



Boron isotopic compositions in growing corals from the South China Sea

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ARTICLE INFO

Article history:

Received 12 April 2012

Received in revised form 24 September 2012

Accepted 2 November 2012

Available online 12 November 2012

Keywords:

Coral
Trace element
Boron isotope
 $\delta^{11}\text{B}$ -pH proxy
South China Sea

ABSTRACT

In order to determine incorporation of boron species, boron isotopic fractionation, and influence of trace elements on isotopic compositions of boron in corals ($\delta^{11}\text{B}_{\text{coral}}$), concentrations of Mg, Sr, Na, B and $\delta^{11}\text{B}_{\text{coral}}$ in growing corals from the South China Sea were measured. Relative to seawater, Sr enriched while Mg depleted in corals in the South China Sea. Although the $\delta^{11}\text{B}_{\text{coral}}$ values were different from various species and were not closely correlated with the element concentrations in corals in the South China Sea, $\text{Mg}(\text{OH})_2$ existed in corals can result in high $\delta^{11}\text{B}_{\text{coral}}$. Thus, it is necessary to examine the existence of $\text{Mg}(\text{OH})_2$ and to choose the same species when $\delta^{11}\text{B}_{\text{coral}}$ is used in the $\delta^{11}\text{B}$ -pH proxy. Based on the measured $\delta^{11}\text{B}$ values of corals and coexisting seawater as well as the seawater pH in the South China Sea, a new isotopic fractionation factor α_{4-3} between $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ was determined to be 0.979. Besides $\text{B}(\text{OH})_4^-$ into corals, our results showed that $\text{B}(\text{OH})_3$ may also be incorporated into corals with variable proportions. The incorporation of $\text{B}(\text{OH})_3$ into corals may challenge the hypothesis of $\delta^{11}\text{B}_{\text{coral}} = \delta^{11}\text{B}_4$, resulting in increasing uncertainty to the calculated seawater pH values to the $\delta^{11}\text{B}$ -pH proxy. We suggested that a best-fit empirical equation between $\delta^{11}\text{B}$ of bio-carbonates and seawater pH needs to be established by the precipitation experiments of inorganic carbonates or culture experiments of corals or foraminifera.

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1. Introduction

In recent years, the reconstruction of ancient seawater pH using the $\delta^{11}\text{B}$ in marine bio-carbonates (such as coral, foraminifera) indirectly, the calculation of the past $p\text{CO}_2$, and the influence of these two factors on changes in the ancient climate have become one of the important issues for the international boron isotope geochemistry community and have been called as the $\delta^{11}\text{B}$ -pH proxy (Hemming and Hanson, 1992; Spivack et al., 1993; Pearson and Palmer, 2000; Pelejero et al., 2005; Wei et al., 2009; Douville et al., 2010). Due to high growth rate and easy sampling, corals become the ideal materials for the $\delta^{11}\text{B}$ -pH proxy (e.g. Gaillardet and Allègre, 1995; Liu et al., 1999, 2009; Hönisch et al., 2004; Wei et al., 2009). Vengosh et al. (1991) firstly analysed the boron isotopic compositions of corals. Gaillardet and Allègre (1995) established the $\delta^{11}\text{B}$ -pH proxy of corals. Coral culture experiments, carried out by Reynaud et al. (2004), showed that corals did not significantly alter ambient seawater for calcification with respect to pH, and that $\delta^{11}\text{B}$ of corals was not temperature dependent. Using the $\delta^{11}\text{B}_{\text{coral}}$, Liu et al. (2009) and Wei et al. (2009) reconstructed the seawater pH in the South China Sea and the Great Barrier Reef of Australia, respectively.

One of the main assumptions of the $\delta^{11}\text{B}$ -pH proxy was that only $\text{B}(\text{OH})_4^-$ incorporated into bio-carbonates, with little or no boron isotopic fractionation (Hemming and Hanson, 1992), so that the $\delta^{11}\text{B}$ value in marine bio-carbonates ($\delta^{11}\text{B}_{\text{carb}}$) recorded the $\delta^{11}\text{B}$ value of $\text{B}(\text{OH})_4^-$ ($\delta^{11}\text{B}_4$) in seawater. A series of inorganic calcite precipitation experiments had shown that $\text{B}(\text{OH})_4^-$ was the only or dominant species incorporated into calcite (Hemming et al., 1995; Sanyal et al., 1996, 2000). However, Klochko et al. (2009) found that both trigonal (36–46%) and tetrahedral coordinated boron existed in biogenic and hydrothermal carbonates. Rollion-Bard et al. (2011) also found that both boron coordination species but in different proportions depend on the coral microstructure, i.e. centres of calcification versus fibres.

The inorganic calcite precipitation experiment (Xiao et al., 2006) indicated that $\delta^{11}\text{B}_{\text{carb}}$ deviated increasingly from the curve of $\delta^{11}\text{B}_4$ as pH increased. The boron isotope fractionation factor between precipitation and solution was even greater than 1. Xiao et al. (2006) reasoned that the presence of Mg^{2+} or other trace elements was the main reasons of this observation. In the former precipitation experiments, only CaCO_3 was considered and their results did support the hypothesis of $\delta^{11}\text{B}_{\text{carb}} = \delta^{11}\text{B}_4$. However, both foraminifera and corals are not pure carbonate and contain other elements, such as Mg and Sr. Sr/Ca and Mg/Ca in corals were mainly used to reconstruct Sea Surface Temperature (SST) (Beck et al., 1992; Sholkovitz and Shen, 1995) and to study the monsoon

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and El Niño (Alibert and McCulloch, 1997; Liu et al., 2008; Mitsuguchi et al., 2008). Brucite ($\text{Mg}(\text{OH})_2$) can exist in modern corals (Nothdurft et al., 2005) and $\text{B}(\text{OH})_3$ incorporate into brucite preferentially (Xiao et al., 2009, 2011). Whether $\text{Mg}(\text{OH})_2$ or other trace elements can influence $\delta^{11}\text{B}_{\text{coral}}$ is worth further studying.

In addition, boron isotopic fractionation factor (α_{4-3}) between $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ is also one of the main parameters for the $\delta^{11}\text{B}$ -pH proxy. The α_{4-3} varied from 0.952 (Xiao et al., 2006) to 0.984 (Hemming et al., 1995) according to different experiments. When different α_{4-3} values are used in the $\delta^{11}\text{B}$ -pH proxy, the calculated pH values will be different. Therefore, accurate determination of α_{4-3} is important.

Fifty-one growing corals and three coexisting seawaters in Weizhou Island, Sanya Bay and Leizhou Peninsula of the South China Sea were collected in this study. Concentrations of Mg, Sr, Na, B and boron isotope composition in corals ($\delta^{11}\text{B}_{\text{coral}}$) were measured. The relationship between these elements and $\delta^{11}\text{B}_{\text{coral}}$, isotopic fractionation of boron and the incorporation of boron species into corals were determined. Those results will shed further lights on the application of the $\delta^{11}\text{B}$ -pH proxy.

2. Site description and analytical methods

2.1. Site description

All corals used in this study were growing corals at three locations, Weizhou Island (21°0'08.22"N, 109°07'24.58"E), Sanya Bay (20°13'24.78"N, 109°55'11.08"E) and Leizhou Peninsula (18°11'22.37"N, 109°29'18.16"E), collected from October 18 to 26, 2006 (Fig. 1). In the same location, there are only few kilometres from each sampling site, so the coexisting seawater for every coral is nearly the same. Therefore, one sample of coexisting seawater was collected in each location. The seawater pH values were measured at the sampling sites with measurement error of ± 0.05 , with values of 8.06, 8.07 and 8.30 in Weizhou Island, Leizhou

Peninsula and Sanya Bay, respectively. The sample ID, locations and species of corals were listed in Table 1.

2.2. Sample preparation and analyses

The fine branches of corals were cut and approximately 5 g of each cut coral was crushed in an agate mortar and washed with double-distilled water to remove soluble salts. Then, the samples were soaked in 30% H_2O_2 for 4 h to remove organic matter from the surface and further cleaned with ultrasonic. After discarding the H_2O_2 solution, corals were dried under an infrared lamp at 60 °C. About 500 mg of the constant weight sample was soaked in 30% H_2O_2 for 2 h and filtrated by pumping. Then, the samples were rinsed with boron-free water repeatedly. The samples were dissolved with enough 1.0 mol/L high-purity HCl for complete dissolution and centrifuged for 1 h. The supernatant were used for chemical separation of boron.

Ca^{2+} , Mg^{2+} , Sr^{2+} and Na^+ were measured by a Leeman Labs Profile ICP-OES at State Key Laboratory of Environmental Geochemistry. Repeated analyses demonstrated reproducibility within 2%. The boron concentration was determined by the azomethine-H spectrophotometric method with the external precision of 2% (Xiao et al., 2011).

Boron was isolated from solution in two chromatographic steps using Amberlite IRA 743 boron-specific resin (Xiao et al., 2003) and a mixed resin of cation-exchanger (H^+ form) and anion-exchanger (ion-exchanger II, HCO_3^- form) (Wang et al., 2002). The isotopic compositions of boron in all samples were measured by a GV IsoProbe T single magnetic sector thermal ionization mass spectrometer and the P-TIMS method using Cs_2BO_2^+ ions with a graphite loading (Xiao et al., 1988). The sample solution was first loaded onto a flat degassed Ta filament coated by 2.5 ml graphite slurry. Data were collected by switching magnetically between the masses 308 ($^{133}\text{Cs}^{10}\text{B}_{16}\text{O}_2^+$) and 309 ($^{133}\text{Cs}^{11}\text{B}_{16}\text{O}_2^+$) and the intensity ratio of the ion beams at masses

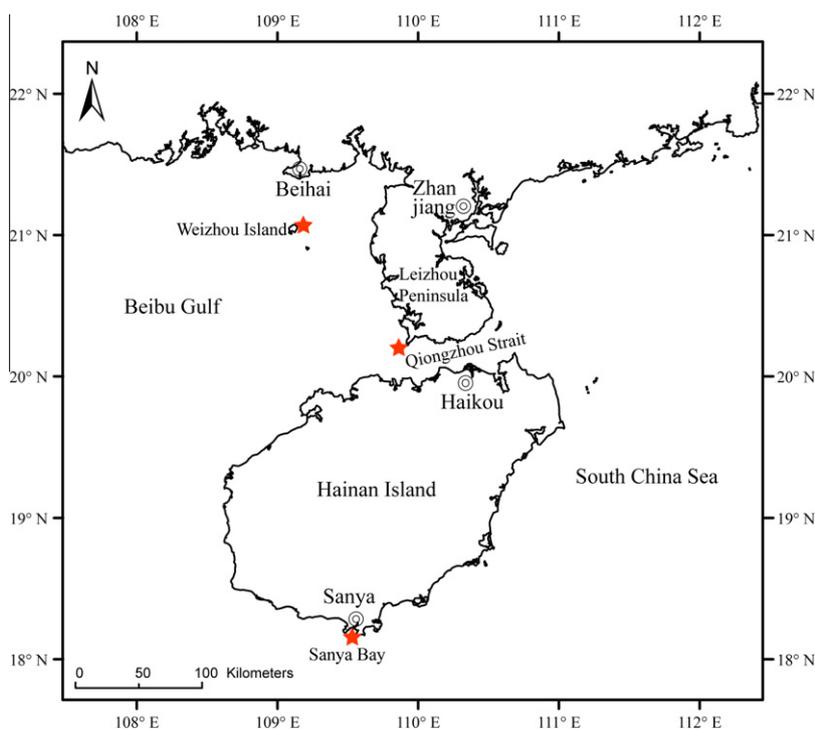


Fig. 1. Sampling locations of corals from South China Sea. Red asterisks represent sampling locations. Eight corals (WZ1 to WZ8) were collected from Weizhou Island, 26 corals (SY2 to SY27) were collected from Sanya Bay and 17 samples (LZ1 to LZ17) were collected from Leizhou Peninsula. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Ion concentrations and the boron isotopic compositions in corals and seawater. K_d is the partition coefficient between coral and seawater. $K_d = [E]_{\text{coral}}/[E]_{\text{seawater}}$, where $[E]_{\text{coral}}$ and $[E]_{\text{seawater}}$ are the ion concentrations in coral and seawater, respectively. WZS, SYS and LZS are the seawater from Weizhou Island, Sanya Bay and Leizhou Peninsula.

Sample	Coral species	Na (mg/g)	Mg (mg/g)	Sr (mg/g)	B ($\mu\text{g/g}$)	$\delta^{11}\text{B}$ (‰)	$\alpha_{\text{carb-sw}}$	$\alpha_{\text{carb-3}}$
WZ1	<i>Favia rotumana</i>	10.91	0.9	7.5	54.6			
WZ2	<i>Acropora brueggemanni</i>	8.2	0.9	7.7	49.7	23.7	0.9834	0.9784
WZ3	<i>Galaxea fascicularis</i>	10.41	1.3	7.7	54.5			
WZ4	<i>Pocillopora meandrina</i>	11.0	0.7	7.4	59.6	24.2	0.9838	0.9789
WZ5	<i>Pectima lactuca</i>	9.8	0.8	6.7	80.5			
WZ6	<i>Favites yamanaril</i>	9.7	1.3	7.3	75.5	26.3	0.9858	0.9815
WZ7	<i>Goniopora gracilis</i>	9.7	1.0	8.6	48.6	23.0	0.9827	0.9775
WZ8	<i>Pocillopora meandrina</i>	7.1	0.6	5.8	74.7			
WZS		7.1	1.2	0.006	4.5	41.0		
K_d^{\dagger}		1.3	0.8	1224	14.0			
LZ1	<i>Stylopora danae</i>	8.1	0.7	7.9	67.7	25.7	0.9851	0.9806
LZ2	<i>Turbinaria peltata</i>	8.2	0.7	7.9	58.3			
LZ3	<i>Coscinaraea exesa</i>	9.0	0.7	7.4	75.2	27.5	0.9868	0.9828
LZ4	<i>Pocillopora meandrina</i>	7.6	0.7	7.9	56.7	24.5	0.9839	0.9790
LZ5	<i>Turbinaria peltata</i>	8.2	0.6	7.8	65.9			
LZ6	<i>Pocillopora meandrina</i>	10.66	0.7	7.8	55.3	24.5	0.9839	0.9790
LZ7	<i>Turbinaria peltata</i>	9.7	0.7	7.8	55.4	25.9	0.9853	0.9809
LZ8	<i>Favites abdita</i>	9.5	0.9	7.3	71.2	25.5	0.9849	0.9803
LZ9	<i>Favites abdita</i>	9.3	1.3	7.7	92.0	25.4	0.9848	0.9802
LZ10	<i>Favites abdita</i>	11.37	1.1	7.4	62.0	25.8	0.9852	0.9807
LZ11	<i>Favites abdita</i>	13.7	1.1	7.6	58.5	25.0	0.9844	0.9797
LZ12	<i>Euphyllia glabrescens</i>	10.39	0.8	7.4	69.4	23.8	0.9833	0.9782
LZ13	<i>Turbinaria peltata</i>	13.1	0.6	7.8	71.4	26.0	0.9854	0.9810
LZ14	<i>Euphyllia glabrescens</i>	9.3	1.0	6.4	68.5	23.7	0.9832	0.9781
LZ15	<i>Turbinaria peltata</i>	10.23	0.6	7.1	54.4			
LZ16	<i>Montipora digitata</i>	12.77	0.8	8.2	73.2			
LZ17	<i>Porites lutea</i>	10.93	1.5	7.0	52.8			
LZS		8.6	1.5	0.009	4.6	41.2		
K_d		1.2	0.6	838	14.0			
SY2	<i>Acropora brueggemanni</i>	9.9	1.0	7.2	65.1			
SY3	<i>Favites abdita</i>	14.56	0.9	7.6	54.3	25.2	0.9847	0.9767
SY4	<i>Acropora brueggemanni</i>	7.8	0.7	7.1	52.6			
SY5	<i>Turbinaria peltata</i>	9.2	0.7	6.5	70.3	25.7	0.9852	0.9774
SY6	<i>Acropora brueggemanni</i>	11.94	0.9	8.1	56.3			
SY7	<i>Favites pectinata</i>	9.6	1.6	8.5	87.2	26.8	0.9863	0.9791
SY8	<i>Euphyllia glabrescens</i>	6.8	1.4	5.8	65.7	23.7	0.9832	0.9744
SY9	<i>Goniopora crossland</i>	7.5	1.2	6.2	50.1			
SY10	<i>Platygyra daedatea</i>	14.89	1.2	7.4	75.3			
SY11	<i>Platygyra sinensis</i>	7.7	0.9	7.0	86.3	27.9	0.9873	0.9806
SY12	<i>Favites pectinata</i>	9.7	0.8	6.7	60.8	26.8	0.9863	0.9791
SY13	<i>Favia rotumana</i>	12.17	1.4	9.2	54.9	22.8	0.9824	0.9732
SY14	<i>Montipora digitata</i>	8.8	0.8	7.9	63.3			
SY15	<i>Montipora digitata</i>	9.9	0.8	7.3	71.7			
SY16	<i>Favites yamanaril</i>	10.46	1.4	7.5	50.3	24.9	0.9844	0.9762
SY17	<i>Coscinaraea exesa</i>	10.8	1.0	9.0	74.4	27.0	0.9864	0.9793
SY18	<i>Acropora brueggemanni</i>	11.06	1.0	8.8	59.5			
SY19	<i>Turbinaria peltata</i>	9.6	1.2	8.0	57.4	25.7	0.9852	0.9774
SY20	<i>Acropora brueggemanni</i>	9.8	0.8	7.6	85.2			
SY21	<i>Acropora carymbosa</i>	10.95	1.1	6.8	65.6			
SY22	<i>Acropora carymbosa</i>	13.93	1.1	6.9	74.6			
SY23	<i>Favites pectinata</i>	9.6	1.1	7.0	90.4	26.8	0.9863	0.9791
SY24	<i>Galaxea fascicularis</i>	9.5	0.9	6.9	78.0			
SY25	<i>Stylocoeniella gnettheri</i>	15.36	1.0	8.8	62.6			
SY26	<i>Acropora brueggemanni</i>	11.16	0.8	7.6	55.4			
SY27	<i>Acropora brueggemanni</i>	11.24	0.9	8.1	57.3	23.3	0.9829	0.9739
SYS		7.2	1.1	0.007	4.5	41.1		
K_d		1.5	0.9	1075	15.0			

308 and 309 ($R_{309/308}$) was calculated. The $^{11}\text{B}/^{10}\text{B}$ ratio was calculated as $R_{309/308} - 0.00078$. The isotopic composition of boron was expressed as $\delta^{11}\text{B}$ value relative to NIST SRM 951 H_3BO_3 according to the following formula:

$$\delta^{11}\text{B}(\text{‰}) = \left\{ \left(\frac{^{11}\text{B}/^{10}\text{B}}{^{11}\text{B}/^{10}\text{B}} \right)_{\text{sample}} / \left(\frac{^{11}\text{B}/^{10}\text{B}}{^{11}\text{B}/^{10}\text{B}} \right)_{\text{standard}} - 1 \right\} \times 1000$$

Here, the standard material is NIST SRM 951 with the recommended value of 4.04362 ± 0.00137 (Catanzaro et al., 1970). The measured average $^{11}\text{B}/^{10}\text{B}$ ratio of NIST SRM 951 was 4.04763 ± 0.00106 (2σ , $n = 8$).

3. Results and discussion

3.1. Ion concentrations in corals in the South China Sea

The concentrations of Mg, Sr, and Na in corals in the South China Sea ranged from 0.6 to 1.6, 5.8 to 9.2, and 6.8 to 15.4 mg/g, with an average value of 0.9, 7.5 and 10.3 mg/g, respectively (Table 1). The boron concentrations ranged from 50.1 to 92.0 $\mu\text{g/g}$, with an average value of 66.1 $\mu\text{g/g}$, which were comparable with the previously reported values (Vengosh et al., 1991; Gaillardet and Allègre, 1995; Liu et al., 1999, 2009; Wei et al., 2009) and

higher than the coexisting seawater. Relative to the coexisting seawater, Sr, B, and Na were enriched in corals in the South China Sea with the K_d values of 1177, 1046, 14 and 1.3, while Mg was depleted in corals with a K_d value of 0.8.

$B(OH)_3$ and $B(OH)_4^-$ are the two species of boron in seawater, which are strongly pH-dependent (Hemming and Hanson, 1992). Slight change of pH in seawater can affect fraction of $B(OH)_3$ and $B(OH)_4^-$ and boron concentration in corals. For example, the calculated fraction of $B(OH)_3$ and $B(OH)_4^-$ at pH = 8.1 and 8.2 are 75%, 25% and 71%, 29%, respectively. Therefore, variation of boron concentrations in corals in the South China Sea mainly reflected the calcification pH variation of growing corals.

3.2. Boron isotopic compositions in corals in the South China Sea

The $\delta^{11}B_{\text{coral}}$ values varied between 22.8‰ and 27.9‰ with an average value of 25.2‰, which were close to the values of 19.1‰ to 25.1‰ reported by Hemming and Hanson (1992), 23.3–25.5‰ by Gaillardet and Allègre (1995), 22.7–24.8‰ by Liu et al. (1999), but were slightly lower than that of 26.7–31.9‰ by Vengosh et al. (1991). The $\delta^{11}B_{\text{coral}}$ of different species from the South China Sea showed a wide variation, apparently indicating a relationship between $\delta^{11}B_{\text{coral}}$ and coral species. *Pocillopora meandrina*, *Turbiniaria peltata*, *Favites pectinata*, *Favites abdita* and *Euphyllia glabrescens* showed average $\delta^{11}B$ values of 24.4‰, 25.9‰, 26.7‰, 25.4‰ and 23.7‰, respectively. Corals of the same species growing at different places showed nearly the same $\delta^{11}B$ values. For example, LZ8, LZ9, and SY3 had $\delta^{11}B$ values of 25.5‰, 25.4‰, and 25.2‰, respectively (Table 1). This discarded the fact that the difference in $\delta^{11}B_{\text{coral}}$ in various species of coral arose from isotopic determination error and indicated that the $\delta^{11}B$ difference in various species of coral actually presented. The $\delta^{11}B$ of seawater ($\delta^{11}B_{\text{sw}}$) was 41.0‰, 41.2‰ and 41.1‰ in WZS, LZS and SYS, respectively. No correlation between $\delta^{11}B_{\text{coral}}$ and element concentrations was observed.

The reported Mg/Ca ratios of corals varied between 3.1 and 5.7 mmol/mol, whereas the Sr/Ca ratios varied between 8.3 and 9.4 mmol/mol (Wei et al., 2000; Watanabe et al., 2001; Peng et al., 2003; Shirai et al., 2008). Mg/Ca and Sr/Ca ratios of the corals in the South China Sea were 2.2–4.4 mmol/mol and 6.4–7.9 mmol/mol, which were comparable with the reported data. $Mg(OH)_2$ can exist in modern corals (Nothdurft et al., 2005) and $B(OH)_3$ incorporates into $Mg(OH)_2$ preferentially (Xiao et al., 2009, 2011). Therefore, if the $Mg(OH)_2$ -bearing corals were sampled and used in the $\delta^{11}B$ -pH proxy, the $\delta^{11}B_{\text{coral}}$ and the calculated pH would be higher than the normal value. For example, if $\delta^{11}B_{\text{coral}}$ values of 23.7‰ and 26.7‰ were used, the calculated pH values will be 8.36 and 8.57, respectively. Rollion-Bard et al. (2011) suggested that careful sampling was necessary before performing boron isotopic measurements in deep-sea corals. The positive relationship between $\delta^{11}B$ and Mg/Ca in corals can be used to judge the existence of $Mg(OH)_2$ in corals (Xiao et al., 2011). There were no relationships between $\delta^{11}B_{\text{coral}}$ and Mg/Ca ratios in our study, indicating the inexistence of $Mg(OH)_2$ in corals in the South China Sea. Thus, when the $\delta^{11}B_{\text{coral}}$ values are used in the $\delta^{11}B$ -pH proxy, it is necessary to examine the existence of $Mg(OH)_2$ and to choose the same coral species.

3.3. Boron isotopic fractionation factor (α_{4-3}) between $B(OH)_4^-$ and $B(OH)_3$

The α_{4-3} is one of the main parameters of the $\delta^{11}B$ -proxy. The first α_{4-3} of 0.981 was determined by Kakihana et al. (1977). Thereafter, a relatively low α_{4-3} of 0.968 and a relatively high α_{4-3} of 0.984 were determined by Palmer et al. (1987) and Hemming et al. (1995), respectively. A new isotopic fractionation factor of 0.976 was subsequently given by Lécuyer et al. (2002) and a lower

α_{4-3} of 0.974 was given by Liu and Toessel (2005) and Klochko et al. (2006).

The boron isotopic fractionation factor between carbonate and $B(OH)_3$ of seawater ($\alpha_{\text{carb-3}}$) can be calculated from the following formula (Pagani et al., 2005):

$$R_4 = R_{\text{sw}} \times (1 + \alpha_{4-3} 10^{\text{pKB-pH}}) / (1 + 10^{\text{pKB-pH}}) \quad (1)$$

α_{4-3} can be given as follows:

$$\alpha_{4-3} = \{(R_4/R_{\text{sw}}) \times (1 + 10^{\text{pKB-pH}}) - 1\} / 10^{\text{pKB-pH}} \quad (2)$$

where R_4 and R_{sw} are the $^{11}B/^{10}B$ ratios of $B(OH)_4^-$ and seawater, respectively. KB is the equilibrium constant for the dissociation of boric acid.

In Eq. (2), KB was given by Dickson (1990), pH values of seawater and R_{sw} can be measured directly whereas R_4 cannot. In our study, R_{coral} was used in calculation of α_{4-3} instead of R_4 . Therefore, the calculated α_{4-3} based on Eq. (2) is actually isotopic fractionation factor between coral and $B(OH)_3$ of seawater ($\alpha_{\text{coral-3}}$). The calculated $\alpha_{\text{coral-3}}$ changed from 0.973 to 0.981 with an average value of 0.979, which was close to the value of 0.981 given by Kakihana et al. (1977). Using this new α_{4-3} of 0.979, $\delta^{11}B_{\text{sw}}$ of 41.1‰ and pK_a of 8.597 (Dickson, 1990), the calcification seawater pH values of corals were calculated by the following equation:

$$\text{pH} = \text{pK}_a - \lg\{(\delta^{11}B_{\text{sw}} - \delta^{11}B_4) / [\alpha_{4-3} - 1 \delta^{11}B_4 - \delta^{11}B_{\text{sw}} + 10^3(\alpha_{4-3} - 1)]\} \quad (3)$$

The calculated calcification pH values of corals in the South China Sea varied between 7.92 and 8.43 with an average value of 8.20. Using published α_{4-3} of 0.968 (Palmer et al., 1987), 0.981 (Kakihana et al., 1977) and 0.984 (Hemming et al., 1995), and the $\delta^{11}B$ values of marine bio-carbonates, the recalculated calcification pH values of seawater were 8.85 ± 0.18 ($n = 187$), 8.17 ± 0.40 ($n = 167$), 7.76 ± 0.54 ($n = 115$), respectively. This implied that the recalculated pH by 0.968 and 0.984 were too high or too low, and only the 8.17 by 0.981 was close to the modern seawater. Therefore, the α_{4-3} values of 0.968 and 0.984 were not suited to calculate seawater pH. The calculated pH of 8.20 in our study was most close to the pH of modern seawater, indicating that $\alpha_{4-3} = 0.979$ might be suitable to calculate ancient seawater pH values.

3.4. Incorporation of boron species into corals

If only $B(OH)_4^-$ or $B(OH)_3$ is incorporated into carbonates, the boron isotopic fractionation factors between carbonates and seawater $B(OH)_3$ ($\alpha_{\text{carb-3}}$), and between $B(OH)_4^-$ and $B(OH)_3$ ($\alpha_{\text{carb-3}}$) are constant. If both $B(OH)_4^-$ and $B(OH)_3$ are incorporated into carbonates with constant proportion, both $\alpha_{\text{carb-sw}}$ and $\alpha_{\text{carb-3}}$ are also constant. However, if both $B(OH)_4^-$ and $B(OH)_3$ are incorporated into carbonates with variable proportion, both $\alpha_{\text{carb-sw}}$ and $\alpha_{\text{carb-3}}$ are inconstant. Our results showed that $\alpha_{\text{coral-3}}$ decreased while $\alpha_{\text{coral-sw}}$ increased with the increasing seawater pH (Fig. 2f). Both $\alpha_{\text{carb-3}}$ and $\alpha_{\text{carb-sw}}$ values were recalculated according to Eq. (2), using the data from the corals (Li et al., 2006), inorganic carbonate precipitation (Sanyal et al., 2000; Xiao et al., 2006), adsorption experiment (Palmer et al., 1987) and culture experiments with foraminifers (Sanyal et al., 1996). The results showed that $\alpha_{\text{carb-3}}$ values varied from 0.937 to 0.965, from 0.960 to 0.971, from 0.970 to 0.976 and from 0.959 to 0.975 from the four experiments above-mentioned, respectively. All of the $\alpha_{\text{carb-3}}$ values decreased whereas $\alpha_{\text{carb-sw}}$ increased with the increasing pH (Fig. 2), which indicated that both $B(OH)_4^-$ and $B(OH)_3$ might be incorporated into carbonates with variable proportion.

The calculated $\delta^{11}B_{\text{coral}}$, $\delta^{11}B_3$ and $\delta^{11}B_4$ in seawater using different α_{4-3} versus pH values of seawater were shown in Fig. 3. The $\delta^{11}B_{\text{coral}}$ were higher than the calculated $\delta^{11}B_4$ using $\alpha_{4-3} = 0.977$

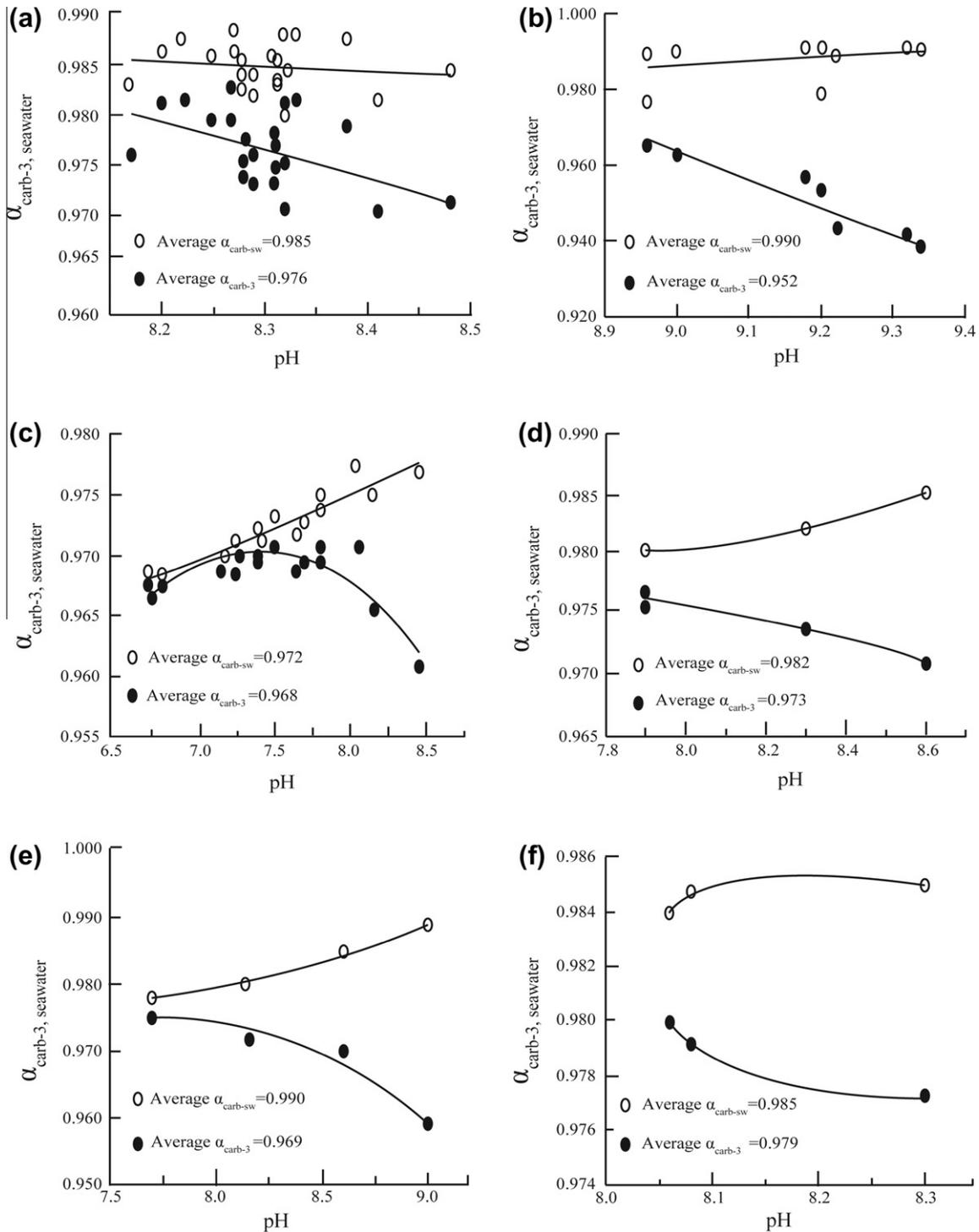


Fig. 2. Plots of calculated $\alpha_{\text{carb-3}}$ and $\alpha_{\text{carb-sw}}$ versus pH value of solution according to the formula reported by Pagani et al. (2005). (a) Coral experiment (Li et al., 2006); (b) inorganic carbonate precipitation (Xiao et al., 2006); (c) adsorption experiment (Palmer et al., 1987); (d) inorganic calcite precipitation (Sanyal et al., 2000); (e) culture experiments with foraminifers (Sanyal et al., 1996); (f) growing corals in this study.

but lower than the $\delta^{11}\text{B}_4$ using $\alpha_{4-3} = 0.980$. Similarly, if only $\text{B}(\text{OH})_4^-$ or $\text{B}(\text{OH})_3$ was incorporated into corals, the $\delta^{11}\text{B}_{\text{coral}}$ must fall on the theoretical $\delta^{11}\text{B}_4$ or $\delta^{11}\text{B}_3$ curves. If both $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ were incorporated into corals, the $\delta^{11}\text{B}_{\text{coral}}$ must fall between the $\delta^{11}\text{B}_4$ and $\delta^{11}\text{B}_3$ curves. The $\delta^{11}\text{B}_{\text{coral}}$ in our study fell between the theoretical $\delta^{11}\text{B}_4$ and $\delta^{11}\text{B}_3$ curves (Fig. 3), which indicated that both $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ may be incorporated into corals. In addition, due to the “vital effects”, the increased microcalcification pH of corals would also increase $\delta^{11}\text{B}$ of calcification,

resulting in a high $\delta^{11}\text{B}_{\text{coral}}$ above the theoretical $\delta^{11}\text{B}_4$ curve. However, it is difficult to distinguish “vital effects” from the effect by the incorporation of $\text{B}(\text{OH})_3$ into corals. There were no “vital effects” in inorganic carbonate precipitation experiments, but the $\delta^{11}\text{B}$ of inorganic carbonate was also higher than theoretical $\delta^{11}\text{B}_4$ curve. In addition, all the $\delta^{11}\text{B}_{\text{carb}}$ in the real samples were higher than best-fit theoretical $\delta^{11}\text{B}_4$ curve, and the $\delta^{11}\text{B}_{\text{carb}}$ at low pH value was higher than that at high pH value (Fig. 2). These indicated that the $\text{B}(\text{OH})_3$ was also incorporated into corals. If

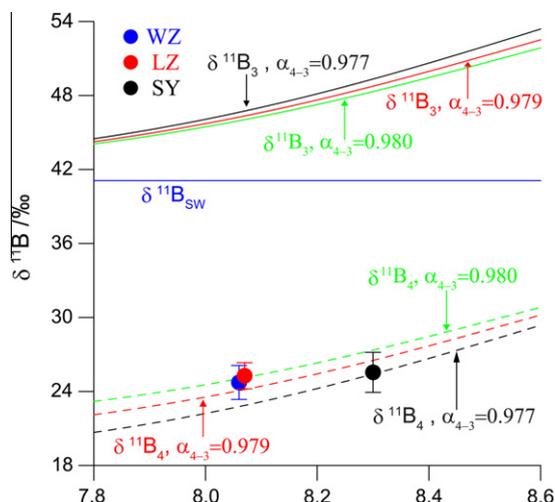


Fig. 3. $\delta^{11}\text{B}$ of corals ($\delta^{11}\text{B}_{\text{coral}}$), $\delta^{11}\text{B}$ of $\text{B}(\text{OH})_3$ ($\delta^{11}\text{B}_3$) and $\text{B}(\text{OH})_4^-$ ($\delta^{11}\text{B}_4$) in seawater calculated using different α_{4-3} versus pH values of seawater. The $\delta^{11}\text{B}_{\text{coral}}$ are higher than the $\delta^{11}\text{B}_4$ calculated using $\alpha_{4-3} = 0.977$ but lower than the $\delta^{11}\text{B}_4$ calculated using $\alpha_{4-3} = 0.980$.

$\text{B}(\text{OH})_3$ was incorporated into corals preferentially, the $\delta^{11}\text{B}_{\text{coral}}$ would be higher than the $\delta^{11}\text{B}_{\text{sw}}$. If $\text{B}(\text{OH})_4^-$ was incorporated into corals preferentially, the $\delta^{11}\text{B}_{\text{coral}}$ would be lower than the $\delta^{11}\text{B}_{\text{sw}}$. Both $\delta^{11}\text{B}_{\text{coral}}$ in our study and reported $\delta^{11}\text{B}_{\text{carb}}$ in the previous studies were lower than $\delta^{11}\text{B}_{\text{sw}}$, which indicated that $\text{B}(\text{OH})_4^-$ was incorporated into corals or marine bio-carbonates preferentially. Therefore, both $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ incorporated into carbonates (corals) with variable proportion and $\text{B}(\text{OH})_4^-$ was incorporated it preferentially. The fraction of $\text{B}(\text{OH})_3$ incorporated into corals can be calculated according to the following equation:

$$\text{B}(\text{OH})_3(\%) = (\delta^{11}\text{B}_{\text{coral}} - \delta^{11}\text{B}_4) / (\delta^{11}\text{B}_3 - \delta^{11}\text{B}_4) \quad (4)$$

where $\delta^{11}\text{B}_3 = [\delta^{11}\text{B}_{\text{sw}} + 1000 \times (1 - \alpha_{4-3}) \times f_4] / (\alpha_{4-3} \times f_4 + f_3)$, $\delta^{11}\text{B}_4 = \delta^{11}\text{B}_3 \times \alpha_{4-3} - 1000 \times (1 - \alpha_{4-3})$; f_4 and f_3 are the fraction of $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ in seawater. The calculated $\text{B}(\text{OH})_3\%$ varied from 0.1% to 5.5% with an average value of 2.2%.

3.5. Influence of $\text{B}(\text{OH})_3$ incorporation into corals on the $\delta^{11}\text{B}$ -pH proxy

One of the hypotheses of $\delta^{11}\text{B}$ -pH proxy is that $\delta^{11}\text{B}_{\text{carb}}$ is equal to $\delta^{11}\text{B}_4$ (Hemming and Hanson, 1992). Our study showed that $\text{B}(\text{OH})_3$ may be also incorporated into carbonates. If it holds true, the hypotheses of $\delta^{11}\text{B}_{\text{carb}} = \delta^{11}\text{B}_4$ might not be tenable and the calculated seawater pH would be inaccurate, which would complicate the $\delta^{11}\text{B}$ -pH proxy. The $\delta^{11}\text{B}_{\text{carb}} \neq \delta^{11}\text{B}_4$ and variable $\alpha_{\text{carb}-3}$ is attributed to the incorporation of $\text{B}(\text{OH})_3$ with variable proportion. The $\alpha_{\text{carb}-3}$ values should become constant only when the incorporated amount of $\text{B}(\text{OH})_3$ is zero. In this case, $\alpha_{\text{carb}-3} = \alpha_{4-3}$. However, this assumption does not exist because of the presence of $\text{B}(\text{OH})_3$ in solution. At present, the reasons and ways of $\text{B}(\text{OH})_3$ incorporated into marine bi-carbonates are still unknown. Xiao et al. (2008) indicated that the empirical equation is much better than the theoretical model for the $\delta^{11}\text{B}$ -pH proxy. When this empirical model is used, the error of measured pH values is lowest and is independent of solution pH. Unfortunately, the “best-fit empirical equation” is still not available at present because of the uncertainties of the experiments, such as the narrow pH range and less pH test points in the previous studies. Therefore, it is necessary and important in future to establish a “best-fit empirical equation” between $\delta^{11}\text{B}_{\text{carb}}$ and pH of seawater based on the precipitation experiments of inorganic carbonates or culture experiments of corals or foraminifera.

4. Conclusions

Relative to coexisting seawater, B and Sr enriched whereas Mg depleted in growing corals in the South China Sea. Due to high $\delta^{11}\text{B}_{\text{coral}}$ resulting from $\text{Mg}(\text{OH})_2$ in corals, it is necessary to examine the existence of $\text{Mg}(\text{OH})_2$ or not by the relationship between $\delta^{11}\text{B}$ and Mg/Ca and to choose the same coral species when $\delta^{11}\text{B}_{\text{coral}}$ is used in the $\delta^{11}\text{B}$ -pH proxy. The α_{4-3} of 0.979 obtained in our study might be suitable to reconstruct ancient seawater pH. Our data indicated that both $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ might be incorporated into corals though $\text{B}(\text{OH})_4^-$ was incorporated preferentially, which complicates the $\delta^{11}\text{B}$ -pH proxy. In the future, it is necessary and important to establish a best-fit empirically equation between $\delta^{11}\text{B}_{\text{carb}}$ and seawater pH based on the precipitation experiments of inorganic carbonates or culture experiments of corals or foraminifera.

Acknowledgements

This work was financially supported by National Science Foundation of China through Grants 40976074, 41003012 and the West Light Foundation of Chinese Academy of Sciences.

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