Letters

The planktic foraminiferal B/Ca proxy for seawater carbonate chemistry: A critical evaluation

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ABSTRACT

The ratio of boron to calcium (B/Ca) in the carbonate tests of planktic foraminifers has been proposed as a proxy for surface ocean pH or carbonate ion concentration ([CO$_3^{2-}$]), with a possible secondary influence of temperature. In both cultured and wild specimens, B/Ca generally increases with [B(OH)$_4^-$/HCO$_3^-$], consistent with the proxy's theoretical basis. However, close examination of the available data reveals that calibrations using the empirical boron partition coefficient, $K_D = [B/Ca]_{calcite}/[B(OH)_4^-/HCO_3^-]_{seawater}$, can be driven by independent relationships between [B(OH)$_4^-$/HCO$_3^-$] and other environmental parameters, not by B/Ca itself. If the influence of B/Ca on a calibration is negligible, it follows that combining that calibration with down-core B/Ca can not yield new information about past ocean conditions. In this study, we evaluate existing calibrations and down-core records with the aim of establishing a framework that allows consistent calibration methods to yield accurate proxy reconstructions from the fossil record. While many issues still need to be addressed, B/Ca does respond to seawater chemistry, and does change across some major climate transitions. Because it may provide insight into major carbon cycle perturbations, we make specific recommendations on how to tackle current uncertainties and develop B/Ca into a more robust proxy.

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1. Introduction

The theoretical basis for pH-dependency of boron (B) incorporation into marine carbonates is rooted in the aqueous speciation of dissolved B. Boron dissolved in seawater exists primarily as boric acid (B(OH)$_3$) and borate (B(OH)$_4^-$). As pH increases, the proportion of boron in the form of borate increases, while boric acid decreases (Dickson, 1990). Because the boron isotopic composition of marine carbonates falls close to the isotopic composition of borate in seawater, Hemming and Hanson (1992) suggested that (B(OH)$_4^-$) is the dominant form adsorbed and incorporated into marine carbonates. On this basis, B/Ca of carbonates is expected to increase with pH (Hemming and Hanson, 1992).

However, B/Ca behavior differs among marine calcifying taxa, defying a simple explanation. For example, B/Ca varies widely within tropical, aragonitic coral skeletons and is not directly related to seawater pH (Allison and Finch, 2010; Sinclair, 2005; Trotter et al., 2011), instead varying inversely with temperature in

some specimens (Trotter et al., 2011). In some coccolithophorids, B/Ca even decreases with pH (Stoll et al., 2012). In the calcite tests of the benthic foraminifer species *Cibicidoides wuellerstorfi* and *Cibicidoides mundulus*, B/Ca is more closely related to ΔCO_3^{2-} (defined as [CO$_3^{2-}$]$_{in\ situ}$ − [CO$_3^{2-}$]$_{saturation}$) than any other oceanographic parameter (Rae et al., 2011; Yu and Elderfield, 2007; Yu et al., 2010), an observation that is not predicted by the theoretical framework of the proxy. B/Ca in several planktic foraminifer species has recently been examined in marine core-top sediments (Foster, 2008; Ni et al., 2007; Yu et al., 2007), sediment traps (Hendry et al., 2009), down-core sediment records (Foster, 2008; Seki et al., 2010; Tripati et al., 2009; Yu et al., 2007), and in culture experiments with live specimens (Allen et al., 2011; Sanyal et al., 1996). These studies reveal that B incorporation is species-specific, where the average modern B/Ca increases from *Neogloboquadrina dutertrei* < *Globigerina bulloides* < *Globorotalia inflata* < *Orbulina universa* < *Globigerinoides sacculifer* < *Globigerinoides ruber*, thus hinting at a potential influence of depth habitat (*N. dutertrei*, *G. inflata*, and *G. bulloides* can live in deeper waters where pH and CO$_3^{2-}$ tend to be lower), and/or symbiosis (*O. universa*, *G. sacculifer*, and *G. ruber* have autotrophic symbionts that consume CO$_2$ and raise local pH) on B incorporation. In addition, questions have been raised about the influence of temperature (Tripati et al., 2011; Yu et al., 2007), the possible

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incorporation of boric acid (Klochko et al., 2009; Pagani et al., 2005; Tossell, 2005), and the influence of other parameters such as carbonate ion or salinity (Allen et al., 2011; Foster, 2008; Hendry et al., 2009; Tripati et al., 2011; Yu et al., 2007).

Here, we examine the existing evidence for planktic foraminiferal B/Ca as a proxy for the carbonate system in the surface ocean. While recent studies show promise for the use of this proxy, we also discuss some problems with the way the empirical B partition coefficient "K_D" has been calibrated and applied ($K_D = $ B/Ca$_{calcite}$/([B(OH)$_4^-$/HCO$_3^-$]$_{seawater}$)). We synthesize the available data from calibrations and paleo-reconstructions, and conclude with implications and recommendations for further proxy development.

2. Calibrations

Several B/Ca calibrations have been published in recent years using different approaches and a variety of foraminifer species. Core-top calibrations include *G. inflata* and *G. bulloides* (Yu et al., 2007), *G. ruber* (white), *G. sacculifer*, and *N. dutertrei* (Foster, 2008). B/Ca has also been measured in *Neogloboquadrina pachyderma* (sinistral) collected from Antarctic sediment traps (Hendry et al., 2009). Calibrations using down-core material include *G. ruber* (white) (Tripati et al., 2009; Yu et al., 2007) and *G. sacculifer* (Tripati et al., 2009). In core-tops, B/Ca of *G. inflata* and *G. bulloides* appears to increase with temperature, but in *G. ruber* and *G. sacculifer* it does not (Fig. 1D). Though B/Ca in many foraminifers appears to increase with pH, the magnitude of B/Ca increase in response to carbonate system parameters also varies by species (Fig. 1A–C, updated from Tripati et al., 2011). Isolating environmental parameters is challenging because several physical and chemical seawater parameters covary in the surface ocean, making it difficult to discern the parameters' separate influences on B/Ca. For example, temperature and carbonate ion [CO$_3^{2-}$] exhibit a broad positive correlation in the top 100 m of the water column ocean-wide (Fig. 2). Temperature and CO$_3^{2-}$ concentrations from previous core-top calibration sites

follow this trend (Foster, 2008; Yu et al., 2007), creating uncertainty regarding specific controls on B/Ca.

Culture experiments with live planktic foraminifers allow isolation of individual chemical and physical parameters, and provide a different way to test environmental controls. Laboratory cultures reveal that raising seawater pH by addition of base (which raises [B(OH)$_4^-$] and [CO$_3^{2-}$], but decreases [HCO$_3^-$]) does increase the boron concentration in *O. universa* calcite (Fig. 1C, Allen et al., 2011; Sanyal et al., 1996). This is consistent with inorganic calcite experiments, most core-top calibrations, and with the theoretical basis proposed for B incorporation (Allen et al., 2011; Sanyal et al., 1996, 2000). The mechanism of this increase with pH is not yet certain, but likely involves the behavior of pH-sensitive ions such as B(OH)$_4^-$, HCO$_3^-$ and CO$_3^{2-}$, discussed in more detail below. In addition, cultured *O. universa* specimens do not record a strong dependence of B/Ca on temperature at constant pH (Fig. 1D and E), suggesting that the inconsistent temperature relationships exhibited by different foraminifer species from core-top sediments may not reflect species-specific temperature sensitivities, but rather the influence of other parameters. Before these laboratory calibrations can be applied, however, they must be ground-truthed in the natural ocean. Specific recommendations for testing these calibrations are given in Section 5.

Here, we discuss the use of K_D, an empirical boron partition coefficient. K_D was first derived by Hemming and Hanson (1992) from a substitution equation:

$$B(OH)_4^- + CaCO_3 \Leftrightarrow CaHBO_3 + HCO_3^- + H_2O$$

In this scenario, borate adsorbed at the CaCO$_3$ surface substitutes for carbonate ion during CaCO$_3$ growth. Hemming and Hanson (1992) then proposed the following partition coefficient:

$$K_D = [HBO_3^{2-}/CO_3^{2-}]_{solid}/[B(OH)_4^-/HCO_3^-]_{fluid}$$

Later, this equation was simplified to:

$$K_D = [B/Ca]_{solid}/[B(OH)_4^-/HCO_3^-]_{fluid},$$

assuming that in calcite, [CO$_3^{2-}$] ≈ [Ca^{2+}] (Yu et al., 2007; Zeebe and Wolf-Gladrow, 2001). Because the boron content of
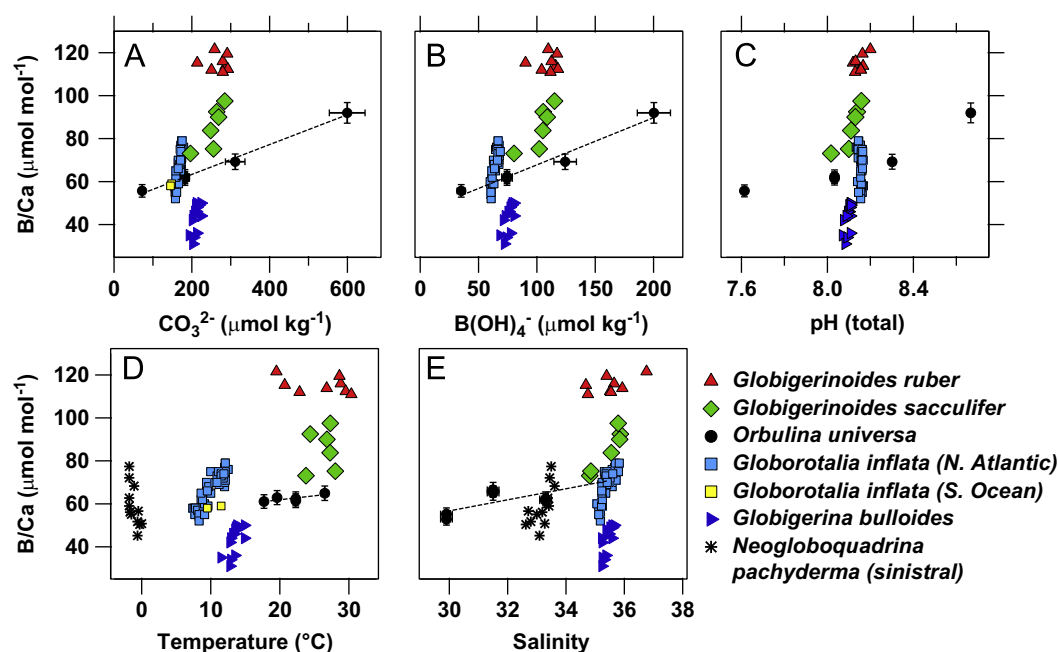

Fig. 1. B/Ca from modern samples vs. [CO$_3^{2-}$], [B(OH)$_4^-$], pH, temperature, and salinity, updated from Tripati et al. (2011). Data shown are from Foster (2008: *G. ruber*, *G. sacculifer*, core-top), Yu et al. (2007: *G. inflata*, *G. bulloides*, core-top), Hendry et al. (2009: *N. pachyderma*, sediment trap), and Allen et al. (2011: *O. universa*, cultured). The wide range of responses indicates species-specific behavior and/or unidentified controls on B/Ca.
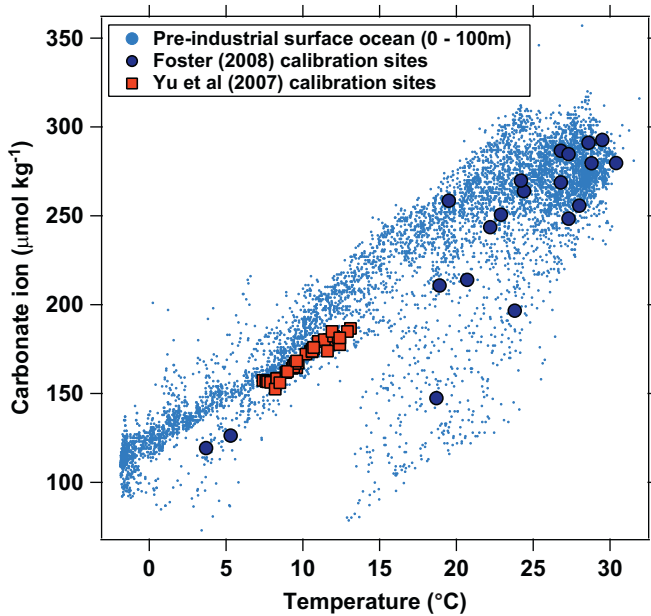
Fig. 2. Temperature and carbonate ion values for core-top sites studied by Foster (2008) and Yu et al. (2007), plotted with modern oceanographic data from the upper 100 m of the water column (Key et al., 2004), which is the typical depth range of the planktic foraminifer species.
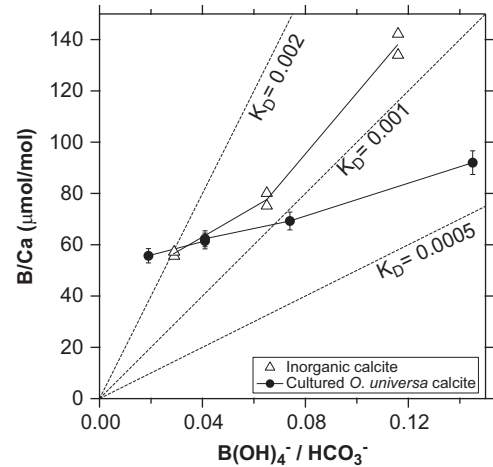

Fig. 3. Comparison of inorganically-precipitated calcite (Sanyal et al., 2000) with calcite from culture experiments with the planktic foraminifer *O. universa* (Allen et al., 2011). Measured B/Ca values are plotted against solution $[B(OH)_4^-/HCO_3^-]$; thus, lines through the origin represent constant K_D values ($K_D = [B/Ca]_{calcite}/[B(OH)_4^-/HCO_3^-]_{solution}$). If samples grow in a steady-state system, and the theoretical incorporation equation is accurate, K_D is expected to remain constant for a given temperature, pressure, solution composition, and ionic strength. These parameters are held constant in both the inorganic precipitation and culture experiments, but contrary to expectations, K_D values vary with pH.
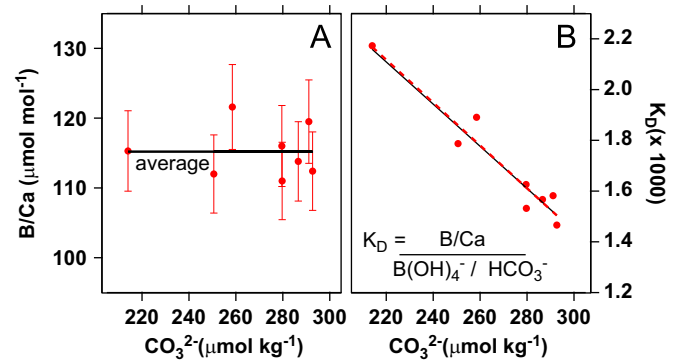
inorganic calcites (Sanyal et al., 2000) and marine carbonates (Hemming and Hanson, 1992) appeared to be well-described by constant K_D values, Yu et al. (2007) expected that planktic foraminiferal calcite should be as well. Instead, measured foraminiferal K_D values were not constant, ranging across an order of magnitude in cultured (Sanyal et al., 1996) and in core-top specimens (Yu et al., 2007). Based on observed co-variation of B/Ca with the temperature-proxy Mg/Ca, Yu et al. (2007) attributed core-top K_D variability to the influence of temperature on B partitioning. However, this mechanism can not explain the wide K_D range observed in foraminifera cultured at constant temperature (Allen et al., 2011; Sanyal et al., 1996). Even in inorganic calcite (Sanyal et al., 2000), K_D ranges from 1.2 to 2.0 (Fig. 3). Given these observations, it seems that the assumption of constant K_D should be revisited.

First, empirical constants (K^*) apply to systems at equilibrium or steady-state. Because foraminiferal life processes have been successfully modeled assuming steady-state conditions (Wolf-Gladrow et al., 1999a; Zeebe et al., 1999), and the diffusional time scale of B ions (1.5 min, assuming a 300 μm boundary layer (Wolf-Gladrow and Riebesell, 1997; Wolf-Gladrow et al., 1999b)) is much faster than the timescale of calcification, it seems reasonable to expect some constant K^* to apply. Second, empirical constants are valid only for the conditions in which they are measured—e.g., a single temperature, pressure, solution composition, and ionic strength (Stumm and Morgan, 1981). Consequently, changes in K_D of planktic foraminifers with temperature and salinity are to be expected. In contrast, although varying pH can affect ion-pairing behavior (Skirrow, 1975), in seawater with a total salt concentration ∼10 × larger than the reacting ions discussed here (i.e. borate and bicarbonate), ion-pairing shifts should not affect K^* values (Stumm and Morgan, 1981). Although K_D decreases from 0.003 to 0.0006 in laboratory culture (Fig. 3), which is not consistent with the expectation above, the almost-linear behavior of K_D with seawater pH still suggests potential as an empirical tool for determining past seawater carbonate chemistry.

However, an important practical issue with K_D is that the division of B/Ca by ($[B(OH)_4^-/HCO_3^-]$) can create artificial correlations and

Fig. 4. Example of an artificial K_D relationship. In this dataset (red circles, panel A, Foster, 2008), B/Ca does not exhibit a relationship with carbonate ion. A relationship only appears when B/Ca is divided by $[B(OH)_4^-/HCO_3^-]$ (panel B). Solid black line in A represents the population B/Ca average; solid black line in B represents a fit through K_D values calculated by combining core-site specific $[B(OH)_4^-/HCO_3^-]$ with this average B/Ca value for each sample. The resulting calibration line is essentially the same as that using the individual, measured B/Ca data (dashed line), illustrating that this K_D relationship is driven by the denominator, and B/Ca only plays a negligible role in this calibration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

obfuscate true ones. This is indicated by the observation that in some core-top suites, B/Ca in planktic foraminifers does not covary with temperature or carbonate ion, but K_D does (Foster, 2008). To demonstrate the artificial nature of this correlation, we examine the *G. ruber* data from Foster (2008) as an example. Fig. 4 illustrates that in this dataset, B/Ca does not depend on seawater carbonate ion, but K_D does. The apparent $[CO_3^{2-}]$ control on K_D stems from the chemical links between CO_3^{2-} and the K_D denominator, $[B(OH)_4^-]/[HCO_3^-]$. The relative abundances of these dissolved species are linked by equilibrium constants, where $[CO_3^{2-}]$ and $[B(OH)_4^-]$ increase, and $[HCO_3^-]$ decreases with pH. In other words, this calibration curve is primarily a function of $1/([B(OH)_4^-]/[HCO_3^-])$ vs. $[CO_3^{2-}]$, where $[B(OH)_4^-]/[HCO_3^-]$ and $[CO_3^{2-}]$ are closely related. As an additional complication, carbonate ion also happens to be roughly correlated with temperature in this dataset, making it

difficult to discern their separate influences (Foster, 2008), see Figs. 1 and 2.

The artificial nature of the K_D relationships is further illustrated by using the average B/Ca value of the sample population instead of the measured B/Ca values to determine individual K_D values. Using this population-average approach, B/Ca equals 115 μmol mol^{-1} for each sample, which is then divided by the sample location-specific $[B(OH)_4^-]/[HCO_3^-]$ ratio. The trend-line resulting from this population-average approach (black line) is essentially the same as that derived from the measured B/Ca (dashed line), suggesting that this K_D calibration is effectively independent of the B/Ca data. It is important to be alert to denominator-driven K_D relationships such as these because they do not depend on the primary measured data (B/Ca) and thus can not provide new paleo-information. This phenomenon is not unique to Foster (2008); other core-top calibrations exhibit denominator-driven behavior as well (e.g., *G. bulloides* of Yu et al., 2007).

Similar to these core-top calibrations, B/Ca of down-core calibration datasets (Tripati et al., 2009; Yu et al., 2007) does not exhibit a relationship with Mg/Ca-derived sea surface temperature (SST) in either *G. ruber* or *G. sacculifer* (Fig. 5A), but K_D does (Fig. 5B). The positive K_D–SST relationship is created solely by dividing B/Ca by $[B(OH)_4^-]/[HCO_3^-]$, which shows a broad negative correlation with SST over the 200-ky study period. This is the same fundamental problem described above for the K_D variation with $[CO_3^{2-}]$ (Fig. 4), except that in this case it is a down-core rather than a core-top calibration (as in the *G. ruber* calibration of Yu et al. (2007).

By contrast, the *G. inflata* data of Yu et al (2007) show a direct correlation between B/Ca and temperature and/or $[CO_3^{2-}]$, and in this case the calibration is not solely driven by the denominator (Fig. 6). Similar to Fig. 4, the average B/Ca value of the sample population (thick black horizontal line in Fig. 6A) is used to determine K_D values. In this dataset, the K_D calibration using the original B/Ca data (circles, dashed line fit) is very different from the calibration using the population average (solid black line), illustrating that the B/Ca data *do* have a significant effect on the calibration. A temperature effect on B incorporation might stem
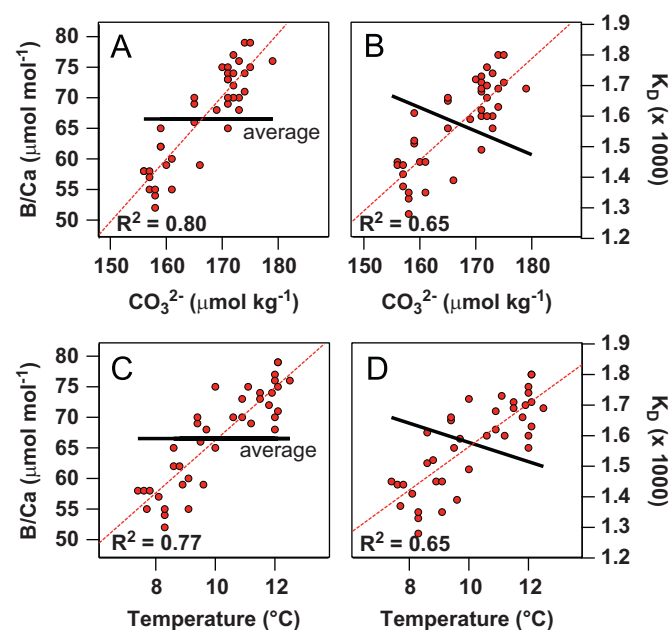

Fig. 6. Example of primary B/Ca relationships in *G. inflata*. In this dataset (Yu et al., 2007), B/Ca increases with $[CO_3^{2-}]$ (A) and temperature (C). In contrast to Fig. 4, the K_D calibration resulting from using the B/Ca population average (solid black lines, B and D) is different from that obtained by using the individual, measured B/Ca data (dashed lines, B and D). This indicates that in this case, B/Ca does have a significant influence on the calibration. The correlation (quantified by R^2 values) of the K_D relationships (B and D) is weaker than that of the B/Ca relationships.

from its influence on the system's free energy. Unfortunately, this thermodynamic effect can not be quantified because formation-energy data are not available for CaHBO$_3$. The temperature and $[CO_3^{2-}]$ correlations with raw B/Ca data ($R^2=0.77$ and 0.80, respectively) are stronger than with calculated K_D values ($R^2=0.65$ for both, Fig. 6), indicating that the division by $([B(OH)_4^-]/[HCO_3^-])$ mutes the B/Ca signal, rather than amplifying it. In light of this correlation decrease, we recommend that the partition coefficient be avoided. Instead, calibrations should be based on primary relationships between B/Ca and environmental parameters, at least until the relevance of individual ion species on B incorporation is better understood.

The second issue is the use of a "down-core calibration", i.e. correlations between B/Ca and environmental parameters through time. Because temperature and pCO$_2$ covary on some geologic and climatic timescales (e.g., Petit et al., 1999), down-core records do not allow separation of these two variables' influences on proxies such as B/Ca and δ^{11}B (Hemming and Hönisch, 2007). Such ambiguous calibrations can not be used to test past climate sensitivity to CO$_2$ because this approach automatically and inappropriately projects the Pleistocene covariation of SST and pCO$_2$ into the past, when their relationship may have been different. For example, when using a Pleistocene K_D–SST calibration as in Yu et al. (2007) and Tripati et al. (2009), a high SST corresponds to a high K_D, which automatically translates into low pH and high pCO$_2$. This forces temperature into a driving role in the reconstruction, and prevents independent evaluation of SST and pCO$_2$ shifts. Consequently, by applying down-core calibrations to previous time periods, we can not learn anything new about how the links between the ocean carbon cycle and climate may have changed through time.
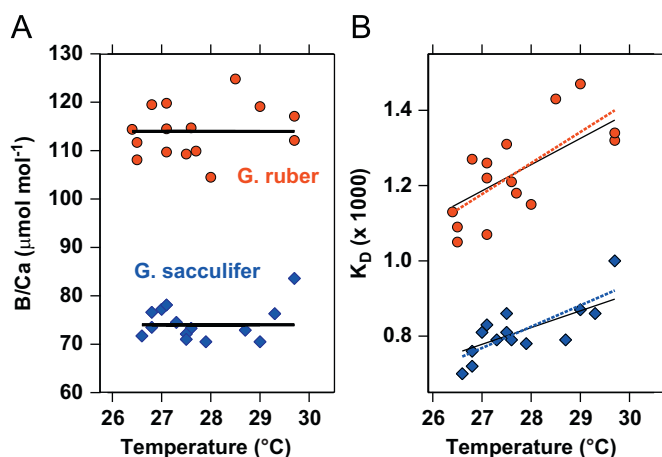

Fig. 5. Down-core calibration. In the Pleistocene calibration dataset of Tripati et al. (2009), B/Ca does not exhibit a relationship with Mg-derived SST (A), but K_D does (B). Similar to Fig. 4, the positive K_D–SST relationship is created by dividing B/Ca by $[B(OH)_4^-]/[HCO_3^-]$. Black horizontal lines in (A) represent the average of all *G. ruber* and *G. sacculifer* data in the calibration dataset (114 and 74 μmol mol^{-1}, respectively). If these average values are divided by core-site specific $[B(OH)_4^-]/[HCO_3^-]$ to determine K_D, the fits to the resulting values (solid lines) are similar to fits reported by Tripati et al. (2009), which use the original B/Ca data (red and blue dotted lines). This implies that in this case, the B/Ca values have little influence on the calibration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Down-core records

Down-core records from planktic foraminifer species show no consistent B/Ca pattern for the past 400,000 years, and recent

G. ruber specimens from different locations yield different B/Ca values despite similar seawater pH (Fig. 7 and Table 1). As a simple test of B/Ca variation in Pleistocene records, we calculated the single-species means for glacial and interglacial periods (as defined by benthic oxygen isotopes, illustrated in Fig. 7), and found that glacial and interglacial B/Ca at each site is the same at a 95% confidence level except for the *G. ruber* (white) record from Foster (2008), whose means were statistically distinct (Table 1). Data that fall within Terminations (rapid transitional periods between glacial and interglacial conditions, as defined by Cheng et al., 2009) were excluded from these averages. The lack of consistent glacial and interglacial B/Ca behavior in Fig. 7 is consistent with the small glacial–interglacial B/Ca range of $10\ \mu\text{mol mol}^{-1}$ predicted from *O. universa* culture experiments. This B/Ca range was predicted assuming interglacial and glacial conditions of 280 and 180 μatm pCO_2, 34.8 and 35.8 salinity, respectively, with alkalinity scaling with salinity as in Hönisch and Hemming (2005). During the last glacial maximum, B/Ca values in the *G. ruber* record of Foster, (2008) were *lower* than Holocene values, which contradicts the expectation of higher B/Ca at higher glacial pH. An additional consideration is if B/Ca of the foraminifer species used in these reconstructions increases with salinity, as it does in cultured *O. universa* (Allen et al., 2011), a salinity effect should be removed before determining pH. Taking

salinity into account for glacial samples—e.g., by subtracting 2.6 μmol/mol B/Ca per salinity unit increase (Fig. 1E)—would slightly exacerbate the issue of already-low glacial–interglacial B/Ca sensitivity.

Given the large differences between existing B/Ca records (Fig. 7) and calibrations, it is remarkable that these studies all yield pCO_2 estimates that closely follow ice-core pCO_2 trends (Foster, 2008; Tripati et al., 2009; Yu et al., 2007). This serves as an indirect illustration of how such K_D-based reconstructions can be and often are driven by other inputs to the pCO_2 calculation, not by B/Ca itself. In one down-core record from the Caribbean, the pCO_2 estimates derived from combining pH ($\delta^{11}B$) with $[CO_3^{2-}]$ (B/Ca) are almost indistinguishable from those derived from pH ($\delta^{11}B$) and alkalinity (salinity) (Foster, 2008). This close similarity is due to the dominant influence of pH on pCO_2 calculations in the Pleistocene carbonate system (e.g., Foster, 2008; Hönisch and Hemming, 2005).

In contrast to the Caribbean record (Foster, 2008), where the pCO_2 estimate agrees with ice core records primarily because of a strong relationship between atmospheric pCO_2 and surface ocean pH (recorded by $\delta^{11}B$), reconstructions using a temperature-dependent K_D (Tripati et al., 2009; Yu et al., 2007) match ice core records primarily because sea surface temperature and atmospheric pCO_2 covary. In these cases, Mg/Ca-derived temperature can be the main
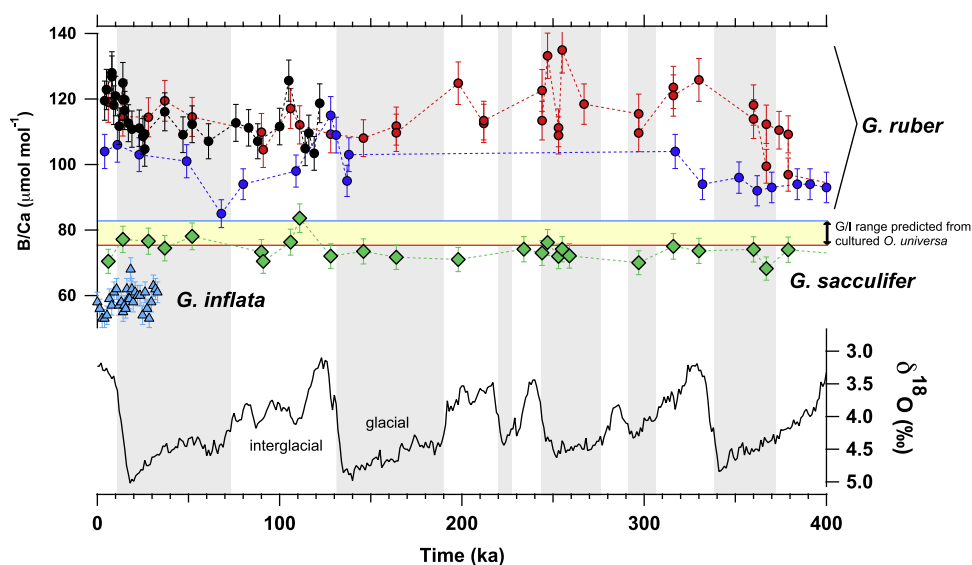

Fig. 7. Glacial–interglacial B/Ca records. Data are from Tripati et al. (2009, red circles and green diamonds), Foster (2008, black circles), and Yu et al. (2007, dark blue circles and light blue triangles). Benthic foraminiferal oxygen isotope data are from Lisiecki and Raymo (2005, black line). B/Ca theory and culture calibrations both predict high B/Ca during glacial intervals (light blue line) and low B/Ca during interglacial intervals (red line). This B/Ca range was predicted assuming interglacial and glacial conditions of 280 and 180 μatm pCO_2, 34.8 and 35.8 salinity, respectively, with alkalinity scaling with salinity as in Hönisch (2005), and the salinity effect on B/Ca observed in culture (Allen et al., 2011, Fig. 1E) taken into account. This predicted behavior is not observed in down-core records, and there is no consistent B/Ca pattern between species and core sites.

Table 1
Comparison of B/Ca averages from glacial and interglacial intervals. The Z value is a standard test value calculated from the means and standard deviations of the populations being compared. The two-tailed critical values against which Z is tested are taken from Borradaile (2003). If the Z value is less than the critical value, the two population means are indistinguishable at a 95% confidence level. Boundaries between glacial and interglacial intervals are based on oxygen isotope data, and data that fall within terminations (as defined by Cheng et al., 2009) are excluded from the glacial and interglacial averages.

Study	Species	Glacial	*n*	Interglacial	*n*	Z value	Critical value
Yu et al. (2007)	*G. ruber*	98.5	11	98.8	12	0.101	2.086
Yu et al. (2007)	*G. inflata*	58.9	12	58.5	12	0.267	2.042
Tripati et al. (2009)	*G. ruber*	111.8	22	115.3	11	1.269	2.042
Tripati et al. (2009)	*G. sacculifer*	73.0	15	74.3	9	0.931	2.060
Foster (2008)	*G. ruber*	110.3	8	115.3	19	2.215	2.042

control on pCO_2 estimates, with B/Ca itself having little impact. Temperature does exert a real, natural influence on the abundances of $[B(OH)_4^-]$ and $[HCO_3^-]$ in seawater through its impact on equilibrium constants K_1, K_2, and K_B (Dickson, 1990; Lueker et al., 2000), but the influence here is very small. The driving mechanism behind the $SST-[B(OH)_4^-]/[HCO_3^-]$ relationship in the case of these glacial–interglacial paleo-records is the systemic climate correlation between surface temperature and pCO_2 (which influences the seawater carbonate system, and thus $[B(OH)_4^-]/[HCO_3^-]$, through air–sea gas exchange). It is the application of this *down-core* relationship, not the B/Ca record, which artificially creates large changes in reconstructed pCO_2 (as discussed in Section 3). An example of this phenomenon is illustrated in Fig. 8. pCO_2 estimates in this figure were calculated according to the temperature-dependent K_D method applied by Yu et al. (2007) and Tripati et al. (2009). To evaluate the impact of B/Ca values on pCO_2 estimates, we compared the original estimates (symbols connected by solid lines) with estimates calculated using the same B/Ca value for all samples across the whole record (symbols connected by dashed lines, using average B/Ca of *G. ruber*$=101$ μmol mol^{-1} for Yu et al, 2007, and *G. ruber*$=108$ μmol mol^{-1}, and of *G. sacculifer*$=75$ μmol mol^{-1} for Tripati et al., 2009). The similarity of these results illustrates that, in these two cases, the influence of B/Ca on pCO_2 estimates is minimal, and it is the assumptions built into the calibration that dominate the final result.

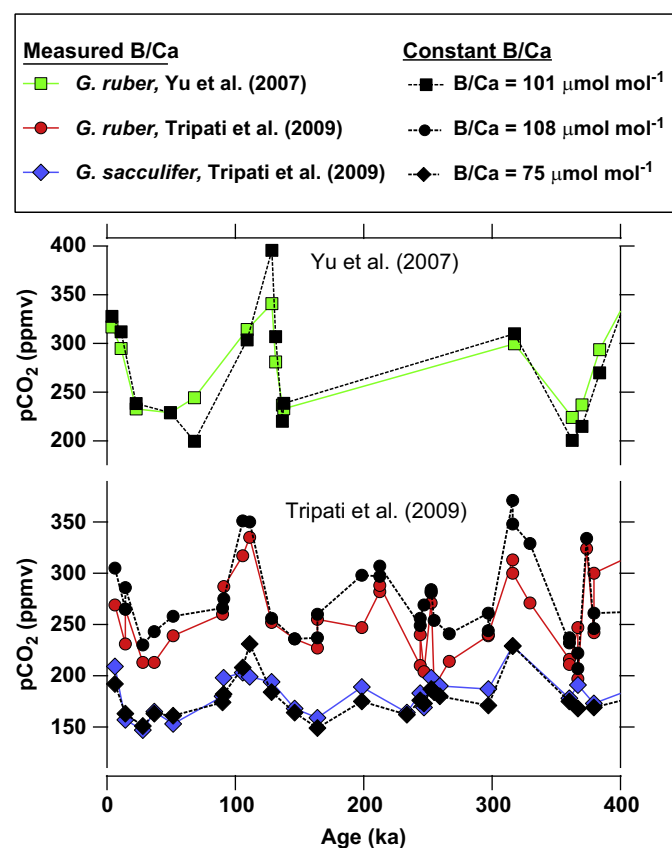**Measured B/Ca**

- □ *G. ruber,* Yu et al. (2007)
- ● *G. ruber,* Tripati et al. (2009)
- ◆ *G. sacculifer,* Tripati et al. (2009)

Constant B/Ca

- ■ B/Ca = 101 μmol mol^{-1}
- ● B/Ca = 108 μmol mol^{-1}
- ◆ B/Ca = 75 μmol mol^{-1}

Fig. 8. Comparison of three paleo-pCO_2 estimates using measured B/Ca data (green, red and blue symbols, data from Yu et al., 2007 and Tripati et al., 2009) and constant B/Ca values (black squares, circles and diamonds), corresponding to the average B/Ca values of each species. All calculations use the temperature-dependent K_D calibrations applied in the original studies. The constant-B/Ca and variable B/Ca methods give similar results, demonstrating the minor role of B/Ca in the reconstruction and the dominance of other input parameters during this time interval. Note also that different species yield different pCO_2 values, which reflects species-specific differences in the calibrations.

4. Recommendations for proxy development

We agree with the recommendation of Tripati et al. (2011) that higher-resolution records with greater spatial distribution are needed to assess the link between pCO_2 and climate, but we also echo the caution of Seki et al. (2010), who suggested that applying K_D is premature in the light of uncertainties controlling B incorporation. We propose that until better constraints are placed on the specific incorporation stoichiometry (and by extension, K_D), direct relationships between raw B/Ca data and well-known modern or recent seawater parameters should instead be used to interpret B/Ca records. B/Ca does change with pH and carbonate ion in culture experiments, and does exhibit some variability across major climate transitions (Seki et al., 2010; Tripati et al., 2011), so while many issues still need to be addressed, the B/Ca proxy may eventually provide insight into past carbon cycle perturbations such as the Paleocene-Eocene Thermal Maximum or Triassic–Jurassic boundary. Below, we make specific recommendations on how to tackle current uncertainties and develop B/Ca into a more robust proxy.

Even if B/Ca is not able to resolve glacial–interglacial shifts in atmospheric pCO_2 (at least not with current analytical precision and with the species investigated to date), it might still be useful in settings where larger carbonate system shifts occurred. A potential target could be upwelling regions, where carbonate system shifts can be several times larger than those driven by atmospheric CO_2. However, the only study available to date measured B/Ca of *G. sacculifer* from the northern Arabian Sea (Palmer et al., 2010), a region characterized by strong seasonal upwelling. In that study, $\delta^{11}B$ of calcite and $\delta^{13}C$ of alkenones both indicate elevated surface seawater CO_2 between 11 and 17 ka, but B/Ca remained relatively constant, suggesting that carbonate system changes were not large enough to be detected by this proxy. Separate and/or competing controls might also explain the lack of B/Ca variability. More data from other upwelling regions (preferably with tight constraints on species depth habitats and seasonal production) are needed to more deeply evaluate these possibilities.

4.1. Distinguish environmental controls

To establish clearer evidence for or against temperature and/or carbonate ion control, we recommend that these relationships should be tested further using more extensive live-plankton and core-top comparisons in areas where temperature and $[CO_3^{2-}]$ are decoupled either spatially or temporally. In the *G. inflata* calibration dataset of Yu et al. (2007), temperature and $[CO_3^{2-}]$ covary ($R^2=0.78$, Fig. 2, squares) and their respective relationships with B/Ca are similar (Figs. 6A and C). Yu et al. (2007) discuss this issue, and point to the inconsistency between K_D and $[CO_3^{2-}]$ relationships observed in their down-core record at 668 B in *G. ruber* (negative) and in the North Atlantic in *G. inflata* (positive) as evidence against CO_3^{2-} control. They also compare core-top specimens grown at similar temperatures but different CO_3^{2-} concentrations (Southern Ocean sites had slightly lower $[CO_3^{2-}]$ than the North Atlantic, Fig. 1). However, it is difficult to draw a firm conclusion from this comparison because of the two Southern Ocean core top samples, one agrees with B/Ca grown at the same temperature in the North Atlantic within error while the other does not. Expanding upon this work would allow firmer conclusions to be drawn regarding environmental controls on B/Ca.

For example, surface waters in the Mediterranean and Black Seas span a wide salinity range (corresponding to a large $[CO_3^{2-}]$ range) but relatively small temperature range (MEDAR, 2001), and there are many areas in which these parameters are

decoupled. At the Hawaii Ocean Time-Series (http://www.hahana.soest.hawaii.edu/), $[CO_3^{2-}]$ and temperature appear largely independent ($R^2=0.28$ for 1989–2010 data, assuming $[CO_3^{2-}]=$ alkalinity$-$DIC). Such areas might serve as useful testing-grounds for temperature vs. $[CO_3^{2-}]$ controls. In addition, using only modern samples will place these investigations on firmer ground because modern seawater properties have been measured directly, and thus are better constrained than past conditions, which must be reconstructed from other proxies.

4.2. Investigate the role of test size

Field studies are also needed to investigate the relationship between test size and B/Ca. In the core-top study of Ni et al. (2007), B/Ca increases with test diameter of G. ruber (white and pink) and G. sacculifer. The authors suggest that variable calcification rates may explain the observed B/Ca behavior. Trace element partitioning often varies with crystal growth rates, possibly due to changes in mass transport or surface reaction kinetics (e.g., Morse and Bender, 1990), but the specific influence of calcification rate on B partitioning has not yet been quantified. Ni et al. (2007) also suggest that habitat depth and proportion of gametogenic to ontogenetic calcite dissolution may influence B/Ca. However, independent estimates of shell corrosion, such as shell weights, were not provided, thus preventing unambiguous identification of the controlling factors. It is important to investigate these possible influences so researchers can make informed decisions about which size fraction(s) to analyze, and to be aware of possible biases in down-core records. For example, previous work suggests that larger individuals are less affected by dissolution and selecting large shells therefore minimizes potential dissolution bias (Hönisch and Hemming, 2004; Ni et al., 2007). Yu et al. (2007) observed no B/Ca difference between G. inflata samples deeper than 3.9 km ($n=4$) and samples shallower than 3.4 km ($n=36$), but a comparison involving more species, more samples, and broader spatial coverage would help assess the general applicability of this result. Comparing individuals from sediment traps (or deep vertical plankton tows) with core-top material at the same sites might further improve our understanding of dissolution effects. Laser ablation ICP-MS could enable separate analysis of ontogenetic and gametogenic calcite layers.

4.3. Establish species-specific calibrations

It is also important to investigate whether the B/Ca of different species may respond differently to changes in carbonate chemistry. In Fig. 8, the pCO₂ estimates given by individual species G. ruber and G. sacculifer are offset. While Tripati et al. (2009) combined $[B(OH)_4^-]/[HCO_3^-]$ ratios from both species to construct a final pCO₂ record, separate calculations for each species yield different results. For samples between 0 and 1 Ma, the average difference between G. ruber- and G. sacculifer-derived pCO₂ is 70 ppm when using a temperature-dependent K_D. Such species offsets can be avoided by applying species-specific calibrations. More culture calibrations, sediment trap studies, and core-top studies should be performed on species used for paleo-reconstructions to determine their individual B/Ca sensitivity to carbonate chemistry, temperature, and salinity.

4.4. Biological processes may influence B uptake

Inorganic calcite growth is primarily controlled by the availability and type of nucleation surfaces, solution trace element composition, ionic strength, and saturation state (Stumm and Morgan, 1981). Biogenic calcite growth is generally subject to the same parameters as inorganic precipitation. However, because organisms have developed many ways to strongly modify the microenvironments in which they grow, the calcite they produce is often characterized by crystal forms, growth rates, and chemical compositions that are very different from inorganic calcite (Erez, 2003; Weiner and Dove, 2003).

The carbonate chemistry in a foraminifer's immediate surroundings (~ 2 mm radius), especially in spinose species, is influenced by a number of physiological processes. These include calcification, respiration and, for those that bear symbionts, photosynthesis (e.g. Zeebe et al., 1999). Calcification consumes DIC and alkalinity in a 1:2 ratio, which raises $[CO_2]$ and lowers local pH. Respiration consumes oxygen and produces CO_2 (lowering pH), while photosynthesis consumes CO_2 (raising pH) and produces oxygen. Photosynthesis exerts only a minor influence on alkalinity through its consumption of nitrate (Wolf-Gladrow et al., 2007). As a result of these processes, foraminifer species hosting photosynthetic symbionts (such as the dinoflagellate Gymnodinium beii) can experience shifts from pH 8.7 to 7.7 (total scale) under light and dark conditions, respectively (Jørgensen et al., 1985; Rink et al., 1998). Such shifts in microenvironment pH alter local aqueous boron speciation, and could ultimately influence the abundance of B incorporated into calcite, as suggested by boron isotope analyses of symbiont-bearing foraminifer shells grown in the light and near-darkness (Hönisch et al., 2003). Experiments to test the effects of these physiological processes on the B/Ca proxy have not yet been performed, but, in theory, first insight into the potential for such effects can be gained from laser-ablation ICP-MS profiles through individual tests. These profiles sample across individual calcite layers precipitated alternately during day and night throughout a foraminifer's lifetime. Such analyses of natural and laboratory-grown foraminifer tests display wide variability, with B/Ca as high as 110 µmol mol^{-1} and as low as 50 µmol mol^{-1} within a single shell (Allen et al., 2011). This suggests a strong biological control on B incorporation, but the observed patterns can not yet be linked to any specific process (Allen et al., 2011; Hathorne et al., 2009). Based on B/Ca variations with test size in core-tops, Ni et al. (2007) have suggested that B incorporation may be influenced by calcification rate. Varying rates of calcification could lead to intra-test B/Ca variation, but this has not yet been tested in culture.

4.5. Constrain past seawater composition

In the modern ocean, boron behaves as a conservative element, with a consistent boron to salinity ratio of 0.1336 ± 0.0005 mg kg^{-1} S^{-1}, which equals 433 µmol B kg^{-1} seawater at $S=35$‰ (Lee et al., 2010). Boron fluxes between major reservoirs have not yet been well-constrained (for review see Tripati et al., 2011). The relatively poor constraints on the secular evolution of the boron cycle limit our ability to apply boron-based proxies to earlier times in Earth history. While relative changes within short intervals (<1 million years) are possible, absolute estimates comparing events that are several million years apart require a much improved understanding of the boron sources and sinks through time. Some paleo-$\delta^{11}B_{SW}$ estimates have been made (e.g., Pearson and Palmer, 1999), but higher-resolution studies and paleo-[B] estimates are needed.

It may be important to consider not only the concentration of B in ancient seawater, but of other elements as well. The balance of $B(OH)_3$ and $B(OH)_4^-$ in solution (described by the equilibrium constant pK_B) depends on temperature, pressure, salinity (Dickson, 1990), and solution composition (Dyrssen and Hansson, 1972–1973). Potentiometric measurements suggest that borate ion activity (i.e., the tendency to interact with other dissolved chemical species) varies with solution composition (Bassett, 1980; Hershey et al., 1986; Simonson et al., 1987). For

example, pK_B values determined in pure Na–Cl, Na–Mg–Cl, and Na–Ca–Cl solutions at ionic strength 0.65 (Hershey et al., 1986) give borate concentrations of 53, 69, and 76 µmol mol^{-1}, assuming a total pH of 8 and total boron (B_T) of 433 µmol kg^{-1}. The results from this study imply that dissolved B may have behaved differently in ancient oceans with higher or lower Mg, Ca, Na, and/ or K concentrations. However, the impact of such variable aqueous B behavior on the incorporation of B into fossil biogenic calcite is uncertain. All studies to date have assumed that the activity of dissolved B species has been constant through time, or at least that any changes did not impact B incorporation.

5. Conclusions

In planktic foraminifer culture experiments, inorganic precipitation experiments, and most sediment core-tops, B/Ca of calcite increases with seawater pH. This increase is consistent with the theoretical basis proposed for B incorporation. The specific mechanism for observed B/Ca behavior is uncertain, but may involve competition between the pH-sensitive anions $B(OH)_4^-$, HCO_3^-, and/or CO_3^{2-} for inclusion in the calcite lattice.

Relationships between K_D and seawater parameters can sometimes be driven by the denominator ([$B(OH)_4^-$]/[HCO_3^-]), and not by B/Ca. Reconstructions based on such B/Ca-independent relationships are susceptible to being driven by other environmental parameters. Application of the empirical boron partition coefficient, K_D, should be avoided until more is known about the relative influences of different chemical species on B incorporation. We recommend that where no direct relationships between B/Ca and environmental parameters can be observed, B/Ca-based reconstructions should not be attempted.

Temperature–K_D calibrations that are based on *down-core* records of both temperature and ocean carbon chemistry inherently contain the relationship between SST and pCO_2 of that particular time period. Such calibrations thus can not be used to test how the SST–pCO_2 relationship may have changed in earlier periods of Earth history.

In Pleistocene down-core records, planktic foraminiferal B/Ca exhibits species- and site-specific offsets but no consistent temporal pattern. B/Ca response to recent shifts in seawater carbonate chemistry (e.g., glacial–interglacial cycles) might be too small to be detected with current methods. However, more dramatic carbonate system shifts should cause larger, more pronounced B/Ca variation in the planktic fossil record. As the controls on this proxy become clearer, planktic foraminiferal B/Ca may yield new insight into past surface ocean chemistry.

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