Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Palaeogeography, Palaeoclimatology, Palaeoecology 218 (2005) 57–73

PALAEO

www.elsevier.com/locate/palaeo

$\delta^{18}O$, Sr/Ca and Mg/Ca records of *Porites lutea* corals from Leizhou Peninsula, northern South China Sea, and their applicability as paleoclimatic indicators

Ke-Fu Yu[a,b,c,*], Jian-Xin Zhao[b,d,*], Gang-Jian Wei[d,1], Xin-Rong Cheng[c,2], Te-Gu Chen[a,3], Thomas Felis[e,4], Pin-Xian Wang[c,2], Tung-Sheng Liu[f,5]

[a] *South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China*
[b] *Advanced Centre for Queensland University Isotope Research Excellence (ACQUIRE), The University of Queensland, Qld 4072, Australia*
[c] *Laboratory of Marine Geology, Tongji University, Shanghai 200092, China*
[d] *Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*
[e] *DFG-Research Center Ocean Margins, University of Bremen, 28359 Bremen, Germany*
[f] *Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China*

Received 17 February 2004; received in revised form 25 October 2004; accepted 9 December 2004

Abstract

Combined seasonal to monthly resolution coral skeletal $\delta^{18}O$, Sr/Ca, and Mg/Ca records are reported for one modern and two late Holocene *Porites lutea* corals from a fringing reef at Leizhou Peninsula, the northern coast of the South China Sea (SCS). All the profiles for the period 1989–2000 reveal annual cycles well correlated with instrumental sea surface temperatures (SST), and display broad peaks in summer and narrow troughs in winter, reflecting seasonal growth rate variations. Calibration against instrumental SST yields the following equations: $\delta^{18}O=-0.174(\pm 0.010)\times SST(^{\circ}C)-1.02(\pm 0.27)$ (MSWD=5.8), $Sr/Ca_{(mmol/mol)}=-0.0424(\pm 0.0031)\times SST(^{\circ}C)+9.836(\pm 0.082)$ (MSWD=8.6), and $Mg/Ca_{(mmol/mol)}=0.110(\pm 0.009)\times SST(^{\circ}C)+1.32(\pm 0.23)$ (MSWD=55). The scatter in the Mg/Ca–SST relationship is much larger than analytical uncertainties can account for, suggesting the presence of SST-unrelated components in the Mg/Ca variation.

Calculated Sr/Ca–SST values for two later Holocene *Porites lutea* samples (U-series ages ~541 BC and ~487 AD, respectively) from the same reef suggest that SST in the SCS at ~541 BC was nearly as warm as in the 1990s (the

* Corresponding authors. Advanced Centre for Queensland University Isotope Research Excellence (ACQUIRE), The University of Queensland, Qld 4072, Australia. Tel.: +61 7 33469753; fax: +61 7 33658530.

E-mail addresses: kyu@earth.uq.edu.au (K.-F. Yu), j.zhao@uq.edu.au (J.-X. Zhao), gjwei@gig.ac.cn (G.-J. Wei), xrchengk@online.sh.cn (X.-R. Cheng), kefuyu@scsio.ac.cn (T.-G. Chen), tfelis@allgeo.uni-bremen.de (T. Felis), pxwang@online.sh.cn (P.-X. Wang), tsliu@public.bta.net.cn (T.-S. Liu).

[1] Fax: +86 20 85290130.
[2] Fax: +86 21 65983207.
[3] Fax: +86 20 84451672.
[4] Fax: +49 421 218 3116.
[5] Fax: +86 10 82661575.

0031-0182/$ - see front matter
doi:10.1016/j.palaeo.2004.12.003

warmest decade of the last century), but at ~487 AD, it was significantly cooler. This observation is consistent with climatic data reported in Chinese historic documents, confirming that the Sr/Ca–SST relationship is a reliable thermometer. Removing the SST component in the $\delta^{18}O$ variation based on calculated Sr/Ca–SST values, the residual $\delta^{18}O$ reflects the deviation of the Holocene seawater $\delta^{18}O$ from the modern value, which is also a measure of the Holocene sea surface salinity (SSS) or the summer monsoon moisture level in mainland China. Such residual $\delta^{18}O$ was close to zero at ~541 BC and −0.3‰ at ~487 AD, suggesting that it was as wet as in the 1990s at ~541 BC but significantly drier at ~487 AD in mainland China, which are also consistent with independent historic records. Calculated Mg/Ca–SST values for the two late Holocene corals are significantly lower than the Sr/Ca–SST values and are also in conflict with Chinese historic records, suggesting that coral Mg/Ca is not reliable proxy for SST. At comparable Sr/Ca ranges, fossil corals always display negative Mg/Ca offsets if compared with the modern coral of the same site. We interpret this observation as due to preferential loss of Mg during meteoric dissolution of cryptic Mg–calcite-bearing microbialites in the exposed fossil corals. Microbialites (MgO up to 17%, Sr only 100–300 ppm) are ubiquitous during reef-building processes and their presence in only a trace amount will have a significant impact on coral Mg/Ca ratios without detectable influence on coral Sr/Ca ratios.

Keywords: O isotopes; Sr/Ca; Mg/Ca; SST; *Porites lutea*; Microbialite; South China Sea

1. Introduction

Massive reef corals with annual growth bands have proved to be excellent archives for the environmental history of the tropical oceans over the past hundreds to thousands of years. So far, coral skeletal $\delta^{18}O$, Sr/Ca, and Mg/Ca are the most widely used tracers in coral-based paleoenvironmental reconstructions.

Since Weber and Woodhead (1972) reported the linear relationship between coral $\delta^{18}O$ and sea surface temperature (SST), significant progress has been made in the study of coral $\delta^{18}O$-based climate records. These studies resulted in a higher temporal resolution (to monthly), longer time series (>350 years), and more environmental information, such as rainfall and salinity variations in addition to SST. Based on coral $\delta^{18}O$, a few long climate reconstructions in seasonal resolution covering the past centuries (Felis et al., 2000; Kuhnert et al., 1999; Linsley et al., 1994; Quinn et al., 1998) have been generated. In recent years, fossil corals are also frequently used to study time-windows during the Holocene and the last interglacial (Felis et al., 2004; Guilderson et al., 2001; Tudhope et al., 2001). Because coral $\delta^{18}O$ is influenced by both SST and seawater $\delta^{18}O$, the interpretation of coral $\delta^{18}O$ as a proxy for SST only can be with large uncertainties, especially in areas with large salinity variations (Cole et al., 1993; McCulloch et al., 1994). Because of this, coral Sr/Ca and Mg/Ca were later developed as proxies for SST, which were thought to be the function of just SST (Beck et al., 1992; Mitsuguchi et al., 1996).

Houck et al. (1977) and Smith et al. (1979) first published the linear relationships of coral Sr/Ca and SST. Beck et al. (1992) first reported high-precision Sr/Ca measurements using the thermal ionization mass spectrometric (TIMS) technique. They obtained a temperature calibration of coral Sr/Ca ratios for *Porites lobata*. Because of the long residence times of Sr and Ca in oceans (~4 Ma), they suggested that high-precision TIMS coral Sr/Ca ratios could be used to recover seasonal records of tropical SST over the past 10^5 years without consideration of seawater conditions. Using the Sr/Ca–SST relationship, some SST reconstructions for time-windows in the past 130 thousand years (Beck et al., 1997; Correge et al., 2000; Linsley et al., 2000; McCulloch et al., 1996, 1999) have been reported.

Mitsuguchi et al. (1996) introduced the coral Mg/Ca thermometry based on the measurements of Mg and Ca with ICP-AES. Wei et al. (2000) indicated that coral Mg/Ca from Sanya Bay at Hainan Island, South China Sea, is a valid SST proxy with a precision better than ±0.5 °C, and it was not affected by coral growth rates and other environmental factors such as precipitation and runoff.

In theory, the $\delta^{18}O$ of coral skeletons reflects a combination of SST and the $\delta^{18}O$ of the seawater with the latter being related to variations in salinity. The Sr/Ca and Mg/Ca of coral skeletons both reflect SST independent of salinity. In this regard, it is possible to use the combination of coral $\delta^{18}O$ and Sr/Ca or Mg/Ca to determine past variations in SST and sea surface salinity (SSS) or precipitation. McCulloch et al. (1994) demonstrated that the combination of the two proxies provides powerful quantitative constraints on past climate. Using combined coral $\delta^{18}O$ and Sr/Ca measurements, Gagan et al. (1998) concluded that the tropical ocean surface in the Great Barrier Reef was 1 °C warmer about 5350 years ago and enriched in ^{18}O by 0.5 per mil relative to modern seawater. Hendy et al. (2002) reconstructed past SST and salinity variations from a Great Barrier Reef coral record during the past 420 years. With the combination of coral Mg/Ca and $\delta^{18}O$, Watanabe et al. (2001b) reconstructed seasonal changes in SST and salinity during the Little Ice Age in the Caribbean Sea.

All these studies have contributed significantly to the understanding of past climate variability, such as tropical climatic forcing and the variability of the El Niño–Southern Oscillation. However, several complicating issues remain to be solved in the application of the coral Sr/Ca and Mg/Ca proxies, such as biological controls on Sr/Ca and Mg/Ca (Devilliers et al., 1994; Mitsuguchi et al., 2003), the effect of chemical pretreatment on coral Mg/Ca due to Mg distribution heterogeneity (Mitsuguchi et al., 2001; Watanabe et al., 2001a) and other factors (Fallon et al., 1999; Sinclair et al., 1998; Wei et al., 1999). In addition, there are obvious differences in the slopes and intercepts of calibrations from different coral reef areas or for different coral genera, which can lead to large offsets in the reconstructed SST if generalized calibration equations are used. Therefore, it is essential to study $\delta^{18}O$, Sr/Ca, and Mg/Ca records in modern corals and their relationships with instrumental SST over coral reef areas worldwide and over different genera before generalized thermometers can be used.

In the present study, we report $\delta^{18}O$, Sr/Ca, and Mg/Ca data for a modern coral and Holocene corals from Leizhou Peninsula at the northern coast of the South China Sea, in an attempt to establish their relationships with SST and test their applicability and reliability as SST proxies. It will also improve the understanding of the utilities of these geochemical tracers in corals from the South China Sea, the biggest closed marginal sea of the western Pacific. In the South China Sea, abundant coral reefs occur over a latitudinal range of 16°, providing excellent materials for coral-based paleoclimate research. However, until now, only a few case studies on corals from Nansha, Xisha, and Hainan Island have been published (Peng et al., 2003; Sun et al., 1999; Wei et al., 2000; Yu et al., 2001). Little has been done on corals at Leizhou Peninsula, part of the so-called “coral triangle” of the Southeast Asia, where numerous important coral species were expected to be found (Roberts et al., 2002).

2. Geographic location and environmental conditions of the coral reef at Leizhou Peninsula

The coral reef at Leizhou Peninsula (Fig. 1) is located at the northern coast of the South China Sea (20°13′ N~20°17′ N, 109°54′ E~109°58′ E). This is the only developed and preserved fringing coral reef on mainland China. The reef flat, dominated by *Goniopora* and *Porites* species, is about 10 km long and 500–1000 m wide (2 km maximum width). From sea to land, eight biogeomorphologic zones can be recognized, with living corals occurring only on the reef front zone (Yu et al., 2002b). Since 1993, more than ten field investigations have been undertaken, which reveal that the coral reef ecosystem is in natural recovery (Yu, 2000). This coral reef documented multiple sea level high-stands during the Holocene (Nie et al., 1997; Yu et al., 2002b; Zhao and Yu, 2002), high frequency, large amplitude, abrupt cold events (“Leizhou Events”) (Yu et al., 2002a) and cold SST-induced coral mortality (cold-bleaching; Yu et al., 2004) during the Holocene climate optimum (7.0–7.5 ka BP).

The study area is part of the tropical monsoon climate regime of Southeast Asia. From June to August, the region is affected by the Southwest Monsoon and tropical cyclones, which bring warm and wet tropical air masses to the study area, resulting in increased precipitation during the summer season. During the winter season from October to March, the region is influenced by the Northeast Monsoon, which brings cold and dry continental air to the study area. Episodic cold air outbreaks from the north can lead to anomalously low winter temperatures in the region.

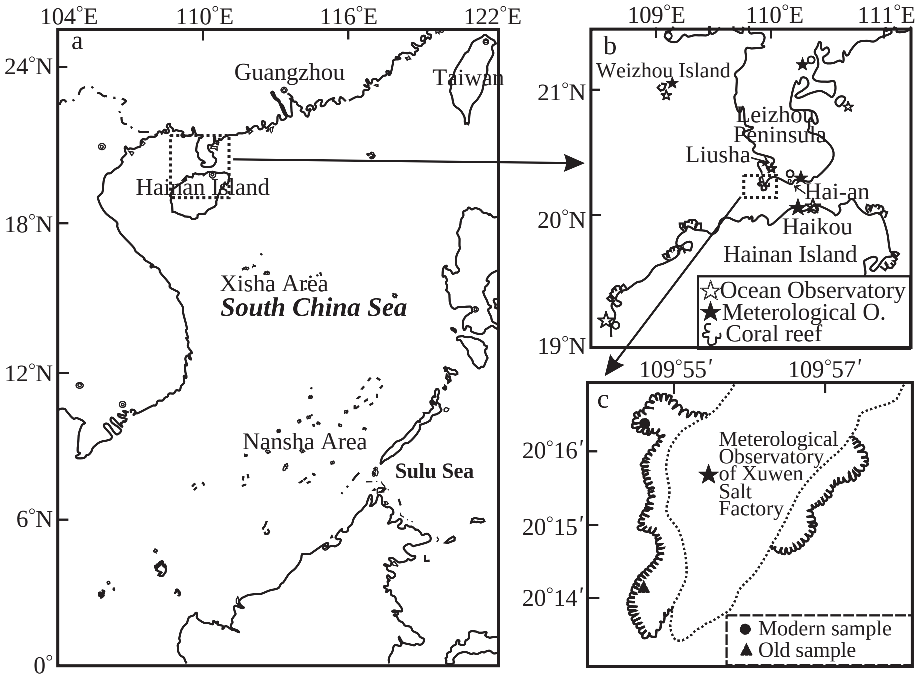


Fig. 1. The location map of the coral reef at Leizhou Peninsula. (a) Location of Leizhou Peninsula at the northern coast of the South China Sea; (b) the coral reef at Leizhou Peninsula and the nearby ocean and meteorology observatories; (c) accurate sample location.

In the vicinity of the coral reef are located more than ten ocean and meteorological observatories, which can provide detailed instrumental records over the past 50 years. The instrumental records show that the seasonal SST in this area varies by up to 11 °C, ideal for the calibration of high-resolution coral thermometers and for high-resolution past climate reconstructions based on fossil corals from the reef area (Yu et al., 2002a). Instrumental data from a nearby Meteorological Observatory at Xuwen Salt Factory, ~1.5 km from the sampling location, show that since 1975 the mean annual air temperature is

Table 1
Monthly climate parameters for the coral reef area

Month	1	2	3	4	5	6	7	8	9	10	11	12	Annual average/total
SST (°)	19.1	19.0	20.8	23.7	27.2	29.2	30.0	29.9	28.9	26.8	23.6	20.6	24.9
Air temperature (°)	17.5	18.2	21.2	24.8	27.5	29.1	29.4	28.9	27.6	25.4	21.7	18.6	24.2
Sunshine duration (h/month)	125.5	103.9	135.9	168.8	215.2	216.1	244.5	209.5	174	189.7	165.8	150.0	2098.8
Cloud cover	6.1	6.7	5.9	5.8	6.3	6.9	6.1	6.6	5.6	5.0	5.0	5.2	5.9
Precipitation (mm/month)	13.0	25.1	23.7	55.4	72.6	149.1	148.5	202.9	220.1	142.4	38.9	20.6	1102.3
Evaporation (mm/month)	93.0	85.4	117.9	144.8	185	186.7	205.8	175.2	149.4	150.3	123.1	104.4	1721.5
SSS (‰)	32.5	32.6	32.5	32.5	32.6	32.0	32.0	31.2	31.5	31.9	31.8	32.1	32.1

Sea surface temperature (SST) data from Haikou Ocean Observatory, located in 47-km distance to the sampling site, are based on the period of 1960–2000 AD. Air temperature, sunshine duration, cloud cover, precipitation, and evaporation data from the Meterological Observatory of Xuwen Salt Factory, located in 1.5 km to the sampling site, are based on the period of 1975–2000 AD. Sea surface salinity (SSS) data from the Ocean Observatory of Weizhou Island, in 110-km distance to the sampling site, are based on the period of 1960 to 1994 AD. See Fig. 1 for locations.

24.2 °C, and the mean annual total precipitation, evaporation, and sunshine duration are 1102.3 mm, 1721.5 mm, and 2098.8 h, respectively. Instrumental records from Haikou Ocean Observatory, at about 47-km distance from the sampling location, indicate that since 1960 the mean seasonal SST cycle is 11 °C with a maximum of 30.0 °C in July and a minimum of 19.0 °C in February. The mean annual SST is 24.9 °C (Yu, 2000). Instrumental records from Weizhou Island Ocean Observatory, at 110-km distance from the sampling location, for the period 1960–1994 show that the mean seasonal cycle of sea surface salinity (SSS) is 1.43‰ with a maximum of 32.6‰ in May and a minimum of 31.2‰ in August. The mean annual SSS is 32.1‰. Table 1 outlines the monthly climate parameters.

3. Material and methods

A modern *Porites lutea* sample (DLL-05) was collected from the living coral cluster within the reef front zone on 3 July 2000. The colony was growing at a water depth of 0.8 m during low tide and is about 30 cm in height with an ellipse spheroid shape. The sampling location is in about 1.5-km distance to the Meteorological Observatory at Xuwen Salt Factory (Fig. 1). For comparison purpose, two late Holocene *P. lutea* samples (DLO-11 with TIMS U-series age of 2541±24 years BP or 541±24 BC; DLO-05, 1513±22 years BP or 487±22 AD; Zhao and Yu, 2002) were also collected from the same reef. Growth rates of the two Holocene corals are similar to that of the modern coral.

The coral samples were soaked and washed with freshwater to eliminate remaining coral tissue, endolithic algae, and salt. Then a 1-cm-thick, 5–7-cm-wide slab for each sample was cut with a high-speed diamond saw along the axis of major growth. Dry coral slabs of the modern coral were X-radiographed in a hospital to reveal the skeletal growth band pattern, which shows that annual growth rates vary from 6 to 10 mm with an average of 8.9 mm for the period 1989–2000.

The coral slabs were soaked in 10% H_2O_2 for 24 h, followed by washing with de-ionized water for 5 to 10 min in order to decompose organic matter completely. Then it was ultrasonically cleaned in de-ionized water for 30 min to eliminate contaminants on the surface, and then dried.

Sub-annual samples were manually sliced or scraped with a very thin surgery blade along the slabs. The average sampling interval is about 0.6–0.8 mm for both samples. From surface downward, a total of 130 samples (No. 1-001 to 1-130) were taken from the modern coral, providing a seasonal to monthly resolution (about 12–13 samples per year). About 307 sub-annual samples were collected from two late Holocene coral slabs. Each sub-annual sample was about 8–10 mg in weight.

Following standard analytical procedures, a fraction of 1–2 mg from each sub-annual sample was taken for $\delta^{18}O$ analyses. The measurements were carried out on a Finnigan MAT 252 mass spectrometer with an automated carbonate device (Kiel III) in the Marine Geology Laboratory of Tongji University, Shanghai (China). All measurements are reported relative to the Pee Dee Belemnite isotopic standard (PDB). Precision was regularly monitored with a Chinese national carbonate standard (GBW04405) and an international standard NBS19. Repeated measurements of the standards vary around a standard deviation (1σ) of 0.07‰ for $\delta^{18}O$ (Tian et al., 2002).

A 2–3 mg fraction from each sub-annual sample was taken for Mg/Ca and Sr/Ca measurements with ICP-AES technology. It is worthwhile to point out that sub-annual samples for the first 2 cm of the modern coral slab are not identical to those used for $\delta^{18}O$ analyses. This is because the surface of the slab was still in light green colour after the above-described pretreatment, implying that organic materials might have not been completely removed. To eliminate this possible problem, we cut a small piece (~2 cm long and ~1 cm wide) from the surface of the pretreated slab for further treatment in 7% NaOH for 12 h. Afterwards, we repeated the treatment process as described in detail above prior to the collection of sub-annual samples. A total of 30 sub-annual samples (No. 1-001r to 1-030r) were taken from this small piece, matching the 26 stable isotope samples (No. 1-001 to 1-026) in approximate location. Thus for this part of the record, the Sr/Ca, Mg/Ca samples may not be exactly the same as the stable isotope samples. However, for the remaining part of the record (samples 1-027 to 1-130), and for the Holocene coral, the samples for $\delta^{18}O$ analyses are identical to those for Sr/Ca and Mg/Ca measurements.

For each sample, about 2–3-mg material was completely dissolved in 1% HNO3, and the solution was diluted to 10,000 times (to 20–30 g in total weight). About 10-ml aliquot was used for Mg/Ca and Sr/Ca measurements. This work was carried out on an ICP-AES at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (China). The instrument is equipped with CCD photomultiplier tubes for simultaneous collection of all spectral lines within the analyzed wave range. This significantly reduces the analytical uncertainty resulting from the fluctuation of signal intensity caused by plasma instability, improving overall analytical precision to better than 1%. Detailed analytical procedures was reported by Wei et al. (2004).

For this study, three spectral lines were used: Ca (183.944 nm), Mg (285.213 nm), and Sr (407.771 nm). To improve the precision, Mg/Ca and Sr/Ca ratios were measured following the method developed by Schrag (1999). In this method, external standardization (to correct for instrumental drift) improves the analytical precision, resulting in an overall precision of 0.4% for Mg/Ca and 0.2% for Sr/Ca, corresponding to SST uncertainties of ~0.4 °C for both Mg/Ca and Sr/Ca. The Mg/Ca and Sr/Ca ratios were calculated by referencing to a laboratory *Porites lutea* coral standard (SY96).

4. Results and discussion

The analytical results (Fig. 2) for the modern coral show that coral $\delta^{18}O$, Mg/Ca, and Sr/Ca have very

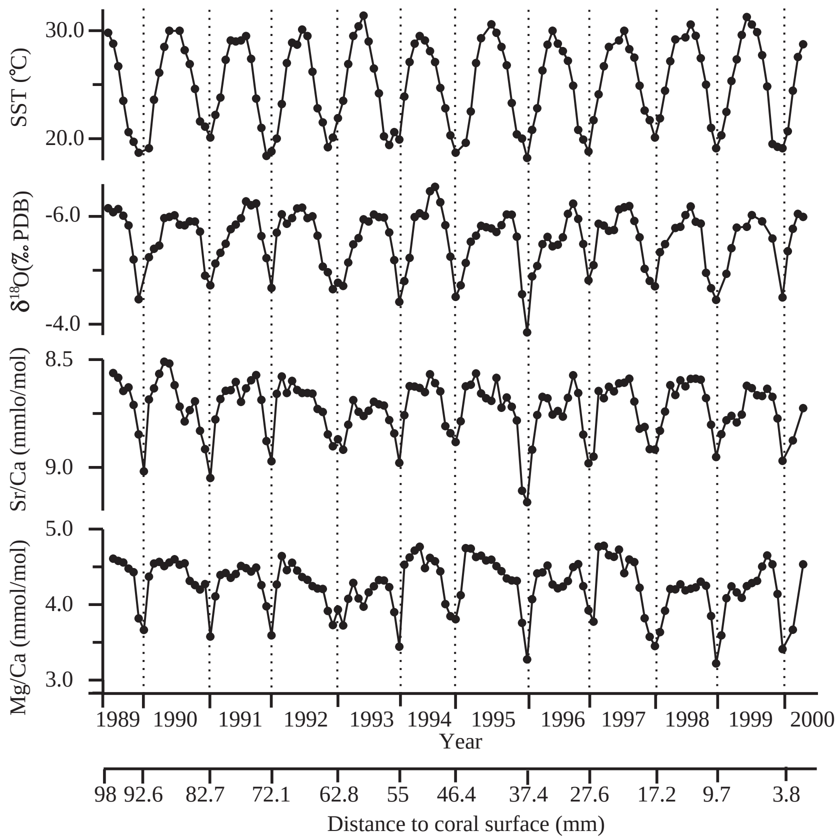


Fig. 2. The experimental results of coral $\delta^{18}O$, Sr/Ca and Mg/Ca for comparison with cycles of instrumental SST.

clear annual cycles similar to the instrumental SST record, and they are well correlated with each other, yielding the following equations:

$$Sr/Ca\,(mmol/mol) = -0.304 \times Mg/Ca\,(mmol/mol) + 10.02\ (n = 134,\ r = -0.83)$$

$$\delta^{18}O = 3.304 \times Sr/Ca\,(mmol/mol) - 34.427\ (n = 103,\ r = 0.81)$$

$$\delta^{18}O = -1.216 \times Mg/Ca\,(mmol/mol) - 0.356\ (n = 103,\ r = -0.73)$$

X-radiography reveals that high values of $\delta^{18}O$ and Sr/Ca and low Mg/Ca values correspond to the high-density bands that are deposited during the winter months and low values of $\delta^{18}O$ and Sr/Ca and high Mg/Ca values to the low-density bands that are deposited during the summer months. Like the *Porites* coral from Ryukyu Islands (Mitsuguchi et al., 2003), all the profiles have broad peaks in summer and narrow troughs in winter, suggesting the coral grew rapidly in summer and slowly in winter.

4.1. Relationships of coral $\delta^{18}O$, Sr/Ca, and Mg/Ca to SST

There are no major rivers along the coast of Leizhou Peninsula. The coral sample was collected from the reef front zone about 500 m away from the beach. Therefore, the influence of salinity variations due to runoff should be negligible. The mean annual SSS variation in the coral reef area is small (maximum 1.43‰ c.f. maximum 17‰ in mid-Pacific) if compared with the mean annual SST change (11 °C c.f. ~4 °C in the southern South China Sea; Table 1). This suggests that SST should have a relatively stronger influence on coral $\delta^{18}O$, Sr/Ca, and Mg/Ca.

Following the method described by Wei et al. (2000) for the calibration and best-fitting of coral $\delta^{18}O$ and instrumental SST, we first smoothed the SST data to the sampling resolution of the coral record, and then matched the maximum $\delta^{18}O$ value with the minimum SST value and the minimum $\delta^{18}O$ value with the maximum SST value in any given year. Then we match the midpoints of the SST curves with those of the $\delta^{18}O$ limbs. The coral $\delta^{18}O$ values between the maximum, minimum, and midpoint values were then matched with the smoothed SST record. The same approach was also taken for the Sr/Ca and Mg/Ca profiles.

Linear regression was applied to establish the relationships between the geochemical proxies and instrumental SST, based on all measured proxy data (Fig. 3). The obtained relationships are similar to those reported from other studies. In order to evaluate uncertainties of the regression equations, Ludwig's (1992) Isoplot program was used, resulting in the following equations with 1σ errors:

$$\delta^{18}O = -0.174(\pm 0.010) \times SST(^{\circ}C) - 1.02(\pm 0.27)\ (MSWD = 5.8) \quad (1)$$

$$Sr/Ca_{(mmol/mol)} = -0.0424(\pm 0.0031) \times SST(^{\circ}C) + 9.836(\pm 0.082)\ (MSWD = 8.6) \quad (2)$$

$$Mg/Ca_{(mmol/mol)} = 0.110(\pm 0.009) \times SST(^{\circ}C) + 1.32(\pm 0.23)\ (MSWD = 55) \quad (3)$$

Eq. (1) indicates a slope for $\Delta\delta^{18}O/\Delta SST$ of −0.174‰/°C, suggesting that an SST increase of 1 °C corresponds to a decrease in skeletal $\delta^{18}O$ of 0.174‰. This value slightly differs from the average slope of 0.19‰/°C derived from several Indo-Pacific *Porites* coral $\delta^{18}O$–SST records (Evans et al., 2000), but similar to *the values* reported from the Great Barrier Reef (0.18‰/°C (Gagan et al., 1994)) and New Caledonia (0.172‰/°C (Quinn et al., 1998); see Fig. 4a).

Eq. (2) indicates a slope for $\Delta(Sr/Ca)/\Delta SST$ of −0.042 mmol/mol/°C, suggesting that an SST increase of 1 °C corresponds to a decrease in skeletal Sr/Ca of 0.042 mmol/mol. This value is different from the average slope of 0.062 mmol/mol/°C reported for *Porites* corals (Gagan et al., 2000), but is within the error of the slope of 0.046 mmol/mol/°C reported for a *Porites lutea* coral at Sanya of Hainan Island (South China Sea; Wei et al., 2000), and is not much different from the value (0.051) reported for a *P. lutea* at Xisha (Fig. 1a) of South China Sea (Sun et al., 2004), and Kenting reef, southern Taiwan (Shen et al., 1996) and

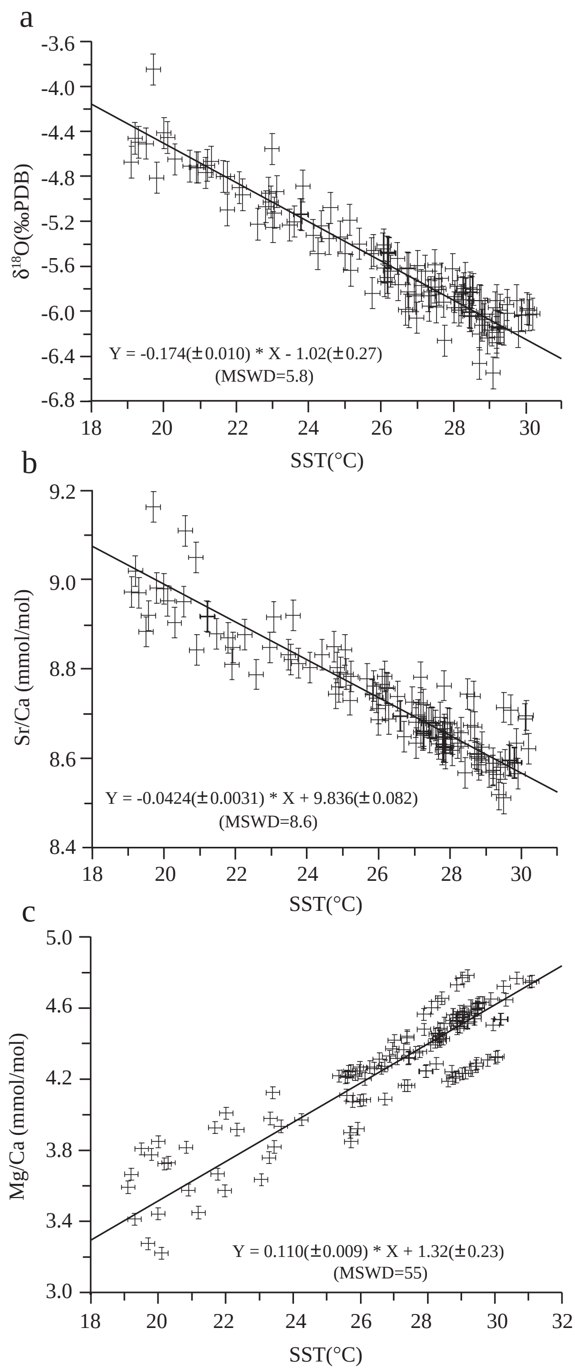


Fig. 3. Linear regressions of coral $\delta^{18}O$, Sr/Ca, and Mg/Ca against instrumental SST.

Galapagos Islands, Eastern Pacific (Schrag, 1999; see Fig. 4b).

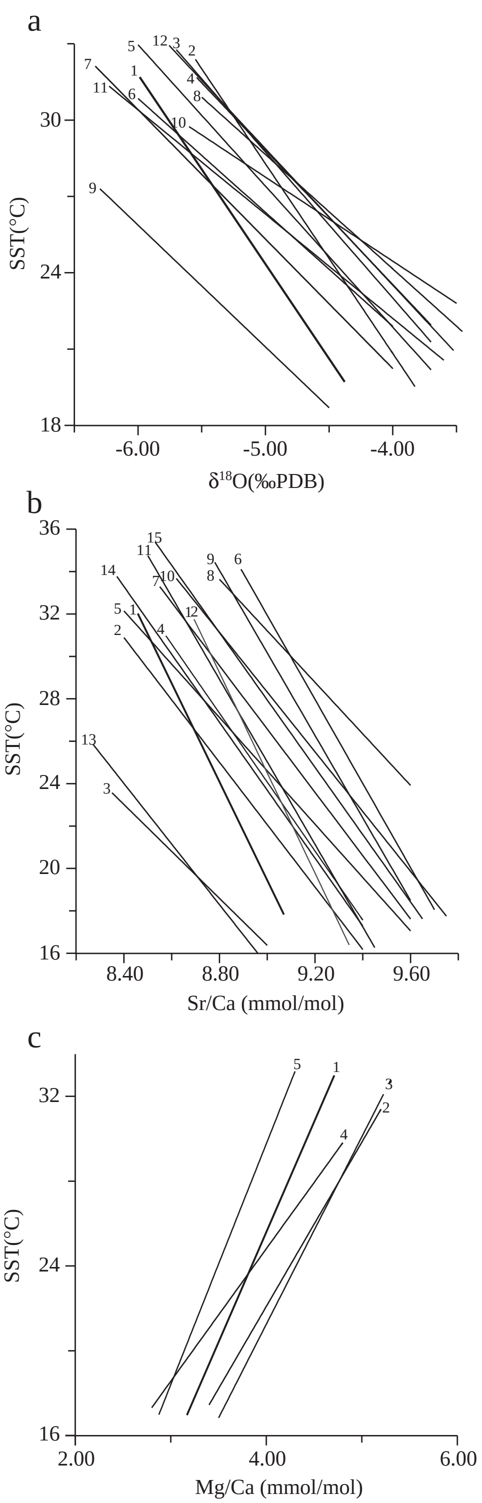
Eq. (3) indicates a slope for Δ(Mg/Ca)/ΔSST of 0.110 mmol/mol/°C, suggesting that an SST increase of 1 °C corresponds to an increase in skeletal Mg/Ca of 0.110 mmol/mol. This value is similar to the Mg/Ca–SST relationship of 0.113 mmol/mol/°C reported for *Porites lutea* coral from Hainan Island (Wei et al., 2000). Published Mg/Ca–SST relationships for *Porites* corals range from 0.088 to 0.16 mmol/mol/°C (average 0.117 mmol/mol/°C; Fig. 4c).

In summary, the approximately seasonal to monthly resolution coral $\delta^{18}O$, Sr/Ca, and Mg/Ca records of our *Porites lutea* colony from Leizhou Peninsula are all well correlated to regional SST variations during the period 1989–2000, with coral $\delta^{18}O$ and Sr/Ca show better correlations with SST than coral Mg/Ca (Figs. 2 and 3).

It is also intriguing to note all three proxies document an anomalously cold winter in 1995/1996 that is not indicated by the instrumental SST record from Haikou Ocean Observatory in 47-km distance to the coral location (Fig. 1). However, the air temperature record from the nearby Xuwen Salt Factory Meteorology Observatory in 1.5-km distance to the reef reveals that the winter of 1995/1996 was anomalously cold in this area. The low air temperatures during this winter, which was the coldest during the period of the coral record (1989–2000), caused mass mortality of banana plants in the vicinity of the coral reef at Leizhou Peninsula. In addition, this winter cooling is clearly seen in instrumental records from many other stations of the northern South China Sea, such as Xisha and Sanya to the south of Haikou. This suggests that the $\delta^{18}O$ and Sr/Ca–SST anomalies in 1995/1996 are real and the lack of a cold SST anomaly in 1995/1996 winter in the Haikou instrumental record is probably due to the fact the Observatory is too close to Haikou City, the capital city of Hainan Province where the cold surge may have been obscured by local anthropogenic factors.

4.2. Interpretation of $\delta^{18}O$, Sr/Ca and Mg/Ca vs. SST relationships

The purpose for establishing coral-based thermometers is to reconstruct past climate and to obtain a



better understanding of climate mechanisms. Numerous studies showed that the slopes and intercepts (Fig. 4) in the relationships of coral $\delta^{18}O$, Sr/Ca, or Mg/Ca vs. SST established for different coral reefs (even for the same coral genera) are significantly different. This leads to great difficulties for climate reconstructions, because reconstructed SST based on a generalized calibration equation may be very different from the true SST at a given location.

The published slopes of the $\delta^{18}O$–SST relationship for *Porites lutea* vary significantly between −0.134 (Mitsuguchi et al., 1996) and −0.189 (Gagan et al., 1998). This is not unexpected because theoretically coral $\delta^{18}O$ is a function of both SST and sea surface salinity (SSS) and thus the large variation in the slope is partially due to SSS variations at different sites. For instance, seasonal SSS in the vicinity of the reef site in this study varies by up to 1.4‰ (Table 1), which may result in ~0.38‰ variation in seawater $\delta^{18}O$ based on the linear relationship between seawater $\delta^{18}O$ and SSS (Fairbanks et al., 1997). This accounts for ~20% of the average seasonal variation observed in the modern coral.

Unlike $\delta^{18}O$, coral Sr/Ca is often considered as a reliable SST proxy independent of the extension rate or SSS change (Alibert and McCulloch, 1997; Beck et al., 1992, 1997; Gagan et al., 1998; Marshall and McCulloch, 2002; McCulloch et al., 1994; Mitsuguchi et al., 2003; Shen et al., 1996; Wei et al., 2000), except for some upwelling zones such as the Eastern Pacific where local artifacts may be produced by upwelling of deep ocean water with an unusual Sr/Ca

Fig. 4. A compilation of coral $\delta^{18}O$, Sr/Ca, and Mg/Ca vs. SST relations for *Porites* corals from different coral reef areas. References quoted for $\delta^{18}O$ equations in panel (a) are (1) this paper; (2) Mitsuguchi et al. (1996); (3) Gagan et al. (1998); (4) Gagan et al. (1998); (5) Evans et al. (2000); (6) Wellington et al. (1996); (7) Wellington and Dunbar (1995); (8) Carriquiry et al. (1994); (9) McConnaughey (1989); (10) Weber and Woodhead (1972); (11) Yu et al. (2001); (12) Abram et al. (2001). References quoted for Sr/Ca equations in panel (b) are (1) this paper; (2) Mitsuguchi et al. (1996); (3) Devilliers et al. (1995); (4) Alibert and McCulloch (1997); (5) Devilliers et al. (1994); (6) Wei et al. (2000); (7) Gagan et al. (1998); (8) Houck et al. (1977); (9) Schrag (1999); (10) Smith et al. (1979); (11) Shen et al. (1996); (12) Cohen et al. (2002); (13) Sinclair et al. (1998); (14) Beck et al. (1992); (15) Fallon et al. (1999). References quoted for Mg/Ca equations in panel (c) are (1) this paper; (2) Mitsuguchi et al. (1996); (3) Wei et al. (2000); (4) Sinclair et al. (1998); (5) Fallon et al. (1999).

ratio (Devilliers et al., 1994). However, both the slope and the intercept of the Sr/Ca–SST relationship also vary significantly at different sites. The slopes in the published calibrations vary between 0.040 to 0.065 mmol/mol/°C (Fig. 4b, also see Gagan et al., 2000), with the value in this study representing the low extreme. In this case, if the average slope of the Sr/Ca–SST relationship for *Porites* genus reported by Gagan et al. (1998) is applied to our data, the average seasonal SST variation will be 6.8 °C, ~3.2 °C lower than the instrumental record. Among all published calibrations, a Sr/Ca value of ~9 mmol/mol will yield a range of SSTs from ~20 °C through to ~28 °C.

Recently many researchers discussed the differences in Sr/Ca–SST calibrations and the potential causes (Devilliers et al., 1995; Gagan et al., 2000; Marshall and McCulloch, 2002; Shen et al., 1996). The slope and intercept of our calibration are significantly lower than those of most other calibrations (Gagan et al., 2000; Marshall and McCulloch, 2002) but are similar to those reported by Sun et al. (2004), Wei et al. (2000) and Shen et al. (1996) for the same region, and by Schrag (1999) for East Pacific. Marshall and McCulloch (2002) considered that the regional variation in coral Sr/Ca–SST relationships is real, depending upon specific environments that control coral physiology. Yu et al. (in press) discussed in detail about other possible causes of the atypical calibration, including mis-match of Sr/Ca data to the instrumental SST and thus artificial rotation of the calibration curve, which may occur if the coral has not recorded the whole winter component of the seasonal cycle or the sampling resolution is too low to reveal the detailed pattern of the winter-time SST. After detailed modelling of different scenarios, it was concluded that the smaller slope in our study is real. To raise the slope to 0.61 mmol/mol/°C, the average values of other typical calibrations, the expected mean winter SST has to be as high as 24 °C, which is unlikely for the reef site in Leizhou Peninsula.

Similar to the Sr/Ca–SST relationship, the slope and intercept of the Mg/Ca–SST relationship also vary significantly. If the published slopes (0.088–0.16 mmol/mol/°C) for Mg/Ca–SST relationships (see Fig. 4c) were used, the magnitude of average seasonal SST changes varies between 6.5 and 12.5 °C, significantly different from the instrumental record of 10 °C.

Therefore, the relationships between coral $\delta^{18}O$, Sr/Ca, or Mg/Ca and SST indeed show significant geographical variations, with the slope of the Sr/Ca–SST relationship being consistently low in the northwest Pacific region. For this reason, to obtain reliable palaeo-SST reconstruction for a given coral reef, individual calibration of the above relationships must be carried out on modern corals in the same region.

4.3. The reliability and applicability of $\delta^{18}O$, Sr/Ca and Mg/Ca vs. SST relationships

As discussed above, coral Sr/Ca is mainly a function of SST, independent of the extension rate or SSS change, and is therefore an ideal and reliable thermometer. To test this, we apply the calibration equation to two late Holocene corals of the same reef site as the modern coral (U-series ages ~541 BC and ~487 AD, respectively). The results (Fig. 5, Table 2) show that the ~541 BC coral yields a mean of Sr/Ca–SST maxima of 29.3 °C and a mean of Sr/Ca–SST minima of 19.5 °C, similar to those of the 1990s (the warmest period of the last century). The ~487 AD coral yields a mean of Sr/Ca–SST maxima of 28.7 °C and a mean of Sr/Ca–SST minima of 16.5 °C, which are 0.7 and 3.8 °C lower than those of the 1990s. Historic records show that it was relatively warm and wet in China during 800–300 BC (Eastern Zhou Dynasty), but was significantly colder and drier in east China during period of 386–589 AD (several degree Celsius colder than today; Chu, 1973; Ge et al., 2003; Man et al., 2000) in east China. For instance, historic literatures documented that it was so warm during early Eastern Zhou Dynasty (770–256 BC) that rivers in today's Shangdong province (35–38 °N) never froze for the whole winter season in 698, 590, and 545 BC. On the other hand, the period of Southern–Northern Dynasties (420–550 AD) was so dry and cold, highlighted by the fact that Beiwei Dynasty (386–534 AD) was forced to move its capital from Pingcheng (today's Datong city, 40.10°N, 113.30°E) to Luoyang (34.67°N, 112.45°E) in 493 AD after a series of severe droughts, with the most severe one occurring in 487 AD (Man et al., 2000). In addition, phenological records from Chinese historic documents also show that the winter temperature around 490 AD in the mid-lower reaches of the Yellow and Yangtze Rivers was ~1 °C lower than the

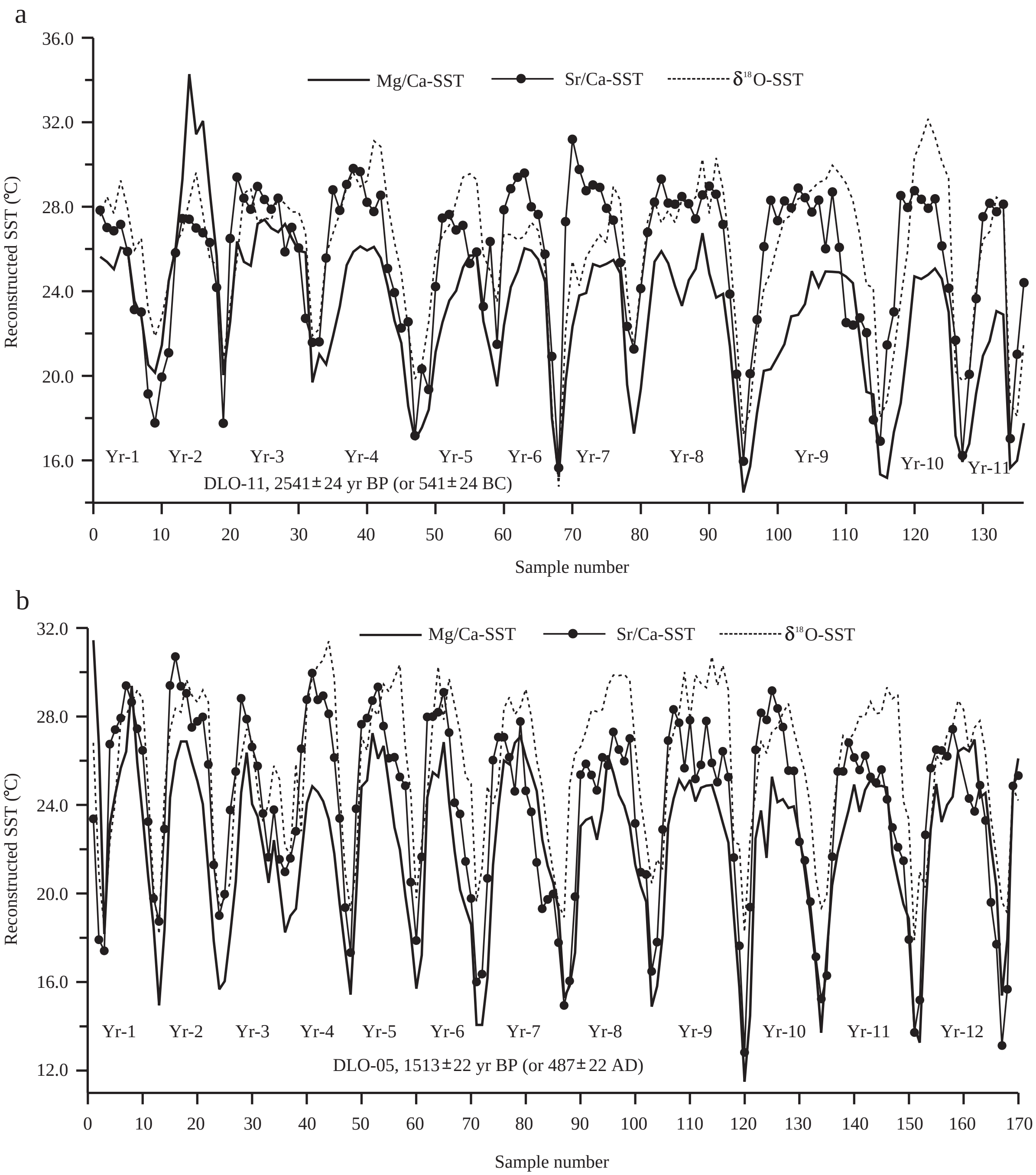


Fig. 5. Coral $\delta^{18}O$-, Sr/Ca-, and Mg/Ca-based SST variations for historical corals: (a) *Porites lutea* sample DLO-11, 2541±24 years BP (or 541±24 BC); (b) *P. lutea* sample DLO-05, 1513±22 years BP (or 487±22 AD). Note that Mg/Ca-based SST values are significantly lower. See text for discussion.

Table 2
Summary of calculated SST (°C) maxima and minima for the later Holocene and modern corals

	Proxy	541 BC (11-year average)	487 AD (12-year average)	Modern coral (11-year average)
SST maximum (°C)	Sr/Ca	29.3	28.7	29.4
	$\delta^{18}O$	28.9	29.6	29.6
	Mg/Ca	25.7	26.8	29.6
SST minimum (°C)	Sr/Ca	19.5	16.5	20.3
	$\delta^{18}O$	18.1	19.3	20.1
	Mg/Ca	17.0	15.4	20.2

present (1951–1980 mean; Ge et al., 2003). As South China Sea (SCS) is the moisture source region for summer monsoon rainfall in the mid-latitude region of East Asia, the above SST records in the SCS are consistent with Chinese historic records.

Unlike coral Sr/Ca, coral $\delta^{18}O$ is controlled by both SST and SSS. In this case, the empirical $\delta^{18}O$–SST equation based on the modern coral may not apply to the Holocene corals if the SSS during the Holocene has changed. This is exactly the case, as calculated $\delta^{18}O$–SST values for the 541 BC and 487 AD corals deviate to opposite directions, if compared with Sr/Ca–SST results, with the $\delta^{18}O$–SST values (Fig. 5; Table 2) for the 487 AD coral being too high, in conflict with historic climatic records. This suggests that the SSS at those times were different from that of the 1990s and therefore its contributions to $\delta^{18}O$ variations were different. This is expected considering the fact that the SCS is a moisture source region for East Asian monsoon rainfall in the mid-latitude region, with present annual evaporation surpassing annual precipitation. For instance, when annual SST increases, effective evaporation would increase, creating elevated moisture for the summer monsoon. This process will distill isotopically lighter oxygen isotope into the water vapour that is transported by atmosphere (e.g., monsoonal winds) polarward, leaving behind a seawater characterised by elevated $\delta^{18}O$ and SSS. On the other hand, when SST decreases, the opposite will occur. Because of this, by extracting the SST component of the $\delta^{18}O$ variation based on the difference between coral Sr/Ca and $\delta^{18}O$ curves (Gagan et al., 1998), the residual $\delta^{18}O$ should represent a measure of change in effective evaporation of the SCS or moisture level of past summer monsoon relative to the present day. The residual $\delta^{18}O$ can be calculated using the following equation: $\Delta\delta^{18}O = d\delta^{18}O/dT^{*}(T_{\delta^{18}O} - T_{Sr/Ca})$, which represents the deviation from mean modern seawater $\delta^{18}O$. In this equation, $d\delta^{18}O/dT$ is the slope of the empirical $\delta^{18}O$–SST relationship, and $T_{\delta^{18}O}$ represent calculated SSTs based on the empirical $\delta^{18}O$– and Sr/Ca–SST relationships, respectively. Using this equation, the calculated mean $\Delta\delta^{18}O$ values are +0.09‰ for the 541 BC coral, and −0.30‰ for the 487 AD coral (Yu et al., in press). The former suggests that the SCS seawater $\delta^{18}O$ at 541 BC, like the SST, was analytically indistinguishable from that of the 1990s (the warmest period of the last century) and the summer monsoon precipitation was also similar to that in the 1990s. On the other hand, the latter suggests that oxygen isotopes of the SCS seawater at 487 AD were significantly lighter (by 0.3‰), the amount of moisture transported out of the SCS was lower, and summer monsoon weaker, than in the 1990s. These findings are clearly consistent with Chinese historical climatic records (Chu, 1973; Ge et al., 2003; Man et al., 2000).

Although coral $\delta^{18}O$ and Sr/Ca have been widely accepted as reliable proxy for SST and SSS and applied in numerous palaeoclimatic studies (Alibert and McCulloch, 1997; Beck et al., 1992; Gagan et al., 1998; Linsley et al., 2000; McCulloch et al., 1994), the applicability of coral Mg/Ca–SST relationship as a thermometer is still a matter of debate (Fallon et al., 1999; Mitsuguchi et al., 2001, 2003; Schrag, 1999; Sinclair et al., 1998). Our results show that coral Mg/Ca–SST relationship has significantly larger scatter (as reflected by large MSWD) than coral $\delta^{18}O$ and Sr/Ca vs. SST relationships, with the bulk of scatter being unrelated to analytical errors of Mg/Ca ratios (if the scatter is only caused by the analytical uncertainty, MSWD should be <1). In other words, although the coral Mg/Ca is generally correlated with SST, SST is not the sole factor that affects coral Mg/Ca in the reef area of Leizhou Peninsula. To assess the applicability of Mg/Ca–SST relationship as a thermometer, we also apply the calibration equation to the two late Holocene *Porites* corals. Although Mg/Ca annual cycles synchronous to those of Sr/Ca and $\delta^{18}O$ are very clear in both samples, the calculated Mg/Ca–SST values are significantly lower than the Sr/Ca–SST values (Table 2; Fig. 5). For instance, the means of summer SST maxima based on Mg/Ca are 1.9–3.6 °C

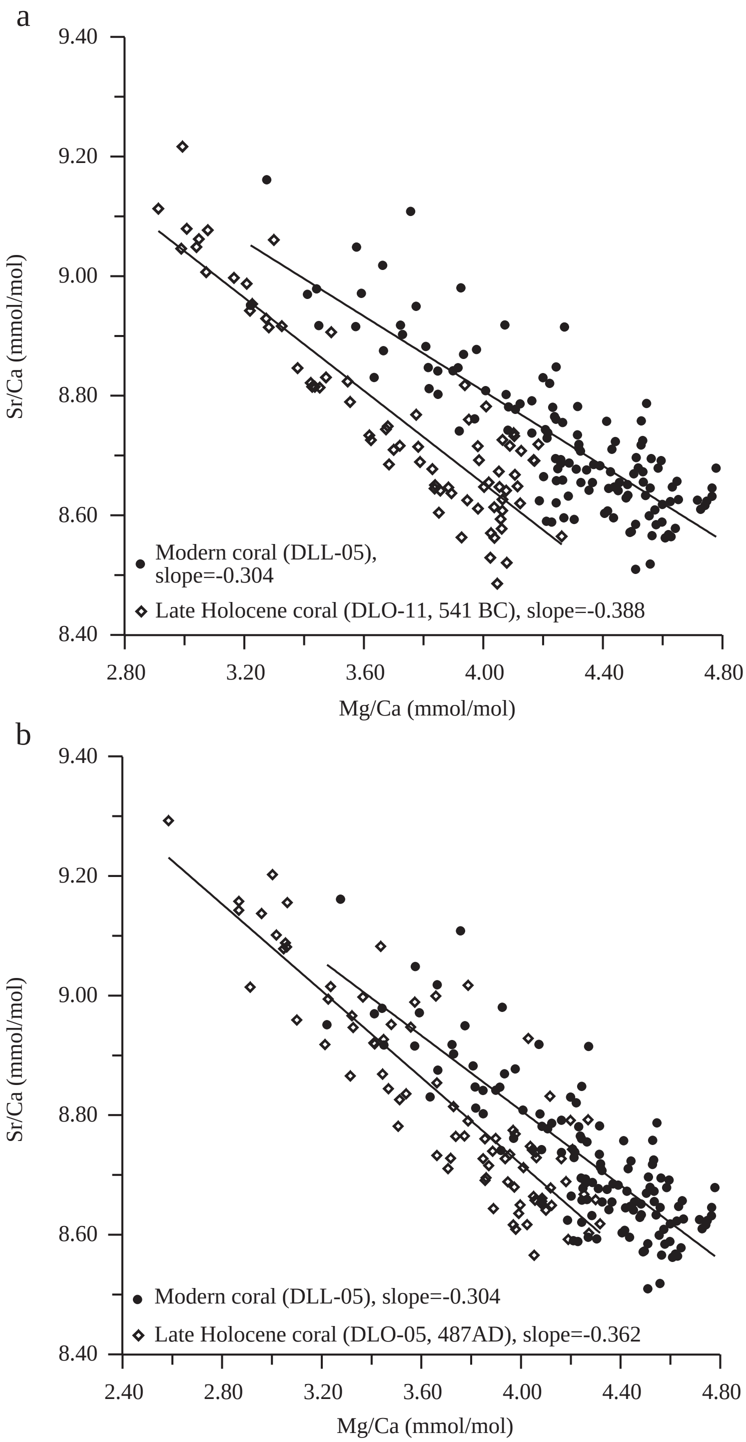


Fig. 6. Comparison between Mg/Ca–Sr/Ca scatter plots for the modern coral (DLL-05) and historical corals (DLO-11, U-series age 2541±24 years BP or 541±24 BC, and DLO-05, U-series age 1513±22 years BP or 487±22 AD). Note that the summer-time Mg/Ca offsets are larger than the winter-time offsets, which probably suggests that microbialites were more abundant in the coral skeletons deposited in the summer season.

lower than those based on Sr/Ca. The means of the winter SST minima based on Mg/Ca are 1.1–2.5 °C lower than those based on Sr/Ca. A summer SST of 25.7 °C and a winter SST of 17.0 °C at ~541 BC are significantly lower than those of the present day, which is clearly in sharp conflict with independent Chinese historic records. This suggests that Mg/Ca–SST relationship cannot be used as a reliable thermometer.

4.4. Possible causes that demise the Mg/Ca–SST relationship

It is intriguing to note that calculated Mg/Ca–SST values for both Holocene corals are lower than expected. In the Mg/Ca vs. Sr/Ca plots (Fig. 6), a clear negative offset in Mg/Ca is displayed by each of two late Holocene corals if compared with the modern coral of a comparable Sr/Ca range, with the older 541 BC sample displaying a larger offset. In each sample, the summer-time Mg/Ca offset is larger than that of the winter-time. For example, in the 541 BC sample, the summer-time offset is ~0.6 mmol/mol, while the winter-time offset, ~0.3 mmol/mol. Mitsuguchi et al. (2001) reported that coral Mg/Ca may be affected by different chemical treatments, decreasing with distilled water treatment, but increasing with H_2O_2 or HNO_3 treatments. However, these treatments were applied to coral powders with up to 60% of each sample being actually dissolved during H_2O_2 or HNO_3 treatments. In this study, only solid sample chips were treated in dilute H_2O_2 without significant dissolution and both late Holocene and modern corals were treated in the same manner. This suggests that coherent Mg/Ca negative offsets in the Holocene corals are unrelated to chemical treatments. It may be argued that the Mg/Ca ratios in the modern and Holocene corals are susceptible to different biological/metabolic effects (Mitsuguchi et al., 2003). This may well be the case, but it is difficult to understand that such biological/metabolic effects should always result in negative offsets in fossil corals. For instance, apart from the two late Holocene corals in this study, the untreated and distilled water-treated fractions of a 7210-year-old coral reported by Mitsuguchi et al. (2001) also displays ~0.2 to 0.5 mmol/mol negative Mg/Ca offset if compared with a modern coral of comparable Sr/Ca ratios. In addition, the mid-Holocene *Porites* and *Goniopora* corals reported in Yu et al. (2004, in press) all show negative Mg/Ca offsets (unpublished).

We interpret this intriguing observation in terms of preferential meteoric dissolution of metastable Mg–calcite formed by cryptic microbialites coexisting with coral skeletons. Cryptic microbialites are ubiquitous during reef-building processes (Webb et al., 1998). As they are mainly composed of metastable Mg–calcite, they may contain up to 17% (molar) MgO (Gregory Webb, personal communication) and only 100–300 ppm Sr (Nothdurft et al., 2004). As Mg–calcite is unstable, it may be preferentially dissolved or convert to low Mg–calcite before aragonite under meteoric conditions if the reef was exposed like the one on Leizhou Peninsula. During such a process, Mg will be lost without appreciable change in Sr, and thus the Mg/Ca ratio will decrease in a coral skeleton containing only a trace amount of cryptic microbialites. This process can easily explain the observation that the fossil corals always display negative Mg/Ca offsets if compared with the modern coral, with the offset being larger in the older 541 BC coral of the Leizhou Peninsula. It is also likely that the microbialites were more abundant in the summer season and thus the summer-time Mg/Ca offset is twice the size of the winter-time Mg/Ca offset in the 541 BC coral. In addition, we speculate that the Mg/Ca offset between the two colonies of modern corals from Ryukyu Islands (Mitsuguchi et al., 2003) could be due to different proportions of microbialites being present in the coral skeletons. Further studies will be undertaken to evaluate the above interpretation.

5. Conclusions

Coral $\delta^{18}O$, Sr/Ca, and Mg/Ca vs. SST relationships were established at seasonal resolutions for a modern *Porites lutea* coral from a fringing reef at Leizhou Peninsula, the northern coast of the South China Sea, which are broadly consistent with those published in the literature. However, the large variations in both the slopes and intercepts of published $\delta^{18}O$–, Sr/Ca–, and Mg/Ca–SST relationships for *Porites* corals from different areas suggest that calibration of these relationships using modern corals and instrumental SST records from different locations is a prerequisite for their application in the reconstruction of past climate using fossil corals.

The applicability and reliability of the above relationships as climatic proxies are tested using two later Holocene *Porites lutea* samples (U-Th ages ~541 BC and ~487 AD, respectively) from the same reef, combined with independent climatic records in Chinese history. The calculated Sr/Ca–SST at ~541 BC was nearly as warm as in the 1990s (the warmest of the last century), but at ~487 AD, it was significantly cooler than in the 1990s. This observation is consistent with climatic data reported in Chinese historic documents, confirming that the Sr/Ca–SST relationship is a reliable thermometer. Removing the SST component in the $\delta^{18}O$ variation based on calculated Sr/Ca–SST values, the residual $\delta^{18}O$ reflects the deviation of the Holocene seawater $\delta^{18}O$ from the modern value, which is also a measure of the Holocene SSS or the summer monsoon moisture level. Such residual $\delta^{18}O$ was close to zero at ~541 BC and -0.3‰ at ~487 AD, suggesting that it was as wet as in the 1990s at ~541 BC but significantly drier at ~487 AD in mainland China, which are also consistent with independent historic records.

In contrast to Sr/Ca and $\delta^{18}O$, calculated Mg/Ca–SST values for the two late Holocene corals are significantly lower than the Sr/Ca–SST and are also in conflict with Chinese historic records. This suggests that Mg/Ca–SST relationship cannot be used as a reliable thermometer. We notice that at comparable Sr/Ca ranges, fossil corals always display negative Mg/Ca offsets if compared with the modern coral of the same site. We interpret this observation as due to preferential meteoric dissolution of cryptic Mg–calcite-bearing microbialites in the exposed fossil corals. Microbialites (MgO up to 17%, Sr only 100–300 ppm) are ubiquitous during reef-building processes and their presence in only a trace amount will have a significant impact on coral Mg/Ca ratios without any influence on coral Sr/Ca ratios.

Acknowledgements

This work was funded by the National Natural Science Foundation of China (No. 40231009), the Chinese Ministry of Science & Technology Special Scheme (No. 2002CCA02700), and the knowledge Innovation Project of the Chinese Academy of Sciences (KZCX3-SW-220). Zhao, Yu, and Wei acknowledge the support of an NSFC Distinguished Young Scholar Award (No. 40028302). Both Yu and Zhao acknowledge the support of a UQ Foundation Research Excellence Award to Zhao. Felis acknowledges the support of Deutsche Forschungsgemeinschaft through DFG—Research Center ‘Ocean Margins’ at Bremen University (No. RCOM0254). Constructive reviews by Dr. Min Sun and Prof. Henry Schwarcz are gratefully appreciated. We enjoy pleasant and constructive discussions with Balz Kamber and Gregory Webb.

References

Abram, N.J., Webster, J.M., Davies, P.J., Dullo, W.C., 2001. Biological response of coral reefs to sea surface temperature variation: evidence from the raised Holocene reefs of Kikai-jima (Ryukyu Islands, Japan). Coral Reefs 20 (3), 221–234.

Alibert, C., McCulloch, M.T., 1997. Strontium/calcium ratios in modern *Porites* corals from the Great Barrier Reef as a proxy for sea surface temperature: calibration of the thermometer and monitoring of ENSO. Paleoceanography 12 (3), 345–363.

Beck, J.W., Edwards, R.L., Ito, E., Taylor, F.W., Recy, J., Rougerie, F., Joannot, P., Henin, C., 1992. Sea-surface temperature from coral skeletal strontium calcium ratios. Science 257 (5070), 644–647.

Beck, J.W., Recy, J., Taylor, F., Edwards, R.L., Cabioch, G., 1997. Abrupt changes in early Holocene tropical sea surface temperature derived from coral records. Nature 385 (6618), 705–707.

Carriquiry, J.D., Risk, M.J., Schwarcz, H.P., 1994. Stable-isotope geochemistry of corals from Costa-Rica as proxy indicator of the El-Nino Southern Oscillation (Enso). Geochimica et Cosmochimica Acta 58 (1), 335–351.

Chu, K., 1973. A preliminary study on the climatic fluctuations during the last 5000 years in China. Science in China. Series B, Chemistry, Life Sciences & Earth Sciences 16 (2), 226–256.

Cohen, A.L., Owens, K.E., Layne, G.D., Shimizu, N., 2002. The effect of algal symbionts on the accuracy of Sr/Ca paleotemperatures from coral. Science 296 (5566), 331–333.

Cole, J.E., Fairbanks, R.G., Shen, G.T., 1993. Recent variability in the southern oscillation—isotopic results from a Tarawa Atoll Coral. Science 260 (5115), 1790–1793.

Correge, T., Delcroix, T., Recy, J., Beck, W., Cabioch, G., Le Cornec, F., 2000. Evidence for stronger El Nino–Southern Oscillation (ENSO) events in a mid-Holocene massive coral. Paleoceanography 15 (4), 465–470.

Devilliers, S., Shen, G.T., Nelson, B.K., 1994. The Sr/Ca–temperature relationship in coralline aragonite—influence of variability in (Sr/Ca) seawater and skeletal growth-parameters. Geochimica et Cosmochimica Acta 58 (1), 197–208.

Devilliers, S., Nelson, B.K., Chivas, A.R., 1995. Biological-controls on coral Sr/Ca and Delta-O-18 reconstructions of sea-surface temperatures. Science 269 (5228), 1247–1249.

Evans, M.N., Kaplan, A., Cane, M.A., 2000. Intercomparison of coral oxygen isotope data and historical sea surface temperature (SST): potential for coral-based SST field reconstructions. Paleoceanography 15 (5), 551–563.

Fairbanks, R.G., Evans, M.N., Rubenstone, J.L., Mortlock, R.A., Broad, K., Moore, M.D., Charles, C.D., 1997. Evaluating climate indices and their geochemical proxies measured in corals. Coral Reefs 16, S93–S100.

Fallon, S.J., McCulloch, M.T., van Woesik, R., Sinclair, D.J., 1999. Corals at their latitudinal limits: laser ablation trace element systematics in Porites from Shirigai Bay, Japan. Earth and Planetary Science Letters 172 (3–4), 221–238.

Felis, T., Patzold, J., Loya, Y., Fine, M., Nawar, A.H., Wefer, G., 2000. A coral oxygen isotope record from the northern Red Sea documenting NAO, ENSO, and North Pacific teleconnections on Middle East climate variability since the year 1750. Paleoceanography 15 (6), 679–694.

Felis, T., Lohmann, G., Kuhnert, H., Lorenz, S.J., Scholz, D., Patzold, J., Al-Rousan, S.A., Al-Moghrabi, S.M., 2004. Increased seasonality in Middle East temperatures during the last interglacial period. Nature 429 (6988), 164–168.

Gagan, M.K., Chivas, A.R., Isdale, P.J., 1994. High-resolution isotopic records from corals using ocean temperature and mass-spawning chronometers. Earth and Planetary Science Letters 121 (3–4), 549–558.

Gagan, M.K., Ayliffe, L.K., Hopley, D., Cali, J.A., Mortimer, G.E., Chappell, J., McCulloch, M.T., Head, M.J., 1998. Temperature and surface-ocean water balance of the mid-Holocene tropical Western Pacific. Science 279 (5353), 1014–1018.

Gagan, M.K., Ayliffe, L.K., Beck, J.W., Cole, J.E., Druffel, E.R.M., Dunbar, R.B., Schrag, D.P., 2000. New views of tropical paleoclimates from corals. Quaternary Science Reviews 19 (1–5), 45–64.

Ge, Q.S., Zheng, J.Y., Fang, X.Q., Man, Z.M., Zhang, X.Q., Zhang, P.Y., Wang, W.C., 2003. Winter half-year temperature reconstruction for the middle and lower reaches of the Yellow River and Yangtze River, China, during the past 2000 years. Holocene 13 (6), 933–940.

Guilderson, T.P., Fairbanks, R.G., Rubenstone, J.L., 2001. Tropical Atlantic coral oxygen isotopes: glacial–interglacial sea surface temperatures and climate change. Marine Geology 172 (1–2), 75–89.

Hendy, E.J., Gagan, M.K., Alibert, C.A., McCulloch, M.T., Lough, J.M., Isdale, P.J., 2002. Abrupt decrease in tropical Pacific Sea surface salinity at end of Little Ice Age. Science 295 (5559), 1511–1514.

Houck, J.E., Buddemeier, R.W., Smith, S.V., Jokiel, P.L., 1977. The response of coral growth rate and skeletal Strontium content to light intensity and water temperature. Proceedings, Third International Coral Reef Symposium, Rosenstiel School of Marine and Atmospheric Science, University of Miami, pp. 425–431.

Kuhnert, H., Patzold, J., Hatcher, B., Wyrwoll, K.H., Eisenhauer, A., Collins, L.B., Zhu, Z.R., Wefer, G., 1999. A 200-year coral stable oxygen isotope record from a high-latitude reef off western Australia. Coral Reefs 18 (1), 1–12.

Linsley, B.K., Dunbar, R.B., Wellington, G.M., Mucciarone, D.A., 1994. A coral-based reconstruction of intertropical convergence zone variability over central-America since 1707. Journal of Geophysical Research, Oceans 99 (C5), 9977–9994.

Linsley, B.K., Wellington, G.M., Schrag, D.P., 2000. Decadal sea surface temperature variability in the subtropical South Pacific from 1726 to 1997 AD. Science 290 (5494), 1145–1148.

Ludwig, K.R., 1992. ISOPLOT—a plotting and regression program for radiogenic–isotopic data, Version 2.57. U.S.G.S. Open-file report 91–445: 40.

Man, Z.M., Ge, Q.S., Zhang, P.Y., 2000. Case studies on the impact of climatic changes on the farming–pastoral transitional zone in historical period. Geographical Research 19 (2), 141–147 (in Chinese with English abstract).

Marshall, J.F., McCulloch, M.T., 2002. An assessment of the Sr/Ca ratio in shallow water hermatypic corals as a proxy for sea surface temperature. Geochimica et Cosmochimica Acta 66 (18), 3263–3280.

McConnaughey, T., 1989. C-13 and O-18 isotopic disequilibrium in biological carbonates: 1. Patterns. Geochimica et Cosmochimica Acta 53 (1), 151–162.

McCulloch, M.T., Gagan, M.K., Mortimer, G.E., Chivas, A.R., Isdale, P.J., 1994. A high-resolution Sr/Ca and Delta-O-18 coral record from the great-barrier-reef, Australia, and the 1982–1983 El-Nino. Geochimica et Cosmochimica Acta 58 (12), 2747–2754.

McCulloch, M., Mortimer, G., Esat, T., Li, X.H., Pillans, B., Chappell, J., 1996. High resolution windows into early Holocene climate: Sr/Ca coral records from the Huon Peninsula. Earth and Planetary Science Letters 138 (1–4), 169–178.

McCulloch, M.T., Tudhope, A.W., Esat, T.M., Mortimer, G.E., Chappell, J., Pillans, B., Chivas, A.R., Omura, A., 1999. Coral record of equatorial sea-surface temperatures during the penultimate deglaciation at Huon Peninsula. Science 283 (5399), 202–204.

Mitsuguchi, T., Matsumoto, E., Abe, O., Uchida, T., Isdale, P.J., 1996. Mg/Ca thermometry in coral-skeletons. Science 274 (5289), 961–963.

Mitsuguchi, T., Uchida, T., Matsumoto, E., Isdale, P.J., Kawana, T., 2001. Variations in Mg/Ca, Na/Ca, and Sr/Ca ratios of coral skeletons with chemical treatments: implications for carbonate geochemistry. Geochimica et Cosmochimica Acta 65 (17), 2865–2874.

Mitsuguchi, T., Matsumoto, E., Uchida, T., 2003. Mg/Ca and Sr/Ca ratios of Porites coral skeleton: evaluation of the effect of skeletal growth rate. Coral Reefs 22 (4), 381–388.

Nie, B.F., Chen, T.G., Liang, M.T., Zhong, J.L., Yu, K.F., 1997. Coral reefs from Leizhou Peninsula and Holocene sea level highstands. Chinese Science Bulletin 42 (5), 511–514 (in Chinese).

Nothdurft, L.D., Webb, G.E., Kamber, B.S., 2004. Rare earth element geochemistry of Late Devonian reefal carbonates, canning basin, Western Australia: confirmation of a seawater REE proxy in ancient limestones. Geochimica et Cosmochimica Acta 68 (2), 263–283.

Peng, Z.C., Chen, T.G., Nie, B.F., Head, M.J., He, X.X., Zhou, W.J., 2003. Coral delta O-18 records as an indicator of winter monsoon intensity in the South China Sea. Quaternary Research 59 (3), 285–292.

Quinn, T.M., Crowley, T.J., Taylor, F.W., Henin, C., Joannot, P., Join, Y., 1998. A multicentury stable isotope record from a New Caledonia coral: interannual and decadal sea surface temperature variability in the southwest Pacific since 1657 AD. Paleoceanography 13 (4), 412–426.

Roberts, C.M., et al., 2002. Coral reef biodiversity and conservation—response. Science 296 (5570), 1027–1028.

Schrag, D.P., 1999. Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates. Paleoceanography 14 (2), 97–102.

Shen, C.C., Lee, T., Chen, C.Y., Wang, C.H., Dai, C.F., Li, L.A., 1996. The calibration of D[Sr/Ca] versus sea surface temperature relationship for Porites corals. Geochimica et Cosmochimica Acta 60 (20), 3849–3858.

Sinclair, D.J., Kinsley, L.P.J., McCulloch, M.T., 1998. High resolution analysis of trace elements in corals by laser ablation ICP-MS. Geochimica et Cosmochimica Acta 62 (11), 1889–1901.

Smith, S.V., Buddemeier, R.W., Redal, R.C., Houck, J.E., 1979. Strontium–Calcium thermometry in coral skeletons. Science 204, 404–407.

Sun, M., Chiu, C.H., Shen, C.C., Lee, T., 1999. Sr thermometer for *Porites* corals: little need to measure Ca? Geochemical Journal 33 (5), 351–354.

Sun, Y.L., Sun, M., Wei, G.J., Lee, T., Nie, B.F., Yu, Z.W., 2004. Strontium contents of a Porites coral from Xisha Island, South China Sea: a proxy for sea-surface temperature of the 20th century. Paleoceanography 19 (2), PA2004, doi:10.1029/2003PA000959.

Tian, J., Wang, P.X., Cheng, X.R., Li, Q.Y., 2002. Astronomically tuned Plio-Pleistocene benthic delta O-18 record from South China Sea and Atlantic–Pacific comparison. Earth and Planetary Science Letters 203 (3–4), 1015–1029.

Tudhope, A.W., Chilcott, C.P., McCulloch, M.T., Cook, E.R., Chappell, J., Ellam, R.M., Lea, D.W., Lough, J.M., Shimmield, G.B., 2001. Variability in the El Nino–Southern oscillation through a glacial–interglacial cycle. Science 291 (5508), 1511–1517.

Watanabe, T., Minagawa, M., Oba, T., Winter, A., 2001a. Pretreatment of coral aragonite for Mg and Sr analysis: implications for coral thermometers. Geochemical Journal 35 (4), 265–269.

Watanabe, T., Winter, A., Oba, T., 2001b. Seasonal changes in sea surface temperature and salinity during the Little Ice Age in the Caribbean Sea deduced from Mg/Ca and O-18/O-16 ratios in corals. Marine Geology 173 (1–4), 21–35.

Webb, G.E., Baker, J.C., Jell, J.S., 1998. Inferred syngenetic textural evolution in Holocene cryptic reefal microbialites, Heron Reef, Great Barrier Reef, Australia. Geology 26 (4), 355–358.

Weber, J.N., Woodhead, P.M.J., 1972. Temperature dependence of Oxygen-18 concentration in reef coral carbonates. Journal of Geophysical Research 77 (3), 463–473.

Wei, G.J., Li, X.H., Nie, B.F., Sun, M., Liu, H.C., 1999. High resolution *Porites* Mg/Ca thermometer for the north of the South China Sea. Chinese Science Bulletin 44 (3), 273–276.

Wei, G.J., Sun, M., Li, X.H., Nie, B.F., 2000. Mg/Ca, Sr/Ca and U/Ca ratios of a *Porites* coral from Sanya Bay, Hainan Island, South China Sea and their relationships to sea surface temperature. Palaeogeography, Palaeoclimatology, Palaeoecology 162 (1–2), 59–74.

Wei, G.J., Yu, K.F., Li, X.H., Zhao, J.X., Sun, Y.L., Sun, M., Nie, B.F., 2004. Coralline Sr/Ca and Mg/Ca temperature for the northern South China Sea: calibration and primary application on high-resolution reconstructing. Quaternary Sciences 24 (3), 325–331 (in Chinese with English abstract).

Wellington, G.M., Dunbar, R.B., 1995. Stable isotopic signature of El-Nino Southern Oscillation events in eastern tropical pacific reef corals. Coral Reefs 14 (1), 5–25.

Wellington, G.M., Dunbar, R.B., Merlen, G., 1996. Calibration of stable oxygen isotope signatures in Galapagos corals. Paleoceanography 11 (4), 467–480.

Yu, K.F., 2000. The sea surface temperature changing trend of the last 40 years in the Lei-Qiong sea area. Tropical Geography 20 (2), 111–115 (in Chinese with English abstract).

Yu, K.F., Chen, T.G., Huang, D.C., Zhao, H.T., Zhong, J.L., Liu, D.S., 2001. The high-resolution climate recorded in the delta O-18 of *Porites lutea* from the Nansha Islands of China. Chinese Science Bulletin 46 (24), 2097–2102.

Yu, K.F., Liu, D.S., Shen, C.D., Zhao, J.X., Chen, T.G., Zhong, J.L., Zhao, H.T., Song, C.J., 2002a. High-frequency climatic oscillations recorded in a Holocene coral reef at Leizhou Peninsula, South China sea. Science in China Series, D: Earth Sciences 45 (12), 1057–1067.

Yu, K.F., Zhong, J.L., Zhao, J.X., Shen, C.D., Chen, T.G., Liu, D.S., 2002b. Biological–geomorphological zones in a coral reef area at southwest Leizhou Peninsula unveil multiple sea level highstands in the Holocene. Marine Geology & Quaternary Geology 22 (2), 27–33 (in Chinese with English abstract).

Yu, K.F., Zhao, J.X., Liu, T.S., Wei, G.H., Wang, P.X., Collerson, K.D., 2004. High-frequency winter cooling and reef coral mortality during the Holocene climatic optimum. Earth and Planetary Science Letters 224 (1–2), 143–155.

Yu, K.F., Zhao, J.X., Wei, G.J., Cheng, X.R., Wang, P.X., 2005. Mid-late Holocene monsoon climate retrieved from seasonal Sr/Ca and d18O records of *Porites lutea* corals at Leizhou Peninsula, northern coast of the South China Sea. Global and Planetary Change (in press).

Zhao, J.X., Yu, K.F., 2002. Timing of Holocene sea-level highstands by mass spectrometric U-series ages of a coral reef from Leizhou Peninsula, South China Sea. Chinese Science Bulletin 47 (4), 348–352.