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Cumulated influence of natural and anthropogenic drivers on surface seawater barium: Evidence from a high-resolution coral record in the northern South China Sea

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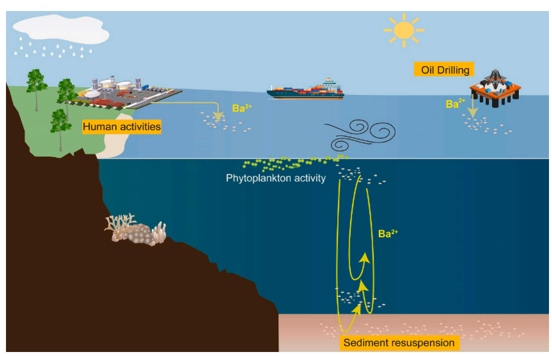
HIGHLIGHTS

- Coral Ba/Ca records reflect the superimposed effects of natural and human factors.
- Winter monsoon-driven sediment resuspension causes seasonal peaks in coral Ba/Ca.
- Coral Ba/Ca records have potentials for the documentation of tropical cyclones.

GRAPHICAL ABSTRACT



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ABSTRACT

Barium (Ba) plays a crucial role as a tracer element in elucidating essential marine biogeochemical processes. However, the limited knowledge regarding Ba sources and variations impedes our comprehension of the diverse array of processes occurring in the marine environment. Although coral Ba/Ca ratios have demonstrated potential as a tracer of oceanic Ba, there remains a scarcity of long-term and high-resolution records to fully utilize this technique. Here, we presented a 32-year record of monthly coral Ba/Ca ratios and $\delta^{18}O$ from the Weizhou Island in the northern South China Sea to elucidate the sources and the influence factors on surface seawater Ba. The results indicated no significant correlation between coral Ba/Ca and sea surface temperature or growth rate, implying that coral Ba/Ca ratios could serve as a dependable proxy for surface seawater Ba concentrations. Significant increases and abrupt fluctuations in coral Ba/Ca ratios were observed during the period of oil drilling exploration and engineering construction, indicating that anthropogenic activities might lead to an elevation of surface seawater Ba levels, subsequently affecting coral Ba/Ca ratios. The winter coral Ba/Ca peaks on monthly timescales were confirmed to be caused by resuspended sediment driven by the winter monsoon. Extreme peaks

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of coral Ba/Ca occurring during the wet season demonstrated the potential of coral Ba/Ca to record tropical cyclones, which has not been found in low-resolution scale studies. The continuous, long-term, and high-resolution coral Ba/Ca time series provides compelling evidence for the combined influence of both natural and anthropogenic factors on seawater Ba concentrations. These findings significantly contribute to the comprehension of the intricate biogeochemical cycling of marine Ba.

1. Introduction

Barium (Ba) is an alkaline earth metal element that exhibits a nutrient-like vertical distribution in the ocean, with low concentrations near the surface and higher concentrations in the deeper layers (Carter et al., 2020; Griffith and Paytan, 2012; Sternberg et al., 2005). The concentration of Ba is influenced by multitude factors in the marine environment, rendering it an invaluable tool for investigating a diverse array of biogeochemical processes (Griffith and Paytan, 2012; Liguori et al., 2016; Saha et al., 2016). Surface seawater typically contains Ba concentrations of 30–50 nmol/kg, while it can extend within the 50 to 200 nmol/kg range in coastal systems. The variations provide reliable information to gain insight into the main sources of the increased seawater Ba concentrations, such as rivers (Brenner et al., 2017; Maina et al., 2012; Yu et al., 2022) and groundwater discharge input (Jiang et al., 2018; Moore, 2010; Shaw et al., 1998). Another source of marine Ba is hydrothermal and cold seep fluids (Griffith and Paytan, 2012; Dymond et al., 1992). Dissolved Ba has a residence time of approximately 8000 years, about four times that of the ocean mixing time (Carter et al., 2020). This characteristic of oceanic Ba has been employed to reconstruct ocean circulation (Hemsing et al., 2018; Lea et al., 1989). The primary mechanism responsible for the removal of Ba from the marine environment is barite precipitation and accumulation in marine sediments (Griffith and Paytan, 2012), which is also associated with carbon cycling. Thus, Ba plays a key role in investigating paleo-productivity (Carter et al., 2020; Liguori et al., 2016) and carbon export (Eagle et al., 2003). However, the absence of direct and long-term seawater Ba data has hindered our understanding of the intricate biogeochemical cycle of seawater Ba.

Hermatypic coral skeletons, characterized by long continuous growth times, ease of dating, wide distribution, and high sensitivity to climate and environmental changes, have been extensively employed to document long-term climatic and environmental variations (Yu, 2012). The abundance of minor and trace elements in coral skeletons can reflect physicochemical changes in the reef environment, acting as geochemical tracers in indicating the marine environment, including the impact of long-term natural change and human activities on the ocean (Jiang et al., 2017; Tanaka et al., 2013). Ba shares similar ionic radii with calcium (Ca), can substitute for Ca in the aragonite lattice, and become incorporated into the coral skeleton. The Ba/Ca ratio of coral is in proportion to the aqueous Ba/Ca ratio (Tudhope et al., 1996; Gonneea et al., 2017; LaVigne et al., 2016), which had been proven to be a valuable proxy for surface seawater Ba (Anagnostou et al., 2011; Weerabaddana et al., 2021). Thus, the coral Ba/Ca ratios have been utilized as indicators of various ocean processes, including upwelling (Tudhope et al., 1996; Lea et al., 1989; Montaggioni et al., 2006; Ourbak et al., 2006), terrestrial input (Brenner et al., 2017; Chen et al., 2020; Lewis et al., 2018; Prouty et al., 2010), submarine groundwater discharge (Horta-Puga and Carriquiry, 2012; Jiang et al., 2018), phytoplankton blooms (Saha et al., 2018b; Sinclair, 2005), stress induced by low sea surface temperatures (Chen et al., 2011), and wind-induced resuspension of sediment (Esslemont et al., 2004). Although these studies have significantly contributed to our understanding of individual climatic and environmental records, they are predominantly focused on estuarine areas, and provided low-resolution (annual) information. Therefore, it is imperative to prioritize the investigation of non-estuarine regions and high-resolution techniques to refine our understanding of coral Ba/Ca and seawater Ba variability in response to environmental and climate change.

The utilization of coralline Ba/Ca ratios as an indicator for changes in surface seawater Ba concentrations has revealed the presence of climatic and environmental factors (Carriquiry and Horta-Puga, 2010; Li et al., 2022; Saha et al., 2018a; Weerabaddana et al., 2021), but the complex interactions between coral Ba/Ca and various climatic and environmental factors still need to be further explored. For instance, in the southern Gulf of Mexico, coral Ba/Ca ratios have been applied to trace land use, river drainage, and oil drilling mud (Carriquiry and Horta-Puga, 2010). Li et al. (2022) observed that coral Ba/Ca ratios recorded oil-drilling muds and the winter monsoon in the northern South China Sea (SCS). These studies confirmed that coral Ba/Ca ratios were influenced by climatic and environmental factors, but the limited resolutions of coral Ba/Ca ratios hindered the identification of such superimposed effects (Saha et al., 2018a). To tackle this challenge, Weerabaddana et al. (2021) suggested that the ideal study site and high-resolution data could be selected to exclude the influences of specific factors to identify the primary influencing factors. Hence, it is imperative to undertake ample high-resolution studies on coral Ba/Ca ratios to effectively discern and elucidate the intricate impacts of climatic and environmental events on marine Ba within the designated study area.

In this study, we obtained a *Porites lutea* coral from the Weizhou Island, located in the northern SCS, and tested the concentrations of Ba and Ca, as well as $\delta^{18}O$, to investigate the effects of natural and anthropogenic factors on surface seawater Ba concentrations. The limitations associated with utilizing coral Ba/Ca ratios as long-term and high-resolution indicators of seawater Ba concentrations were addressed. This region of coral growth provides extensive climatic and environmental data, that can be utilized to comprehensively comprehend the climatic and external environmental drivers influencing surface seawater Ba concentrations. The age of coral growth was determined by counting the annual growth bands and validated by establishing the relationship between $\delta^{18}O$ and instrumental sea surface temperature (SST) data. Subsequently, the influences of climatic and environmental drivers (e.g., SST, average wind speed, maximum wind speed, oil drilling, and engineering construction) on seasonal and annual variations in coral Ba/Ca ratios were examined. The data revealed that the annual and seasonal fluctuations in coral Ba/Ca ratios were driven by the cumulative impacts of natural and anthropogenic factors. These findings contribute significantly to the advancement of enhancing our understanding of the role of coral Ba/Ca in specific regions and underscore the importance of considering the impacts of climatic and environmental drivers on seawater Ba concentrations.

2. Material and methods

2.1. Study area

The Weizhou Island is located in the northernmost tropics at coordinates 20°54′ - 21°10′ N and 109°00′ - 109°15′ E, covering an area of 26 km^2 (Fig. 1). It holds the distinction of being the largest island in the Beibu Gulf and is also recognized as China's youngest and largest Quaternary volcanic island. The geological foundation of the island predominantly consists of basaltic and pyroclastic rocks formed during volcanic activities in the early Pleistocene (Fan et al., 2006). It falls within the subtropical marine monsoon climate zone, characterized by mild climatic conditions and abundant sunshine. The annual average temperature, maximum temperature, and minimum temperature are recorded as 22.6 °C, 35.4 °C, and 2.9 °C, respectively. The surface seawater salinity is measured at 31.9 ‰, and the average annual rainfall amounts to 1682.7 mm, with a concentration during the wet season spanning from July to September. The island experiences an average of 2234 h of sunshine per year, and the frost-free period extends for 359–363 days. Common natural disasters in the region encompass tropical cyclones, thunderstorms, rainstorms, and tornadoes, with tropical cyclones being the most prominent climate-related events.

2.2. Coral samples and isotope analyses

In October 2015, a *Porites lutea* coral (W3) was collected at 4 m depth from the northwest side of Weizhou Island (21°4′7″N, 109°5′24″E), situated at the northern edge of the coral reefs in the SCS (Fig. 1). In the laboratory, the coral core was sliced along the main growth axis using a cutting machine, resulting in thick slices with a width of approximately 8 cm and a thickness of around 1 cm. These slices were subsequently washed with Milli-Q water and dried. X-ray photos were taken of the dried coral slices to visualize the annual growth bands and establish the chronology by assigning annual growth density bands (Xu et al., 2018). The coral slabs were immersed in 10 % H_2O_2 for 48 h, followed by three ultrasound washes, and then dried in an oven at 60 °C for 48 h. Using radiographs as a reference, powder samples were intensively etched from top to bottom along the main growth axis by using a stainless steel blade of the skeletal lamellae, with a spacing of approximately 0.5–0.8 mm. Each sample weighed between 15 and 20 mg, resulting in a total of 415 samples being collected. Approximately 3 mg of each sample was weighed into centrifuge tubes, and approximately 18 *g* of 2 % HNO_3 was added to achieve a final dilution factor of approximately 1:6000. The concentrations of Ba and Ca in the samples were measured using inductively coupled plasma mass spectrometry. To correct for instrumental drift and matrix effects, a 100 mL of 100 ppb internal standard reserve solution was prepared using reference elements (^{103}Rh, ^{115}In, ^{187}Re). National geochemical standards GBW07129, GBW07133, and GBW07135 were utilized as external standards, and 1 mL of 100 ppb internal standard reserve solution was added, followed by dilution to a 2000-fold with 2 % HNO_3. The coral powder samples underwented a reaction with 100 % H_3PO_4 at 75 °C, and the oxygen/carbon isotope ratio of the coral was measured using a Finnigan MAT-253 stable isotope mass spectrometer. The isotopic ratios were reported in the per mil (‰) convention, normalized to the Vienna Pee Dee Belemnite (V-PDB), and standardized against the GBW04405 standard ($\delta^{18}O = -8.49$ ‰). The $\delta^{18}O$ data have been previously reported in our previous research (Xu et al., 2018).

2.3. Marine and meteorological data collecting

The SST data were obtained from the 0.25° × 0.25° ERA5 monthly mean dataset (https://cds.climate.copernicus.eu/cdsapp#!/dataset/10.24381/cds.f17050d7?tab=overview/). Rainfall and wind speed data were collected from the Weizhou Island Weather Station. Chlorophyll-a concentrations (Chl-α) were obtained from the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) Level 3 binned data with a spatial resolution of 9 km. Data on tropical cyclones were collected from the China Typhoon Network (https://dtbank.gistinker.com/fy/wxapp/RealTyphoon.html).

2.4. Coral age models

The construction of a coral chronology for the W3 coral from the Weizhou Island was identified and calculated by high-density bands and low-density bands visible in X-ray photographs, reflecting the annual growth pattern within the coral skeletons (Knutson et al., 1972). The sampling year was designated as the final year of coral growth, and the W3 coral age framework was establish by calculating the number of the inverse growth bands. Furthermore, the chronological framework was validated using $\delta^{18}O$ data and SST. The narrow peaks and broad valleys of the $\delta^{18}O$ annual curve were used as control points to validate the annual growth cycle of W3 coral, with low $\delta^{18}O$ values corresponding to winter SST extremes, specifically in January. Integrating the

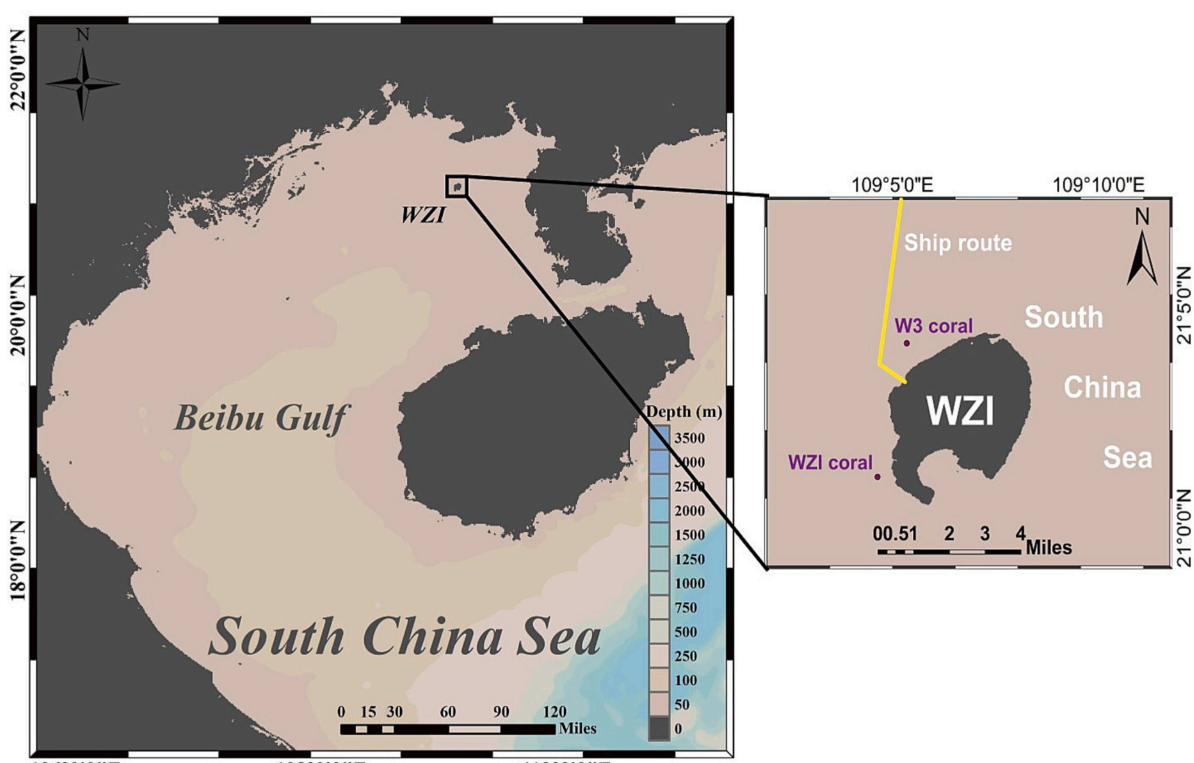

Fig. 1. The location of the study area, the location of the W3 and WZI coral, and the ship route indicated by a yellow line.

information obtained from X-ray photographs and the $\delta^{18}O$ cycle (Fig. 2), the growth period of the W3 coral was determined to be from 1984 to 2015 CE. To determine the annual linear extension (mm), the distance between the maximum values of coral $\delta^{18}O$ (representing winter values) was measured, and a linear extension rate of 7.15 mm/year (ranging from 5.5 to 8.2 mm/year) was determined for the age model (Fig. S1 in Supplementary materials).

2.5. Statistic analysis

All statistical analyses were performed in Origin 2021, including linear interpolation, Pearson correlations, significance analyses, regressions, and running-standard deviations. The Pearson correlation coefficient was applied to examine the consistency and relationships between the different parameters. The two-tailed *t*-test were used to evaluate the statistical significance from the correlation and regression analyses using. Based on the chronology established using $\delta^{18}O$ and SST, the assigned time corresponding to the coral $\delta^{18}O$ profiles were applied to the respective coral Ba/Ca records. The Ba/Ca data between $\delta^{18}O$ peaks were interpolated using linear interpolation at monthly resolution. Subsequently, the monthly resolution time series data were aggregated to a yearly resolution by calculating the average monthly values.

3. Results

Based on the annual laminae and oxygen isotope, the geochemical record of W3 coral spans from 1984 to 2015 CE. The monthly variability of coral Ba/Ca ratios over the entire period ranges from 7.68 to 37.80 μmol/mol, with a mean value of 11.82 ± 3.09 μmol/mol (Fig. 2). Evidently, the Ba/Ca ratios exhibited a higher value in W3 coral in comparison to those obtained from the regions without artificial disturbances, such as Southern Oman (Tudhope et al., 1996), New Ireland (Alibert and Kinsley, 2008), Papua New Guinea (Alibert and Kinsley, 2008), and Antongil Bay (Grove et al., 2012). The monthly coral Ba/Ca record exhibits notable seasonal variability across the entire temporal span, characterized by distinct peaks occurring during the winter season (Fig. 3).

The annual average Ba/Ca ratios exhibit fluctuating trends, ranging from 8.42 to 17.09 μmol/mol, with a mean value of 11.82 ± 1.93 μmol/mol (Fig. 4). The annual Ba/Ca data surpass the previously reported values associated with river runoff (Maina et al., 2012; Sinclair and McCulloch, 2004), upwelling (Montaggioni et al., 2006), and sediment input (Prouty et al., 2010). Nevertheless, it is worth noting that the annual Ba/Ca ratios in W3 coral display a resemblance to the reported values in the Gulf of Westward of Mexico Park Bank, where the influences of oil production on coral Ba/Ca ratios have been confirmed (Weerabaddana et al., 2021). The annual coral Ba/Ca ratios of the W3 coral demonstrates a significant elevation compared to the values reported in other regions of SCS. For instance, a *Porites* coral Ba/Ca ratio of ~5 μmol/mol was reported in the Luzon Strait (Liu et al., 2019). This notable discrepancy strongly implies that the W3 coral may have been subjected to anthropogenic activities or distinct regional climatic or environmental factors.

4. Discussion

4.1. Reliability of coral Ba/Ca indicating seawater Ba

Ba is incorporated into the aragonite calcium carbonate skeleton of corals through a relatively straightforward ionic substitution process (eg. Ba^{2+} replaces Ca^{2+}). Coral Ba/Ca ratio is proportional to the surrounding seawater Ba concentration, which is frequently employed as a proxy for evaluating coastal seawater chemistry, and assessing the environmental dynamics that influence the surface seawater composition (Tudhope et al., 1996; Dietzel et al., 2004). Nevertheless, the mechanisms governing the incorporation of elements into coral skeletons continue to be a topic of ongoing discussion and debate. Several studies have reported an inverse relationship between coral Ba/Ca ratios and temperature, with a factor of 1/3 or 1/2 (Gaetani and Cohen, 2006;

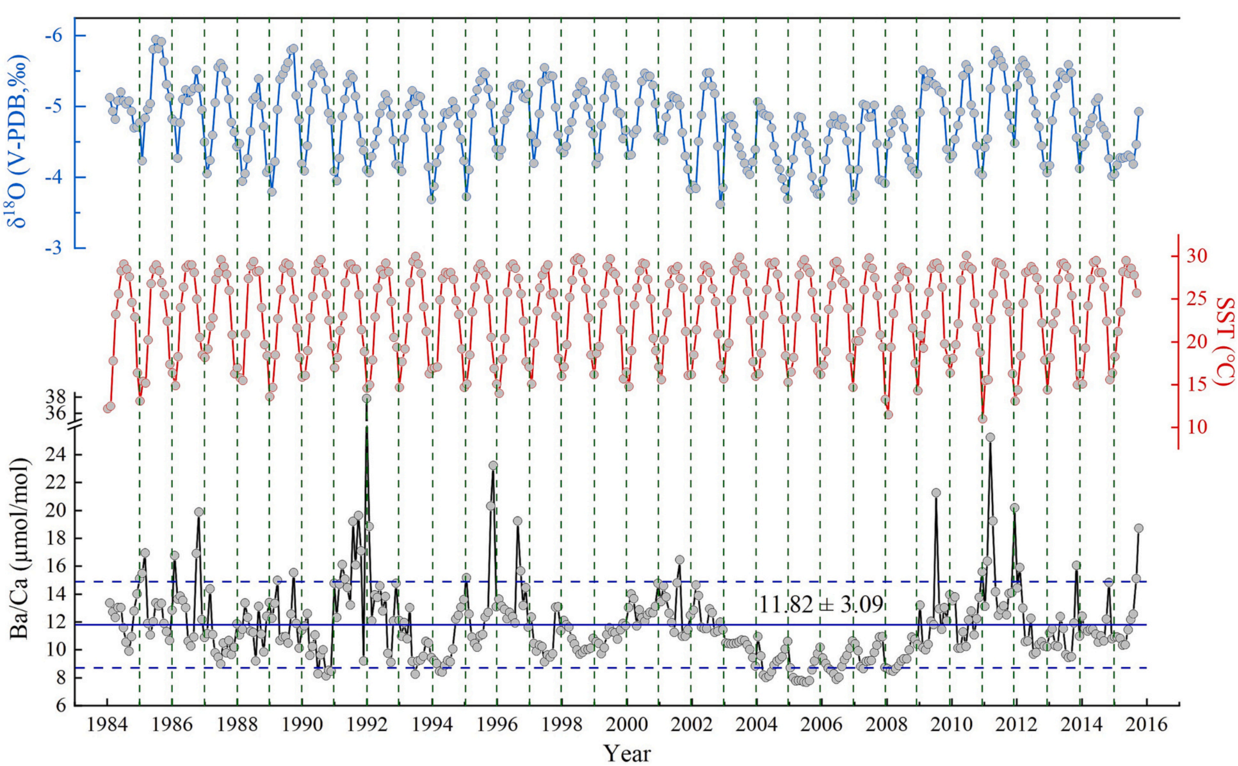

Fig. 2. A comparison of the Ba/Ca ratio, $\delta^{18}O$, and SST, the green chain line is January of each growth year. Coral skeleton Ba/Ca ratios are shown as mean ± standard deviation (SD), where the dark blue solid line presents the mean and the dark blue broken lines indicate mean ± SD.

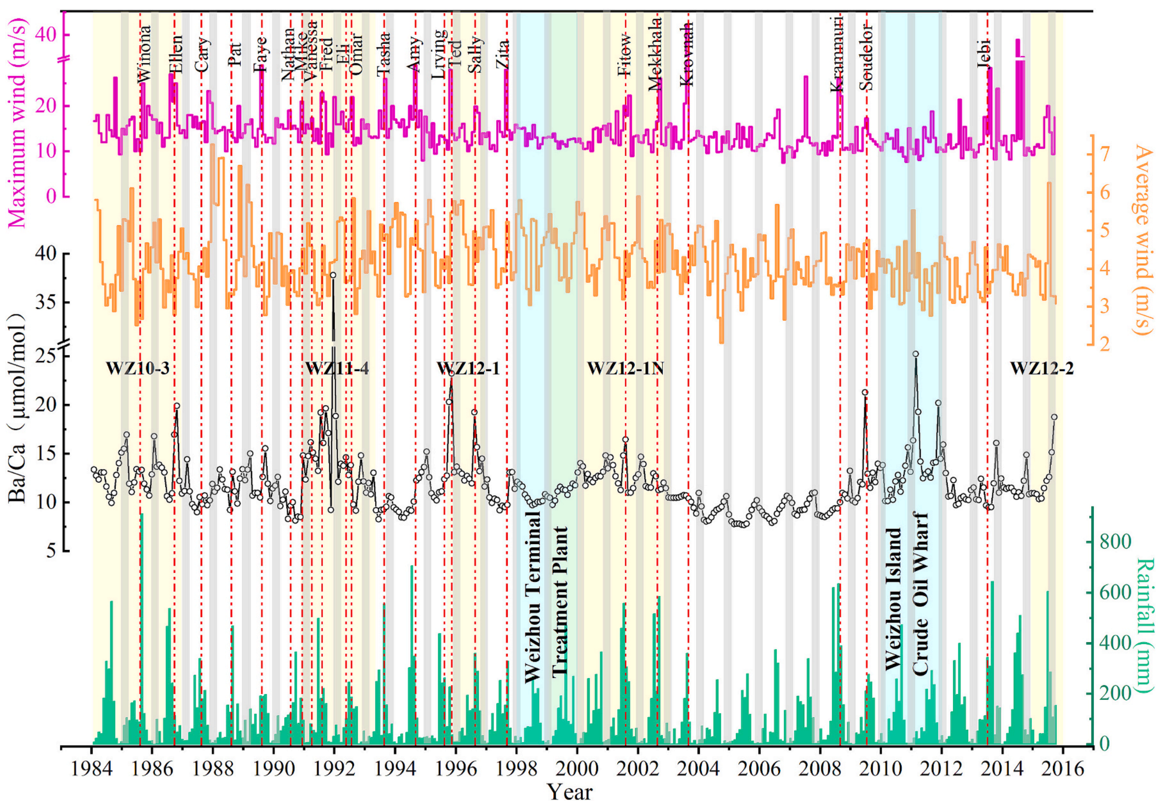

Fig. 3. A comparison of coral Ba/Ca and rainfall, average wind, and maximum wind from 1984 to 2015 CE. The red chain lines indicate the abrupt peak values of coral Ba/Ca data that may be related to tropical cyclones (near the line is the name of the typhoon in the corresponding month) and the yellow/cyan shades are the known oil field production events/coastal engineering near the study area. Gray shades correspond to the peak of coral Ba/Ca in winter during the year.

Lea et al., 1989). Conversely, other investigations proposed that the temperature dependency of the distribution coefficient governing the Ba partitioning between seawater and aragonite was negligible (Gonneea et al., 2017; Tanaka et al., 2013).

To investigate the potential influence of SST on the incorporation of Ba into the W3 coral, a comparative analysis was conducted between monthly coral Ba/Ca ratios and local SST. No significant correlation was observed between coral Ba/Ca and SST in the W3 coral, suggesting that the influence of temperature on the alteration of coral Ba/Ca ratios may not be statistically significant. This finding was consistent with previous studies of Gonneea et al. (2017), who reported a temperature-influenced value of 1.1 μmol/mol for *Favia fragum* coral with an SST range of approximately 20–28 °C and surface seawater Ba concentration of 50 nmol/kg. Based on the experiment of Gonneea et al. (2017), the SST range, and surface seawater Ba concentration (60 nmol/kg) in the Weizhou Ialand reported by Li et al. (2022), the anticipated variation in coral Ba/Ca ratios in the W3 coral was estimated to be around 1.9 μmol/mol. However, the observed monthly coral Ba/Ca ratios (ranging from 6.62 to 37.8 μmol/mol) greatly exceeded the expected temperature-driven variation, in which case the existence of interspecific differences between *Favia fragum* and *Porites* corals was negligible. The time series of monthly coral Ba/Ca ratios exhibited substantial fluctuations, while SST showed cyclical annual variations (Fig. 2). The significant disparity in fluctuations between coral Ba/Ca ratios and SST provided further evidence that the variations in coral Ba/Ca ratios should be contributed by other factors, which might mask the effects of temperature. That was to say that factors beyond temperature contributed to the significant variability in W3 coral Ba/Ca ratios. We also examined the relationship between the annual coral Ba/Ca and SST. However, there was no statistical correlation between annual coral Ba/Ca and SST ($p > 0.05$). It suggested that SST did not exert a significant influence on annual coral Ba/Ca ratios.

In addition to SST, previous studies have proposed a link between coral growth rates and the incorporation of elements in the coral skeleton (Hsieh et al., 2022; Liu et al., 2019; Matthews et al., 2008). However, no significant correlation between coral Ba/Ca ratios and growth rates ($p > 0.05$) (Fig. S1) in W3 coral effectively ruled out the influence of growth rates on the Ba/Ca ratios. Additionally, Gonneea et al. (2017) suggested that calcification rate, aragonite saturation state, and precipitation effectiveness could potentially affect coral Ba/Ca ratios, yet a comprehensive understanding of these relationships remains difficult. Given that the Ba/Ca ratios of W3 coral were not influenced by SST or growth rates, it implied that climatic or environmental factors played a key role in the observed variations. Thus, the Ba/Ca ratios of W3 coral should be a reliable proxy for surface seawater Ba concentrations.

4.2. Monthly resolution Ba/Ca indicates natural drivers

Despite significant fluctuations, the monthly coral Ba/Ca ratios have consistently displayed a cyclic pattern characterized by winter peaks (Fig. 3). It is postulated that seasonal climatic or environmental factors play a pivotal role in influencing seasonal peaks in coral Ba/Ca ratios. Previous researches have confirmed the existence of several potential factors contributing to the seasonal variations in coral Ba/Ca ratios, including river runoff (Maina et al., 2012), upwelling (Montaggioni et al., 2006), sediment resuspension induced by winds and waves (Esslemont et al., 2004), and the seasonal biogeochemical cycling (Saha et al., 2018b). To comprehend the underlying reasons for the seasonal fluctuations in the Ba/Ca ratios of W3 coral, we explored the potential impacts of these possible factors.

4.2.1. Terrestrial runoff

Terrestrial runoff plays a fundamental role as a primary source of dissolved and particulate Ba in the ocean, particularly in coastal

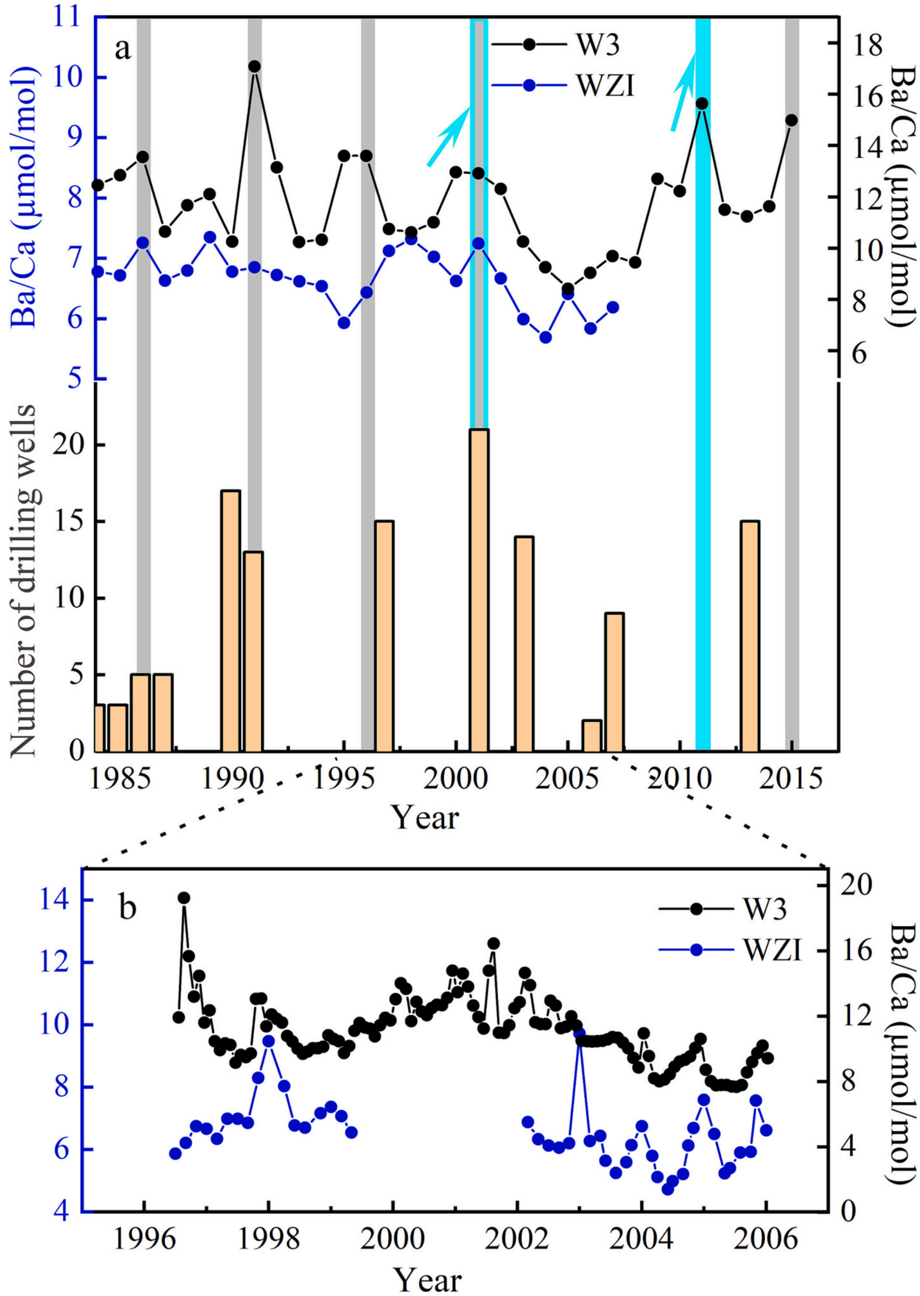

Fig. 4. a) A comparison of annual Ba/Ca between coral W3, coral WZI, and and the Number of drilling wells; b) A comparison of monthly coral W3 Ba/Ca and bi-monthly coral WZI Ba/Ca. The gray/cyan shades represent the known oil field production events/coastal engineering.

estuaries (Carter et al., 2020; Alibert et al., 2003). Within estuarine regions, substantial quantities of dissolved and particulate Ba are introduced into the ocean and subsequently incorporated into coral skeletons, thereby influencing coral Ba/Ca ratios (Alibert et al., 2003; D'Olivo and McCulloch, 2022). The significant association between coral Ba/Ca ratios and river discharge, and the peaks of coral Ba/Ca ratios coinciding with flood events provided robust evidence of coral Ba/Ca ratios emerged as a reliable proxy for quantifying the influences of river runoff in many studies (Brenner et al., 2017; Chen et al., 2020; McCulloch et al., 2003). However, some studies held a doubtful attitude toward that (Lewis et al., 2018; Sinclair, 2005). Recently, Saha et al. (2021) reported that the effectiveness of coral Ba/Ca as a proxy for terrestrial runoff might depend on whether Ba behaved conservatively or non-conservatively in the Great Barrier Reef, and it might be influenced by catchment geology, degree of weathering and river flow magnitude.

The Weizhou Island is geographically isolated from the mainland, limiting the direct influence of nearby rivers on seawater Ba levels. The likelihood of a significant contribution of river runoff-derived Ba to the coastal waters should be considered low. Surface runoff and submarine groundwater discharge have the potentials to introduce Ba from terrestrial sources into the coastal seawater, strongly associating with rainfall. The dominant presence of sedimentary rocks in the island's geology enables direct recharge of the aquifer through rainfall. Additionally, the intense precipitation can transport terrestrial materials to the ocean, increasing the elemental fluxes in seawater and incorporating them into coral skeletons. However, no significant correlation ($p > 0.05$) between the coral Ba/Ca ratios and rainfalls was observed. Furthermore, the Weizhou Island falls within the East Asian monsoon climate zone, characterized by concentrated rainfall between May and September. But the timing of peaks in monthly coral Ba/Ca ratios mostly occured in winter, did not align with the timing of rainfall (Fig. 3). To further explore the relationship between rainfall and coral Ba/Ca ratios, we analyzed the relationship between them in the dry and wet seasons, respectively. We observed that the coral Ba/Ca ratios in most years were higher during the dry season compared to the rainy season, as demonstrated in Fig. S4. This finding provides compelling evidences that the seasonal variation in coral Ba/Ca ratios cannot be predominantly attributed to terrestrial runoff.

4.2.2. Upwelling

The distribution of Ba in the ocean exhibits a similar pattern to that of nutrients, characterized by lower concentrations in surface waters and higher concentrations in deeper regions (Roy-Barman et al., 2019). During upwelling, there is a vertical displacement of nutrient-depleted surface waters by colder, nutrient-rich waters from deeper layers (Lea et al., 1989). This process results in an elevation of surface seawater Ba levels, subsequently recorded in coral skeletons, thereby rendering coral Ba/Ca ratio a valuable indicator of upwelling activity (Shen et al., 1992; Lea et al., 1989; Montaggioni et al., 2006). In our study area, the depth of the surrounding seawater is about 60 m, and there are no reports of upwelling activity. In addition, in the northern shelf of the SCS, upwelling events typically occur between April and September (Liu et al., 2013). However, the peaks of coral Ba/Ca ratios in the winter (Fig. 3) did not correspond to the time of upwelling. Therefore, the results strongly ruled out the hypothesis that upwelling plays a prominent role in driving variations of coral Ba/Ca ratios.

4.2.3. Phytoplankton activity

The depletion of Ba in shallow surface seawater is primarily attributed to its uptake by phytoplankton organisms (Bishop, 1988; Sternberg et al., 2005) and its adsorption onto biogenic particles (Dehairs et al., 1980). To investigate the impacts of marine biochemical factors on the Ba/Ca ratios in W3 coral, the concentration of chlorophyll-α (Chl-α) was utilized, which was considered as a indicator of phytoplankton activity (Chen et al., 2011; Saha et al., 2018b). It was important to note that Chl-α data were only available during 1998–2015 in the study area, with occasional data gaps. Nevertheless, these data also exhibited consistent seasonal peaks during the winter (Fig. 5), indicating active phytoplankton biomass.

Theoretically, the feeding and sorption processes of phytoplankton would lead to a decrease in the surface seawater Ba concentration, subsequently resulting in reduced Ba incorporation into the coral skeletons. Previous studies have cautioned that seasonal coral Ba/Ca ratios significantly diminished during the phytoplankton bloom and post-bloom phases (Saha et al., 2018b; Sinclair, 2005). However, seasonal Ba/Ca peaks of W3 coral were synchronized with the peaks of Chl-α appearances (Fig. 5). Moreover, the correlation analyses revealed a weak interaction between Chl-α and coral Ba/Ca ratios during 1998–2006 ($r = 0.21$, $p < 0.05$). It suggested that the involvement of other climatic or environmental factors that influenced coral Ba/Ca variations can also influence the phytoplankton activities. Sun et al. (2022) reported that the vertical mixing of seawater induced by the winter monsoon enhanced surface concentrations of cadmium (Cd), which masked the effects of biological processes associated with the phytoplankton growth stimulated by simultaneously increased nutrients. It was reasonable to speculate that similar dynamics might occur for Ba. Hence, we proposed that the winter monsoon could serve as a driving factor for seasonal peaks in both coral Ba/Ca ratios and Chl-α. In conclusion, the findings suggested that phytoplankton activities might contribute to coral Ba/Ca variations, but be confounded by other climatic and environmental factors. The concomitant changes in Chl-α and coral Ba/Ca ratios during seasonal fluctuations implied their interdependence.

4.2.4. Winter monsoon and tropical cyclones

Sediment resuspension, arising from the vertical mixing of seawater, represents a noteworthy factor that contributes to the heightened concentration of the trace element in surface seawater (Ogston et al., 2004; Presto et al., 2006). It has been identified as a significant mechanism responsible for the increased levels of Ba in the surface seawater. This process also plays a crucial role in the seasonal variations of coral Ba/Ca ratios (Alibert et al., 2003; Esslemont et al., 2004; Maina et al., 2012). For instance, Esslemont et al. (2004) found that the peaks of coral Ba/Ca ratios coincided with the resuspension of fine sediments influenced by the southeast trade winds. Substantial quantities of sediments originating from the neighboring rivers are transported toward the SCS, resulting in the accumulation of fluvial sediments (Liu et al., 2016). These sediments can be carried by currents into the Beibu Gulf, contributing to the enrichment of elements and other substances in the surface seawater under the influence of winds or other external forces. To investigate the contribution of sediment resuspensions on Ba/Ca

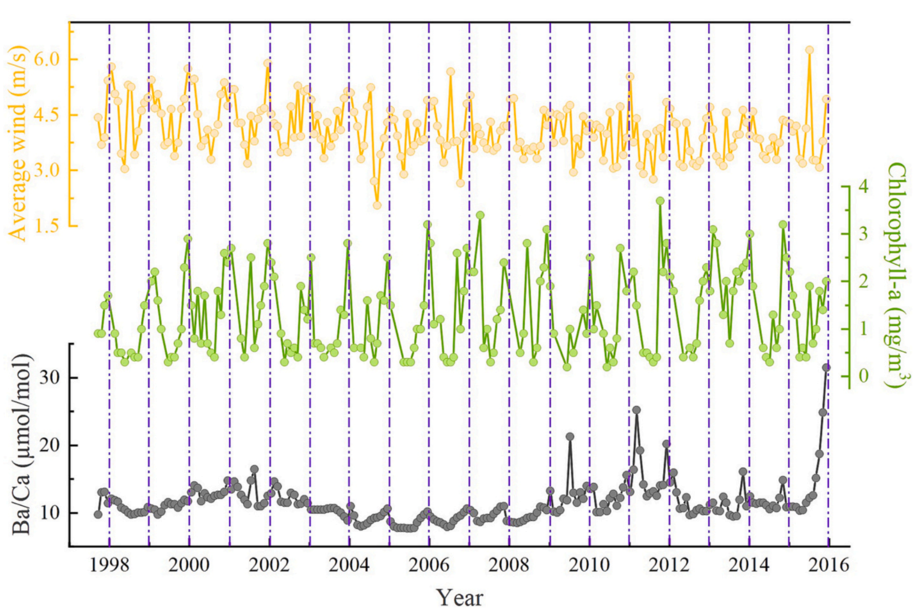

Fig. 5. A comparison of coral Ba/Ca and Chlorophyll-a, average wind from 1998 to 2015 CE. The purple chain lines represent January of each growth year.

ratios in the W3 coral, we examined the correlation between coral Ba/Ca ratios and the average surface wind speeds. The result showed a significant positive relationship between multi-year average coral Ba/Ca ratios and multi-year average wind speeds ($r = 0.73$, $p < 0.01$) (Fig. 6), confirming the influence of surface winds on coral Ba/Ca ratios. Booth et al. (2000) reported that when the wind speed exceed 4 m/s, approximately 50 % of bottom sediments could be resuspended, with the value increasing to over 80 % at the wind speed of 10 m/s. Fig. 3 showed that the average wind speed in the Weizhou Island fluctuated between 2.05 and 7.26 m/s, with a slight decreasing trend since 2001. The average value of wind speed was 4.2 m/s, which was a favorable condition for sediment resuspensions. Influenced by the East Asian monsoon, wind speeds on the Weizhou island exhibited notable seasonal variations, characterized by low wind speed in summer and high wind speed in winter. The average winter wind speed of 4.83 m/s exceeded that of summer by 1 m/s, which was recorded at 3.97 m/s. The presence of winter peaks in the monthly-resolved coral Ba/Ca ratios, which was consistent with elevated average wind speed (Fig. 3), implied a seasonal response to the winter monsoon. In contrast, despite fluctuationed in average wind speeds from June to August, coral Ba/Ca ratios remained consistently low during the summer. It suggested that the impact of summer monsoon on surface seawater Ba levels might be minimal. The higher wind speeds in the winter had a greater impact on enhancing the vertical mixing of seawater and resuspending sediment than the lower wind speeds in the summer. This discrepancy in wind speeds likely accounted for the observed variations in coral Ba/Ca ratios between the winter and summer. These findings provided evidences for the influence of the winter monsoon on the seasonal cycle variations of seawater Ba levels. Similarly, Li et al. (2022) reported the influence of winter monsoon on the bimonthly coral Ba/Ca record from the southwest coast

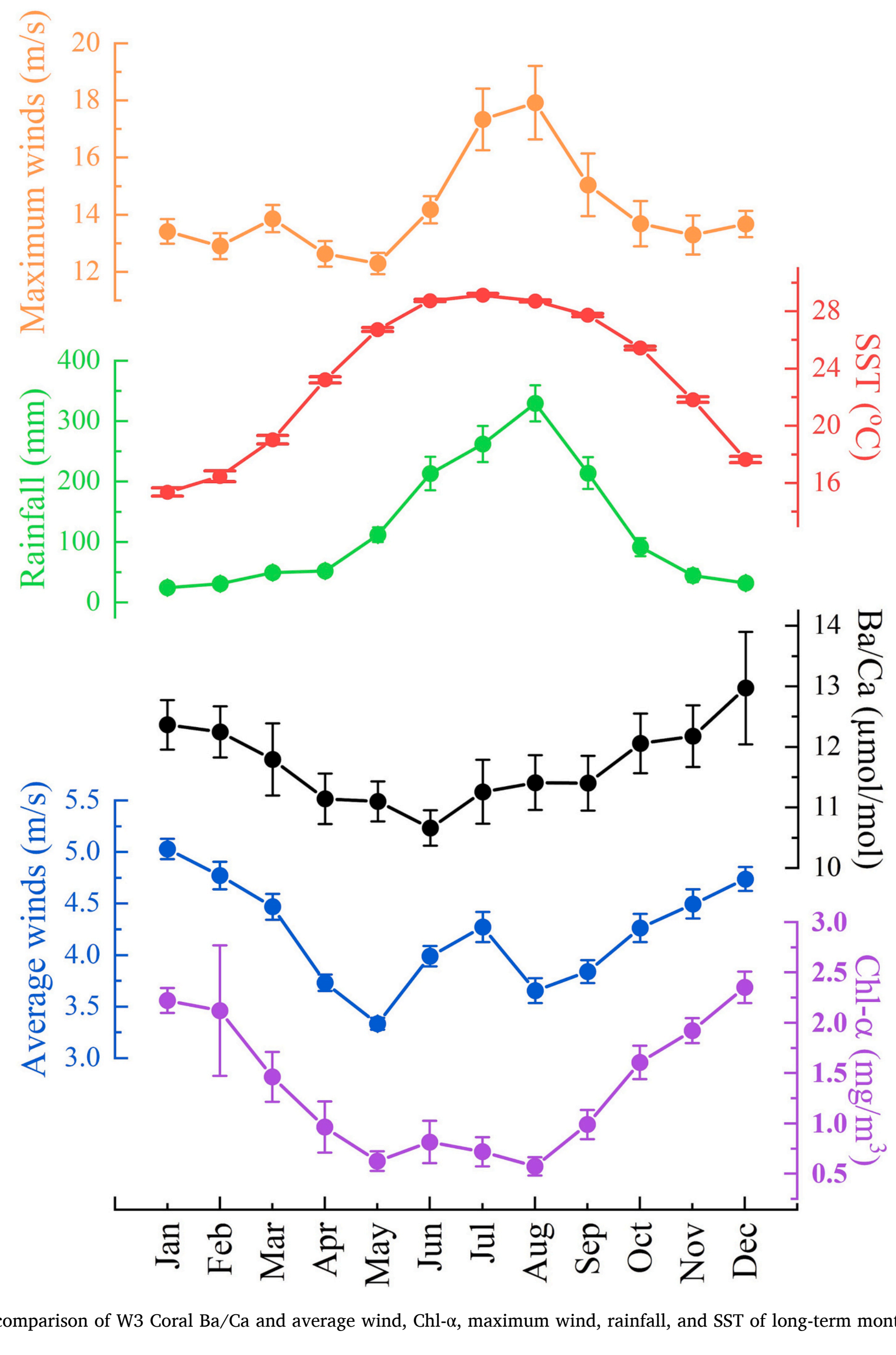

Fig. 6. A comparison of W3 Coral Ba/Ca and average wind, Chl-α, maximum wind, rainfall, and SST of long-term month averages.

of Weizhou Island (Fig. 4b). The Ba/Ca records of W3 coral offered higher resolution (Fig. 4b) allowed for clearer visualization of Ba/Ca changes. We concluded that Ba/Ca ratios of W3 coral provided more reliable climatic records of winter monsoon in the Weizhou Island. Our findings supported by Li et al. (2022), provided valuable insights into the seasonal dynamics of coral Ba/Ca ratios and their relationship with winter monsoon, and highlighted the strength of coral Ba/Ca records in capturing climatic variations.

However, some certain peaks in the coral Ba/Ca ratios were observed during anomalous periods not correspond to the time of winter monsoon, indicating the influence of an additional factor on coral Ba/Ca ratios. These peaks occurred in the summer or autumn of most years (Fig. 3). To ensure the validity of our findings and rule out the possible impacts from interpolation, we conducted a comprehensive comparison between the surface wind speeds and coral Ba/Ca ratios during both the dry and wet season. Results revealed that coral Ba/Ca ratios were higher during the dry season compared to the wet season, confirming the significant role of winter monsoon. However, we also observed a contrary relationship in 1989, 1996, 2001, 2002, 2003, and 2009 CE (Fig. 7). Given that the seasonal peaks of coral Ba/Ca ratios primarily occurred due to the high wind speed, we explored the potential influence of tropical cyclones. The high wind speeds of tropical cyclones possess the capacity to induce vertical mixing of seawater (Walker et al., 2005) and weaken seawater stratification (Guan et al., 2021).

The rapid ventilation of the thermocline induced by tropical cyclones can lead to sediment resuspensions increased, facilitating the mixing of bottom Ba-rich waters with surface seawater. Moreover, tropical cyclones often bring heavy precipitations, resulting in a short period of terrestrial runoff that transports significant amounts of terrigenous material into the ocean (Brenner et al., 2017). To accurately assess the impacts of tropical cyclones on coral Ba/Ca ratios, we gathered comprehensive information on tropical cyclones occurring within a 500 km radius of Weizhou Island, including details such as duration, magnitude, and wind speed. Based on the data from the local meteorological station, the Weizhou Island typically experiences 2–4 tropical cyclones with strong winds every summer or autumn. Notably, the specific tropical cyclones named Faye, Sally, Fitow, Mekkhala, Krovanh and Soudelor were recorded in the October 1989, August 1996, August 2001, September 2002, August 2003 and July 2009 (Fig. 3), respectively, coinciding with the non-winter peaks observed in the coral Ba/Ca time series (Fig. 7). During these periods, the coral Ba/Ca ratios exhibited a rapid increase, then reached a peak, subsequently followed by a subsequent rapid decline. This short-term effect showed the same consequences as the effect of tropical cyclones. This finding was in line with the research by Yamazaki et al. (2011), which revealed that the highest peaks of coral Ba/Ca ratios were observed from August to September, corresponding to the passage of typhoons.

However, Weerabaddana et al. (2021) concluded that coral Ba/Ca ratios might not have the ability to reliably record tropical cyclones due to the limitations of its temporal resolution. In our research, the tropical cyclones occurred in closer proximity to the island, with wind speeds surpassing 10 m/s, which were highly conducive to the vertical mixing of seawater. And the synchronized timing of coral Ba/Ca spikes with these tropical cyclones suggested that monthly coral Ba/Ca ratios exhibited a response to these extreme weather events. Additionally, the lower coral Ba/Ca ratios during the dry season compared to the wet season in 1989, 1996, 2001, 2002, 2003 and 2009 CE may also be attributed to the weakened winter monsoon and possible intensified human activities during the wet season (Fig. 3).

4.3. Coral Ba/Ca ratio responds to anthropogenic drivers

The time series of W3 coral Ba/Ca ratio reveals significant fluctuations in monthly resolution records, ranging from 7.68 to 37.80 μmol/mol. Considering the reported distribution coefficient of ~1.2 between *Porites* coral skeletons and surface seawater Ba (LaVigne et al., 2016), the concentration of Ba in the surface seawater had been estimated to range between 56 nmol/kg and 275.63 nmol/kg. These concentrations exceed those typically observed in natural settings (Hsieh and Henderson, 2017), suggesting an elevated level of Ba in the surrounding

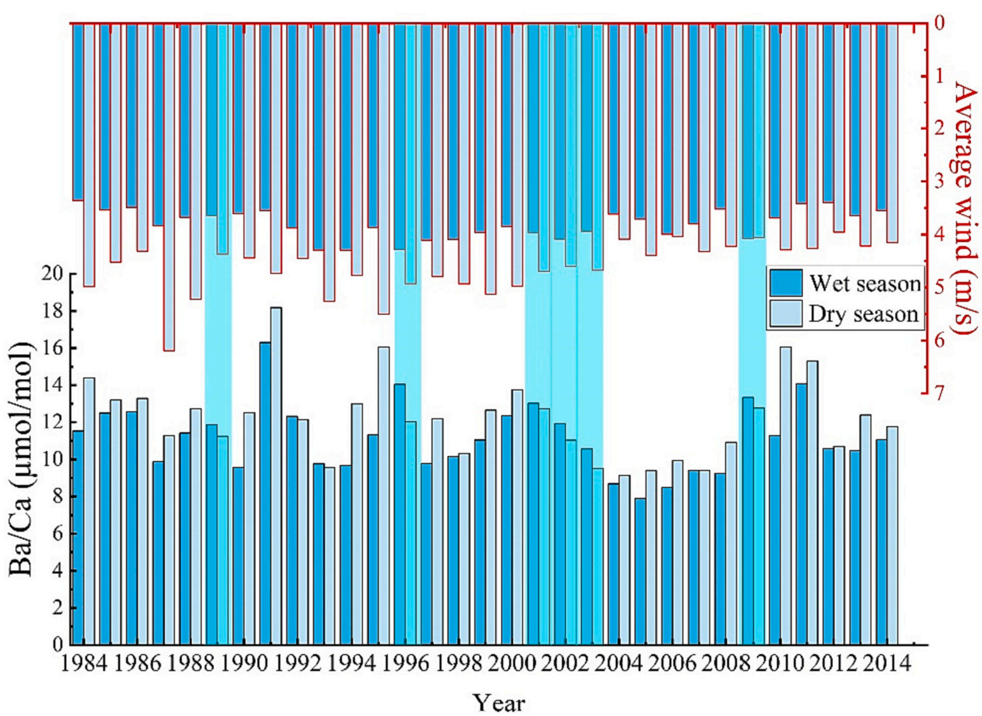

Fig. 7. A comparison of W3 coral Ba/Ca ratios and Average wind in the dry season and wet season. The black border light blue and dark blue color represents the average values of coral Ba/Ca in the dry season and wet season, respectively. The red border light blue and dark blue color represent the rainfall in the dry season and wet season, respectively. The blue shadow represents the year with inconsistent trends.

seawater. As the Weizhou Island is an isolated island, several environmental factors, including tourism development, seawater pollution, engineering construction, and oil drilling, could contribute to increasing element concentration in the surface layer of seawater (He et al., 2009). Notably, the use of barite as a drilling mud additive in oil drilling operations can contribute to seawater pollution and serve as an additional source of Ba in the water column (Carriquiry and Horta-Puga, 2010), ultimately incorporating into coral skeletons. Weerabaddana et al. (2021) concluded that coral Ba/Ca ratios exceeding 9 μmol/mol were associated with land use changes, minings, and oil drillings. The average Ba/Ca ratio of W3 coral was about 11.82 μmol/mol, which is approximate to the ratios observed in *Siderastrea siderea* coral Ba/Ca (~11 μmol/mol) affected by oil drillings in Mexico. Given the absence of significant land use changes reported on Weizhou Island, the relatively elevated Ba/Ca ratios observed in the W3 coral may be attributed to the influence of oil drilling activities.

The Weizhou Island is the largest oil drilling development area in the northern SCS, with drilling operations commencing in August 1974 and persisting to the present day. The available historical data reveals a notable positive correlation between historical oil production data and barite production data from the Weizhou oil field ($r = 0.73$, $p < 0.01$) within the time 1990–2010 (Figs. S2 and S3). This correlation substantiates the demand for barite in oil drilling activities near Weizhou Island. The concentration of dissolved Ba in seawater is controlled by equilibrium with solid barite (Neff, 2008), therefore it can significantly increase when the drilling starts. Although barite is limited in dissolution in seawater, the large quantities and the continuation of oil drilling and extraction operations introduced barite in large quantities. Under the influence of temperature or pressure, it can dissolve and release Ba and make a significant increase in the surrounding seawater. To confirm the response of coral Ba/Ca to oil drilling, we compared the number of exploratory and drilled wells of the six major oil field developments with the annual coral Ba/Ca records (Fig. 4a). The results indicate that the peaks or increasing trends in coral Ba/Ca ratios in 1986, 1991, 1996, 2001, and 2015 (Fig. 4a) correspond to the timing of exploration and drilling activities. Due to insufficient drilling data, interpolation errors and lags in time series, there is a lack of strict correspondence between the magnitude of the coral Ba/Ca ratios and the number of wells drilled. In addition, the peaks in monthly coral Ba/Ca occur in the development timeline of historical data of the six major oil field developments of the WZ10-3 (1983–1986), WZ11-4 (1990–1993), WZ12-1 (1996), WZ12-1N (1999–2003), and WZ12-2 (2015) oil fields (Fig. 3). The drilling mud in seawater diminishes rapidly as drilling activities are completed, and there is only about 1 % of Ba remains preserved in the sediment one year after drilling (Boothe and Presley, 1987).The sharp declines in annual coral Ba/Ca ratios were observed in 1987, 1992, and 2003 CE (Fig. 4a), while the monthly resolution coral Ba/Ca of 1991 CE rapidly decreased to relatively low levels (Fig. 3), potentially linked to diminished oil drilling activities during those periods. Weerabaddana et al. (2021) reported similar sharp declines in coral Ba/Ca ratios resulting from reduced offshore oil well operations. Comparing the periods with oil drilling activities and without oil drillings, we found that the coral Ba/Ca ratios were significantly higher in the years with oil drillings than those in the other years, like 1986 and 1987, 1991 and 1992, etc. These findings suggest that annual coral Ba/Ca ratios can capture the signal of oilfield production, and the significantly high values and increased levels of coral Ba/Ca in W3 coral were influenced by oil drilling activities. Similarly, Li et al. (2022) reported a pronounced signal of oil exploration and drilling activities along the southwestern coast of Weizhou Island based on the annual Ba/Ca record of WZI coral spanning 1977–2007. The Ba/Ca ratios of W3 coral can compensate for the post-2007 Ba/Ca ratios data of coral WZI (Fig. 4a). Notably, the Ba/Ca ratios of W3 coral are significantly higher than those of coral WZI (Fig. 4), indicating location-specific variations in trace elements influenced by oil drilling activities (Jiang et al., 2020). The continuous and higher-resolution Ba/Ca ratios of W3 coral yield a detailed and uninterrupted record of seawater Ba concentrations (Fig. 4b). These observations suggest that the coral Ba/Ca ratio have potentials to serve as an indicator of oil drilling activities, which are valuable for understanding the impact of oil field production on the marine environment.

To establish the relationship between the coral Ba/Ca record and local oil exploitation at a monthly resolution, we collected detailed data on oil exploration and drilling. Historical records revealed that the WZ10-3 oil field commenced production in August 1986 CE, which coincided with exceptionally high annual-resolution coral Ba/Ca value (Fig. 4a) and pronounced fluctuations in monthly-resolution coral Ba/Ca ratios (Fig. 3). The WZ11-4 oil field began production in February 1990 CE and continued until October 1993 (Wang, 2017). The time series showed the monthly coral Ba/Ca ratios peaked in December 1991 CE, aligning with the period of substantial oil field development for WZ11-4. Additionally, the production of WZ12-1N and WZ12-2 fields corresponded to the peaks in coral Ba/Ca occurring in December 2003 and September 2015, respectively (Fig. 3). In summary, the coral Ba/Ca ratios display increased fluctuations and dramatic peaks in the year of oil production, suggesting that monthly coral Ba/Ca was influenced by oil production. The time lag of 2–3 months between coral Ba/Ca peaks and field production time may be attributable to interpolation or hysteresis of elemental incorporation into the coral skeleton, but it falls within the acceptable error tolerance.

Surface seawater Ba concentrations can be augmented not only through oil drilling activities but also as a result of enhanced sediment deposition associated with coastal engineering (Carriquiry and Horta-Puga, 2010; Lewis et al., 2007). The Weizhou Terminal Treatment Plant attained its official completion and commenced operations in August 1998, which is affiliated with the Zhanjiang Branch of China National Offshore Oil (China) Company Limited. The construction of the Weizhou Island Crude Oil Wharf and its supporting project in Beihai was initiated in 2010 CE, with a planned completion date before June 2011 CE. In the construction phase, dredgers are capable of resuspending dredged materials deposited on the seabed due to mechanical disturbances, overflows and spill, substantial utilization of mud was used and discharged continuously, leading to an increase of suspended dredged materials in the water column (Ito et al., 2020). This process may serve as a significant influential element in regulating the concentration of surface seawater Ba, then affecting coral Ba/Ca ratios. There was a consistent upward trend observed in the coral Ba/Ca ratios from 1998 to 2000 (Fig. 4), corresponding to the commencement of operations at the Weizhou Terminal Treatment Plant. This observation strongly suggests a discernible impact of industrial production on the coral Ba/Ca ratios. The variations in coral Ba/Ca exhibited a significant increase during the period from 2010 to 2011 (Fig. 4), ultimately culminating in a peak value of 25.24 μmol/mol in March 2011 CE (Fig. 3). Notably, these peak values coincided precisely with the time of the crude oil terminal construction, suggesting the influence of coastal engineering on coral Ba/Ca ratios. These findings provide evidence that industrial activities such as oil drilling and crude oil terminal projects have a significant impact on the Ba/Ca ratios of coral and emphasize the substantial impact of human activities on Ba levels in surface waters. In addition, the coral Ba/Ca ratios are a potential indicator of oil drilling operations and engineering efforts. Thus, the integration of coral Ba/Ca analysis provides a semi-quantitative method for monitoring and documenting environmental events associated with these activities.

5. Conclusion

We conducted a comprehensive analysis of monthly variations in coral Ba/Ca ratios and $\delta^{18}O$, comparing them with detailed climatic and environmental data, such as SST, chlorophyll-a (Chl-a), rainfall, average and maximum wind speeds, and tropical cyclone events. The results showed that the coral Ba/Ca ratios had a negligible relationship with SST and growth rates, confirming their reliability as an indicator of surface seawater Ba concentration. Notably, we found that the substantial increases and pronounced fluctuations in surface seawater Ba levels were predominantly attributed to human activities, particularly oil drillings and coastal engineering constructions. The Ba/Ca ratios of W3 coral showed distinct seasonal characteristics, exhibiting higher values in the winter and lower values in the summer. Significant seasonal peaks in the winter resulted from the contribution of winter monsoon-induced sediment resuspensions. It was worth emphasizing that the occurrence of non-winter peaks in coral Ba/Ca ratios coincided with the tropical cyclone events. Our study provided valuable insights into human activities and natural factors compounding effects on seawater Ba in a complex marine environment. As such, these findings provided the database to ensure the reliability and accuracy of coral Ba/Ca ratio as a unique proxy for understanding the dynamics of environmental and climate change.

CRediT authorship contribution statement

Chunmei Feng: Investigation, Formal analysis, Writing-Original draft preparation; Wei Jiang: Conceptualization, Methodology, Formal analysis, Writing-Reviewing and Editing, Funding Acquisition, Resource; Kefu Yu: Data curation, Funding Acquisition, Resource, Supervision; Yinan Sun: Investigation; Sirong Xie: Investigation; Yansong Han: Methodology; Chaoshuai Wei: Methodology, Data Curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.167414.

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