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Key Points:

- The seasonal and bulk zinc (Zn) isotope compositions in shallow-water coral skeletons were first reported
- The correlations between seasonal Zn isotope composition in coral skeletons and environmental variables are poor
- Interspecific differences in coral skeletal Zn isotope compositions suggest a biologically controlled fractionation process

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A Pilot Study on Zinc Isotopic Compositions in Shallow-Water Coral Skeletons

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Abstract The trace metal element zinc (Zn) participates in coral metabolic processes and therefore accumulates in their skeletons. These metabolic processes are largely controlled by the changes of environment in which they live, so Zn isotopic compositions (δ^{66}Zn) in coral skeletons may possibly serve as potential tracers for climate and environmental changes. In this study, we first reported the δ^{66}Zn in shallow-water coral skeletons by investigating with monthly resolution δ^{66}Zn values in the skeleton of a modern *Porites* coral 10AR2 from the Great Barrier Reef of Australia, and the bulk skeletal δ^{66}Zn values of several coral species from the Luhuitou Reef of Hainan Island in the northern South China Sea. Correlations between δ^{66}Zn and other climate and environmental proxies (Sr/Ca, δ^{18}O, and δ^{13}C) and instrumental environmental variables (sea surface temperature, river runoff, and chlorophyll *a*) are poor, suggesting that the effects of external environmental changes on monthly variations in δ^{66}Zn in coral skeletons are not significant. However, significant interspecific differences in the skeletal δ^{66}Zn of corals growing under identical external environments may suggest the occurrence of biologically controlled δ^{66}Zn fractionation during coral skeletons formation. In addition, the monthly δ^{66}Zn in the 10AR2 coral skeleton roughly decreases with increasing temperature, which is in agreement with the recent finding that δ^{66}Zn in coral tissues and zooxanthellae increases with increasing temperature and can serve as a proxy for thermal stress in corals. We thus suggest that the complicated coral internal biological processes hinder the use of skeletal δ^{66}Zn as a climate and environmental proxy.

Plain Language Summary Zinc (Zn) is an essential micronutrient during the growth process of corals, and its contents in coral skeletons have been investigated for tracing the history of marine environmental pollution. However, the characteristics and potential applications of δ^{66}Zn in coral skeletons have not been reported so far. In order to better understand the significance of δ^{66}Zn in coral skeletons, we first investigated the monthly resolution δ^{66}Zn values in the skeleton of a modern *Porites* coral from the Great Barrier Reef, and the bulk skeletal δ^{66}Zn values of other shallow water coral species from the Hainan Island in the northern South China Sea. The results indicate that the changes of monthly δ^{66}Zn values in coral skeletons may not be primarily controlled by external climate and environmental factors. The significant differences of skeletal δ^{66}Zn values among different coral species imply that internal biological activities of coral holobiont play an important role in Zn isotopic fractionation in shallow-water coral skeletons. In this regard, the application of δ^{66}Zn in shallow water coral skeletons as a climate and environmental indicator is limited.

1. Introduction

Stable isotopes (e.g., δ^{18}O and δ^{13}C) and elemental ratios (e.g., Sr/Ca, Mg/Ca, U/Ca) in massive reef-building coral skeletons are excellent proxies for tracing past seawater environments, such as surface seawater temperature (SST) and surface seawater salinity, thus are widely used in the reconstruction of tropical ocean paleoclimate (Beck et al., 1992; Gagan et al., 2000; Lough, 2010; Smith et al., 1979). Advances in analytical instruments and techniques over the past two decades have allowed nontraditional stable isotopes to be

used as unique tracers of different cosmochemical, geological, and biological processes (Teng et al., 2017). Under such context, nontraditional stable isotopes have been broadly applied in coral geochemistry studies, including B (Pelejero et al., 2005; Wei et al., 2009), Ca (Bohm et al., 2006; X. F. Chen et al., 2016), Mg (Saenger et al., 2013; Yoshimura et al., 2011), stable Sr (Fruchter et al., 2016; Rüggeberg et al., 2008), Mo (Voegelin et al., 2009; Z. B. Wang et al., 2019), Cr (Pereira et al., 2016), and Ba (Liu et al., 2019; Pretet et al., 2015). These isotopic systems have created new opportunities for coral-based paleoclimate research. For example, they may be used as proxies to identify climate and environmental changes (Bohm et al., 2006; Fruchter et al., 2016; Pelejero et al., 2005; Wei et al., 2009), responses of coral biological activities to climate change (X. F. Chen et al., 2016; Z. B. Wang et al., 2019) and oceanic elemental cycling (Liu et al., 2019).

Zinc (Zn) is a trace element in coral skeletons, which can be preserved in the aragonite skeleton by replacing Ca^{2+} during the calcification process of the coral (Esslemont, 2000; Fallon et al., 2002). In recent decades, Zn contents in coral skeletons have usually been used to track the pollution history of seawater during coral growth (Al-Rousan et al., 2007; T. R. Chen et al., 2010; Nour & Nouh, 2020; B. S. Wang et al., 2011). However, the characteristic and significance of Zn isotopes of coral skeletons have not been reported so far. Zn has five naturally stable isotopes: ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn, and ^{70}Zn (Rosman, 1972). Zn isotope composition is expressed in delta notation, that is, $\delta^{66}Zn = (^{66}Zn/^{64}Zn_{sample}/^{66}Zn/^{64}Zn_{standard} - 1) \times 1{,}000$, which is the relative deviation of the $^{66}Zn/^{64}Zn$ ratio of a sample from Zn reference material in parts per 1,000.

Although excess Zn is toxic, Zn is still an essential nutrient element for coral growth because it is an important cofactor for many enzymes (e.g., superoxide dismutase and carbonic anhydrase) in corals and endosymbiotic zooxanthellae, which are important for the photosynthesis of zooxanthellae and calcification of polyps (Ferrier-Pagès et al., 2005, 2018). Therefore, Zn isotopic fractionation may occur during its participation in biological activities of symbiotic zooxanthellae and coral polyps, and the heat stress-induced change in the Zn isotopic composition in coral symbionts and host tissues has been identified (Ferrier-Pagès et al., 2018). Considering coral biological processes are largely controlled by the changes of environment in which they live, the coral skeletal $\delta^{66}Zn$ could possibly be used as a proxy for climate and environmental change.

Aiming to explore the possibility of coral skeletal $\delta^{66}Zn$ as a proxy for climate and environmental change, we measured monthly resolved $\delta^{66}Zn$ and other geochemical proxies (Sr/Ca, $\delta^{18}O$, and $\delta^{13}C$) in the skeleton of a modern *Porites* coral from the Great Barrier Reef (GBR) of Australia to study the relationships between $\delta^{66}Zn$ values and instrumental environmental parameters (SST, river runoff, and chlorophyll *a* concentration) as the coral grew. We also measured the bulk $\delta^{66}Zn$ values in skeletons of different coral species from the Luhuitou (LHT) Reef in Sanya Bay of the northern South China Sea (SCS) to identify possible Zn isotopic fractionation related with coral biological activities. According to current knowledge, this is the first study reporting the Zn isotope compositions in shallow-water coral skeletons, which will benefit the understanding of the Zn isotope fractionation in biogenic carbonate and the developing of new potential proxy in coral-based climate and environmental research.

2. Materials and Methods

2.1. Coral Sampling

The GBR coral core 10AR2 was extracted in April 2010 using an underwater pneumatic drill from a living *Porites* colony at a water depth of ~ 4 m on the Arlington Reef (16°38′17″S, 146°06′13″E), which is a middle-shelf crescentic reef located ~44 km offshore from the Barron River mouth in northeastern Australia (Figures 1a and 1b). The coral core was first cut into slabs of 7 mm thick. Then, X-ray photographs were taken to reveal regular and well-defined annual density bands, which were used to guide the subsampling process. Next, the coral slabs were soaked in 10% H_2O_2 for 24 h to remove organic matter followed by ultrasonic cleaning in deionized water for 30 min (×3 times) to remove surface contaminates (Wei et al., 2007). Powder samples for geochemical analysis (Sr/Ca, $\delta^{13}C$, $\delta^{18}O$, Zn content, and $\delta^{66}Zn$) were collected from the top of the skeleton at 1–2 mm intervals along the main growth axis using a milling machine with a high speed steel drill bit, and ultrapure water and dust-free paper were used to clean the drill bit between sample collections. A total of 52 subsamples were collected, covering a time span of ~4–5 years. Each subsample was further ground using an agate mortar to evenly mix the sample, and the pestle and mortar were washed with dilute acid and ultrapure water to avoid cross-contamination between samples. The coral core had been previously

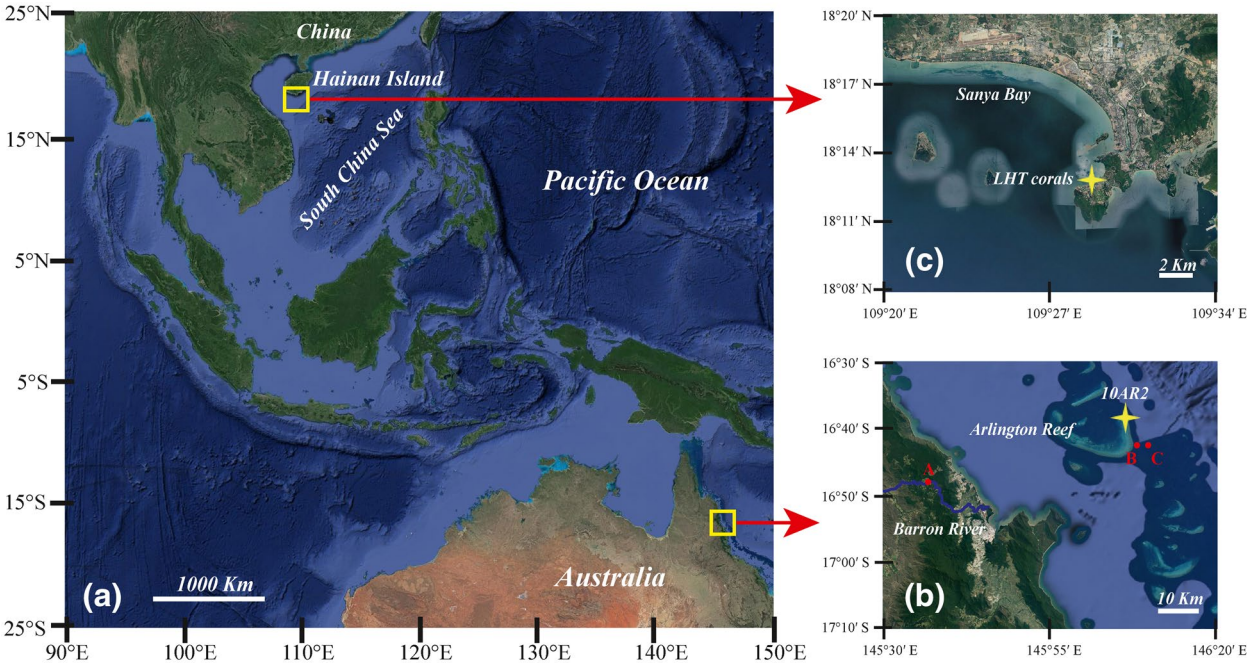


Figure 1. Satellite image of the sampling site for coral samples. (a) Regional location map of the GBR and Sanya Bay, Hainan Island, (b) the 10AR2 sampling site in Arlington Reef, (c) the LHT coral sampling site. Yellow stars indicate sampling locations. Red solid circles represent the observation locations for the data of Barron River runoff (A), chlorophyll *a* (B), and SST (C), and they are about 55, 8.5, and 10 km away from the sampling site of coral 10AR2, respectively. GBR, Great Barrier Reef; LHT, Luhuitou; SST, surface seawater temperature.

used for monthly to annual resolution studies of elemental ratios and isotopic compositions, including Sr/Ca, Mg/Ca, $\delta^{13}C$, $\delta^{18}O$, $\delta^{44/40}Ca$, and $\delta^{98}Mo$ (X. F. Chen et al., 2016; Deng et al., 2014; Z. B. Wang et al., 2019).

Six different species of living scleractinian corals were used for the bulk skeletal $\delta^{66}Zn$ analysis. These samples were collected in June of 2014 from the LHT Reef platform in Sanya Bay located at the southernmost edge of Hainan Island in the northern SCS (18°12′-18°13′, 109°28′-109°30′E; Figures 1a and 1c), and have been used to investigate $\delta^{98}Mo$ compositions in coral reef systems (Z. B. Wang et al., 2019). The sampling work was carried out on the same reef platform by divers at a water depth of ~5 m, which means that these samples were grown under similar environmental conditions. Pretreatments of these samples followed the strategy described above for the coral core 10AR2.

2.2. Geochemical Analysis

Zn content analyses were performed on a Thermo Fisher iCAP RQ inductively coupled plasma-mass spectrometry at Guizhou Tongwei Analytical Technology Co., Ltd. Approximately 50 mg of each coral powder sample was poured into a Teflon PFA beaker which was preadded with 0.5 ml ultrapure water. After 15.34 N HNO_3 was added dropwise into the beaker until there was no foaming, an additional 300 μl was added to ensure complete digestion of the sample. The dissolution was maintained on an oven at 90°C for half an hour, and after cooling down, 5 ml 2% HNO_3 was added into the digested sample solution. Finally, sample solution was diluted to 2,000 times with 2% HNO_3 and added with 6 ppb Rh, In, and Re internal spikes. USGS standard W-2a was used as reference standard and crossed checked with Basalt, Hawaiian Volcanic Observatory-2 and other reference materials. Instrument drift and mass bias were corrected with internal spikes and external monitors. The external precision for Zn content was generally better than 1.52% (relative standard deviation [RSD]).

The separation and measurement of Zn isotopes in coral samples were carried out following the methods described by J. B. Chen et al. (2009). Acids used in this study were further purified by subboiling distillation in Teflon stills. All solutions were prepared with ultrapure water (18.25 MΩ·cm resistivity) obtained from a Millipore water purification system. All work was carried out under clean laboratory conditions in "class

100" clean hoods. First, ~0.2 g of fine coral powder was directly dissolved in 3 ml 6N HCl and was evaporated to dryness. Then, the evaporated sample was dissolved in 1.2 ml 6 N HCl again and used for further chemical separation. Finally, an aliquot of the dissolved sample (1 ml) was loaded onto a column filled with 1.6 ml AGMP-1M anion resin (Bio-Rad). After matrix elution with 10 ml 6 N HCl, Cu, Fe, and Zn were collected from 20 ml 6 N HCl, 10 ml 2 N HCl, and 10 ml 0.5 N HNO_3, respectively. The final Zn fraction was evaporated and conditioned for isotopic measurement (dissolution in 2% HNO_3 and Cu addition).

Zn isotopic analyses were carried out using a Neptune Plus multiple-collector ICP-MS (Thermo-Fisher Scientific). All Zn isotope ratios were measured relative to the standard reference material Zn (Alfal Aesar solution) from the Institut de Physique du Globe de Paris (IPG) and reported relative to the Johnson Matthey (JMC) Lyon Zn isotopic standard ($\delta^{66}Zn_{IPG/JMC} = 0.04 \pm 0.03\%$, Guinoiseau et al., 2016). Replicate analyses of the NIST SRM 683 standard yielded a reproducibility of 0.06% ($\delta^{66}Zn_{SRM683/JMC} = 0.11 \pm 0.06\%$, $n = 131$, n is replicated times of the same solution, 2 standard deviation [SD]). In addition, coral standards JCp-1 (an international coral standard sample, Inoue et al., 2004) and AR-std (an in-house coral standard sample) were repeatedly measured in this study using the above chemical and analytical protocols for quality control. The $\delta^{66}Zn$ values of JCp-1 and AR-std were $-0.05 \pm 0.12\%$ ($n = 6$, 2 SD, n is replicated times of the whole procedure) and $0.56 \pm 0.10\%$ ($n = 6$, 2 SD, n is replicated times of the whole procedure), respectively, which are first reported in this study. The total Zn procedural blank was less than 10 ng, representing <10% of all Zn in the samples.

Coral skeletal $\delta^{18}O$ and $\delta^{13}C$ analyses were conducted using a GV Isoprime II stable isotope ratio mass spectrometer coupled with a MultiPrep carbonate device that used 102% H_3PO_4 at 90°C to extract CO_2 from the coral samples following the procedures described by Deng et al. (2009). Isotope data were normalized to Vienna Pee Dee Belemnite using the NBS-19 standard. Multiple measurements conducted based on this standard yielded a reproducibility of 0.05% for $\delta^{13}C$ and of 0.07% for $\delta^{18}O$.

Analyses of Sr/Ca ratios were conducted on a Varian Vista Pro inductively coupled plasma atomic emission spectrometer using the method reported by Wei et al. (2007). The standard reference material for calibration is the JCp-1 *Porites* standard. All Sr/Ca data were normalized to JCp-1 with Sr/Ca = 8.838 mmol/mol (Hathorne et al., 2013). Replicate analyses of an in-house *Porites* coral standard solution BH-7 showed excellent levels of reproducibility with an external precision of 0.16% (RSD).

2.3. Chronology Construction

To perform a comparative study of coral skeletal $\delta^{66}Zn$ values and other geochemical proxies or monthly instrumental records, the chronological years of the coral 10AR2 were constructed using the Sr/Ca ratios which track changes in ambient seawater temperature and while assuming that each Sr/Ca cycle represents 1 year (Deng et al., 2009; X. J. Wang et al., 2018). Minima of Sr/Ca ratios were assigned to the start of each year, which is generally the hottest period (January) in the southern hemisphere. Monthly data from each chronological year were obtained by linear interpolation (for an annual cycle with <12 data points) or nearest neighbor smoothing (for an annual cycle with >12 data points) in each Sr/Ca cycle assuming the linear growth of corals (X. J. Wang et al., 2018). According to the drilling time and after removing the upper three data points that may be subject to organic contamination, the final growth chronology for this study was assigned to January 2006 to January 2010.

2.4. Climatic and Environmental Records

As recent in situ instrumental climatic and environmental records for the Arlington Reef were not available, those from neighboring areas were employed to evaluate the controlling factors and fractionation mechanisms of $\delta^{66}Zn$ in the skeleton of the 10AR2 coral. Monthly SST data at a 0.01° spatial resolution centered on 16.71°S, 146.16°E were extracted from the Multiscale Ultra-high Resolution SST data set (https://coastwatch.pfeg.noaa.gov/erddap/griddap/jplMURSST41mday.html). Monthly resolution Barron River runoff records for the nearest Myola station (~27.1 km away from the Barron River estuary) were acquired from the Water Monitoring Information Portal of the Queensland Government (https://water-monitoring.information.qld.gov.au/). Monthly chlorophyll *a* (Chl *a*) concentrations at a 0.1° spatial resolution centered on 16.71°S, 146.13°E were obtained from the Sea-viewing Wide Field-of-view Sensor data set (https://coastwatch.pfeg.noaa.gov/erddap/griddap/erdSW2018chlamday.html).

2.5. Statistical Analysis

To explore potential factors affecting the Zn isotopic variations in coral skeletons, correlation analyses were performed between the monthly δ^{66}Zn and geochemical and instrumental parameters by the Excel Pearson function. As serial correlation in time series regression will reduce the degrees of freedom for the calculation of the significance level, the *p* values were calculated according to Hu et al. (2017) to avoid overestimation of significance level.

3. Results

The geochemical results for 10AR2 are reported in Table 1 and plotted in Figure 2. Skeletal Zn content ranges from 0.38 to 2.54 μg/g with an average of 0.77 μg/g (Figure 2a). With the exception of sample 10AR2-50, which shows abnormally high levels of Zn content relative to the other samples, all other 10AR2 samples have a Zn content level of less than 2 μg/g (Figure 2a). Therefore, this sample is an outlier and will not be considered in the following discussion of the data. The δ^{66}Zn values in the skeleton of 10AR2 do not have pronounced annual cycles showing in Sr/Ca, δ^{18}O, and δ^{13}C time series over time, and display a large variation of 0.62% (from −0.01% to 0.61%) with an average of 0.39 ± 0.27% ($n = 52$, 2 SD, Figure 2).

Based on the chronological frame constructed by Sr/Ca ratios, other monthly geochemical time series including δ^{18}O, δ^{13}C, and δ^{66}Zn series for January 2006 to January 2010 for the 10AR2 coral were obtained by linear interpolation or nearest neighbor smoothing, and they are shown with monthly instrumental climatic and environmental records including SST, river runoff, and Chl *a* concentration records for the same time period (Figure 3). Although some of the correlations are significant, the strengths of linear correlation between δ^{66}Zn values and other climate and environmental proxies and instrumental environmental variables are weak or very weak (i.e., *r* values are far from +1 or −1; Figure 4).

The elemental contents and isotopic compositions of Zn in the skeletons of six different coral species in LHT are listed in Table 2 and plotted in Figure 5. Significant interspecies differences are found in both Zn and δ^{66}Zn values, which range from 0.20 to 9.39 μg/g and from −0.20% to 0.13%, respectively.

4. Discussion

4.1. Temperature

Correlations between the δ^{66}Zn time series of 10AR2 coral and Sr/Ca, δ^{18}O, and SST are poor (Figure 4), which suggests that temperature cannot be a predominant factor in controlling the variations in skeletal δ^{66}Zn. The correlation between δ^{66}Zn values and SST records were found to be statistically significant ($r = -0.38$, $n = 49$, $p < 0.01$, Figure 4d), showing that SST may possibly affect changes in skeletal δ^{66}Zn. However, the linear regression of SST and δ^{66}Zn produced a small slope (−0.028%/°C, Figure 4d), indicating that δ^{66}Zn sensitivity to SST is not strong. Satellite records show that the overall seasonal variation amplitude of SST is ~ 6°C for the studied period, which can result in an isotope variation of roughly 0.17%. The predicted amplitude is much smaller than the observed range of 0.62% in the skeleton of coral 10AR2. This means that even temperature plays a role, monthly SST changes can explain only 14% of Zn isotope variation observed in the skeleton while fractionation may be predominantly caused by other factors. Previous studies have demonstrated that the incorporation of some trace metals (e.g., Mg and Sr) into coral skeleton aragonite is temperature-dependent (Armid et al., 2011; Cohen & Gaetani, 2010; Kinsman & Holland, 1969). However, the effect of temperature on the distribution coefficient (K_d) of Zn between seawater and coral aragonite is not significant (Jiang et al., 2020). Thus, the weak correlation between SST and δ^{66}Zn may also result from the weak temperature dependence of the K_d of Zn between seawater and coral aragonite.

4.2. Changes in Seawater δ^{66}Zn

The skeleton of the coral forms by precipitation from the calcifying fluid in its semiclosed calcification space (Tambutté et al., 2011), and seawater can enter the calcification space to form the most basic calcifying fluid compositions (Gaetani & Cohen, 2006; Gagnon et al., 2007, 2012; Tambutté et al., 2011). Therefore, the composition of calcifying fluid may inherit some of the characteristics of seawater and the Zn isotopic

Table 1
Geochemical Results for 10AR2 Coral Core

Sample name	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	Sr/Ca (mmol/mol)	$\Delta\delta^{18}O$ (‰)	Zn content (μg/g)	$\delta^{66}Zn$ (‰)	2SD	*N*
10AR2-1	−3.44	−4.79	8.998	−0.52	0.75	0.28	0.05	3
10AR2-2	−3.30	−5.02	8.964	−0.61	0.53	0.31	0.04	2
10AR2-3	−3.03	−5.23	8.871	−0.46	0.44	0.24	0.14	2
10AR2-4	−2.89	−5.34	8.865	−0.55	0.38	0.27	0.04	2
10AR2-5	−3.08	−4.93	8.896	−0.26	0.51	0.19	0.17	2
10AR2-6	−3.38	−4.67	9.035	−0.55	0.56	0.45	0.06	2
10AR2-7	−3.59	−4.36	9.061	−0.34	0.63	0.47	0.09	2
10AR2-8	−3.74	−4.43	9.011	−0.21	0.64	0.30	0.11	2
10AR2-9	−3.61	−4.23	9.090	−0.32	0.65	0.49	0.07	2
10AR2-10	−3.50	−4.60	9.042	−0.51	0.57	0.30	0.03	2
10AR2-11	−3.20	−4.89	8.965	−0.50	0.54	0.23	0.14	2
10AR2-12	−3.21	−5.17	8.904	−0.53	0.52	0.32	0.05	2
10AR2-13	−3.01	−5.04	8.911	−0.43	0.51	0.47	0.09	2
10AR2-14	−2.74	−4.95	8.905	−0.31	0.56	0.36	0.01	2
10AR2-15	−2.58	−4.77	8.924	−0.21	0.72	0.21	0.07	2
10AR2-16	−2.65	−4.61	8.962	−0.20	0.69	0.32	0.01	2
10AR2-17	−2.85	−4.55	8.998	−0.29	0.74	0.41	0.00	3
10AR2-18	−3.06	−4.24	9.065	−0.24	0.78	0.37	0.06	2
10AR2-19	−3.37	−4.31	9.063	−0.30	0.97	0.43	0.01	2
10AR2-20	−3.69	−4.38	9.102	−0.53	0.96	0.36	0.01	3
10AR2-21	−3.69	−4.43	8.981	−0.10	0.74	0.52	0.01	2
10AR2-22	−3.51	−4.69	8.949	−0.22	0.71	0.44	0.11	2
10AR2-23	−3.38	−4.74	8.893	−0.06	0.99	0.21	0.05	2
10AR2-24	−3.49	−4.93	8.813	0.07	0.62	0.09	0.03	2
10AR2-25	−3.55	−4.86	8.864	−0.06	0.74	0.38	0.03	2
10AR2-26	−3.44	−4.89	8.922	−0.32	0.61	0.46	0.02	2
10AR2-27	−3.34	−4.82	8.932	−0.29	0.70	0.51	0.06	2
10AR2-28	−3.53	−4.65	9.018	−0.46	0.75	0.58	0.00	2
10AR2-29	−3.24	−4.61	9.004	−0.37	0.79	0.26	0.02	2
10AR2-30	−3.19	−4.54	8.978	−0.19	0.92	0.35	0.01	2
10AR2-31	−3.32	−4.42	9.087	−0.51	0.86	0.52	0.02	2
10AR2-32	−3.44	−4.36	9.113	−0.55	0.99	0.55	0.06	3
10AR2-33	−3.68	−4.25	9.123	−0.48	0.91	0.45	0.01	2
10AR2-34	−3.79	−4.60	9.135	−0.88	0.80	0.51	0.03	3
10AR2-35	−3.95	−4.74	9.135	−1.01	0.88	0.57	0.02	2
10AR2-36	−3.82	−4.96	9.004	−0.71	0.83	0.57	0.03	2
10AR2-37	−3.53	−5.12	8.978	−0.77	0.83	0.54	0.07	2
10AR2-38	−3.52	−5.26	8.939	−0.76	0.80	0.56	0.05	2
10AR2-39	−3.32	−5.18	8.948	−0.71	0.68	0.47	0.06	2
10AR2-40	−3.06	−5.01	8.845	−0.14	0.67	0.51	0.04	2
10AR2-41	−2.94	−5.03	8.856	−0.20	0.76	0.47	0.05	2
10AR2-42	−2.96	−4.85	8.841	0.04	0.68	0.39	0.03	2
10AR2-43	−3.01	−4.76	8.981	−0.42	0.82	0.29	0.01	2

Table 1
Continued

Sample name	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	Sr/Ca (mmol/mol)	$\Delta\delta^{18}O$ (‰)	Zn content (μg/g)	$\delta^{66}Zn$ (‰)	2SD	*N*
10AR2-44	−2.97	−4.64	9.006	−0.40	0.82	0.42	0.00	2
10AR2-45	−3.10	−4.53	9.002	−0.28	0.85	0.51	0.02	2
10AR2-46	−3.07	−4.56	9.121	−0.78	0.73	0.48	0.02	2
10AR2-47	−3.28	−4.63	9.130	−0.89	0.88	0.61	0.05	2
10AR2-48	−3.47	−4.69	9.035	−0.57	0.89	0.56	0.01	2
10AR2-49	−3.43	−4.80	8.956	−0.36	0.85	0.30	0.05	2
10AR2-50	−3.31	−5.02	8.998	−0.75	2.54	−0.01	0.06	3
10AR2-51	−3.18	−5.08	8.926	−0.52	1.05	0.48	0.02	3
10AR2-52	−3.04	−5.24	8.897	−0.57	0.84	0.23	0.02	3

Note. *N* is replicated times of the same solution.
Abbreviation: Zn, zinc.

composition of seawater is likely to affect the $\delta^{66}Zn$ values of coral skeletons. It has been found that seasonal variations in $\delta^{66}Zn$ occur in the upper water column (0–150 m), with heavier $\delta^{66}Zn$ values in the late autumn than in the summer (Samanta et al., 2017). Therefore, effects of river input and biological uptake were studied to determine whether the monthly variations of skeletal $\delta^{66}Zn$ are derived from those in seawater $\delta^{66}Zn$, as they may play a role in the monthly variations of coral skeletal $\delta^{66}Zn$ by affecting the chemical composition of seawater.

4.2.1. River Input

The Arlington Reef lies ~44 km offshore from the Barron River, which is the largest river on the northeast coast of Australia. Thus, river input from the Barron River may modify the chemical compositions of reef water. Considering that no $\delta^{66}Zn$ data are available for Barron River water and the total amount of Zn and the $\delta^{66}Zn$ in seawater would be altered by seasonal changes in river runoff, the correlation between coral $\delta^{66}Zn$ and river runoff was analyzed. However, there is no significant relationship between the two parameters (Figure 4e), indicating that the impact of freshwater input may not be the main reason for the seasonal change in skeletal $\delta^{66}Zn$. Even so, it should be noted that Zn content and $\delta^{66}Zn$ in river water may change depending on climatic conditions and weathering mechanisms (e.g., Little et al., 2019), so the explanation on the correlation between coral $\delta^{66}Zn$ and river runoff should be cautious.

Residual $\delta^{18}O$ ($\Delta\delta^{18}O$), a proxy for river runoff (McCulloch et al., 1994), was also used to assess the effect of runoff on coral skeletal $\delta^{66}Zn$ (Table 1). The $\Delta\delta^{18}O$ was calculated by subtracting the effect of temperature from coral $\delta^{18}O$ using the equation $\Delta\delta^{18}O = d\delta^{18}O / dT \times \left[T_{\delta^{18}O} - T_{Sr/Ca}\right]$ (Gagan et al., 1998). In the equation, $d\delta^{18}O/dT$ is the slope (0.23‰/°C) reported by Gagan et al. (2012), and $T_{\delta^{18}O}$ and $T_{Sr/Ca}$ are the apparent temperatures from the $\delta^{18}O$ values and Sr/Ca ratios, respectively. The Sr/Ca-SST relationship was employed from Deng et al. (2014). The weak correlation between interpolated $\Delta\delta^{18}O$ and interpolated $\delta^{66}Zn$ of 10AR2 ($r = -0.31$, $n = 49$, $p < 0.05$) also shows that the role of changes in seawater $\delta^{66}Zn$ by river runoff in coral skeletal $\delta^{66}Zn$ is likely limited.

4.2.2. Biological Uptake

Zn is the second most prevalent micronutrient in phytoplankton biomass, playing a fundamental role in DNA replication and transcription and serving as a cofactor in carbonic anhydrase and alkaline phosphatase enzymes (Weber et al., 2018). It has been reported that phytoplankton in the upper seawater column generally absorb lighter ^{64}Zn at a faster rate relative to its heavier counterparts (Gelabert et al., 2006; John & Conway, 2014; John et al., 2007; Samanta et al., 2018), leaving the heavier $\delta^{66}Zn$ composition in surface seawater (Bermin et al., 2006; John & Conway, 2014; Zhao et al., 2014). As bioabsorption increases, more ^{64}Zn is absorbed, and the $\delta^{66}Zn$ in seawater becomes heavier. Therefore, the $\delta^{66}Zn$ value of seawater

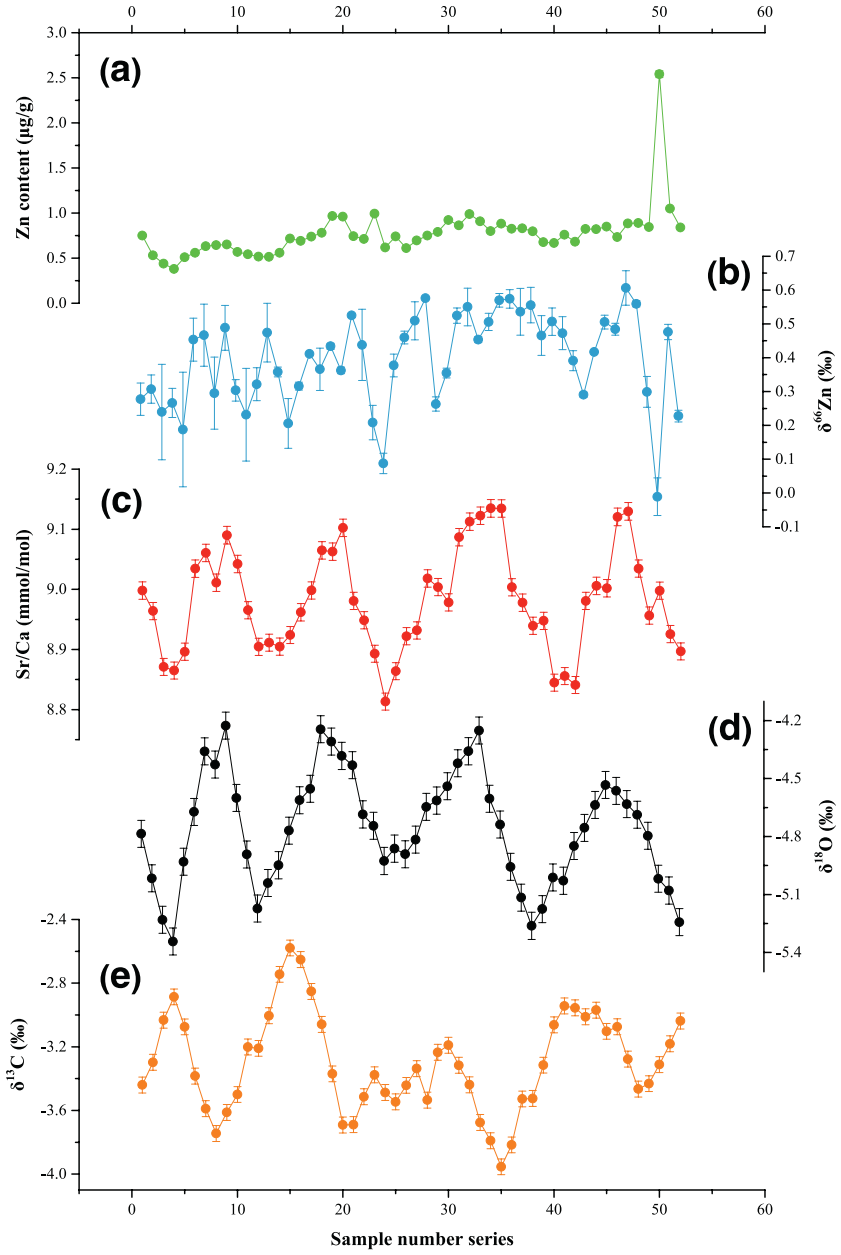
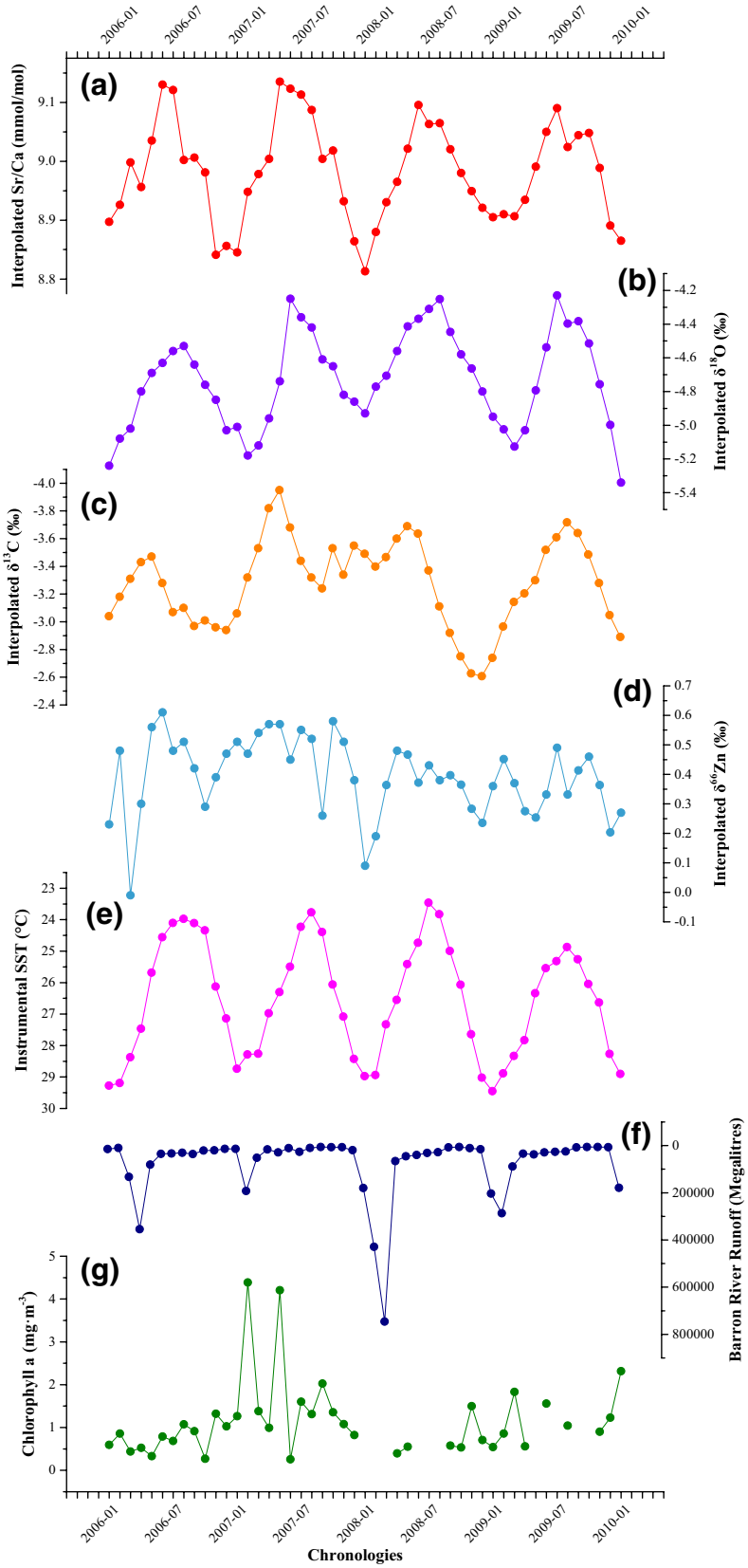


Figure 2. Test results for various geochemical parameters of the 10AR2 coral skeletal samples and coral ages as the sample number increases. (a) Zn content, (b) δ^{66}Zn values, (c) Sr/Ca ratios, (d) δ^{18}O values, (e) δ^{13}C values. The error bars for Zn content are too short to be visible. Zn, zinc.

should show similar seasonal changes with the seasonal variation of surface marine productivity (Samanta et al., 2017), which may affect the δ^{66}Zn composition of coral skeletons.

The concentration of Chl *a* in water is generally considered to represent the biomass of phytoplankton with higher Chl *a* concentrations denoting the presence of more phytoplankton, and higher concentrations of Chl *a* are often observed during warm seasons (Ye et al., 2017). Here, we compared the relationship between coral δ^{66}Zn and Chl *a* concentrations (Figures 3d and 3g) and found the correlation to be very weak (r = 0.18, n = 39, $p > 0.05$, Figure 4f). Moreover, as biomass increases during the warm season, the δ^{66}Zn of seawater should theoretically become higher. If changes in seawater δ^{66}Zn are responsible for controlling the monthly variations in δ^{66}Zn in coral skeletons, then skeletal δ^{66}Zn should be positively correlated with SST, which runs contrary to the weak negative correlation between coral δ^{66}Zn and SST (Figure 4d). Thus,


2006-01
2006-07
2007-01
2007-07
2008-01
2008-07
2009-01
2009-07
2010-01
(a)
Interpolated Sr/Ca (mmol/mol)
9.1
9.0
8.9
8.8
(b)
Interpolated δ18O (‰)
-4.2
-4.4
-4.6
-4.8
-5.0
-5.2
-5.4
(c)
Interpolated δ13C (‰)
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
-2.6
-2.4
(d)
Interpolated δ66Zn (‰)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
(e)
Instrumental SST (°C)
23
24
25
26
27
28
29
30
(f)
Barron River Runoff (Megalitres)
0
200000
400000
600000
800000
(g)
Chlorophyll a (mg·m-3)
5
4
3
2
1
0
Chronologies

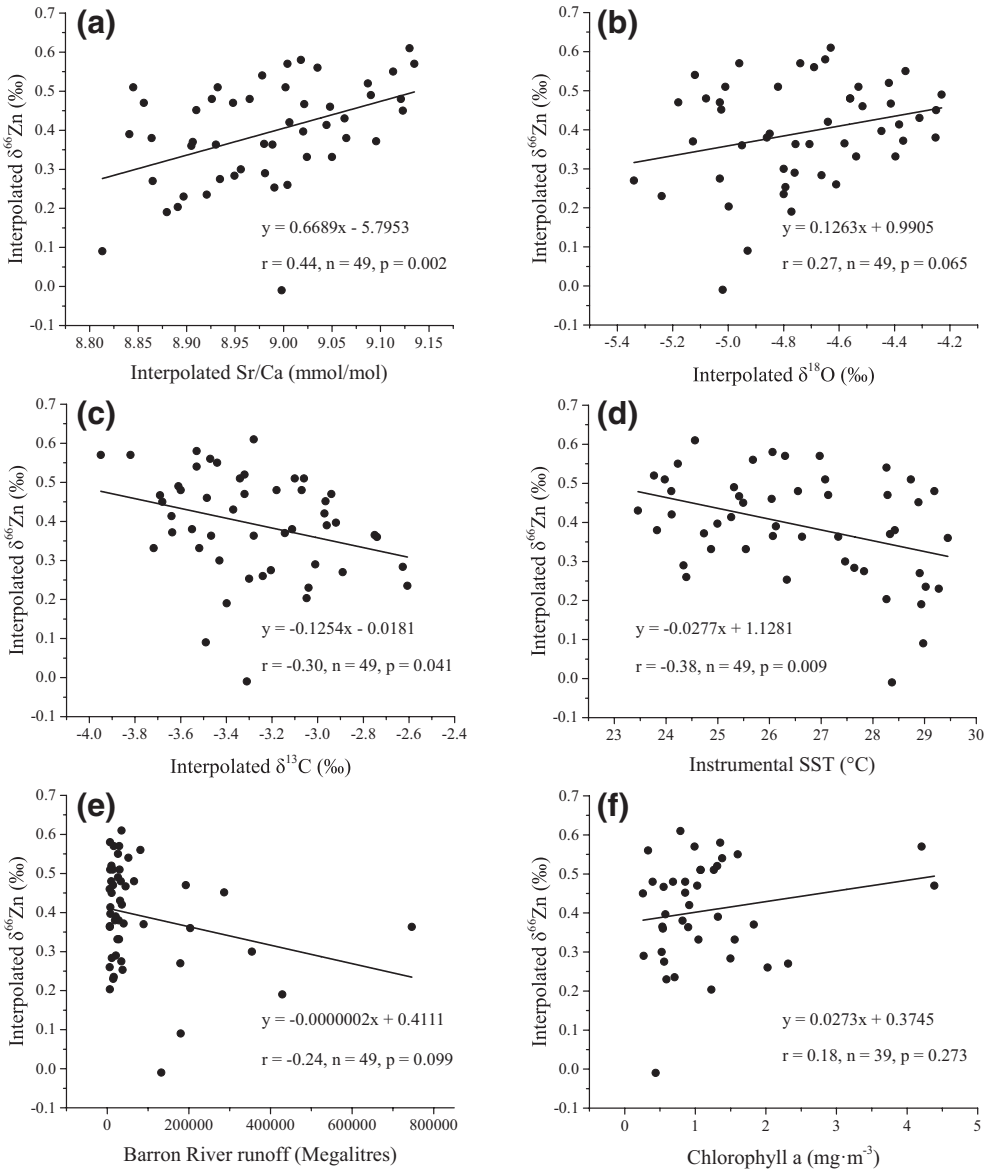


Figure 4. Relationship between interpolated δ^{66}Zn data of 10AR2 and other climate proxies and instrumental environmental variables: (a) Sr/Ca values, (b) δ^{18}O values, (c) δ^{13}C values, (d) SST data, (e) Barron River runoff data, (f) chlorophyll *a* concentration data. SST, surface seawater temperature; Zn, zinc.

in combining these two points, we can infer that the change in seawater δ^{66}Zn caused by external biological uptake is not the main reason for the monthly variations in skeletal δ^{66}Zn.

4.3. Internal Biological Processes

For zooxanthellate corals, calcification depends on a mutualistic partnership between coral and endosymbiotic zooxanthellae (Cohen & McConnaughey, 2003; McCulloch et al., 2017), and so variations of geochemical proxies in coral skeletons are inevitably affected by biological effects (i.e., vital effect) of coral and

Figure 3. Interpolated geochemical time series of 10AR2 coral skeletal samples and corresponding instrumental records for the period 2006–2010. (a) Sr/Ca ratios, (b) δ^{18}O values, (c) δ^{13}C values, (d) δ^{66}Zn values, (e) satellite SST (plotted on an inverted scale on the *y* axis), (f) Barron River runoff, (g) chlorophyll *a* concentration. SST, surface seawater temperature; Zn, zinc.

Table 2
The Elemental Content and Isotopic Compositions of Zn in Six Different Species of Corals in LHT Corals

Sample name	Species	Zn content (μg/g)	δ^{66}Zn (‰)	2SD	*N*
LHT001	*Porites*	0.20	−0.20	0.05	2
LHT002	*Fungia*	1.16	−0.14	0.06	3
LHT003	*Hydnophora*	1.27	−0.10	0.03	3
LHT004	*Montipora*	9.39	0.02	0.06	3
LHT005	*Acropora*	1.75	0.13	0.01	3
LHT006	*Pocillopora*	2.24	0.01	0.03	3

Note. *N* is replicated times of the same solution.
Abbreviations: LHT, Luhuitou; Zn, zinc.

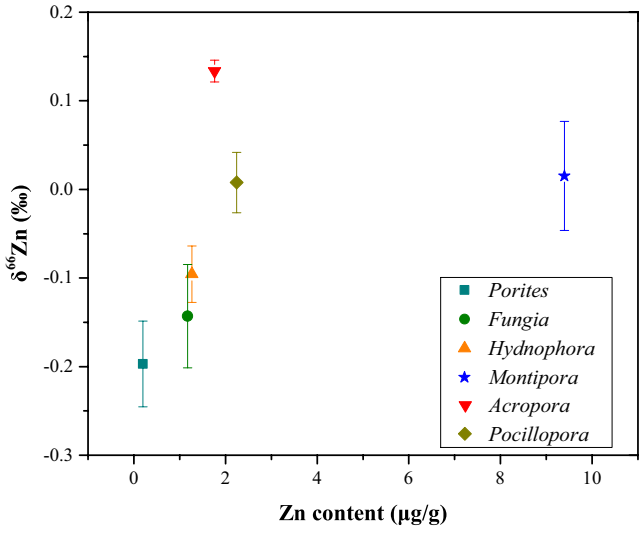


Figure 5. The δ^{66}Zn values and Zn content of different coral species from the Luhuitou reef. Zn, zinc.

zooxanthellae. It has been demonstrated that Zn is involved in multiple biological processes in corals and notably acts as a cofactor in enzymatic photosynthetic reactions (Houlbreque et al., 2012). Therefore, the fractionation of Zn isotopes in coral skeletons may be related to the role of Zn in internal biological activities, and fractionation may occur during its participation in various metabolic activities. Skeletal δ^{13}C is generally considered to be mainly affected by vital effects (X. F. Chen et al., 2016; McConnaughey et al., 1997; Swart et al., 1996). Thus, we compared the skeletal δ^{13}C with the skeletal δ^{66}Zn of coral 10AR2 and found a weak but significant correlation between them ($r = -0.30$, $n = 49$, $p < 0.05$, Figure 4c), which means that variations in skeletal δ^{66}Zn may possibly be regulated by internal biological processes occurring in the coral organism. On the other hand, δ^{66}Zn compositions and Zn content in the skeletons of different coral species in the LHT reef have significant interspecies differences (Figure 5, Table 2). Since these corals grew under identical natural environments, the interspecific differences in Zn content and isotope composition should not be attributable to environmental variables and may be triggered by the internal metabolic and biological regulation of the corals themselves.

A recent study found a significant increase in the δ^{66}Zn signature of symbionts and host tissues (polyps) at high temperatures (Ferrier-Pagès et al., 2018), and it is believed that such isotopic variations can be related to an increase in reactive oxygen species (ROS) by thermal stress in coral tissue (Cunning & Baker, 2013; Ferrier-Pagès et al., 2018). ROS is a by-product of normal cell metabolism in plants and animals (Karuppanapandian et al., 2011; Thannickal & Fanburg, 2000; Turrens, 2003), but it is a core biological constituent and regulates the metabolic changes of zooxanthellae and coral hosts (Suggett & Smith, 2019). Meanwhile, metabolic changes caused by external environmental factors in turn cause fluctuations in the "ROS reservoir" of the coral holobiont, which affects the absorption of nutrients and the physiological functions of certain substances in the coral holobiont (e.g., protein, lipids, and DNA; Suggett & Smith, 2019). For example, under high temperature stress, the balance between the production and elimination of ROS will be disturbed (Ferrier-Pagès et al., 2018; Karuppanapandian et al., 2011). When cells produce more ROS than their antioxidant capacity allows, the excess ROS will damage macromolecules such as lipids, proteins, and DNA (Thannickal & Fanburg, 2000). In the process of destruction, as light isotopes create weaker links with molecules than heavy isotopes (Schauble, 2004), bonds with light isotopes are more easily disrupted by ROS and are preferentially released from polyps and zooxanthellae, resulting in heavier δ^{66}Zn in coral tissue and symbionts (Ferrier-Pagès et al., 2018). The released light isotopes of Zn may then be actively transported along with Ca^{2+} from the coelenteron to calcifying fluid for calcification via the Ca-ATPase pump (Nakamura et al., 2013), leading to lighter δ^{66}Zn in coral skeletons.

Although the negative correlation between SST and δ^{66}Zn is weak, the discovery that δ^{66}Zn in coral skeletons decreases with increasing temperature is in agreement with Ferrier-Pagès et al. (2018)'s finding that elevated δ^{66}Zn in coral tissues and zooxanthellae during heat stress events. These phenomena reflect the biogeochemical cycling of Zn within corals and the coordinated integration of tissues, zooxanthellae, and skeletons. Thus, we suggest that when temperatures increase the light Zn isotopes released from coral tissue and zooxanthellae are imported and preserved in the coral skeleton, leading to depleted skeletal δ^{66}Zn results and vice versa (Figure 6). It is possible that the 10AR2 coral did not undergo severe thermal stress during the study period, so the correlation between SST and δ^{66}Zn is weak. Even though their correlation is not strong, the minima of δ^{66}Zn almost always occurred during warm summers (Figures 3d and 3e). Therefore, the monthly variation in skeletal δ^{66}Zn would likely result from the changes in the metabolic intensity of polyps and zooxanthellae, and the correlation between

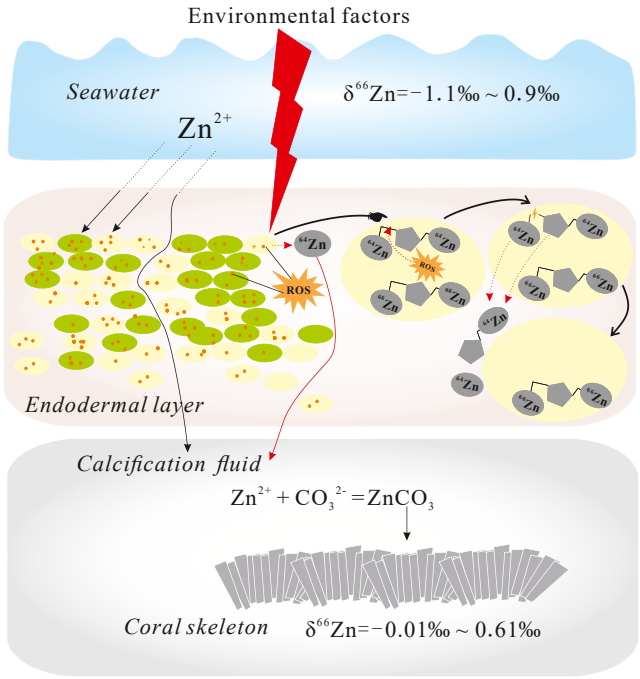


Figure 6. Conceptual illustration of Zn incorporated into coral skeletons. Free Zn^{2+} ions in the seawater enter the coral body (here using the endodermal layer containing symbiotic zooxanthellae as an example); some are absorbed and used by cells of polyps (yellow ovals) and zooxanthellae (green ovals) and some directly enter the calcifying fluid and coprecipitate with carbonate ions and are preserved in the coral skeletons. External environmental factors drive the metabolism of the coral holobiont, creating fluctuations in the intracellular reactive oxygen species (ROS; orange dots within the cells). Gray pentagons and ovals represent all substances containing Zn in the cell and isotopes (^{64}Zn and ^{66}Zn), respectively, and polygonal lines connecting pentagons with ovals represent chemical bonds with ^{64}Zn and ^{66}Zn. Relative to the bonds with ^{66}Zn, excess ROS will preferentially destroy those with ^{64}Zn. The ^{64}Zn of broken bonds is released from the cells and then transported into the calcifying fluid for precipitation and preservation. The $\delta^{66}Zn$ range (−1.10% ~ 0.90%) of the surface seawater (<100 m depth) is from Conway and John (2014). Zn, zinc.

skeletal $\delta^{66}Zn$ and SST originates from the fact that SST mediates the metabolic processes of polyps and zooxanthellae.

5. Conclusions

Our findings indicate that the internal biological activities of zooxanthellae and polyps may cause Zn isotopic fractionation recorded in shallow-water coral skeletons and are most likely responsible for monthly variations in skeletal $\delta^{66}Zn$ rather than changes in the environmental conditions of surrounding seawater. We suggest that the amount of ROS produced by internal biological processes may induce Zn isotopic fractionation in coral skeletons while environmental factors (e.g., SST) only partially affect changes in skeletal $\delta^{66}Zn$ by mediating biological processes. While the role of coral skeletal $\delta^{66}Zn$ is limited as a proxy for paleoenvironmental and paleoclimatic reconstruction, it may provide valuable insight into the responses of biological activities to environmental change. Given that a change in skeletal $\delta^{66}Zn$ may be directly related to ROS and as we still know little about whether it can contribute to trace ROS changes, future culture experiments are needed to determine the intrinsic relationship between the $\delta^{66}Zn$ variations of coral organism (tissue and zooxanthellae) and coral skeletons and the role of ROS.

Data Availability Statement

The data for this study are available in Mendeley: Xiao et al. (2020), Data for: A pilot study on zinc isotopic compositions in shallow-water coral skeletons. Mendeley Data, v6 (http://dx.doi.org/10.17632/ypyj4d5b5g.6).

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