

**Examining the boron isotope-pH proxy: the role of vital effects on  $\delta^{11}\text{B}$  of  
Porites coral and implications for proxy use**

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**Abstract:** The fundamental study on the ion-exchange separation of boron isotopes, *Kakihana et al.* (1977), set the stage for the further study of the boron isotope-pH proxy to be used in climate reconstructions. The proxy is based on a number of assumptions, which have proven difficult to constrain experimentally. Boron occurs in such small concentrations that it is difficult and sensitive to work with. Additionally, both biological and inorganic processes may affect the concentration and incorporation of boron in the carbonate lattice. However, many labs throughout the world are still doing important work on the topic and the future use of the proxy looks hopeful. This paper will begin by examining the historical and current studies on the boron isotope-pH proxy in order to synthesize the large amount of information available. Under the time and resource constraints of this senior project, individual research unfortunately was not possible. However, work done by *Wang et al.* (2013) will be used to analyze the vital effects of the *Porites* coral from Australia's Great Barrier Reef, concurrently with available literature on the topic, in order to draw conclusions regarding the importance of vital effects for future use of the boron isotope-pH proxy. With more research into the mechanisms behind the  $\delta^{11}\text{B}$  changes due to vital effects in biogenic marine carbonates, future use of the proxy for paleoclimate reconstruction is still quite viable.

## 1. Introduction

Since the realization of anthropogenic affects on Earth's atmosphere and oceans over 100 years ago (Fourier, 1824; Tyndall, 1861; Arrhenius, 1896), scientists have attempted to reconstruct Earth's past climates in order to help determine the potential future of the Earth. This is a daunting task and over the years scientists have tried a number of methods. Quantification of past  $\text{CO}_2$  concentrations is necessary in order to understand the exact sensitivity of climate to changing greenhouse gas concentrations. The pH of the surface ocean is a function of its alkalinity and total inorganic carbon concentration, properties which also control the partial pressure of  $\text{CO}_2$  in the atmosphere. By 2001, ocean acidification increased 0.1 pH units relative to industrial times and is predicted to increase another 0.8 pH units by 2300 (Pelejero, 2005). While qualitative representations can provide a general picture of the relationship between  $p\text{CO}_2$  and climate forcings, direct quantitative

measurements of historic CO<sub>2</sub> levels are also necessary in order to fully understand implications for future climate change (Pagani et al., 2005).

Ice core data provides the groundwork for quantitative climate reconstruction data, and has been complimented by climate model simulations (Berner and Kothavala, 2001), the carbon isotopic composition of organic and carbonate carbon (Arthur et al., 1988; Freeman and Hayes, 1992; Pagani et al., 1999), carbon isotopic compositions of soil carbonates (Cerling, 1991) and the boron isotopic composition of marine carbonates (Sanyal et al., 1995; Pearson and Palmer, 2000). Marine bio-carbonates are one of the main reservoirs of boron in the ocean; this includes coral, foraminifera, brachiopoda, gastropoda, and bivalve (Xiao et al., 2013). There is a relationship between the isotopic concentration of boron in marine carbonates and the pH of the oceans, which, if reliably constrained, may provide a much better understanding of the history of Earth's climate. This relationship between boron isotopic composition and pH is termed the  $\delta^{11}\text{B}$ -pH proxy and foraminifera and corals are the main materials used to study the potential of the proxy. Given the growing importance of climate research and paleoclimate evidence for the nature of earth's systems, boron isotope studies have increasing scientific and public interest and its implications are important in the larger climate debate. For example, the Cenozoic record of pCO<sub>2</sub> and ocean pH of *Pearson and Palmer (2000)* based on  $\delta^{11}\text{B}$  measurements of ancient foraminifers appears in the IPCC AR4 report as part of the case for CO<sub>2</sub> causing natural climate change (Foster et al., 2012).

This proxy is an exciting development in paleoclimate reconstruction research because it is the first and only known proxy for direct CO<sub>2</sub> reconstructions. There are a number of factors and assumptions in the proxy, however, that must be further constrained or better understood in order to utilize the proxy more broadly. This paper will enumerate each of the potential concerns regarding the use of the proxy and the work being done to better constrain them. Current debate focuses on the potential vital effects and offsets caused by biological processes in both coral and foraminiferal carbonates as well as the importance of interlaboratory comparisons of boron isotope analyses. Understanding the vital effects of different species will allow for the use of different species within the same reconstruction and the comparison of results between species. Additionally, the use of laboratory standards and common methodologies in approaching boron analysis will allow for the certainty to

compare results between labs and use multiple datasets from different labs in the same analysis and reconstruction.

## 2. Literature Review: Boron and pH

Dissolved boron in seawater primarily includes mononuclear species  $\text{B(OH)}_3$  (boric acid; planar, trigonally coordinated) and  $\text{B(OH)}_4^-$  (borate; tetrahedrally coordinated) (Kakihana et al., 1977). However, polyborate anions containing the tetrahedral groups,  $\text{B}_3\text{O}_3(\text{OH})_4^-$ ,  $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ , must also be considered if the concentrations of boron are  $>0.025$  M (Kakihana et al., 1977; Ingri, 1963; Ingri et al., 1957; Xiao et al., 2013) because these species may contribute to the high separation factor between a cation exchange resin phase and solution below pH 8.7 (Kakihana et al., 1977). However, for our purposes, polynuclear boron species are assumed to be inconsequential because they are effectively absent at modern total boron concentrations in seawater ( $0.416 \text{ mmol kg}^{-1}$  at  $S=35$ ; Miller, 1982; Zeebe et al., 2001; Klochko et al., 2006).

The consistency of the boron isotopic composition in the oceans is due to the long residence time of about 16 million years in the world's oceans (Taylor and McLennan, 1985; Hemming and Hanson, 1992). Comparatively, the isotopic value of boron in river water is much more negative. Marine boron is more  $^{11}\text{B}$ -enriched than fluvial boron because the active surfaces in the marine environment that adsorb boron select the tetrahedral  $\text{B(OH)}_4^-$ , which is  $^{11}\text{B}$  depleted relative to  $\text{B(OH)}_3$  (Hemming and Hanson, 1992). When boron is incorporated into the carbonate lattice of marine organisms, several factors determine the isotopic composition of the resulting carbonate, including ambient pH because of its control on the distribution of aqueous boron species, borate to carbonate ratio in seawater, temperature, mineralogy, biological controls and vital effects, and other kinetic factors (Hemming and Hanson, 1992). It has long been assumed that the tetrahedral and negatively charged borate is preferentially incorporated into the carbonate lattice (Hemming et al., 1995; Sanyal et al., 1996; 2000; 2001); however, recent studies (Klochko et al., 2009) have re-evaluated this assumption, concluding that both trigonal and tetrahedral boron is incorporated in almost equal amounts in both calcite and aragonite samples. Additionally,

Zeebe *et al.* (2001) established that kinetic isotope effects are unlikely to affect the incorporation of boron into the carbonate lattice.

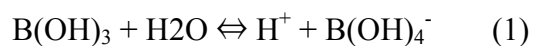
The pH of the surface ocean is a function of the ratio of alkalinity to total dissolved inorganic carbon. The combination of these factors controls dissolved  $p\text{CO}_2$ . Therefore, if the pH of seawater and either the alkalinity or the dissolved inorganic carbon concentrations are known, atmospheric  $p\text{CO}_2$  can be calculated. The boron isotope-pH proxy is therefore a tool to reconstruct past seawater pH, as a means to then estimate atmospheric  $p\text{CO}_2$ .

### 2.1 Assumptions of the Boron-pH proxy

The boron isotope-pH proxy relies on a number of assumptions to predict past  $p\text{CO}_2$  and therefore changes in global sea surface temperatures (SST). (1) The proxy relies on the assumption that dissolved  $\text{CO}_2$  is in equilibrium with atmospheric  $\text{CO}_2$ . Therefore, a change in atmospheric  $\text{CO}_2$  means that more  $\text{CO}_2$  is likely dissolved in the surface ocean, resulting a decrease in its pH (Pearson and Palmer, 2000; Pagani *et al.*, 2005). (2) In seawater, boron is present in two significant forms,  $\text{B}(\text{OH})_4^-$  and  $\text{B}(\text{OH})_3$ , the relative concentrations of which are pH dependent. Also, boron isotopes are fractionated between these two species with  $\text{B}(\text{OH})_3$   $^{11}\text{B}$ -enriched relative to  $\text{B}(\text{OH})_4^-$  (Ingri, 1963; Kakihana *et al.*, 1977; Xiao *et al.*, 2013). (3) The proxy also assumes that the  $\delta^{11}\text{B}$  value of carbonate boron is similar or identical to borate in solution (Figure 2). This assumption remains questionable and the validity of the assumption also depends on the accuracy of the parameters that create the theoretical  $\delta^{11}\text{B}$ -pH curve,  $pK_B^*$ ,  $\alpha_{4-3}$ , and  $\delta^{11}\text{B}$  of seawater. (4) Due to the long residence time of boron in seawater,  $\delta^{11}\text{B}_{\text{sw}}$  is stable at  $\sim 39.5\%$  for at least the past 20 Ma (Spivack and Edmond, 1987; Pearson and Palmer, 2000). (5) There is no significant “vital” effect on the boron isotopic composition of foraminifera (Sanyal *et al.*, 2000; Zeebe *et al.*, 2003; Hönisch *et al.*, 2003). Particular vital effects will be discussed later in this paper.

### 2.2 Dissociation Constant ( $K_B^*$ )

Assuming the trigonal and tetrahedral mononuclear boron species dominate, the dissociation of boric acid is a function of salinity, temperature, and pressure, and is given by the following equilibria:



Equation (1) illustrates the dependence of the ratio between boric acid and borate on the pH of the solution (Hemming and Hanson, 1992). In order to determine this ratio, the

dissociation constant of boric acid ( $K_B^*$ ) must be known. The equation for the dissociation constant is

$$K_B^* = \frac{[H^+][B(OH)_4^-]}{[B(OH)_3]} \quad (2)$$

The equation relating the distribution of each species in seawater to the pH of seawater is the following:

$$\log \left( \frac{[B(OH)_4^-]}{[B(OH)_3]} \right) = \text{pH} - \text{p}K_B^* \quad (3)$$

The actual value of  $K_B^*$  is debated; however, the value most widely accepted is from *Dickson* (1990) is  $\text{p}K_B = 8.579$ , using the  $\text{pH}_T$  scale (Roy et al., 1993; Hansson, 1973). The value of  $\text{p}K_B^*$  has been studied in a range of temperatures and media including freshwater, ionic solutions (Owen and King, 1943; Dyrssen and Hansson, 1973; Byrne and Kester, 1974; Hershey et al., 1986), and synthetic seawater (Hansson, 1973; Dickson, 1990; Roy et al., 1993), and using various pH scales (Pagani et al., 2005). The different pH scales include the NBS scale ( $\text{pH}_{\text{NBS}}$ ), total scale ( $\text{pH}_T$ ), free scale ( $\text{pH}_F$ ), and the seawater scale ( $\text{pH}_{\text{SWS}}$ ). It is important to understand which scale was used when the  $\text{p}K_B^*$  value was determined because in order to calculate  $\text{pCO}_2$  from pH the dissociation constants for  $\text{CO}_2$  equilibria must also be determined on the same pH scale (Gebbinck, 2013).

**Table 1: Acid Dissociation Constants for  $B(OH)_3$  at 25°C**

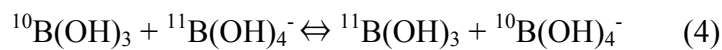
Author	pH Scale	Ionic Strength	Media	$\text{p}K_B^*$
Hansson (1973)	$\text{pH}_T$	0.7	$\text{Na}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Cl}^-, \text{SO}_4^{2-}$	8.61
Byrne and Kester (1974)	$\text{pH}_{\text{NBS}}$	0.7	$\text{Na}^+, \text{Ca}^{2+}, \text{Cl}^-$	8.774 <sup>a</sup>
			$\text{Na}^+, \text{Mg}^{2+}, \text{Cl}^-$	8.715 <sup>a</sup>
Hershey et al. (1986)	$\text{pH}_T$	0.68	$\text{Na}^+, \text{Cl}^-$	8.83
			$\text{Na}^+, \text{Mg}^{2+}, \text{Cl}^-$	8.725
			$\text{Na}^+, \text{Ca}^{2+}, \text{Cl}^-$	8.675
Dickson (1990)	$\text{pH}_T$	0.7	$\text{Na}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Cl}^-, \text{K}^+, \text{SO}_4^{2-}$	8.597
Tossell (2005)	n/a	n/a	Computational	9.2
Byrne et al. (2006)	$\text{pH}_T$	0.6	$\text{K}^+, \text{Cl}^-$	8.64

<sup>a</sup>Corrected by Millero, 1992  
Gebbinck, 2013

Generally,  $pK_B^*$  increases with decreasing temperature and salinity but differences in  $pK_B^*$  are attributed to differences in ionic media and measurement techniques, as well as the pH scale applied (Pagani et al., 2005; Xaio et al., 2013). Under normal conditions, the variation in  $pK_B^*$  is minor and can be neglected; for example, when temperature varies 5°C,  $pK_B^*$  changes only 0.04 and the calculated pH results in a 0.004 unit change (Dickson, 1990; Xaio et al., 2013).

### 2.3 Isotopic Fractionation Factor ( $\alpha_{4-3}$ )

While the dissociation constant expresses the propensity for boron to separate into the trigonal or tetrahedral species, the isotopic fractionation factor expresses the propensity for boron *isotopes* to fractionate between the trigonal or tetrahedral species. At low pH (<7), virtually all the boron in seawater is present as  $B(OH)_3$  and at high pH (>10), virtually all the boron in seawater is present as  $B(OH)_4^-$  (Figure 1b; Hemming and Hanson, 1992). As the relative concentration of the two species changes with pH, so does their isotopic concentration. It is also different from the equilibrium constant for the isotope exchange reaction (4), which illustrates the relative enrichment in  $^{11}B$  of boric acid and borate. This results from differences in molecular geometries and vibrational energies of the trigonal and tetrahedral species (Urey, 1947; Pagani et al., 2005) and is illustrated by the following equation:



All three factors discussed above, the isotopic fractionation factor ( $\alpha_{4-3}$ ), the equilibrium isotopic fractionation ( ${}_{11}^{10}K$ ), and the dissociation constant ( $K_B^*$ ) are related through this equation:

$$\alpha_{4-3} = \frac{1}{{}_{11}^{10}K} = \frac{R_{B(OH)_4^-}}{R_{B(OH)_3}} \quad (5)$$

where  $\alpha_{4-3}$  is less than unity and R is the  $^{11}B/^{10}B$  ratio of borate and boric acid (Pagani et al., 2005).

Calculations of  $\alpha_{4-3}$  can be either theoretical or experimental. Disadvantages may hinder the results of theoretical calculations due to sensitivity surrounding experimentally-obtained vibrational energy values as well as to the theoretical methods that are applied to calculate molecular forces (Klochko et al., 2006). *Kakihana et al.* (1977) provided the first theoretical estimate for isotopic exchange between borate and boric acid, ( ${}_{11}^{10}K_B = 1.0194$ ;  $\alpha_{4-3}$



$_3 = 0.981$ ) using reduced partition function ( $f_3$  and  $f_4$ ) ratio calculations from spectroscopic data on molecular vibrations. The magnitude of this fractionation corresponds to:

$$f_4/f_3 = \alpha = \frac{(\delta^{11}\text{B}(\text{OH})_4^- + 10^3)}{(\delta^{11}\text{B}(\text{OH})_3 + 10^3)} \quad (6)$$

Since then, predictions using various theories and computations have supported values much lower (Oi et al., 1991) than this and also much higher (Zeebe, 2005) than this value. The fractionation factor ( $\alpha_{4-3}$ ) for boron is determined to be between 0.96-1.027 (Klochko et al., 2006; Kakihana et al., 1977; Gaillardet and Allégre, 1995). Zeebe (2005) asserted that further research and experimental work is necessary to fully understand the true fractionation factor. The value at 25°C from Kakihana et al. (1977) is  $\alpha_{4-3} = 1.0194$ . However, using *ab initio* molecular orbital theory, the Zeebe (2005) result is  $\alpha_{4-3} = 1.0361$ , and using the Urey-Bradley Force Field for  $\text{B}(\text{OH})_4^-$  theory,  $\alpha_{4-3} = 1.0533$  (Zeebe, 2005). This is a wide range of values, which prompted Zeebe (2005) to suggest further research was critical. The next year, Klochko et al. (2006) determined current most accurate value of  $^{10}K_B = 1.0272$ ;  $\alpha_{4-3} = 0.974$ , by based upon spectrophotometric measurements using a range in total boron concentrations (Klochko et al., 2006; Pagani et al., 2005; Xaio et al., 2013). This is considered the most accurate value at present because it is purely experimental with no reliance on theoretical deductions and it is in agreement with more recent *ab initio* calculations (Klochko et al., 2009). However, there is still need for this factor to be better constrained in order to determine climate reconstructions more certainly, based on the boron-pH proxy.

The equilibrium constant ( $^{10}K$ ) for the isotope exchange reaction is greater than unity (Kakihana et al., 1977), and therefore  $\text{B}(\text{OH})_3$  is enriched in  $^{11}\text{B}$  relative to  $\text{B}(\text{OH})_4^-$ . Naturally occurring boron contains 19.8% boron-10 and 80.2% boron-11 (Kakihana et al., 1977).

Equations (3) and (5) with mass balance for each isotope in seawater (sw) lead to:

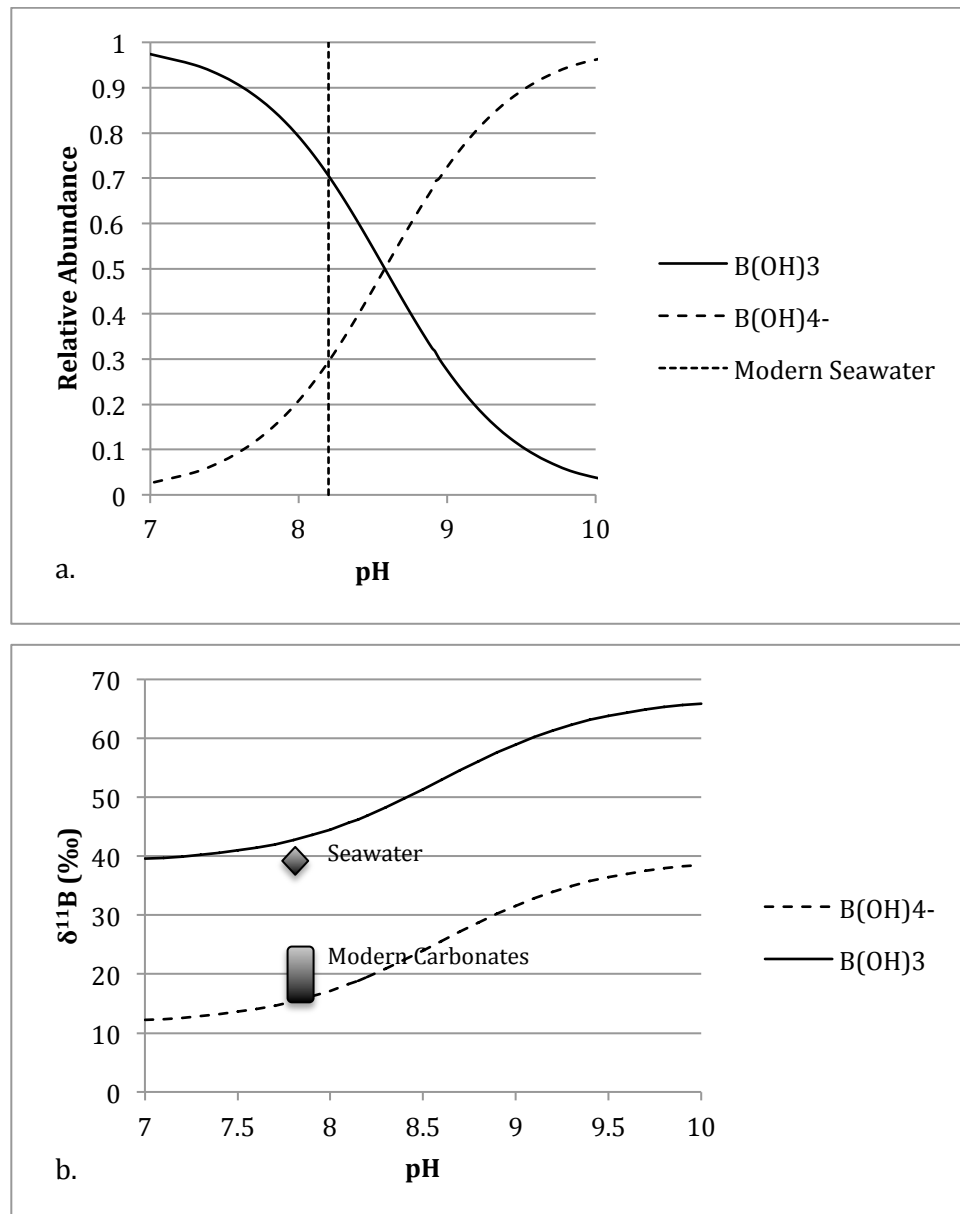
$$^{10}\text{B} = ^{10}\text{B}(\text{OH})_3 + ^{10}\text{B}(\text{OH})_4^- \quad (7)$$

$$^{11}\text{B} = ^{11}\text{B}(\text{OH})_3 + ^{11}\text{B}(\text{OH})_4^- \quad (8)$$

From this, we can solve the system of equations for the isotopic composition of boric acid and borate relative to that of the total for the solution:

$$R_{\text{B}(\text{OH})_4^-} = R_{\text{sw}} \left( \frac{1 + \alpha_{4-3} 10^{pK_B^* - \text{pH}}}{1 + 10^{pK_B^* - \text{pH}}} \right) \quad (9)$$

where:  $R_{sw} = {}^{10}\text{B}/{}^{11}\text{B}$  ratio of seawater;  $pK_B^*$  is for the  ${}^{11}\text{B}$  isotope. Figure 1b represents the theoretical relationship between the boron isotopic compositions of boric acid and borate in seawater, using Equation (9) (Hemming and Hanson, 1992; Pagani et al., 2005). Due to variation in molecular coordination and vibrational frequencies between the aqueous species of boron,  $\text{B}(\text{OH})_3$  is enriched in  ${}^{11}\text{B}$  relative to  $\text{B}(\text{OH})_4^-$  by  $\sim 27\text{‰}$  (Klochko et al., 2006; Kakihana et al., 1977; Vengosh et al., 1991; Hönisch et al., 2007).



**Figure 1: a. Distribution of boric acid and borate in seawater b. Theoretical relationship between boron isotopic compositions of boric acid and borate in seawater,  $T=25^\circ\text{C}$ , using a  $\delta^{11}\text{B}$  of  $39.6\text{‰}$  (Spivack and Edmond, 1987),  $pK_B^*=8.6$  (Dickson, 1990), and  $\alpha_{4-3} = 0.974$  (Klochko et al., 2006).**

The relationship between the boron isotopic composition of carbonate and the pH of seawater is summarized as:

$$\text{pH} = \text{pK}_B^* - \log\left(\frac{\delta^{11}\text{B}_{\text{sw}} - \delta^{11}\text{B}_{\text{carb}}}{\delta^{11}\text{B}_{\text{sw}} - \frac{10}{11}K\delta^{11}\text{B}_{\text{carb}} - 1000\left(\frac{10}{11}K - 1\right)}\right) \quad (10)$$

### 2.3 Isotopic Composition of Boron in Seawater ( $\delta^{11}\text{B}_{\text{sw}}$ )

The use of the boron isotope-pH proxy relies on a detailed understanding of the isotopic composition of boron in seawater ( $\delta^{11}\text{B}_{\text{sw}}$ ), as it is used as the basis of the reconstruction (Equation 9, 10). Seawater boron concentration and the  $\delta^{11}\text{B}_{\text{sw}}$  value are controlled by the boron input and output processes. The input processes include river input, dry and wet deposition, seafloor hydrothermal activity, organisms' oxidation, and rock weathering (LeMarchand et al., 2000; 2002; Xaio et al., 2013). The output processes include evaporation, biological uptake, diagenesis, and adsorption of clay minerals and suspended matter (Sanyal et al., 1996; Xaio et al., 2013).

The global carbon cycle allows for the ocean to have a buffering capacity in which  $\text{CO}_2$  from the atmosphere enters the ocean and combines with  $\text{H}_2\text{O}$  to form carbonic acid,  $\text{H}_2\text{CO}_3$ , which quickly transforms to  $\text{HCO}_3^- + \text{H}^+$  and then further to  $\text{CO}_3^{2-} + 2\text{H}^+$ . Free  $\text{Ca}^{2+}$  ions in the ocean can combine with  $\text{CO}_3^{2-}$  to produce calcium carbonate,  $\text{CaCO}_3$ . Considering this entire system, a slight change in pH of the ocean implies a much larger atmospheric fluctuation. For example, assuming a constant total dissolved inorganic carbon (DIC) concentration in the ocean, a 0.2 unit decrease in pH illustrates a  $p\text{CO}_2$  increase to twice the present value (Pagani et al., 2005). Because the proxy-calculated pH values are a function of  $\delta^{11}\text{B}_{\text{sw}}$  at the time of calcite formation (Equation 9, 10), constraining the uncertainty of pH values within 0.2 requires that  $\delta^{11}\text{B}_{\text{sw}}$  is known with a precision better than  $\pm 1.5\%$  (Pagani et al., 2005).

The modern value of  $\delta^{11}\text{B}_{\text{sw}}$  is well constrained at 39.61‰ (Foster et al, 2010). However, in order to use the boron isotope-pH proxy for reconstructing past conditions, pH values must be similarly highly constrained through at least the Cenozoic. The estimated residence time of boron in the ocean is between 14-20 Myr, meaning geologically rapid fluctuations in  $\delta^{11}\text{B}_{\text{sw}}$  are unlikely (Spivack and Edmond, 1987; LeMarchand et al., 2000). Therefore, the constancy of seawater boron concentrations and  $\delta^{11}\text{B}_{\text{sw}}$  over the past 20 Myr makes it unlikely that short-term changes in the  $\delta^{11}\text{B}$  value of foraminifera result from

fluctuations in  $\delta^{11}\text{B}_{\text{sw}}$ , which allows for the changes in foraminifera  $\delta^{11}\text{B}$  compositions to be interpreted as a change in pH (Palmer et al., 1998; Spivack et al., 1993). Extending beyond the residence time of boron, however, we cannot fully exclude the possibility of a slight variation in  $\delta^{11}\text{B}_{\text{sw}}$ . This variation could explain the change in foraminiferal  $\delta^{11}\text{B}$  values between *Palmer et al.* (1998) middle Miocene and late Pleistocene samples, extending approximately to the accepted residence time of  $\delta^{11}\text{B}_{\text{sw}}$  (14-20 Myr).

*LeMarchand et al.* (2002) suggests that boron cannot be used as a paleo-pH proxy on longer timescales (>14 Myr) until the evolution of  $\delta^{11}\text{B}_{\text{sw}}$  is constrained by further data. *LeMarchand et al.* (2000; 2002) also indicated that boron exchange between continental rivers and oceans led to a balanced oceanic boron budget. They predicted  $\delta^{11}\text{B}_{\text{sw}}$  lower during the Cenozoic and slightly higher during the Cretaceous than today, with a typical rate of  $\delta^{11}\text{B}_{\text{sw}}$  change of 0.1‰/Myr, which could be increased up to 0.6‰/Myr during the Cretaceous (Xaio et al., 2013).

### 2.3.1 $\delta^{11}\text{B}_{\text{sw}}$ Beyond Residence Time (>20 Myr)

*Pearson and Palmer* (2000) calculated pH-depth profiles from  $\delta^{11}\text{B}$  values of depth-stratified foraminifera using a range of  $\delta^{11}\text{B}_{\text{sw}}$  values in order to estimate paleo- $\delta^{11}\text{B}_{\text{sw}}$  for discrete time intervals. Different species of planktonic foraminifera calcify from the surface mixed layer to the lower pH conditions of deeper waters, below the thermocline. The level of biological production in the surface waters controls the pH and magnitude of pH decline because more productive waters have a higher flux of organic material that sinks and oxidizes in the water column, reducing the pH at depth (Pearson and Palmer, 2000). From six previously studied time intervals during the Cenozoic, large differences were observed in the carbonate  $\delta^{11}\text{B}$  differentials between surface and deep-water environments, which was therefore a reflection of differences in pH and therefore  $\delta^{11}\text{B}_{\text{sw}}$  (Pearson and Palmer, 1999; 2000). *Pearson and Palmer* (2000) created a model using the carbonate  $\delta^{11}\text{B}$  differential and resulting  $\delta^{11}\text{B}_{\text{sw}}$  values to interpolate  $\delta^{11}\text{B}_{\text{sw}}$  for other samples from each of the six time windows studied. Further, given Equation (9), a foraminiferal  $\delta^{11}\text{B}$  value will yield a specific pH value, for a given  $\delta^{11}\text{B}_{\text{sw}}$ . Therefore, a pH-depth profile can be constructed using a number of foraminiferal species with distinct, known calcification depths. It was necessary to use different species because no one species survived throughout the entire time interval, spanning the past 60 Myr. However, species were chose that are understood to have no vital

effect. In this interpretation, the value of  $\delta^{11}\text{B}_{\text{sw}}$  used determines the character of the pH-depth profile (Pearson and Palmer, 2000; Pagani et al., 2005). Within this model lies a fairly large uncertainty regarding the slope of the pH decrease with depth, which derives from the difficulty in assigning a narrow range of calcifying depths to individual foraminiferal species, species-dependent isotope effects, the analytical uncertainty of the carbonate  $\delta^{11}\text{B}$  value, and the accuracy of the carbonate  $\delta^{11}\text{B}$ -pH technique itself (Pagani et al., 2005).

Temporal trends of  $\delta^{11}\text{B}$  predicted from numerical models (LeMarchand et al., 2000) appear distinctly different from *Pearson and Palmer* (2000). As described above, these studies propose that the first order driver of  $\delta^{11}\text{B}$  fluctuations is the balance of continental supply and uptake from seawater during the low temperature weathering of oceanic crust, with other drivers being adsorption on clastic sediments and co-precipitation in carbonates (LeMarchand et al., 2000; 2002). Because the flux of boron into and out of the oceans of the past is not known, a better-understood geological process defines each flux. For example, the co-precipitation of boron in carbonate is proportional to total carbonate deposition, boron adsorption onto clays is related to the suspended sediment supply by rivers and uptake by oceanic crust alteration, and hydrothermal inputs are assigned to estimates of sea-floor spreading rates. Rivers, hydrothermal vents, and fluid expelled from accretionary prisms in subduction zones are the proposed balances to the suggested outputs from the oceans (LeMarchand et al., 2000). *LeMarchand et al.* (2000) considers two scenarios of riverine input: constant riverine flux and changes of riverine runoff with time. When the runoff values show relatively important variations ( $\sim 25\%$  in the Cretaceous), there is a difference in both marine B concentration and  $\delta^{11}\text{B}_{\text{sw}}$  observed (LeMarchand et al., 2002). However, the models show similar evolutions of marine boron over time and a continuous increase of  $\delta^{11}\text{B}_{\text{sw}}$  over the past 60 Myr is observed. Together, the two models lead to a calculation of a typical rate of change of boron isotope composition in the oceans of about  $0.1\text{‰ Myr}^{-1}$ , with analytical errors  $\sim 0.3\text{‰}$  (LeMarchand et al., 2000; 2002). Therefore, the paper concludes that hypothesizing a strictly constant  $\delta^{11}\text{B}_{\text{sw}}$  does not hold longer than 3 Myr before present.

Comparing the two studies, *Pearson and Palmer* (2000) and *LeMarchand et al.* (2000), reveals possibly important discrepancies between data sets. The two studies are in relatively close agreement back to 20 Ma (upper bound on the residence time of marine boron) but reflect opposite trends in  $\delta^{11}\text{B}_{\text{sw}}$  beyond 20 Myr. *LeMarchand et al.* (2002)

proposes alternatives to the riverine boron flux modeled in order to produce a more similar estimate of  $\delta^{11}\text{B}_{\text{sw}}$  toward 42 Ma to what was proposed by *Pearson and Palmer* (2000). If the riverine boron flux follows a sinusoidal curve with period of 100 Myr, a magnitude of 20% modern values and increasing over the past 50 Myr, causing the  $\delta^{11}\text{B}_{\text{sw}}$  around 42 Ma to be similar to today's value, *LeMarchand et al.* (2000; 2002) model would match *Pearson and Palmer* (2000) much more closely. Accurate knowledge of  $\delta^{11}\text{B}_{\text{sw}}$  beyond its residence time is limited, considering the dramatic differences between results of these studies, and others. *Pagani et al.* (2005) therefore concludes that this unknown represents a limitation in the application of the boron isotope-pH proxy.

## 2.4 Analytical Techniques for $\delta^{11}\text{B}$

There are six different techniques used to analyze boron isotope compositions of foraminifera. It is difficult to judge the accuracy of boron isotope analysis through interlaboratory comparisons because there are so many different techniques utilized, however attempts are currently being made to do so (*Gonfiantini et al.*, 2003; *Aggarwal et al.*, 2009; *Foster et al.*, 2012). Disagreement may arise from sample preparation, laboratory or sample contamination, or due to the instrumental techniques utilized. The boron concentration in modern marine carbonates can range from 1-100 ppm and in foraminifera is between 10-15 ppm (*Hemming and Hönisch*, 2007). Therefore, analysis must be efficient and potential laboratory contamination must be carefully controlled (*Rae et al.*, 2011). Boron is a light element with only two stable isotopes ( $^{10}\text{B}$  and  $^{11}\text{B}$ ). The isotopes have a relatively large difference in mass, which may generate potential instrumental mass fractionation, and to correct for this, mass fractionation must be identical between samples and normalizing standards (*Foster et al.*, 2006; *Rae et al.*, 2011). Table 2 summarizes the six different methods of analysis, the sample size needed to use each method, and their precision.

**Table 2: Analytical Techniques for Boron Isotope Composition**

Method	Acronym	Sample Size (ng)	Precision (‰)
<b>Multi-Collector Inductively Coupled Plasma Mass Spectrometry</b>	MC- ICPMS	250	$\pm 0.2$
<b>Negative Ion Thermal Mass Spectrometry</b>	NTIMS	1	$\pm 0.8$

<b>Total Evaporation Negative Ion Thermal Mass Spectrometry</b>	TE-NTIMS	<0.5	± 0.7
<b>Positive Ion Thermal Mass Spectrometry</b>	PTIMS	1000	± 0.4
<b>High Resolution Inductively Coupled Plasma Mass Spectrometry</b>	HR-ICPMS	250	± 2
<b>Quadruple Inductively Coupled Plasma Mass Spectrometry</b>	Q-ICPMS	100	± 14
<b>Secondary Ion Mass Spectrometry</b>	SIMS	<0.1	± 4

Early measurements of boron isotope analysis utilized positive ion thermal mass spectrometry (PTIMS). This was followed by negative ion thermal mass spectrometry (NTIMS), which allows for analysis of smaller samples (1 ng); however, mass interferences are a major problem with this technique (Hemming and Hanson, 1994). Multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) requires a slightly larger sample size compared to some approaches, but is the most precise (<1‰) method for analyzing boron isotopes (Foster, 2008).

### 3. Boron Incorporation

The best setting from which to take carbonate samples to measure  $\delta^{11}\text{B}$  is low-latitude gyre systems, where a mixed layer of warm, low-density surface water interacts with the atmosphere and is underlain by cold deep waters with little intermixing. This is because the pH and aqueous  $\text{CO}_2$  concentrations of the surface waters vary spatially based on deep-water upwelling, local productivity regimes, and freshwater inflows. Therefore, the farther from these influences that the carbonates precipitated, the more closely they will reflect atmospheric  $p\text{CO}_2$  (Pearson and Palmer, 2000).

There is a higher content of boron in marine biogenic aragonite (15ppm) than in calcite (9 ppm). This may be because there is a larger percentage of organic matter than inorganic matter in the calcite shells relative to aragonite and the boron is present within the inorganic constituents of the shells (Gebbinck, 2013). Biogenic effects may also have an effect on the concentration of boron in the carbonate matrix (Vengosh et al., 1991).

One important assumption of this technique is that  $\delta^{11}\text{B}$  of boron incorporated into the carbonate lattice of marine organisms is identical to borate ( $\text{B}(\text{OH})_4^-$ ) in solution. This implies that the boron incorporation is an equilibrium process between solution and carbonate and that the trigonal/tetrahedral fractionation in the carbonate is identical to that which occurs in solution (Pagani et al., 2005). The following lines of evidence lead to this assumption:

1. Bulk seawater  $\delta^{11}\text{B}$  composition is about 39.5‰, which is only slightly lower than the dominant  $\text{B}(\text{OH})_3$   $\delta^{11}\text{B}$  composition of about 40.4-45.2‰. However, this is much different than in modern marine carbonates, which is much closer to that of  $\text{B}(\text{OH})_4^-$ , and has a range of  $\delta^{11}\text{B}$  values of 19.4-24.1‰ (Hemming and Hanson, 1992).
2. Boron from solution is incorporated into the carbonate structure, or some other solid phase within the carbonate, and not present just in the fluid inclusions because if that were the case, the isotopic composition would be that of modern seawater and the boron concentration in the carbonate would be much lower (Hemming and Hanson, 1992).
3. There is a large range in the abundance of boron in marine carbonates (10.9-75.1 ppm) which parallels the steep slope in the  $\text{B}(\text{OH})_4^-$  vs. pH curve. This slope indicates that a slight change in pH can dramatically change the concentration of borate in solution (Hemming and Hanson, 1992).
4.  $\text{B}(\text{OH})_4^-$  is charged and is therefore more likely to be attracted to the crystal lattice than is  $\text{B}(\text{OH})_3$  (Hemming and Hanson, 1992).

However, deviation from the  $\delta^{11}\text{B}$ -solution pH curve (Figure 1b) under equilibrium conditions could occur for a number of reasons.

1. The isotopic fractionation between solid phase and solution may differ from those occurring between aqueous boron species, which would result in an offset of the isotopic composition from that of the dissolved species (Pagani et al., 2005).
2. Equilibrium may be established between the carbonate and another microenvironment, or a chemically distinct ‘pool’ of solution, rather than the bulk solution (Elderfield et al., 1996; Zeebe et al., 2003).

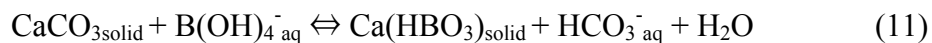


3. Solid phase boron could instead be a combination of both trigonal and tetrahedral boron species that change as a function of pH (Pagani et al., 2005; Vengosh et al., 1991; Xaio et al., 2013; Klochko et al., 2009).
4. The theoretical  $\delta^{11}\text{B}$ -pH curve displayed in Figure 1b is wrong.

### 3.1 Coordination of Carbonate Boron

The relative molecular dimensions of  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  are similar to that of  $\text{CO}_3^{2-}$  and could therefore both substitute for the carbonate ion in the carbonate lattice (Pagani et al., 2005). *Hemming and Hanson* (1992) theorized that the charged  $\text{B}(\text{OH})_4^-$  species is more likely to be attracted to the positively charged particles on the calcium carbonate surface than  $\text{B}(\text{OH})_3$ .  $\text{B}(\text{OH})_3$  substitution would substitute for both  $\text{CO}_3^{2-}$  and  $\text{Ca}^{2+}$  (Pagani et al., 2005). However, it is generally assumed that the charged borate species incorporates highly selectively into marine carbonates, rather than  $\text{B}(\text{OH})_3$ . With this assumption in mind, the cause for increased incorporation of borate at higher pH values may be related to the change in boron speciation, dependent on pH. At pH 7.9, the relative percentages of the species  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  are 91 and 9%, respectively and at pH 8.6, they are 68 and 32% (Sanyal et al., 2000). Therefore, if borate is the dominant species incorporated into the calcite, the increase in abundance of borate at higher pH very likely explains the greater amount of boron incorporated into calcite overall (Sanyal et al., 2000).

Considering charge balance, coupled substitution is necessary to make the ultimate molecular charge equal to zero.  $\text{B}(\text{OH})_4^-$  substitution could be charge balanced by the coupled substitution of an alkali for  $\text{Ca}^{2+}$ , it is also possible that boron exists as  $\text{Ca}(\text{HBO}_3)$  with  $\text{HBO}_3$  substituting for  $\text{CO}_3^{2-}$ , illustrated in Equation 11 (Hemming and Hanson, 1992).



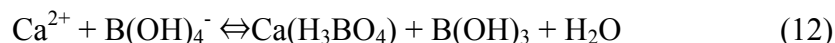
The coordination of boron likely plays a significant role in the incorporation of boron into the carbonate lattice. *Sen et al.* (1994) used  $^{11}\text{B}$  magic angle spinning nuclear magnetic resonance (MAS NMR) techniques to study the local coordination of boron in natural calcite and aragonite, synthetic calcite and aragonite, and a phase changed calcite. The study concluded that natural and synthetic calcite contained 90%  $\text{B}(\text{OH})_3$  and 10%  $\text{B}(\text{OH})_4^-$ . The natural and synthetic aragonite contained only  $\text{B}(\text{OH})_4^-$ . Calcite that had been altered from aragonite by being finely crushed and heated contained only  $\text{B}(\text{OH})_3$ . This suggested that a potential change in coordination during the incorporation of boron into calcite might be

required, generating an energy barrier. This energy barrier may have a greater impact on the boron inclusion than that of size or charge (Sen et al., 1994). Interestingly, this implies that the larger, tetrahedral anion,  $\text{B}(\text{OH})_4^-$ , appears to be substituted into the smaller lattice sites in aragonite, whereas the smaller, trigonal  $\text{B}(\text{OH})_3$  is substituted into the larger lattice sites in calcite (Gebbinck, 2013).

*Klochko et al.* (2009) observed equal abundances of trigonal and tetrahedral boron in biogenic calcite and aragonite samples using MAS NMR studies and did not conclude that carbonate crystal structures preferentially incorporated one boron coordination over another. However, the  $\delta^{11}\text{B}$  data available for both natural and synthesized carbonates suggest that changes in coordination of boron species occurs during carbonate precipitation (Hemming and Hanson, 1992; Sen et al., 1994; Klochko et al., 2009). These discrepancies suggest that the boron isotope-pH proxy is not as simple as previously speculated.

The considerations that there may be changes in coordination through intermediate phases of incorporation, suggest that boron inclusion does not occur by basic adsorption onto the carbonate surface (Tossell, 2006). Instead, chemical reactions between  $\text{HCO}_3^-$  and either  $\text{B}(\text{OH})_3$  or  $\text{B}(\text{OH})_4^-$  take place on carbonate surfaces during early growth stages, referred to as “chemisorption” (Tossell, 2006). During this stage,  $\text{B}(\text{OH})_3\text{CO}_3^-$  isomers of either trigonal or tetrahedral coordination form on the surface. These reconstructive processes that occur at the crystal surface may involve boron isotope fractionation.

*Trotter et al.* (2011) suggested the following reaction for the incorporation of the borate ion, which may switch between coordinations during adsorption and incorporation:

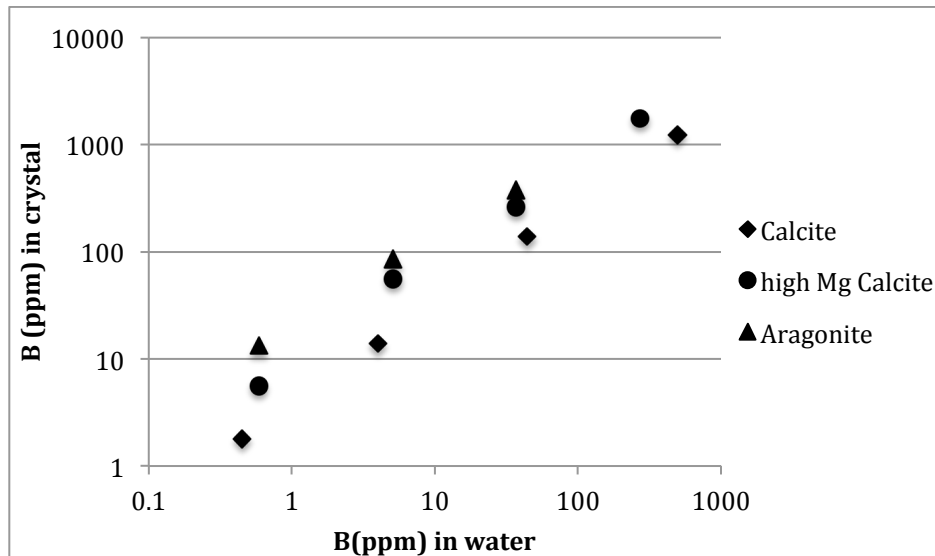


If this is the case, the spectroscopic studies that observe the coordination of carbonate boron in order to identify the boron source coordination may be misleading (Klochko et al., 2009; Sen et al., 1994; Rae et al., 2011).

### 3.2 Effects of Boron Concentration on Incorporation

Regardless of mineral dynamics, it is assumed that boron incorporation into a carbonate mineral is an equilibrium process between the precipitating carbonate and the parent solution (Vengosh et al., 1991). A number of experimental studies have shown the increase in B incorporated into the carbonate crystal lattice as a direct result of increased

boron in solution (Vengosh et al., 1991; Hemming and Hanson, 1992; Hemming et al., 1995; Hobbs and Reardon, 1999).



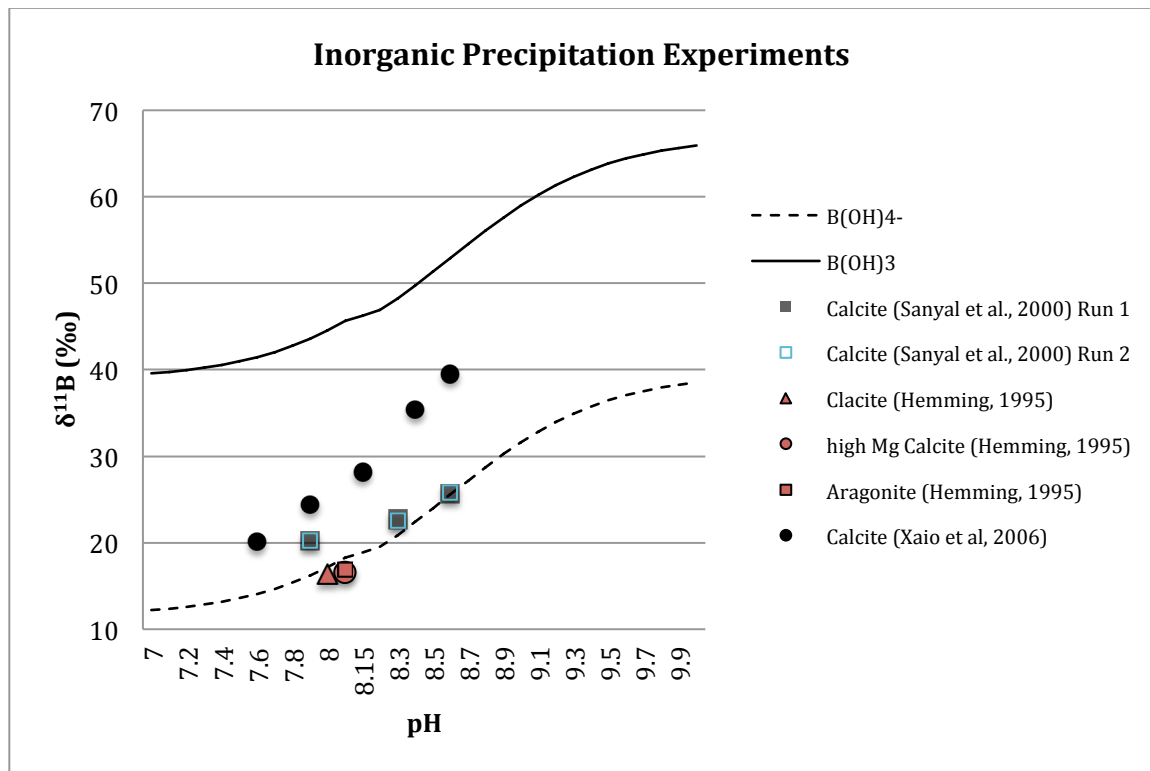
**Figure 2: Boron concentrations of synthetic calcite (diamonds), high Mg calcite (circles), and aragonite (triangles) plotted with respect to initial boron concentration of parent solutions (Hemming, 1995). Note: logarithmic scale.**

If it follows that only  $B(OH)_4^-$  is incorporated into the carbonate lattice, without significant fractionation further, the carbonate  $\delta^{11}B$  value should be equal to the boron isotope composition of  $B(OH)_4^-$ ,  $\delta^{11}B_{B(OH)_4^-}$ . The boron concentration in both calcite and aragonite increases as the boron concentration in parent solution increases (Figure 2; Vengosh et al., 1991; Hemming et al., 1995). When the pH of a parent solution increases, a higher concentration of boron is measured in carbonates (Kitano et al., 1978; Hemming et al., 1995; Hobbs and Reardon, 1999). If boric acid, which is more abundant at lower pH (Figure 1a), were being incorporated into the carbonate structure, a higher boron concentration in carbonates should be seen at a lower pH instead of at a higher pH, as seen experimentally. Consequently, these experimental observations support the hypothesis that only the borate ion is contributing to the boron isotope composition of the precipitating calcium carbonate.

### 3.3 Experimental Evidence for Boron Incorporation in Inorganic Carbonates

By considering the range of isotopic values in modern marine carbonates, it is possible to evaluate the likelihood that the boron incorporation includes both trigonal and tetrahedral boron or solely the tetrahedral borate species. Figure 1b illustrates  $\delta^{11}B$  data from

modern marine inorganic carbonates, which lie over the theoretical curve for  $\text{B}(\text{OH})_4^-$  and not  $\text{B}(\text{OH})_3$  (Hemming and Hanson, 1992; Hemming, 1995; Sanyal et al., 2000). Figure 2 illustrates the same curve with *Sanyal et al.* (2000) empirical data of  $\delta^{11}\text{B}$  values of the inorganic calcite precipitated at pH 7.9, 8.3, and 8.6 from artificial seawater, *Hemming* (1995) empirical data of  $\delta^{11}\text{B}$  values of the inorganic calcite, high Mg calcite, and aragonite precipitated at  $\sim$ pH 8.1, and *Xaio et al.* (2006)  $\delta^{11}\text{B}$  values of the inorganic calcite precipitated at pH ranging between 7.6-8.6.



**Figure 3: Theoretical curve from Figure 1b, with additional empirical data from Sanyal et al., 2000; Hemming, 1995 (average  $\delta^{11}\text{B}$  value from range of [B]); and Xaio et al., 2006.**

Results of *Sanyal et al.* (2000) and *Hemming et al.* (1995) support the assumption that only the charged borate species is incorporated into the carbonate mineral with little and insignificant fractionation during uptake. *Sanyal et al.* (2000) performed inorganic calcite precipitation experiments at varied pH levels and concluded that isotopic fractionation between seawater and calcite followed the theoretical trend for  $\text{B}(\text{OH})_4^-$ .

However, there was no temperature control used in *Sanyal et al.* (2000), it was simply carried out at ambient laboratory conditions. Also, the calcite growth rate was not

consistent between the experiments for the three different pH values, and *Sanyal et al.* (2000) assume that no potential kinetic effects were at play because the resulting  $\delta^{11}\text{B}$  values for the carbonates follow the theoretical curve of *Kakihana et al.* (1977). A confirmation of isotopic equilibrium would have more accurately depicted whether or not kinetic effects played a part in the synthesis of calcium carbonate (Gebbinck, 2013).

*Hemming et al.* (1995) investigated mineral fluid partitioning and isotopic fractionation of boron into carbonates by growing aragonite, high-Mg calcite, and Mg-free calcite under monitored laboratory conditions. The result of the study illustrated that  $\delta^{11}\text{B}$  of the synthetic minerals was identical to the calculated  $\delta^{11}\text{B}$  of the  $\text{B}(\text{OH})_4^-$  species in the parent solution, which is evidence of strong interaction of the borate with the crystal surface (Hemming et al., 1995). The carbonate samples in this study, however, were only synthesized from a single pH value and no stirrer was used in the experimental setup; therefore, uniform conditions are not guaranteed throughout the precipitating solution. The pH of the solution in this experiment increased from 5.6 to 8.0 over the first two days, during which it is unclear how *Hemming et al.* (1995) ensured that no crystals had precipitated; the study mentions only that none were visible. When trying to determine if the  $\delta^{11}\text{B}$  of the carbonate is equal to that for the  $\text{B}(\text{OH})_4^-$  ion at the same pH value, the pH must not change over the course of carbonate synthesis because the incorporation of boron may have occurred over a range of pH values and then cannot be precisely compared.

Although they generally follow the  $\text{B}(\text{OH})_4^-$  curve, there is a slight offset between *Hemming et al.* (1995) and *Sanyal et al.* (2000) in  $\delta^{11}\text{B}_{\text{carb}}$ , compared to the predicted equilibrium  $\delta^{11}\text{B}_{\text{B}(\text{OH})_4^-}$ . The exact reason for this offset is unknown. The experimental method and ionic strength applied in each study was different, which could be the potential cause for disagreement. Both studies adjusted pH manually. *Hemming et al.* (1995) adjusted  $\text{pCO}_2$  in the reaction chamber in order to adjust pH, whereas *Sanyal et al.* (2000) added acids and bases (HCl and NaOH) in order to obtain the desired pH, and added  $\text{Na}_2\text{CO}_3$  in order to maintain the constant pH throughout synthesis. In general, neither study synthesized calcium carbonate samples from a wide enough pH range to reliably depict boron isotope incorporation into carbonates (Gebbinck, 2013). Both studies were successful in showing correlation between boron isotope composition of calcium carbonate and solution pH;

however, the disagreement implies that more studies are necessary to obtain a better constraint on boron isotope systematics.

A number of other inorganic calcite experiments (Xiao et al., 2006; He et al., 2013) have also been conducted in order to test and verify this assumption. An unusual result in Xiao et al. (2006) indicated that  $\delta^{11}\text{B}$  of inorganic calcium carbonate was not parallel with the theoretical borate curve (Figure 3). Instead, the fractionation deviates from the curve more with increasing pH; the ratio of  $\text{B}(\text{OH})_3$  to  $\text{B}(\text{OH})_4^-$  incorporated increases with increasing pH (Xiao et al., 2006). The reasoning was that the presence of  $\text{Mg}^{2+}$  or other microelements caused this because  $\text{B}(\text{OH})_3$  preferentially incorporated into brucite,  $\text{Mg}(\text{OH})_2$ . The presence of Mg in the parent solutions increased the boron uptake, relative to Mg-free solutions (Xiao et al., 2006). This prediction is not illustrated, however, in the carbonates from Hemming (1995), but the singular pH value studied may be the cause for this. Sanyal et al. (2000) used Mg-free artificial seawater, so this effect is non-existent.

Although there are potential experimental flaws that may have had an effect on the results of these studies, both Sanyal et al. (2000) and Hemming (1995) support the assumption that  $\text{B}(\text{OH})_4^-$  is preferentially incorporated into inorganic carbonate. However, recent studies have proposed complications to this assumption (Xiao et al., 2013). In a critical review of the proxy, Pagani et al. (2005) highlighted that the data of Sanyal et al. (2000) deviated slightly from the theoretical  $\delta^{11}\text{B}$ -pH curve, indicating an incorrect assumption that incorporated boron was identical to borate in solution or that some proportions of the trigonal species was also incorporated into biogenic carbonates. Alternatively, if incorporation occurs through kinetic fractionation, this would imply a non-equilibrium process in which one species is preferentially and irreversibly incorporated. This results from fast carbonate growth rates versus boron exchange rates. In this case, the boron isotopic concentration in the carbonate would reflect the isotopic concentration of the dissolved species plus the associated kinetic fractionation, which could change under varying conditions (Pagani et al., 2005).

#### 4. Biogenic Carbonate Sources

It is challenging to develop a geochemical proxy based on natural samples due to the difficulty in precisely tracing the environments in which the samples formed (e.g. pH,

salinity, and temperature) (Gebbinck, 2013). The effects of dissolution of calcium carbonate on applying the boron isotope-pH proxy can be minimized by incorporating samples from areas of low productivity and large shell size fractions (Hönisch et al., 2007). Culture studies allow even more control of the external environment. However, they are also subject to the influence of unknown biogenic effects during calcium carbonate precipitation. The application of culture studies is beneficial in terms of identifying species-specific vital effects that must be taken into consideration once the principles of the boron isotope-pH proxy have been better understood. It is important to continue to conduct laboratory studies where all aspects of growth can be controlled in order to better understand the boron isotope systematics of marine carbonates.

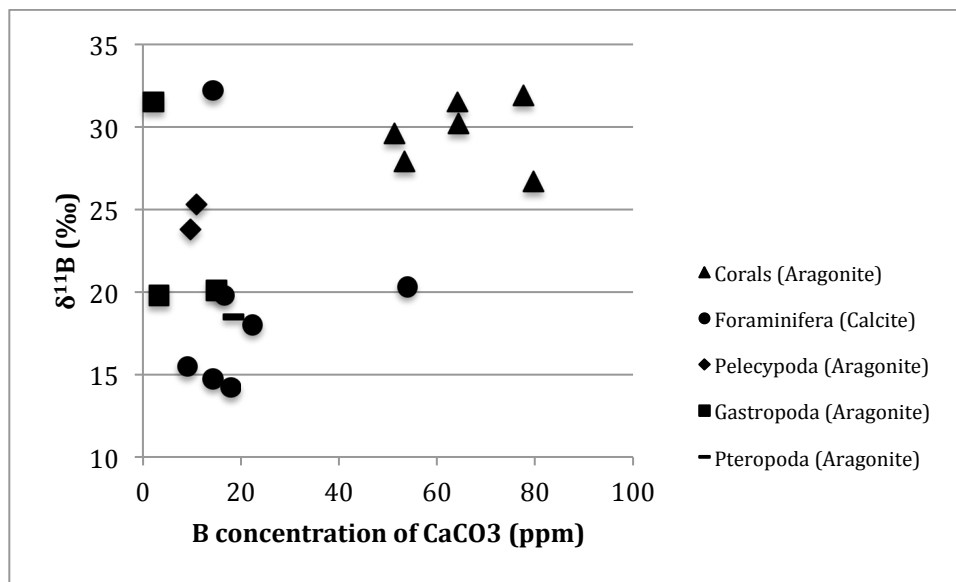
#### 4.1 Experimental Evidence for Vital Effects in Biogenic Carbonates

The assumption that there is no significant biogenic effect on the boron isotopic composition of coral and foraminifera must be reconsidered. There is clear evidence for species dependent “vital” effects on the boron isotopic composition of biogenic carbonates and these effects cannot be ruled out for most species (Sanyal et al., 1996; Hönisch et al., 2004). Vital effects include photosynthesis of the symbiotic algae, respiration of the host-symbiont system, and calcification (Zeebe et al., 2003). To test the vigor of these vital effects, Sanyal et al. (1996) cultured the symbiont-bearing foraminifera species *Orbulina universa* in natural seawater at four different pH values in order to establish the pH-dependence of boron isotope fractionation (Figure 4). Sampling ambient coretop foraminifera of the same species checked any possible cultural artifact. The cultured samples of *O. universa*, as well as the coretop species studied, had a significantly lighter boron isotopic ratio, consistently ~1‰ lighter, than the similarly symbiont-bearing *Globigerinoides sacculifer* species which has a much slower calcification process (Sanyal et al, 1995; Wolf-Gladrow et al, 1999), suggesting that a vital effect must have been active, at least in the *O. universa* species. Depending on size, *O. universa* harbors between 3000-7000 symbionts, distributed between and on the spines in a halo around the calcite shell (Wolf-Gladrow et al., 1999; Spero and Parker, 1985). The results of Sanyal et al. (1996) further implicate a clear pH dependence on the isotopic ratio of boron in calcite and they also support the hypothesis that the charged borate species is the only boron species incorporated into the carbonate lattice; however, the results also suggest that there is a significant

biogenic effect at play, which must be recognized and accounted for in order to use the paleoceanographic boron-pH proxy (Sanyal et al., 1996).

The assumption that the incorporation of boron accurately follows the curve of the concentration of  $B(OH)_4^-$  species in solution (Sanyal et al., 2000; Hemming et al., 1995; He et al., 2013) does not include evidence for biogenic carbonates, which implicate vital effects and pH up-regulation as biological controls on the microenvironment of carbonate precipitation and therefore the  $\delta^{11}B$  concentration in the carbonate.

Figure 4 illustrates the incorporation of  $\delta^{11}B$  vs. the total boron concentration in the sample. Five types of organic carbonate are plotted, each illustrating a different behavior of incorporation. It is clear that biogenic “vital” effects have a large control over the relative preferential incorporation (corals) and exclusion (gastropods) of boron (Vengosh et al., 1991).



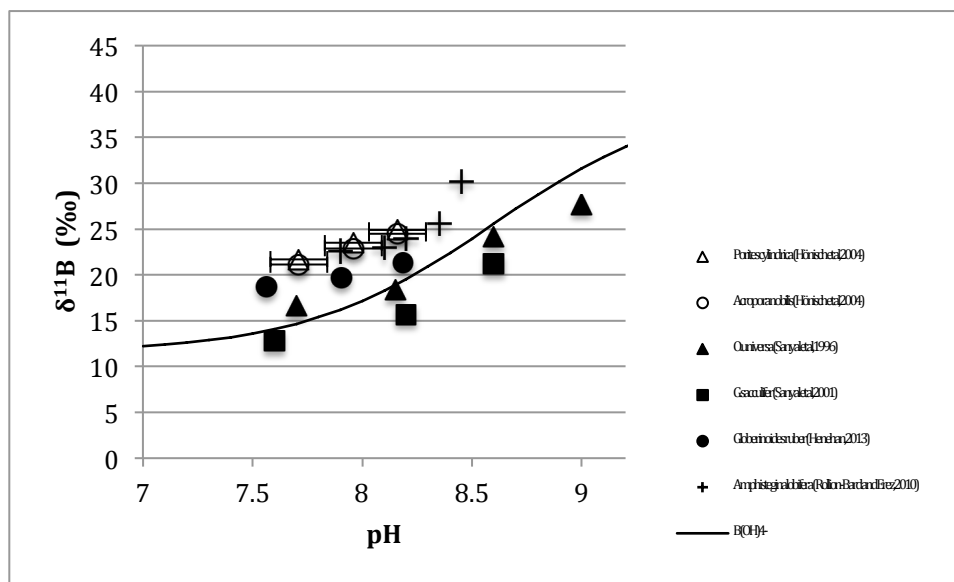
**Figure 4: Abundance and isotopic compositions in select biogenic carbonate species (Vengosh et al., 1991).**

*Sanyal et al.* (2000) found that the boron isotopic fractionation between seawater and inorganic calcite was lower than that for *Orbulina universa*, the cultured biogenic foraminifera species in the experiment, indicating the presence of a biogenic effect on the boron isotopic composition of the *O. universa* (Sanyal et al., 2000; 1996). *Sanyal et al.* (2000) suggests that once species-specific  $\delta^{11}B$ -pH relationships are established, they can be used to correct offsets from the theoretical  $B(OH)_4^-$ . However, *Pagani et al.* (2005) counters



that the magnitude of the offsets in relation to the theoretical curve varies with pH, which makes precise and accurate corrections difficult and sensitive. The corrections are also dependent on the value used for the isotopic fractionation factor and the possibility of pH differences between seawater and the calcifying microenvironment.

*Klochko et al.* (2009) found that both trigonally (36-46%) and tetrahedrally coordinated boron species existed in both biogenic and hydrothermal carbonates, using MAS NMR spectroscopy. This result was different from that of *Sen et al.* (1994), which concluded from spectral analysis that the trigonal species was predominantly incorporated into calcite. The differences between the experimental results are likely due to the large differences in the symmetry of the electric field gradient ( $\eta$ ) as well as in the magnitude of the quadrupolar coupling parameter (Cq) (Klochko et al., 2009).



**Figure 5: Boron isotopic composition of six coral (open symbols) and foraminifera (filled symbols) species vs. pH, plotted against the theoretical  $\text{B}(\text{OH})_4^-$  curve, using  $\delta^{11}\text{B}$  of 39.6‰ (Spivack and Edmond, 1987),  $\text{pK}_B^* = 8.6$  (Dickson, 1990), and  $\alpha_{4-3} = 0.974$  (Klochko et al., 2006). It is clear that the  $\delta^{11}\text{B}$  is pH dependent and somewhat closely follows the  $\text{B}(\text{OH})_4^-$  curve; however, each species has a particular offset from the curve, which is likely caused by vital effects.**

*Rae et al.* (2011) further argues with both of these studies because this test of boron coordination in the crystal lattice is not a test of which molecule, borate or boric acid, is incorporated from solution. As *Klochko et al.* (2009) explicitly state, boron may switch between coordination with 3 or 4 oxygens during adsorption and incorporation into

borocarbonate, independent of the species initially adsorbed. Isotope composition is a powerful indirect test of boron species incorporation, due to the large isotopic offset between  $\text{B(OH)}_3$  and  $\text{B(OH)}_4^-$  (Figure 1b). Although seawater boron is dominated by  $\text{B(OH)}_3$  (~90%), at the environmental conditions in the core-top dataset from *Rae et al.* (2011), the  $\delta^{11}\text{B}$  data provide evidence for exclusive  $\text{B(OH)}_4^-$  incorporation in foraminiferal calcite: just 2%  $\text{B(OH)}_3$  would offset the data from the close match to the calculated  $\delta^{11}\text{B}$  of seawater  $\text{B(OH)}_4^-$  (Rae et al., 2011).

There is clear discrepancy between datasets and conclusions made regarding the potential vital effects of foraminifera. More work must be done to verify the results of these studies in order to increase the confidence in using the boron isotope-pH proxy.

#### 4.2 Effects of the Microenvironment on Foraminiferal Carbonates

The question remains whether foraminifera record the pH of the bulk seawater or that of the microenvironment, which is strongly influenced by biological processes. *Zeebe et al.* (2003) presents a diffusion-reaction model to test this question. The model includes chemical reactions, diffusion and uptake or release of the three carbonate species  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and the two borate compounds  $\text{B(OH)}_3$  and  $\text{B(OH)}_4^-$ , which buffer the shift in pH (Wolf-Gladrow et al, 1999). It then calculates the concentrations in the vicinity of the shell depending on diffusion, chemical conversion, and the fluxes generated by vital effects (Wolf-Gladrow et al, 1999). The speeds of diffusion and chemical reaction of the aforementioned species implicate which pH is recorded in the calcite shell: the microenvironment or the bulk solution. If the speed of the reaction is much faster than diffusion, the concentrations of chemical species are in local equilibrium and are tightly coupled, meaning the microenvironment pH must be different from the bulk solution and is recorded in the calcite structure (Zeebe et al., 2003). However, if the speed of diffusion is similar to the chemical reaction, then the concentrations of chemical species are relatively independent from each other (Zeebe et al., 2003). For example, photosynthesis on a symbiont-bearing foraminifera species increases the pH of the microenvironment when the symbiotic algae takes up  $\text{CO}_2$ , creating a more alkaline environment. In response,  $\text{CO}_2$  from the bulk medium diffuses towards the shell and chemical conversion from  $\text{HCO}_3^-$  to  $\text{CO}_2$  replaces the removed  $\text{CO}_2$  after some seconds to reach equilibrium again. However, due to the difference in diffusion and chemical reaction rates, photosynthetic activity causes the pH

of the microenvironment to increase incrementally in light environments relative to dark environments (Zeebe et al., 2003).

The reacto-diffusive length scale is used to measure the relative importance of diffusion and reaction:  $\lambda = \sqrt{D/k}$ , where  $D$  is the diffusion coefficient,  $k$  is the reaction constant, and  $\lambda$  may be thought of as the mean length a molecule diffuses before it reacts (Zeebe et al., 2003; Wolf-Gladrow et al., 1999). Zeebe et al (2003) estimates the reacto-diffusive length scale of the boric acid-borate equilibrium in seawater to be  $\sim 0.2 \mu\text{m}$ , which is much smaller than the typical diffusive boundary layer, equal to the radius of a foraminifer ( $\sim 300 \mu\text{m}$ ). Therefore, the boron compounds and the pH of the microenvironment are tightly coupled in this reaction.

The results of the model conclude that the  $\delta^{11}\text{B}$  in planktonic foraminifera is primarily controlled by the pH of the microenvironment and not that of the bulk solution (the diffusive boundary layer,  $\sim 300\text{-}500 \mu\text{m}$ ) (Zeebe et al., 2003). Therefore, in using the boron-pH proxy, an offset must accompany the  $\delta^{11}\text{B}$  measurements for different species or differing growth environments (i.e. light or dark environments), if relating them to the measurements of inorganic calcite (Zeebe et al., 2003). Symbiont-bearing species should be enriched in  $^{11}\text{B}$  relative to symbiont-barren species due to the elevated pH experienced during photosynthesis of the symbiont-bearing species in the light. Importantly, the offset applied is constant over a large range of pH, which implies that the vitality of the proxy as a paleo-pH indicator is not compromised by these findings (Zeebe et al., 2003; Hönisch et al., 2003). Unless the life processes of foraminifera vary significantly based on pH, the changes recorded in shells of a given species through time should still be a valid proxy for pH changes of past oceans even though vital effects do result in differences in the absolute  $\delta^{11}\text{B}$  value of different species (Zeebe et al., 2003).

This theoretical model was written concurrently with an assenting experimental study (Hönisch et al., 2003). In this study, culture experiments were carried out on planktonic foraminifer *Orbulina universa* under high and low light levels in order to determine the effects of photosynthetic activity on the boron isotopic composition of shell calcite. The experiments show about  $\sim 1.5\%$  lower  $\delta^{11}\text{B}$  in the reduced light scheme, with therefore reduced photosynthetic rates, which corresponds to a pH reduction of about 0.2 units (Hönisch et al., 2003). These cultured samples are compared to plankton tow samples

and illustrate similar  $\delta^{11}\text{B}$  values to those grown in the laboratory under low light conditions. In addition, this study presents the first data for symbiont-barren foraminifer species *Globigerina bulloides*, which fall  $\sim 1.4\%$  below the *O. universa* data (Hönisch et al., 2003).

Coral boron concentrations are about 5 times that in foraminifera ( $>50$  ppm vs 5-15 ppm, respectively) (Hemming et al., 1998). Due to the difficulty in obtaining accurate boron isotope measurements on small amounts of foraminifera samples, Hönisch et al (2003) employ an experimental method of increasing the boron concentration in the culture water to tenfold the natural seawater in order to proportionately increase the boron concentration in the foraminifer and therefore reduce the large sample size required for  $\delta^{11}\text{B}$  measurements from  $\sim 200$  to  $\sim 60-70$  shells. This seems to work well; however, it also reduces the pH of the culture water, which must be countered with either the addition of a basic solution to raise the pH back to ambient conditions or to lower the DIC by bubbling an inert gas, such as  $\text{N}_2$ , into solution (Hönisch et al., 2003). The latter compensation for increased boron concentration, however, would reduce the concentration of carbonate species possible in solution, reducing the final shell weight for analysis and therefore reversing the purpose of the increased boron concentration in the first place. Hönisch et al (2003) therefore utilized the addition of NaOH to bring the pH of the culture solution back to ambient conditions. One possible result of increased boron concentration is a buffer effect on the changes of pH at the site of calcification caused by photosynthesis and respiration (Zeebe et al., 2003). Due to this effect, the  $\delta^{11}\text{B}$  offset between foraminifera grown under high light and low light conditions in the study is about  $2.6\%$  smaller than expected for shells grown in natural seawater on the basis of the Zeebe et al (2003) diffusion-reaction model. Hönisch et al (2003) suggests that in order to effectively rule out any potential effect of the increased boron concentration on  $\delta^{11}\text{B}$ , the experiment of Sanyal et al (2001) must be repeated and laboratory grown (1 X B) and (10 X B) exclusively compared, rather than laboratory (10 X B) and field grown (1 X B) foraminifera.

However, Rae et al. (2011) asserts that there is no systematic offsets caused by vital effects in his 76 benthic foraminiferal samples. There is one exception in the study, the species *H. elegans*, which has relatively low and constant  $\delta^{11}\text{B}$  (Rae et al., 2011). The apparent absence of vital effects on  $\delta^{11}\text{B}$  in the wide range of calcite benthic foraminifera studied provides more certainty in applying the technique to extinct epifaunal species to

reconstruct ancient ocean pH.(Rae et al., 2011). This study also offers a powerful argument for exclusive  $B(OH)_4^-$  incorporation in foraminiferal calcite, conflicting with the work of *Klochko et al.* (2009).

### 4.3 Vital effects and pH up-regulation in Coral Species

Corals should provide an ideal material for recording the paleo-pH of surface water. Their growth rates are high, providing ample sample at high resolution, and they have high concentrations of boron (five times higher than in calcitic foraminifera), since boron uptake in aragonite is significantly greater than in calcite (Reynaud et al., 2004). However, understanding the mechanics and controls of boron uptake in coral is essential to attain accurate conclusions using the boron isotope–pH proxy.

Coral polyps exert strong control over the calcification process, which can be achieved by drawing seawater into a space between the calicoblastic ectoderm and the skeleton, isolating it from the external environment, and modifying it to achieve a higher aragonitic saturation state ( $\Omega_{Arag}$ ). A potential mechanism for increasing  $\Omega_{Arag}$  of what was initially seawater is for the polyp to use the enzyme  $Ca^{2+}$ -ATPase to add  $Ca^{2+}$ , coupled with  $H^+$  removal that increases carbonate ion concentration (Gaetani et al., 2011).

In his study of both deep-sea and shallow water scleractinian corals, *McCulloch et al.* (2012) determined that the ability to up-regulate internal pH of the calcifying fluid ( $pH_{cf}$ ), and consequently the seawater aragonitic saturation state ( $\Omega_{cf}$ ), of the calcifying fluid is a process present in both azooxanthellate and zooxanthellate aragonitic corals, and is attributed to the action of  $Ca^{2+}$ -ATPase in modulating the proton gradient between seawater and the site of calcification. The findings also show that aragonitic corals display a boron isotopic composition that is highly systematic and consistent with direct uptake of the borate species present within the biologically controlled extracellular calcifying medium (McCulloch et al., 2012).

The relatively strong up-regulation of pH and consequent elevation of the internal carbonate saturation state ( $\Omega_{cf} \sim 8.5$  to  $\sim 13$ ) at the site of calcification by cold-water corals, facilitates calcification at or in some cases below the aragonite saturation horizon, providing a greater ability to adapt to the already low and now decreasing carbonate ion concentrations. Although providing greater resilience to the effects of ocean acidification and enhancing rates of calcification with increasing temperature, the process of internal  $pH_{cf}$

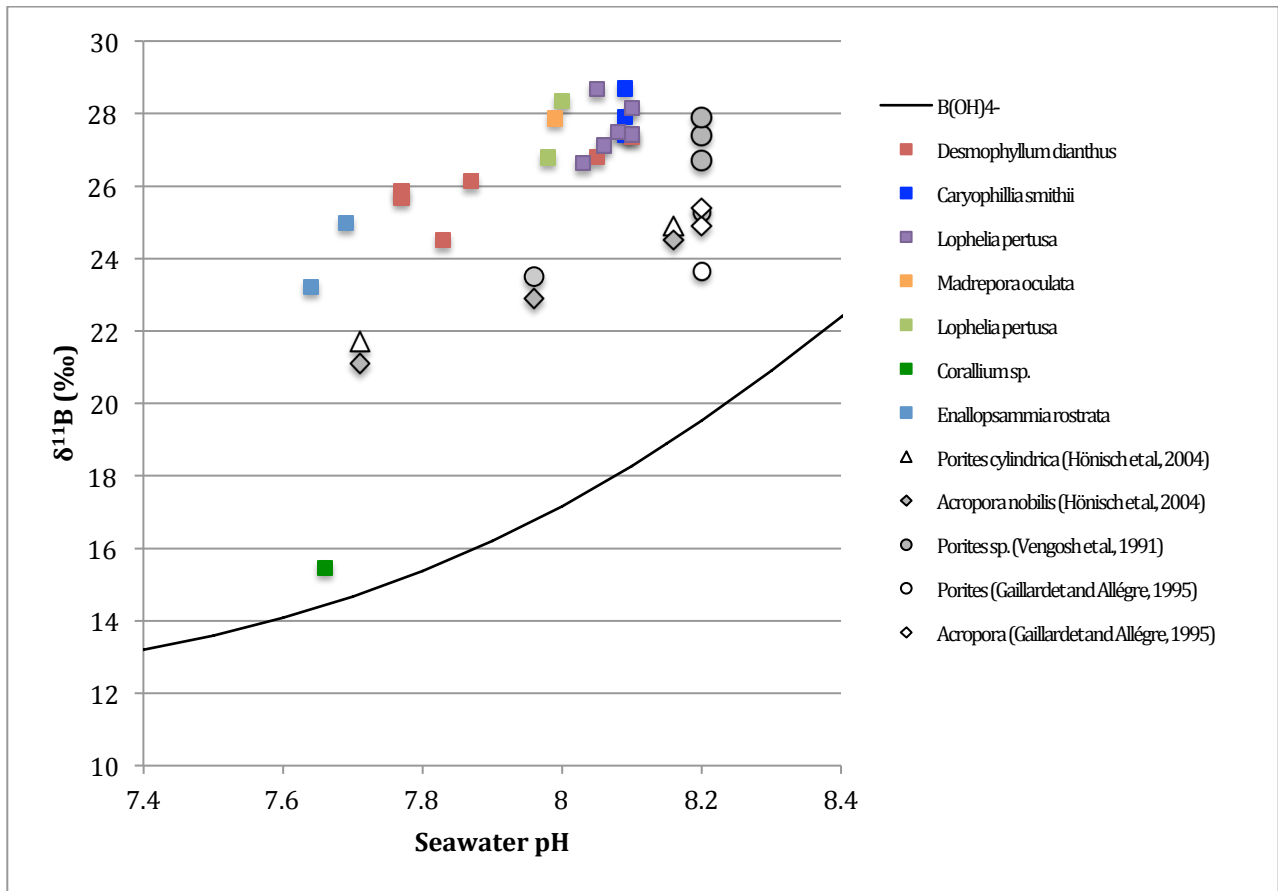
up-regulation has an associated energetic cost, and therefore growth-rate cost, of ~10% per 0.1 pH unit decrease in total seawater pH (McCulloch et al., 2012).

Linear correlations between seawater pH and either the internal pH of the calcifying fluid or the differential pH ( $\Delta\text{pH}$ ) relative to ambient seawater ( $\Delta\text{pH} = \text{pH}_{\text{cf}} - \text{pH}_{\text{T}}$ ) indicates pH up-regulation according to this formula:

$$\text{pH}_{\text{cf}} = (m-1)\text{pH}_{\text{T}} + C_{\text{sp}} \quad (13)$$

where  $m$  is the gradient of the linear array and  $C_{\text{sp}}$  denotes the species-dependent value of the intercept (McCulloch et al., 2012).

*McCulloch et al.* (2012) boron isotopic measurements for a suite of azooxanthellate corals from various ocean basins and collected at a range of depths, in addition to keeping well-constrained seawater  $\text{pH}_{\text{T}}$  measurements for *D. dianthus*, or reasonable quantitative estimates (with noted caveats) for the other corals, which are essential to define the systematics of biologically mediated pH regulation. The species in the study comprise the aragonite species, *C. smithii*, *D. dianthus*, *E. rostrata*, *L. pertusa*, and *M. oculata*, as well as the calcitic coral, *Corallium sp.* All the aragonitic cold water coral samples lie well above the  $\text{B}(\text{OH})_4^-$  speciation curve from *Klochko et al.* (2006).



**Figure 6: Measured boron isotopic compositions ( $\delta^{11}\text{B}$ ) of cold-water corals (colored symbols from McCulloch et al., 2012) plotted against seawater  $\text{pH}_T$ . Measurements of tropical corals from previous literature (see legend) are represented by grey or open symbols. The black curve represents the  $\delta^{11}\text{B}$  composition of the borate species  $[\text{B}(\text{OH})_4^-]$  as a function of seawater pH, assuming the boric/borate isotopic fractionation factor of 1.0272 (Klochko et al., 2006);  $T = 25\text{C}$ ,  $S = 35$ , depth = 5 m. Aragonitic cold-water corals have higher  $\delta^{11}\text{B}$  values than their tropical/sub-tropical counterparts (grey symbols), indicative of greater extracellular pH up-regulation. The calcitic cold-water coral *Corallium sp.* (green) lies near the borate curve suggesting that pH up-regulation is minimal or absent.**

## 5. Study of Vital Effects in Porites Coral

### 5.1 Introduction

Many scleractinian corals grow continuously over several centuries and record useful information within their aragonite skeletons, providing a valuable archive of seasonally resolved oceanographic data that is unavailable from any other source (Gaetani et al., 2011). However, interpretation of this information is not always straightforward. For example, different parts of the same skeleton accreted at the same time may have significantly

different isotopic compositions. Coral polyps exert strong control over the calcification process. This is achieved by drawing seawater into a space between the calciblastic ectoderm and the skeleton, isolating it from the external environment, and modifying it to achieve a higher  $\Omega_{\text{Arag}}$ . A potential mechanism for increasing  $\Omega_{\text{Arag}}$  of what was initially seawater is for the polyp to use the enzyme  $\text{Ca}^{2+}$ -ATPase to add  $\text{Ca}^{2+}$ , coupled with  $\text{H}^+$  removal that increases carbonate ion concentration (Gaetani et al., 2011). These vital effects cause discrepancies between expected and measured boron isotopic values, and therefore pH values, and have made it very difficult to create a model for the pH-proxy from experimental results of biogenic carbonates.

Wara et al. (2003) presented the first continuous records from 0-5 Ma of paired boron/calcium (B/Ca) ratios and boron isotopes ( $\delta^{11}\text{B}$ ) in the planktonic foraminifera *Globogerinoides sacculifer* from ODP site 806 in the western equatorial Pacific Ocean. These measurements, in conjunction with the calcification temperature measurements (Mg/Ca ratios) and average shell mass measurements, suggest that pH is not the sole environmental variable controlling boron in planktonic foraminiferal calcite (Wara et al., 2003). The data show that calcification temperature plays an important role in controlling B concentration and isotopic composition in planktonic foraminifera. These results define new aspects of calibrating the  $\delta^{11}\text{B}$  paleo-pH tracer; the need to include calcification temperature in pH and  $\text{pCO}_2$  estimates from boron isotope measurements introduces new uncertainties in the process (Wara et al., 2003).

Promisingly, relationships among elemental ratios in coral skeleton provide insights into the mechanisms that produce vital effects as well as the temperature effects on both the calcifying fluid and the trace elemental ratios in the precipitated aragonite. Correlations among Sr/Ca, Ba/Ca, Mg/Ca, U/Ca, and B/Ca ratios have been documented in a number of studies (e.g. Gaetani et al., 2011; Wang et al., 2013; Allison and Finch, 2010). Recent studies have demonstrated that elemental fractionations during coral biomineralization are influenced by Rayleigh fractionation, which depends on SST and the amount of precipitation, and the fact that coral fractionation occurs from a semi-isolated fluid reservoir (Wang et al., 2013a; Allison and Finch, 2010). Rayleigh fractionation equations can be used to identify trace elemental ratios if the relative concentrations of each element in the “batch” of calcifying fluid at the beginning of precipitation are known, as well as the mass fraction



of the initial fluid that remains when precipitation ends, and the Nernst aragonite-seawater partition coefficients (Gaetani et al., 2011). When expressions describing T-dependent element partitioning derived from abiogenic precipitation experiments are substituted for the aragonite-seawater partition coefficients, the Rayleigh fractionation becomes T-dependent as well. Temperature cannot be derived from a singular trace element ratio, such as Sr/Ca, unless the ratio in the calcifying fluid is constant over time, which is not usually the case, as seen in the following results of *Wang et al.*, (2013a). Increasing the number of measured element ratios improves this situation because each additional Rayleigh equation adds only a single unknown; it therefore becomes possible to solve for T (Gaetani et al., 2011).

The primary influence on skeletal composition is the amount of aragonite precipitated from each “batch” of calcifying fluid, which can have daily, seasonal, and annual fluctuations. Thus, coral colonies growing adjacent to one another can have significantly different relationships between temperature and elemental ratios because they differ in the amount of aragonite that they precipitate from each “batch” of calcifying fluid (Gaetani et al., 2011).

*Gaetani et al.* (2011) presents a new approach to coral thermometry that separates the influence of water temperature on skeleton composition from that of “vital effects,” and has the potential to provide estimates of growth temperatures that are accurate to within a few tenths of a degree Celsius from both tropical and cold-water corals. The results provide support for a physico-chemical model of coral biomineralization, and imply that  $Mg^{2+}$  substitutes directly for  $Ca^{2+}$  in biogenic aragonite. Temperature is resolved from the Rayleigh fractionation signal by combining information from multiple element ratios (e.g., Mg/Ca, Sr/Ca, Ba/Ca) to produce a mathematically over-constrained system of Rayleigh equations (Gaetani et al., 2011).

The Rayleigh-based, multi-element (RBME) approach to coral thermometry from *Gaetani et al.* (2011) differs from previous coral thermometers because it does not rely on an initial calibration of coral skeletal composition to an instrumental temperature record. Rather, considering coral skeletogenesis as a biologically mediated physico-chemical process, it provides a means to extract temperature information from the skeleton composition using the Rayleigh equation and a set of experimentally determined partition coefficients (Gaetani et al., 2011). Because this approach is based on a quantitative

understanding of the mechanism that produces the “vital effect” it should be possible to apply it both across scleractinian species and to corals growing in vastly different environments.

It has long been recognized that both the  $\delta^{18}\text{O}$  and Sr/Ca ratio of a coral skeleton correlate with SST. Both of these factors can be highly variable among individual corals and have a very different relationship in abiogenic aragonite than in corals, which illustrates the significance of “vital effects” on the composition of coral (Gaetani et al., 2011). With the proposed Rayleigh-based, multi-element (RBME) approach to coral thermometry, *Gaetani et al.* (2011) is able to accurately capture temperature (T) variability without the need to calibrate element ratios of coral skeleton to known SST. An in depth description of the coral thermometry can be found in *Gaetani et al.* (2011).

Another study, *Allison and Finch*, (2010), estimated calcification site pH from skeletal  $\delta^{11}\text{B}$  and it ranged from 8.3 to 8.8 ( $\pm \sim 0.1$ ) with a mean of  $\sim 8.6$ . Sr/Ca and B/Ca heterogeneity was not simply correlated with calcification site pH, as expected if Ca-ATPase activity increases the pH and decreases the Sr/Ca and  $\text{B}(\text{OH})_4^-/\text{CO}_3^{2-}$  ratios of the extracellular calcifying fluid (ECF). During periods of rapid calcification, enzymatic pumping of  $\text{Ca}^{2+}$  into the calcification site may dilute the trace element/Ca ratios of the ECF and the skeleton subsequently deposited from it (Allison and Finch, 2010). However, the relationship between the pH and Sr/Ca of the ECF is dependent on the concentration of DIC at the calcification site. At higher DIC concentrations the ECF has a high capacity to buffer the  $[\text{H}^+]$  changes induced by Ca-ATPase pumping. Conversely, at low DIC concentrations, this buffering capacity is reduced and ECF pH changes more rapidly in response to Ca-ATPase pumping. The absence of a simple correlation between ECF pH and skeletal Sr/Ca implies that calcification occurred under a range of DIC concentrations, reflecting variations in the respiration and photosynthesis of the coral and symbiotic zooxanthellate in the overlying coral tissues. To further our understanding of the processes affecting coral skeletal chemistry, *Allison and Finch* (2010) correlated Sr/Ca, B/Ca, Mg/Ca and boron isotopic variations in a modern *Porites lobata* coral from Hawaii. The  $\delta^{11}\text{B}$  values from the coral were correlated with Sr/Ca, B/Ca and Mg/Ca to test the hypothesis that variations in trace element geochemistry reflect pH changes at the calcification site dependent on Ca-ATPase

activity, which, in turn, serves to dilute the Sr/Ca, Mg/Ca and  $\text{B(OH)}_4^-/\text{CO}_3^{2-}$  ratios of the calcifying fluid.

In this study, *Allison and Finch* (2010) observed significant variations in B/Ca, Mg/Ca, Sr/Ca and  $\delta^{11}\text{B}$  over short skeletal distances (<500  $\mu\text{m}$ , nominally equivalent to periods of <20 days). No seasonal pattern in the magnitude of short temporal resolution Mg/Ca variations were observed. A significant correlation ( $r^2 = 0.47$ ) between skeletal Sr/Ca and B/Ca was observed in the dataset, but correlations between Sr/Ca and Mg/Ca as well as between B/Ca and Mg/Ca are insignificant. It is most likely that the geochemical heterogeneity reflects variations in the fluid from which the coral precipitates (*Allison and Finch, 2010*).

*Wang et al.* (2013a) produced measurements of elemental ratios over a two-year study period, in addition to measurements of  $\delta^{11}\text{B}$  values for samples of a *Porites* coral from the Great Barrier Reef, Australia. From these measurements, conclusions were drawn regarding constraints on partition coefficients for trace elements Uranium, Boron, and Lithium, as well as the temperature control on the trace elemental ratios and the pH up-regulation capability of the *Porites* coral (*Wang et al., 2013a*).

## 5.2 Methods

Boron is a highly volatile substance on which conducting laboratory experiments is difficult and time consuming. Unfortunately within the scope of and time allotted to this undergraduate research study, I was unable to obtain results for boron analyses of my own. Here I present the work of Zhengrong Wang, Assistant Professor of Geochemistry at Yale University and my research advisor, in order to further evaluate the vital effects of biogenic corals from Australia's Great Barrier Reef and the implications for the boron isotope-pH proxy.

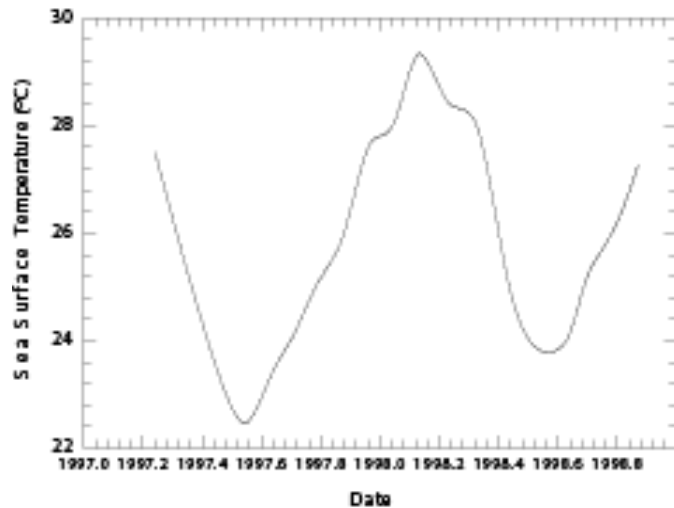
The samples used were *Porites lutea*, an aragonitic coral with finger-like morphology collected from Rib Reef, within Australia's Great Barrier Reef (GBR). Corals composed of aragonite are ideal for applying boron isotope-pH proxy as they contain a high concentration of boron, approximately 60 ppm (*Hemming and Hanson, 1992*). The growth of corals also occurs at the epidermis, in contact with seawater, as opposed to internal shell growth, associated with internal fluids at a lower pH, as observed in molluscs (*Hemming and Hanson, 1992*).

Long term monitoring of the GBR provides valuable records of *in situ* sea surface temperature (SST), salinity and other variables, against which geochemical proxies can be compared (Wang et al., 2013). Working from the study by Gaetani et al. (2011), Wang et al. (2013) presents measurements of trace element concentrations, including boron(B), lithium(Li), magnesium(Mg), strontium(Sr), barium(Ba), uranium(U) and calcium(Ca), oxygen ( $\delta^{18}\text{O}$ ), Mg ( $\delta^{26}\text{Mg}$ ) and B ( $\delta^{11}\text{B}$ ) isotope compositions of a Porites coral to understand the origin(s) of the vital effects evident in each proxy.

A series of powder samples were milled at ~1 mm intervals along the coral's axis of maximum growth, providing ~monthly temporal resolution across a ~2 year growth period. Aliquots of the aragonite powders were cleaned and prepared using established methods for trace metal, B isotope, and Mg isotope analysis (Foster, 2008; Wang et al., 2013a; Wang et al., 2013b).

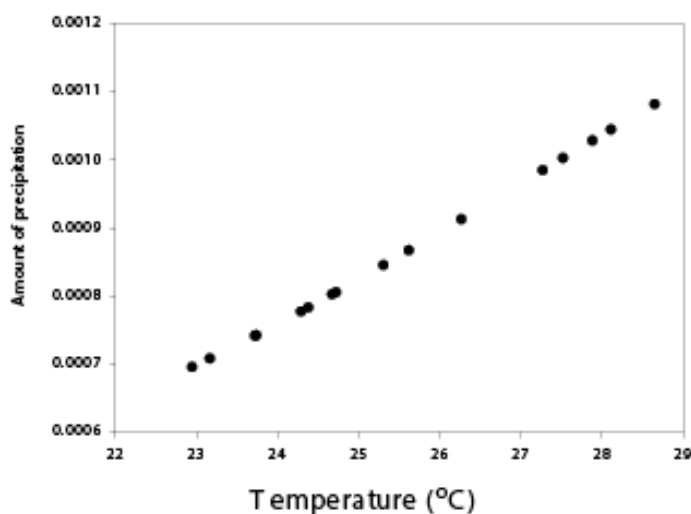
### 5.3 Results

Relationships among elemental ratios in coral skeleton provide insights into the mechanisms that produce “vital effects” (Gaetani et al., 2011). Three conclusions can be made regarding the results from this study. The first is regarding the temperature control on the trace elemental ratios in the coral samples, on annual cycles. The variations can be understood by a Rayleigh process, which depends on SST and the amount of precipitation. The second result is focused on calibrating the partition coefficients of boron, lithium, and uranium, assuming the calcifying solution has similar concentrations of these three elements to seawater. The partition coefficients are required for use in the Rayleigh fractionation equation, which characterizes the behavior of the trace elemental ratios in the coral (Gaetani et al., 2011). The third conclusion illustrates that the pH during annual growth of the Porites coral is does not vary with temperature, indicating a strong control over the internal pH of the calcifying fluid (Wang et al., 2013a).

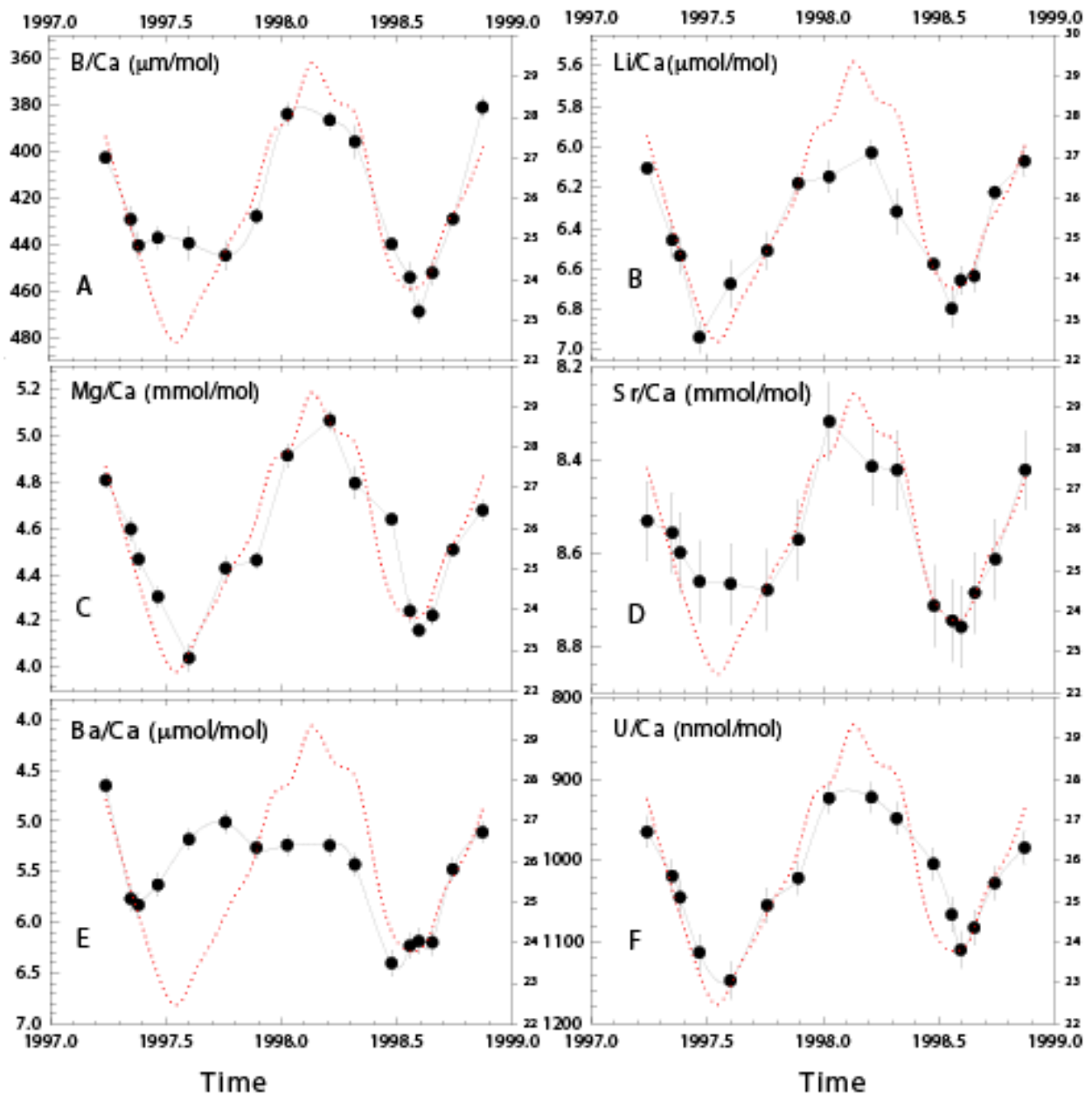


**Figure 7: Sea Surface Temperature variations (degrees Celsius) over the two-year study period from 1997-1999 (Wang et al., 2013a).**

In general, there is a temperature control observed for the trace elemental ratios, which is not the case for the  $\delta^{11}\text{B}$  values measured (Wang et al., 2013a). The trace elemental ratios follow a Rayleigh process, as discussed. This process depends on temperature and the amount of aragonite precipitation, which can be calculated for each growth band using the methods of *Gaetani et al* (2011). The relationship between SST and calcite precipitated is illustrated in Figure 8 (Wang et al, 2013a).



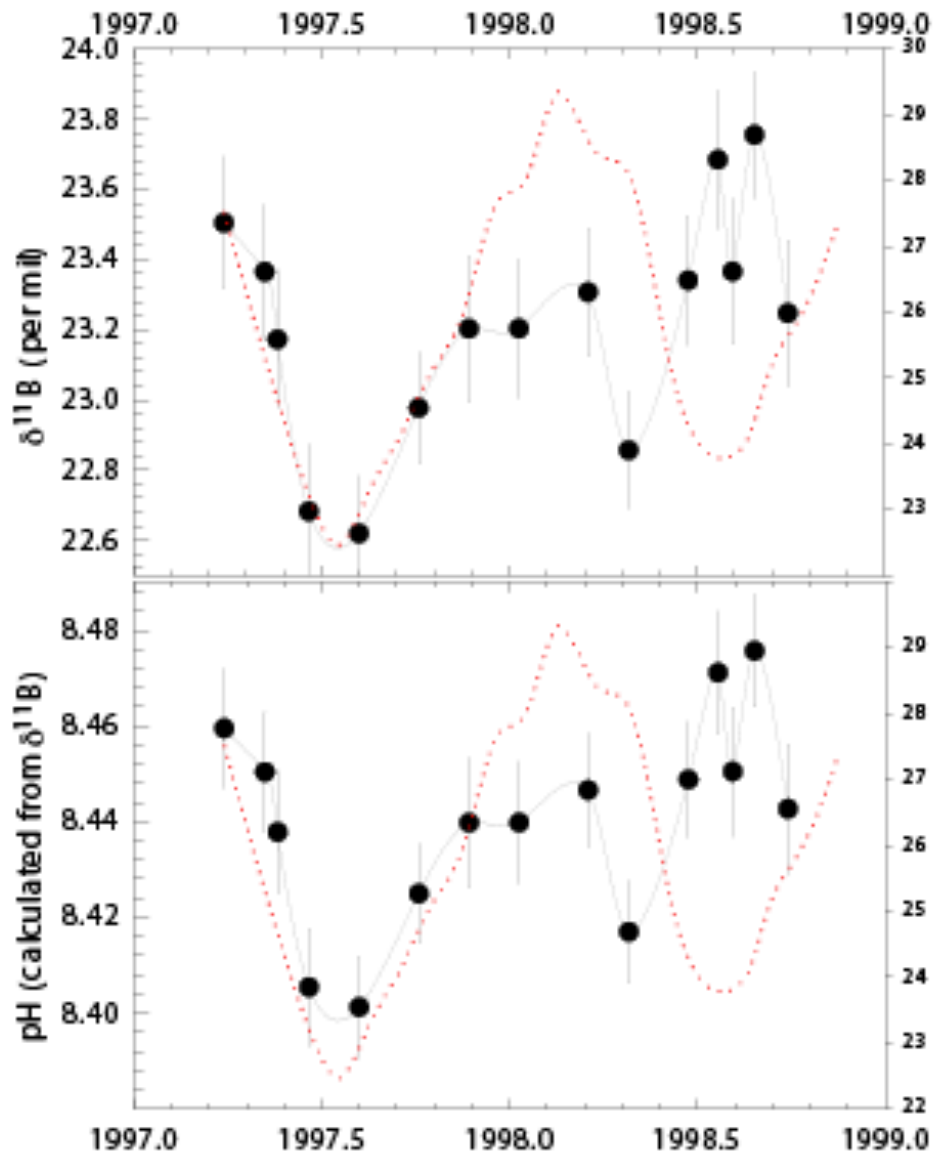
**Figure 8: Relationship between SST and the amount of aragonite precipitation (Wang et al., 2013a). A precipitation value of 1 would indicate that all of the calcium in the solution was precipitated.**



**Figure 9: B/Ca, Li/Ca, Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca values and correlations with SST (red) variations (Wang et al, 2013a).**

Figure 9 illustrates that B/Ca, Li/Ca, Sr/Ca, Ba/Ca and U/Ca have a positive correlation with SST, whereas Mg/Ca,  $\delta^{18}\text{O}$  and  $\delta^{26}\text{Mg}$  values have a negative correlation with SST (Wang et al., 2013a). As illustrated by Figure 10, there is no significant correlation between temperature and boron isotopic composition in these samples (Wang et al., 2013a). There is a weak correlation between 1997.0 and about 1997.8, but then there seems to be a

shift to an anti-correlation between 1997.8 and 1999.0. Using a fractionation factor of 1.027 and assuming the  $\delta^{11}\text{B}_{\text{cf}}$  is equal to  $\delta^{11}\text{B}_{\text{sw}} = 39.61\text{‰}$ , the average pH value calculated is 8.44 over the two-year time period; this is higher than the bulk seawater pH, which is about 8.2 (Gaetani et al., 2011). The lack of seasonal variation in pH indicates a strict control over the internal pH of the calcifying fluid of the *Porites* coral.



**Figure 9: Isotopic composition of boron in samples and temperature variations during time of carbonate formation (top). pH calculated using the boron isotope-pH proxy and the measured boron isotopic compositions (bottom) (Wang et al, 2013a).**

## 5.4 Discussion

*Wang et al.*, (2013) observed that B/Ca, Li/Ca, Sr/Ca, Ba/Ca and U/Ca have a positive correlation with SST, whereas Mg/Ca,  $\delta^{18}\text{O}$  and  $\delta^{26}\text{Mg}$  values have a negative correlation with SST. From the study of the RBME approach, *Gaetani et al.* (2011) predict the same relationships and conclude:

- 1) coral calcification rate is influenced by changes in the mass of aragonite precipitated from each “batch” of calcifying fluid, which, in turn, is sensitive to T,
- 2) T directly influences Mg/Ca and Sr/Ca ratios in coral skeleton, although the signal is relatively weak, and this information can be recovered using RBME thermometry,
- 3) there is no evidence to support the existence of independent mechanisms for controlling the transport and incorporation of Sr and Mg into coral skeleton.

It is important to note, as is illustrated in Figure 9, both Sr/Ca and Ba/Ca decrease with increasing aragonite precipitation, but the Rayleigh effect on these element ratios is weak relative to Mg/Ca.

In another study, *Reynaud et al.* (2007) investigated the effects of T on the skeletal composition of the tropical coral *Acropora* sp. to evaluate the use of Sr/Ca and Mg/Ca ratios as paleo-temperature proxies. Their conclusions differ from those of *Wang et al.* (2013a) and *Gaetani et al.* (2011). *Reynaud et al.*, (2007) concludes that variations in Mg/Ca ratio are driven by changes in calcification rate and, therefore, are only indirectly related to T, which influences the coral calcification rate, and the different T sensitivities of Sr/Ca and Mg/Ca indicate that Sr and Mg are transported to the site of calcification and incorporated into the skeleton by different mechanisms. However, there is clearly a strong correlation between the temperature of the calcifying fluid and the calcification rate. *Gaetani et al.* (2011) illustrates that the RBME method predicts the temperatures observed in cultured samples with great accuracy, proving the validity of the method.

The Rayleigh fractionation mechanism is understood to be the dominant “vital effect” in the coral species studied. These fractionations depend on both T and the mass of aragonite precipitated from each “batch” of calcifying fluid. The latter signal is what is commonly referred to as “vital effects” (*Gaetani et al.*, 2011). Further understanding of the mechanisms behind the “vital effects” in biogenic carbonates, which affect the



microenvironment of the carbonate and therefore the chemical composition, will aid in our ability to reliably constrain the use of the  $\delta^{11}\text{B}$ -pH proxy.

## 6. Interpreting the Proxy

### 6.1 Post-depositional Alterations

It is important to take into account the possibility for post-depositional alterations such as diagenesis in analyzing boron isotopes for paleoclimate reconstruction. Evidence that diagenesis causes enrichment of  $^{10}\text{B}$  is supplied by *Gaillardet and Allégre* (1995) for corals and *Spivack and You* (1997) for bulk core-sample carbonate (Pagani et al., 2005). This additional factor poses an important limitation to boron isotope-based pH determinations.

Using positive thermal ionization mass spectrometry and a chemical procedure for B separation and purification both for the first time, *Gaillardet and Allégre* (1995) observe a linear correlation in both  $\delta^{11}\text{B}$  vs. total B concentrations and  $\delta^{11}\text{B}$  vs.  $1/\text{B}$  plots for ancient corals but not for modern corals. The samples used in this study all contain almost pure aragonite. Unusually,  $\text{B}(\text{OH})_4^-$  is enriched in  $^{10}\text{B}$ , compared to  $\text{B}(\text{OH})_3$ , which clearly alters the pH values calculated from the measured  $\delta^{11}\text{B}$  values, if used as equivalent to non-diagenetic samples. Because of this, it is important that only well preserved samples are used for pH determinations using the  $\delta^{11}\text{B}$ -pH proxy (*Gaillardet and Allégre*, 1995).

### 6.3 Interlaboratory Calibrations

As mentioned previously, due to the nature of the boron isotope-pH proxy, there are major implications of relatively small changes in  $\delta^{11}\text{B}$  (<2‰). Therefore, it is important to be sure that different laboratories working on boron produce comparable results, within a reasonable uncertainty, in order to be able to use each other's findings to further the research on the topic. However, accurate measurements of boron isotope ratio by mass spectrometry is difficult because of the relatively large mass difference between the isotopes which causes large fractionation during measurement as well as the fact that there are only two naturally occurring isotopes of boron and it is therefore impossible to use the double spike approach that works for other isotopic measurements, such as Zn (*Foster et al.*, 2012). Previous studies on interlaboratory comparisons for boron isotope measurements (*Gonfiantini et al.*, 2003; *Aggarwal et al.*, 2009) show an interlaboratory range of  $\delta^{11}\text{B}$  measurements typically

between 2-3‰ and even up to 11‰. However, this is too large to be compatible with the important and sensitive paleo-pH implications, where differences of >1‰ is often too great.

*Hönisch et al* (2003) raises the important discrepancy between interlaboratory calibration issues. In response to the unexplainable +2.7‰ offset between these results and those of *Sanyal et al* (1996), the most likely responsible difference between the two experiments was the laboratory and mass spectrometer used. The study therefore concludes that there is a need to define an international carbonate standard for boron isotopic analysis. *Wara et al* (2003) performed an interlaboratory comparison with *Sanyal et al.* (1995, 1996, 1997, 2000) by exchanging samples, and produced significantly similar results. Without a carbonate standard for boron isotopic analysis, this type of cross-calibration is important to perform in order to compare results with previous work.

*Foster et al.* (2012) presents the first report on the interlaboratory comparison of boron isotope analyses of boric acid, seawater and marine CaCO<sub>3</sub> in four laboratories, each using a different technique of MC-ICPMS and/or NTIMS. The study distributed samples to four chosen laboratories whose primary analyst has a history and specific interest in marine carbonate boron isotope analysis. The samples distributed comprise 15 different samples of CaCO<sub>3</sub>, ranging from inorganic calcite to aragonitic corals, and 3 samples of boric acid, which require no chemical treatment before analysis and were therefore used first to determine any pre-existing systematic analytical biases (Foster et al., 2012). Each laboratory also used somewhat different analytical methods, specifics of which can be found in *Foster et al.* (2012).

Among the four different laboratories in the study, there were no reportedly significant interlaboratory biases in  $\delta^{11}\text{B}$  for boric acids or seawater (2 standard deviation (sd) = 0.31-0.61‰) (Foster et al., 2012). This confirms that there were no inherent analytical biases between the different analytical techniques used in the different labs, given strict protocols (Gonfiantini et al., 2003; Foster et al., 2012). Similar agreement was found in the analysis of seawater, which produced a mean  $\delta^{11}\text{B} = 39.65 \pm 0.41\text{‰}$  2sd. The discrepancy here is much lower than was found in *Gonfiantini et al.* (2003).

However, there is a significant variation for  $\delta^{11}\text{B}$  of calcium carbonate samples (2sd=1.6‰). This variation is relatively systematic between laboratories and can be partially reduced by secondary normalization. It seems that the B/Ca ratio (i.e. boron content of the

samples) and overall sample size (available B) may play a role in the variation but the exact mechanism responsible for the offset is not yet certain (Foster et al., 2012). After the normalization correction, the uncertainty is reduced to less than 0.65‰ 2sd for about 75% of the samples (Foster et al., 2012). A significant correlation is observed between the ratio of boron to CaCO<sub>3</sub> matrix (B/Ca ratio) and the level of interlaboratory variability; smaller samples with lower amounts of boron are more susceptible to the influence of the error introduced by differing “blanks” and/or matrix effects. If the matrix is removed, the blank contribution is increased; however, if the matrix is not removed, samples with different matrices will inevitably behave differently during analysis (Foster et al., 2012). Therefore, the normalization correction attempts to account for this by grouping the samples with a common matrix or similar total B and averaging the results for each sub-set. This also allows outliers to be identified (Foster et al., 2012).

Although it is important to determine the exact cause of discrepancy in future studies and minimize it, the error was largely systematic which is important because relative differences in  $\delta^{11}\text{B}$ , rather than absolute values, can often be used in paleoclimate or paleoceanographic interpretations.

From the results of this study, *Foster et al.* (2012) lays out a number of suggestions for future boron measurements including:

- i. Minimizing and quantifying the extent of boron contamination in every step of sample processing
- ii. Assessing the effect of sample size on measured  $\delta^{11}\text{B}$  and external reproducibility
- iii. Understanding and minimizing the causes of “matrix” effects specific to each particular sample type and analytical protocol

In addition, it is suggested that well characterized marine carbonate reference materials are very much needed for future boron isotope analysis (Foster et al., 2012). This would allow for better interlaboratory comparisons as well as minimize variations in absolute  $\delta^{11}\text{B}$  measurements.

#### 6.4 Future Study

At present, the research on the  $\delta^{11}\text{B}$ -pH proxy has studied mostly coral and foraminifera. However, this limits the possibility of using the proxy past ~180 Ma because foraminifer-bearing deep-sea sediments are limited to that time frame. Therefore, extending

the use of the proxy beyond the earlier Phanerozoic must rely on different carriers.

Brachiopods are the most promising candidate for extending the boron isotope record as far as the Cambrian (Xaio et al., 2013). However, little is known about the controls on boron isotopes on such large time scales and possible vital effects; therefore, these problems are worth studying further.

With regard to the need for future study, among the controlling factors of the  $\delta^{11}\text{B}$ -pH proxy, ( $\text{pK}_{\text{B}}^*$ ,  $\delta^{11}\text{B}_{\text{sw}}$ ,  $\delta^{11}\text{B}_{\text{carbonate}}$ , and  $\alpha_{4-3}$ ), the controversy as to  $\text{pK}_{\text{B}}^*$  and  $\delta^{11}\text{B}_{\text{sw}}$ , and  $\alpha_{4-3}$  is relatively less, while the hypothesis regarding which and how boron species are incorporated into biogenic carbonates remains doubtful. If trigonal boron is also incorporated into bio-carbonates, the proxy becomes much more complicated (Xaio et al., 2013).

*Wang et al.* (2013) and *Gaetani et al.*, (2011) have illustrated a further depth of research the proxy can and will take in order to better constrain the activity of biogenic carbonates and the temperature effects on trace elemental ratios. With this quantitative Rayleigh fractionation research, we may not have to rely so heavily on empirical calibrations of each coral species; it is therefore possible to extrapolate to more species of coral in order to use the boron isotope-pH proxy, and other geochemical proxies, for paleo-reconstructions. With continued research on the topic, we heighten the possibilities of using geochemical proxies applied to coral and foraminiferal skeletons in order to reconstruct past climate, and possibly to predict the effects of the changing earth systems on future climate.

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