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Interannual variation of rare earth element abundances in corals from northern coast of the South China Sea and its relation with sea-level change and human activities

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ABSTRACT

Here we present interannual rare earth element (REE) records spanning the last two decades of the 20th century in two living *Porites* corals, collected from Longwan Bay, close to the estuarine zones off Wanquan River of Hainan Island and Hong Kong off the Pearl River Delta of Guangdong Province in the northern South China Sea. The results show that both coral REE contents (0.5–40 ng g^{-1} in Longwan Bay and 2–250 ng g^{-1} in Hong Kong for La–Lu) are characterized with a declining trend, which are significantly negative correlated with regional sea-level rise (9.4 mm a^{-1} from 1981 to 1996 in Longwan Bay, 13.7 mm a^{-1} from 1991 to 2001 in Hong Kong). The REE features are proposed to be resulted from seawater intrusion into the estuaries in response to contemporary sea-level rise. However, the tendency for the coral Er/Nd time series at Hong Kong site is absent and there is no significant relation between Er/Nd and total REEs as found for the coral at Longwan Bay site. The observations are likely attributed to changes of the water discharge and sediment load of Pearl River, which have been significantly affected by intense human activities, such as the construction of dams/reservoirs and riverbed sediment mining, in past decades. The riverine sediment load/discharge ratio of the Pearl River decreased sharply with a rate of 0.02 kg m^{-3} a^{-1}, which could make significant contribution to the declining trend of coral REE. We propose that coastal corals in Longwan Bay and similar unexplored sites with little influences of river discharge and anthropogenic disruption are ideal candidates to investigate the influence of sea-level change on seawater/coral REE.

1. Introduction

The combination of abundant geochemical tracers, weekly-to-monthly resolution, and applicability to both contemporary and Pleistocene climatic and environmental changes provides coral as one of the richest of natural archives (Shen, 1996). Coral skeletal $\delta^{18}O$, $\delta^{11}B$, and elemental contents (e.g., Mg, Sr, Ba, Cd, and Pb) have been used for decades to reconstruct natural dynamics of El Niño-Southern Oscillation (ENSO), East Asian monsoon, and anthropogenic pollution (Dodge and Gilbert, 1984; Shen and Boyle, 1987; Wellington and Dunbar, 1995; Shen et al., 1996, 2005; Wei et al., 2000; Cobb et al., 2003; Peng et al., 2003; Sun et al., 2004; Yu et al., 2004; Liu et al., 2008, 2009). Recent studies suggest that corals can accurately record seawater rare earth element (REE) composition with constant REE distribution coefficients even if the seawater REE concentrations change by a factor of 10 (Akagi et al., 2004; Wyndham et al., 2004). This unique character has drawn wide attention in using coral REE for modern and paleo-environmental studies after the 1990s (Sholkovitz et al., 1999; Nozaki et al., 2000a; Webb and Kamber, 2000). The REE abundances in corals have, for example, been used in investigating monsoon variability, mining contamination, and biological activity in coastal seawater (Sholkovitz and Shen, 1995; Naqvi et al., 1996; Fallon et al., 2002; Akagi et al., 2004; Wyndham et al., 2004).

Seawater and fresh water are characterized by different REE patterns: seawater has much lower REE concentration and is more

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enriched in the heavy REEs (HREEs, Eu–Lu) as compared that with fresh water (Wyndham et al., 2004; Lawrence and Kamber, 2006). The REE abundances in estuarine mixing zones are influenced by river plumes. At the high-salinity regime the REEs are largely conservative; the concentrations decrease slightly toward typical coastal water values together with an enrichment in HREE (Nozaki et al., 2000a; Wyndham et al., 2004). This is in contrast to the low-salinity region where complex removal and remineralization of dissolved REEs occur by reaction with suspended particles and uptake by phytoplankton (e.g., Nozaki et al., 2000b; Lawrence and Kamber, 2006).

When a river plume is retreating relative to previous decades, pushing the salinity front further into the estuary, as a result of either reduced river discharge (or reduced water level in the estuary or reduced sediment load) or higher mean sea level, there is a possibility that the aragonite skeleton of corals may record the variation of seawater REE. It implies that REE in the massive corals near estuaries is a potentially valuable proxy for tracing interactions between fresh water and seawater.

In this paper, we analyzed 2-decade records of REE abundances in two coastal corals, collected from Longwan Bay near the Wanquan River estuary of Hainan Island and Hong Kong off the Pearl River Delta in the northern South China Sea (SCS). The results show that coral REE can reflect estuarine seawater condition and the site-specific variability is closely associated with changes of riverine discharge/sediment and sea level.

2. Geographic location and the environment of sample areas

The climate in the northern SCS, where living *Porites lutea* corals were collected (Fig. 1a), is characterized with typical conditions in the subtropical–tropical East Asian monsoon region. The ocean circulation pattern in the SCS is clearly modulated by seasonal changes of the East Asian monsoon (Su et al., 2006). During the period of the summer monsoon with prevailing southwest wind, the surface ocean currents flow broadly northeastward, bringing warm tropical water into the SCS. During the winter monsoon with northeast wind, a counter-clockwise gyre circulation draws cold non-tropical water into the SCS through the Taiwan Strait.

Longwan Bay, where coral LW6 was collected, is located on the east side of Hainan Island and 20 km to the north of Wanquan River estuary (Fig. 1b). Sea surface temperature (SST) is 30 °C in summer and 19 °C in winter and the mean precipitation is 1962 mm with 70% in summer (data from Qinglan Meteorological Observatory located ~10 km north to the coral sampling site). An extensive cover of corals has developed in the shallow coastal area around eastern and southern Hainan Island. The 163 km-long Wanquan River, with a drainage area of 3693 km^2 (Zhu et al., 2005), originates from the central mountainous region of the island.

The second coral sample HK1 was collected from a marine park in Hong Kong at the east side of the Pearl River estuary (Fig. 1c). The local SST is ~28 °C in summer, and 17 °C in winter. The mean annual precipitation is 2200 mm (data from Hong Kong Observatory). The 2214 km-long Pearl River, with a drainage area of 453,700 km^2 (Zhang et al., 2008), is the 13th largest river in the world and the second largest river entering into the SCS in terms of annual water discharge. The river extends from Yunnan Province in southwest China to Guangdong Province before pouring into the SCS.

The primitive Wanquan River has been well-protected with natural landscape, a dense vegetation cover, and a small annual discharge of 5 billion m^3 and low sediment load (Zhu et al., 2005). The region has been little disrupted by human activities. In contrast, the Pearl River with a large annual discharge of 300 billion m^3 and high sediment load (Zhang et al., 2008), has been significantly affected by intense human activities, such as construction of huge dams/reservoirs and riverbed sediment mining (Lu et al., 2007; Zhang et al., 2008).

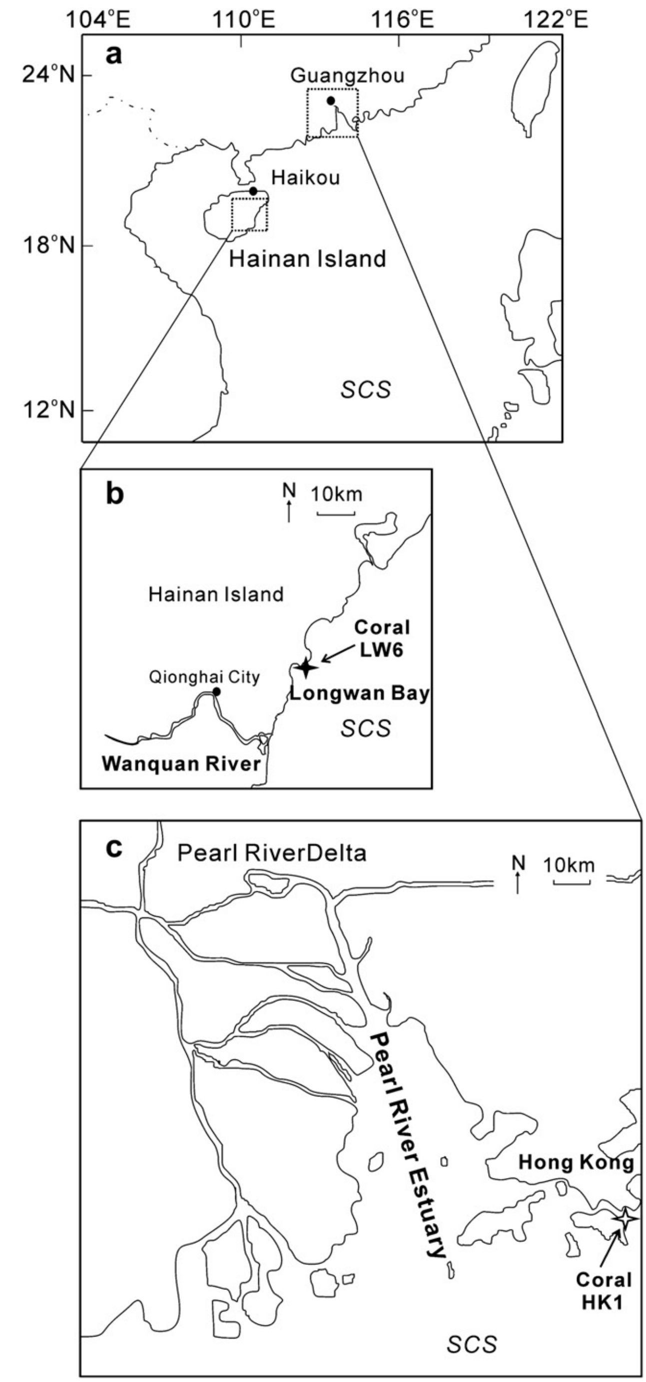

Fig. 1. (a) Location map of coral sample collection sites in the SCS. (b) A coral core was drilled from a living *Porites lutea* coral LW6 from Longwan Bay (solid star) near the north Wanquan River estuary in Hainan Island. (c) A living *Porites lutea* star coral head HK1 was collected offshore Hong Kong (hollow star), the east side of Pearl River Estuary.

3. Coral samples and analytical methods

3.1. Coral LW6 from Longwan Bay, Hainan Island

A core, 2 m in length and 5 cm in diameter, was drilled from the top of a living *Porites lutea* coral LW6 at a depth of 5 m from Longwan Bay (19°20′N, 110°39′E) near the north Wanquan River estuary in August 1998 (Fig. 1b). Slabs, 0.5 cm in thickness, were cut from core segments and washed with pure water and dried, followed by X-ray photographing. Annual-resolution subsamples from 1981 to 1996 were taken along the axis of maximum growth (Fig. 2).

About 50 mg of each subsample was weighted and dissolved in 2 mL of 2 N HCl. The solution was passed through an ion-exchange column (AG-50X8) to separate alkaline metals. The eluate containing REE was dried, re-dissolved in 1 mL of 1.2 N HNO_3, and then diluted by a factor of 50 to acidity at 4% HNO_3. An aliquot of 4 mL was mixed with an appropriate amount of internal standard Rh solution. The REE abundances were measured on a PE Elan 6000 ICP-MS at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Detailed operating parameters and instrumentation were described in Liu et al. (1996). The detection limits of REE are 1×10^{-13}–1×10^{-12} g g^{-1}, determined with 3σ of the procedure blank. MISA-Rare Earth Elements (MISA-01-1) was used as the working standard. The accuracy was determined by repeated measurements of USGS standards W-2 and AGV-1. The relative standard deviations (RSD) for most REE are less than ±8%, except for Nd, which is ±12% for W-2 and ±10% for AGV-1. Barium could not be completely removed during column separation and the isobaric interferences of its oxides, $^{135}Ba^{16}O$, $^{137}Ba^{16}O$, hindered the possibility of precise determination of Eu (^{151}Eu, ^{153}Eu) for coral LW6 with high Ba contents.

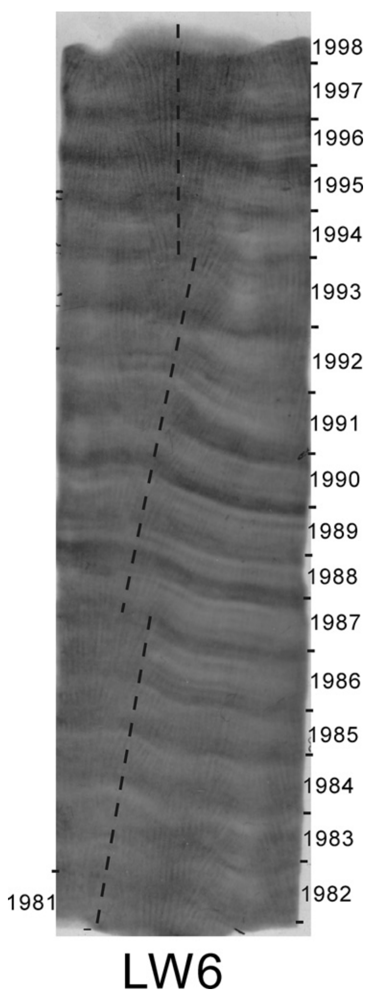

Fig. 2. X-radiograph of the Longwan *Porites lutea* coral LW6 slab with annual high- and low-density band couplets. The dashed line denotes the subsampling path.

3.2. Coral HK1 from Hong Kong

A living *Porites lutea* coral head HK1, 14 cm in diameter, was collected at a depth of 4 m offshore Hong Kong (22°20′N, 114°16′E), the east side of Pearl River Estuary in October 2002 (Fig. 1c). This coral head was sectioned into 0.6 cm thick slices. The annual subsamples (1991–2001) were taken along the axis of maximum growth from the clear density bands (Fig. 3). Due to high REE contents in HK1, about 50 mg of each subsample was directly dissolved in 25% HNO_3 and then diluted 1000 times to the acidity of solution at 4% HNO_3 for direct ICP-MS analysis (Liu et al., 1996). Relative standard deviations (RSDs) of the AGV-1 standard for most REE are less than ±10% and only ±19–30% for Tb and Tm because of their low abundances.

4. Results

The measured annual REE abundances of corals LW6 and HK1 are tabulated in Tables 1 and 2. The REE abundances are 3–20 ng g^{-1} for light REEs (LREEs, La–Sm) and 1–6 ng g^{-1} for HREEs in coral LW6 and 20–120 ng g^{-1} for LREEs and 4–28 ng g^{-1} for HREEs in coral HK1. The most striking feature of the annual REE data for corals LW6 and HK1 is a declining trend during the periods of 1981–1996 and 1991–2001, respectively (Tables 1 and 2). The levels of total REEs decrease from 80–90 ng g^{-1} in 1981–1984 to 50–60 ng g^{-1} in 1992–1996 for coral LW6 (Table 1) and from 500–900 ng g^{-1} in 1991–1993 to ~200 ng g^{-1} in 2000–2001 for coral HK1 (Table 2). In addition, coral HK1 is much higher in both average REE abundances (total REEs: 418.7 ng g^{-1}) and proportional rates of change (PRC) (total REEs: 15.3% a^{-1}) than those (total REEs: 78.9 ng g^{-1}, PRC: 3.9% a^{-1}) for coral LW6, where PRC = (*declining rate*/*mean concentration*) × 100%.

5. Discussion

5.1. Seawater and coral REE

The REE abundances of seawater are mainly controlled by scavenging processes in the estuarine zone, in which LREEs are preferentially adsorbed onto particle surfaces and settle in the sediments, while HREEs are favorably compounded with the

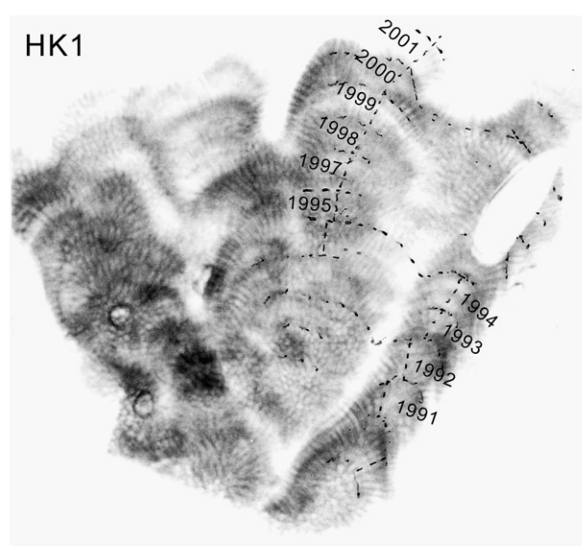

Fig. 3. X-radiograph of the Hong Kong *Porites lutea* coral HK1 slab with annual high- and low-density band couplets. The dashed line denotes the subsampling path.

Table 1
REE abundances (ng g^{-1}) and proportional rates of change (PRC, % a^{-1}) in coral LW6 from offshore Hainan Island, China, from 1981 to 1996.

Year/Element	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	PRC	*p*
La	18.3	20.5	18.9	40.4	18.4	15.6	26.9	16.8	13.9	14.4	16.2	10.0	10.3	12.9	12.2	12.1	−5.4	0.015
Ce	23.1	24.7	23.2	41.6	21.7	20.5	23.8	21.3	16.9	17.2	21.5	13.0	11.6	13.7	13.9	15.0	−5.2	0.002
Pr	3.4	3.5	3.5	4.8	3.5	3.0	4.5	3.1	2.6	2.8	2.9	2.0	1.9	2.3	2.4	2.2	−4.3	0.001
Nd	13.1	15.9	14.7	18.2	14.1	12.5	17.4	12.3	11.1	11.9	11.5	7.4	8.1	10.1	11.2	9.0	−4.0	0.001
Sm	3.1	3.7	3.4	4.1	3.7	3.2	4.0	3.3	2.8	3.3	3.0	2.1	2.1	2.5	3.0	2.5	−2.9	0.002
Gd	4.6	5.1	5.3	5.4	4.7	4.6	4.9	4.6	4.1	4.6	3.8	2.9	3.1	3.9	4.2	3.7	−2.8	<0.001
Tb	0.70	0.86	0.76	0.75	0.71	0.67	0.75	0.77	0.65	0.68	0.63	0.52	0.51	0.62	0.67	0.53	−2.4	0.001
Dy	5.0	5.8	5.7	5.2	5.1	4.9	5.2	5.3	4.4	5.2	4.5	3.2	3.4	4.5	4.8	4.1	−2.3	0.002
Ho	1.3	1.3	1.5	1.4	1.4	1.3	1.3	1.3	1.2	1.3	1.2	0.9	1.0	1.2	1.2	1.1	−1.9	0.001
Er	4.3	5.0	5.0	4.7	4.8	4.6	4.6	4.6	4.4	4.5	4.4	3.4	3.4	4.1	4.1	3.8	−1.8	0.001
Tm	0.68	0.74	0.78	0.73	0.76	0.74	0.74	0.76	0.75	0.81	0.70	0.54	0.57	0.66	0.67	0.66	−1.4	0.040
Yb	6.1	5.9	6.4	6.4	6.3	6.1	5.7	5.9	6.3	6.3	5.8	5.1	5.2	5.3	5.2	5.3	−1.4	<0.001
Lu	0.93	1.00	1.02	1.02	1.01	1.08	0.92	0.97	0.98	1.02	0.86	0.79	0.80	0.94	0.88	0.95	−1.1	0.030
Total REEs	84.7	94.0	90.2	134.7	86.2	78.8	100.8	81.0	70.0	73.9	77.0	51.9	52.0	62.7	64.4	61.0	−3.9	0.002

complex and/or carbonate ions and retained in the seawater due to their smaller ionic radii (Nozaki et al., 2000b). As a result, seawater is much lower in REE concentrations compared to fresh water and estuarine water, and is more enriched in the HREE (Wyndham et al., 2004). The post-Archean Australian shale (PAAS, McLennan, 1989) normalized REE patterns clearly show that there is a strong REE content gradient and REE pattern difference between the Pearl River water (Ouyang et al., 2004) and the coastal seawater in the Pearl River estuary (Hong et al., 1998) and surface seawater of the SCS(Nozaki et al., 2000b) (Fig. 4).

The PAAS-normalized REE patterns of corals LW6 and HK1 are similar to that in seawater with a negative Ce anomaly and HREE enrichment (Fig. 4). The coral REE patterns from the SCS are consistent with other reported coastal *Porites* coral records from the Great Barrier Reef (GBR) in the western South Pacific (WSP) (Wyndham et al., 2004), the Okinawa island in the western North Pacific (WNP) (Akagi et al., 2004), and Bermuda in the North Atlantic (NA) (Sholkovitz and Shen, 1995).

The variation of Er/Nd ratio can be used to describe the changes of REE compositions and the degree of HREE enrichment (Nozaki et al., 2000b). The Er/Nd ratio of Pearl River water, coastal seawater in the Pearl River estuary, and surface seawater in the SCS is 0.094 (Er: 7.9 pg g^{-1}; Nd: 84 pg g^{-1}) (Ouyang et al., 2004), 0.34 (Er: 2.9 pg g^{-1}; Nd: 8.4 pg g^{-1}) (Hong et al., 1998) and 0.49 (Er: 0.77 pg g^{-1}; Nd: 1.6 pg g^{-1}) (Nozaki et al., 2000b), respectively, showing a remarkable increase from river water to seawater (Fig. 5). The observation suggests that corals growing offshore have lower REE concentrations and stronger HREE enrichment (higher Er/Nd ratio) than those growing inshore or in the estuarine zone. Due to short residence time of 0.5–2 thousand years for seawater REE (Lawrence and Kamber, 2006), coral REE pattern is also significantly influenced by local hydrographic settings. Okinawa corals, although with low skeletal REE contents (Er: 0.9–3.7 ng g^{-1}; Nd: 6.0–27 ng g^{-1}), in the WNP (Akagi et al., 2004) are characterized with a smaller Er/Nd ratio than the Hong Kong coral HK1 in the SCS (Fig. 5). The potential aeolian dust input from the loess deposits of Asia with low Er/Nd ratio by westerly winds (Greaves et al., 1999) may cause the low Er/Nd ratio in Okinawa corals. The REE records of *Porites* corals in Misima Island, Papua New Guinea (PNG), experiencing high terrestrial sediment flux at sites with intense open-cut mining, exhibit the lowest Er/Nd ratio (0.009 ng/ng) in literature (Fallon et al., 2002). Our data and previous studies (Nozaki et al., 2000b; Wyndham et al., 2004) suggest that coral REE abundances and Er/Nd ratio can capture the main features of ambient seawater REE.

5.2. Interannual variability of coral REEs

The REE records of two corals, LW6 and KH1, are both characterized with a declining trend during the last two decades of the 20th century (Tables 1 and 2). The trend indicates that REE concentrations in the local coastal seawater decreased over the course of annual growth bands. This decreasing seawater REE abundances could be attributed to several possible factors, including (a) reduced fresh water discharge (WD), (b) low riverine sediment load (SL), and/or (c) sea-level rise.

5.2.1. Coral LW6 in Longwan Bay, Hainan Island

Total REEs in coral LW6 show an average PRC of 3.9% a^{-1} over 1981–1996. The relationships between total REEs in coral LW6 and

Table 2
REE abundances (ng g^{-1}) and proportional rates of change (PRC, % a^{-1}) in coral HK1 from offshore Hong Kong, China, from 1991 to 2001.

Year/Element	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	PRC	*p*
La	231.2	250.6	152.1	106.5	94.1	107.9	92.0	66.0	87.0	60.6	49.8	−15.0	<0.001
Ce	161.4	173.5	86.4	54.0	49.9	68.7	47.3	26.7	37.2	34.7	19.3	−19.4	0.001
Pr	38.2	41.5	24.6	17.2	16.1	17.4	15.6	10.8	15.5	10.2	8.5	−14.8	0.001
Nd	156.2	168.0	107.5	68.4	65.9	66.2	56.4	39.9	68.8	41.3	35.9	−14.7	0.001
Sm	40.1	42.6	23.7	17.4	16.1	14.3	15.7	10.0	11.9	10.8	8.0	−16.2	0.001
Eu	8.0	7.9	6.1	4.0	4.0	3.7	3.1	2.5	3.3	2.7	2.1	−13.2	<0.001
Gd	44.7	53.3	39.0	22.8	16.3	19.5	14.2	11.6	14.2	9.5	7.6	−18.3	<0.001
Tb	7.8	9.1	5.8	4.2	3.7	2.6	2.7	2.2	2.5	2.2	1.7	−16.6	<0.001
Dy	47.8	51.0	42.6	31.6	22.4	22.8	21.7	18.1	19.0	15.5	12.7	−13.7	<0.001
Ho	10.5	12.1	10.2	7.2	6.6	5.1	4.8	4.3	4.7	3.7	2.8	−13.3	<0.001
Er	28.2	32.9	27.0	22.3	21.1	15.0	12.5	12.3	13.7	11.4	9.3	−12.3	<0.001
Tm	4.5	5.8	4.7	3.3	3.4	2.6	2.4	2.6	2.2	1.8	1.5	−12.0	<0.001
Yb	29.3	35.3	30.2	23.9	25.1	19.1	17.9	19.3	15.7	16.2	10.6	−9.1	<0.001
Lu	5.7	6.7	5.1	4.3	3.5	3.8	3.2	3.4	3.0	2.7	2.4	−9.2	<0.001
Total REEs	813.5	890.1	565.1	387.2	348.2	368.6	309.5	229.7	298.8	223.2	172.1	−15.3	<0.001

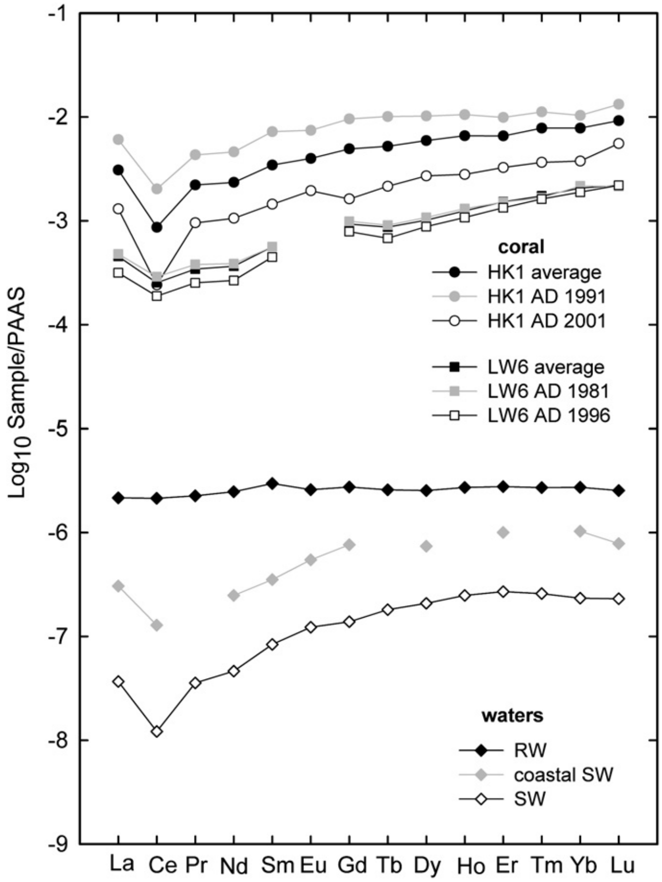

Fig. 4. PAAS-normalized REE abundances in corals HK1 (circles) and LW6 (squares), surface seawater (SW) in the SCS (hollow diamond; Nozaki et al., 2000b), coastal SW of Pearl River estuary (gray diamond; Hong et al., 1998), and Pearl River water (RW) (solid diamond; Ouyang et al., 2004).

WD, SL, and the ratio of SL/WD of Wanquan River (Zhu et al., 2005) are given in Fig. 6.

An insignificant correlation ($R^2 = 0.13$, $n = 16$, $p = 0.166$) is exhibited between records of Wanquan River WD (Fig. 6a) and total coral REEs (Fig. 6d). In the years with heavy (low) discharge, such as 1981 and 1989 (1987 and 1991), the annual-resolution coral subsamples were not featured with high (low) REE levels (Fig. 6d). It is suggested that water discharge was not a dominant factor for determining coral REE levels at this site. A poor relationship ($R^2 = 0.002$, $n = 16$) between total coral REEs in LW6 and the river SL (Fig. 6b) also indicates that the decreasing trend of coral REE abundances was not associated with terrestrial sedimentation flux.

Heavy rainfalls usually brought a large amount of sediments from the island to the reef zones and caused an increase of REE contents in corals near the open-cut mining site in Misima Island, PNG (Fallon et al., 2002). The missing linkage between rainfall/runoff and coral REE in Hainan Island is likely attributed to a dense vegetation cover, which restrains the terrestrial supply of labile REEs to the Wanquan River. Besides, the coral LW6 lived 20 km from the mouth of the river with an annual discharge of only ~5 billion m^3 and low SL density of 0–0.012 kg m^{-3} of river water (Zhu et al., 2005). Very limited discharge REE signal could be recorded in the coral. An alternative explanation is the change of local or regional monsoon rainfall as a direct source of REE. Due to low REE contents, annual subsamples were used. This subsampling resolution hinders to evaluate possible relationship between seasonal REE and monsoon rainfall. However, the REE pattern of rainfall is featured with a convex-up shale-normalized pattern, enrichment in the middle REE, and depletion in the HREE (Sholkovitz et al., 1993), very different from those in seawater, and our corals. It suggests that rainfall is not the dominated factor controlling REE in the corals or seawater near sample sites in this study.

Recent decadal sea-level rise has been suggested to enhance offshore seawater intrusion at the estuarine zones in East Asia and North America due to the global warming and ice-sheet melting (Rosenzweig et al., 2007; Cruz et al., 2007). The rising rate of the South China Sea (SCS) is about one order of magnitude higher than the global rate in the 1990s. Li et al. (2002) showed that the average rate of the sea-level rise in the SCS is 10 mm a^{-1} with some areas as high as 27 mm a^{-1}, based on TOPEX/POSEIDON satellite altimetry data (T/P). We suggest that when sea level rapidly rises, the intrusive

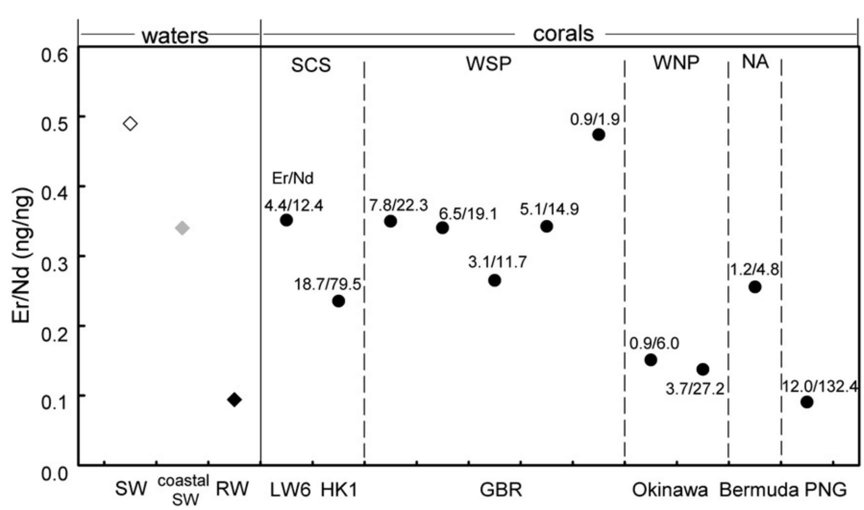

Fig. 5. Er/Nd ratios (ng ng^{-1}) of surface seawater (SW) in the SCS (hollow diamond; Nozaki et al., 2000b), coastal SW of Pearl River estuary (gray diamond; Hong et al., 1998), Pearl River water (RW) (solid diamond; Ouyang et al., 2004), and of corals used in this study, LW6 and HK1, and collected from the Great Barrier Reef (GBR) in the western South Pacific (WSP) (Wyndham et al., 2004), Okinawa in the western North Pacific (NSP) (Akagi et al., 2004), Bermuda in the North Atlantic (NA) (Sholkovitz and Shen, 1995), and Misima Island in PNG (Fallon et al., 2002). The values of coral Er and Nd abundances (ng g^{-1}) are given just above the Er/Nd ratio.

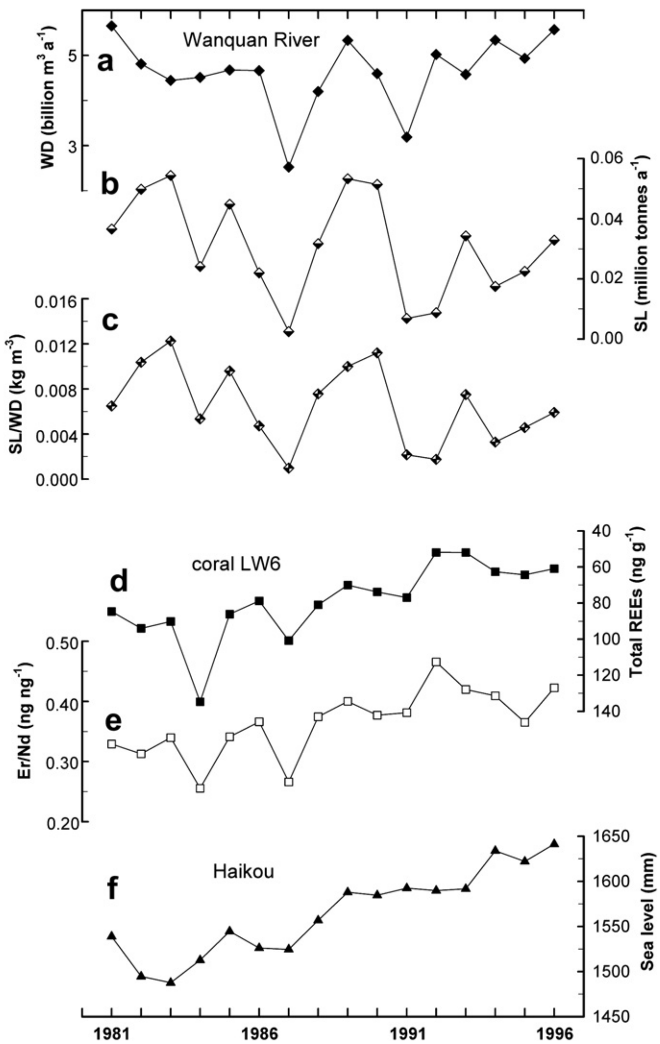

Fig. 6. Comparison of (a) the water discharge (WD), (b) sediment load (SL), and (c) the SL/WD ratio of the Wanquan River (Zhu et al., 2005) with (d) total REEs and (e) Er/Nd ratio in coral LW6 and (f) sea level at Haikou, Hainan Island. Note that the axis of total REEs is plotted reversely.

open-ocean saline seawater, with low REEs contents of $\sim$0.008 ng g^{-1} (Nozaki et al., 2000b), can dilute the REE levels and change their signatures at the estuarine zone of the Wanquan River with low WD and SL.

On the basis of the local tide gauge data (22.01° N, 110.17° E; University of Hawaii Sea Level Center; http://ilikai.soest.hawaii.edu/uhslc/htmld/d0329B.html), the sea-level rise at Haikou, Hainan Island (Fig. 1a), was at a rate of 9.4 mm a^{-1} from 1981 to 1996. The decrease of total REEs in coral LW6 is significantly coupled with the local sea-level rise during 1981–1996 ($R^2 = 0.55$, $n = 16$, $p = 0.001$) (Fig. 6d and f). The increasing annual coral Er/Nd ratios, with a rate of 0.0083 a^{-1} from 1981 to 1996 ($R^2 = 0.50$, $p = 0.001$) (Fig. 6e), also show a significant correlation with sea-level rise ($R^2 = 0.53$, $n = 16$, $p = 0.001$). Combined with a high correlation between coral total REEs and Er/Nd ratio ($R^2 = 0.86$, $n = 16$, $p < 0.001$), indicating an additional simple source for this binary mixing in the estuarine region, the observations of decreasing total REEs and increasing Er/Nd suggest an intensification of offshore seawater intrusion in response to recent sea-level rise.

Another possible factor for the decline trend of total REEs in LW6 is the variability of the upwelled offshore subsurface REE-rich seawater, inducing by summer monsoon wind (Jing et al., 2007). However, the coral REE record has no relation with summer wind speed ($R^2 = 0.02$ for total REEs with summer wind speed) or annual wind speed ($R^2 = 0.05$ for total REEs with annual wind speed) [wind speed data from the meteorological observatory at Xisha (16°50′N, 112°20′E)]. The weak correlation suggests a trivial influence of seasonal upwelling on coral REE variation.

5.2.2. *Coral HK1 in Hong Kong*

The features of coral REEs at this site are different from those at Longwan Bay in Hainan Island. For example, the REE abundances in coral HK1 are 5–10 times higher than those in coral LW6 during the overlapping years of 1991–1996 and HK1 decreased during the overlapping period, but LW6 did not. Besides, an average PRC, 15.3% a^{-1}, of total REEs for coral HK1 is about 4 times higher than that for coral LW6. The Er/Nd ratio in HK1 is also lower than LW6 (Fig. 5).

The local tide gauge data (22.18° N, 114.13° E; Hong Kong-B marine station) show that the local offshore sea level raised at a rate of 13.7 mm a^{-1} from 1991 to 2001. The total REEs in coral HK1 significantly correlates with sea level ($R^2 = 0.57$, $n = 11$, $p = 0.008$; Fig. 7d and f). Mao et al. (2004) showed that the saltwater intrusion of eastern side of the estuary is very intense, at a site close to where

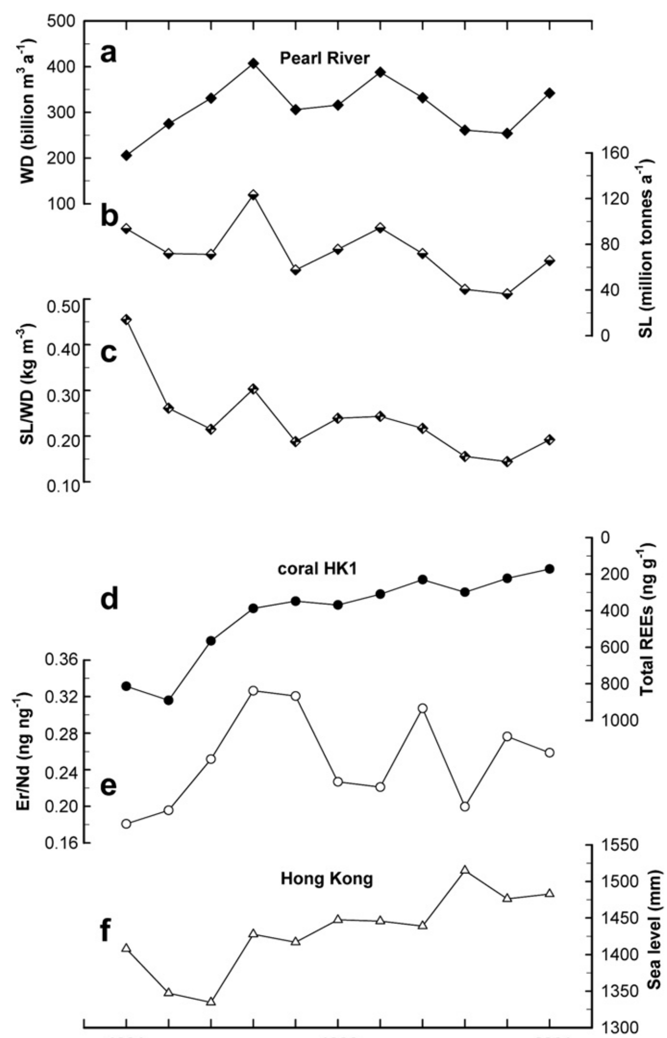

Fig. 7. Comparison of (a) the water discharge (WD), (b) sediment load (SL) and (c) the SL/WD ratio of the Pearl River (Zhang et al., 2008) with (d) total REEs and (e) Er/Nd ratio in coral HK1 and (f) sea level at Hong Kong. Note that the axis of total REEs is plotted reversely.

HK1 was collected. However, in contrast to coral LW6 in Longwan, a poor relation is expressed for Hong Kong coral Er/Nd ratio with sea level ($R^2 = 0.004$, $n = 11$, Fig. 7e) and for the coral total REEs with Er/Nd ratio ($R^2 = 0.30$, $n = 11$, $p = 0.08$). The above-mentioned evidences suggest that the features of coral REEs could not be attributable to only sea-level change. A substantial decrease of terrestrial REE source is likely to be the additional factor at Hong Kong site.

The Pearl River has been significantly affected by intense human activities. The total population in the Pear River Delta region is about 50 million with an urbanization rate of >70% (Lu et al., 2007). High population density and rapid economic development have resulted in a heavy burden to the aquatic environment. Zhang et al. (2008) found the annual WD of the Pearl River showed no significant trend or abrupt shift from 1954 to 2004 (1991–2001 data shown in Fig. 7a). The SL of the river has declined since the early 1990s due to the construction of dams/reservoirs and the mining of riverbed sediments (Fig. 7b) (Zhang et al., 2008). A total of 387 large and medium reservoirs with a storage capacity of 46.7 billion m^3 had been constructed by 2005 in the Pearl River Basin (Zhang et al., 2008). The sediment mining has been intensive and a huge amount of sand, 0.7–1 billion m^3 from 1983 to 1998, has been mined from the riverbed of the Pearl River due to a booming economy in the Delta region (Huang and Zhang, 2005). Sediment mining in the Pearl River made not only a contribution to the significant decrease of sediment load, but also a rapid channel incision across the whole delta area. Lu et al. (2007) reported a dramatic channel incision with >10 m in the deepest cut during the past 10 years in the lower Pearl River.

Although the correlation between the total coral REEs and SL of the Pearl River is poor ($R^2 = 0.09$), the total REEs in HK1 is significantly positively correlated with the river SL/WD ratio (Zhang et al., 2008) ($R^2 = 0.46$, $n = 11$, $p = 0.023$). A dramatic decreasing trend, from 0.45 kg m^{-3} in 1991 to 0.19 kg m^{-3} in 2001, is observed for the river SL/WD ratio (Fig. 7c). It indicates the Pearl River water has been getting “clear”, likely resulting in the declining trend of coral REEs. In contrast, the annual SL/WD ratio of the less disrupted Wanquan River did not show a significant trend from 1981 to 1996 and the relation of the total REEs in coral LW6 with the SL/WD ratio of the Wanquan River is poor (Fig. 6c and d, $R^2 = 0.01$). Er/Nd ratio in coral HK1 is also negatively correlated with the SL/WD of the Pearl River ($R^2 = 0.12$, $n = 11$, $p = 0.306$), although it is not significantly which may indicate strong human disruptions on fractions of REE.

Accordingly, we suggest that a combination of local and regional factors, such as the decreasing sediment load, rapid channel incision caused by dams and riverbed sediment mining, and sea-level rise, could decrease terrestrial input and lead to high saline seawater intrusion into Pearl River estuary, resulting in the REE record in coral HK1. At present, it is difficult to distinguish the contribution of sea-level rise and the anthropogenic decrease of SL/WD ratio in the Pearl River to the declining trend of REEs in coral HK1 in such a complex estuary region. A comprehensive REE study of the estuarine waters along the salinity gradient and longer coral records of multiple elemental proxies with sea level in the coastal region are high priorities.

6. Conclusions

REE records in corals LW6 of Longwan Bay in Hainan Island and HK1 of Hong Kong off Pearl River Delta both display a declining trend during the last two decades of the 20th century. Total REEs and Er/Nd ratio in coral LW6 are significantly correlated with local sea level, but not with terrestrial input. The results suggest that the decrease of REE abundances in coral LW6 is mainly influenced by sea-level rise. A significant negative correlation between REE abundances in coral HK1 and the sea level indicates that the REE abundances in the HK1 are also influenced by sea-level rise. However, poor correlations are exhibited between the coral Er/Nd ratio and total REEs and between coral Er/Nd ratio and sea level. Additional local factors, such as construction of dams/reservoirs and riverbed sediment mining, are suggested to reduce SL/WD ratio of Pearl River, enhance the intrusion of offshore saline seawater, and affect the REE pattern in coral HK1. Coastal corals at sites with the similar hydrographic settings, with small river discharge, low terrestrial sedimentation flux, and trivial anthropogenic disruption, in Longwan Bay, Hainan, are ideal locations for evaluating the impact of sea-level change on local/regional nearshore seawater and coral REE abundances.

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