Vital Effects and Beyond: A Modeling Perspective on Developing Paleoceanographic Proxy Relationships in Foraminifera

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Abstract. This paper primarily reviews our recent work on the biology and geochemistry of foraminifera with respect to their use as paleoceanographic proxies. Our approach to proxy validation and development is described, primarily from a modeler's point of view. The approach is based on complementary steps in understanding the inorganic chemistry, inorganic isotope fractionation, and biological controls that determine paleo-tracer signals in organisms used in climate reconstructions. Integration of laboratory experiments, field and culture studies, theoretical considerations, and numerical modeling holds the key to the method's success. We describe effects of life-processes in foraminifera on stable carbon, oxygen, and boron isotopes as well as Mg incorporation into foraminiferal calcite shells. Stable boron isotopes will be used to illustrate our approach. We show that a mechanism-based understanding is often required before primary climate signals can be extracted from the geologic record because the signals can be heavily overprinted by secondary, non-climate related phenomena. Moreover, for some of the proxies, fundamental knowledge on the thermodynamic, inorganic basis is still lacking. One example is stable boron isotopes, a paleo-pH proxy, for which the boron isotope fractionation between the dissolved boron compounds in seawater was not precisely known until recently. Attempts to overcome such hurdles are described and implications of our work for paleoceanographic reconstructions are discussed.

1 Introduction

Development and validation of paleoceanographic proxy relationships in foraminifera have evolved rapidly over the past few years. During the early years of paleoceanography, offsets from isotopic and elemental geochemical equilibrium that were attributed to life processes were often referred to as biological 'vital effects'. In the case of stable carbon and oxygen isotopes, the black box was opened, resulting in a precise characterization of biological effects on geochemical signals recorded in the calcite shells of foraminifera. Interspecific variations have long been recognized in the stable carbon and oxygen isotope system (for review, see Wefer and Berger, 1991; Spero, 1998). However, the breakthrough in understanding inter- as well as intraspecific isotope variability came with culture experiments of live foraminifera under controlled laboratory conditions (Bijma et al., 1998; Bouvier-Soumagnac and Duplessy, 1985; Hemleben et al., 1985; Spero and DeNiro, 1987; Spero and Williams, 1988; Spero and Lea, 1993; 1996) as pioneered by Bé et al. (1977) and Hemleben et al. (1977).

The profound consequences of controlled culture experiments for paleoceanographic interpretations were widely recognized in 1997, when Spero and co-workers demonstrated that the seawater carbonate chemistry significantly affects $\delta^{13}C$ and $\delta^{18}O$ in planktonic foraminifera (Spero et al., 1997; Bijma et al., 1999). This phenomenon has been referred to as the carbonate ion effect. While paleoceanographers had long been aware that temperature and continental ice volume affect foraminiferal $\delta^{18}O$ (Emiliani, 1955; Shackleton, 1967), another important player, the ocean's CO_2 chemistry, had to be

added to the list. As a result, $\delta^{18}O$-based temperature estimates are likely too low for geologic periods in the more distant past of high atmospheric CO_2 concentrations and low oceanic pH (Zeebe, 2001; Royer et al., 2004; Bice et al., 2006).

With respect to quantitative modeling of life processes in foraminifera, a first attempt to open the 'vital effect' black box by means of a mathematical approach was provided by Spero et al. (1991). Their work outlined an abstracting concept, transforming geometry and fluxes in the living organism (Figure 1) into mathematical equations which allowed the calculation of stable carbon isotope fractionation in a model foraminifer. But it was not until after the discovery of the carbonate ion effect that more sophisticated tools such as numerical models of the chemical microenvironment (Figure 2) were developed to understand life processes, stable isotope fractionation, the carbonate ion effect, and prospectively, trace metal incorporation into foraminiferal calcite (Wolf-Gladrow and Riebesell, 1997; Wolf-Gladrow et al., 1999; Zeebe et al., 1999; Zeebe, 1999). Elderfield et al. (1996) proposed a Rayleigh distillation model for trace element incorporation into foraminiferal $CaCO_3$, which is consistent with data in benthic but not in planktonic foraminifera. As suggested by Zeebe and Sanyal (2002), the process of metal incorporation is, particularly in the case of Mg^{2+}, most likely intimately intertwined with the energetics of the precipitation mechanism itself (cf. also Erez, 2003). Development of a comprehensive theory of element incorporation in foraminifera by means of mathematical and numerical modeling is currently an active area of paleoceanographic research.

Parallel to the refinement of well-established proxy relationships such as $\delta^{13}C$ and $\delta^{18}O$ in foraminifera, other important geochemical proxies have been revitalized or newly developed over the past years, including metal/Ca ratios of Mg, Sr, U, Li, and stable calcium and boron isotopes. Stable boron isotope ratios in foraminifera provide a tool for reconstructing the pH of ancient seawater (e.g. Spivack et al., 1993; Hemming and Hanson, 1992; Sanyal et al., 1995; Pearson and Palmer, 2000; Hönisch and Hemming, 2005). The biogeochemical and physico-chemical aspects of this 'paleo-acidimetry' proxy have been intensively examined over the past years by culture studies with live planktonic species, inorganic precipitation experiments, and theoretical means including *ab initio* molecular orbital theory (Sanyal et al., 1996; 2000; 2001; Hönisch et al., 2003; Hönisch and Hemming, 2004; Zeebe et al., 2001; 2003; Zeebe, 2005a).

In this paper, we highlight some of our recent work on the development and validation of paleoceanographic proxy relationships in foraminifera, primarily from a modeler's point of view. Section 2 briefly describes the philosophy of our approach which is spelled out in terms of stable isotope fractionation in Section 3. In Section 4, we show that foraminifera strongly perturb their chemical and isotopic microenvironment, which has immediate consequences for the paleoceanographic interpretation of stable isotopes in foraminifera from the fossil record. Application of our method to stable boron isotopes and a down-core reconstruction of Late Pleistocene glacial-interglacial cycles in surface ocean pH is presented in Section 5. Finally, Section 6 describes our findings that foraminifera seem to control their Mg/Ca ratio by a rather expensive

method in terms of energy requirements. The final section also points to several gaps in our understanding of biomineralization in foraminifera.

2 Vital effects and beyond: The approach

Our approach to proxy validation and development is based on complementary steps in exploring the inorganic chemistry, inorganic isotope fractionation, and biological controls on proxy relationships in organisms relevant to climate reconstructions. In many cases, the integration of laboratory experiments, field and culture studies, theoretical considerations, and numerical modeling has turned out to be a successful method for this task.

The foremost goal of this research is to improve climate reconstructions. Climate signals extracted from the geologic record can be heavily overprinted by secondary, non-climate related phenomena because in the case of foraminifera, climate fluctuations are recorded by living organisms rather than by chemical compounds of inorganic origin. The long-term prospect of this work is to achieve refined paleoceanographic interpretations of proxy relationships and to apply those relationships to the actual down-core record. The practical field application of our work to deep-sea sediment records has been documented by several authors of the present paper (e.g. Sanyal and Bijma, 1999; Zeebe, 2001; Spero and Lea, 2002; Hönisch and Hemming, 2005).

3 Stable isotope fractionation

A great deal of our recent efforts has been focused on developing a comprehensive

theory of stable isotope fractionation in foraminifera, focusing on the elements of carbon,

oxygen, and boron. While the inorganic CO_2 chemistry and isotope fractionation of

carbon in the CO_2-H_2O-$CaCO_3$ system has been rather well known for quite some time

now (for summary, see Millero, 1995; Zhang et al., 1995; Zeebe and Wolf-Gladrow,

2001), this is not the case for oxygen (Usdowski and Hoefs, 1993; Zeebe, 1999; Zeebe,

2005b) and less so for boron. In the following, the inorganic chemistry and stable isotope

fractionation of dissolved boron in aqueous solution is used as an example to illustrate

the steps taken in the process of understanding the thermodynamic basis of a proxy

such as the $\delta^{11}B$ paleo-pH proxy.

3.1 Inorganic chemistry

Dissolved boron in seawater comes mainly in two forms − as boric acid, $B(OH)_3$,

and borate ion, $B(OH)_4^-$. The boric acid - borate equilibrium can be written as:

$$B(OH)_3 + H_2O \Leftrightarrow B(OH)_4^- + H^+$$
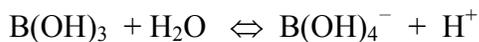
with stoichiometric equilibrium constant K_B:

$$K_B = [B(OH)_4^-][H+]/[B(OH)_3] , \qquad (1)$$

while the total boron concentration B_T is given by

$$B_T = [B(OH)_4^-] + [B(OH)_3] . \qquad (2)$$

The concentration of the dissolved boron species as a function of pH is shown in

Figure 3a. There is little discussion regarding the chemical thermodynamics of the

boron equilibrium (cf. Zeebe and Wolf-Gladrow, 2001). A value frequently used for the

dissociation constant of boric acid, pK_B , is 8.60 at $T = 25^{\circ}C$, $S = 35$ (DOE, 1994). It is also noted that at typical total boron concentration of ~420 μmol kg^{-1} in seawater, polynuclear boron species can probably safely be ignored. Cotton and Wilkinson (1988) state that polynuclear boron species are negligible at concentrations < 25 mM [see also Su and Suarez (1995) and references therein]. Using pK's for the polynuclear B_3 species given in Kakihana et al. (1977), the concentration of $B_3O_3(OH)_4^{-}$, for example, is 3×10^{-11} M at typical total seawater boron concentration.

On the other hand, the kinetics of the boric acid−borate equilibrium are less well known. Yet in order to calculate fluxes, pH gradient, and boron isotope distribution in the vicinity of a foraminifer, the kinetics, i.e. the speed of the conversion between the two dissolved boron species, is crucial. At the time when we developed the numerical models of the chemical microenvironment of foraminifera, there was, to the best of our knowledge, no measured value for this rate constant available in the literature. The problem was eventually solved by considering sound absorption data in seawater, which is described in Zeebe et al. (2001).

3.2 Inorganic isotope fractionation

Boron has two stable isotopes, ^{10}B and ^{11}B, which make up 19.82% and 80.18% of the total boron (IUPAC, 1998). As can be seen in Figure 3a, at low pH all dissolved boron is essentially boric acid, $B(OH)_3$, whereas at high pH all dissolved boron is essentially borate ion, $B(OH)_4^{-}$. Because the stable isotope ^{11}B is enriched in $B(OH)_3$ compared to $B(OH)_4^{-}$, the isotopic composition of the dissolved species change with pH

(Figure 3b). At low pH the isotopic composition of $B(OH)_3$ is equal to the isotopic

composition of the total dissolved boron, ~39.5‰. In contrast, at high pH the isotopic

composition of $B(OH)_4^-$ is equal to the isotopic composition of the total dissolved

boron. In between, the $\delta^{11}B$ of the two species increase. Based on the assumption

that the charged species, $B(OH)_4^-$, is incorporated into foraminiferal calcite (Hemming

and Hanson, 1992), the $\delta^{11}B$ of calcite also increases with pH and a paleo-pH proxy is

constructed (Figure 3b).

One uncertainty regarding the inorganic basis of this proxy is the value of

the thermodynamic equilibrium fractionation factor between $B(OH)_3$ and $B(OH)_4^-$,

$\alpha(B(OH)_3 - B(OH)_4^-)$, or short $\alpha_{(B3-B4)}$. Based on the theory of thermodynamic properties

of isotopic substances (Urey, 1947), Kakihana and Kotaka (1977) calculated

$\alpha_{(B3-B4)} = 1.0193$ at 300 K. Due to the absence of an experimental value, this theoretical

value has widely been used in geochemical applications over the past 25 years or so.

However, recent theoretical work suggests a larger fractionation factor. In June and

August of 2005, two theoretical articles were published indicating $\alpha_{(B3-B4)} > \sim 1.030$

and $\alpha_{(B3-B4)} = 1.027$ at 300 K, respectively (Zeebe, 2005a; Liu and Tossell, 2005).

These results were based on various theoretical, analytical methods and on numerical

approaches using *ab initio* molecular orbital theory and point towards a larger value

for $\alpha_{(B3-B4)}$, as also indicated by Oi (2000). Thus, theory predicts a value for the boron

isotope fractionation factor between $B(OH)_3$ and $B(OH)_4^-$ at 25ºC of about 30‰ rather

than 20‰. In fact, in April 2006 an experimental value of 28.5‰ was published (Byrne

et al. 2006). It is emphasized that this is the fractionation factor between the dissolved

boron compounds in solution and is not to be confused with fractionation

factors involving stable boron isotope ratios in carbonates. The latter is discussed in the

next section. In that context, it is important to note that using a fractionation of 28.5‰ to

calculate the isotopic composition of borate, the shape and inflection point of the borate

curve does not match the shape of the empirical carbonate data (Figure 4).

The above example illustrates an aspect of a proxy relationship which requires more

fundamental work because it is of basic, thermodynamic nature. Such hurdles need to

be overcome by experimental and theoretical efforts. However, it would be erroneous

to draw the general conclusion that a proxy approach whose inorganic basis is not yet

completely understood is *per se* invalid. In the case of boron, for example, uncertainties

in $\alpha_{(B3-B4)}$ do not bias pH reconstructions provided that organism-specific calibrations

are used.

3.3 Biological controls

Some organism-specific calibrations are shown in Figure 4. They include results

from controlled culture experiments with the two planktonic foraminiferal species

Globigerinoides sacculifer and *Orbulina universa* (Sanyal et al., 1996; 2001) and the

coral species *Porites cylindrica* and two species of *Acropora* (Hönisch et al., 2004;

Reynaud et al., 2004). First, the δ^{11}B of boron incorporated into the biogenic carbonates

of all these coral and foraminiferal species increase with pH. This is the basis of the

δ^{11}B -pH proxy.

Second, there are offsets between different groups and species. The corals appear to be isotopically heavier (enriched in ^{11}B) compared to the foraminifera. It is interesting to note that the coral skeletons consist of the $CaCO_3$ polymorph aragonite, while the foraminifera *G. sacculifer* and *O. universa* produce calcite shells. The offset between the two foraminiferal species is about 2‰. It is discussed in the next section that changes in the microenvironment of foraminifera can lead to light/dark shifts in shell δ^{11}B. However, the offset between *G. sacculifer* and *O. universa* is difficult to explain with this mechanism (Zeebe et al., 2003). Also shown in Figure 4 are results for inorganically precipitated calcite (Sanyal et al., 2000) which falls between the foraminifera. In summary, the δ^{11}B -*p*H relationship has been found in the biogenic carbonates tested. The foraminifera are offset from the inorganic calcite and the corals seem to be generally enriched relative to that.

So far only the isotopic fractionation between a standard and the carbonates as a function of *p*H has been discussed. Now let us look at the dissolved species of boron in aqueous solution. The upper black solid, the dotted, and the dashed black lines in Figure 4 represent the δ^{11}B of $B(OH)_4^-$ ($\delta^{11}B_{B(OH)4-}$) as a function of *p*H calculated using $\alpha_{(B3-B4)}$ = 1.019, 1.027, and 1.030 (Kakihana and Kotaka, 1977; Liu and Tossell, 2005; Zeebe, 2005a). The dot-dashed black line represents the experimental $\alpha_{(B3-B4)}$ = 1.0285 of Byrne et al. (2006). It is obvious that no matter what the true value of $\alpha_{(B3-B4)}$ is, the assumption that $B(OH)_4^-$ is exclusively incorporated into the carbonates without further fractionation cannot hold for all biogenic and inorganic carbonates. If this

assumption was correct, then all carbonates would fall on a single line and this line would be the δ^{11}B of B(OH)$_4^-$. As a corollary, δ^{11}B$_{B(OH)4-}$ cannot be deduced from the δ^{11}B of the carbonates and *vice versa*. In the future, some remaining issues of the δ^{11}B -*p*H proxy need to be addressed: (1) How does temperature, seawater salinity/composition, and total boron concentration affect the results for $\alpha_{(B3-B4)}$ published by Byrne et al. (2006) and (2) what causes the offsets between the δ^{11}B of the boron species in solution and in the carbonates. Meanwhile, neither of these questions compromises the use of δ^{11}B in carbonates as a paleo-*p*H indicator.

4 Foraminifera dramatically alter their chemical and isotopic micro-environment

If one considers an organism of the size of a foraminifer ($R < 1$ mm), being surrounded by a comparatively large volume of seawater, it may be difficult to see that the organism would have any significant influence on its environment. One would rather assume that the environmental properties the organism 'sees', and thus records in its shell, are dictated by the bulk seawater properties. Strictly, this is not the case. Although not independent of ambient conditions, the chemistry and isotopic ratios in the vicinity of the shell are primarily set by the properties within the diffusive boundary layer of the organism. The reason is that the typical length scale of the organism, R, is smaller than the so-called Kolmogorov scale, η, roughly the 'size of the smallest eddie':

$$\eta = (v^3/\varepsilon)^{1/4} \tag{3}$$

where v is the kinematic viscosity and ε is the energy dissipation. In most parts of the ocean, η is typically > 10 mm, and > 1 mm in the wind mixed layer (Lazier and Mann, 1989). This means that the transport within the boundary layer of a foraminifer,

for instance, is dominated by slow molecular diffusion rather than rapid turbulent mixing. The diffusion time scale on the millimeter scale ($L = 10^{-3}$ m) is given by $\tau = L^2/D \cong 1000$ s where $D = 10^{-9}$ m^2 s^{-1} is a diffusion coefficient characteristic for small molecules in seawater (note that diffusion on the length scale of single symbiotic algae, say a few micrometer, is much quicker). The combination of long diffusion time scales with high concentrations of symbionts and large rates of respiration and calcification of the foraminifera can drastically alter the microenvironment of the organism. As a result, the signal it 'sees' can be significantly different from that of the bulk medium. But how different?

Regarding foraminifera, this question has comprehensively only recently been addressed using microsensor studies and numerical modeling (Jørgensen et al., 1985; Rink et al., 1998; Wolf-Gladrow et al., 1999; Zeebe et al., 1999; Zeebe et al., 2003). Figure 5 shows an example of a model experiment simulating a foraminifer under dark conditions (for details, see Wolf-Gladrow et al., 1999). Due to respiration, the CO_2 concentration at the shell increases, while the pH drops (panels a and d). Model results agree well with microsensor pH transects measured by B. B. Jørgensen and co-workers (diamonds in panel d). It is interesting to note that microsensor observations of pH and our model simulations are generally in good agreement also with more recent pH electrode studies (Rink et al., 1998; Wolf-Gladrow et al., 1999). However, recent microelectrode measurements of dissolved CO_2 show smaller dark/light CO_2 amplitudes at the shell surface than the model (Köhler-Rink and Kühl, 2005). One possible explanation is that reaction rate constants as implemented in the model (based

on inorganic chemistry) and those in the vicinity of the organism are different. Another

is that in comparison to pH electrodes, the full potential of microsensor CO_2 technology

is yet to be reached.

Nevertheless, the important message is that at typical radii and life process fluxes

of planktonic foraminifera, a boundary layer with strong chemical gradients is

developed (this is not necessarily the case for other plankton, cf. Wolf-Gladrow and

Riebesell, 1997). This leads to substantial differences between e.g. pH, and O_2/CO_2

concentrations in the vicinity of the organism and the ambient seawater. For example,

in symbiotic foraminifera under high-light conditions, O_2 has been measured to be 2 to

2.5 times higher at the shell than in the bulk medium, while measured and simulated

pH rises by more than 0.4 units at the shell (Jørgensen et al., 1985; Rink et al., 1998;

Wolf-Gladrow et al., 1999; Köhler-Rink and Kühl, 2005). During night time, and when

ambient pH is lowered below typical seawater values (pH < ~7.7, H. J. S. and J. B.,

unpublished results), acidic conditions at the shell due to CO_2 respiration can lead to

actual dissolution of calcite chambers.

But not only is the chemistry within the foraminiferal boundary layer drastically

perturbed. Stable isotope ratios are also affected, which bears directly on

paleoceanographic interpretations of stable isotopes in fossil foraminifera. For example,

preferential uptake of ^{12}C during symbiotic photosynthesis under light conditions leads to

enrichment of shell-$\delta^{13}C$ by up to 1.5‰ (Spero and Williams 1988), in agreement with

results of diffusion-reaction models which include stable carbon isotopes (Zeebe et al.,

1999). Likewise, it is not difficult to imagine that stable boron isotope ratios at the shell

are different under light vs. dark conditions, considering the substantial pH variations at

the shell (Figure 5d). In fact, controlled laboratory experiments and numerical modeling

has shown this to be case (Hönisch et al., 2003; Zeebe et al., 2003).

Figure 6 illustrates the differences in shell δ^{11}B in the dark and light, respectively. In the

dark, pH at the shell is lowered, and, considering that δ^{11}B$_{B(OH)4-}$ decreases with pH

(Figure 3b), shell δ^{11}B is lowered as well − provided that B(OH)$_4{}^-$ is preferentially

incorporated into the calcite. The opposite applies to high-light conditions. Although the

sign of the light/dark induced δ^{11}B shift is clear, its magnitude could not be calculated

until the kinetics of the boric acid−borate ion reaction were understood. (Note that the

boundary layer chemistry is properly described by a steady-state of fluxes involving

diffusion and reaction kinetics. It is not chemical equilibrium!) Taking advantage of our

previous work on the boric acid−borate ion kinetics described in Section 3.1 (Zeebe et

al., 2001), the light/dark induced δ^{11}B shift was calculated (Figure 6). The model results

using 10 times elevated total boron concentration (as in culture experiments) and a

symbiont halo thickness of 200 μm match experimental results well (Hönisch et al., 2003;

Zeebe et al., 2003).

5 Planktonic foraminifera are reliable recorder of the ocean's paleo-pH

Reliable proxies for the ocean's CO_2 chemistry are of utmost importance because

they can provide information about past atmospheric CO_2 concentrations and clues

to the causes of carbon cycle variations. In turn, such information is crucial to

comprehending feedbacks of Earth's climate system. For example, due to lack of

adequate CO_2 records, it is still controversial whether CO_2 was the primary driver of the

Cenozoic cooling trend. Moreover, we still lack a sound understanding

of the link between glacial-interglacial changes in atmospheric CO_2 and deep ocean

chemistry. These problems need to be solved by reliable CO_2-system reconstructions.

As described earlier, stable boron isotope ratios in foraminifera provide a tool for

reconstructing the pH of ancient seawater (Spivack et al., 1993; Sanyal et al., 1995;

Pearson and Palmer, 2000; Hönisch and Hemming, 2005); combined with information on

one other parameter of the carbonate system (e.g. CO_3^{2-}, total CO_2, or total alkalinity),

past atmospheric pCO$_2$ may be estimated (e.g. Tyrrell and Zeebe, 2004).

Efforts to understand and calibrate this proxy, including culture experiments,

inorganic precipitation studies, and theoretical approaches hitherto indicate that

planktonic foraminifera are reliable recorders of the ocean's paleo-pH (Sanyal et al.,

1995; 1996; 2000; 2001; Hönisch et al., 2003; Hönisch and Hemming, 2004; Zeebe et

al., 2001; 2003; Zeebe, 2005a). Assuming the modern relationship between alkalinity

and salinity remained constant over the course of the Pleistocene, Sanyal et al. (1995)

and Hönisch and Hemming (2005) translated their δ^{11}B -pH reconstructions (Figure 8)

and estimated alkalinities into aqueous PCO$_2$ estimates, which quantitatively reflect

atmospheric pCO$_2$ reconstructions measured in ice cores (Petit et al. 1999; Siegenthaler

et al. 2005).

Whereas surface ocean pH estimates have never been questioned, boron isotope

estimates of a dramatic glacial deep-sea increase in pH and $[CO_3^{2-}]$ (Sanyal et al.,

1995) could not be confirmed by sedimentary records of carbonate preservation and

other geochemical proxy records. Deep sea pH estimates have therefore been criticized

(Broecker and Henderson, 1998). The major uncertainty of those estimates was the use

of mixed benthic foraminifer species, which are likely to record a mix of pH conditions

from pore and bottom waters. A recent sediment study now focusing on the use of the

single epibenthic foraminifer species *Cibicidoides wuellerstorfi*, found glacial deep water

pH in the Atlantic similar to or no higher than +0.08 pH units relative to interglacials

(Hönisch et al., in prep.). These new data no longer support the hypothesis of a much

more basic deep ocean which could explain the entire glacial drop in atmospheric

pCO$_2$. More validation studies for the Pacific Ocean are underway but the studies

mentioned above demonstrate that the boron isotope proxy works, if carefully applied.

6 Foraminifera appear to control their shell-Mg/Ca ratio by a luxurious method

Mg/Ca ratios in carbonates and seawater affect the thermodynamic equilibrium

between solution and the solid state, as well as the kinetics during crystal precipitation

and dissolution. These properties are relevant for global carbon, calcium, and magnesium

fluxes (Morse and Mackenzie, 1990) and were likely important drivers of switches

between Phanerozoic calcite and aragonite seas (Stanley and Hardie, 1998). More

recently, Mg/Ca ratios in foraminifera have received great attention because of their use

as a paleothermometer (e.g. Nürnberg et al., 1996, Lea et al., 2000; Tripati and Elderfield,

2005).

Planktonic foraminifera seem to have strong control over their shell Mg concentration because the Mg/Ca ratio is significantly smaller than, for instance, of abiotic marine calcite or inorganically precipitated calcite in the laboratory (Figure 8). The latter two fall in the category of high-magnesian calcites. Because Mg^{2+} is also known to be an inhibitor of calcite growth, one viable strategy of planktonic foraminifera to initiate calcite precipitation may be the removal of Mg^{2+} ions from the site of calcification. If there are other advantages to produce low- instead of high-magnesian calcite (related to thermodynamic stability, for instance), then Mg^{2+} removal would serve two purposes at the same time. Zeebe and Sanyal (2002) investigated such a scenario by means of inorganic precipitation experiments. The purpose of the experiments was to mimic the chemistry of a calcifying fluid during precipitation, analogous to a simple calcification scheme as depicted in Figure 9 (for a recent review of biomineralization in foraminifera, see Erez, 2003).

The evaluation of the experimental results plus consideration of H^+, CO_2, and Ca^{2+} fluxes indicate that it is energetically much more efficient to initiate calcite precipitation by removal of protons, rather than Mg^{2+} ions (Zeebe and Sanyal, 2002). This result is puzzling because the low Mg concentrations in planktonic foraminifera are then difficult to explain by considering cost-effectiveness during 'house building'. Of course, it is well known that the cheaper house is not necessarily the better one and other factors may be important for the low Mg/Ca ratios in planktonic foraminifera. Alternatively, calcification mechanisms could also involve Mg^{2+}-binding organic ligands. Such avenues should be explored in the future in order to solve the puzzle of biomineralization in

foraminifera.

Recent advances in measurement techniques allow analysis of ever smaller samples. Eggins et al. (2004) used high-resolution microanalysis techniques to study the spatial distribution of Mg in the final chamber of the planktonic foraminifer *Orbulina universa*. They found paired bands of low and high Mg/Ca ratios which were interpreted as diurnal growth bands reflecting *p*H changes in the foraminiferal microenvironment driven mainly by variations in photosynthesis and respiration of the symbionts. They speculate that the Mg banding may be accompanied by similar variations in oxygen, carbon, and boron isotopes. If this is true and measurable (cf. Rollion-Bard, 2005) it would open the door to investigating stable isotope variations at the sub-shell/sub-chamber scale of foraminifera. Element and isotope variations across a single foraminiferal shell pose a new challenge for models of biomineralization.

7 Conclusions

In this paper we have primarily reviewed some of our recent work on developing and validating paleoceanographic proxy relationships in foraminifera. Several aspects of the biology and geochemistry of planktonic foraminifera relevant to climate reconstructions have been explored in great detail over the last 10 years or so. A few conclusions derived from this research were discussed in the current paper: (1) foraminifera dramatically alter their chemical and isotopic micro-environment, (2) planktonic foraminifera are reliable recorder of the ocean's paleo-*p*H, and (3) foraminifera appear to control their shell-Mg/Ca ratio by a luxurious method. Our results were obtained by a team effort,

combining culture studies of live foraminifera, laboratory studies, and theoretical work. In order to employ the full potential of paleoceanographic proxies that involve once living organisms, the approach outlined in the current paper has turned out to be successful in many cases. We conclude that future research should continue to employ this approach.

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Figure Captions

Figure 1. Light microphotographs of the symbiotic, planktonic foraminifer *Orbulina universa* (top) and the non-symbiotic species *Globigerina bulloides* (bottom). After Spero (1998).

Figure 2. Schematic of life processes. Photosynthesis, respiration, and calcification perturb the chemical and isotopic microenvironment of the organism. The distance to the center of the shell is denoted by r, while R_1 and R_2 refer to the radius of the foraminiferal shell and edge of symbiont halo, respectively. Dissolved inorganic carbon enriched in ^{12}C is taken up during photosynthesis, while ^{12}C-enriched CO_2 is released during respiration (after Wolf-Gladrow et al., 1999; Zeebe et al., 1999).

Figure 3. (a) The concentration of dissolved boron species as a function of pH at $T = 25°C$, $S = 35$, and total boron concentration of 416 μmol kg^{-1} (DOE, 1994). (b) Boron isotopic composition of $B(OH)_3$ and $B(OH)_4^-$ as a function of pH assuming $\alpha_{(B(OH)3-B(OH)4-)} = 1.030$ (cf. Hemming and Hanson (1992); Zeebe, 2005a).

Figure 4. Empirical relationships between $\delta^{11}B$ and culture seawater pH measured in three species of corals (*Porites* and *Acropora*), two species of planktonic foraminifera (*Globigerinoides sacculifer* and *Orbulina universa*), and inorganically precipitated calcite. Paleoceanographic reconstructions use the empirical curves for reconstructing past seawater pH. The upper black solid, the dotted, and the dashed black line represent the $\delta^{11}B$ of $B(OH)_4^-$ using $\alpha_{(B3-B4)} = 1.019$, 1.027, and 1.030 (Kakihana and Kotaka, 1977; Liu and Tossell, 2005; Zeebe, 2005a). The dot-dashed black line represents the experimental $\alpha_{(B3-B4)} = 1.0285$ of Byrne et al. (2006). Note that $\delta^{11}B_{B(OH)4-}$ and the $\delta^{11}B$ in carbonates are two different quantities and that one cannot be deduced from the other (see text).

Figure 5. Results of a diffusion-reaction model of the foraminiferal microenvironment under dark conditions. (a) Respiration raises CO_2 at the shell, while $[CO_2^{3-}]$ and pH decrease (c, d). (b) The HCO_3^- pool is large and shows no dramatic change under dark conditions (this is different under high-light, Wolf-Gladrow et al., 1999). Microsensor pH transects (diamonds in panel d) were measured by B. B. Jørgensen and co-workers.

Figure 6. Light/dark induced shift in shell $\delta^{11}B$ of *O. universa* as measured in culture experiments (stars) and numerically simulated (diamonds). $\Delta\delta^{11}B$ is the difference relative to bulk $\delta^{11}B_{B(OH)4-}$ at pH 8.16; HL = High Light. Experimental and modeled total dissolved boron concentration were 10 times elevated over natural seawater concentrations. In the model, a symbiont halo thickness of 200 μm was assumed (HL200).

Figure 7. Reconstruction of surface ocean pH over glacial cycles based on δ^{11}B (Hönisch and Hemming, 2005). (a) Past atmospheric CO_2 concentration from the Vostok ice core (Petit et al., 1999). (b) δ^{11}B in *Globigerinoides sacculifer* from ODP core 668B in the eastern equatorial Atlantic, Sierra Leone Rise at 2693 m water depth (right axis, red symbols) superimposed on δ^{18}O of *Globigerinoides ruber* (left axis, black symbols) (c) Record of δ^{18}O of seawater (Waelbroeck et al., 2002), reflecting changes in global ice volume. Note that surface pH reconstructions track the glacial-interglacial climate oscillations.

Figure 8. Typical values of mole % $MgCO_3$ in planktonic foraminifera, abiotic marine calcite, and inorganic precipitates from laboratory studies.

Figure 9. Simple calcification scheme of $CaCO_3$ precipitation from a calcifying fluid. Organisms may control precipitation by separating a certain space from the ambient seawater by a membrane which is permeable to H_2O and CO_2 diffusion. Ion transport across the membrane may be mediated by H^+-ATPase and Ca^{2+}-ATPase. Note that whether such transport systems are active in foraminifera remains to be tested; even less is known about magnesium transporters.
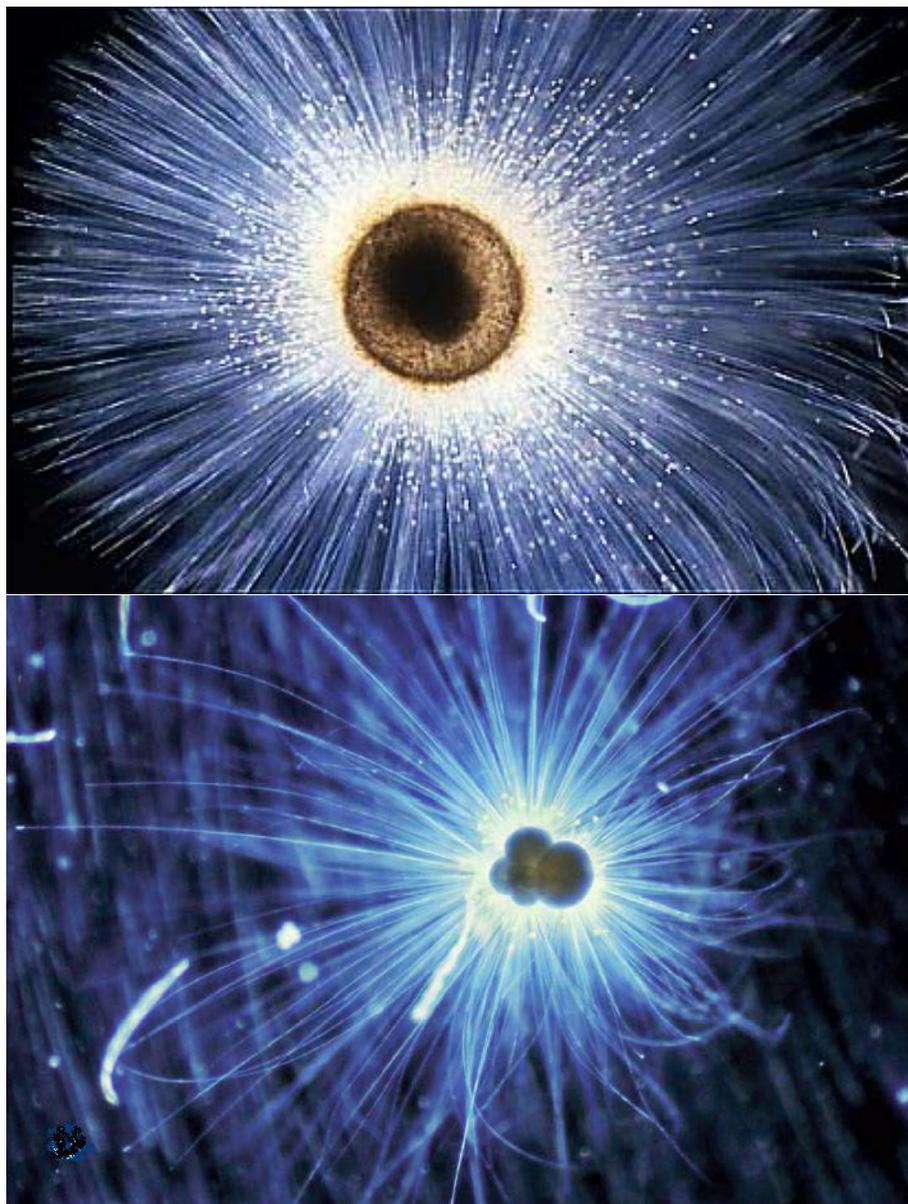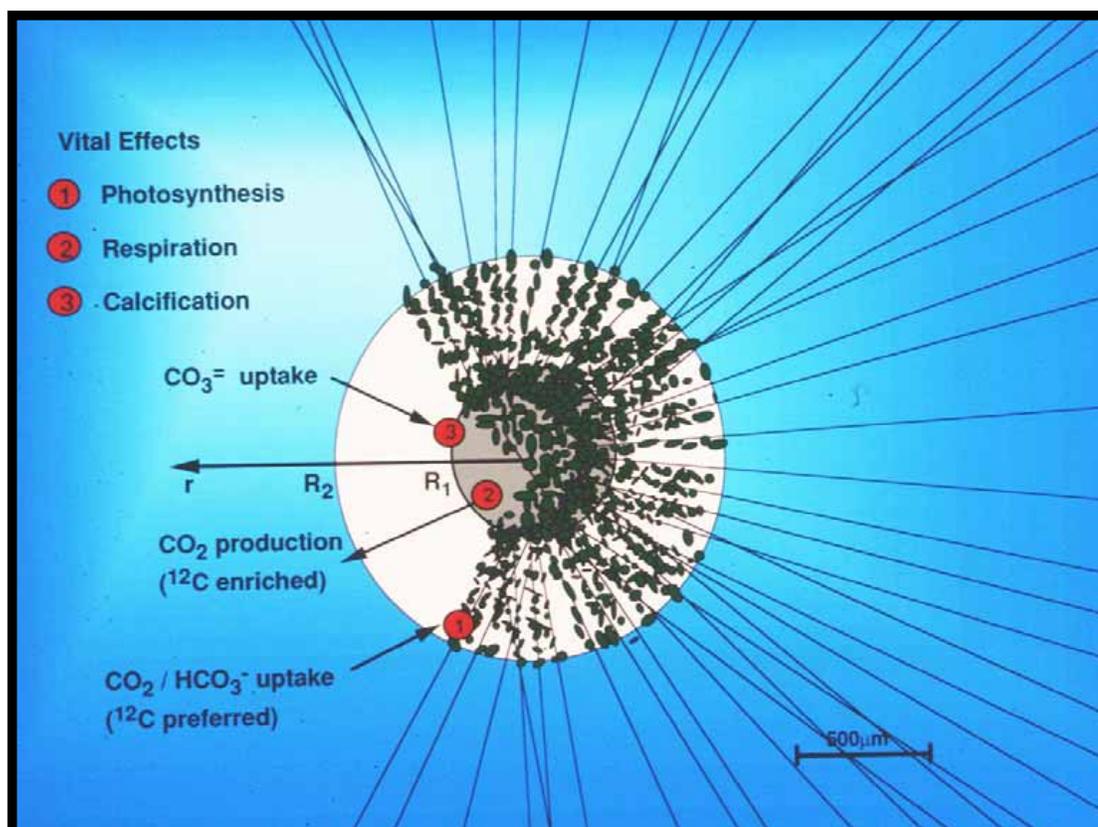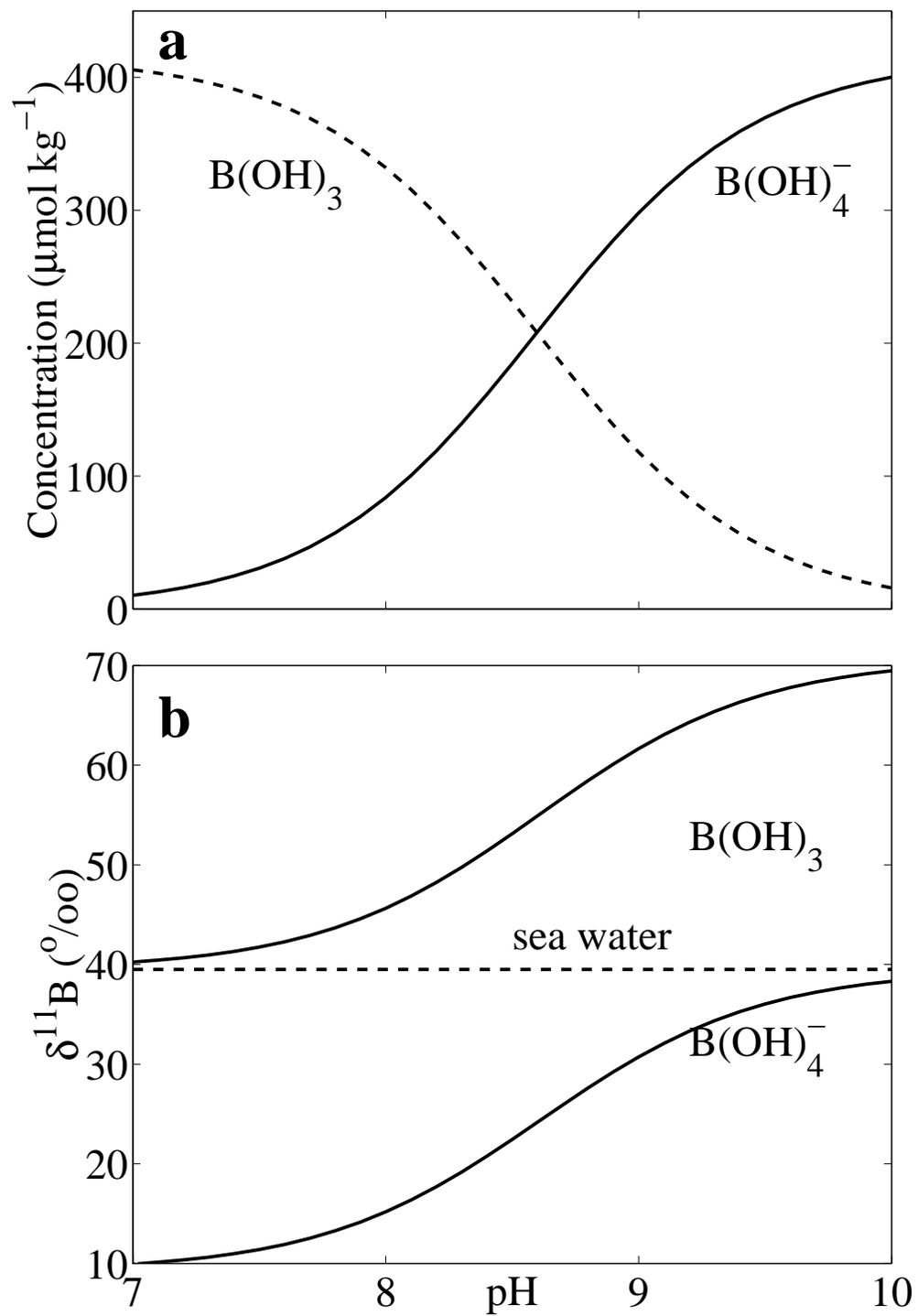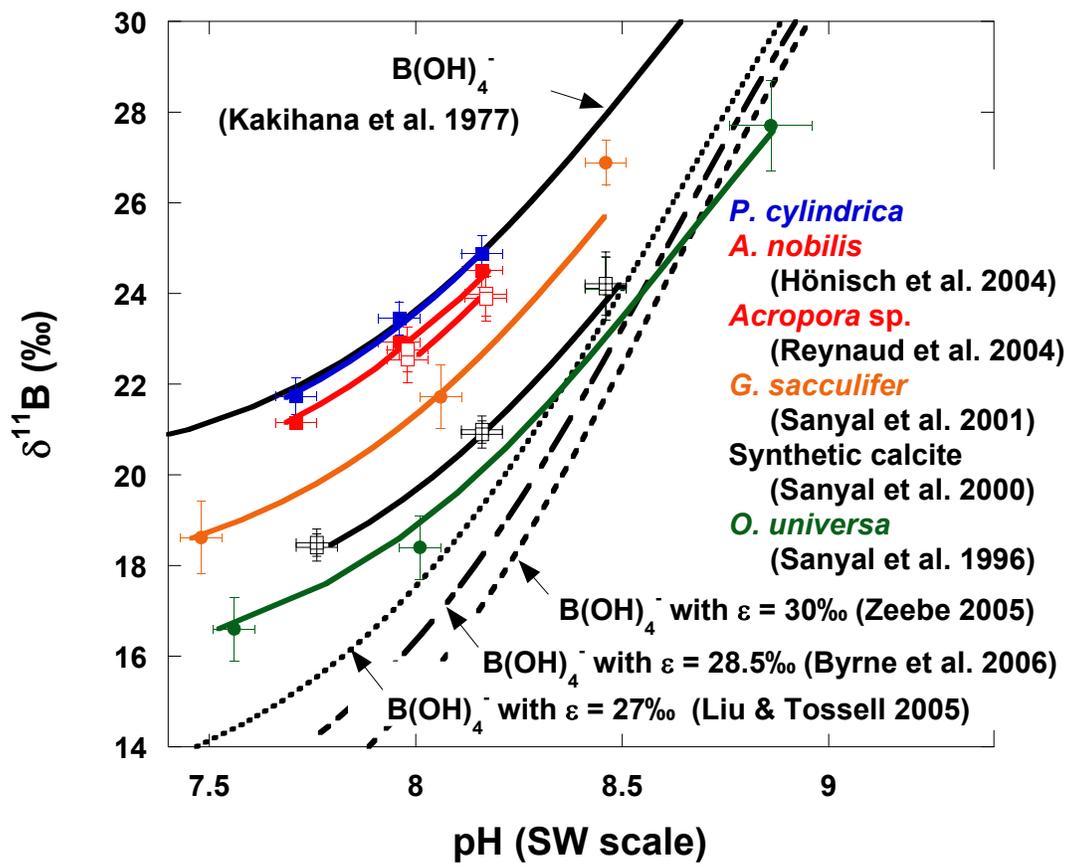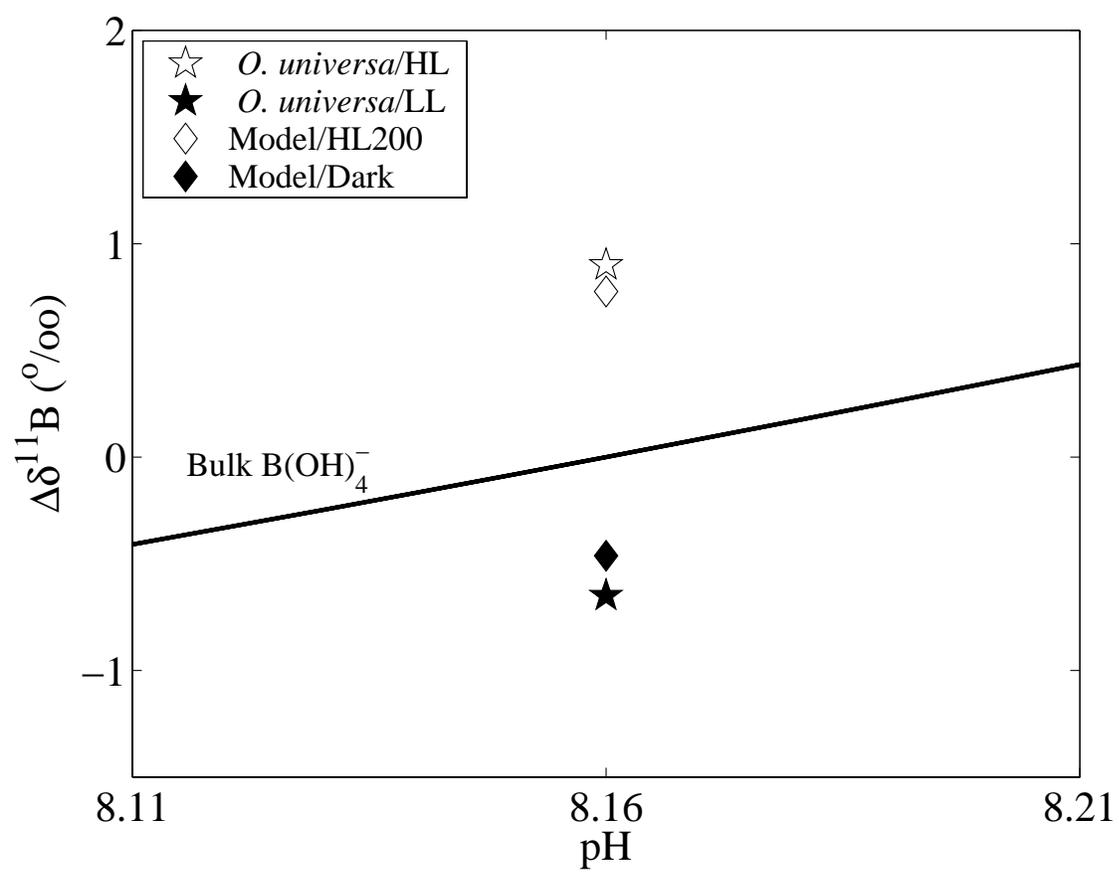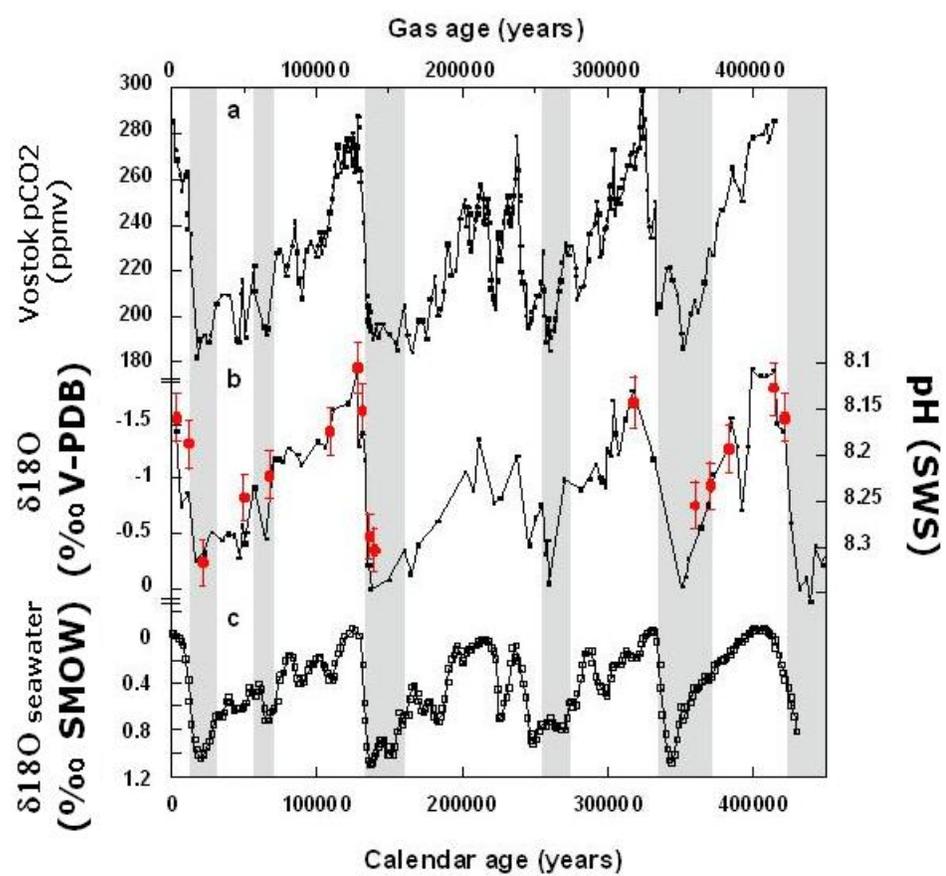
Figure 1.

Figure 2.
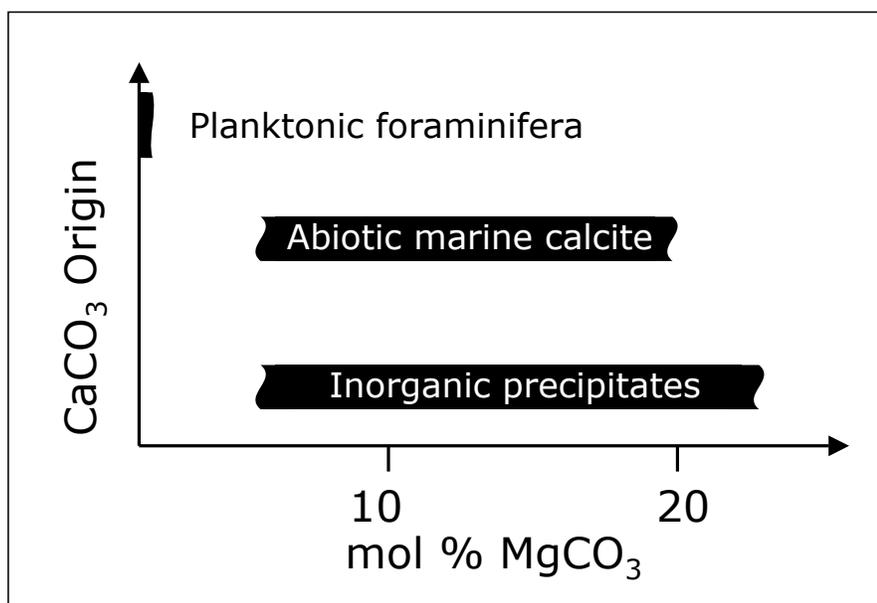
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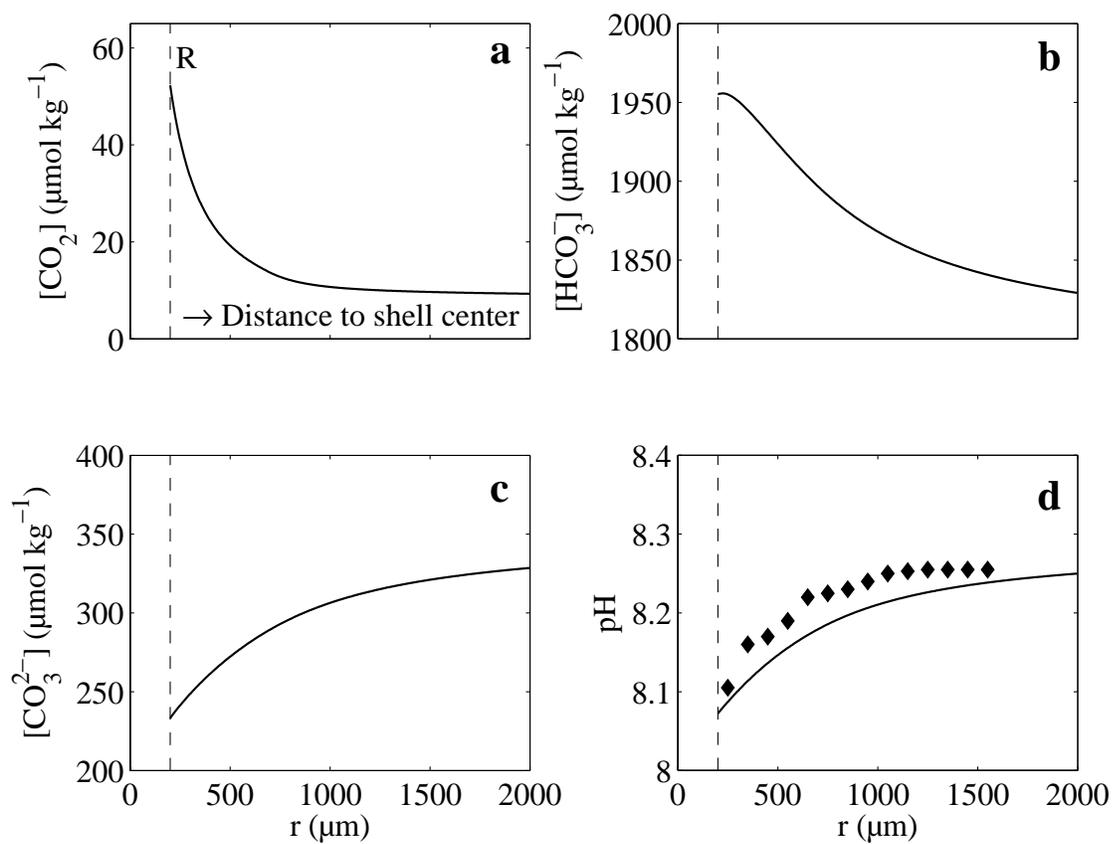
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