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RESEARCH ARTICLE
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Key Points:

- Coral skeletal Cd/Ca ratios in monthly resolution were first reported
- Seawater mixing process and sediments resuspension caused by winter monsoon are responsible for Cd seasonal variations in surface seawater
- Coral skeletal Cd/Ca ratios have potential to be a novel proxy for winter monsoon

Supporting Information:

Supporting Information may be found in the online version of this article.

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High-Resolution Coral Records of Cadmium in Surface Seawater: Biogeochemical Cycling and a Novel Proxy for Winter Monsoon

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Abstract Cadmium (Cd) geochemical cycle plays a significant role in the composition and function of the marine ecosystem. Skeletal cadmium-to-calcium (Cd/Ca) ratios in hermatypic corals have been applied to reconstruct the historical changes of oceanic and climatic processes, yet there was no systematic evaluation of this tracer's natural variability in high resolution over time. Here, we reported a coral skeletal Cd/Ca record in monthly resolution from 1999 to 2008 CE and reconstructed the history of Cd contents in surface seawater in the northern South China Sea. A significant seasonal variation (higher in the winter but lower in the summer) of Cd contents in surface seawater can be identified. We found that the seasonal variations in coral skeletal Cd/Ca ratios exhibited significant trends coupled with the surface wind speeds, indicating that strong winds had likely driven the vertical seawater mixing process and then induced the process of sediment remobilization on the shelf, which significantly increased Cd contents in surface seawater. The reduction in Cd contents in surface seawater due to biological processes might be masked by the impacts of surface winds. Importantly, we also observed that coral skeletal Cd/Ca records in the winter showed significant correlations with the winter monsoon index, highlighting the possibility as a new proxy of winter monsoon in the non-upwelling shelf environments.

Plain Language Summary Cadmium (Cd) is a nutrient element absorbed by phytoplankton in surface seawater, showing a distribution of low surface content and high bottom content. In order to determine the seasonal variations of Cd content in surface seawater in the northern South China Sea, we analyzed the coral skeletal Cd/Ca ratios in monthly resolution (1999–2008 CE) and finally concluded that the process of sediment resuspension and vertical mixing of seawater driven by winter monsoons is the main reason. The reduction of Cd contents in surface seawater due to biological processes was masked by the impacts of surface winds. In the past, Cd content in seawater/coral has been used to track the history of upwelling and El Niño Southern Oscillation, but the potential indicative on winter monsoon has not been reported so far. Considering that the trend between coral skeletal Cd/Ca ratios and average wind speeds showed a great agreement, we suggested that coral skeletal Cd/Ca ratios in the winter might be a potential proxy of winter monsoon.

1. Introduction

Cadmium (Cd) is a toxic trace metal element, which can be transferred or accumulated through the food chain, and is one of the elements that must be measured in marine monitoring (Jurado-González et al., 2003). The behavior and distribution of Cd in the seawater are similar to that of macro-nutrient, being biologically depleted in surface seawater (Xu et al., 2008) and enriched at depth through dissolution of sinking organic matter (Boyle et al., 1976; Bruland et al., 1978), forming a scavenged depth profile of nutrient types (Grottoli et al., 2013). Cd is also considered as a micro-nutrient associated with a carbonic anhydrase that is ubiquitous in the bacteria, plants and animal kingdoms (Lionetto et al., 2005). Some researches suggested that Cd was an essential trace metal element in phytoplankton (Lane & Morel, 2000; Lane et al., 2005), but others suggested that Cd was non-specifically exploited by phytoplankton and stored intracellularly to avoid toxicity (Horner et al., 2013). Whichever mechanism may explain the nutrient-like behavior of Cd, its strong correlation with phosphate reflects its involvement in biological cycling processes (Delgadillo-Hinojosa et al., 2015). However, the geochemical

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behavior of Cd in surface seawater is still poorly resolved, despite its potentially critical impacts on the nearshore biosphere.

In the modern ocean, the primary source of Cd is land runoff in particulate forms (Libes, 2009; Wang et al., 2010). As river water moves downstream into estuaries, a large amount of particulate matters enter the ocean, most of which is decomposed and bound in surface seawater by various organisms (Collier & Edmond, 1984; Martin & Knauer, 1973), while a small portion is adsorbed by particulate matters and settles on the seafloor along with other organic debris, which also remains in a state of continued decomposition during the sinking process (Boyle, 1988). As a nutrient-like trace metal element, Cd below the light-transmitting layer increases rapidly with depth and reaches a maximum near the thermocline (~1,000 m) (Libes, 2009). After that, it no longer changes significantly with the water depth and remains constant basically (Feng & Tian, 2018; Libes, 2009). The retention time of Cd in seawater is ~300,000 years, much longer than the sufficiently mixing time of seawater, so that Cd from natural and anthropogenic sources is mainly deposited in the bottom sediments (Zhang et al., 2019). The Cd contents in sediments vary in the range of 0–8.6 μg/g (Yang et al., 2021). The ocean has a scavenging effect, usually in the form of suspended sediments adsorption (Turner et al., 2008), metal-sulfide formation (Jiann et al., 2005) and biological ingestion (Liu et al., 2012). Cd may be re-released into the surface seawater by upwelling and ocean currents (Delgadillo-Hinojosa et al., 2015), as a "new" source (Souri et al., 2020). Little environmental concern is warranted for the remobilization of Cd (Choi et al., 2006), and the desorption of Cd from sediments by resuspension in seawater is greater than for any other heavy metals, controlled by the redox potential (Simpson, 1978). In addition, Cd content is low in surface seawater of the tropical and subtropical regions, but high in middle and deep water of the Southern Ocean (Feng & Tian, 2018). This feature is mainly related to the mixing of water masses, which also indicates that Cd is sensitive to oceanic processes such as vertical mixing and upwelling (Carriquiry and Villaescusa, 2010). Therefore, the variation of Cd contents in seawater is often used as an indicator of ocean current changes.

Aragonite skeletons of corals are ideal geochemical indicators, providing the marine environment and meteorological information (Saha et al., 2016), and the Metal/Ca ratios in coral skeletons with the properties of high-resolution and continuous records are unique archives recording temporal variations of trace metals in surface seawater (Saha et al., 2016). The coral cadmium/calcium (Cd/Ca) is generally regarded as an indicator of upwelling (Reuer et al., 2003). Shen et al. (1987) believed that Cd in reef corals is a sensitive tracer of natural and anthropogenic disturbances to the surface seawater in history, and can be used to evaluate the onset/termination timing patterns of El Niño Southern Oscillation (ENSO). Pretet et al. (2014) found that in laboratory experiments Cd/Ca radios and salinity revealed a positive correlation for each coral genus. Carriquiry and Villaescusa (2010) found that the interannual variation of coral skeletal Cd/Ca radios in the eastern North Atlantic is related to ENSO, and suggested that Cd/Ca radios in biogenic carbonates could be used as a tracer of increasing seawater stratification and weakening trade winds. At present, there are few reports on coral skeletal Cd/Ca records in coastal and continental shelf, and most of the existing studies were restricted to annual-decadal variations, which seriously hinders the in-depth study of the geochemical behavior of Cd. In this paper, we used a monthly resolution coral skeletal Cd/Ca record, obtained from the Weizhou Island (WZI) in the northern of South China Sea (SCS), to analyze the variation mode and potential influencing factors of Cd in surface seawater, and to discuss the feasibility of coral skeletal Cd/Ca record as an alternative indicator of sea surface winds.

2. Materials and Methods

2.1. Study Area

Weizhou Island is a volcanic island located in the north SCS (Figure 1), isolated from the Asian continent. The island resides in the East Asian monsoon realm but non-upwelling areas with subtropical maritime climate. WZI has suitable surface seawater temperature (SST, from ~16°C to ~32°C, average of ~25.0°C), surface seawater salinity (SSS, average of ~32.9‰), and annual precipitation (~1,423 mm) for coral reefs. Thus, there are a large number of corals, including *Porites*, distributed here with adequate light, excellent water exchange conditions, and smooth coastal slopes. During the wet season (May–October), the southwest summer monsoon and occasional typhoons bring more than 84% of annual precipitation (Figure S1 in Supporting Information S1). In the dry season (November–April), the prevailing winter monsoon brings cold and dry air masses from the Siberian High. Meanwhile, as a famous tourist resort, the local government pays great attention to the protection and monitoring

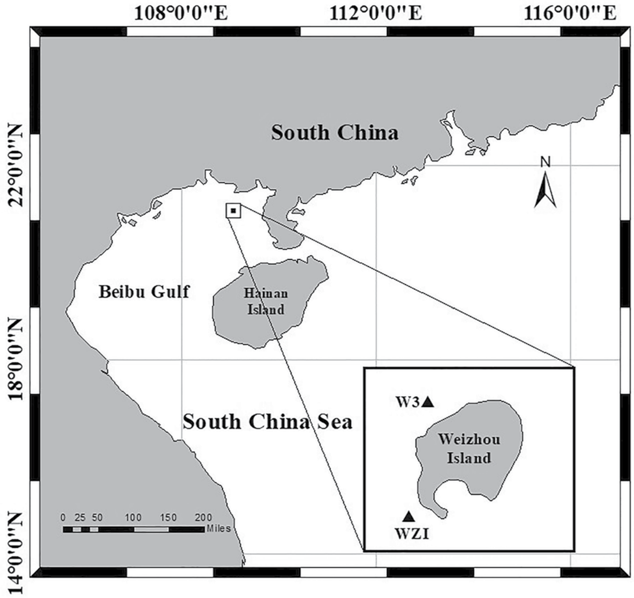

Figure 1. Location map of the coral sampling site and study area. The black rectangle indicates Weizhou Island (WZI). The black triangle indicates the sample site (W3 and WZI) used in this study.

of marine environment, thus human activities have been clearly recorded in the statistical yearbook or the bulletin of the environment.

2.2. Analytical Methods

The *Porites* coral was taken from the northwest of WZI (W3: 21°4′7′′N, 109°5′24′′E, as shown in Figure 1) in October 2015, at a sampling depth of 4 m. In the laboratory, the collected coral samples were cleaned and then dried, cutting into a plate (approximately 8 cm wide and 1 cm thick) along the growth axis. After that, we used X-ray to take photos of the interlaced light and dark density bands. To remove surface organic matter and contaminants, all the samples were soaked in 10% H_2O_2 for 48 hr, then cleaned with Milli-Q water (3 times), and finally air-dried for 48 hr at 60°C. Details of sampling and age models can be referred to our previous research (Xu et al., 2018).

After the pretreatment of the coral samples, a total of 416 powder samples with ∼3 mg in each, were extracted along the coral growth axis, dissolved with 2% HNO_3 at a sample: solution ratio of 1:6,000, and finally liquid samples were obtained for instrumental determination of the macronutrient and trace element contents. In order to correct the matrix effect of instrument drift, internal standard elements (^{103}Rh, ^{115}In, and ^{187}Re) were added to all samples, and the concentration was 6 ppb. In addition, national geochemical standard materials GBW07129, GBW07133, and GBW07135 were selected as external standards. Cd and Ca contents of all samples were determined by the Thermo Fisher inductively coupled plasma-mass spectrometer (ICP-MS). Oxygen isotopes were analyzed by Finnigan MAT-253 stable isotope mass spectrometer. Details of elements and isotopes can be referred to the previous researches of Xu et al. (2018) and Jiang et al. (2020).

In this study, assuming consistent intra-annual growth rates of the coral, each annual cycle was determined based on the maximum δ^{18}O values (the lowest temperature) and minimum δ^{18}O values (the highest temperature) points, and the coral skeletal data were processed to monthly resolution by linear interpolation. However, due to the complex biological structure of corals and the multivariate changes in surrounding environment, the actual intra-annual growth rate of corals cannot be consistent. Therefore, this method may result in a certain deviation in the time series of monthly resolution, which requires extra attention in data analysis, so that we use 12-month sliding-window correlation to analysis the data that can effectively eliminate the effect of interference. This method takes 12-month data for local averaging, continued calculation on an interval-by-interval basis, and finally makes the correlation analysis results more credible. The relevant equation as follows ($N = 12$):

$$\overline{x} = \frac{X_{n-(N-1)} + X_{n-(N-2)} + \ldots + X_{n-1} + X_n}{N}$$

$$\overline{y} = \frac{y_{n-(N-1)} + Y_{n-(N-2)} + \ldots + Y_{n-1} + Y_n}{N}$$

$$\mathrm{Correl}\,(X, Y) = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}$$

According to our previous research (Wu et al., 2022), the coral Ni/Ca ratios during the P2 period (1994–2008 CE) were relatively low and stable, which is lower than worldwide average (∼8.2 nmol/kg). Before 1994, exploration, production, and transportation in oilfields near the WZI had a great impact on the heavy metal contents; after 2008 CE, there were several oil spills in the region, with the development and operation of the Beibu Gulf Economic Zone. Thus, we chose the decade (1999–2008 CE) that is not affected by oil extraction or other representative anthropogenic activities around WZI, with a more pronounced trend as the focus of this paper.

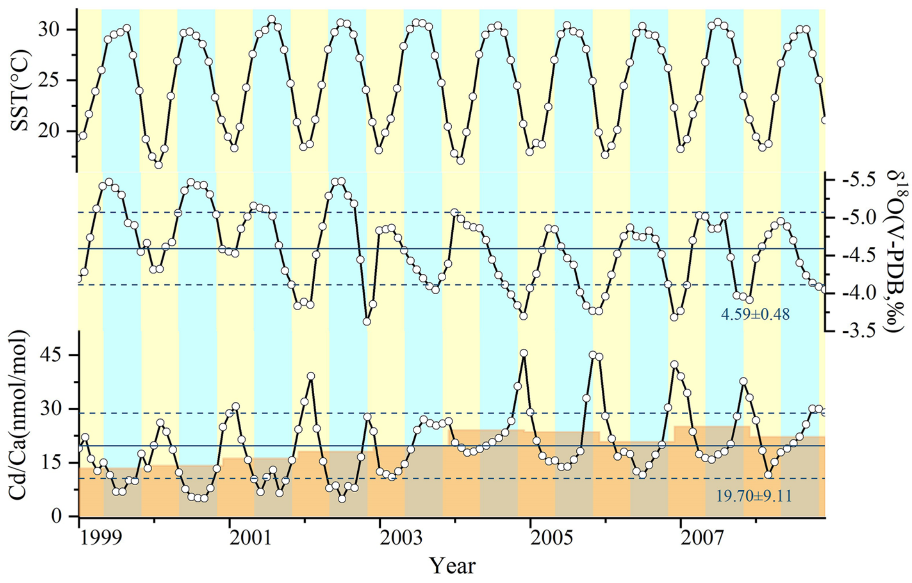

Figure 2. Comparison of surface seawater temperature, $\delta^{18}O$ and Cd/Ca ratios in *Porites lutea* coral skeletons from 1999 to 2008. Data for the dry and wet seasons are divided by two background colors (light yellow and light blue). Coral skeleton Cd/Ca ratios and $\delta^{18}O$ are shown as mean ± standard deviation (SD), where the dark blue solid line presents mean and the dark blue broken lines indicate mean ± SD. The orange shaded area is the annual mean of coral Cd/Ca ratios from 1999 to 2008 CE.

2.3. Climate and Environmental Data

The SST data from 0.25° × 0.25° ERA5 monthly mean data (Hersbach et al., 2019) were utilized in this study (https://cds.climate.copernicus.eu/cdsapp#!/dataset/10.24381/cds.f17050d7?tab = overview/). The 0.5° × 0.5° SSS data were from the Simple Ocean Data Assimilation (SODA, http://apdrc.soest.hawaii.edu/las/v6/constrain?var=4785/). Rainfall and wind speed data were collected from the WZI Weather Station. The 0.1° × 0.1° monthly average Chlorophyll-a (Chl-a) concentration data were acquired using NOAA database (https://coastwatch.pfeg.noaa.gov/erddap/griddap/jplMURSST41.html). The East Asian summer/winter monsoon indexes were obtained from the National Tibetan Plateau Data Center (http://data.tpdc.ac.cn/zh-hans/data/1c0c4197-5e5d-4f0d-bd38-03dae3658a06/) and China Climate Bulletin.

3. Results

As shown in Figure 2, coral skeletal Cd/Ca ratios ranged from 4.85 to 45.58 nmol/mol, with an average value of 19.70 ± 9.11 nmol/mol, which is consistent with the range of Cd/Ca ratios in different species of corals (6.53~62.90 nmol/mol) (Pretet et al., 2014). It is worth noting that obvious seasonal fluctuations can be observed with the peaks occurring in the dry season and the low values occurring in the wet season. The average Cd/Ca ratios in the dry season are 23.81 ± 4.81 nmol/mol, and the average Cd/Ca ratios in the wet season are 15.59 ± 6.13 nmol/mol. In addition, the annual average values during the decade ranged from 13.4 to 25.1 nmol/mol, showing a slight upward trend overall (Figure 2).

Cd contents in surface seawater are usually in the range of 0.002–0.909 μg/L all over the world (Li et al., 2010, 2013; Lian et al., 2001; Yang et al., 2017; Yu, 2003). According to the distribution coefficient of Cd between *Porites lutea* coral skeletons and surface seawater (0.6, referring to Jiang et al. (2020)), the Cd content in surface seawater can be calculated combined with the relatively stable content of Ca in surface seawater (~10.3 mmol/kg) (Kelly et al., 2009; Quinby-Hunt & Turekian, 1983). Results showed that the Cd contents in surface seawater ranged from 0.009 to 0.088 μg/L, with an average value of 0.038 ± 0.018 μg/L (Figure 3). Obviously, the Cd content in surface seawater from WZI was close to the natural seawater, although it was slightly higher than the background value of surface seawater in the northern of SCS (0.002–0.017 μg/L, Yu, 2003) and the measured value in the open ocean (e.g., 0.04 μg/L in Xisha Island, Zhou et al., 2007). Comparing with the content of Cd in the near-shore surface seawater (e.g., 0.14 μg/L in Daya Bay, Yang et al., 2017), it was still relatively low. Meanwhile,

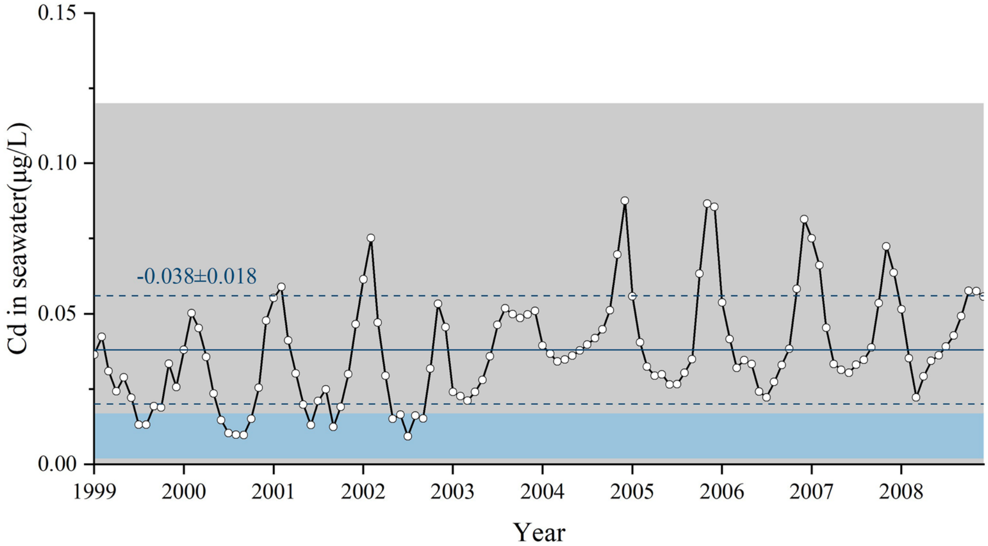

Figure 3. Plot showing Cd content in surface seawater calculated from the Cd/Ca ratios of W3 coral. The dark blue solid line presents mean and the dark blue broken lines indicate mean ± SD. The blue background indicates the background value of surface seawater in the northern of South China Sea. The gray background indicates the surface seawater measurements from Weizhou Island (data from Yang et al. (2017)).

it is much lower than the national standard of first-class sea water quality. Therefore, it can be inferred that the surface seawater around WZI is not significantly affected by human activities during 1999–2008 CE.

4. Discussion

4.1. Source of Cd in Surface Seawater

The ocean is an important sink for most trace metals (Sabarathinam et al., 2019). According to previous researches, Cd in surface seawater is mainly imported by runoff (Goldstein & Jacobsen, 1988), atmospheric input (Duce & Hoffman, 1976; Marx et al., 2005; Mason, 2013), and remobilization from sediments (Choi et al., 2006; Ni et al., 2016; Sakellari et al., 2011; Simpson, 1978). Moreover, abnormal content variations are usually associated with natural events (e.g., volcanic eruptions) and pollutant inputs (Sun et al., 2016).

4.1.1. Runoff

Terrestrial input, especially runoff, is the primary access to the sea for trace metals (Feng & Tian, 2018; Wang et al., 2010), usually affected by river input and precipitation. Cd mainly exists in zinc, copper and aluminum ores, so it can be transferred from land to the ocean through mining and weathering (Ye et al., 2005). Moreover, the erosion and transport of terrestrial materials on tropical islands occur frequently in high temperature and rainy seasons (Saha et al., 2019). More than 84% of annual precipitation (1999~2008 CE) in the WZI is concentrated from May to October (Figure S1 in Supporting Information S1), which usually carries a large amount of land-based Cd to coastal seawater. However, the peaks of skeletal Cd/Ca ratios all occur in the dry season with poor precipitation (Figure S2 in Supporting Information S1). Therefore, runoff associated with precipitation cannot be responsible for the temporal distribution of Cd in coral skeletons. In addition, WZI is far away from the mainland (~24 nautical miles) and lacks direct input from rivers. Thus, the river source of Cd near the WZI can be ignored. This conclusion is consistent with Li et al. (2019) regarding the sources of rare earth elements in the WZI.

4.1.2. Atmospheric Input

Atmospheric dry/wet deposition is another important source for Cd in surface seawater. Accompanied by wind or precipitation, solid particles usually fall into the sea and dissolve/release trace elements in the sinking process (Libes, 2009). According to Wang et al. (2017), the mean content of Cd in atmospheric input in China (1995~2015) exceeded the primary standard of Environmental Quality Standard for Soils (GB15618-1995) by

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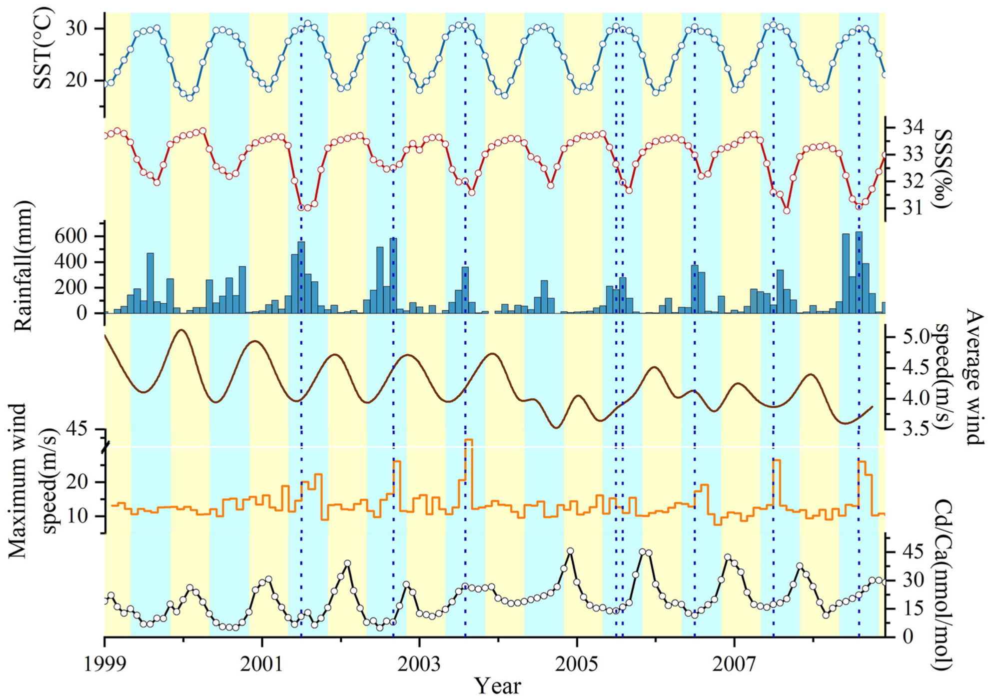

Figure 4. Comparison of surrounding environmental parameters and the coral skeletal Cd/Ca ratios in the Weizhou Island (WZI) from 1999 to 2008. This figure shows the relationship between coral Cd/Ca ratios, maximum wind speed, average wind speed, precipitation, surface seawater salinity (SSS) and surface seawater temperature (SST) in the WZI from 1999 to 2008. Data for the dry and wet seasons are divided by two background colors (light yellow and light blue). The blue dotted lines indicate tropical cyclones around WZI (wind speed data from the Weizhou Island Weather Station; SST data from ERA5; SSS data from Simple Ocean Data Assimilation).

16.5 times. It is worth noting that there is more precipitation in the South China, so wet deposition is the main atmospheric source around the WZI. In addition, previous studies have shown that wet depositions can account for 80%–90% of atmospheric input flux of Cd in the oceans around the world (Duce et al., 1991; Patterson & Duce, 1991). However, our data suggested that the precipitation and the Cd/Ca ratios are negatively correlated ($r = -0.32$, $p < 0.05$, Figure 4). Meanwhile, the Cd/Ca ratios in the dry season were much higher than those in the wet season during most years (Figure 5), ruling out the possibility of contribution from the atmospheric wet depositions. Therefore, we believed that the atmospheric wet deposition was not the main source of Cd around the WZI. This conclusion is consistent with Duce and Hoffman (1976), which indicated that the contribution of this process to the Cd in the ocean was very limited, although a small amount of land-based materials could be carried to the open ocean through the atmosphere transport. On the other hand, the dry deposition process is affected by the wind forces. As shown in Figure 4, the average wind speeds and coral skeletal Cd/Ca ratios have a similar trend. However, the contents of ^{210}Pb in the surface water of the SCS, as a tracer of atmospheric inputs, have been reported extremely low (Nozaki et al., 1998). Therefore, we considered that the dust carried by the winds contributed little, but the similar trend between wind speeds and Cd/Ca ratios suggested that winds, especially winter monsoons, made a significant contribution to the Cd levels in surface seawater around the WZI.

4.1.3. Seawater Vertical Mixing and Sediment Remobilization

Coral skeletons can record the fluctuations of Cd contents in surface seawater during the upwelling process, when deep water is lifted to the surface (Shen et al., 1987, 1992). Thus, the increase of coral skeletal Cd/Ca ratios are often associated with vertical exchange between warm nutrient-limited surface waters and cold nutrient-enriched bottom waters (Lea et al., 1989). In the northern SCS, upwelling is a regular summer phenomenon caused by the southwest monsoon (Chen et al., 2011), while the peaks of Cd/Ca ratios mainly occurred in winter and the study area is relatively shallow without distinct upwelling. Therefore, the seasonal changes of the skeletal Cd/Ca ratios were unlikely to be caused by the upwelling.

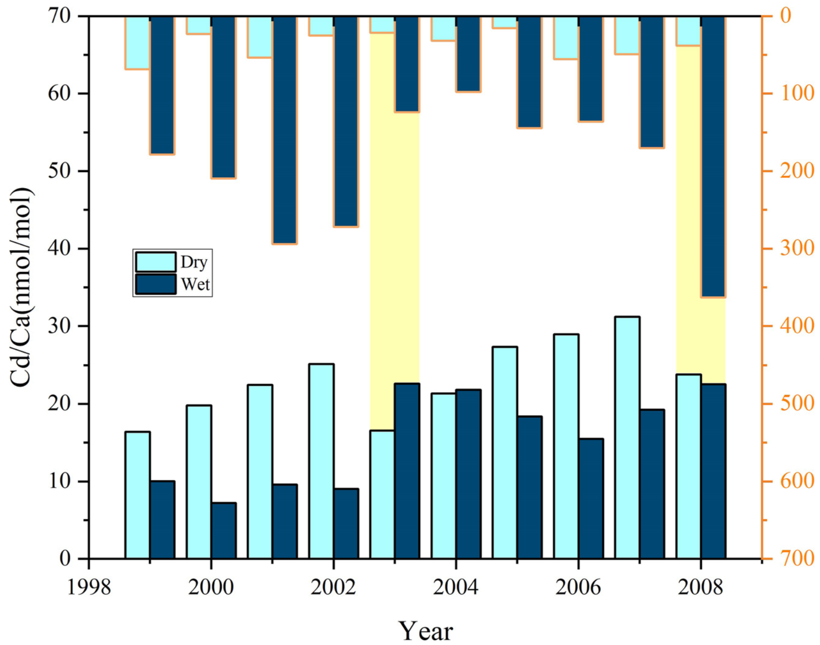

Figure 5. Time series highlighting annual changes in coral skeletal Cd/Ca ratios in Weizhou Island (WZI) (1999~2008) and precipitation in dry and wet seasons. This picture shows the comparison of Cd/Ca ratio and precipitation in the WZI from 1999 to 2008. The black-bordered light blue and dark blue column bars represent annual averages of Cd/Ca ratios in the dry and wet seasons, respectively, while the orange-bordered light blue and dark blue column bars represent annual averages of precipitation in the dry and wet seasons, respectively. The yellow background indicates periods of inconsistent trends.

The direct input of dissolved Cd from rivers to coastal seawater is very limited, but the northern SCS receives a large amount of sediments transported by surrounding rivers and accumulates in the continental shelf (Liu et al., 2016), including Pearl River (84 tons/year), Red River (130 tons/year) and Mekong River (160 tons/year) (Cai et al., 2011). The fluvial input of dissolved metals has a very limited impact on the ocean, but those sediments can be transferred to the continental shelf (Rea & Ruff, 1996). Therefore, shelf sediments are also considered to be an potential significant source of dissolved trace metals in the ocean (Souri et al., 2020). Due to the obvious seasonal changes and the prevailing monsoons around WZI, we compared the monthly average wind speeds with the coral skeletal Cd/Ca ratios (Figure 6). It was worth noting that there was a high agreement between the multi-year monthly average wind speeds and coral skeletal Cd/Ca ratios (Figure 6, $r = 0.83$, $p < 0.05$). To eliminate effects of deviations in the interpolation time series, we used a 12-month sliding-window correlation analysis testing the strength and stationarity of the relationship between monthly average wind speeds and the monthly coral skeletal Cd/Ca ratios from 1999 to 2008 CE (Figure 7). As shown in Figure 7, the average wind speeds and coral skeletal Cd/Ca ratios were significantly correlated because most sliding correlation coefficients were >0.3 ($p < 0.01$). Thus, we considered that the seasonal variations of Cd in surface seawater are related to the vertical mixing of coastal seawater induced by winds, which might lead to the re-release of particulate adsorbed Cd from sediments into seawater.

At the bottom of the ocean, Cd can be divided into dissolved phase, particulate phase and sedimentary phase (Zhang et al., 2018). Affected by reductant-oxidant conditions (Jiann & Ho, 2014), Cd content is usually higher in sediments and particulates, and can be reversibly adsorbed on iron and manganese oxides. The interaction between ions is enhanced, leading to the reversal of the adsorption process, and part of the combined Cd can be transformed into free Cd when surrounding salinity increases (Guinoiseau et al., 2018; Jiann & Ho, 2014; Lao et al., 2019). As shown in Figure 4, the SSS was lower in the wet season but higher in the dry season. Therefore, the regular seasonal variation of Cd in surface seawater should be related with the wind speed: in summer, the wind speeds dropped, which conduced to the seawater stratification; in winter, the wind speeds rose, which significantly promoted the vertical mixing process (Tang et al., 2003). This suggested that the processes of seawater vertical mixing and sediment remobilization caused by winds were the main reasons for the seasonal variations of Cd contents in surface seawater. In addition, we noticed that the multi-year monthly average wind speeds

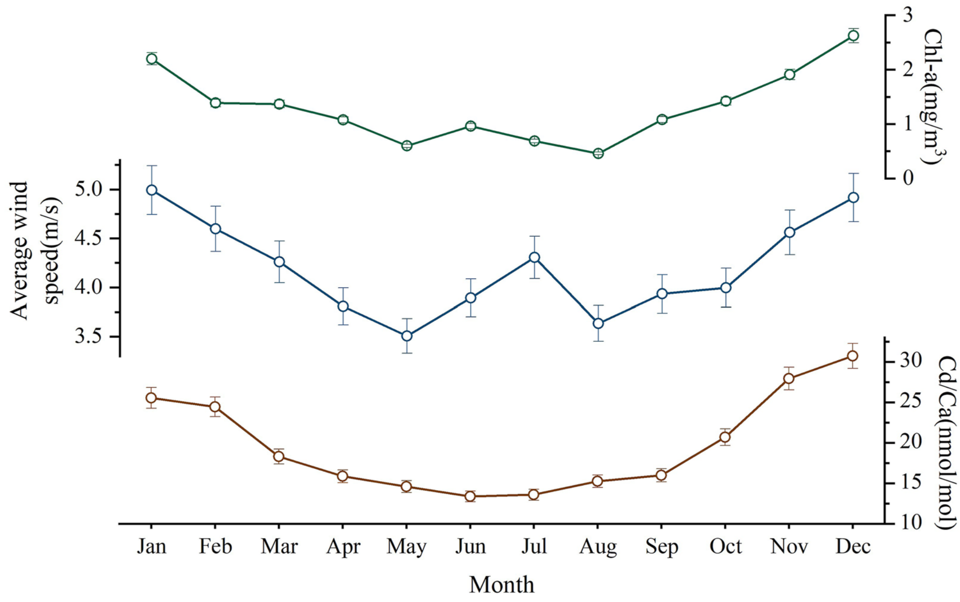

Figure 6. Comparison of the annual trend of coral Cd/Ca ratio, average wind speed and Chl-a in each month from 1999 to 2008 in the Weizhou Island.

showed a significant increase in June–July (Figure 6). Considering it only occurred in individual years from 1999 to 2008 CE (Figure 4), it was likely to be related to tropical cyclones.

4.2. Biogeochemical Process

In winter, the strong winter monsoon in the WZI brings a large amount of nutrients to the surface seawater, which is conducive to the growth and reproduction of phytoplankton and produces many bio-particles (Ma et al., 2014).

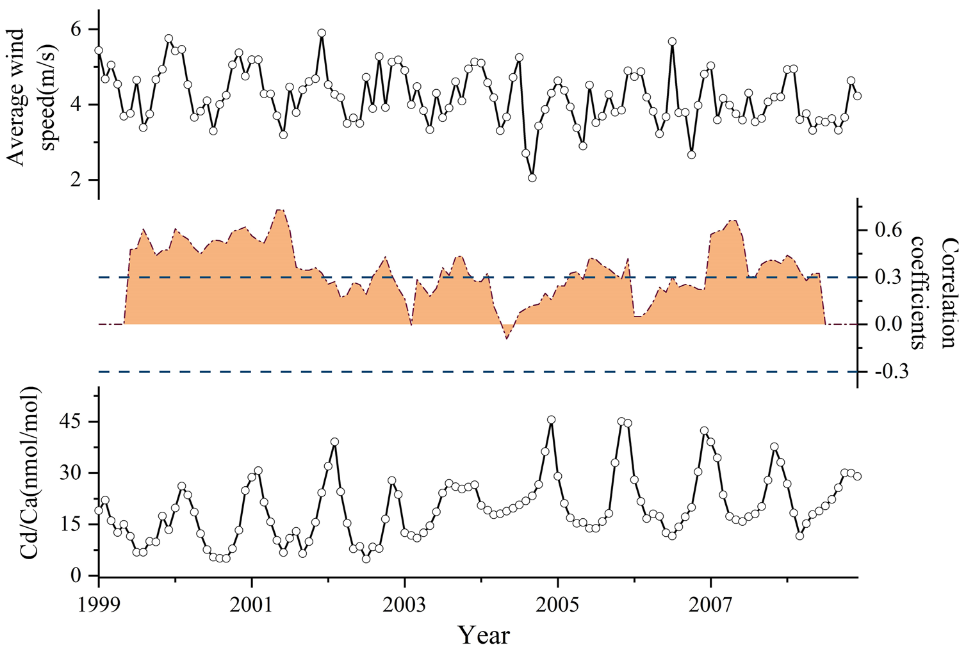

Figure 7. Comparison of coral skeletal Cd/Ca ratio, average wind speed and their 12-month running correlation coefficients ($p < 0.01$) in the Weizhou Island (1999–2008 CE). The dark blue broken lines represent $r = \pm 0.3$, which indicates that the correlations between skeletal Cd/Ca ratio and average wind speed are very significant.

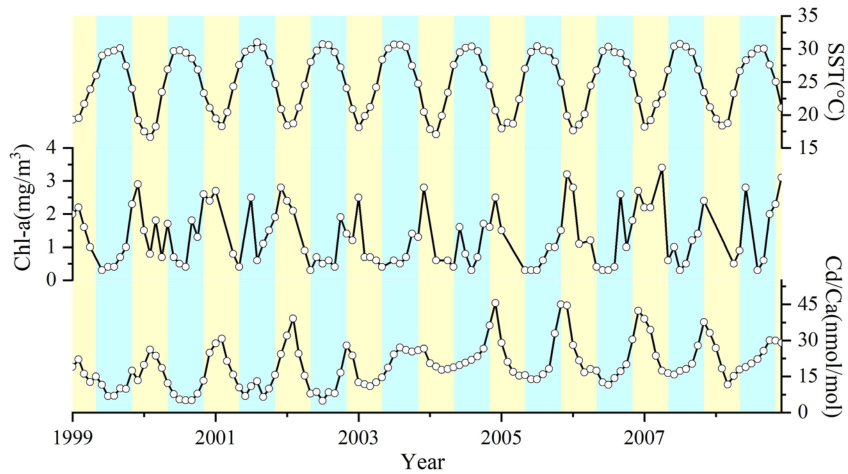

Figure 8. Comparison of the coral surface seawater temperature (SST), Chl-a and Cd/Ca ratios in the Weizhou Island (WZI) from 1999 to 2008. This figure shows the relationship between coral SST, Chl-a and Cd/Ca ratios in the WZI from 1999 to 2008. Two background colors (light yellow and light blue) are used to make a distinction between the dry and wet season (SST data from ERA5; Chl-a data from NOAA).

Chl-a concentration is an important indicator of the biomass (Cai et al., 2002), reflecting eutrophication in the water body (Liu & Zhao, 2019; Oh & Suh, 2006). We found that Chl-a contents in the WZI were relatively high in winter, but began to decrease after spring as the northeast monsoons subsided (Figure 8), and were significantly positive correlated with Cd/Ca ratios ($r = 0.50$, $p < 0.05$). Therefore, we believed that the seasonal changes of Chl-a and SST revealed an event of phytoplankton bloom during the winter. In general, Chl-a contents are higher in summer and lower in winter (Wang et al., 2016), and should be negatively correlated with Cd/Ca ratios, due to the fact that an increase in biomass leads to a decrease in dissolved Cd content in surface seawater (Bruland, 1980; Guinoiseau et al., 2018). However, the situation in our research is apparently opposite, suggesting that the reduction in Cd contents in surface seawater due to biological processes might be masked by the impacts from seawater vertical mixing and sediment remobilization caused by surface winds. In addition, the enhanced phytoplankton leads to the forming excess organic matter, which sinks to the bottom and decomposes rapidly (Bruland et al., 1994). This process requires the consumption of dissolved oxygen, but the accelerated movement of the seawater under the action of winter winds weakens the effect of organic matter decomposition. The uptake of Cd by phytoplankton is directly proportional to dissolved Cd concentrations (Sunda & Huntsman, 2000), while the nutrient-rich bottom seawater transported to the surface by winter monsoon, creating a positive feedback process, but gradually subsides as the winter passes. In some years, the peak of Chl-a also appeared in summer, but due to the weakening of seawater mixing, the dissolved oxygen consumed by organic matter degradation cannot be replenished in time, resulting in the state of hypoxia of the seawater which is not conducive for the dissolution of particle Cd. It also confirmed that winter monsoons were strong enough to transport nutrients in bottom water to the surface more efficiently in the study area. In the contrary, the summer monsoons were too weak to have a marked impact on both seawater vertical mixing and sediment remobilization.

4.3. Coral Cd/Ca Ratio as an Indicator of Surface Wind

Coral skeletal Cd/Ca ratios have been successfully applied as a tracer of wind-driven coastal upwelling (Delgadillo-Hinojosa et al., 2015; Geen, 1996), but there is no upwelling near the WZI. The perennial monsoons in the WZI have obvious seasonal variability, characterized by northeast monsoon in the dry season and southwest monsoon in the wet season. During the winter, surface seawater driven by winter monsoon moves, and the lower layer of Cd-rich seawater produces the compensation lift to replenish the surface seawater loss (Reissmann et al., 2009). Meanwhile, the seawater vertical mixing increases the oxygen content of the underlying water to induce sediment remobilization of Cd (Reissmann et al., 2009). In contrast, this effect is limited due to the relatively weak summer monsoon during the summer.

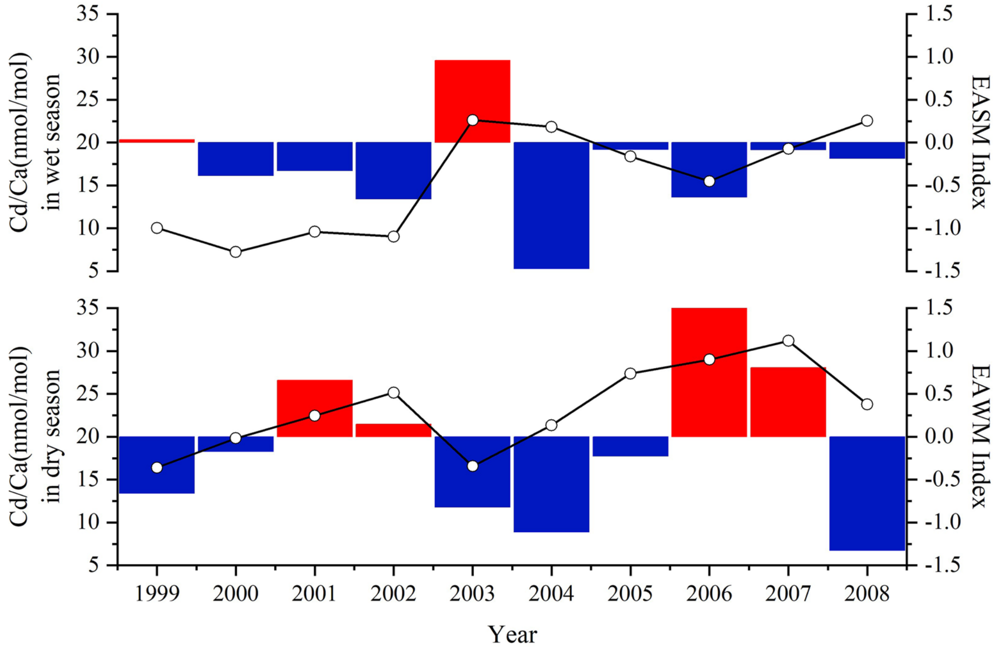

Figure 9. Comparison of the East Asian summer/winter monsoon indexes and coral skeletal Cd/Ca ratios in the Weizhou Island from 1999 to 2008 CE. This figure shows the annual average of Cd/Ca ratios in dry and wet seasons and compared with annual monsoon indexes. Depending on the occurrence time of monsoon, we used summer monsoon indexes from 1999 to 2008 CE and winter monsoon indexes from 1998 to 2007 CE. The East Asian summer/winter monsoon indexes were obtained from Huang and Zhao (2019), Zhao et al. (2015) and China Climate Bulletin.

In present study, the wind speed data were used to present that the winds in the dry season were much higher than those in the wet season, which can give expression to the key role of winter monsoon. Although the site data we used can reflect the correlation, it can not fully reflect the wind intensity of the whole region. Thus, we introduced the Asian summer/winter monsoon indexes, which can present the wind strengths of the entire region, in order to explain the increase of Cd/Ca ratios with no concurrent shift in wind speed. It can be seen from Figure 4 that Cd/Ca ratios increased in summer since 2003, while this change in winter significantly occurred in 2005. The increase in Cd/Ca ratios in the wet/dry season can respond to the strengthen of Asian summer/winter monsoon indexes (Figure 9). During 2003–2008 CE, the Asian summer monsoon indexes trend is similar to Cd/Ca ratios, higher than those during 1999–2002 CE. Likewise, the Asian winter monsoon indexes during 2005–2008 CE were higher than those during 1999–2004 CE. We believed that the strengthen of Asian monsoons might be responsible to the increase in coral Cd/Ca ratios. Comparing the East Asian summer/winter monsoon indexes with the coral skeletal Cd/Ca ratios from 1999 to 2008 CE (Figure 9), we found that the summer monsoon was very weak and had no correlation with the summer average of Cd/Ca ratios ($r = 0.15$, $p > 0.05$), while the winter monsoon was strong and had significant correlation with the winter average of Cd/Ca ratios ($r = 0.64$, $p < 0.05$). Thus, we can explain the different patterns of coral skeletal Cd/Ca ratios in the dry and wet seasons in 2003 and 2008 CE (Figure 5), relating to the weakening winter monsoon or the strengthening summer monsoon (Figure 9).

Tropical cyclone is also associated with wind speed in the wet season besides monsoons. The coral skeletal Cd/Ca ratios showed a significant correlation ($r = 0.45$, $p < 0.05$) with the maximum wind speeds in the summer. However, the peaks of coral skeletal Cd/Ca ratios were not corresponding to the typhoons affecting WZI from 1999 to 2008 CE (Figure 4), indicating that tropical cyclones contributed limited to the rise of Cd levels in surface seawater probably due to the short duration of tropical cyclones or geochemical sensitivity of Cd (Simpson, 1978). Therefore, considering the high consistency between coral skeletal Cd/Ca ratios and average wind speeds, we suggested that coral skeletal Cd/Ca ratios in the winter might be a potential novel proxy for winter monsoons.

In order to make our conclusions more convincing, we introduced a coral Ba/Ca data set from W3 and a bimonthly coral Ba/Ca data set (2002–2005 CE) from another *Porites lutea* coral (Figure 1, WZI coral) near WZI reported by Li et al. (2022) as an extended multiproxy approach. Considering the effects on the Ba/Ca ratios from the high barite ($BaSO_4$) consumption used for oil exploration and drilling activities before 2004 CE reported by Li et al. (2022), we selected the Ba/Ca time series from 2004 to 2005 CE of WZI coral to compare with the Ba/Ca and Cd/Ca ratios (2004–2008 CE) of W3 coral (Figure S3 in Supporting Information S1). Coincidentally, the Ba/Ca records from two corals both exhibited strong seasonal variations, similar to Cd/Ca ratios. Therefore, we believed that the data set of W3 coral should be representative.

5. Conclusion

This is the first to report the relationship between monthly resolution Cd/Ca ratios of coral and winter monsoons, revealing its great potential for the documentation of prehistoric changes in winter monsoons. In the absence of anthropogenic source, the coral Cd/Ca ratios exhibited obvious seasonal fluctuations, and had significant correlations with the speeds of sea surface winds. Under the influences of strong surface winds, the vertical mixing process can change the redox conditions of bottom seawater, leading to the release of the adsorbed Cd in sediments into seawater. Despite that this process also leads to an increase of nutrients, which promotes the growth of phytoplankton resulting in the depletion of Cd the surface seawater, the reduction of Cd levels in surface seawater connected with biological processes is masked by sediment remobilization caused by winter monsoons. Compared with strong winter monsoons, summer monsoons are always very weak and tropical cyclones occur for a short period of time, indicating a limited effect on Cd contents in surface seawater. Therefore, we considered that the sediment remobilization and mixing processes driven by winter monsoons should play a key role in the seasonal variations of Cd contents in surface seawater, and coral skeletal Cd/Ca ratios in the winter have potentials to be a potential novel proxy for winter monsoons in the non-upwelling shelf environments.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The data used in this paper will be deposited in a general data repository (https://doi.org/10.6084/m9.figshare.21087820.v1).

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