



Assessment of coral $\delta^{44/40}\text{Ca}$ as a paleoclimate proxy in the Great Barrier Reef of Australia



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ARTICLE INFO

Article history:

Received 18 December 2015

Received in revised form 21 April 2016

Accepted 23 April 2016

Available online 26 April 2016

Keywords:

Calcium isotopic composition

Porites coral

Geochemical proxy

ABSTRACT

The Ca isotopic composition ($\delta^{44/40}\text{Ca}$) in a *Porites* spp. coral from the Great Barrier Reef was analyzed at monthly intervals for two consecutive years. It was found that variations in skeletal $\delta^{44/40}\text{Ca}$ values over the 2-year period are slightly greater than the analytical precision of the measurements, although other coralline geochemical records (i.e., $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{11}\text{B}$ and Sr/Ca ratios) show remarkable variations. To evaluate the potential of $\delta^{44/40}\text{Ca}$ as a paleoclimate proxy in corals, we compared $\delta^{44/40}\text{Ca}$ with other well-established indicators, and found that $\delta^{44/40}\text{Ca}$ values show little relationship to $\delta^{18}\text{O}$, Sr/Ca, $\Delta\delta^{18}\text{O}$, or $\delta^{11}\text{B}$ values, thus suggesting that the influence of seawater temperature, seawater pH and river inputs on skeletal $\delta^{44/40}\text{Ca}$ is limited or overwhelmed by other factors. However, skeletal $\delta^{44/40}\text{Ca}$ values are significantly related to $\delta^{13}\text{C}$ values ($r = 0.46$, $p < 0.05$; $n = 27$), thus indicating that Ca isotopic fractionation in corals is subjected to vital effect. The strong influence of biogenic factors on $\delta^{44/40}\text{Ca}$ in corals, limit the applicability of coral $\delta^{44/40}\text{Ca}$ to paleoclimate reconstruction.

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1. Introduction

Massive reef-building corals are distinguished paleoclimate recorders, providing high-resolution geochemical archives of past climatic conditions over time scales of weeks to centuries (Felis and Pätzold, 2003; Gagan et al., 2000; McCulloch et al., 1994). To date, a number of elemental and isotopic compositions in coral skeletons have turned out to be effective paleoclimate proxies, containing $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^{11}\text{B}$ and elemental ratios (e.g. Sr/Ca, Mg/Ca and Ba/Ca etc.) (Deng et al., 2013; McCulloch et al., 2003; Wei et al., 2000, 2009; Zinke et al., 2014). These geochemical proxies have allowed reconstructions of seasonal to annual variations in sea surface temperature (SST), seawater pH, and terrestrial inputs in reef waters back to the Pleistocene (Deng et al., 2014a, 2014b; Liu et al., 2014; McCulloch et al., 1999; McGregor et al., 2013; Yu et al., 2005).

The element Ca, a major constituent of aragonitic coral skeletons, is generally included in many paleoclimate proxies, such as multiple elemental ratios. In addition to elemental compositions, its isotopic compositions of corals also appear to be controlled by environmental factors (Böhm et al., 2006; Inoue et al., 2015) and such isotopic compositions could be of use in paleoclimate studies.

Calcium isotopic composition of marine carbonates, defined as $\delta^{44/40}\text{Ca} = [(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}} / (^{44}\text{Ca}/^{40}\text{Ca})_{\text{SRM 915a}} - 1] \times 1000$, has received considerable attention due to the essential roles of Ca in both marine sediments and the biosphere (DePaolo, 2004; Fantle and Tipper, 2014; Zhu and Macdougall, 1998). Calcium isotopic compositions offer the potential to reveal the evolutionary history of seawater chemistry and the Ca balance in the oceans, which can benefit our understanding of the global Ca cycle (Blättler et al., 2012; De La Rocha and DePaolo, 2000; Farkaš et al., 2007a).

Values of $\delta^{44/40}\text{Ca}$ vary among marine organisms. Calcium isotopic fractionation in some taxa resembles inorganic trends, but this pattern is not observed in all taxa (Böhm et al., 2006; Blättler et al., 2012; Gussone et al., 2003, 2005, 2006). Gussone et al. (2006) and Böhm et al. (2006) suggested that in coccolithophores and corals, Ca isotopic fractionation occurs during Ca transport across the cellular membrane during which dehydration of the Ca aquo-complex can induce $\delta^{44/40}\text{Ca}$ offsets. Culture experiments also show that calcium isotopic fractionation in both inorganic and biogenic carbonates is temperature dependent (Böhm et al., 2006; Gussone et al., 2003, 2005; Inoue et al., 2015; Marriott et al., 2004; Nägler et al., 2000). On the other hand, Lemarchand et al. (2004) argued that the temperature dependence of Ca isotopic fractionation in inorganic and some biogenic carbonate is relatively small ($\sim 0.02\text{‰}/^\circ\text{C}$), and can be attributed to the temperature-dependent speciation of carbonic acid (Millero, 1995). Nevertheless, these findings all suggest that skeletal $\delta^{44/40}\text{Ca}$ might be

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an indicator of environmental conditions (e.g., seawater temperature or pH).

In contrast, Pretet et al. (2013) compared $\delta^{44/40}\text{Ca}$ with both $\delta^{18}\text{O}$ and Sr/Ca ratios in a fossil coral, and suggested that the use of coral $\delta^{44/40}\text{Ca}$ as a temperature proxy is problematic. Their results showed that the amplitude of paleo-SST variations reconstructed from Sr/Ca ratios and $\delta^{18}\text{O}$ was only 3 °C (Pretet et al., 2013). Given the small temperature dependence of calcium isotopic fractionation in cultured *Porites* corals ($0.021 \pm 0.009\text{‰/K}$; Inoue et al., 2015), a temperature variation of 3 °C can only induce a change in $\delta^{44/40}\text{Ca}$ values of $\sim 0.06\text{‰}$, which is less than the analytical precision ($\sim 0.1\text{‰}$). Thus, the $\sim 0.28\text{‰}$ amplitude of $\delta^{44/40}\text{Ca}$ variations determined by Pretet et al. (2013) suggests that factors other than temperature mainly control $\delta^{44/40}\text{Ca}$ variations in Tahiti corals (Pretet et al., 2013).

In the present study, we measured monthly values of $\delta^{44/40}\text{Ca}$ and other geochemical proxies (including $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{11}\text{B}$, and Sr/Ca ratios) in the coral skeleton of a *Porites* spp. from the Great Barrier Reef, an area which experiences a relatively wide annual range of seawater temperatures (as large as 7 °C). Climatic and environmental changes can therefore be assessed by comparing the response of $\delta^{44/40}\text{Ca}$ values to well-established paleoclimate proxies. These results will help to interpret climatic and environmental information related to the calcium isotopic composition of coral skeletons, and will benefit the understanding for coral $\delta^{44/40}\text{Ca}$ being used as a paleoclimate proxy.

2. Materials and methods

2.1. Coral sampling

Coral cores were collected in April 2010 from a living *Porites* spp. coral colony at a water depth of ~ 4 m on the back of Arlington Reef, which is a middle-shelf crescentic reef located ~ 44 km offshore of the Barron River mouth on the northeast coast of Australia. The core (10AR2), which was 1.24 m in length was cut into slices (~ 7 mm thick) along the plane of the vertical growth axis, and X-rayed to reveal annual growth banding that was used to as a guide for collecting the monthly to annual time series data. Details of the cores, are presented by Deng et al. (2014a).

To prepare the samples, the slabs were first immersed in 10% H_2O_2 for 24 h, followed by ultrasonic cleaning in Milli-Q water for 30 min, rinsing three times, and then drying at 40 °C prior to sampling. To avoid contamination, preliminary milling along the designated sample track was undertaken to remove ~ 1 mm from the surface. Guided by the annual bands identified in the X-ray images, subsamples were collected continuously at 1–2 mm intervals for a period of two consecutive years (i.e. 2007–2008; Fig. 1) along the main growth axis using a

drill bit, ground to a fine powder (~ 200 mesh) using an agate mortar and pestle, and then well mixed to yield a homogenous sample. All geochemical measurements were performed on aliquots of the homogenous powder samples.

2.2. Geochemical analyses

Calcium isotopic analyses were performed using a thermal ionization mass spectrometer (TIMS Finnigan Triton) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, following the methods described by Zhu et al. (2015). Approximately 5 mg of fine coral powder was directly dissolved in 1.6 M HNO_3 and was evaporated to dryness. To remove interfering organic molecules, the sample was treated with a 1:3 HNO_3 –HCl mixture, dried and then dissolved in a certain volume of 1.6 M HNO_3 . An aliquot of sample solution containing ~ 50 μg Ca was pipetted into a Savillex beaker, and a ^{42}Ca – ^{43}Ca double spike was added. Finally, the coral samples were dried and dissolved in 10 μl 10% v/v HNO_3 for TIMS determination. Details of the analysis are presented by Zhu et al. (2015). The long-term $\delta^{44/40}\text{Ca}$ of NIST SRM 915a and IAPSO seawater are $-0.01 \pm 0.11\text{‰}$ ($n = 41$; 2 standard deviation, SD) and $1.81 \pm 0.10\text{‰}$ ($n = 19$, 2 SD), respectively. These values are in good agreement with those reported in previous studies (e.g., Amini et al., 2009; Farkaš et al., 2007b; Hippler et al., 2003; Huang et al., 2011). The total procedural Ca blanks ranged from 20 to 70 ng, and were all $< 2\%$ of the amount of Ca analyzed. Errors are reported as 2 SD for samples measured in triplicate. If the sample was measured only once or twice, the error for $\delta^{44/40}\text{Ca}$ was set as 0.11‰ based on 2 standard deviations of our long-term standard analyses (Table 1).

Boron isotopic analyses were also performed at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, following the methods described in Wei et al. (2009, 2013). The dissolved sample was first loaded onto a cation-exchange column containing AG50W- $\times 8$ resin to remove major constituents of the carbonate solution (Ca, Mg, and Sr), and then treated with a second column prepared using Amberlite IRA-743 B-specific ion-exchange resin to concentrate and purify the B. The $\delta^{11}\text{B}$ was determined using a Thermo Fisher Scientific Neptune plus multi-collector inductively couple plasma mass spectrometry (MC-ICP-MS). Typical operating conditions and measurement strategies are summarized by Wei et al. (2013). To reduce the possible B memory of the introduction system, a low-flow PFA Microflow nebulizer, PFA spray chamber, sapphire injector, Ni sampler cone and Pt skimmer cone were used. Instrumental mass bias and boron background levels were corrected using a sample–standard bracketing method and on a peak zero blank correction (Wei et al., 2013). The JCP-1 (*Porites* spp.: Geological Survey of Japan) and B1

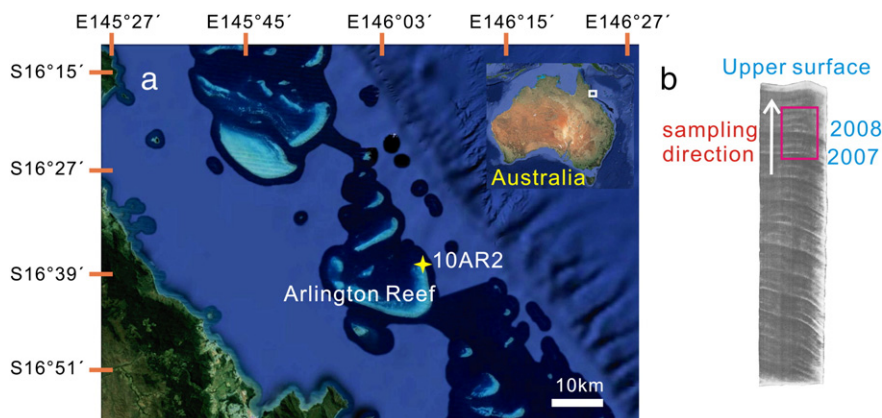


Fig. 1. a. Map showing the location of the Arlington Reef on the Great Barrier Reef (GBR). Yellow Star indicates the sampling position. b. X-ray radiographs (negative prints) of 10AR2 coral core section with sampling intervals along the maximum growth axis.

Table 1
Geochemical records of Arlington Reef in two successive years.

Sample	$\delta^{44}\text{Ca} \text{‰}$	2SD	n	$\delta^{13}\text{C} \text{‰}$	$\delta^{18}\text{O} \text{‰}$	Sr/Ca mmol/mol	$\Delta \delta^{18}\text{O} \text{‰}$	$\delta^{11}\text{B} \text{‰}$
1	0.78	0.07	3	-3.21	-4.95	8.85	0.04	24.88
2	0.73	0.16	3	-3.15	-5.45	8.97	-0.84	22.24
3	0.69	0.10	3	-3.58	-5.28	8.99	-0.68	22.96
4	0.78	0.04	3	-3.27	-5.36	8.85	-0.44	24.40
5	0.73	0.12	3	-3.13	-5.22	8.86	-0.31	23.68
6	0.74	0.11	1	-3.38	-4.94	8.92	-0.11	24.40
7	0.73	0.13	3	-3.69	-4.79	8.91	0.05	24.67
8	0.70	0.11	1	-3.85	-4.68	9.08	-0.23	22.53
9	0.70	0.11	1	-4.11	-4.71	9.05	-0.20	24.09
10	0.70	0.11	1	-3.69	-4.66	9.17	-0.42	22.22
11	0.78	0.11	1	-3.52	-4.48	9.08	-0.01	22.08
12	0.77	0.11	1	-3.15	-4.72	9.09	-0.31	21.86
13	0.72	0.08	3	-2.73	-4.89	9.01	-0.31	23.30
14	0.85	0.08	3	-2.75	-5.35	8.95	-0.68	23.26
15	0.74	0.06	3	-2.91	-5.35	8.91	-0.58	23.65
16	0.76	0.07	3	-3.17	-5.49	8.98	-0.91	22.15
17	0.70	0.07	3	-3.16	-5.28	9.00	-0.71	22.03
18	0.68	0.11	3	-3.51	-5.05	9.09	-0.66	22.60
19	0.66	0.07	3	-4.11	-4.89	9.12	-0.57	23.46
20	0.71	0.09	3	-4.12	-4.71	9.14	-0.40	23.50
21	0.67	0.06	3	-4.01	-4.50	9.28	-0.51	22.08
22	0.69	0.08	3	-3.91	-4.83	9.20	-0.68	23.00
23	0.84	0.09	3	-3.88	-4.64	9.11	-0.26	23.21
24	0.63	0.07	3	-3.74	-4.87	8.99	-0.22	22.30
25	0.72	0.07	3	-3.59	-4.81	8.63	0.73	22.39
26	0.74	0.07	3	-3.49	-4.99	9.08	-0.58	22.32
27	0.80	0.07	3	-3.46	-5.06	9.00	-0.46	22.53

(Seawater: IAEA) standards were chemically treated repeatedly and measured along with the coral samples to monitor the analytical quality of the samples. The measurements yielded $\delta^{11}\text{B}$ values of $24.19 \pm 0.46\text{‰}$ ($n = 7$, 2 SD) for JCP-1 and $39.32 \pm 0.41\text{‰}$ ($n = 5$, 2 SD) for B1, which are consistent with previously reported values within analytical errors (e.g. Foster et al., 2006; Gonfiantini et al., 2003; McCulloch et al., 2014; Wang et al., 2010). The long-term total procedure blank for B was in the range of 10–20 ng.

Coral skeletal $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were measured at the same laboratory on a GV Isoprime II stable isotope ratio mass spectrometer (IRMS) coupled with a MultiPrep® carbonate device in which 102% H_3PO_4 was reacted with the coral samples (ca. 0.2 mg) at 90 °C to extract CO_2 ; details of the procedure are described by Deng et al. (2009). Isotope data were normalized to the Vienna Pee Dee Belemnite (VPDB) using standard NBS-19 ($\delta^{13}\text{C} = 1.95\text{‰}$ and $\delta^{18}\text{O} = -2.20\text{‰}$). Repeated measurements ($n = 30$) of this standard yielded a standard deviation of 0.05‰ for $\delta^{13}\text{C}$ and 0.08‰ for $\delta^{18}\text{O}$.

Sr/Ca measurements of samples (ca. 1 mg) were performed on a Varian Vista Pro inductively coupled plasma atomic emission spectrometer (ICP-AES) at the same laboratory. Replicate analyses of an in-house coral standard solution showed excellent reproducibility, with an external precision of 0.16% for Sr/Ca measurements. All the samples were measured repeatedly, and differences between the results of the repeated measurements were within the range of analytical error. Details of the method are presented by Wei et al. (2007).

2.3. Statistical analyses

The program PAST (Hammer et al., 2001) was employed in this study to calculate the correlation coefficients between all the geochemical parameters and to assess the serial correlation among the seasonal time series. As autocorrelation is prone to exist among such time series which may compromise the results of correlation analyses, we adopted the Durbin–Watson test (implemented in the PAST software) to verify whether the correlation coefficients between $\delta^{44/40}\text{Ca}$ and other geochemical parameters are influenced by their autocorrelations. The test statistic shows that both d and $(4 - d)$ values are all above the upper critical value, implying that there is no statistical evidence that

the correlation coefficients between $\delta^{44/40}\text{Ca}$ and other geochemical parameters would be affected by serial correlation.

3. Results

The results of the $\delta^{44/40}\text{Ca}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{11}\text{B}$ and Sr/Ca determinations are listed in Table 1. The $\delta^{44/40}\text{Ca}$ values vary slightly with time, and are in the range of 0.63‰–0.85‰ (average, $0.73 \pm 0.10\text{‰}$), which is consistent with previous results (e.g. Böhm et al., 2006: $0.81 \pm 0.05\text{‰}$, Pretet et al., 2013: $0.81 \pm 0.18\text{‰}$). The $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and Sr/Ca values all show seasonal cycles, with higher $\delta^{13}\text{C}$ accompanying lower $\delta^{18}\text{O}$ and Sr/Ca values, and vice versa. The $\delta^{44/40}\text{Ca}$ values also appear to follow seasonal cycles (Fig. 2), with lower values generally occurring in winter months and higher values in summer months, as indicated by $\delta^{18}\text{O}$ and Sr/Ca ratios values; however, some erratic points disturb the pattern of cyclicity. The $\delta^{44/40}\text{Ca}$ shows a significant positive correlation with $\delta^{13}\text{C}$ ($r = 0.46$, $p < 0.05$, $n = 27$), whereas no statistically significant relationship is observed between $\delta^{44/40}\text{Ca}$ and $\delta^{18}\text{O}$, or between $\delta^{44/40}\text{Ca}$ and Sr/Ca ratios (Table 2). Skeletal $\delta^{11}\text{B}$ varies from 21.86‰ to 24.88‰ and show no significant seasonal cycles, and is barely related to $\delta^{44/40}\text{Ca}$ (Table 2).

The $\delta^{11}\text{B}$ values of samples were converted into pH values of seawater (pH_{sw}), using the equation (e.g. Zeebe et al. (2001)):

$$\text{pH}_{\text{cf}} = \text{pK}_B - \log \left[\frac{\delta^{11}\text{B}_{\text{sw}} - \delta^{11}\text{B}_{\text{carb}}}{\alpha_{\text{B3-B4}} \delta^{11}\text{B}_{\text{carb}} - \delta^{11}\text{B}_{\text{sw}} + 1000(\alpha_{\text{B3-B4}} - 1)} \right]$$

and the equation calibrated for vital effects in *Porites* spp. coral (Trotter et al., 2011):

$$\text{pH}_{\text{sw}} = (\text{pH}_{\text{cf}} - 5.954) / 0.32.$$

The parameters pK_B and $\alpha_{\text{B3-B4}}$ are the equilibrium constant and the fractionation factor for isotope exchange between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ in the calcifying fluid, respectively. The $\delta^{11}\text{B}_{\text{sw}}$ and $\delta^{11}\text{B}_{\text{carb}}$ indicate the $\delta^{11}\text{B}$ in seawater and in carbonate, respectively. Using the $\alpha_{\text{B3-B4}}$ value of 1.0272 (Klochko et al., 2006), the pK_B value of 8.60 (DOE, 1994; Hönisch et al., 2004), and the $\delta^{11}\text{B}_{\text{sw}}$ value of 39.5‰ (Foster, 2008),

the calculated monthly-resolved seawater pH varies in the range of 7.52–8.14.

4. Discussion

The overall variation in skeletal $\delta^{44/40}\text{Ca}$ values is $\sim 0.22\%$, which is only slightly greater than the analytical precision ($\sim 0.11\%$). This small variability in the Ca isotopic composition of *Porites lutea* corals from the GBR resembles the variability in cultured corals (0.33% in *Acropora* spp., Böhm et al., 2006; 0.24–0.40% in *Porites* spp., Inoue et al., 2015) and in the open-ocean corals (0.13% in *Porites* spp., Böhm et al., 2006; 0.34%, Pretet et al., 2013; 0.22% in *Pavona clavus*, Böhm et al., 2006). The small $\delta^{44/40}\text{Ca}$ variation in this study may to some extent

compromise the confidence level of the comparison study between calcium isotopes and other geochemical parameters in corals.

4.1. Comparisons with other paleoclimate proxies

The evident seasonal cycles of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Sr/Ca ratios in coral 10AR2 reveal a continuous two-year record, with higher $\delta^{13}\text{C}$ and lower $\delta^{18}\text{O}$ and Sr/Ca occurring in summer months and lower $\delta^{13}\text{C}$ and higher $\delta^{18}\text{O}$ and Sr/Ca occurring in winter months (Fig. 2). Such seasonal variations are generally induced by environmental factors: e.g., temperature, solar radiation, or river input (Deng et al., 2013; Gagan et al., 1996; Wei et al., 2000). To evaluate the geochemical significance of skeletal $\delta^{44}\text{Ca}$, we compared it with other well-defined geochemical proxies in corals (i.e. $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{11}\text{B}$, and Sr/Ca ratios).

4.1.1. Temperature

As indicated in previous studies, $\delta^{44/40}\text{Ca}$ values in corals show a small but significant relationship with temperature, with a regression slope of $0.020 \pm 0.015\%$ /°C (Böhm et al., 2006; Inoue et al., 2015). In the 10AR2 coral, $\delta^{44/40}\text{Ca}$ values show weak seasonal cycles similar in periodicity to those of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Sr/Ca values (Fig. 2); such trend are possibly driven by temperature. Given that Sr/Ca ratios in corals are considered as a tool for elucidating SST variations (McCulloch et al., 1999; Smith et al., 1979; Weber, 1973), we therefore compared Sr/Ca ratios to $\delta^{44/40}\text{Ca}$ and found that the two parameters are not well correlated ($r = 0.27$, $p = 0.17$, $n = 27$; Table 2). A similar weak relationship between Sr/Ca and $\delta^{44/40}\text{Ca}$ was found in a fossil coral record from Tahiti (Pretet et al., 2013), suggesting that the weak relationship between temperature and $\delta^{44/40}\text{Ca}$ may not be precisely revealed by comparing Sr/Ca ratios to $\delta^{44/40}\text{Ca}$, or that the influence of temperature on $\delta^{44/40}\text{Ca}$ values is obscured by other effects.

The instrumental records show that the amplitude of seasonal temperature variations is as large as $\sim 7\text{ }^\circ\text{C}$ (AIMS, 2015). The weak temperature sensitivity of $\delta^{44/40}\text{Ca}$ in cultured *Porites* corals ($0.021 \pm 0.009\%$ /°C, Inoue et al., 2015) indicates that a temperature variation of $\sim 7\text{ }^\circ\text{C}$ can induce a $\delta^{44/40}\text{Ca}$ change of $\sim 0.14 \pm 0.02\%$. This change in $\delta^{44/40}\text{Ca}$ values is only slightly higher than the analytical precision (0.11%) but comparable to the observed overall variation of the range of skeletal $\delta^{44/40}\text{Ca}$ ($\sim 0.22\%$).

For a direct comparison of skeletal $\delta^{44/40}\text{Ca}$ and SSTs, we used the Sr/Ca–SST relationship to correlate geochemical records with instrumental data. Because annual boundary is difficult to identify using growth bands during sampling, it is possible that the starting point of the time series was in the preceding year. Because of this, guided by Sr/Ca–SST, the top three and the bottom two points of the time series were removed firstly, as the Sr/Ca ratios for these points varied from the trend of instrumental SST values. Then, the maximum Sr/Ca value was matched to the minimum SST value and the minimum Sr/Ca value was matched to the maximum SST. Next, the remainder of the time series data was interpolated to correspond to SST variation. The procedure (results of which are shown in Fig. 3) yields a regression equation for the $\delta^{44/40}\text{Ca}$ –SST for the Arlington Reef with a small slope ($0.009 \pm 0.004\%$ /°C, $r = 0.42$, $p < 0.05$, $n = 24$) which is identical within uncertainty to the results obtained from culturing experiments (Böhm et al., 2006: $0.020 \pm 0.015\%$ /°C; Inoue et al., 2015: $0.021 \pm 0.009\%$ /°C)

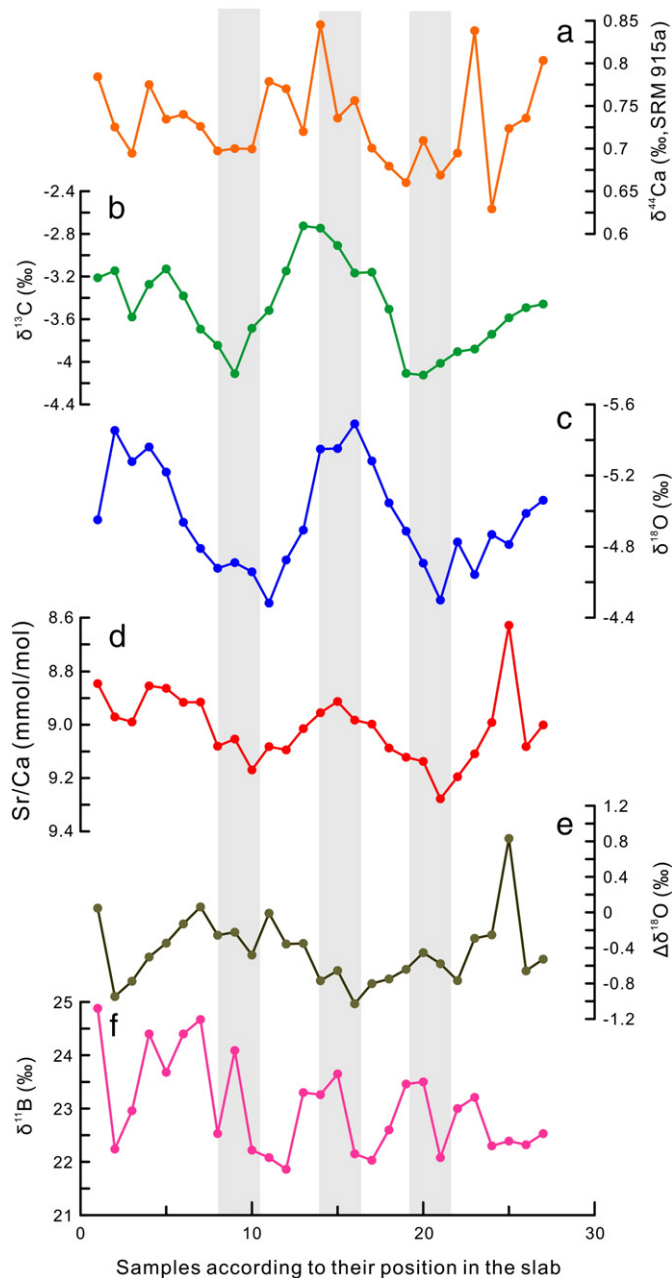


Fig. 2. Monthly-resolved geochemical records in 10AR2 coral plotted as the samples according to their position in the coral slab (Fig. 1b): a, $\delta^{44}\text{Ca}$; b, $\delta^{13}\text{C}$; c, $\delta^{18}\text{O}$; d, Sr/Ca; e, $\Delta\delta^{18}\text{O}$; f, $\delta^{11}\text{B}$. Note that the axis of $\delta^{18}\text{O}$ and Sr/Ca is reversed. Gray bars indicate synchronous variations in all the geochemical proxies.

Table 2
Intercorrelations between the $\delta^{44}\text{Ca}$ and coral geochemical parameters*.

	$\delta^{11}\text{B}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Sr/Ca	$\Delta\delta^{18}\text{O}$
$\delta^{44}\text{Ca}$	0.19	0.46	−0.19	−0.27	0.08
$\delta^{11}\text{B}$		0.01	−0.09	−0.37	0.26
$\delta^{13}\text{C}$			− 0.65	− 0.48	−0.18
$\delta^{18}\text{O}$				0.47	0.53
Sr/Ca					− 0.50

* Correlation coefficients with p value below 0.05 are in bold. For all the parameters, $n = 27$.

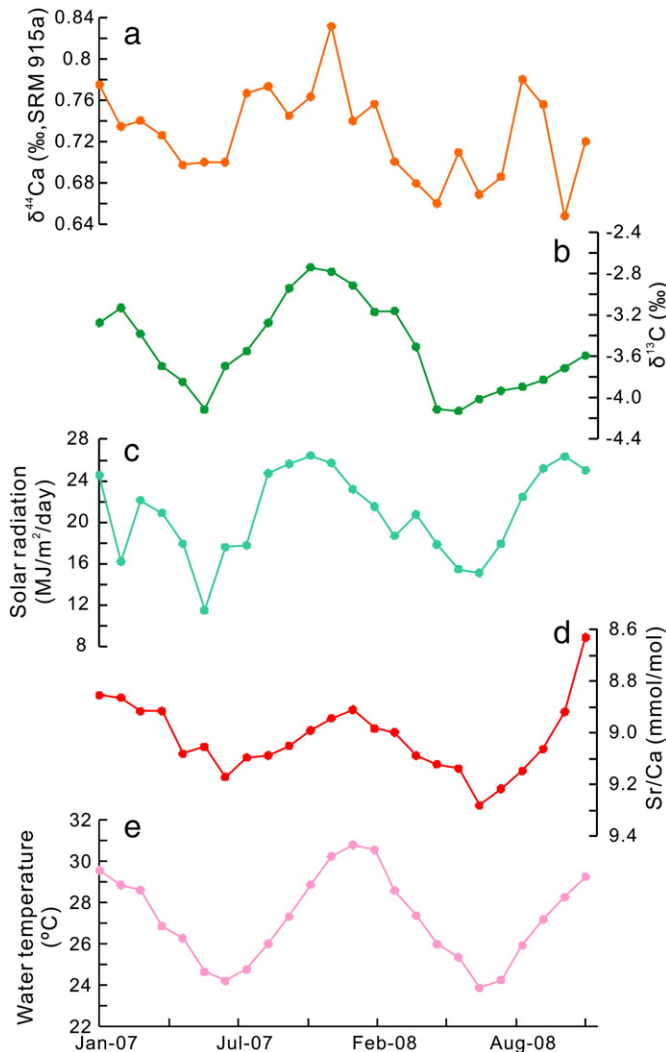


Fig. 3. Interpolated geochemical records in 10AR2 coral and the corresponding instrumental records for year 2007 and 2008: a, interpolated $\delta^{44}\text{Ca}$ record; b, interpolated $\delta^{13}\text{C}$ record; c, solar radiation (Location: 16.6° S, 146.1° E; Data available from NASA/POWER Agroclimatology Daily Averaged Data: http://power.larc.nasa.gov/common/AgroclimatologyMethodology/Agro1d0_Methodology_Content.html; d, interpolated Sr/Ca ratios; e, water temperature for Arlington Reef (Data available from Australian Institute of Marine Science: <http://data.aims.gov.au/aimstrds/datatool.xhtml>).

(Fig. 3). These results suggest that temperature changes can explain only part of the observed $\delta^{44/40}\text{Ca}$ variation, and that the remaining variability may be the result of other environmental factors (river inputs, salinity, or water pH), vital effects, or analytical technique.

4.1.2. River runoff

In inshore area of the GBR, river inputs can modify the chemical composition of seawater, and can thus leave an imprint on the chemistry of coral skeletons (D'Olivo et al., 2015; Lewis et al., 2007; McCulloch et al., 2003). The isotopic composition of riverine Ca, which is the main input to the oceanic Ca reservoir, shows a mean $\delta^{44/40}\text{Ca}$ value of 0.86‰, which is much lower than that of seawater (1.85‰; Fantle and Tipper, 2014). River runoff not only alters the $\delta^{44/40}\text{Ca}$ values of inshore waters, which can be recorded by corals, but also influences water salinity, which in turn might affect $\delta^{44/40}\text{Ca}$ in corals, as changes in salinity may exert a positive influence on coral $\delta^{44/40}\text{Ca}$ (Pretet et al., 2013). In the region of the Great Barrier Reef, seawater salinity remains generally stable around an average of 35 part per thousand (Andutta et al., 2011), but the inflow from the rivers may cause extensive fluctuations in salinity (Schaffelke et al., 2009). Moreover, heavy rainfall and evaporation at

the ocean surface can also change surface salinity. As the Arlington Reef is a mid-shelf reef, only in wet season with heavy rainfall and enhanced river flow the salinity may fluctuate, otherwise during dry season the salinity stays stable. (Andutta et al., 2011; Schaffelke et al., 2009). Therefore, on the Arlington Reef, freshwater inputs dominate the seawater chemical composition and salinity.

To acquire freshwater information, residual $\delta^{18}\text{O}$ ($\Delta\delta^{18}\text{O}$) was calculated by subtracting the SST contribution from coral $\delta^{18}\text{O}$ values (Gagan et al., 1998) using the following equation:

$$\Delta\delta^{18}\text{O} = d\delta^{18}\text{O}/dT \times [T_{\delta^{18}\text{O}} - T_{\text{Sr/Ca}}],$$

where $d\delta^{18}\text{O}/dT$ is the slope of the empirical $\delta^{18}\text{O}$ -SST function (0.23‰/°C, as reported by Gagan et al., 2012), and $T_{\delta^{18}\text{O}}$ and $T_{\text{Sr/Ca}}$ are the apparent SSTs calculated from $\delta^{18}\text{O}$ values and Sr/Ca ratios, respectively. In this study we use the Sr/Ca-SST relationship reported by Deng et al. (2014a).

Results of $\Delta\delta^{18}\text{O}$ calculations are shown in Fig. 2. The coral $\Delta\delta^{18}\text{O}$ represents changes in the oxygen isotopic composition of seawater, which are commonly associated with river runoff or precipitation (Gagan et al., 1998; McCulloch et al., 1994). The great variability of $\Delta\delta^{18}\text{O}$ suggests intense variations of freshwater input and salinity fluctuations, which is consistent with the increase of Barron River annual flow and total rainfall in Cairns in 2008 (Data available from Queensland Department of Environment and Resource Management, and Cairns Aero Weather Station). However, no evident correlation was observed between $\Delta\delta^{18}\text{O}$ and $\delta^{44/40}\text{Ca}$ ($r = 0.08$, $p = 0.71$, $n = 27$). Thus, freshwater inputs apparently do not influence coral skeletal $\delta^{44/40}\text{Ca}$ values on the Arlington Reef.

4.1.3. Seawater pH

Lemarchand et al. (2004) indicated that in inorganic carbonates, variations in $\delta^{44/40}\text{Ca}$ values show a linear dependence on CO_3^{2-} concentration ($[\text{CO}_3^{2-}]$) and hence pH, thus arousing the interest in the use of skeletal $\delta^{44/40}\text{Ca}$ as a proxy for seawater pH. However, culture experiments using various organisms have shown diverse relationships between pH (or $[\text{CO}_3^{2-}]$) and $\delta^{44/40}\text{Ca}$ in biogenic carbonates (Gussone and Filipsson, 2010; Inoue et al., 2015; Kisakürek et al., 2011; Taubner et al., 2012). Kisakürek et al. (2011) found a minor dependence of Ca isotope fractionation on $[\text{CO}_3^{2-}]$ in *Globigerinella ruber* ($0.0005 \pm 0.0003\text{‰}/\mu\text{mol/l}$), which is identical to the isotopic fractionation in inorganic calcite precipitated from stirred solution ($0.0008 \pm 0.0004\text{‰}/\mu\text{mol/l}$; Lemarchand et al., 2004). However, for benthic foraminifers, temperature and carbonate chemistry exert mutual effects on $\delta^{44/40}\text{Ca}$, and result in a complex relationship between $\delta^{44/40}\text{Ca}$ and $[\text{CO}_3^{2-}]$ (Gussone and Filipsson, 2010). In addition, water pH plays a limited role in calcium isotopic fractionation in *Orbulina universa* and *Emiliania huxleyi* (Gussone et al., 2003, 2006). In corals, Taubner et al. (2012) observed an apparent $\delta^{44/40}\text{Ca}$ dependence on pH in soft corals (*Alcyonarian spicules*), whereas for scleractinian corals $\delta^{44/40}\text{Ca}$ is barely influenced by pH (Inoue et al., 2015). To assess pH effects on coral $\delta^{44/40}\text{Ca}$, we compared $\delta^{44/40}\text{Ca}$ with $\delta^{11}\text{B}$, as $\delta^{11}\text{B}$ is a well-defined pH indicator in marine carbonates (Hönisch et al., 2004; Pelejero et al., 2005; Wei et al., 2009). However, results of this comparison show no significant relationship between $\delta^{11}\text{B}$ and $\delta^{44/40}\text{Ca}$ (Fig. 2, Table 2).

Monthly resolved $\delta^{11}\text{B}$ time series behaved differently than those of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data. In particular, seasonal cycles are weak, but $\delta^{11}\text{B}$ values show remarkable variability (range, $\sim 3.00 \pm 0.71\text{‰}$), which translates to a pH variation of $\sim 0.62 \pm 0.11$. This range of pH values is comparable to that found in culturing experiments (Inoue et al., 2015; Taubner et al., 2012). However, as indicated by Inoue et al. (2015), such pH variations exert only a limited influence on skeletal $\delta^{44/40}\text{Ca}$ in *Porites australiensis* corals. Therefore, the absence of a relationship in corals between $\delta^{44/40}\text{Ca}$ and $\delta^{11}\text{B}$ indicates that $\delta^{44/40}\text{Ca}$ in coral skeletons may not be a potential proxy for pH, and that calcium isotope

fractionation in biogenic carbonates is far more complex than that observed on synthetic calcite; the difference is likely related to vital effect.

4.1.4. Biological effects

Corals exert a strong command over the biomineralization processes, as coral skeletons calcify extremely faster than inorganic carbonates and even other calcareous organisms (Cohen and McConnaughey, 2003). As a result, most geochemical proxies in corals are subjected to vital effects (Juillet-Leclerc et al., 2009; Meibom et al., 2006; Trotter et al., 2011). Taken it into consideration that calcium and inorganic carbon are the two important elements for photosynthesis and calcification (Brand and Becker, 1984; Gattuso et al., 1999), it is likely that metabolic processes induce the fractionation of calcium and carbon isotopes. We therefore compared skeletal $\delta^{44/40}\text{Ca}$ and $\delta^{13}\text{C}$ values, and as expected, found a significant positive correlation between the two ($r = 0.46$, $p < 0.05$; $n = 27$). As Ca and C are basic components of CaCO_3 , it is possible that the relationship between $\delta^{44/40}\text{Ca}$ and $\delta^{13}\text{C}$ is inherited from kinetic effects happening during CaCO_3 precipitation. However, kinetic fractionation of Ca isotopes only occurs during its transport across the cell membrane (Böhm et al., 2006), while carbon dioxide hydration and hydroxylation result in kinetic fractionation of both C and O isotopes (McConnaughey, 1989). Furthermore, as shown by Inoue et al. (2015), growth rates may not be a crucial driving forcing in Ca isotope fractionation in corals. Consequently, we believe that the positive relationship between $\delta^{13}\text{C}$ and $\delta^{44/40}\text{Ca}$ may not be caused by kinetic effects during precipitation, but rather the result of other processes operating collectively that influence the systematics of both isotopes in corals.

The $\delta^{13}\text{C}$ in tropical zooxanthellate coral skeletons is influenced by many factors, including carbon source, metabolic effects, and other environmental variables (e.g., Allison et al., 2012; Deng et al., 2013; Grottole, 2002; McConnaughey et al., 1997, McConnaughey, 2003; Swart et al., 1996a, 1996b). Depending on the dominance of different processes, $\delta^{13}\text{C}$ values can show diverse relationships with skeletal $\delta^{18}\text{O}$ values, which can be positive, negative or insignificant in zooxanthellate corals (McConnaughey, 1989). On the Arlington Reef, skeletal $\delta^{13}\text{C}$ varies seasonally and shows inverse relationship with $\delta^{18}\text{O}$ ($r = -0.65$, $p < 0.0001$, $n = 27$), with $\delta^{13}\text{C}$ maxima corresponding to $\delta^{18}\text{O}$ minima in the warm season as indicated by both $\delta^{18}\text{O}$ and Sr/Ca ratios. During the warm season, higher temperatures lead to higher rates of photosynthesis and respiration, and photosynthesis is also enhanced by increased sunlight (McConnaughey, 1989; Swart, 1983). These patterns indicate that enhancement of photosynthesis by symbiotic algae during the warm season consumes more ^{13}C -depleted CO_2 , leaving the calcifying fluid enriched in ^{13}C . Given that corals typically occur in waters with temperatures more optimal for photosynthesis than for respiration (Swart, 1983), and given the positive relationship between $\delta^{13}\text{C}$ and SST, the $\delta^{13}\text{C}$ variability in coral 10AR2 appears to be driven mainly by photosynthesis rather than respiration (as

Table 3
Relationship between interpolated geochemical records in 10AR2 coral and environmental parameters^a.

	$\delta^{13}\text{C}$	Sr/Ca	$\delta^{18}\text{O}$	SST	Solar radiation
$\delta^{44}\text{Ca}$	0.59	-0.27	-0.32	0.41	0.49
$\delta^{13}\text{C}$	-0.47	-0.68	0.74	0.59	
Sr/Ca		0.52	-0.78	-0.47	
$\delta^{18}\text{O}$			-0.87	-0.32	
SST				0.62	

^a Data available from Australian Institute of Marine Science: <http://data.aims.gov.au/aimsrtds/datatool.xhtml>

^b Data available from NASA/POWER Agroclimatology Daily Averaged Data: http://power.larc.nasa.gov/common/AgroclimatologyMethodology/Agro1d0_Methodology_Content.html

* Correlation coefficients with p value below 0.05 are in bold. For all the parameters, $n = 24$.

respiration drives skeletal $\delta^{13}\text{C}$ values in a direction opposite to that of photosynthesis). Furthermore, interpolated $\delta^{13}\text{C}$ time series show a positive correlation with solar radiation, which is consistent with a previous finding that light levels influence $\delta^{13}\text{C}$ values (Grottole, 2002). However, the intercorrelations between $\delta^{13}\text{C}$, SST, and solar radiation indicate that temperature accounts for ~56% of the $\delta^{13}\text{C}$ variations, while light explains only 35% of the variation in $\delta^{13}\text{C}$ that is comparable to the observation that temperature accounts for roughly 38% solar radiation variability (Table 3). This implies that $\delta^{13}\text{C}$ variations in coral 10AR2 are mainly subject to the temperature-dependent photosynthetic processes.

As Ca isotope fractionation is a function of temperature, it is possible that the apparent positive relationship between $\delta^{44/40}\text{Ca}$ and $\delta^{13}\text{C}$ is a result of temperature effects. However, no correlation has been found between $\delta^{44/40}\text{Ca}$ and $\delta^{18}\text{O}$ (or Sr/Ca) whereas the latter is more sensitive to temperature. This suggests that temperature may not be the dominant factor controlling variations in $\delta^{44/40}\text{Ca}$ in coral 10AR2, or the dominant factor controlling the positive correlation between $\delta^{44/40}\text{Ca}$ and $\delta^{13}\text{C}$, as its weak $\delta^{44/40}\text{Ca}$ dependence of temperature in corals may be obscured by other factors. In particular, coral $\delta^{13}\text{C}$ is strongly influenced by metabolic effects, which suggests that relationships between $\delta^{13}\text{C}$ and $\delta^{44/40}\text{Ca}$ are a result of biological effects on Ca isotopic fractionation.

4.2. Factors controlling calcium isotope fractionation in corals

Temperature-dependent calcium isotopic fractionation has been demonstrated in the precipitation of both inorganic and biogenic carbonate (Böhm et al., 2006; Gussone et al., 2003, 2005; Marriott et al., 2004; Nägler et al., 2000). Regression line slopes for different aragonitic and calcitic carbonates are basically identical (Fig. 4), which shows that temperature is an essential factor controlling calcium isotopic fractionation in carbonates. It has also been noted that fractionation factors (α) for different carbonates generally vary under a certain temperature condition, with α values being normally highest for inorganic calcite and lowest for inorganic aragonite (Fig. 3), and intermediate for biogenic carbonates. These findings indicate that mineralogy and CaCO_3 biomineralization have strong influences on $\delta^{44/40}\text{Ca}$ values, accounting for the offset of ~0.6‰ between inorganic aragonite and calcite, and the relatively small difference between varieties of biogenic

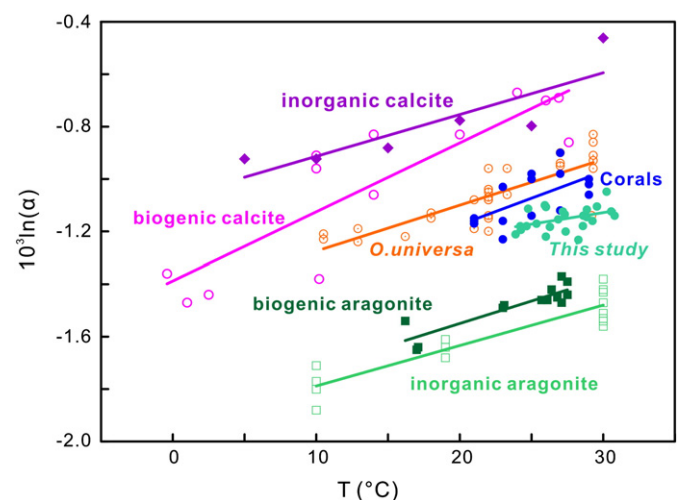


Fig. 4. Temperature dependent calcium isotopic fractionation in biogenic and inorganic carbonates. The fractionation factor (α) calculated from interpolated $\delta^{44/40}\text{Ca}$ are also plotted against the corresponding SST, displaying a weak temperature dependent trend. Inorganic calcite data are from Marriott et al. (2004), ($\delta^{44/42}\text{Ca}$ values have been converted to $\delta^{44/40}\text{Ca}$ values); Biogenic calcite and biogenic aragonite data are from Gussone et al. (2005); O.universa and inorganic aragonite data are from Gussone et al. (2003); Corals data are from Böhm et al. (2006).

carbonate (Gussone et al., 2005). However, there is some biogenic carbonate showing identical fractionation with respect to inorganic carbonate, implying that calcium isotopes fractionation in biogenic carbonate is complicated and suffers from multiple factors' influences.

With respect to corals, it seems that skeletal $\delta^{44/40}\text{Ca}$ values are weakly influenced by temperature, and strongly affected by biological effects, as calcification takes place at a closed, biologically controlled system with respect to calcium. Scleractinian corals precipitate aragonitic CaCO_3 from an internal fluid, extracytoplasmic calcifying fluid (ECF), which underlies the calcicoblastic epithelium. The calcium and inorganic carbon in ECF used for calcification are supplied by ambient seawater through both active and passive transport across the coral polyp cells (Cohen and McConnaughey, 2003). Böhm et al. (2006) suggested that calcium isotopic fractionation occurs during the passage of Ca through the calcicoblastic layer, and that no further fractionation occurs after the fractionated Ca is transported into the calcifying fluid for calcification. Our results show that $\delta^{44/40}\text{Ca}$ is significantly related to $\delta^{13}\text{C}$, suggesting that metabolic effects play an important role in the isotopic fractionation of both calcium and carbon. Calcium is a particularly important biogenic element, and may function directly in several aspects of photosynthesis (Brand and Becker, 1984; Rocha and Vothknecht, 2012). For instance, chloroplasts contain an especially large amount of calcium (15–25 mM; Rocha and Vothknecht, 2012). We therefore suspect that the involvement of Ca in photosynthesis may underlie the positive correlation between $\delta^{44/40}\text{Ca}$ and $\delta^{13}\text{C}$, as chloroplasts generally contain high large amounts of Ca^{2+} (Rocha and Vothknecht, 2012); however, further studies are needed to test this hypothesis.

5. Conclusion

We evaluated the potential of coral $\delta^{44/40}\text{Ca}$ as a proxy for paleoclimate. Skeletal time series data for two consecutive years showed little correlations between $\delta^{44/40}\text{Ca}$ and Sr/Ca ratios, $\delta^{18}\text{O}$, $\delta^{11}\text{B}$ and $\Delta\delta^{18}\text{O}$, indicating that water temperature, seawater pH, and river runoff are not the dominant forcing controlling calcium isotopic fractionation in coral skeletons. However, in symbiotic *P. lutea* corals, $\delta^{44/40}\text{Ca}$ is positively related to $\delta^{13}\text{C}$, suggesting the influence of metabolic effects on $\delta^{44/40}\text{Ca}$. This positive relationship indicates that fractionation processes occurring during coral growth are more complex than those demonstrated in culturing experiments, which show that temperature, and to a certain extent water pH, control the fractionation of calcium isotopes in carbonate. It appears that the impacts of biological processes may overwhelm those of ambient environmental conditions, at least with respect to $\delta^{44/40}\text{Ca}$ values. Therefore, additional studies are needed to reveal the role of biological processes in controlling $\delta^{44/40}\text{Ca}$ in corals, before it is used as a paleoclimate proxy.

Acknowledgments

The authors thank Dr. Liu Fang and Dr. Liu Yufei from the State Key Laboratory of Isotope Geochemistry, GIG-CAS, for their assistance with TIMS measurements. Thanks also go to the Editor Michael E. Böttcher and two anonymous reviewers for their helpful comments and constructive suggestions. This work was financially supported by the National Natural Sciences Foundation of China (41325012 and 41076025) and the National Basic Research Program of China (2013CB956103) and the State Key Laboratory of Isotope Geochemistry (SKLIG-RC-14-02). This is contribution IS-2230 from GIGCAS.

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