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Deconvolving the biogeochemical controls on coral Sr/Ca and Ba/Ca proxies: New perspectives from paired stable Ca, Sr and Ba isotope compositions

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Abstract. This study introduces a novel approach to disentangle the biogeochemical controls on Sr/Ca and Ba/Ca signatures in coral skeletons using paired stable Ca, Sr and Ba isotopes to assess their specific uptake dynamics during coral biomineralization. The observed seasonal variations in stable Ca ($\delta^{44/42}$Ca) and Sr isotopes ($\delta^{88/86}$Sr) underscore the capability of corals to actively mediate the transport of Ca^{2+} and Sr^{2+} ions to the calcifying fluid prior to aragonite precipitation. We suggest that while the individual concentrations of Ca and Sr in the calcifying fluid vary seasonally, the Sr/Ca ratio of the fluid is likely comparable to that of seawater due to similar ion uptake dynamics. In contrast, the observed coral stable Ba isotope compositions ($\delta^{138/134}$Ba) remain essentially constant, suggesting a passive transport mechanism of Ba^{2+} ions, possibly through direct seawater leakage. The contrasting ion transport behaviours of Ba and Ca elucidate the underlying cause of the temperature-dependent variations in coral Ba/Ca records. By evaluating the uptake dynamics of Ca, Sr and Ba via their respective isotope systems, this study provides useful implications for the accurate application of coral Sr/Ca and Ba/Ca as proxies for paleoclimate reconstructions.

1 Introduction

Reef-building corals provide valuable records of past climate conditions, especially in periods and regions where instrumental data are limited (Beck et al., 1992; Lea et al., 1989; McCulloch et al., 2003; Wei et al., 2000). Different coral geochemical proxies have been used to reconstruct ambient seawater properties, such as Sr/Ca for sea surface temperature (SST, Beck et al., 1992), and Ba/Ca for site-specific processes like freshwater input (McCulloch et al., 2003) and upwelling dynamics (Lea et al., 1989). The development of these geochemical proxies typically begins with inorganic precipitation experiments under controlled laboratory settings (e.g., Gaetani and Cohen, 2006; Mavromatis et al., 2018). In such experiments, environmental variables are systematically adjusted to evaluate their individual effects on elemental partitioning between the culturing fluid and aragonite precipitate. In natural environments, however, coral biomineralization

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fundamentally differs from inorganic aragonite precipitation due to physiologically mediated ion transport. Unlike inorganic precipitation, coral calcification does not take place directly from seawater but rather from a semi-isolated extracellular calcifying fluid (Cohen and McConnaughey, 2003). While the calcifying fluid originates from the ambient seawater, its chemical compositions is affected by the selective transport of different ions (Allison et al., 2011; Gattuso et al., 1999).

To date, studies on ion transport during coral biomineralization have mainly focused on the uptake of Ca into the calcifying fluid. The delivery of Ca^{2+} ions to the fluid is thought to involve both a passive step through Ca channels and an energy-requiring step via Ca-ATPase pumps (Al-Horani et al., 2003). This two-step mechanism elevates Ca concentrations in the fluid and thus leads to oversaturation with respect to $CaCO_3$ precipitation (Allemand et al., 2004; Cohen and McConnaughey, 2003). Direct microsensor measurements have confirmed that corals can actively raise the concentration of Ca^{2+} ions in the fluid above that in surrounding seawater to facilitate aragonite precipitation (Al-Horani et al., 2003; Sevilgen et al., 2019). This active transport mechanism may also be crucial for the transport of other ions, but the ability to measure and quantify the fluxes of trace elements is limited by the technical challenges of microsensor measurements.

An alternative way to gain insights into the distributions of trace elements is based on the observed skeletal chemistry. However, this method is complicated by the fact that most geochemical proxies rely on elemental ratios that include both trace element and Ca concentrations. For example, the Sr/Ca ratio in coral skeletons exhibits a strong negative correlation with SST and is thus widely used as a paleothermometer (Beck et al., 1992; Smith et al., 1979). Although it is generally accepted that the partitioning of Sr/Ca between aragonite skeleton and calcifying fluid is temperature dependent (Gaetani and Cohen, 2006; Smith et al., 1979), the composition of the fluid may be altered from that of the surrounding seawater by selective ion uptake. This means that the observed skeletal Sr/Ca records may partly reflect variations in the Sr/Ca ratios of the calcifying fluid rather than solely changes in SST. Similarly, coral Ba/Ca ratios have been applied to reconstruct river runoff (McCulloch et al., 2003), dust deposition (Bryan et al., 2019) and oceanic upwelling (Lea et al., 1989), depending on the sources of excess Ba to surface waters. Despite that Ba^{2+} has chemical properties similar to Ca^{2+} given that both are alkaline earth metals, it is not clear if Ba^{2+} follows the same transport pathway as Ca^{2+} ions during coral biomineralization.

To overcome the limitations of using elemental ratios to trace the uptake dynamics of Ca, Sr and Ba, we employ their individual stable isotope systems ($\delta^{44/42}$Ca, $\delta^{88/86}$Sr and $\delta^{138/134}$Ba) to unravel the biogeochemical controls on their distributions during coral biomineralization. It has been proposed that stable Ca isotope fractionation is physiologically mediated and thus provides valuable insights into Ca uptake dynamics (Chen et al., 2016; Inoue et al., 2015). For example, Böhm et al. (2006) suggested that the active process of transcellular Ca uptake mainly drives the observed temperature-dependent fluctuations in skeletal $\delta^{44/42}$Ca signatures. Similar to Ca, an incubation study on the scleractinia coral *Acropora verweyi* using the radiotracer ^{85}Sr indicated that the uptake of Sr is also modulated by temperature (Reynaud et al., 2004). In

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contrast, Ba, a non-biologically essential element, shows little temperature-dependent isotope fractionations across multiple *Porites* colonies (Hsieh et al., 2022; Liu et al., 2019).

Despite the fact that stable Ca, Sr and Ba isotopes are increasingly used as independent proxies for biological and/or environmental parameters, no study has to date integrated these three isotope systems to compare the uptake dynamics of different ions into coral skeletons. Considering their similar chemical properties as alkaline earth elements but different biological functions, the joint examination of their stable isotope compositions and elemental ratios presents a novel approach to evaluate the nature and extent of the biomineralization controls on coral geochemical proxies.

2 Materials and Methods

2.1 Study area and coral sample collection

The South China Sea (SCS) is situated between the Pacific and Indian Oceans, with Xisha Island positioned approximately 600 km southwest of the Pearl River estuary (Fig. 1). This area is dominated by the South Asian monsoon system, with south-westerly winds during summer and north-easterly winds during winter (Wei et al., 2000). These seasonal wind reversals drive corresponding shifts in surface ocean circulation, forming a cyclonic gyre in winter and an anticyclonic gyre in summer (Wong et al., 2007). The observed SST shows an annual average value of 27 °C, ranging from 23 °C in January to 30 °C in June (Tseng et al., 2005).

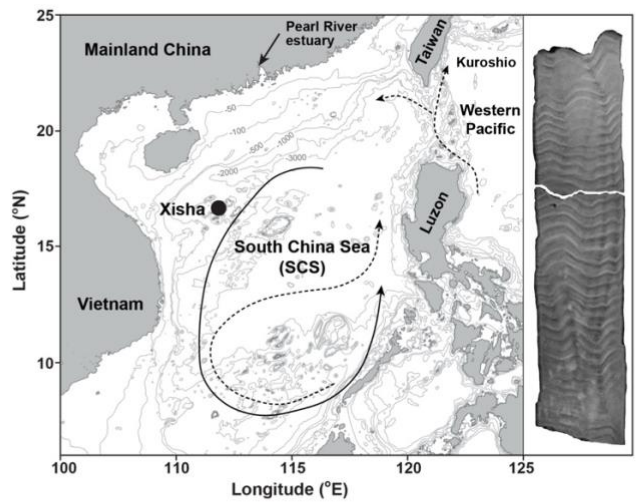

Figure 1: Map of the South China Sea (SCS) illustrates the location of coral sampling site in Xisha (black dot). Ocean circulation patterns reveal a basin-wide cyclonic gyre in winter (solid line) and an anticyclonic gyre in summer (dashed line, Wong et al., 2007). The Kuroshio current and its intrusions into the northern SCS are also indicated with dashed lines (Wong et al., 2007). In addition, an X-ray image of a sectioned coral core is displayed on the right side of the figure. The map was generated using the Ocean Date View software (Schlitzer, 2009) and modified after Cao et al. (2020).

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In 2015, a living *Porites* coral was drilled at Xisha Island (Fig. 1). The coral core was subsequently sectioned into slabs that are perpendicular to its vertical axis of growth. X-ray imaging of the sectioned coral cores reveals distinct high- and low-density bands, corresponding to annual growth increments (Fig. 1). Guided by these annual density bands, sub-samples from the upper section of the coral slab were collected along the main growth axis to obtain an approximately monthly resolution. The dissolution of sub-samples was carried out by immersing the powdered carbonate in Milli-Q water and adding drops of 1 M acetic acid stepwise. Brief ultrasonic agitation was used to enhance the dissolution process, allowing for complete dissolution of coral aragonite as gently as possible (Yu et al., 2022).

2.2 Geochemical analysis

The determination of trace element/Ca ratios in the coral samples was conducted at GEOMAR using a standard-sample bracketing method with an Agilent 7500ce ICP-MS. A matrix-matched standard was used to correct for instrumental mass bias and matrix effects as outlined by Yu et al. (2022). Measured intensities were blank corrected and normalised to ^{43}Ca before calculating the element/Ca ratios following the technique of Rosenthal et al. (1999). Coral reference material JCp-1 was analysed as an unknown, yielding mean values of 8.80 ± 0.04 (1SD) mmol/mol for Sr/Ca and 7.28 ± 0.15 (1SD) µmol/mol for Ba/Ca, which are consistent with the values reported by Hathorne et al. (2013).

Coral skeletal carbon isotopes ($\delta^{13}C$) analyses were conducted at GEOMAR using a Finnigan MAT 253 mass spectrometer connected to a Kiel IV Carbonate device system. For carbon isotopic analysis, 200 µg of aragonite samples were reacted with anhydrous 105% H_3PO_4 under vacuum at 70 °C to release CO_2. Carbon isotopic compositions are reported in δ notation as per mil (‰) deviation from the Vienna Pee Dee Belemnite (VPDB) standard. Calibration to the VPDB scale was achieved using the National Bureau of Standards (NBS) 19 and an in-house standard. The analytical precision for $\delta^{13}C$ measurements was better than 0.10‰ (2SD, N = 34).

Stable Ca isotope analyses were performed at GEOMAR using a Thermo Fisher Neptune Plus MC-ICP-MS, following the protocols outlined by Eisenhauer et al. (2019). Instrumental mass fractionation was corrected using a standard-sample bracketing method with an in-house Ca standard solution. Stable Ca isotope compositions are reported in per mil (‰) relative to the NIST SRM 915a Ca standard as $\delta^{44/42}Ca$ (‰) = ($^{44/42}Ca_{sample}/^{44/42}Ca_{NIST\ SRM\ 915a} - 1$) × 1000. Repeated analyses of NIST SRM 1486 (–0.50 ± 0.04‰, 2SD), NIST SRM 915b (0.34 ± 0.04‰, 2SD) and IAPSO seawater standard (0.93 ± 0.02‰, 2SD) showed good agreement with published values (Heuser et al., 2016; Heuser and Eisenhauer, 2008; Hippler et al., 2003; Tacail et al., 2014). The long-term reproducibility (2SD) for all analysed reference materials was better than 0.04‰.

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Stable Sr isotope measurements were performed on a Finnigan Triton TIMS at GEOMAR, following the methods described by Krabbenhöft et al. (2009). The ^{87}Sr-^{84}Sr double spike was added to one aliquot before chemical separation while the other remained un-spiked. Sr was purified from the matrix elements using Eichrom Sr-spec resin, achieving a recovery rate of over 90%. Stable Sr isotope compositions are reported relative to the NIST SRM 987 Sr standard as $\delta^{88/86}Sr$ (‰) = ($^{88/86}Sr_{sample}/^{88/86}Sr_{NIST\ SRM\ 987} - 1) \times 1000$. The coral JCp-1 standard was analysed repeatedly, yielding an average $\delta^{88/86}Sr$ value of 0.20 ± 0.02‰ (2SD, N = 10).

Stable Ba isotope analyses of coral samples were conducted at GEOMAR using a Neptune Plus MC-ICP-MS, following the methods detailed by Yu et al. (2020). The ^{130}Ba-^{135}Ba double spike was added to correct for instrumental mass fractionation. Ba was purified twice from the matrix elements using 1.4 mL of Bio-Rad AG 50W-X8 resin. Stable Ba isotope measurements were conducted at a matrix tolerance state defined by a high Normalized Ar Index value (NAI, which is an index of plasma temperature, Fietzke and Frische, 2016; Yu et al., 2024, 2020). Stable Ba isotope compositions are reported relative to the NIST SRM 3014a Ba standard as $\delta^{138/134}Ba$ (‰) = ($^{138/134}Ba_{sample}/^{138/134}Ba_{NIST\ SRM\ 3104a} - 1) \times 1000$. Repeated analyses of coral reference material JCp-1 yielded a $\delta^{138/134}Ba$ value of 0.29 ± 0.04‰ (2SD, N = 12), which agrees well with reported values (Cao et al., 2021, 2020; Geyman et al., 2019; Hemsing et al., 2018; Horner et al., 2015; Pretet et al., 2015; Yu et al., 2022; Zeng et al., 2019).

2.3 Coral age model

The distinct annual cycles in the observed skeletal Sr/Ca data were used to establish the chronology of the Xisha coral core. The seasonal maxima and minima of coral Sr/Ca data were correlated with the corresponding seasonal extreme values in the monthly HadISST records (Hadley Centre Global Sea Ice and Sea Surface Temperatures, Rayner et al., 2003). This approach allows for the construction of an age model for the coral core that extends from the year of collection (2015) back to 2004. Note that time series data for the uppermost section of the coral head (2014 - 2015) were excluded from this study, considering the anomalously low Sr/Ca ratios associated with less clearly defined annual density bands as shown in Fig. 1.

3 Results

The skeletal Sr/Ca and Ba/Ca records are shown in Fig. 2 and detailed in Table S1. In addition, two-year records (2007 - 2009) of skeletal Ba isotopes ($\delta^{138/134}Ba$), Ca isotopes ($\delta^{44/42}Ca$) and Sr isotopes ($\delta^{88/86}Sr$) are plotted alongside the corresponding SST and coral $\delta^{13}C$ data in Fig. 3 and also presented in Table S1.

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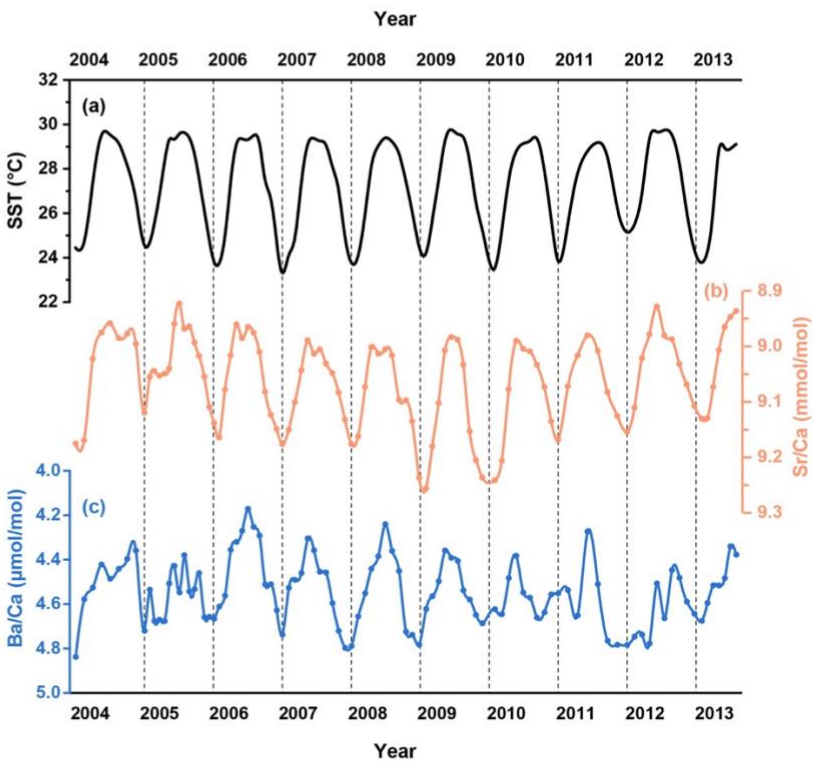

Figure 2: (a) The U.K. Meteorological Office Hadley Centre Global Sea Ice and Sea Surface Temperature (HadISST, Rayner et al., 2013). Monthly resolved coral geochemical data for (b) Sr/Ca and (c) Ba/Ca from the coral samples in the South China Sea.

Coral Sr/Ca ratios exhibit well-defined cyclic fluctuations on a seasonal timescale and show strong agreement with the HadISST dataset ($R^2 = 0.70$, $p < 0.05$) for the period between 2004 and 2013 (Fig. 2b). Coral Ba/Ca data display similar seasonal variations (Fig. 2c) that show a statistically significant correlation with the HadISST dataset ($R^2 = 0.36$, $p < 0.05$). The skeletal $\delta^{13}C$ variability generally tracks the seasonal cycles displayed by SST, with higher $\delta^{13}C$ values accompanying elevated SST (Fig. 3c). The time series data for coral $\delta^{138/134}Ba$ (Fig. 3e) show negligible variations over the two-year period of coral growth and do not exhibit any correlation with SST ($R^2 = 0.03$, $p > 0.05$). In contrast, the time series data for coral skeletal $\delta^{44/42}Ca$ (Fig. 3f) exhibit small but well-resolved seasonal fluctuations that align well with changes in SST (Fig. 4a, $R^2 = 0.26$, $p < 0.05$). Similar to Ca isotopes, coral skeletal $\delta^{88/86}Sr$ (Fig. 3g) displays clear seasonal variations that show a statistically significant correlation with SST (Fig. 4b, $R^2 = 0.30$, $p < 0.05$), with consistently lower $\delta^{88/86}Sr$ values during summer months and higher $\delta^{88/86}Sr$ values during winter months. This includes a notable decline in $\delta^{88/86}Sr$ during the summer of 2008, coinciding with elevated SST and increased $\delta^{13}C$ values.

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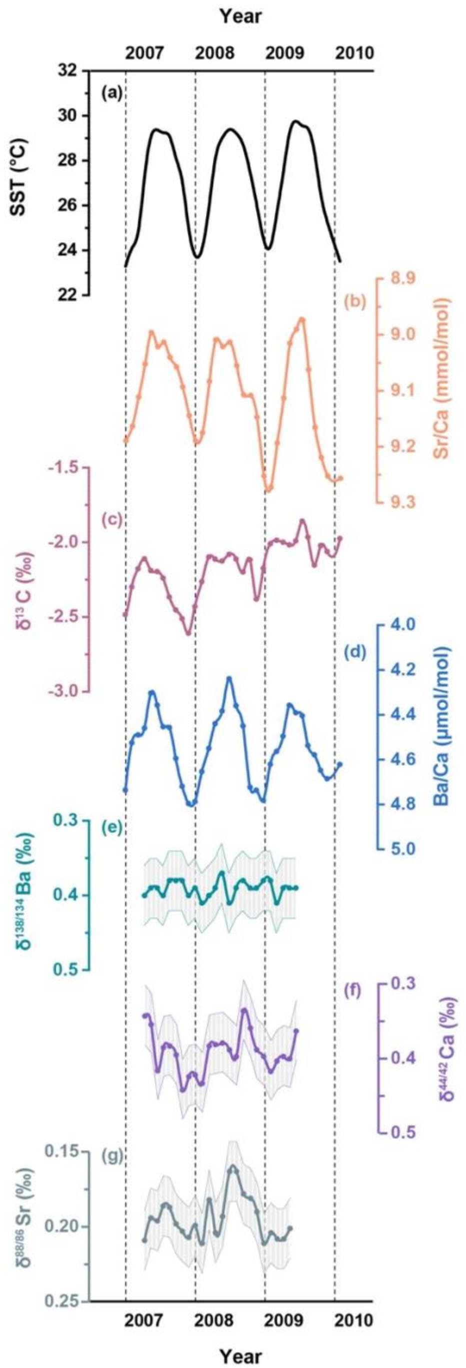

165 **Figure 3: A two-year record (2007-2009) of (a) the U.K. Meteorological Office Hadley Centre Global Sea Ice and Sea Surface Temperature (HadISST, Rayner et al., 2013), and skeletal geochemical data for (b) Sr/Ca; (c) δ^{13}C; (d) Ba/Ca; (e) $\delta^{138/134}$Ca; (f) $\delta^{44/42}$Ca; (g) $\delta^{88/86}$Sr from the coral samples in the South China Sea. Shaded bands represent analytical uncertainties (2SD) for each dataset.**

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4 Discussion

4.1 Surface seawater chemistry

The SCS is a semi-enclosed marginal sea situated between the Asian continent and the western Pacific Ocean, strongly affected by the seasonal Asian monsoon circulation (Fig. 1). Given that the relatively long residence time of Ca (~ 1 Ma) and Sr (~ 4 Ma) in seawater (Drever, 1988), dissolved Ca and Sr concentrations in surface seawater are expected to be constant on seasonal timescales. In contrast, terrestrial input from river runoff, such as the Pearl River, serves as a major source of excess Ba to the nearshore SCS (Cao et al., 2021). However, our coral sampling site is geographically remote (~ 600 km, Fig. 1) from the Pearl River discharge plume and thus is unlikely to be influenced by terrestrial Ba contributions. In addition, the observed coral Ba/Ca ratios are consistently high during the dry winter monsoon periods (Fig. 2c), indicating that neither precipitation nor runoff can account for the regular Ba/Ca peaks in dry seasons.

Apart from riverine inputs, the observed Ba/Ca peaks are potentially related to the advection of the Kuroshio Branch Water from the North Pacific during the winter monsoon (Fig. 1). However, no evidence of such contributions can be found in the surface Ba concentrations ([Ba]) in the SCS, which has surface [Ba] values similar to those observed in the western North Pacific (Bacon and Edmond, 1972; Monnin et al., 1999). Furthermore, dissolved stable Ba isotope compositions in the surface seawater of the SCS sampled in January are characterised by a value of 0.63 ± 0.04‰ (Cao et al., 2020), which is comparable to those observed in the open Pacific sampled in September (0.64 ± 0.03‰, Hsieh and Henderson, 2017). Therefore, we suggest that water mass advection has a negligible effect on the distinct seasonal patterns observed in coral Ba/Ca.

It has been shown that increased wind speeds during the northeast monsoon enhance vertical mixing (Tseng et al., 2005). Although Xisha is located outside the main upwelling areas, the influence of wind-driven vertical mixing is reflected in seasonal fluctuations of the mixed layer depth (MLD). Within the coral sampling area, the MLD is relatively shallow (20 - 40 m) during the summer monsoon and markedly deeper (~ 90 m) during the winter monsoon (Tseng et al., 2005). Consequently, the entrainment of deeper waters with higher [Ba] would be expected in winter as a result of the nutrient-like depth profile of dissolved [Ba] in water column (Monnin et al., 1999b). However, the vertical distributions of dissolved [Ba] are essentially constant within the upper 150 m in the SCS (Cao et al., 2020), suggesting that the intensified wind-induced mixing and the consequent MLD deepening are unlikely to explain the observed seasonal variations in coral Ba/Ca. Therefore, we propose that the seasonal fluctuations in coral skeletal Ba/Ca and Sr/Ca ratios are not driven by changes in surface seawater compositions.

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4.2 Uptake dynamics of ions

4.2.1 Ca^{2+} ion transport

During the processes of Ca transport in corals, there are likely two stages of Ca transport where its stable isotopes ($\delta^{44/42}$Ca) could potentially undergo fractionation (Böhm et al., 2006). In the first stage, Ca channels permit passive diffusion of seawater Ca^{2+} ion into cells (Allemand et al., 2011). Considering coral channels have relatively narrow pores, the large, hydrated seawater Ca^{2+} ions must be dehydrated at the channel entrance before being transported into the cell interior (S. Tambutté et al., 2011). In the second stage, the cell exports the Ca^{2+} ions into the extracellular calcifying fluid via the active Ca-ATPase pumps (Allemand et al., 2011). This step requires energy to move Ca^{2+} ions against their concentration gradient, leading to high Ca^{2+} concentration in the fluid to form $CaCO_3$ (S. Tambutté et al., 2011).

The observed monthly resolved coral $\delta^{44/42}$Ca values are typically lower during summer months associated with elevated SST, resulting in a statistically significant ($p < 0.05$) negative correlation between $\delta^{44/42}$Ca and SST (Fig. 4a, solid circles). This negative correlation between temperature and coral Ca isotope fractionation differs from results of previous studies. For example, Böhm et al. (2006) identified a significant ($p < 0.05$) but positive correlation between $\delta^{44/42}$Ca and temperature in both cultured *Acropora* and open ocean *Porites* and *Pavona* corals (Fig. 4a, empty circles). Similarly, coral culturing experiments also found a positive correlation between the mean skeletal $\delta^{44/42}$Ca of *Porites* colonies and temperature (Fig. 4a, empty squares, Inoue et al., 2015).

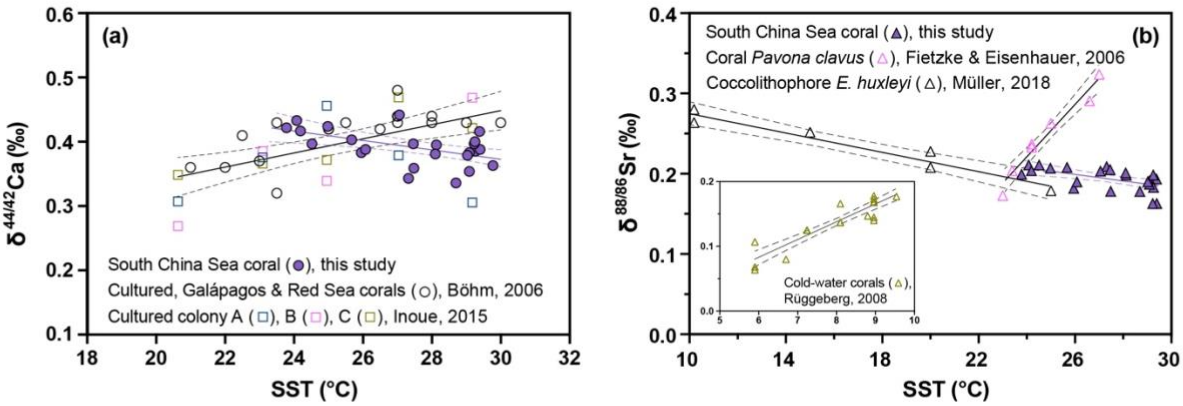

Figure 4: (a) Correlations between $\delta^{44/42}$Ca and SST for the South China Sea coral (solid circles), the cultured, Galápagos and Red Sea corals (empty circles, Böhm et al., 2006), and three different cultured coral colonies (empty squares, Inoue et al., 2015); (b) Correlations between $\delta^{88/86}$Sr and SST for the South China Sea coral (solid triangles in purple), coral *Pavona clavus* (empty triangles in pink, Fietzke & Eisenhauer, 2006), coccolithophore *E. huxleyi* (empty triangles in black, Müller et al., 2018), and cold-water corals *L. pertusa* (empty triangles in olive drab, Rüggeberg et al., 2008).

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Böhm et al. (2006) proposed that the isotope fractionation of Ca in corals occurs primarily during the diffusion of Ca^{2+} ions from seawater into the calicoblastic layer. This mechanism was firstly introduced by Gussone et al. (2006), who suggested that the dominant process driving Ca isotope fractionation in coccolithophores (*Emiliania huxleyi*) is likely associated with the initial uptake of Ca^{2+} ions across the cell membrane via Ca channels. This kinetic isotope effect was later quantified in an ion dehydration model by Mejía et al. (2018). At higher temperatures, corals often increase the rates of Ca uptake and calcification (Cohen and McConnaughey, 2003). According to prior models (e.g., Gussone et al., 2003), faster uptake rate of Ca^{2+} ions should reduce Ca isotope fractionation (i.e. higher $\delta^{44/42}Ca$ values) because there is less opportunity for isotopic selection between ^{42}Ca and ^{44}Ca.

However, our results show a negative correlation between $\delta^{44/42}Ca$ and temperature (Fig. 4a). Considering that ions uptake is energy-dependent and metabolically controlled, it is expected that Ca dehydration at the channel entrance and subsequent transcellular Ca transport likely respond to changes in temperature. On the other hand, light Ca isotopes (e.g., ^{42}Ca) are more readily dehydrated compared to heavier Ca isotopes (e.g., ^{44}Ca) because lighter isotopes require less energy to remove water molecules (Hofmann et al., 2012). Therefore, the observed apparent temperature dependence of $\delta^{44/42}Ca$ is likely a result of the more selective dehydration of lighter Ca isotopes, resulting in more pronounced isotope fractionation (i.e. lower $\delta^{44/42}Ca$ values) at increasing transport rates under elevated SST (Fig. 4a).

In line with our suggestion, a temperature-controlled culturing experiment on scleractinian coral colonies found s similar negative correlation between $\delta^{44/42}Ca$ and temperature at temperatures above 24 °C (colony A, Fig 4a, Inoue et al., 2015). In addition, we observe an increase in skeletal $\delta^{13}C$ in the summer months (Fig. 3c). The preferential utilization of the light carbon isotope (^{12}C) by zooxanthellae during photosynthesis results in an increased concentration of $^{13}CO_2$ in the pool of inorganic carbon accessible for coral calcification. The formation of coral skeleton during periods of intense photosynthetic activity is thus associated with higher skeletal $\delta^{13}C$ values (Felis et al., 1998; McConnaughey et al., 1997). Consequently, the energy supply by the photosynthesis of zooxanthellae increases the rate of dehydration and ions transport for calcification (Al-Horani et al., 2003; Allemand et al., 2011). Therefore, we suggest that temperature plays an important but probably indirect role in regulating the uptake of Ca^{2+} ions and related Ca isotope fractionation.

4.2.2 Sr^{2+} ion transport

Similar to Ca, the time series data for coral skeletal $\delta^{88/86}Sr$ (Fig. 3g) display clear seasonal changes over a continuous two-year period, with consistently lower $\delta^{88/86}Sr$ values in summer months and higher $\delta^{88/86}Sr$ values in winter months. As the magnitude of Sr isotope fractionation increases (i.e. lower $\delta^{88/86}Sr$ values) with rising SST, the negative $\delta^{88/86}Sr$-temperature relationship observed in this study differs from previous studies (Fig. 4b). For example, both Fietzke and Eisenhauer (2006) and Rüggeberg et al. (2008) reported a positive relationship between $\delta^{88/86}Sr$ and temperature in inorganic aragonite,

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shallow- and cold-water corals (Fig. 4b). However, subsequent studies found either very muted variability in in coral $\delta^{88/86}$Sr or no clear positive temperature dependence (Fruchter et al., 2016; Raddatz et al., 2013).

Considering the similar chemical properties and ionic radius of Sr^{2+} and Ca^{2+} (Shannon, 1976), both ions are likely transported and fractionated via a similar biologically-mediated pathway. An incubation study using the radiotracer ^{85}Sr indicated that the uptake of Sr is a function of temperature and follows the same pattern as Ca uptake (Reynaud et al., 2004). The significant ($p < 0.05$) negative correlation observed in the $\delta^{88/86}$Sr-SST plot (Fig. 4b) suggests that the variations in $\delta^{88/86}$Sr are likely regulated by the temperature-dependent uptake of Sr^{2+} ions. If this is true, the magnitude of Sr isotope fractionation will reflect the strength of Sr^{2+} ion dehydration and flux. While we cannot conclude that Sr uptake occurs solely through Ca channels and pumps, our data indicate that seasonal changes in the rates of Sr^{2+} ion desolvation and Sr transport kinetics represent an important mechanism contributing to the observed variations in skeletal $\delta^{88/86}$Sr.

A similar significant negative correlation of $\delta^{88/86}$Sr and temperature has been reported for culturing experiments on coccolithophores, where a larger fractionation in $\delta^{88/86}$Sr was observed with elevated temperature (Fig. 4b, Müller et al., 2018). This negative relationship between coccolithophore $\delta^{88/86}$Sr and temperature (Fig. 4b) is consistent with previous results obtained for three different coccolithophore species (Stevenson et al., 2014). Unlike corals, coccolithophores as unicellular organisms with intra-cellular calcification, exclusively use trans-membrane transport, whereas corals may use a combination of transcellular and paracellular transport mechanisms (Hohn and Merico, 2015). Despite that the relative contribution of the paracellular transport to coral Sr uptake is largely unknown, the similarity of Sr isotope fractionation patterns between coccolithophores and corals indicates that Sr is likely transported primarily via transcellular pathways in corals. The negative temperature dependence of both Sr and Ca isotope fractionation highlights the significant impact of temperature on metabolic and ion uptake processes during coral biomineralization.

4.2.3 Ba^{2+} ion transport

Compared to Sr^{2+} (1.31 Å), the Ba^{2+} ion is characterised by a significantly larger ionic radius (1.47 Å) than that of Ca^{2+} ion (1.18 Å), with a difference of approximately 25% (Shannon, 1976). This substantial difference in ion radius may prevent Ba from using the same transcellular pathway as Ca (Gaetani and Cohen, 2006). In addition, Ba is a non-essential element for biological processes and can be toxic to organisms at elevated concentrations (Kravchenko et al., 2014), indicating that Ba is less likely to be regulated and transported by the active transcellular pathway. More importantly, the essentially invariant fractionation behaviours of stable Ba isotopes implies that the incorporation of Ba^{2+} ions differ from that of Ca^{2+} ion (Fig. 3e).

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The results of our study indicate that stable Ba isotope fractionation between coral skeletons and seawater (0.63 ± 0.04‰, Cao et al., 2020) is constant at a calculated value of –0.24 ± 0.05‰. This fractionation factor is generally comparable with the reported factor of –0.30‰ in the SCS (Liu et al., 2019), and an average value of –0.28 ± 0.06‰ from multiple *Porites* colonies located near Singapore (Hsieh et al., 2022). Like Ca and Sr, the stable Ba isotope fractionation can be attributed to the weaker ion-water bond of lighter isotopes (e.g., ^{134}Ba) compared to heavier isotopes (e.g., ^{138}Ba) during the processes of ion dehydration. The observed constant coral $\delta^{138/134}$Ba signatures indicate that Ba uptake and associated isotope fractionation are likely controlled by a mechanism that is largely independent of changes in environmental factors.

Experiments using membrane impermeant fluorescent dye-tracer, such as calcein, have indicated the existence of a paracellular pathway by which seawater may bypasses the cytoplasm, and directly enter the calcifying fluid (Allemand et al., 2011; Gagnon et al., 2012; E. Tambutté et al., 2011). This paracellular route facilitates diffusive or advective exchange of ions between the calcifying fluid and the surrounding seawater. A recent culturing experiment on the incorporation of anions into coral skeletons provides additional support for direct transport of seawater to the fluid (Ram and Erez, 2023). Therefore, we suggest that this paracellular pathway and Ba dehydration likely dominate the Ba transport and its isotope fractionation during coral biomineralization, respectively.

Considering that the ionic radius of Ca^{2+} is smaller than that of Ba^{2+}, it is possible that seawater Ca^{2+} ions may also enter the coral calcifying fluid directly via the paracellular pathway. However, the paracellular pathway relies on the Ca concentration gradient between seawater and the fluid, but currently available data suggest higher Ca concentrations in the fluid compared to seawater (Al-Horani et al., 2003; Sevilgen et al., 2019). In addition, the paracellular pathway allows for passive diffusion or advection, which does not require any energy cost. In contrast, the transcellular transport requires ATP to actively move ions against their concentration gradients into the fluid (S. Tambutté et al., 2011). We assume that during periods of elevated SST, the Ca channels and Ca-ATPase pumps become more active in supplying Ca^{2+} ions via the transcellular pathway. In contrast, the transport of non-essential Ba^{2+} ions is primarily governed by the passive paracellular transport that is less sensitive to SST changes. As a result, the uptake of Ca increases more at higher SST, while Ba uptake remains more stable and does not respond much to temperature changes. Therefore, the seasonal variations in the observed Ba/Ca ratios of the coral skeleton are likely driven by changes in the flux of Ca^{2+} ions rather than that of Ba^{2+} ions. The contrasting ion transport behaviours between Ba and Ca elucidates the mechanism underlying seasonal variations in coral Ba/Ca and $\delta^{44/42}$Ca, while also accounting for the invariable coral $\delta^{138/134}$Ba records.

4.3 Implications for coral geochemical proxies.

Although the empirical correlation between coral Sr/Ca ratios and SST has been widely used for the establishment of high-resolution SST records (Beck et al., 1992; Smith et al., 1979), a major uncertainty arises from the potential for corals to actively modulate the incorporation of trace elements into the calcifying fluid prior to aragonite precipitation. The seasonal

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fluctuations observed in coral skeleton $\delta^{44/42}$Ca and $\delta^{88/86}$Sr indicate that Ca and Sr concentrations in the fluid could vary over seasonal timescales, likely driven by changes in environmental factors like SST and related coral physiological processes. However, if Sr flux changes linearly with Ca flux as SST varies, then their elemental ratio (i.e. Sr/Ca) in the calcifying fluid remains relatively constant despite absolute changes in concentrations of both ions. Therefore, the temporal fluctuations in the uptake rates of Sr and Ca ions are unlikely to explain the observed monthly changes in skeletal Sr/Ca ratios. Instead, the temperature-sensitive partitioning of Sr and Ca into coral aragonite is likely the primary driver of seasonal variations in skeletal Sr/Ca records. This result supports the wealth of empirical results demonstrating coral Sr/Ca ratios provide a reliable proxy for reconstructing past SST.

On the other hand, the limited Ba isotope fractionation suggests that the concentration of Ba in the fluid is nearly constant and does not respond strongly to SST changes. The elevated Ca concentrations in the fluid, driven by enhanced transport of Ca^{2+} ions, likely account for the seasonal variations in skeletal Ba/Ca records observed. Culturing experiments have shown that coral Ba/Ca ratios vary in response to temperature and light conditions, even when seawater Ba concentrations are kept constant (Sakata et al., 2024; Yamazaki et al., 2021). These observations demonstrate that elevated temperature or light intensity, both of which can enhance coral metabolic activity, likely drive the changes in skeletal Ba/Ca ratios through their influence on Ca transport dynamics. Therefore, this metabolic component of coral Ba/Ca needs to be removed to improve the reliability of coral Ba/Ca for tracing past ocean chemistry. In comparison, coral stable Ba isotopes are largely independent from such biological effects, thereby supporting the use of coral $\delta^{138/134}$Ba as a more robust proxy to reconstruct seawater Ba isotope compositions and related geochemical cycling over time.

5 Conclusions

Coral biomineralization consists of two individual steps: Modifications of the extracellular calcifying fluid and subsequent aragonite precipitation. Our monthly resolved coral geochemical records from the South China Sea indicate that the first step of transporting Ca^{2+} and Sr^{2+} ions from seawater to the fluid is tightly regulated by physiological processes and thus exhibits a distinct temperature dependence. This is supported by the corresponding stable Ca and Sr isotope fractionations, showing consistently decreasing $\delta^{44/42}$Ca and $\delta^{88/86}$Sr values with elevated temperatures. Although the respective concentrations of Sr and Ca in the fluid likely fluctuate seasonally, the elemental ratio of Sr/Ca remains constant in the fluid, thus supporting the use of coral Sr/Ca as a proxy for sea surface temperature reconstructions. In contrast, the transport of Ba^{2+} ions likely occurs through a passive mechanism such as seawater leakage, which is independent of environmental factors as evidenced by the invariable coral $\delta^{138/134}$Ba records. Therefore, the different incorporation behaviours of Ba and Ca ions likely drive the observed seasonal variations in coral Ba/Ca records. Overall, our study highlights the complex interplay between biological processes and environmental factors during coral biomineralization, emphasising the importance of understanding the uptake dynamics of different ions for accurate paleoclimate reconstructions.

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Data availability

All data are provided in the Supplement.

Author contributions

YY and EH conceived and designed the study; YY and AH performed the analyses; YY carried out the investigation and visualization; YY wrote the manuscript draft; YY, EH, XC, GW, FB, AH, AE, CS, and MF reviewed and edited the manuscript; MF supervised and administered the project; MF acquired funding; XC and GW provided resources.

Competing interests

The authors declare that they have no conflict of interest.

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