Anomalous Ba/Ca signals associated with low temperature stresses in Porites corals from Daya Bay, northern South China Sea

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Abstract

Barium to calcium (Ba/Ca) ratio in corals has been considered as a useful geochemical proxy for upwelling, river flood and other oceanic processes. However, recent studies indicated that additional environmental or biological factors can influence the incorporation of Ba into coral skeletons. In this study, Ba/Ca ratios of two Porites corals collected from Daya Bay, northern South China Sea were analyzed. Ba/Ca signals in the two corals were ‘anomalous’ in comparison with Ba behaviors seen in other near-shore corals influenced by upwelling or riverine runoff. Our Ba/Ca profiles displayed similar and remarkable patterns characterized by low and randomly fluctuating background signals periodically interrupted by sharp and large synchronous peaks, clearly indicating an environmental forcing. Further analysis indicated that the Ba/Ca profiles were not correlated with previously claimed environmental factors such as precipitation, coastal upwelling, anthropogenic activities or phytoplankton blooms in other areas. The maxima of Ba/Ca appeared to occur in the period of Sr/Ca maxima, coinciding with the winter minimum temperatures, which suggests that the anomalous high Ba/Ca signals were related to winter-time low sea surface temperature. We speculated that the Ba/Ca peaks in corals of the Daya Bay were most likely the results of enrichment of Ba-rich particles in their skeletons when coral polyps retracted under the stresses of anomalous winter low temperatures. In this case, Ba/Ca ratio in relatively high-latitude corals can be a potential proxy for tracing the low temperature stress.

Key words: Ba/Ca; barium; Porites coral; cold water stress; northern South China Sea

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Introduction

Barium (Ba) has a nutrient-like distribution in the ocean, generally depleting in surface waters and enriching in deep waters, and such concentration profiles indicate involvement in biological processes (Dehairs et al., 1987; Bishop, 1988; Lea and Boyle, 1989; Dymond and Collier, 1996; Stecher and Kogut, 1999; Paytan and Griffith, 2007). The concentrations of Ba in seawater (Sternberg et al., 2008) and sediment (Pfeifer et al., 2001; Paytan and Griffith, 2007) have been recently employed as proxies for past biogeochemical processes. Ba incorporated into bivalve shells has been used as a tracer of local primary productivity (Stecher et al., 1996; Vander et al., 2000; Elliot et al., 2009).

In scleractinian corals, Ba can substitute for Ca into the crystal lattice of coral aragonite (Lea et al., 1989; Fallon et al., 1999; Sinclair and McCulloch, 2004), with a partition coefficient $D_{Ba} \approx 1$ (Lea et al., 1989; Alibert et al., 2003). Its skeletal concentration faithfully records the concentration of Ba in the ambient ocean, thus making it a potential tracer of a number of different oceanographic processes. Coralline Ba/Ca has been explored as a geochemical proxy for historical variability in upwelling of cold nutrient-rich deep waters to the surface ocean (Lea et al., 1989; Fallon et al., 1999; Reuer et al., 2003; Montaggioni et al., 2006; Ourbak et al., 2006; Alibert and Kinsley, 2008a, 2008b) or flux of suspended sediment into coastal waters from rivers and associated land-use changes (Alibert et al., 2003; McCulloch et al., 2003; Sinclair and McCulloch, 2004; Fleitmann et al., 2007; Prouty et al., 2010). However, compared with these ‘normal’ patterns of coral Ba/Ca associated with seasonal upwelling and river flood, new patterns have been observed recently.

The Ba/Ca ratio, especially for the ‘abnormal’ Ba/Ca peaks, in the corals from some regions did not show a simple response to the intensity of upwelling events (Hart and Cohen, 1996; Tudhope et al., 1996; Montaggioni et al., 2006; Ourbak et al., 2006) or suspended sediment transport in flood events (Sinclair, 2005a; Lewis et al., 2007), clearly indicating that additional environmental or biological factors can influence the incorporation of

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Ba into coral skeletons. In fact, the mechanisms of Ba incorporation and the forms of Ba in coral skeletons are not yet fully understood. A better understanding of the biogeochemical behavior of Ba in corals is essential for developing and applying it as a tool for geochemical and paleo-oceanographic studies.

In this work, we analyzed Ba/Ca ratios in the skeletons of two Porites corals collected from Daya Bay, a shallow semi-enclosed bay located at the northern South China Sea, and reported an ‘anomalous’ pattern of Ba variation. We compared our results with other anomalous Ba behaviors in corals published previously, and sought an explanation for this pattern.

1 Materials and methods

1.1 Study site

Daya Bay is located at 22°30′–22°50′N, 114°30′–114°50′E, in a subtropical region of the northern South China Sea (Fig. 1). It is a semi-enclosed bay, with an area of 600 km$^2$ and an average depth of 10 m. Apart from some small seasonal streams, there are no large rivers flowing into the bay. The annual mean air temperature is approximately 22°C in this region. The lowest (January or February) and the highest (July or August) monthly mean air temperature are around 14°C and 30°C, respectively.

Non-reefal coral communities are patchily and sporadically distributed along the offshore islands and in some coastal areas. Corals generally occur from 0.5 to 5 m below the mean sea level, growing on basement rocks. There are 34 species of scleractinian corals locally, including cosmopolitan Porites corals (Chen et al., 2009).

1.2 Coral collection

Two coral specimens of living Porites were collected. One (DLJ-1) was collected in June 2006, from a depth of approximately 1 m on the rocky substratum off Dalajia Island (Fig. 1). The other specimen (XLJ-1) was collected in August 2007, from a depth of approximately 3 m off Xiaolajia Island (Fig. 1). The two islands are both uninhabited, characterized by low topography with large boulders.

1.3 Sub-sampling procedure

The coral samples were washed with freshwater, and then sectioned by a masonry saw to obtain 8 mm thick slabs, containing the axis of maximum growth of the corals. Dry coral slabs were X-radiographed to expose density banding (Fig. 2). The coral slabs were soaked in 10% H$_2$O$_2$ for 48 hr, then cleaned for 20 min, 3 times in an ultrasonic bath containing Milli-Q water (18.2 MΩ, Millipore, USA), and then oven dried at 60°C for 48 hr.

Using the X-radiographs as guides, skeletal sub-samples were manually scraped with a thin blade along the slabs. Care was taken to avoid obvious bioerosion from bivalves, worms or sponges within the skeletal slabs. From the surface downward, approximately 400 and 500 sub-samples were taken from the two specimens DLJ-1 and XLJ-1, respectively.

1.4 Analytical methods

Sr/Ca and Mg/Ca values in coral skeletons vary with the ambient sea surface temperature (SST) and display seasonal cycles (Beck et al., 1992; Mitsuguchi et al., 1996). Using this relationship, we confirmed coral growth chronologies and time series of Ba/Ca by measuring Sr/Ca and Mg/Ca values.

![Fig. 1 Map of Daya Bay. The coral sampling sites are indicated.](image1)

![Fig. 2 Sr/Ca, Mg/Ca ratios and X-radiography positive prints for Porites corals from Daya Bay. Annual banding within the skeleton is indicated by the cycles of high (dark) and low (light) density. Sub-sampling transects are indicated by white lines. Contrary to Mg/Ca, Sr/Ca ratios are inversely correlated with sea surface temperature (SST) so that the maximum of the sine-like record corresponds to the lowest winter temperature. The corresponding monthly SST was recorded at adjacent Zhelang Ocean Observation (22°39’N, 115°34’E).](image2)
For each sub-sample, 1.5 mg of powdered sample was taken into a centrifuge tube and weighed, dissolved in 3% HNO₃, and the solution was accurately diluted to 10,000 times. Before analysis, the mixture was centrifuged at 4000 rpm for 7 min. Sr/Ca and Mg/Ca analyses were performed using an inductively coupled plasma atomic emission spectrometer (Varian Vista-Pro ICP-AES, USA). Procedural blank and calibration standards were reanalyzed every 20 samples, and a quality control standard was reanalyzed every 5 samples for monitoring and correcting of instrumental drift. Calibration standards were made with high Ca concentrations to match the chemical matrix of the samples.

For specimen DLJ-1, the top 350 sub-samples were selected for further Ba/Ca analysis; for XLJ-1, 190 sub-samples were selected, based on Sr/Ca and Mg/Ca chronologies (six sub-samples were selected within each annual growth band). The analytical method for Ba/Ca was similar to that for Sr/Ca and Mg/Ca, except that more powdered samples were weighed and the sub-sample solutions were accurately diluted to 2000 times.

The analytical wavelengths selected for Sr, Mg, Ca and Ba elements were 407.771, 285.213, 318.127 and 455.403 nm, respectively. The relative standard deviation (RSD) of Sr/Ca, Mg/Ca and Ba/Ca measurements were 0.3%, 0.7% and 3% respectively, based on analysis of 12 replicates of the Chinese national carbonate standard (GBW07129).

In the experiment, all chemical pre-treatments were conducted in a super-clean laboratory in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Sub-boiling distilled high purity grade nitric acid and acid-cleaned bottles and centrifuge tubes were used in the chemical analysis. A 3% HNO₃ solution (diluted with Milli-Q water) was prepared for blanks, dilution of standard solutions and sub-sample digestion.

2 Results

2.1 Coral chronologies derived from skeletal Sr/Ca and Mg/Ca

Coral Sr/Ca and Mg/Ca are often described as robust SST proxies (e.g., Beck et al., 1992; Mitsuguchi et al., 1996). In this study, both Sr/Ca and Mg/Ca profiles from the two specimens DLJ-1 and XLJ-1 showed clear seasonal cycles roughly matched with sea surface temperature (SST) (Fig. 2). The best matching is in cold winters with low SST, showing sharp Sr/Ca and Mg/Ca peaks. Based on Sr/Ca and Mg/Ca profiles, DLJ-1 was identified to span the period between 1982 and 2006 (totally 25 years) and XLJ-1 between 1976 and 2007 (totally 32 years). Annual variations of Ba/Ca were then constructed based on seasonal cycles of Sr/Ca and Mg/Ca.

2.2 Ba/Ca profiles

The Ba/Ca ratios of the two *Porites* corals were similar, with the average 8 μmol/mol, within the range of 6–15 μmol/mol. The Ba/Ca profiles from the two corals displayed similar and remarkable patterns characterized by low-level background signals periodically interrupted by sharp and large synchronous peaks (Fig. 3), this clearly indicates an environmental forcing. Besides, the reproducibility of the Ba/Ca patterns between the two coral slabs is an evidence for the reliability of the data.

3 Discussion

Normally, coralline Ba/Ca ratio represents a powerful proxy for seasonal upwelling (e.g., Lea et al., 1989) or riverine discharge and sediment transport in flood events associated with intense rainfall during the wet season (e.g., McCulloch et al., 2003). In this study, however, the Ba/Ca ratios in both corals displayed an anomalous behavior. The sharp and intense Ba/Ca peaks observed here seem exceeding the scope of the upwelling (Lea et al., 1989; Fallon et al., 1999; Reuer et al., 2003), SST (Lea et al., 1989; Ourbak et al., 2006) and ‘vital effects’ (Sinclair, 2005b) influences on Ba incorporation in modern corals. Moreover, the reproducibility between the Ba/Ca profiles in the coral skeletons strongly suggests that these synchronous Ba/Ca peaks are not derived from an endogenous process, but are a response to an exogenous factor.

3.1 Precipitation and terrestrial input

The South China Sea is dominated by the East Asian monsoon system. In summer, the southwest monsoon prevails and brings rainfall to the northern South China Sea. The wet season in Daya Bay is from May to September (Fig. 4), and often brings heavy precipitation associated with typhoons in summer.

There are no major riverine inputs in Daya Bay, thus avoids any flood plumes interferences. Therefore, if the Ba/Ca signals reflect terrestrial inputs, coastal rainy runoff could be the only source for Ba flux. However, these anomalous Ba/Ca peaks do not correlate with peaks in precipitation (Fig. 4), and therefore rules out the potential influence of terrestrial Ba on the anomalous coral Ba/Ca peaks although there appears to be some small Ba/Ca peaks that are correlated with summer-time precipitation peaks,

![Fig. 3 Time series for Ba/Ca ratios in the two *Porites* corals.](image-url)

especially during summers of 1995, 1997, 1999 and 2001 (Fig. 4), suggesting that coral Ba/Ca may carry a faint precipitation signal.

3.2 Upwelling

Upwelling is a regular phenomenon during summer (June, July and August) in the northern continental shelf of the South China Sea. Eastern Guangdong Coastal Upwelling (EGCU) is mainly induced by the alongshore component of the summer southwesterly monsoon, and the alongshore wind pumps the cold and nutrient-rich deep waters up to the surface and sub-surface layers over the broad shelf (Kuo et al., 2000; Jing et al., 2007; Gan et al., 2009). However, these anomalous Ba/Ca peaks mostly occurred in cold winters (Fig. 3), not in the upwelling season or summer. Furthermore, so far, there is no evidence showing EGCU can affect the inner bay.

3.3 Anthropogenic impacts

Greater sediment input into coastal zones caused by increase in soil erosion due to land-based activities (e.g., deforestation, agricultural practices, livestock farming and coastal development) can cause elevated Ba/Ca values in coral skeletons (Fleitmann et al., 2007; Lewis et al., 2007; Prouty et al., 2008, 2010).

Significantly high Fe and Mn concentrations were observed in 1984–1989 growth bands of the two Porites corals, coincided with period of the Daya Bay Nuclear Power Station construction (Chen et al., 2010). Increased sediment input as a direct result of human alteration of the landscape (e.g., deforestation, blasting, coastal land-filling and land-leveling) for the construction was the primary source of elevated levels of Fe and Mn (Chen et al., 2010). The concentration of Zn in the two corals increased dramatically relative to the baseline value since 1994, corresponding well to the period of rapid local population and industrial development. The elevated levels, which have gradually increased through to the present, were most likely caused by contributions from domestic and industrial sewage discharges into Daya Bay (Chen et al., 2010).

The Ba/Ca signals, however, did not peak in phase with either Fe/Ca and Mn/Ca or Zn/Ca. Therefore, the possibility that anomalous Ba peaks are caused by anthropogenic impacts such as coastal constructions and sewage discharges seems unlikely.

3.4 Phytoplankton bloom

The anomalous Ba/Ca peaks in the two Porites corals could be associated with local phytoplankton blooms. As discussed in previous studies, barite (BaSO₄) content in the water column has been shown to be linked with oceanic primary production (Dehairs et al., 1987; Stecher and Kogut, 1999). Bioshop (1988) presented strong evidences (scanning electron microscopy and energy dispersive X-ray fluorescence analysis) that barites are formed almost exclusively in microenvironments containing decaying organic matter and the remains of diatoms. Ganeshram et al. (2003) found an increase in the number of barite crystals in diatoms (Stephanopyxis palmerina) and coccolithophorids (Emiliania huxleyi) decaying in their experiments. Their studies also showed that living plankton contains a relatively large pool of labile Ba, which is released during decomposition and acts as the main source of Ba for barite formation in microenvironments.

The phytoplankton density during blooms in highly productive bays is much greater than that in the open seas, suggesting a greater abundance of biogenic microenvironments suitable for barite formation. Stecher et al. (1996), Vander et al. (2000) and Thebault et al. (2009) found Ba/Ca profiles in mollusk shells were characterized by a background level punctuated by sharp peaks (like the Ba/Ca pattern observed in our study), and suggested that the formation of the sharp peaks was linked with high levels of Ba associated with the precipitation of barite inside organic-rich, siliceous microenvironments, formed primarily by assemblages of decaying diatoms. They concluded that the sharp Ba/Ca peaks in mollusk shells may provide excellent markers for diatom blooms. Daya Bay is considered to have undergone eutrophication caused by increased nutrient load as a result of rapidly expanding aquaculture and increasing human population.
(Wang et al., 2008). Shallow, semi-enclosed topography, appropriate SST and eutrophic regime, may play important roles in the high level of phytoplankton biomass and frequent outbreaks of red tides in the bay (Song et al., 2004, 2009). The seawater Chl-\(\alpha\) concentration is supposed to reflect phytoplankton biomass, exhibited a general pattern with an intense maximum occurring in spring and summer (Fig. 5). Most of the phytoplankton is diatoms (Wang et al., 2006a, 2006b), suggesting that a substantial flux of barite should accompany phytoplankton blooms in Daya Bay.

We compared the Ba/Ca ratios against the local Chl-\(\alpha\) concentration obtained using the SeaWiFS satellite dataset for the period 1998–2007 (Fig. 5). Time lag between the occurrence of maximum Chl-\(\alpha\) concentration and Ba/Ca ranged from 1 to 2 months from 1999 to 2001, and their profile shapes were totally different. For example, in 2000, a particularly productive year, the maxima of Ba/Ca peaks in both corals were surprisingly weak; whereas in 1999, the year with relatively low productivity, the peaks in both corals were great, higher than in 2000. After 2002, high productive summers occurred every year. Ba/Ca peaks should then have coincided, which is not observed. These results highlight that the extent of Ba/Ca maxima is not directly related to the Chl-\(\alpha\) concentration in seawater. Barite formation in diatom decaying, or the Bar-rich phytoplankton itself, is clearly not the direct cause of these Ba/Ca peaks.

We may conclude that bivalves are better bio-monitors than scleractinian corals in tracing phytoplankton blooms. The differences of feeding behavior between them may be the major factor. Bivalves filter particles from the seawater, whereas scleractinian corals largely depend on symbiotic zooxanthellae which provide energy and essential nutrients for the invertebrate host via photosynthesis (Hoegh-Guldberg, 1999).

### 3.5 Low sea surface temperature in cold winter

Similar Ba behaviors were observed in *Porites* corals from South Africa (Hart and Cohen, 1996; Hart et al., 1997), the Arabian Sea (Tudhope et al., 1996), New Caledonia (Quinn and Sampson, 2002) and coastal Queensland (Sinclair, 2005a) (Table 1). Sinclair (2005a) summarized the anomalous Ba/Ca peaks were characterized by (1) larger than most upwelling and flood signals, (2) typically narrow and sharply defined, (3) resistant to oxidative cleaning and (4) seasonality. Several hypotheses were presented (Table 1), but none was confirmed as interpretations for the anomalous Ba spikes.

In this study, one of the outstanding features of the anomalous Ba/Ca peaks is their seasonality. This strongly suggests that these Ba/Ca peaks have some connection with a seasonal environmental parameter which cues a short-lived biological event that is responsible for the enriched Ba. We compared Ba/Ca with Sr/Ca and SST profiles (Fig. 6), and found that the maxima of Ba/Ca appear to occur in the period of Sr/Ca maxima, coinciding with the winter minimum SSTs, suggesting that winter low SST may be the cause of the anomalous Ba/Ca peaks.

We speculate that the possible origin for Ba/Ca peaks could be the incorporation of Ba-rich particles when coral tissues retract. Temporary tissue retraction may occur when corals are exposed to stressful conditions. During such retraction, mucus covering the spines would preferentially bind metals (Brown et al., 1991; Marshall, 2002). Subsequent tissue recovery and calcification can trap the metal compounds which provide a visible environmental signature in the coral skeleton. This mechanism of metal incorporation into the coral involved direct precipitation of metal compounds onto the mucus-covered skeleton, rather than deposition of metal ions via calcifying tissues (Brown et al., 1991). Daya Bay is located in the relative high-latitude regions for scleractinian coral growth (Chen et al., 2009). The winter lowest SST can drop below 14°C (Fig. 6) which can lead to mass coral mortality in other regions (Veron and Minchin, 1992). Tissue retraction and mucus-covered colonies for *Porites* corals at Daya Bay during the 2008 extreme cold event (Chen et al., 2009) and in an experimental temperature-regulated mesocosm (Li et al., 2009) when the water temperature fell to 14°C have been certainly observed. Forming mucus membrane may be a unique defense mechanism for *Porites* that prevent the further losing of symbiotic algae under extreme cold stresses (Li et al., 2009). Thus, particulate phases enriched in Ba could be trapped in the coral skeleton when tissues retract due to stressing events like a sudden drop in SST.

In our case, the phase of anomalous Ba in *Porites* is probably not lattice-bound but instead is incorporated as Ba-rich particles by occlusion (Pingitore et al., 1989; Hart and Cohen, 1996). However, the presence of particulate phases has not been documented to date, and their source could be problematic. Anomalous Ba is probably associated with coral tissues which have very high concentrations of Ba than either the zooxanthellae or the skeleton (Esslemont et al., 2000; Reichelt-Brushett and McOrist, 2003). If it is true, the outmost layers for the two corals could contain significant high levels of Ba/Ca, which is not observed, but instead is no significant Ba/Ca peaks appeared after 2002 in both DLJ-1 and XLJ-1 skeletons (Fig. 6).

In fact, this part of organic phases in skeletons can be removed by...
rigorous oxidative cleaning procedures. Another potential source of Ba could be barite and other detrital materials which are universal components of suspended matter in the World Ocean (Dehairs et al., 1980). Ba-rich particles were trapped into the skeletal interstices and micro-porosities after tissue retraction and mucus secretion, and rigorous strong oxidative cleaning had no effect on this part of Ba (Tudhope et al., 1996; Sinclair, 2005a).

Most timing of Ba/Ca peaks correspond well with the periods of the minima of SSTs in winters (Fig. 6). For example, distinctively large and sharp Ba/Ca spikes in 1992 correspond very well with the contemporaneous extreme cold winter (the satellite SST record was 11.5°C). The correlation between the maximum Ba/Ca values for DLJ-1 and the minimum monthly satellite SSTs was statistically significant at the 0.05 level \((r = -0.7, p = 0.034, n = 9)\) (Fig. 7), suggesting that anomalous Ba/Ca could be a potential tracer for coral resistance and resilience to extreme low SST stresses. However, no significant correlation relationship was found between maximum Ba/Ca values in the XLJ-1 coral and minimum SSTs, probably due to the sub-sampling resolution, suggesting that sampling resolution is very important for the studies of geochemical coralline tracers. Moreover, we do not consider a simple linear but a more complex non-linear relationship existing between coralline Ba/Ca and low SST in our study, although significant correlation was found. The exact physiological mechanisms of acclimatization in coral-zooxanthellae symbiosis are still unclear. This could be used to explain that no anomalous Ba/Ca peaks occurred in some equivalent cold winters such as 1993, 1995, 1996, 1998 and 2003 (Fig. 6).

Our interpretation on the relationship between the anomalous Ba behavior and cold SST seems cannot be used to explain the similar patterns observed in *Porites* corals from the Two-Mile Reef, South Africa (Hart and Cohen, 1996; Hart et al., 1997), Marbat, southern Oman (Tudhope et al., 1996), Amédée Island, New Caledonia (Quinn and Sampson, 2002) and Orpheus Island, Australia (Sinclair, 2005a), because their Ba peaks appeared in summer (Table 1). Furthermore, in our coral samples, there are also some second Ba/Ca peaks occurred in summer.
Porites lutea
Daya Bay, China ICP-AES 6–15 Mid winter Low SSTs This study

Porites sp.
Orpheus Island, ICP-MS 4–12 Mid spring to summer Ba-rich organic
 Sinclair, 2005a

Porites lutea
Amédée Island, ICP-MS 4–9 Mid summer Ba-rich organic Quinn and Sampson, 2002

Porites sp.
Marbat, ICP-MS 5–120 Mid summer Ba-rich organic Tudhope et al., 1996

large synchronous peaks, yet not correlated with external background signals periodically interrupted by sharp and large peaks by occlusion.

Anomalous Ba/ Ca peaks are characterized by low-level background signals periodically interrupted by sharp and large synchronous peaks, yet not correlated with external causes, such as upwelling, river discharge, anthropogenic impacts or phytoplankton blooms.

The maxima of Ba/ Ca appear to occur in the period of Sr/ Ca maxima, coinciding with the winter minimum SSTs. This suggests that low SST in winter may be the cause of anomalous Ba/ Ca peaks. We speculate that the possible origin for Ba/ Ca peaks could be the incorporation of Ba-rich particles when coral tissues retrace. In our case, the phase of anomalous Ba in the Porites corals is probably not lattice-bound but instead is incorporated as Ba-rich particles by occlusion.

The significant correlation relationship between the maximum Ba/ Ca values for DLJ-1 and the minimum monthly SSTs was found. This suggests that Ba/ Ca appears to be a potential tracer of the resistance and resilience of the stress-tolerant Porites coral to sub-optimal SST or other environmental stresses. Further research should be carried out to better understand the complex significance of the geochemical proxy.

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Conclusions
Ba/ Ca ratios were analyzed in the aragonite skeletons of two Porites corals collected from Daya Bay, northern South China Sea. The Ba/ Ca values of the two Porites corals were similar, with the average 8 μmol/mol, within the range of 6–15 μmol/mol.

In oceanic corals, upwelling is a possible source of pulsed Ba input. In this study, however, the Ba/ Ca ratios measured in both Porites corals displayed an anomalous behavior. Moreover, the reproducibility between the Ba/ Ca profiles strongly suggests that these synchronous Ba/ Ca peaks are not derived from an endogenous process, but are a response to an exogenous factor in both Porites corals. Anomalous Ba/ Ca peaks are characterized by low-level background signals periodically interrupted by sharp and large synchronous peaks, yet not correlated with external causes, such as upwelling, river discharge, anthropogenic impacts or phytoplankton blooms.

Table 1 Anomalous Ba/ Ca values from comparative worldwide studies of Porites corals

<table>
<thead>
<tr>
<th>Species</th>
<th>Location</th>
<th>Analysis method</th>
<th>Ba/ Ca (μmol/mol)</th>
<th>Timing of Ba/ Ca peaks</th>
<th>Interpretation &amp; hypotheses</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Porites lutea</td>
<td>Two-Mile Reef, South Africa (27°31.2’S, 12°40.8’E)</td>
<td>Ion microprobe</td>
<td>3–90</td>
<td>Late summer</td>
<td>Ba-rich organic matter</td>
<td>Hart and Cohen, 1996; Hart et al., 1997</td>
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<tr>
<td>Porites sp.</td>
<td>Marbat, southern Oman (17°N, 55°E)</td>
<td>ICP-MS</td>
<td>5–120</td>
<td>Mid summer</td>
<td>Ba-rich organic matter, upwelling</td>
<td>Tudhope et al., 1996</td>
</tr>
<tr>
<td>Porites lutea</td>
<td>Amédée Island, New Caledonia (22°29’S, 116°28’E)</td>
<td>ICP-MS</td>
<td>4–9</td>
<td>Mid summer</td>
<td>Ba-rich organic matter</td>
<td>Quinn and Sampson, 2002</td>
</tr>
<tr>
<td>Porites lutea</td>
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<td>ICP-MS</td>
<td>4–15</td>
<td>Mid winter</td>
<td>Diatom blooms, blue-green algae blooms, coral mass spawning</td>
<td>Sinclair, 2005a</td>
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<td>Mid spring to early summer</td>
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<td>Porites lutea</td>
<td>Daya Bay, China (22°37’N, 114°37’E)</td>
<td>ICP-AES</td>
<td>6–15</td>
<td>Mid winter</td>
<td>Low SSTs in winters</td>
<td>This study</td>
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References

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