life processes of the foraminifer constitute a perturbation of the seawater carbonate chemistry equilibrium within the microenvironment, producing a steady state that deviates from equilibrium. The degree of deviation from equilibrium depends on the buffer present in solution. At 10 times higher boron concentrations the buffer provided by the conversion between $B(OH)_3$ and $B(OH)_4^-$ is significant and any large perturbation of the carbonate system is suppressed. As a result, at elevated boron concentrations the *p*H difference between microenvironment and bulk medium is reduced and so is the difference in δ^{11}B.

[19] Also shown in Figure 5 is one δ^{11}B measurement of calcite of the symbiont-barren species *Globigerina bulloides* (closed square) from plankton tows [*Hönisch et al.*, 2003]. As expected from the model predictions, its δ^{11}B is smaller than that of the symbiont-bearing species *O. universa*. However, at first glance it appears puzzling why its δ^{11}B is about 1.5‰ lighter than that of *O. universa* grown under low-light conditions (closed star). One may expect the δ^{11}B of a symbiont-barren species to be similar to that of a symbiont-bearing species under dark conditions because microenvironment *p*H should be similar. The model offers an explanation for the unexpected difference which has to do with boron concentrations. Shells of *G. bulloides* are from plankton tows grown in natural seawater with natural boron concentrations, while *O. universa* was cultured with 10 times enriched boron as discussed above. With natural boron concentrations, the model calculates a much larger negative offset (Figure 5, closed diamond left column) than at enriched boron concentrations (right column). This offset is close to the observed one in *G. bulloides*.

[20] In summary, the comparison of model and data is truly satisfactory. It was very encouraging to see how the model predictions, which were made before the measurements were completed, were eventually confirmed by the culture data. Note also that our findings regarding dark/light differences in δ^{11}B are consistent with stable boron isotope data on aragonite precipitation in natural corals, pointing to an analogous mechanism [*Hemming et al.*, 1998].

3.5. Vital Effects at Different Bulk *p*H

[21] In sections 3.3 and 3.4 we have shown that there may be significant offsets between the δ^{11}B-signal recorded in the foraminiferal shell and that of $B(OH)_4^-$ in the bulk medium. However, this is not a drawback for the paleo-*p*H proxy if those offsets are constant at different *p*H. Provided that single species are used for paleoceanographic reconstructions, the slope is important and not the absolute value. In order to test this, model runs were performed at different bulk *p*H and normal seawater boron concentrations (Figure 6). For

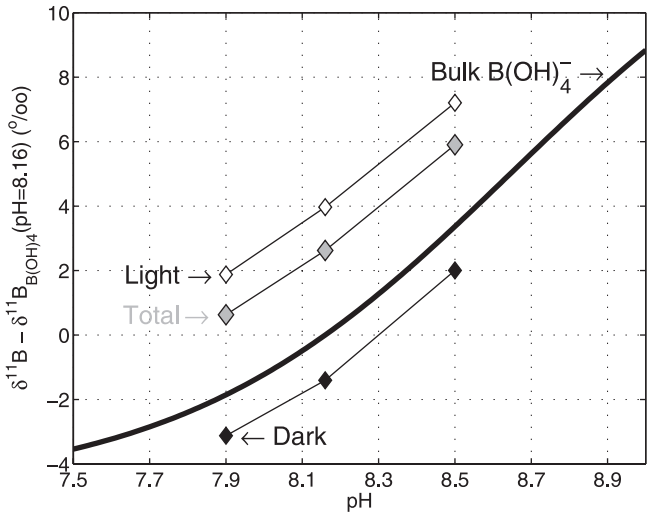

Figure 6. Offset of calculated $\delta^{11}B$ values of foraminiferal calcite from bulk $\delta^{11}B_{B(OH)_4^-}$ at *p*H 8.16. Open and closed diamonds: High-light and dark conditions. The final or total $\delta^{11}B$ value of the calcite (gray diamonds) was calculated using a dark:light calcification ratio of 1:3. Note that the offset between $\delta^{11}B$ (calcite) and $\delta^{11}B_{B(OH)_4^-}$ (bulk) is constant over the considered *p*H range.

convenience, the results refer to the boundary conditions of the culture experiments discussed in section 3.4. However, the main conclusions given in the current section hold in general and do not pertain to a certain foraminiferal species. Our aim here is to demonstrate the basic effect of life processes at different bulk *p*H and we found that it is of very minor importance whether photosynthesis, respiration, and calcification rates vary by, say a factor of two. Assumptions regarding dark:light calcification ratios do not enter the discussion at this stage because model results in the light and in the dark are examined separately.

[22] Our model foraminifer has a radius of 250 μm; photosynthesis, respiration, and calcification rates are 0, 2, and 1 nmol C h^{-1} in the dark and 10, 2, and 3 nmol C h^{-1} in the light. The bulk *p*H values chosen are 7.9, 8.16, and 8.5 and the rates of the life processes are assumed constant over this *p*H range. Furthermore, $T = 22°C$, $S = 33.7$. The model was run for each of these bulk *p*H values under dark and light conditions, and the calculated $\delta^{11}B_{B(OH)_4^-}$ at the foraminiferal shell was recorded. The model results are presented in Figure 6. As expected, the shell is isotopically heavier than the bulk $B(OH)_4^-$ in the light and isotopically lighter in the dark. This holds for all bulk *p*H values. Most importantly, our results indicate that the offset of $\delta^{11}B$ (calcite) from the $\delta^{11}B_{B(OH)_4^-}$ (bulk) is constant over this entire *p*H range.

4. Discussion

[23] Our results are good news for paleoacidimetry. First, our model is a major step forward in understanding stable boron isotope incorporation into the shells of live foraminifera. This is a fundamental prerequisite before environmental information can be extracted from stable boron isotopes of fossil foraminiferal shells from the sediment record. The consistency of model predictions and experimental data-in regard to both differences in $\delta^{11}B$ between dark/light calcification and differences between symbiont-bearing and symbiont-barren species - strongly suggests that we have indeed taken a step into the right direction. However, there is a lot more to do. For example, we cannot explain the whole offset between *O. universa* and *G. sacculifer*. Furthermore, if the thermodynamic fractionation between the dissolved boron species as calculated by *Kakihana et al.* [1977] is correct, the low-end member *p*H culture data for *O. universa* [*Sanyal et al.*, 1996] is very difficult to understand (see below).

[24] Second, consistent with the observation that the offset between *G. sacculifer*, *O. universa* and the $\delta^{11}B_{B(OH)_4^-}$ of bulk seawater appears to be constant at different *p*H (Figure 2), the model predicts that any offset from the inorganic line due to vital effects should be constant at different bulk *p*H. The major implication for paleoceanographic studies is that *p*H variations of the bulk seawater over time should be clearly reflected in the change of $\delta^{11}B$ within the shells of a given foraminiferal species. In other words, vital effects in foraminifera do result in differences in the absolute $\delta^{11}B$ value in different species. However, the changes of $\delta^{11}B$ recorded in the shells of a given species through time should still be a valid proxy for *p*H changes of the ocean in the past. If, in contrast to the model assumptions, the rates of the life processes in foraminifera significantly vary at different *p*H, the latter statement may have to be revised.

4.1. HCO_3^- Versus CO_3^{2-} Uptake

[25] Throughout this paper we have assumed HCO_3^- uptake for calcification. This is in contrast to earlier work where CO_3^{2-} uptake was favored [*Wolf-Gladrow et al.*, 1999]. Currently, we believe that recent studies on foraminiferal calcification suggest HCO_3^- uptake—or at least favor HCO_3^- as the major source for calcification. First, the modeled *p*H increase in the very vicinity of the shell if HCO_3^- is taken up for calcification is in better agreement with microsensor data [*Wolf-Gladrow et al.*, 1999]. Second, *Zeebe* [1999] demonstrated that the stable oxygen isotope composition of foraminiferal calcite is very well explained by uptake of HCO_3^- and CO_3^{2-} in proportion to their respective concentrations in solution of which the vast majority is HCO_3^-. These results lead us to conclude that HCO_3^- is the major source for calcification in planktonic foraminifera. If, however, this conclusion turns out to be wrong after all, one might ask: What is the modeled $\delta^{11}B$ of the shells if only CO_3^{2-} is taken up for calcification?

[26] We reran the model for all results shown in Figure 6 assuming CO_3^{2-} uptake. The outcome (not shown) is that all calculated $\delta^{11}B$ values for CO_3^{2-} uptake are ~0.5‰ lighter than those for HCO_3^- uptake. The reason is that for CO_3^{2-} uptake the *p*H at the shell is a little lower than for HCO_3^- uptake. Note, however, that the fundamental result that offsets resulting from vital effects are constant over the considered *p*H range was not affected.

4.2. Foraminiferal Size

[27] An issue worth discussing in regard to stable boron isotope fractionation in planktonic foraminifera is the

potential effect of size. Although size should not affect paleoceanographic reconstructions if foraminifera are picked from a single size fraction, it would be advantageous for our understanding if the model could predict the $\delta^{11}B$ of foraminifera of different size classes. However, in order to examine this we need input data of life processes (photosynthesis, respiration, and calcification) on foraminifera of different sizes. These data are, to the best of our knowledge, not available. The only two studies that supply input data to the model do not address the effect of size on the measured rates [*Jørgensen et al.*, 1985; *Rink et al.*, 1998]. Because our model cannot predict the rates of life processes as a function of size, a definite statement on the size effect on $\delta^{11}B$ cannot be made at this stage. This has to await experiments that either determine rates of life processes or $\delta^{11}B$ as a function of size directly.

[28] At the moment one can make different assumptions relating foraminiferal rates to their size and then calculate the resulting $\delta^{11}B$, given these assumptions. First of all, if rates would not depend on size (which is highly unlikely), then offsets due to vital effects would decrease with size. A more realistic relationship is that the rates in planktonic foraminifera scale with some power (n) of their radius, R. While there are certainly a number of arguments for and against n being equal to 1, 2, or 3 (the correct rate law would then scale with radius, surface area, or volume) we omit this discussion as it is purely academic and instead present the results for $\delta^{11}B$, given $n = 1$, 2, and 3.

[29] The model was run for the conditions corresponding to the results shown in Figure 6 at bulk pH = 8.16 (R was 250 μm in those experiments) but for a foraminifer of only R = 125 μm and a symbiont halo of 100 μm thickness. Figure 7 shows the calculated $\delta^{11}B$ under dark and high-light conditions assuming a rate law for the fluxes of photosynthesis, respiration, and calcification (symbol F) proportional to R, R^2, and R^3. This allows us to calculate the fluxes for the smaller foraminifer from those of the larger. The model predicts that life processes in smaller foraminifera produce a smaller offset in $\delta^{11}B$ (calcite) from $\delta^{11}B_{B(OH)_4^-}$ (bulk), given $F \propto R$, R^2, and R^3 in all cases. The only exception occurs under high-light conditions and $F \propto R$ which produces the same offset. The differences among the three cases shown in Figure 7 are large. If the fluxes scale with R, the offsets are as large/almost as large as in a foraminifer which has twice the size. On the other hand, if the fluxes scale with R^3, the offsets are small. The latter case may be unrealistic as estimates of photosynthesis, respiration, and calcification in *G. sacculifer* can be interpreted to roughly scale with R, R^2, and R, respectively [*Hemleben and Bijma*, 1994].

[30] In summary, our tentative prediction is that offsets from $\delta^{11}B_{B(OH)_4^-}$ (bulk) in the $\delta^{11}B$ of foraminiferal calcite is increasing with size but we are unable to say by how much, given the data currently available. In order to avoid any complications for paleoceanographic reconstructions, the common practice should be followed that foraminifera are picked from a single size fraction.

4.3. Thermodynamic Fractionation Factor

[31] As noted above, there are fundamental issues of paleoacidimetry that need to be addressed in the future. If

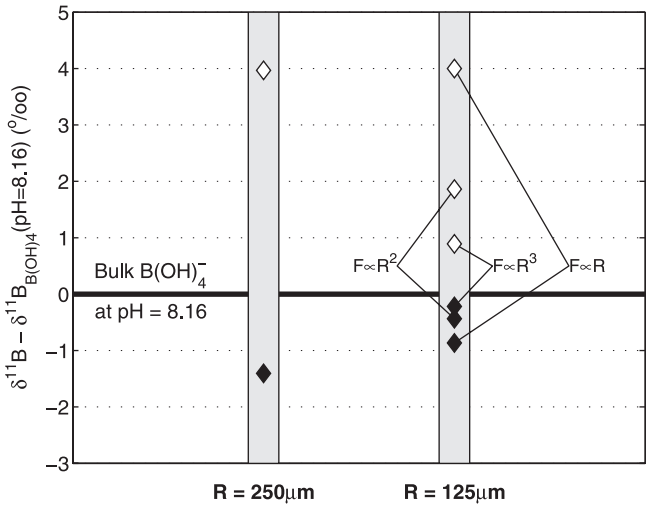

Figure 7. Potential effect of foraminiferal size on stable boron isotopes. Model runs refer to two foraminifera of radius R = 250 μm (left column) and R = 125 μm (right column) and a symbiont halo thickness of 200 μm and 100 μm, respectively (other boundary conditions are the same as in Figure 6 at bulk pH = 8.16). The $\delta^{11}B$ of the smaller foraminifer was calculated assuming a rate law for the fluxes of photosynthesis, respiration, and calcification (symbol F) proportional to R, R^2, and R^3 for dark and highlight conditions (closed and open diamonds). Our tentative conclusion is that dark/light offsets in $\delta^{11}B$ of foraminiferal calcite from $\delta^{11}B_{B(OH)_4^-}$ (bulk) increase with the size of the foraminifer.

the thermodynamic fractionation between $B(OH)_3$ and $B(OH)_4^-$ calculated by *Kakihana et al.* [1977] is correct, then the $\delta^{11}B$ of $B(OH)_4^-$ in natural seawater is given by the curve shown in Figure 1. The lowest possible $\delta^{11}B$ of $B(OH)_4^-$ is 19.7‰ (at pH < 6). The lowest $\delta^{11}B$ measured in *O. universa*, however, is even lower than that, 16.6‰. It is by no means possible to explain this value by a simple shift to lower pH values within the microenvironment of the foraminifer. Even if the pH dropped below 7, which is extremely unlikely, the lowest $\delta^{11}B$ value theoretically possible would be the minimum of $\delta^{11}B$ of $B(OH)_4^-$ which is 19.7‰.

[32] One way to solve this paradox is to challenge the calculated value of the thermodynamic fractionation between $B(OH)_3$ and $B(OH)_4^-$ [*Kakihana et al.*, 1977]. If the fractionation factor was larger than ~20‰, the curve of $\delta^{11}B$ of $B(OH)_4^-$ shown in Figure 1 would be shifted downward and the microenvironment pH shift may explain the low values of 16.6‰ measured in *O. universa*. One of the authors (R.E.Z.) has recalculated the fractionation factor given by *Kakihana et al.* [1977] and preliminary results include the possibility that the true value may indeed be larger than ~20‰. This is because the calculation is sensitive to the vibrational frequencies of the molecules involved for which different values have been reported in the literature. This problem is subject of a separate paper as the calculations are lengthy and not yet complete. The

thermodynamic fractionation factor is not a serious problem for paleoceanographic reconstruction provided that calibrations for single species are used because then it does not enter the equation. Nevertheless, we have to figure out what the true value of the fractionation factor is because our understanding of the inorganic basis of stable boron isotope fractionation hinges on it.

5. Conclusions

[33] Our model predicts that the $\delta^{11}B$ in planktonic foraminiferal shells is primarily controlled by the *p*H of the microenvironment. This leads to an offset of shell $\delta^{11}B$ from the $\delta^{11}B$ of $B(OH)_4^-$ in the bulk medium. The model explains about half of the observed offset between *G. sacculifer* and *O. universa*, the other half is uncertain. The model is very useful to investigate the basics of paleoacidimetry regarding the incorporation of stable boron isotopes in living foraminifera which was demonstrated by the comparison with observational data. We hypothesize that dark/light offsets in $\delta^{11}B$ increase with size. The most important finding is that offsets resulting from vital effects are constant over a large *p*H range (7.9–8.5). This is consistent with measured $\delta^{11}B$ values in *G. sacculifer* and *O. universa* at different *p*H. In conclusion, the model results suggest that the use of stable boron isotopes in planktonic foraminifera as a paleo-*p*H recorder is not compromised through vital effects as examined in the current paper.

Appendix A: Reacto-Diffusive Length Scale

[34] The reacto-diffusive length scale, λ, is a measure of the relative importance of diffusion and chemical conversion when disequilibria are considered on small spatial scales. In general, λ may be written as:

$$\lambda = \sqrt{\frac{D}{k}} \tag{A1}$$

where D is the diffusion coefficient and k is the reaction constant. To derive λ for the boron compounds, we start with the diffusion-reaction equation for $B(OH)_4^-$ (cf. equation (7)). We substitute $b_4 = [B(OH)_4^-]$, $b_3 = [B(OH)_3]$, $oh = [OH^-]$ to simplify the notation:

$$0 = \frac{D}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\,b_4}{\mathrm{d}r}\right) + k_+ b_3 oh - k_- b_4. \tag{A2}$$

For a small perturbation of b_4, the concentrations b_3 and oh may be assumed constant and equal to their respective bulk values (superscript "eq"). Using

$$\frac{k_+}{k_-} = \frac{b_4^{\mathrm{eq}}}{b_3^{\mathrm{eq}} oh^{\mathrm{eq}}},$$

equation (A2) can be rewritten in terms of a small perturbation, $x' = (b_4 - b_4^{\mathrm{eq}})$:

$$0 = \frac{D}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\,x'}{\mathrm{d}r}\right) - k_- \cdot x'. \tag{A3}$$

Furthermore, substituting $x = x'/r$, the diffusion term becomes

$$\frac{D}{r}\frac{\mathrm{d}^2 x}{\mathrm{d}r^2}$$

and the simplified diffusion-reaction equation reads:

$$0 = D\frac{\mathrm{d}^2 x}{\mathrm{d}r^2} - k_- \cdot x. \tag{A4}$$

This is a well-known equation and the solution shows that perturbations decay exponentially over the length scale λ:

$$x = x_0 \cdot \exp(-r/\lambda) \tag{A5}$$

Inserting equation (A5) into equation (A4), one obtains

$$\lambda = \sqrt{\frac{D}{k_-}}. \tag{A6}$$

This is the reacto-diffusive length scale. With $D \simeq 10^{-9}$ m^2 s^{-1} and $k_- \simeq 250$ s^{-1} [*Zeebe et al.*, 2001], its value for the conversion between $B(OH)_4^-$ and $B(OH)_3$ is:

$$\lambda \simeq 2\mu m. \tag{A7}$$

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References

Anderson, O. R., and W. W. Faber Jr., An estimation of calcium carbonate deposition rate in a planktonic foraminifer *Globigerinoides sacculifer* using ^{45}Ca as a tracer: A recommended procedure for improved accuracy, *J. Foraminiferal Res.*, *14*, 303–308, 1984.

Boudreau, B. P., and D. E. Canfield, A comparison of closed- and open-system models for porewater pH and calcite-saturation state, *Geochim. Cosmochim. Acta*, *57*, 317–334, 1993.

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

Hemleben, C., and J. Bijma, Foraminiferal population dynamics and stable carbon isotopes, in Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change, edited by R. Zahn et al., pp. 145–166, Springer-Verlag, New York, 1994.

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

Hönisch, B., J. Bijma, A. D. Russell II, H. J. Spero, M. R. Palmer, R. E. Zeebe, and A. Eisenhauer, The influence of symbiont photosynthesis on the boron isotopic composition of foraminifera shells, *Mar. Micropaleontol.*, in press, 2003.

Jørgensen, 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*(6), 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, and H. J. Spero, Calcium uptake and calcification rate in the planktonic foraminifer *Orbulina universa*, *J. Foraminiferal Res.*, *25*, 14–23, 1995.

Palmer, M. R., P. N. Pearson, and S. J. Cobb, Reconstructing past ocean *p*H-depth profiles, *Science*, *282*, 1468–1471, 1998.

Pearson, P. N., and M. R. Palmer, Atmospheric carbon dioxide concentrations over the past 60 million years, *Nature*, *406*, 695–699, 2000.

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

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., J. Bijma, H. J. Spero, and D. W. Lea, Empirical relationship between pH and the boron isotopic composition of *Globigerinoides sacculifer*: Implications for the boron isotope paleo-pH proxy, *Paleoceanography*, *16*, 515–519, 2001.

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

Wolf-Gladrow, D. A., J. Bijma, and R. E. Zeebe, Model simulation of the carbonate system in the microenvironment of symbiont bearing foraminifera, *Mar. Chem.*, *64*, 181–198, 1999.

Zeebe, R. E., An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotopes, *Geochim. Cosmochim. Acta*, *63*, 2001–2007, 1999.

Zeebe, R. E., and D. A. Wolf-Gladrow, *CO_2in Seawater: Equilibrium, Kinetics, Isotopes*, 346 pp., Elsevier Sci., New York, 2001.

Zeebe, R. E., A. Sanyal, J. D. Ortiz, and D. A. Wolf-Gladrow, A theoretical study of the kinetics of the boric acid—Borate equilibrium in seawater, *Mar. Chem.*, *74*(2), 113–124, 2001.

Zeebe, R. E., J. Bijma, and D. A. Wolf-Gladrow, A diffusion-reaction model of carbon isotope fractionation in foraminifera, *Mar. Chem.*, *64*, 199–227, 1999.

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