

Isotopic fractionation of boron in growing corals and its palaeoenvironmental implication

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Isotopic compositions of boron ($d^{11}\text{B}_c$ value) and elemental concentrations of B, Ca, Mg, Fe and Al in growing corals from Sanya Bay, China and Kavaratti Lagoon, India along with $d^{11}\text{B}_{sw}$ values and pH values of the coexisting sea water have been measured in this study using TIMS. The $d^{11}\text{B}_c$ values of growing corals behave inconsistently and are not related to the concentrations of Fe and Al in corals. The higher $d^{11}\text{B}_c$ values of corals imply additional amount of trigonal species of boron to be incorporated into corals. Based on the measured $d^{11}\text{B}$ values of growing corals and coexisting sea water as well as the pH of co-existing sea water, a new isotopic fractionation factor a_{43} between two boron species, $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$, has been measured to be 0.980, consistent with the well accepted a_{43} of 0.981 established by earlier workers.

The significance of a_{43} value established by recalculating the sea water pH considering the published $d^{11}\text{B}$ values of marine carbonates and using the reported a_{43} values of 0.968, 0.981, 0.984 and one a_{43} of 0.980 observed in this study, gave the average pH values of sea water to be 8.85, 8.17, 7.76 and 8.22 respectively. This indicates the closeness of a_{43} value of 0.980 with that of the well-accepted reported a_{43} of 0.981 as the recalculated pH values of sea water obtained using these are nearly the same. The a_{43} value of 0.980 observed in this study can therefore be considered an acceptable value for reconstructing the past sea water pH values.

Keywords: Boron, coral, isotopic compositions, isotopic fractionation, sea water.

THE use of boron isotopes in marine biogenic carbonate for the reconstruction of palaeo-pH of sea water relies on a large isotopic fractionation between the two aqueous species, $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ of boron¹⁻⁴. Their relative abundance in sea water is strongly pH-dependent. Isotopic fractionation of boron between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ occurs due to different reduced partition function ratios for the two molecular species, resulting in ¹⁰B enrichment in the $\text{B}(\text{OH})_4^-$. Boron uptake in marine biogenic carbonate takes place by $\text{B}(\text{OH})_4^-$ incorporation, with little or no boron

isotopic fractionation⁵, so the $d^{11}\text{B}$ value in marine biogenic carbonate potentially records the $d^{11}\text{B}$ value of $\text{B}(\text{OH})_4^-$ of sea water, i.e. the pH of sea water. The first isotopic fractionation factor a_{43} of 0.981 between $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ was determined⁶ based on both theoretical partition function calculations and boron adsorption experiments on ion exchange resin. Thereafter, a lower a_{43} of 0.968 was determined⁷ based on adsorption experiments of boron onto marine clays. Moreover, Hemming *et al.*⁸ calculated a fractionation factor of 0.984 and a new isotopic fractionation factor of 0.976 was subsequently given by Lécuyer *et al.*⁹ by deriving an isotopic fractionation curve ($a_{\text{calcite sea water}} = 0.023X_{[\text{B}(\text{OH})_4^-]} + 0.976$) between brachiopod calcite and sea water. The $a_{\text{calcite sea water}} = 0.976$ when $X_{[\text{B}(\text{OH})_4^-]}$ equates to 0 and $a_{\text{calcite sea water}}$ of 0.976 corresponds to isotopic fractionation between $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$. The isotopic fractionation factor a_{43} is an extremely important parameter in the calculation of palaeo-pH values of sea water for studying the oceanic palaeoenvironments and are based on the isotopic composition of boron ($d^{11}\text{B}_c$) in marine biogenic carbonates. Using these a_{43} values, Sanyal *et al.*¹⁰ estimated that the deep Atlantic and Pacific Oceans had a pH 0.3 ± 0.1 units higher during the last Glaciation. Pearson and Palmer¹¹ found that the pH was significantly lower during early Palaeogene than in the Neogene period. Spivack *et al.*¹² reported that the surface ocean pH, about 21 Myr ago was only 7.4 ± 0.2 , which then increased to 8.2 ± 0.2 around 7.5 Myr ago, by using the lower isotopic fractionation factor a_{43} of 0.968.

Here, we present results of isotopic fractionation observed between $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ using the measured $d^{11}\text{B}$ of sea water and growing corals, as well as the pH of coexisting sea water. The significance of the new isotopic fractionation factor a_{43} has been evaluated for its suitability of use in reconstructing the paleo-pH of the oceans.

Materials and methods

Description of samples

All corals used in this study are growing corals. Of these, ten corals (SYC-1–10) pertained to seven different species:

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Table 1. Locations and species of corals studied

Sample	Location	Sampling date	Species of coral
SYSW (sea water) [†]	Sanya Bay, Hainan Prov., China	7 October 2001	–
SYC-1 (coral)			<i>Acropora pulchra</i>
SYC-2 (coral)			<i>Acropora prostrata</i>
SYC-3 (coral)			<i>Acropora corymbosa</i>
SYC-4 (coral)			<i>Acropora prostrata</i>
SYC-5 (coral)			<i>Stylophora pistillata</i>
SYC-6 (coral)			<i>Pocillopora brevicornis lamarck</i>
SYC-7 (coral)			<i>Pocillopora danae verill</i>
SYC-8 (coral)			<i>Pocillopora danae verill</i>
SYC-9 (coral)			<i>Montipora ramosa bernard</i>
SYC-10 (coral)			<i>Acropora pulchra</i>
SSC-1 (coral)	Southern China Sea		<i>Poritidae</i>
SSC-2 (coral)			<i>Poritidae</i>
SKLC (coral)	Southern Kavaratti lagoon	31 January 2001	<i>Porites leutea</i>
CKLC (coral)	Central Kavaratti lagoon		<i>P. leutea</i>
NKLC (coral)	Northern Kavaratti lagoon		<i>P. leutea</i>

[†]pH value and temperature of sea water are 8.12 and 28.6°C respectively.

2 *Acropora pulchra*, 2 *Acropora prostrata*, 1 *Acropora corymbosa*, 1 *Stylophora pistillata*, 1 *Pocillopora brevicornis lamarck*, 2 *Pocillopora danae verill* and 1 *Montipora ramosa bernard*, and the coexisting sea water (SYSW) from Sanya Bay, Hainan, China and were collected during 7 October 2001. The sampling areas are only a few kilometres from each sampling site, so the coexisting sea water for every coral is nearly the same. The pH and temperature of sea water were measured immediately after sample collection. Besides, two corals (SSC-1, 2) from Southern China Sea, with no coexisting sea water were provided by South China Institute of Oceanology, Chinese Academy of Sciences and three corals (SKLC, CKLC, NKLC) from Kavaratti lagoon (72°38'E, 10°33'N) in Lakshadweep Islands of the Arabian Sea, collected on 31 January, 2001 were provided by NIO, Goa. All these corals have not been studied before. The sample data including sampling date, locations, species of corals and the pH of sea water are given in Table 1.

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 it was dipped in 30% hydrogen peroxide solution and kept overnight to remove organic matter from the surface. After discarding the hydrogen peroxide solution, coral samples were dried under an infrared lamp at 60°C. The dried coral samples were powdered into 100–200 mesh and washed few times with a warm 30% hydrogen peroxide and then low-boron water with 0.4 ng B/ml of boron concentration to remove organic matter. About 500 mg of each cleaned coral powder was dissolved in just enough 1.0 M high-purity HCl for complete dissolution. The pH of the resulting solution was adjusted to 6 using

0.5 M NaOH and sample solutions were centrifuged for 1 h. Almost all sample solutions were clear and the supernatant was ready for chemical separation of boron.

Boron was isolated from solution in two chromatographic steps using Amberlite IRA 743 boron-specific resin¹³ and a mixed resin of cation-exchanger (H⁺ form) and anion-exchanger (ion-exchanger II, HCO₃⁻ form)¹⁴. Sample solutions were first loaded onto a column with 0.4 cm diameter. The column was filled with 0.25 ml of Amberlite 743 boron-specific resin (~80 mesh) pre-conditioned by 10 ml of 2 M HCl, 20 ml of H₂O and 10 ml of 3 M NH₄OH. The column was then rinsed sequentially by 10 ml of high purity water, 10 ml of 2M NH₄OH and 10 ml of high-purity water. The boron absorbed by the resin was eluted by 5 ml of 0.1 M HCl at 75°C. After cooling the elution of 0.1 M HCl, it was loaded into the second column filled with a mixed resin of 2 ml cation-exchange resin (H⁺ form) and 2 ml anion-exchange resin (ion-exchanger II, HCO₃⁻ form). The boron here was eluted by 10 ml of low-boron water. After appropriate mannitol and Cs₂CO₃ additions, the eluate was evaporated in a clean oven at 60°C to produce a boron solution with boron concentration of around 1 µg B/µl.

The boron isotopic compositions of samples were measured based on the measurement of Cs₂BO₂⁺ with a graphite loading using a single magnetic sector thermal ionization mass spectrometer¹⁵, VG 354. The sample solution was first loaded onto a flat degassed Ta filament coated by 2.5 µl graphite slurry. Data were collected by switching magnetically between the masses 308 (¹³³Cs₂¹⁰B¹⁶O₂⁺) and 309 (¹³³Cs₂¹¹B¹⁶O₂⁺) and the intensity ratio of the ion beams at masses 308 and 309 ($R_{309/308}$) was calculated. The ¹¹B/¹⁰B ratio was calculated as $R_{309/308} - 0.00078$. The isotopic composition of boron was expressed as $d^{11}\text{B}$ value relative to NIST SRM 951 H₃BO₃ according to the following formula:

$$d^{11}\text{B} (\text{‰}) = \left[\left(\frac{{}^{11}\text{B}}{{}^{10}\text{B}} \right)_{\text{sample}} / \left(\frac{{}^{11}\text{B}}{{}^{10}\text{B}} \right)_{\text{NIST 951}} - 1 \right] \times 1000, \quad (1)$$

where the standard material is NIST SRM 951. The measured ${}^{11}\text{B}/{}^{10}\text{B}$ value of NIST SRM 951 was 4.05048 (SD) \pm 0.00034 ($2S_m$, $n = 6$) with an analytical uncertainty of 0.1‰. The analytical uncertainties of boron isotopes for most of samples are lower than 0.5‰.

Boron concentration was determined by the azomethine-H spectrophotometric method¹⁶ with a reproducibility of 2%. The chemical compositions were measured using conventional methods.

Results and discussion

Boron isotopic compositions and chemical compositions of growing corals

The $d^{11}\text{B}$ values and chemical constituents measured in growing corals and sea water are presented in Table 2. The $d^{11}\text{B}_c$ values of corals are shown in Figure 1. For all samples, repetitive analyses have been done. The $d^{11}\text{B}_c$ values show that the corals can be divided into two groups. In group I, nine corals have lower $d^{11}\text{B}_c$ values ranging from 22.5 to 25.5‰, with an average of $23.3 \pm 1.1\text{‰}$ and are consistent with those of (a) $22.1 \pm 3\text{‰}$ reported by Hemming and Hanson⁵; (b) 23.3 to 25.5‰ reported by Gailardet and Allègre¹⁷; (c) 22.7 to 24.8‰ reported by Liu *et al.*¹⁸ and (d) 25.6 and 25.7‰ reported by Lécuyer *et al.*⁹. In group II, three corals have higher $d^{11}\text{B}_c$ values ranging from 28.3 to 29.0‰, with an average of 28.6‰ and are consistent with those reported by Vengosh *et al.*¹⁹, i.e. from 26.7 to 31.9‰. The boron isotopic composition of sea water ($d^{11}\text{B}_{\text{sw}}$) in Sanya Bay has been found to be 40.5‰.

The measured boron concentrations of growing corals range from 50.2 to 117.5 $\mu\text{g B/g}$ with an average of 70.5 $\mu\text{g B/g}$. The reported boron concentrations of corals are from 49 to 58 ppm¹⁷, 58.7 to 79.7 ppm¹⁸ and from 43 to 68 ppm¹⁹. The average value of 70.5 $\mu\text{g B/g}$ obtained in this study is comparable with the reported values.

The measured concentrations of Ca, Mg, Fe and Al in growing corals are also listed in Table 2. Ca is a major constituent of coral and exists as CaCO_3 . The abundance of CaCO_3 in coral signifies its purity. The measured abundances of CaCO_3 in corals range from 48 to 103.9% with an average value of $87.0 \pm 12.0\%$, suggesting that the whole coral is not composed of pure CaCO_3 . The measured CaCO_3 abundance of 103.9% was, perhaps, caused by analytical error. The concentration of Mg, Fe and Al in corals ranges from 0.37 to 3.90 mg/g with an average of 1.37 ± 0.80 mg Mg/g, 35.2 to 165.2 $\mu\text{g/g}$ with an average value of 73.3 ± 38.9 $\mu\text{g Fe/g}$, and 9.7 to 36.5 $\mu\text{g/g}$ with an average value of 18.7 ± 7.2 $\mu\text{g Al/g}$ respectively. No relationship between $d^{11}\text{B}_c$ values and element concentrations is observed.

The $d^{11}\text{B}$ values in growing corals of seven different species from Sanya Bay show a wide variation from 22.5 to 29.0‰ and apparently indicate a relationship between $d^{11}\text{B}_c$ values and coral species. The species *Acropora corymbosa* (SYC-3), *Stylophora pistillata* (SYC-5) and *Pocillopora brevicornis lamarck* (SYC-6) show higher $d^{11}\text{B}$ values of 28.3, 29.0 and 28.4‰ respectively, compared to others giving an average $d^{11}\text{B}$ of 23.3‰. Corals of the same species growing at different places in Sanya Bay show nearly the same $d^{11}\text{B}$ values (e.g. SYC-1 and 10 show $d^{11}\text{B}$ of 22.5 and 23.5‰ respectively; SYC-2 and 4 give $d^{11}\text{B}$ of 22.5 and 22.9‰ respectively, while SYC-7 and 8 give $d^{11}\text{B}$ of 23.3 and 22.7‰ respectively). The $d^{11}\text{B}$ values of two *Poritidae* corals are the same (25.2 and 25.4‰). These results therefore discard the fact that the difference in $d^{11}\text{B}$ values in various species of coral arises from isotopic determination error and indicate that the difference in $d^{11}\text{B}$ values in various species of coral actually present.

Calculation of isotopic fractionation factor (a_{43}) between $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$

Various isotopic fractionation factors (a_{43}) of 0.981, 0.968, 0.984 and 0.976 have been reported by different workers using various experimental methods as stated earlier⁶⁻⁹. The new isotopic fractionation factor a_{43} of 0.980 observed in this study has been confirmed based on the $d^{11}\text{B}_c$ values of growing corals, $d^{11}\text{B}_{\text{sw}}$ value of coexisting sea water and the pH of sea water in Sanya Bay. Figure 2 shows a plot of $d^{11}\text{B}_4$ (i.e. $d^{11}\text{B}_c$ vs isotopic fractionation factor a_{43}), and a_{43} between two boron species ranging from 0.95 to 1. $d^{11}\text{B}_4$ is calculated as follows:

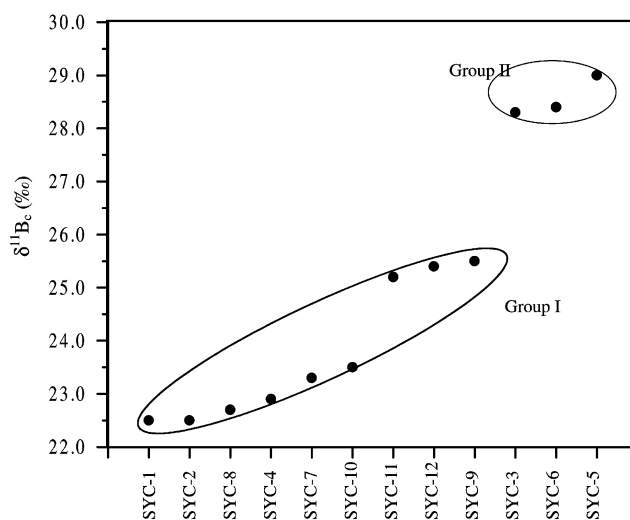


Figure 1. Isotopic compositions of boron in growing corals from Sanya Bay and Southern China Sea. (SYC-1, 10, *Acropora pulchra*; SYC-2, 4, *Acropora prostrata*; SYC-7, 8, *Pocillopora danae verril*; SYC-11, 12, *Poritidae*; SYC-9, *Montipora ramosa bernard*; SYC-3, *Acropora corymbosa*; SYC-6, *Pocillopora brevicornis lamarck*; SYC-5, *Stylophora pistillata*).

Table 2. Chemical composition and isotopic composition of boron in coral and coexisting sea water

No.	Ca (mg/g)	CaCO ₃ (%)	Mg (mg/g)	Fe (μg/g)	Al (μg/g)	B (μg/g)	<i>d</i> ¹¹ B ± 2 <i>s</i> (%)	<i>a</i> _{cs} between coral and sea water (2 <i>s</i>)	Calculated <i>a</i> ₄₃ between B ₄ and B ₃	Calculated pH
1						4.61	40.5 ± 0.6 (4) [†]	–		
2	354.0	88.5	0.82	41.6	10.8	72.5	22.5 ± 0.9 (4)	0.9827 ± 0.0009	0.9794	
3	349.9	87.5	0.37	43.7	17.0	59.9	22.5 ± 0.4 (4)	0.9827 ± 0.0005	0.9794	
4	332.2	83.0	0.596	35.2	13.0	66.6	28.3 ± 0.3 (5)*	0.9882 ± 0.0003*	0.9860*	8.67
5	415.5	103.9	1.38	46.3	20.7	66.7	22.9 (2)	0.9831	0.9799	
6	361.6	90.4	1.45	84.7	19.9	61.6	29.0 ± 0.6 (5)*	0.9889 ± 0.0006*	0.9868*	8.73
7	359.3	89.8	1.28	41.6	14.0	70.4	28.4 ± 0.1 (4)*	0.9884 ± 0.0001*	0.9861*	8.68
8	353.1	88.3	1.44	41.3	19.4	72.5	23.3 ± 0.7 (8)	0.9835 ± 0.0006	0.9803	
9	191.9	48.0	0.918	81.4	29.0	67.4	22.7 ± 1.5 (3)	0.9829 ± 0.0015	0.9796	
10	327.6	81.9	1.06	141.7	24.0	76.1	25.5 ± 0.2 (6)	0.9856 ± 0.0004	0.9828	
11	338.4	84.6	1.75	108.8	36.5	67.1	23.5 ± 0.4 (5)	0.9837 ± 0.0004	0.9806	
Average 2–11	–	–	–	–	–	68.1 ± 5.0 (SD)	23.3 ± 1.1 (SD)	0.983 ± 0.001	0.980 ± 0.001 (SD)	
12	361.6	90.4	1.35	165.2	15.8	61.7	25.2 ± 0.4 (4)	–	–	8.39
13	375.7	93.9	1.08	71.3	21.7	61.6	25.4 ± 0.4 (5)	–	–	8.40
14	369.8	92.4	3.90	79.5	9.68	50.2	24.4 ± 0.7 (5)	–	–	8.28
15	369.2	92.3	1.68	60.9	12.2	86.2	23.7 ± 0.4 (5)	–	–	8.18
16	362.3	90.5	1.50	56.5	17.2	117.5	24.0 ± 0.2 (4)	–	–	8.22
Average	348.1	87.0 ± 12	1.37 ± 0.8	73.3 ± 39	18.7 ± 7.2	70.5	–	–	–	–

*Data were not included in calculation of average *d*¹¹B and *a*.

†Data in parenthesis are the number of repetitive analyses.

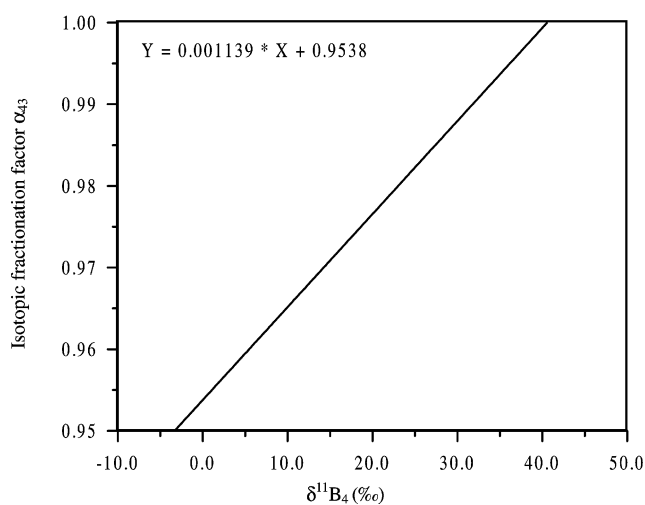


Figure 2. Calculated *d*¹¹B₄ vs isotopic fractionation factor *a*₄₃ ranging from 0.95 to 1 for Sanya Bay sea water with pH of 8.12.

$$d^{11}B_4 = (d^{11}B_{sw} + f_3 * 1000 - f_3 * 1000 / a_{43}) / (f_4 + f_3 / a_{43}). \quad (2)$$

Here *f*₃ and *f*₄ are molar fractions of B(OH)₃ and B(OH)₄[−] respectively, as decided by pH value of sea water shown in Figure 3 *a*. The *d*¹¹B_{sw}, *f*₃ and *f*₄ are 40.5‰, 0.8368 and 0.1632 respectively, for Sanya Bay sea water with pH 8.12. The calculated *d*¹¹B₄ values corresponding to *a*₄₃ of 0.950 to 1, range from −3.4 to 40.5‰. An isotopic fractionation curve can be derived based on the relationship between calculated *d*¹¹B₄ and *a*₄₃ as follows from Figure 2:

$$a_{43} = 0.001139 \times d^{11}B_4 + 0.9538. \quad (3)$$

It is assumed that only the charged borate species is incorporated into carbonate minerals in corals and this incorporation occurs with a small and nearly constant isotopic fractionation. Therefore, the *d*¹¹B_c values in corals equal the *d*¹¹B₄ value of sea water. The *a*₄₃ values between two species of boron for individual growing corals in Sanya Bay were calculated using eq. (3) and are shown in Table 2. The *a*₄₃ ranges from 0.979 to 0.983 with an average of 0.980 ± 0.001 (SD) for group I and from 0.986 to 0.987 with an average of 0.986 for group II. The average *a*₄₃ of 0.980 ± 0.001 observed is closer to the theoretical value of 0.981 reported by Kakihana *et al.*⁶, but is lower than the measured average *a*_{cs} of 0.983 between coral and sea water. This is perhaps an actual isotopic fractionation of boron occurring between B(OH)₄[−] and B(OH)₃ in sea water. The pH values of sea water from which the corals SSC-1, SSC-2, SKLC, CKLC and NKLC were collected are calculated using *d*¹¹B_{sw} of 40.5‰ and *a*₄₃ of 0.980 as shown below¹⁶:

$$pH = 8.83 - \log\left\{\frac{(d^{11}B_{sw} - d^{11}B_4)}{[a_{43}^{-1}d^{11}B_4 - d^{11}B_{sw} + 1000(a_{43}^{-1} - 1)]}\right\}. \quad (4)$$

The pH values calculated based on the measured *d*¹¹B_c are shown in Table 2. The pH value of sea water in Southern China Sea is 8.40, which is slightly higher than that of sea water in Sanya Bay, but falls into a typical pH range of sea water⁵, 7.5–8.4. The pH values of sea water in Kavaratti lagoon are 8.28, 8.18 and 8.22 with an average

value of 8.23, which is closer to the present sea water pH value¹⁷ of 8.2. The $d^{11}B$ values of $B(OH)_3$ and $B(OH)_4^-$, the two dominant aqueous species of boron in Sanya sea water as a function of pH, calculated from the fractionation factor a_{43} of 0.980 obtained in this study (solid line) and from the fractionation factor a_{43} of 0.981 (broken line)⁶, as well as the measured $d^{11}B_{sw}$ value of sea water and $d^{11}B_c$ of growing corals are shown in Figure 3b. The $d^{11}B_3$ and $d^{11}B_4$ at pH 8.12 are 43.8 and 23.3‰ for a_{43} of 0.980. The $d^{11}B_3$ and $d^{11}B_4$ were calculated as follows:

$$d^{11}B_3 = (40.5 + 20 \times f_4) / (0.980 \times f_4 + f_3), \quad (5)$$

and

$$d^{11}B_4 = d^{11}B_3 \times 0.980 - 20. \quad (6)$$

Here $f_3 = 0.8368$ and $f_4 = 0.1632$ based on Figure 3a.

The results of Figure 3b indicate that the $d^{11}B_c$ values of SYC-3, 5 and 6 are much higher than $d^{11}B_4$ of 23.3‰,

i.e. average value for SYC-1, 2, 4, 7–10. This could be due to the following: (1) The sea water surrounding the corals have a distinctly higher $d^{11}B_{sw}$. In case the pH and a_{43} are constant and only the charged borate species is incorporated into the corals, the $d^{11}B_{sw}$ of sea water surrounding SYC-3, 5 and 6 can be calculated to be 46.2, 46.9 and 46.3‰ respectively, which is much higher than the measured $d^{11}B_{sw}$ of 40.5‰ and exceeds the $d^{11}B_{sw}$ variation range²⁰ of 38.4 to 44.4‰. Such high $d^{11}B_{sw}$ values are unlikely to occur in Sanya Bay. (2) The microenvironment of the coral cell has a distinctive pH. Microsensor studies of the living symbiotic species *Globigerinoides trilobus* and related taxa show that pH increases over short distances as the foraminifer shell is approached^{21,22}. This condition perhaps is present for the growing corals. The pH value of sea water surrounding SYC-3, 5 and 6 is calculated to be 8.67, 8.83 and 8.68 respectively only if charged borate species is incorporated into the corals and a_{43} is 0.980 and the $d^{11}B_{sw}$ is 40.5‰. Comparing this with measured pH value of 8.12, the occurrence of large fluctuations in pH in the crystallizing environment is also unlikely. (3) A smaller isotopic fractionation between $d^{11}B_3$ and $d^{11}B_4$ occurs. The calculated a_{43} values are 0.9860, 0.987 and 0.986 with an average of 0.986 (Table 2). The highest isotopic fractionation, a_{43} of 0.984, was reported by Hemming *et al.*⁸. The a_{43} of 0.986 may not be accepted. (4) $B(OH)_3$ and $B(OH)_4^-$ are incorporated into corals simultaneously. Most of the studies on boron isotopes suggest that only $B(OH)_4^-$ anion is incorporated into the marine carbonate^{5,19}. Here, a mechanism for incorporating a substantial amount of the heavier $B(OH)_3$ species must be invoked. The adsorption of boron species onto the mineral surfaces indicated that for pH values below 9.24, $B(OH)_3$ may be preferentially adsorbed onto the mineral surface. When the solution pH exceeds 9.24, $B(OH)_4^-$ becomes dominant and may be preferentially adsorbed²³. In the case of sea water pH of 8.12 in Sanya Bay, it is possible that a substantial amount of $B(OH)_3$ incorporates into the coral cell. Based on the measured $d^{11}B_c$, the calculated $d^{11}B_3$ and $d^{11}B_4$ are shown in Figure 3b. The fractions of $B(OH)_3$ in coral cell can be calculated to be 0.2439, 0.2780 and 0.2488 for SYC-3, 5 and 6 respectively. This application is vital to the use of $d^{11}B_c$ values of biological carbonate from the ocean in reconstructing the past ocean pH. The incorporation of $B(OH)_3$ into biological carbonate in the ocean suggests that it is not possible to apply the $d^{11}B_c$ value of biological carbonate in the ocean to calculate oceanic pH. At present, we cannot rule out the factors causing an incorporation of $B(OH)_3$ into biological carbonates in the ocean.

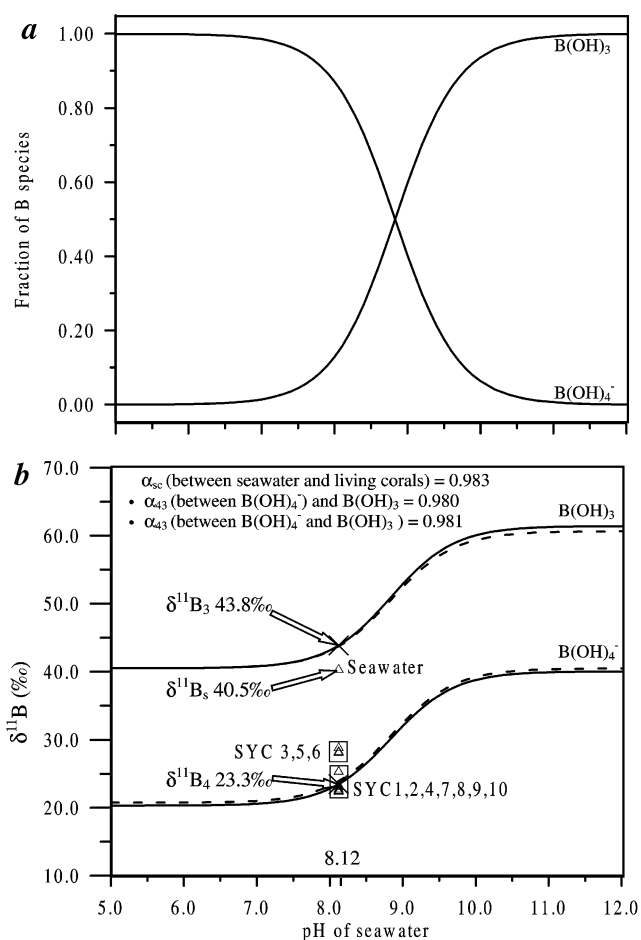


Figure 3. a, Distribution of aqueous boron species vs pH calculated using pK (dissociation constant of boric acid) value of 8.83 (Hershey *et al.*²⁶). b, $d^{11}B$ values of $B(OH)_3$ and $B(OH)_4^-$, two dominant aqueous species of boron in Sanya sea water, as a function of pH calculated from isotopic fractionation factor of 0.980 obtained in this study (solid line) and from the fractionation factor of 0.981 reported by Kakihana⁶ (broken line). Measured $d^{11}B$ value of sea water and growing corals are shown. $d^{11}B_3$ and $d^{11}B_4$ at pH 8.12 are 43.8 and 23.3‰ respectively for isotopic fractionation factor of 0.980.

Application of isotopic fractionation factor for the calculation of pH value of sea water

It is important to apply an actual a_{43} for calculation of pH value of sea water based on the measured $d^{11}B_c$ value. In

the typical pH range of sea water⁸, 7.5–8.4, the calculated $d^{11}B_4$ of sea water vs the a_{43} , ranging from 0.95 to 1 is shown in Figure 4. The results suggest that $d^{11}B_4$ increases with increase in a_{43} and reaches the $d^{11}B_{sw}$ when a_{43} is 1, based on the eq. (2). Similarly, at a typical pH range of sea water, 7.5–8.4, using the $d^{11}B_{sw}$ of 39.8‰, the ranges of variation for the measured $d^{11}B_c$ values would be from 8.6 to 16.0‰, 20.9 to 25.5‰, 21.5 to 25.9‰ and 24.6 to 28.3‰, when a_{43} has values of 0.968, 0.980, 0.981 and 0.984 respectively. Moreover, the maximum variation ranges of $d^{11}B_4$ are 6.5–39.8‰, 19.3–39.8‰, 20.0–39.8‰ and 23.2–39.8‰ for $a_{34} = 0.968, 0.9803, 0.981$ and 0.984 respectively. The measured $d^{11}B_c$ values falling into the normal variations ranges are used to calculate the pH of sea water. The measured $d^{11}B_c$ values exceeding the maxi-

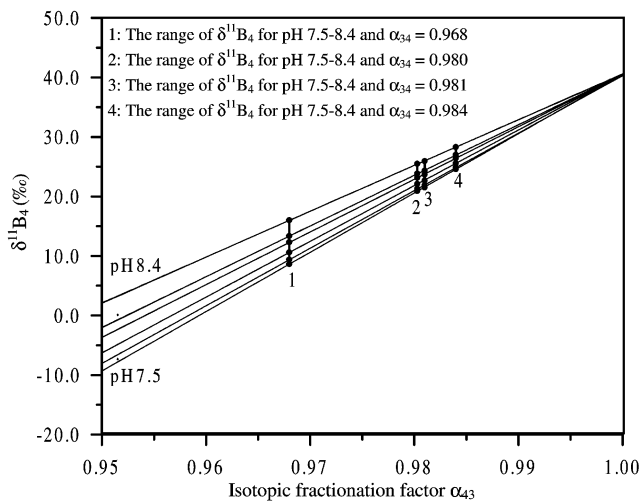


Figure 4. Calculated $d^{11}B_4$ for sea water with pH ranging from 7.5 to 8.4 vs isotopic fractionation factor a_{43} ranging from 0.95 to 1 vs.

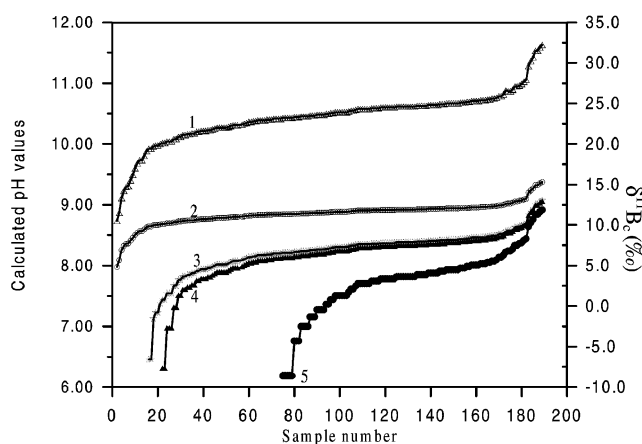


Figure 5. Comparison of calculated pH values based on published $d^{11}B_c$ of marine biogenic carbonates (line 1, $d^{11}B_c$ values from 10.5 to 32.2‰) using $a_{43} = 0.968$ ($n = 187$, average pH = 8.85). Line 2, $a_{43} = 0.980$ ($n = 173$, average pH = 8.23). Line 3, Obtained in this study; $a_{43} = 0.981$ ($n = 167$, average pH = 8.17). Line 4, $a_{43} = 0.984$ ($n = 115$, average pH = 7.76) (line 5).

um variations ranges cannot be used to calculate the pH values. Using published a_{43} of 0.968 (ref. 7), 0.981 (ref. 6), 0.984 (ref. 8) and 0.980 observed in this study, we re-calculate the pH values of sea water based on the published $d^{11}B_c$ values of marine biological carbonates^{5,10–12,17–19,24,25} (total $n = 189$, Figure 5, line 1). The re-calculated pH values show the average values of 8.85 ± 0.18 ($n = 187$, only two measured $d^{11}B_c$ values are lower than 6.5‰), 8.23 ± 0.37 ($n = 173$, 16 measured $d^{11}B_c$ values are lower than 19.3‰), 8.17 ± 0.40 ($n = 167$, 21 measured $d^{11}B_c$ values are lower than 20.0‰), 7.76 ± 0.54 ($n = 115$, 74 measured $d^{11}B_c$ values are lower than 23.2‰) and when $a_{43} = 0.968, 0.980, 0.981, 0.984$ respectively. The results imply that a_{43} values of 0.968 and 0.984 are not suited to calculate pH value because the re-calculated pH values of 8.85 and 7.76 are either too high for using $a_{43} = 0.968$ or too low for using $a_{43} = 0.984$ respectively, when compared with the pH of modern sea water. The re-calculated pH values of 8.22 and 8.17 using measured a_{43} of 0.980 in this study and a_{43} of 0.981 given by Kakihana *et al.*⁶, are close to the pH of 8.2 for modern sea water. Our measured a_{43} of 0.980 strongly demonstrates itself the a_{43} value of 0.981 reported by Kakihana *et al.*⁶ and therefore can be used as a standard a_{43} value for calculating the past oceanic pH values.

Conclusion

The isotopic fractionation of boron that takes place during the uptake of boron from sea water for its incorporation into the carbonate structure of growing corals indicates that the fractionation is different in different species of corals. The relatively higher $d^{11}B_c$ values observed in different species of corals indicate an additional amount of trigonal species of boron to be incorporated into the coral cell. The fractionation factor can be used for measuring the pH of sea water in which the coral was growing and has an implication in palaeo-pH measurements of sea water or the oceans. The fractionation factor (a_{43}) observed in the present study, which is 0.980, is nearly the same as 0.981 – one of the best fractionation factors proposed by Kakihana *et al.*⁶. The pH values of sea water recalculated using the two a_{43} values (0.981 and 0.980), gave pH values close to those of modern sea water compared with the other published a_{43} values, as they give either high or low pH values for modern sea water. The measured a_{43} of 0.980 in the present study can therefore be considered as a standard a_{43} value for palaeo-pH measurements.

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