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Original Article

A Preliminary study of Sr/Ca thermometry in Chang Islands, Gulf of Thailand

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Abstract

Variations in ratios of strontium-to-calcium (Sr/Ca) for two *Porites* sp. coral specimens collected from Wai (PW) and Loa Ya (PLY) islands, part of Chang islands, Gulf of Thailand, were determined. Inductively coupled plasma optimal emission spectrometry (ICP-OES) was used to analyze this ratio, which demonstrates annual cycles and the data is assumed to reflect the sea surface temperature (SST). Comparing the ratios with SST data, following Sr/Ca–SST relationships were determined PW: Sr/Ca (mmol/mol) = 11.56–0.070×SST, PLY: Sr/Ca (mmol/mol) = 11.89–0.081×SST. Our correlations are different from those previously reported; a discrepancy that may involve differences in analytical methods employed and abnormally low sea surface salinity (SSS) (<30 psu) in the Gulf of Thailand.

Keywords: Sr/Ca ratio, coral skeletons, sea surface temperature, Chang Islands, Gulf of Thailand

1. Introduction

Corals incorporate a variety of trace elements in their skeletons, the contents of which vary with the formative marine environment (Smith *et al.*, 1979; Shen and Boyle, 1988). Magnesium (Mg), Strontium (Sr), and Uranium (U) have relatively long remainder times in seawater (Swart, 1981; Swart and Hubbard, 1982) and provide geochemical proxies for reconstructing environmental conditions during coral growth. Moreover, their ratios to Calcium (Ca in $CaCO_3$) in coral skeletons can be linked to seawater temperature (Beck *et al.*, 1992; Min *et al.*, 1995; Mitsuguchi *et al.*, 1996; Wei *et al.*, 2000). Several studies, mostly in the Pacific, have used the coral Sr/Ca ratio as a proxy for sea surface temperature (SST) (review in Corrège, 2006). The ratio of Sr/Ca in coral skeleton varies inversely with SST when seawater Sr/Ca is constant (Weber, 1973; Smith *et al.*, 1979; Beck *et al.*, 1992). The Sr/Ca ratio from skeletons of large and old hermatypic corals (in particular *Porites* sp.) has proved an excellent recorder of past SST seasonal cycles (e.g., Mitsuguchi *et al.*, 1996; Shen *et al.*, 1996; Wei *et al.*, 2000; Cardinal *et al.*, 2001; Sun *et al.*, 2005; Yu *et al.*, 2005; Ayling *et al.*, 2006; Cahyarini *et al.*, 2008 and Liu, 2008). *Porites* sp. corals live more than 100 years. Because their annual extension rate is approximately 1–2 cm/yr (Knutson *et al.*, 1972; Buddemeier *et al.*, 1974; Dodge and Thomson, 1974), one can retrieve high-resolution (weekly to monthly) SST records by investigating Sr/Ca ratios.

Paleoclimate data available for Thailand has scarcely been recorded and few paleoclimatic studies have even been performed in coral specimens. It is therefore necessary to extrapolate the SST record to produce a database for SST reconstruction. The aim of this study is to examine the correlation between the Sr/Ca ratio of coral skeletons of *Porite* sp. and SST of Chang islands, Trat Province in the Gulf of Thailand for climate reconstruction.

2. Materials and Methods

2.1 Study sites

The Chang islands are located at 11.5°N/102.5°E in the eastern region of Thailand, Trat Province. Specific study

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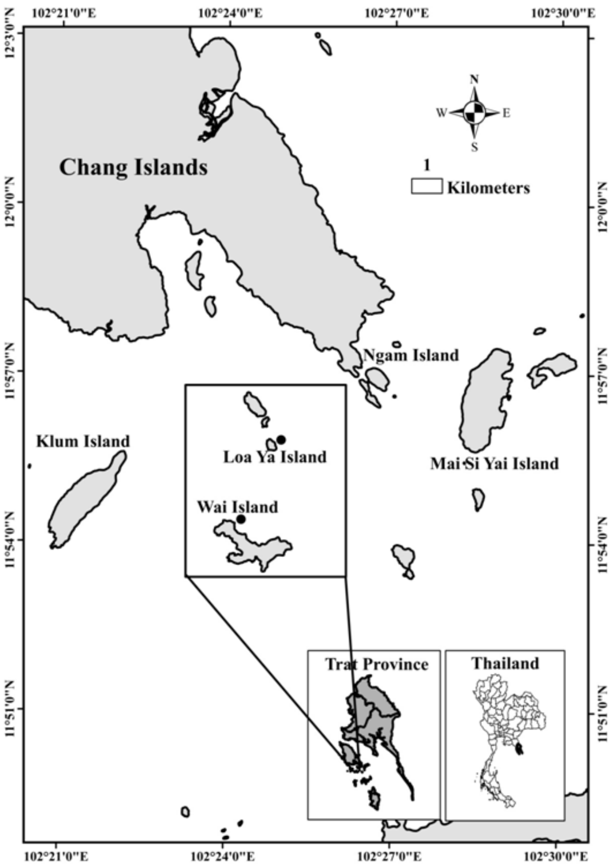

Figure 1. Map of Chang islands, highlighting sample collection sites, Wai and Loa Ya islands. Two black circles represent sampling sites.

sites include Wai and Loa Ya islands (Figure 1). Climate data was not recorded for these islands, but was obtained at a nearby meteorological station at Klong Yai, approximately 55 km from the study sites.

The climate of these islands is characterized by two seasons: a summer season from November to April, and a rainy season from May to October. The northeast monsoon brings dry, hot air during summer season, and the southwest monsoon brings wet, cold air during rainy season. Climate records from the Thai Meteorological Department show that the annual mean air temperature is 27.3±0.3°C (1982-2011). The lowest mean monthly temperature is recorded in January (26.4°C), and the highest in April (28.5°C). The annual mean rainfall averages 4,871 mm (1982-2011), with the lowest recorded in December (22.4 mm) and the highest in August (1,021 mm). Rainfall is concentrated from May to October.

SST data was obtained from the 4-weeks of NOAA SST data (NOAA NCEP EMC CMB GLOBAL Reyn_ SmithOlv2 weekly SST) from a 1 degree × 1 degree grid (11.5°N, 102.5°E) between 1995 and 2011. The mean sea surface temperature was 29.3±0.9°C, with the maximum and minimum SST for each year not considerably different and ranging from approximately 30.1°C to 31.7°C and 27.1°C to 29.4 °C, respectively. The highest SST recorded was from 1998, and the lowest was from 2009. The interannual variability of SST was relatively small. The SST generally reached a maximum from April to June and a minimum in January (Figure 2).

Coral reefs of interest were found around both Wai and Loa Ya Islands in a depth of 5-8 m from the sea surface. *Porites* sp. corals are the most commonly found constituents of these reefs. Chemical and physical properties as SST, pH, dissolved oxygen (DO), salinity, and conductivity were measured on July 15, 2011; SST: 30.7 °C, pH: 8.2, DO: 5.30 mgO_2/l, salinity: 28.2 psu (practical salinity unit), and conductivity: 89.3 µS/cm.

2.2 Coral specimens

In July 2011, two large living *Porites* sp. corals were collected off Wai (PW) and Loa Ya (PLY) islands. Their diameters were >30 cm and were collected using a hammer and a chisel at 5 m below the water surface. Specimens were rinsed and soaked in distilled water at room temperature for 24 hrs and then dried for several weeks. They were cut into 5-7 mm thick slabs along the direction of growth with a circular rock saw. Slabs were then ultrasonically cleaned with distilled/deionized water repeatedly to remove surface contamination and dried in an oven at 60°C for 24 hrs (Al-Rousan *et al.*, 2007). Coral slabs were X-rayed using a Philips Optimus. Extension rates were directly measured along the major growth axes from computed radiography. Each group of high/low-density bands represented an annual extension rate, and the upper band was assigned to the collection date (Figure 3).

2.3 Elemental analysis

Chemical treatment and analysis methods were conducted as reported by Mitsuguchi *et al.* (2003). To analyze the Sr/Ca ratio, microsamples of coral skeletons, each weighing 2-3 mg, were manually collected at 1 mm intervals with an etching needle; the cross-section of the micro-sampling plane measured approximately 1.5 mm × 1.5 mm.

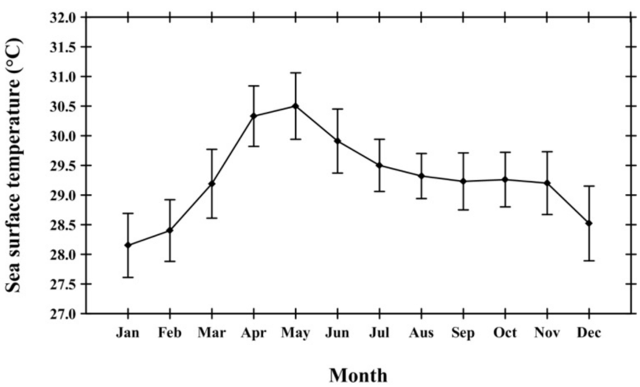

Figure 2. Monthly mean SST with standard deviation between 1995 and 2011 at Chang islands from NOAA.

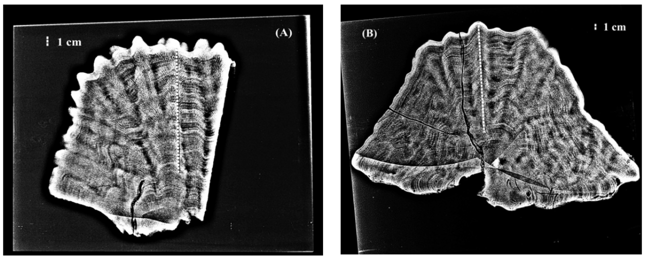

Figure 3. X-radiograph positive print of *Porites* sp. coral (A) PW and (B) PLY. The sampling profiles for Sr/Ca ratio are indicated with white dashed lines.

Each subsample was crushed, transferred into an acid cleaned 5-mL glass vial, and sequentially treated with distilled/deionized water at room temperature, 4 mM HNO_3 at room temperature, and 30% H_2O_2 at 60°C. Each treatment consisted of 1 ml of the treatment solution per subsample with ultrasonic agitation for 15 min. At the end of each step, vials were centrifuged for 10 min (15 cm radius; 2,000 rpm), and supernatants were carefully removed by a micropipette. Microsamples were dried in vacuum desiccators at 60°C without a drying agent for 8 hrs and individually dissolved in HNO_3 to standardize the Ca concentration of the sample solution to 95 ppm ± 10%. Finally, Sr and Ca contents of the solutions were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) at Faculty of Science, Silpakorn University, with Agilent 710 ICP-OES. Reproducibility (relative standard deviation) of the Sr/Ca measurement was approximately 0.5%. A linear least-squares regression was used to analyze the correlation of the Sr/Ca ratio and SST.

3. Results

3.1 Annual extension rates

Dark (high-density) and light (low-density) bands were seen within the annual extension via X-radiograph (Figure 3). For the positive X-radiograph, the total number of counted growth bands was 12 for coral PW and 17 for coral PLY, with annual extension incrementing from 8.9 to 14.8 mm and 7.9 to 15.3 for coral PW and PLY, respectively (Figure 4). The average annual extension rate of coral PW was 11.5±1.7 mm/yr, slightly higher than that of PLY (11.3±0.7 mm/yr). Overall, the average annual extension rates of the two corals were similar to coral from Con Dao Island, Vietnam (Dang *et al.*, 2004) and Pulau Tioman, Malaysia (Lee and Mohamed, 2009). Our two coral samples were drilled at 1-mm intervals, yielding a monthly resolution for this sampling interval.

3.2 Variation of Sr/Ca ratio of coral skeletons

In this study, 129 and 179 subsamples were analyzed from coral PW and PLY, respectively, with Sr/Ca ratios presented in Figure 5. We report the Sr/Ca ratio as a range from 9.30 to 9.81 mmol/mol for coral PW and from 9.27 to 9.76 mmol/mol for coral PLY. The results showed little difference for both the coral skeletons, indicating that both corals are influenced by similar environmental conditions. X-radiography revealed that high Sr/Ca values correspond to the high-density bands deposited during the rainy season (May to October), and low Sr/Ca values to low-density bands deposited throughout summer (November to April). Our results mirrored those of Mitsuguchi et al. (2003) on *Porites* coral from Ryukyu Islands, suggesting that coral grew slowly in winter and rapidly in the summer.

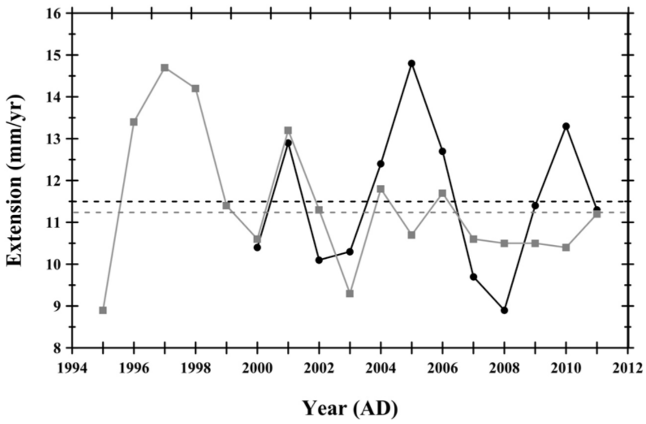

Figure 4. Linear annual extension rates of coral PW (black circles with black lines) and PLY (gray rectangles with gray lines) for 1995-2011. The dashed black and gray lines represent the average annual extension rates for corals PW and PLY, respectively.

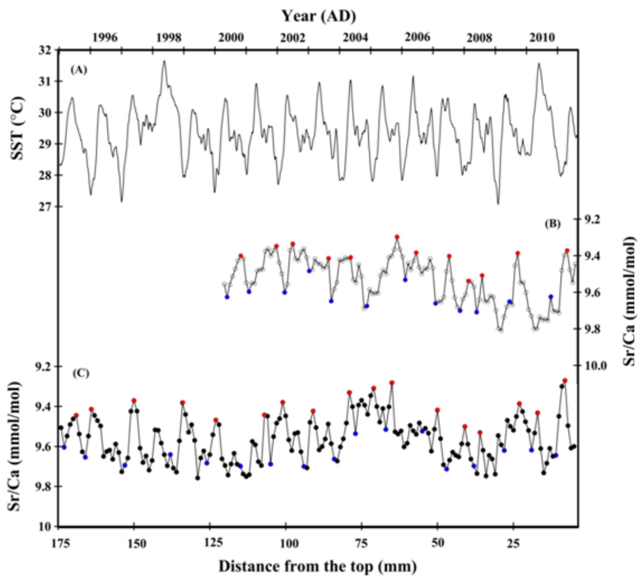

Figure 5. Variation of (A) SST from NOAA and Sr/Ca ratios of *Porites* (B) coral PW and (C) PLY. Red and blue cycles represent data points used for calibration.

3.3 Relationship of Sr/Ca ratios with SST

To calibrate Sr/Ca ratios against SST with a least-squares regression analysis, the annual maximum and minimum SST values were used. The resulting plot is shown in Figure 6. Published intermediate values also assume that coral skeletal growth rate is constant between extreme values (e.g. Mitsuguchi *et al.*, 1996; Marshall and McCulloch, 2002), while some have used this calibration procedure with only extreme values (e.g. Gagan *et al.*, 1998; Cardinal *et al.*, 2001; Sun *et al.*, 2004).

A total of 24 data points for coral PW and 34 data points for coral PLY were analyzed (Figure 6), and a calibration equation for coral PW was generated:

$$\text{Sr/Ca (mmol/mol)} = 11.56 - 0.070\,\text{SST}; \quad r = 0.89,\ p < 0.001 \tag{1}$$

This was similar to the calibration equation calculated for coral PLY:

$$\text{Sr/Ca (mmol/mol)} = 11.89 - 0.081\,\text{SST}; \quad r = 0.87,\ p < 0.001 \tag{2}$$

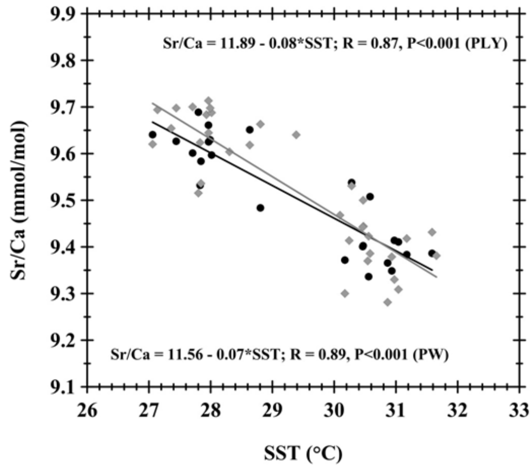

Figure 6. Linear least-squares regression of Sr/Ca ratio vs. SST for *Porites* sp. corals PW and PLY. Black circles with black lines and gray rectangles with gray lines represent coral PW and PLY, respectively.

4. Discussion

Table 1 presents a literature review of Sr/Ca calibrations against SST for genus *Porites*. The slopes from these calibrations revealed large variations (Figure 7). Comparing the results of our study with previous ones, our regressions have steeper slopes ($|b| = 0.07$ and 0.08) than most previously published relationships ($|b| = 0.04$–0.06) that exhibited greatest divergence. However, prior reports highlight Sr/Ca thermometry with a slightly higher slope ($|b| = 0.06$–0.09) from a inductively coupled plasma mass spectrometer (ICP-MS) (Sinclair *et al.*, 1998; Corrège *et al.*, 2000), including Sr/Ca thermometry from Koh Chueak located at the south of the Gulf of Thailand (Sirianansakul *et al.*, 2012). de Villiers *et al.* (1994) suggested that the effects of extension rates on skeleton Sr/Ca may either be the result of variations in extension and/or calcification rate, or higher Sr/Ca values associated with slower extension rates. Later publications implied that these are not important factors in influencing the Sr/Ca ratio for *Porites* corals (e.g. Wei *et al.*, 2000; Mitsuguchi *et al.*,

Table 1. Summary of Sr/Ca-SST calibrations published to date by using the genus *Porites*.

References	*Porite* species	Location	a	b	r^2
This study	*Porites* sp.	Wai Island	11.56	-0.070	0.79
This study	*Porites* sp.	Lao Island	11.89	-0.081	0.75
de Villiers *et al.* (1994)	*Porites lobata*	Hawai'i	10.956	-0.0795	0.95
Shen *et al.* (1996)	*Porites lutea*	Taiwan	10.29	-0.051	>0.90
Mitsuguchi *et al.* (1996)	*Porites lutea*	Ryukyu, Japan	10.5	-0.0608	0.73
Bessat (1997)	*Porites* sp.	Moruroa	11.302	-0.0815	0.66
Sinclair *et al.* (1998)	*Porites mayeri*	GBR, Australia	10.8	-0.07	0.68
Fallon *et al.* (1999)	*Porites lobata*	Shikoku, Japan	10.76	-0.063	0.59
Corrège *et al.* (2000)	*Porites lutea*	Amédée, NewCal	10.73	-0.0657	0.64
Linsley *et al.* (2000)	*Porites lutea*	Rarotonga	11.12	-0.065	0.75
Wei *et al.* (2000)	*Porites lutea*	South China Sea	10.6	-0.05	0.56
Quinn and Sampson (2002)	*Porites lutea*	Amédée, NewCal	10.524	-0.067	0.84
Sun *et al.* (2005)	*Porites* sp.	Xisha Island	10.33	-0.053	0.96
Yu *et al.* (2005)	*Porites lutea*	Leizhou Pen	9.84	-0.042	N.A.
Mitsuguchi *et al.* (2008)	*Porites* sp.	Con Dao Island	10.11	-0.045	0.95
Deng *et al.* (2009)	*Porites lutea*	Hainan Island	9.82	-0.043	N.A.
Sirianansakul *et al.* (2012)	*Porites lutea*	Chueak Island	11.83	-0.098	0.96

NewCal – New Caledonia, France

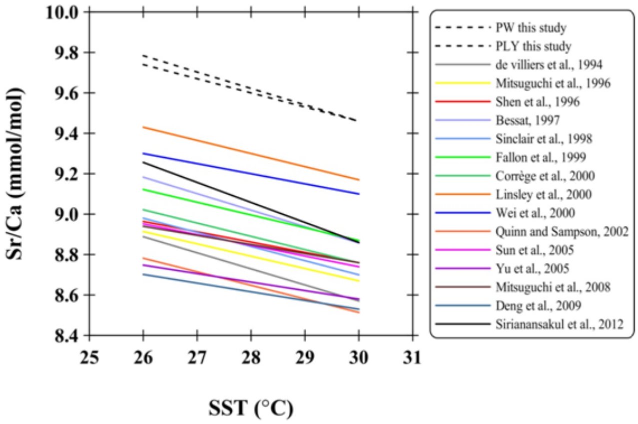

Figure 7. Calibrationof Sr/Ca thermometry for *Porites* corals.

2003). In this study, average annual extension rates of coral PW are similar to coral PLY.

We consider potential factors disturbing Sr/Ca thermometry in this study include. First, analytical error of Sr/Ca (RSD: 0.5%) is probably too large to correctly capture skeletal Sr/Ca variations induced by SST variation from Chang islands (approximately 3°C in the annual range). Second, the anomalously low sea surface salinity (SSS) (<30 psu) in the Gulf of Thailand may distort Sr/Ca thermometry to cause unclear annual cycles. Mitsuguchi *et al.* (2008) found that the Sr/Ca thermometry in *Porites* coral collected from Con Dao island (90 km off the Mekong Delta in the southern South China Sea) was significantly altered during the warm/wet season when SSS decreased to ~30 psu.

Recently, several researchers discussed the divergence in Sr/Ca–SST calibrations and potential causes (Shen *et al.*, 1996; Gagan *et al.*, 2000; Marshall and McCulloch, 2002), considering that local variation in coral Sr/Ca-SST calibrations is real and dependent on environments that control coral growth. Enmar *et al.* (2000) suggested that variation in skeletal Sr/Ca ratio is mainly due to coral Sr composition variation. Variation was explained by differences in minor elemental seawater composition that are important factors controlling the intake of minor elements into coral skeletons. Sun *et al.* (2005) suggested that variations in seawater Ca do not significantly affect calcium content in coral skeletons. Furthermore, elemental ratios also result from growth rate and chemical treatment (Yoshioka *et al.*, 1985; Mitsuguchi *et al.*, 2001). Results reported by Mitsuguchi *et al.* (2001) and Mitsuguchi and Kawakami (2012) suggested that Sr/Ca ratios showed slight or little variation throughout treatment sequences.

We did not investigate any other factors that are causes of Sr/Ca thermometry disturbance. Hence, we do not yet have sufficient data or knowledge about the sea-surface conditions around Wai and Loa Ya Islands. Our analyses suggested that differences arise from sampling procedure discrepancies. Analytical uncertainties could be partially ascribed to Sr/Ca differences.

5. Conclusions

Sr/Ca ratios from annually banded *Porites* sp. specimens collected from Wai and Loa Ya islands in the Gulf of Thailand were analyzed by their relationship to SST. Coral samples grew between 2000 and 2011 and 1995 and 2011 AD, respectively. The Sr/Ca time series revealed an exceptionally unclear annual cycle, primarily reflecting seasonal SST variation for Wai and Loa Ya islands. The Sr/Ca ratio in two coral skeletons correlated with SST, but Sr/Ca thermometry showed higher slopes than in the previously studies. The specific reasons for the discrepancy are still unclear, but possible reasons include analytical methods used and low SSS (<30 psu) in the Gulf of Thailand.

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