CHAPTER 17

Boron Isotopes in Marine Carbonate Sediments and the pH of the Ocean

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Contents

1. Introduction

Until recently, our understanding of ancient seawater pH has relied on model predictions, despite its being an important chemical parameter of the oceans. Exchange between the surface ocean and the atmosphere means that changes in PCO_2 (ocean) and pCO_2 (atmosphere) are coupled, so knowing one can provide information on the other. If we could measure ancient ocean pH, then constraints can be placed on natural, pre-industrial pCO_2. This may help us better understand these natural fluctuations and controls on atmospheric chemistry so that we may better understand the recent anthropogenic perturbations and their future implications. One of the most critical environmental threats today is global warming, attributed to the industrial increase in atmospheric CO_2, making the development of a proxy for paleo-pH both timely and necessary.

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A promising candidate for a paleo-pH proxy is the boron isotope composition of marine calcium carbonate. Since the first published analysis of the boron isotope composition of modern marine carbonates (Hemming & Hanson, 1992; Vengosh, Kolodny, Starinsky, Chivas, & McCulloch, 1991), there has been a steady increase in our knowledge of this proxy. Although complications have been identified, confidence in the proxy has strengthened as our understanding of the mechanisms and controls on boron isotope uptake and fractionation in carbonates has increased. The goal of this paper is to present a history of the development of the boron isotope paleo-pH proxy as well as the theory behind it, identify the caveats, complications, and assumptions, and briefly review the applications of the proxy.

2. EMPIRICAL OBSERVATIONS AND THEORETICAL BACKGROUND

Our understanding of the boron isotope composition of seawater begins with an early study by Schwarcz, Agyei, and McMullen (1969). They proposed that the isotopically heavy value of seawater ($\sim+40‰$ relative to the NIST standard SRM951 boric acid) is due to the fact that boron is adsorbed onto clay particles as they enter the ocean. The clays flocculate and are deposited, thus removing some boron from the marine system. The boron that is removed is isotopically light, leaving seawater isotopically heavy. Normally one would expect the adsorbed species to be isotopically heavier than the water, as the lower vibration energy of the heavier isotope is typically favored in adsorption reactions. However, because boron does not occur as a metal in most natural systems, the aqueous boron species must be considered. Boron is present in seawater primarily as the trigonal $B(OH)_3$ species and the tetrahedral $B(OH)_4^-$ species (~80 and 20%, respectively, in seawater). The distribution of these species is pH controlled (Figure 1a). Because of coordination-controlled vibration differences between the species, there is an isotopic offset. The isotope exchange reaction

$$^{11}B(OH)_3 + {}^{10}(BOH)_4^- \leftrightarrow {}^{10}B(OH)_3 + {}^{11}B(OH)_4^-$$

has a equilibrium constant <1, which means the trigonal species is isotopically heavy relative to the tetrahedrally coordinated species. Thus, as the distribution of aqueous species changes with pH, so does the isotopic composition of the species (Figure 1b). The suggestion by Schwarcz et al. (1969) that adsorbed boron on clays is isotopically light gave the first clue that there could be a pH control on the isotope composition of adsorbed boron. Subsequent work on boron isotopes focused on distinguishing marine vs. non-marine origins of borate deposits (see Swihart, Moore, & Callis, 1986) until Spivack, Palmer, and Edmond (1987) presented their study of the sedimentary cycle of boron isotopes. This study represented a great leap in our understanding of boron isotope systematics. This was soon followed by an experimental study of boron adsorption on clays (Palmer, Spivack, & Edmond, 1987), which supported the early work of Schwarcz et al. (1969). At about this same time, two groups were beginning the first analyses on marine carbonates. Vengosh et al. (1991) and Hemming and Hanson (1992)
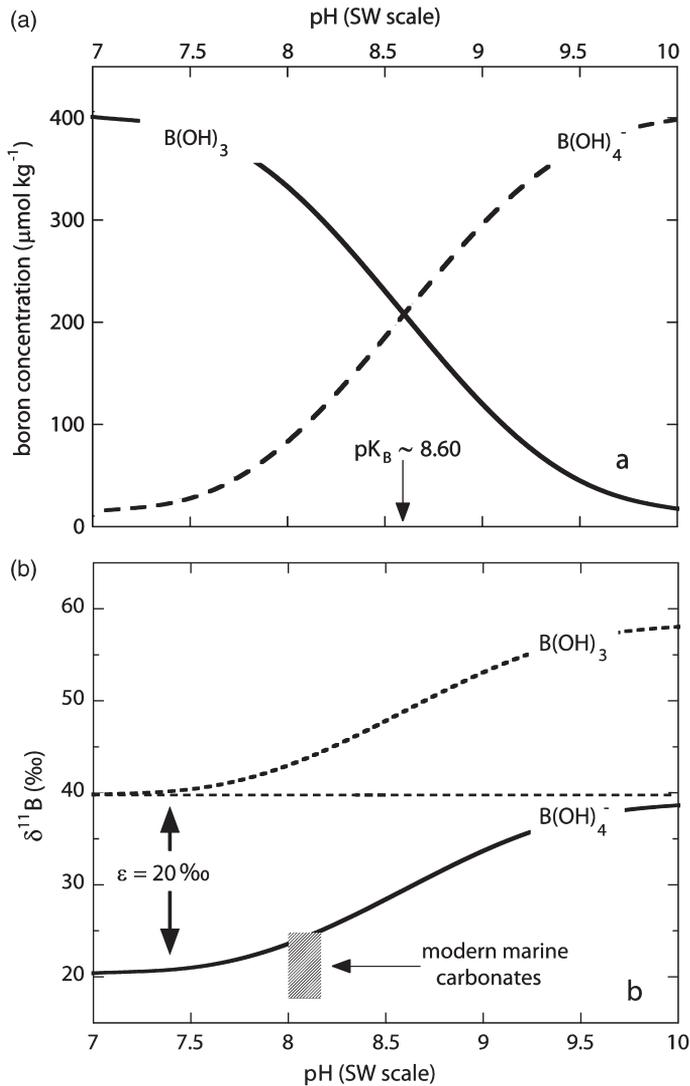
(a)

(b)

Figure 1 (a). The pH controlled distribution of the two dominant aqueous species of boron in seawater (pKB value from Dickson, 1990). (b). The isotopic composition of the two dominant aqueous species of boron in seawater (calculated using the theoretical fractionation factor of Kakihana et al., 1977). The box represents the range of measured modern carbonates analyzed by Hemming and Hanson (1992) and include bivalves, corals, echinoderms, calcareous algae, and ooids. Since the exact growth pH for those samples is not known, data are plotted at typical surface seawater-pH (after Hemming & Hanson, 1992).

pursued an improved negative thermal ionization method (NTIMS) of boron isotope analysis following initial work on this method by Duchateau and de Bièvre (1983) and Heumann and Zeininger (1985). Both the Hemming and Hanson (1992) and Vengosh et al. (1991) studies took the survey approach, measuring a

variety of marine carbonates, and both found significant offsets from seawater. The Hemming and Hanson (1992) study reported a relatively narrow range in boron isotope compositions considering the wide variety of samples analyzed (corals, echinoderms, brachiopods, ooids, bivalves, etc.), representing calcite, high–Mg calcite, and aragonite (Figure 1b). Hemming and Hanson (1992) proposed that the range in boron isotope composition was due to the fact that only the $B(OH)_4^-$ aqueous species is involved in reactions incorporating boron into the carbonate structure, as the survey data plotted remarkably close to the isotopic composition of the tetrahedral species in seawater as calculated using the only available estimate of the fractionation factor at that time (Kakihana, Kotaka, Satoh, Nomura, & Okamoto, 1977). In contrast, Vengosh et al. (1991) reported a much larger range in boron isotope values for modern carbonates, from +13.3‰ for a foraminifera sample to +31.9‰ for a coral sample. It is not clear why there is a difference between these two studies, but a later study by Gaillardet and Allègre (1995) reported modern coral analyses that overlap within analytical uncertainty of the Hemming and Hanson (1992) data (+24 to +27‰). This study used a positive ion technique similar to that used by Spivack and Edmond (1986), and gave support to the Hemming and Hanson (1992) interpretation.

2.1. Synthetic Carbonate Studies

The next step in the development of the proxy was to determine if the interpretation of Hemming and Hanson (1992) was robust. The uncertainties of the survey study (the exact pH at sample localities, as well as salinity, temperature, and other factors, was not known), did not allow quantitative analysis of the controls on boron uptake and fractionation. Therefore, a laboratory-based study was initiated to test the Hemming and Hanson (1992) hypothesis. In that study, synthetic calcite was grown from solutions with similar ionic strength to seawater, and a range of boron concentrations (Hemming, Reeder, & Hanson, 1995). The boron isotope standard, NIST SRM951, was used so the starting composition of the fluid was known. The results showed a remarkable agreement to the $B(OH)_4^-$ isotope composition of the solution, and thus lent strong support for the initial hypothesis (Figure 1b). There was no indication from that study that mineralogy (calcite, high-Mg calcite, or aragonite) played a significant role in the isotopic fractionation. This set the stage for the use of boron isotopes as a paleo–pH proxy, as it was now clear that the boron isotope composition of the precipitated carbonate matched perfectly with the known pH of the experimental solution. A second experimental study of inorganic precipitates confirmed the tight coupling between boron isotopes in synthetic carbonates and the pH of the growth solution over a range of pH conditions (Sanyal, Nugent, Reeder, & Bijma, 2000). However, there was an offset of approximately −2‰ between the growth solution $B(OH)_4^-$ composition and the carbonate. It is not known why there is a discrepancy between the Hemming et al. (1995) and Sanyal et al. (2000) studies, but the experimental setup was quite different. Whereas Hemming et al. (1995) adjusted pH by controlling pCO_2 in the experiment chamber, Sanyal et al. (2000) controlled pH by the addition of salts, which also altered alkalinity. Perhaps the differences in the experimental controls

had an influence on the results, but to date these experiments have not been replicated. Regardless, both studies show the strong dependence of boron isotope compositions of calcium carbonate with pH.

2.2. Culture Experiments

While it is impossible to recreate natural conditions in the laboratory, coral and foraminifera culture experiments come closest to simulating true conditions, while allowing control of environmental parameters. Coral and foraminifera experiments over a range of pH values (Hönisch et al., 2004; Reynaud, Hemming, Juillet-Leclerc, & Gattuso, 2004; Sanyal, Bijma, Spero, & Lea, 2001; Figure 2, Sanyal et al., 1996) all faithfully reproduce the shape of the Kakihana et al. (1977) $B(OH)_4^-$ curve, although they are variably offset from the curve (see discussion on this offset below). Hönisch et al. (2003, 2004) further evaluated the effects of variable light intensity and respiration on the boron isotope composition of cultured foraminifers and corals, respectively. Whereas planktic foraminifers quantitatively record the influence of those physiological parameters on pH in their microenvironment (Hönisch et al., 2003), corals are not strongly affected by these controls, thus reflecting the different calcification mechanism of the corals (Hönisch et al., 2004).

3. Caveats and Complications

3.1. Isotope Fractionation Factor

There has been a flurry of activity recently to recalculate and measure the isotope fractionation between aqueous $B(OH)_3$ and $B(OH)_4^-$ (Byrne, Yao, Klochko, Tossell, & Kaufman, 2006; Liu & Tossell, 2005; Oi, 2000; Pagani, Lemarchand, Spivack, & Gaillardet, 2005a; Sanchez-Valle et al., 2005; Zeebe, 2005). Whereas Pagani et al. (2005a) merely fitted a curve to the synthetic calcite calibration established by Sanyal et al. (2000), most of these studies attempt to refine the fractionation factor (α) using *ab initio* calculations of the theoretical isotope effect based on the vibrational energies of the two coordinations. All but one of these studies results in α significantly greater than that determined by Kakihana et al. (1977). The range in α determined in these studies is from 1.0176 to 1.030 (see discussion in Zeebe et al., in press). This large range is an indication of the problems with determining α that stems from uncertainties in the vibration frequency data and assumptions used in the calculations. Byrne et al. (2006) provide the first true experimental estimate of $\alpha = 1.0285$. Although this estimate is consistent with other theoretical estimates, the shape of the empirical calibration curves discussed above (Figure 3, Hönisch et al., 2004; Reynaud et al., 2004; Sanyal et al., 2001; Sanyal et al., 1996, 2000) is remarkably consistent with a fractionation factor of ~1.020, close to the Kakihana et al. (1977) fractionation factor. The discrepancy between the empirically determined and the experimentally determined fractionation factors is not understood at this time. This is an unsatisfying aspect of the boron isotope paleo-pH proxy. It should be noted that a larger fractionation factor
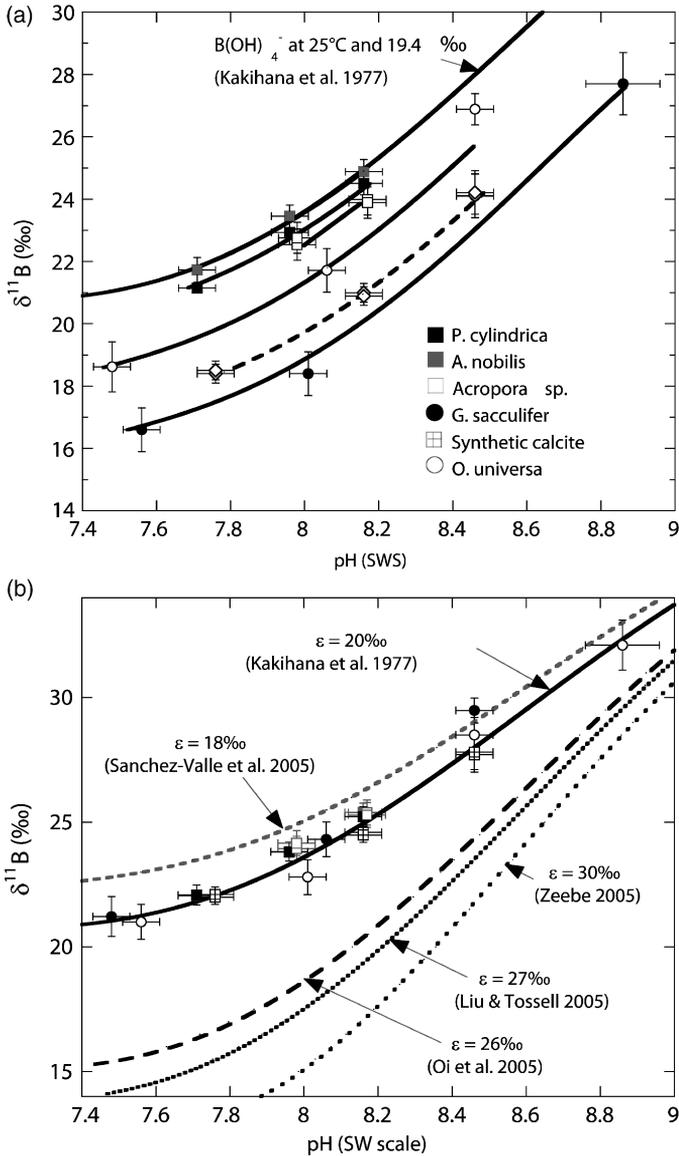
Figure 2 (a) Data for all published calibration studies (solid and shaded squares after Hönisch et al., 2004; open squares after Reynaud et al., 2004; open circles after Sanyal et al., 2001; open diamond after Sanyal et al., 2000; closed circles after Sanyal et al., 1996). Note that all empirical curves are parallel to each other but show constant offsets relative to each other and to the theoretical borate curve by Kakihana et al. (1977). (b) Empirical data from Figure 2a corrected for their specific offsets, and five theoretical borate curves. Empirical data match the shape of the borate curve by Kakihana et al. (1977). Note that minor variability between theoretical and empirical curves may be due to differences in experimental temperature and salinity.

cannot explain the observed δ^{11}B offsets from the Kakihana et al. (1977) B(OH)$_4^-$ curve, as vital effects would move the curves left or right on Figure 2. Further, it is unlikely to be a problem with the empirical fractionation factor, as other values for α change the shape of the curve and therefore do not fit the calibration data. Zeebe (2005) and (Zeebe et al., in press) recognize the importance of the empirical calibrations, stating that the current uncertainty in α does not preclude the use of the proxy, and that the proxy is robust as long as single species, empirical calibrations are used. Further study, particularly with synthetic carbonate approaches, may help to solve this conundrum.

3.2. Foraminifera Size and Dissolution Effects

In an effort to evaluate all potential complications behind the boron isotope paleo–pH proxy, Hönisch and Hemming (2004) analyzed natural foraminifers from core top samples over a depth range representing variable calcite saturation (Ontong-Java Plateau in the Pacific and the 90° East Ridge in the Indian Ocean). It was found that both shell size and shell weight influence the boron isotope values measured. Shell size relates to the depth of calcification of the species analyzed (the symbiont-bearing *Globigerinoides sacculifer*). Smaller shells are consistent with the foraminifers residing deeper in the water column, where light levels are lower and the pH-elevating effect of symbiont photosynthesis is reduced (Figure 3). The lighter δ^{11}B values of smaller individuals are also in good agreement with Mg/Ca measurements on these same individuals and the expected cooler temperatures at depth. Shells from deeper location core tops have lower size–normalized shell weights, indicative of the amount of dissolution the foraminifera test has experienced in the corrosive bottom waters. The isotopic composition of those shells picked from deeper sediment cores is offset from pristine, unaltered samples, towards lighter boron isotope values (Figure 3). The conclusion of this study is that, in order to make robust interpretations of paleo–pH using the boron isotope proxy in foraminifera, one must select large (>400 μm), pristine shells of single calibrated species. Previous authors were not aware of these potential complications so those studies need to be interpreted with caution (see application discussion below).

3.3. Analytical Challenges

Perhaps the biggest obstacle that must be overcome in order to bring the boron isotope paleo–pH proxy into widespread use is the analytical challenge. Early work relied on positive ion methods, beginning with procedures that measured the Na$_2$BO$_2^+$ ion (Oi et al., 1989; Swihart et al., 1986). This method was capable of measuring geologic samples to a precision of $\pm 2‰$ and required large amounts of boron (>100 μg), but was adequate for early studies of borate minerals where sample size was not a problem. However, the method also required high sample purity, and was sensitive to ionization temperature, as well as fractionation during the analysis. The introduction of the Cs$_2$BO$_2^+$ method (Leeman, Vocke, Beary, & Paulsen, 1991; Nakamura, Ishikawa, Birck, & Allegre, 1992; Ramakumar, Khodade, Parab, Chitambar, & Jain, 1985; Spivack & Edmond, 1986; Xiao, Beary,
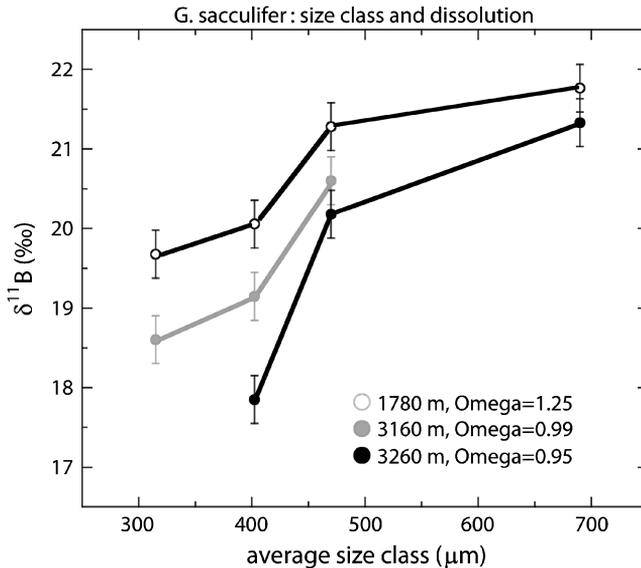
G. sacculifer : size class and dissolution

Figure 3   The δ^{11}B of *G. sacculifer* shells from the Ontong-Java Plateau decrease with shell size and with increasing dissolution (with permission from Hönisch & Hemming, 2004). Note that δ^{11}B of the large shells show less difference between shallow and deep sites, and the authors recommend only selecting large shells with no evidence of dissolution for paleo-reconstructions.

& Fassett, 1988) improved on the previous methods by a reduction in sample size to 0.5–1 µg, and the heavier compound reduced problems with in-run fractionation. However, sample purity is still a problem with this method.

In order for the boron isotope paleo-pH proxy to have wide application to marine chemistry and climate change studies, a method that would allow the analysis of very small samples is necessary. Foraminifer shells are currently the most useful archive for paleo-climate proxies, but only contain on the order of 10–15 ppm boron. An unreasonably large sample size would be necessary in order to analyze foraminifers from marine sediment cores using the positive ionization methods. Improvements to NTIMS first developed by Duchateau and de Bièvre (1983), Heumann and Zeininger (1985), and Vengosh, Chivas and McCulloch (1989) opened the door to analysis of very small amounts of boron with high precision (Hemming & Hanson, 1992, 1994). Because the negative ion species BO_2^- ionizes extremely efficiently, sub-nanogram quantities of boron could be analyzed with precision of better than 0.7‰. Recent refinements of this method now result in reported precision of <0.3‰, on par with the positive ion method (see Hönisch & Hemming, 2005; Pelejero et al., 2005).

Obtaining this precision comes at a price. Each sample must be replicated at least three times (Hönisch & Hemming, 2004, 2005) and extreme care must be taken in order to reproduce running conditions. Because internal normalization is not possible as with stable isotope analysis, mass fractionation during acquisition must be corrected by repeated analysis of standards using exactly the same analytical protocol as the samples. The protocol we have developed includes consistent sample

loading procedures, filament heating procedures, strict acceptance criteria for in-run fractionation, and a minimum of three replicate analyses. Some samples must be analyzed 10 times or more in order to obtain three runs that meet all of these criteria. While we think this protocol is essential in order to obtain high precision data, few labs apply these criteria. This makes it difficult to compare results from one lab to another. One lab that has adhered to these guidelines has produced perhaps the best data published to date (Pelejero et al., 2005). Following is a brief review of our procedure.

Samples for data published by Hemming, Sanyal, and Hönisch were measured a minimum of three times, and a minimum of 50–60 isotope ratios are collected over a period of 20–30 min. Data are rejected if the increase in the measured ratio during that time interval exceeds 1‰. Data are also rejected if a signal is observed at mass 26 ($^{12}C^{14}N$ ions), an indication that an isobaric interference may be present. NTIMS measures BO_2^- ions on masses 43 and 42 ($^{11}B^{16}O_2^-$ and $^{10}B^{16}O_2^-$) and organic matter contamination interferes on mass 42 ($^{12}C^{14}N^{16}O$), which results in an underestimate of the original $\delta^{11}B$ of the carbonate (Hemming & Hanson, 1992). As a consequence, samples need to be treated with an oxidizing solution to remove organic matter. Samples are crushed and bleached overnight in commercial bleach or NaOCl. We refrain from H_2O_2 because it is too aggressive and may cause partial dissolution during the cleaning process. The oxidizing solution, as well as potentially adsorbed boron and clay particles, are then removed by repeated rinsing (10 times) and ultrasonication in distilled water. The cleaned carbonate sample is then dissolved in distilled HCl and measured at approximately $980°C$ on an outgassed Re filament. The filament temperature and heat-up time are critical for the analyses. Experience has shown that it is best to heat the filament slowly, over 20–30 min. Our goal is to collect three analyses that fall within $\pm 0.5‰$ for every sample, but excessive fractionation and/or isobaric interference through organic matter contamination sometimes require up to ten or more analyses of a single sample solution to reach that goal. Over the years we have optimized heat up time, analysis temperature and we now refrain completely from waiting after filament heat up. We can measure boron amounts as small as 1 ng and obtain 2σ analytical uncertainties of $\pm 0.3‰$ or better. Daily analysis of SRM NBS 951 and/or a seawater standard allows for monitoring of the mass spectrometer performance and data reference relative to SRM NBS 951. Sample cleaning and analysis are always done in exactly the same manner and resulting data for monospecific samples of similar age are internally consistent.

3.4. Secular Variation in Seawater $\delta^{11}B$

The boron isotope paleo-pH proxy requires the knowledge of the isotope composition of the parent fluid in order for it to work. Since boron has a relatively long residence time in seawater, (∼3–5 Myr, Lemarchand, Gaillardet, Lewin, & Allègre, 2000, 2002; ∼16 Myr, Taylor & McLennan, 1985), it is reasonable to assume there has not been significant variation in the isotopic composition of seawater over those time scales. However, there has been some concern regarding studies that report pH interpretations going back tens of millions of years (Palmer, Pearson, & Cobb, 1998;

Pearson & Palmer, 1999, 2000; Spivack, You, & Smith, 1993). In response to this concern Lemarchand et al. (2000) modeled the expected limits of boron isotope composition of seawater going back ~120 Ma. Their model predicts boron isotope fluctuations over a range of ~6‰, related primarily to continental discharge, alteration of oceanic crust, and mechanical erosion of continents as it supplies a source of sediment for adsorption of boron. They suggest that the relatively large pH changes reported by Pearson and Palmer (2000) and Spivack et al. (1993) may therefore be incorrect. If pH is calculated using the boron isotope data in foraminifers and the modeled boron isotope composition of seawater, little change in pH is seen over that time period. A secular variation of 0.1‰/Ma is estimated by the Lemarchand et al. (2000) model. However, evidence from past seawater Ca^{2+} and Mg^{2+} concentration and calcite compensation depth suggests that pH has probably increased over the past 100 Ma and that variations have occurred over the Cenozoic (Tyrrell & Zeebe, 2004). Given this independent evidence, an almost constant seawater pH based on the estimated $\delta^{11}B_{seawater}$ (Lemarchand et al., 2000) appears unrealistic.

Clearly, for paleo-pH studies of deep time, a boron isotope secular variation curve must be constructed similar to the Sr isotope curve. There are several potential approaches to this goal:

1) analysis of a deep marine carbonate that grew at low pH values (<7.8) which would represent the maximum offset from the seawater value and allow calculation of the bulk seawater composition; problems with this method include uncertainties in the habitats of benthic foraminifers and ancient species and species-specific offsets as reported in Figure 2;
2) analysis of an extant species (such as brachiopods) that have spanned a large part of the Phanerozoic; problems with this approach again include uncertainties in species-specific offsets (although less likely for this particular organism), the habitat of ancient species, and the ocean pH, increasing the uncertainty of the ocean isotope composition estimate;
3) pristine seawater fluid inclusion analysis of calcium carbonate or other marine mineral precipitates; problems with this method include the difficulty in extraction of the fluid for analysis, and uncertainties in determining whether the inclusion is pristine;
4) analysis of two minerals with known (and different) fractionation from seawater would allow calculation of the seawater isotope composition, however a second suitable mineral (besides $CaCO_3$) has not been identified.

4. APPLICATIONS OF THE BORON ISOTOPE PALEO-pH PROXY

To date, there are surprisingly few published applications of the boron isotope paleo-pH proxy. This is most likely due to the fact that the proxy is still in development, as well as the fact that the analyses are difficult. However, some interesting records are now available, and it is expected that, with the recent

increase in our knowledge of the proxy (Hönisch et al., 2003, 2004; Hönisch & Hemming, 2004, 2005), more application studies will be forthcoming.

The first attempt at applying the proxy was the study of Spivack et al. (1993), who completed down-core analyses of mixed species of foraminifers and associated pore water going back approximately 21 Ma. This early attempt suffered from several problems not recognized at the time, including potential species effects, shell size effects, and dissolution effects which could be present in a bulk sample. Further, the interpretation that seawater $\delta^{11}B$ was 5‰ lighter than today prior to ~7.5 Ma is unlikely, and the interpretation that seawater pH was as low as 7.4 is highly suspect.

The second attempt at applying the proxy addressed many of these potential problems by analyzing mono-specific samples, and restricting the study to glacial–interglacial time scales, thus avoiding potential complications with seawater secular variation and reducing the potential for diagenetic effects (Sanyal, Hemming, Hanson, & Broecker, 1995). In this study, the pH of glacial surface water was calculated to be ~0.3 pH units more basic than present-day seawater based on the boron isotope composition of glacial age planktonic foraminifers. The authors showed this was reasonable by calculating the expected surface ocean pH difference based on the known atmospheric pCO_2 of glacial times as measured in air trapped in ice cores. Whereas the authors used a single species for the surface water pH part of this study, and met many of the analytical criteria described previously, the determination of bottom water pH was based on analysis of bulk, mixed benthic foraminifer species. As with the Spivack et al. (1993) study, interpretations based on mixed species analysis are suspect, and the very high bottom water pH (~0.3 pH units greater than Holocene) was not accepted by the paleoceanographic community. The mismatch between the boron isotope estimate and reconstructions based on carbonate preservation (Anderson & Archer, 2002) and Zn/Ca ratios in benthic foraminifers (Marchitto et al., 2005), which suggested a much smaller increase in deepwater saturation, had the unfortunate side effect of making people suspicious of the proxy. Although we still do not know the reason for the heavy boron isotope values measured in that study (perhaps resulting from using mixed benthic species), a recent application of the boron isotope pH proxy using *Cibicidoides wuellerstorfi* has shown that the glacial ocean was at most ~0.1 pH units more basic than today (Hönisch, unpublished data). Sanyal, Hemming, and Broecker (1997) followed up their first study with an application of the boron isotope paleo-pH proxy to a core in the eastern equatorial Pacific. In that study, no surface water change was seen through the marine isotope stage 5–6 transition, which they interpreted as a result of higher glacial upwelling intensity at that site. As with the Sanyal et al. (1995) study, mixed benthic species were analyzed for bottom water pH determinations. The absolute isotope values obtained from those samples were ~2‰ lower, and the relative difference between glacial and Holocene samples was ~1‰ greater as compared to the earlier study, indicating the poor consistency and large uncertainty of the mixed benthic species approach. So again caution should be exercised in interpreting the high bottom water pH values reported there.

Two studies used the boron isotope pH proxy to interpret changes in upwelling over glacial–interglacial time scales (Palmer & Pearson, 2003; Sanyal & Bijma, 1999). The basis for using boron isotopes in this context is that increased upwelling

at a particular site will decrease the surface water pH at the site, which should be reflected in the boron isotope composition of foraminifers. Sanyal and Bijma (1999) compared glacial–interglacial changes in pH at two locations, off northwest Africa and in the eastern equatorial Pacific. They interpret the minimal change in pH of surface water in the Pacific core as an indication this area was a significantly greater source of CO_2 to the atmosphere than was the northwest Africa region, which showed a 0.2 pH unit higher value than today. Similarly, the Palmer and Pearson (2003) study of a western equatorial Pacific core interprets the calculated low surface water pH values as disequilibrium between the surface ocean and atmosphere. According to that study, the deglacial surface Pacific had excess CO_2 relative to the atmosphere, and thus the tropical oceans were a source of CO_2 to the atmosphere, so may have triggered or amplified Holocene warming.

Palmer et al. (1998) used the boron isotope composition of various foraminifer species that represent a range of depth of calcification and thus can be used to create a pH-depth profile. Using the same $\delta^{11}B/pH$ relationship for all species investigated, similar pH-depth profiles at five time slices going back ∼16 Ma are obtained and suggest little change in the ocean pH structure. Although this approach provides potential for reconstructing the boron isotope composition of seawater through time, it does not take into account specific differences in the isotopic composition recorded by foraminifer species uncalibrated for their $\delta^{11}B$-pH relationship. So again, caution should be applied in interpreting those data.
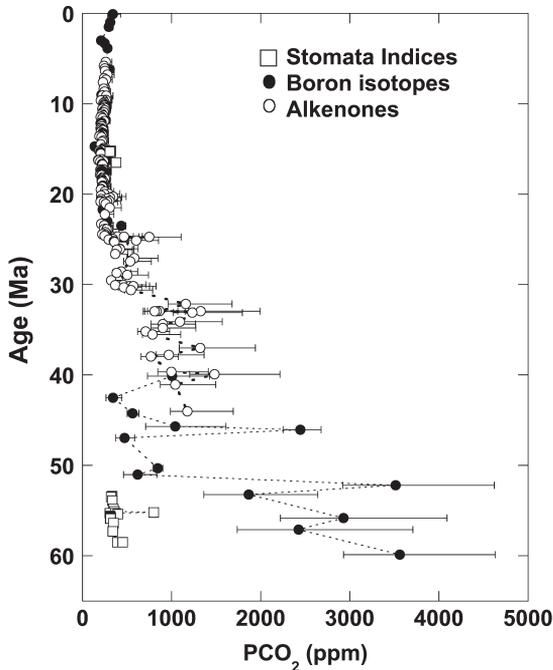

Figure 4 Estimates of pCO_2 through the Cenozoic using boron isotopes (Pearson & Palmer, 2000), alkenones (Pagani et al., 1999, 2005), and stomata indices (Royer et al., 2001).

Pearson and Palmer (1999) and Pearson and Palmer (2000) represent attempts to take the proxy back to deep time. As with the Spivack et al. (1993) study, there is concern whether there has been secular variation of the boron isotope composition of seawater as suggested by models (Lemarchand et al., 2000, 2002). Pearson and Palmer (1999) measured pH-depth profiles from planktic foraminifers over the past 43 Ma and concluded pCO_2 was similar or only slightly elevated relative to pre-industrial levels. The Pearson and Palmer (2000) study analyzed foraminifer samples going back 60 Ma. They construct a surface ocean pH curve that shows relatively small deviations going back ~20 Ma, but then erratic fluctuations and significantly more acidic surface ocean pH conditions from 40 to 60 Ma (there is a gap in the time series between 20 and 40 Ma). These data can be compared with other proxies for pCO_2 (Figure 4), such as stomata indices (Royer et al., 2001) and the photosynthetic carbon isotope fractionation as reported in alkenones (Pagani, Freeman, & Arthur, 1999; Pagani, Zachos, Freeman, Tipple, & Bohaty, 2005b). As discussed above, Lemarchand et al. (2002, 2000) reinterpret the Pearson and Palmer (2000) data in light of their model secular variation calculations and find that pH variations over the past 60 Ma may be minor.
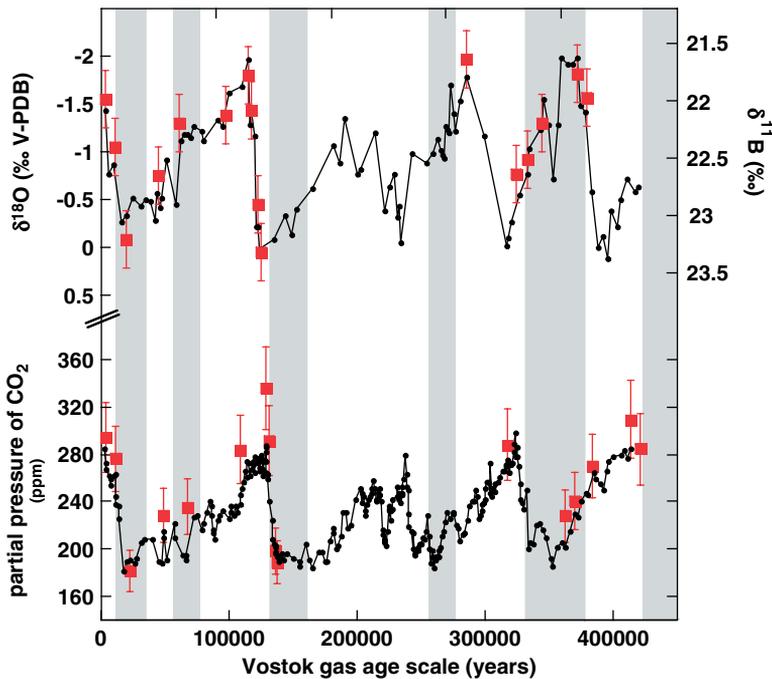

Figure 5 Boron isotope evidence for pH changes at ODP site 668B in the eastern equatorial Atlantic in synchrony with atmospheric pCO_2 variations recorded in the Vostok ice core (Hönisch & Hemming, 2005). In the top panel the black curve is the $\delta^{18}O$ of *G. ruber* from the sediment core, and the red symbols are the measured $\delta^{11}B$ of *G. sacculifer*. In the lower panel, the black curve is the pCO_2 record from Vostok, and the solid symbols are the calculated PCO_2 based on the $\delta^{11}B$ as well as temperature, salinity and alkalinity estimates (for a detailed description see Hönisch & Hemming, 2005).
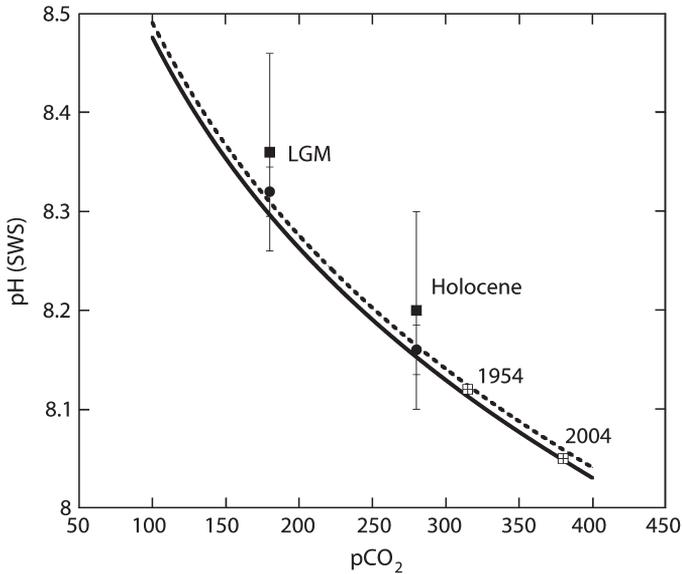
Figure 6 Plot of calculated surface ocean pH for a given atmospheric pCO_2. The two curves are calculated for salinities and temperatures estimated for open tropical waters in the Holocene (34.8 psu, 27°C, 2,300 μmol kg^{-1} alkalinity), and the LGM (35.8 psu, 25°C, 2,370 μmol kg^{-1}). Also shown are reconstructed pH data from planktic foraminifers (black squares: Sanyal et al., 1995, and black circles: Hönisch & Hemming, 2005). The error bars for both are propagated according to the description in the publications. Offsets for data from Sanyal et al. (1995) and Hönisch and Hemming (2005) are due to differences in the analytical protocols used for those two studies. Also shown are the atmospheric pCO_2 data for 1954 and 2004 from Keeling and Whorf (2005), plotted along the calculated pH profiles.

Finally, the most recent study by Hönisch and Hemming (2005) represents a rigorous test of the boron isotope paleo-pH proxy by using boron isotope data of mono-specific foraminifers representing two glacial cycles, calculating aqueous PCO_2 from the pH data, and comparing the results directly with the known atmospheric pCO_2 as measured in air trapped in ice cores. The results are a remarkable success, with PCO_2 values from the proxy matching the ice core data to within $+/-20$ ppmv (Figure 5). Glacial/Holocene studies from ocean areas where atmospheric pCO_2 and aqueous PCO_2 are in equilibrium (Hönisch & Hemming, 2005; Sanyal et al., 1995, 1997) can also be used to assess the robustness of the proxy, as ice core pCO_2 data are available for this time period. Figure 6 compares these studies and demonstrates the good agreement between boron isotope-pH reconstructions and measured changes in atmospheric pCO_2.

5. SUMMARY AND CONCLUSION

While the development of the boron isotope paleo-pH proxy continues, the general understanding of the proxy allows it to be applied if done carefully. The

observations and lessons learned from calibration studies and first attempts at applying the proxy include:

1) data quality is of utmost importance, so any application of the proxy must include evidence that strict analytical protocol has been adhered too, and include replicate analysis of all samples;
2) core locations must be selected carefully, depending on the question being pursued with the proxy (i.e., evidence that upwelling or other major oceano-graphic changes have not occurred at the location; water depths are above the lysocline);
3) calibrated, mono-specific foraminifera samples of the appropriate size range and with no signs of dissolution or recrystallization must be chosen; extinct species must be calibrated to extant species;
4) absolute pH values can only be reconstructed within the residence time of boron in the oceans, as secular variation of the boron isotope composition of seawater cannot yet be determined beyond this time; until past variations of $\delta^{11}B$ seawater are satisfactorily determined, older samples can only be interpreted with regard to relative pH changes within 3–5 Myr time intervals (i.e., intervals similar to the residence time of boron in seawater).

These observations allow application of the proxy to an important time window that could provide invaluable information on the controls on climate, and thus addresses ocean–atmosphere interactions resulting from recent anthropogenic perturbations.

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