Sea Surface Temperature and Salinity Reconstruction from Geochemical Tracers of a Massive Coral in the Persian Gulf

Forouzan, F., Ghazban, F.,* and Ardestani, M.

Department of Environmental Engineering, Faculty of Environment, University of Tehran, P.O. Box14155-6135, Tehran, Iran

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ABSTRACT: The δ^{18} O, δ^{13} C, and strontium/calcium (Sr/Ca)-record was measured from a 7-year old *Platygyra sinensis* coral located offshore Larak Island in the Persian Gulf at a resolution of 22 samples/year. An increased sampling resolution of 55 samples/year over two annual cycles was also compared with the 22 sample resolution to evaluate the effectiveness of the sampling procedure. The resulting data exhibited identical results between the two methods. By means of previously reported equations, Sr/Ca-derived sea surface temperatures (SST) ranged between 17 to 30 °C, with an average of 24.7 °C. The inter-annual variability in the *Platygyra sinensis* indicated a significant correlation with COADS data. In addition, the relation between the δ^{18} O in *Platygyra sinensis* coral and the Sr/Ca-estimated SST data was assessed. Subtracting the Sr/Ca-based SST values from the δ^{18} O of the coral, the δ^{18} O of water was calculated. These data were then used to construct ranges of sea surface salinity (SSS) in the region.

Key words: Coral, Persian Gulf, Temperature, Salinity, Geochemical tracers

INTRODUCTION

In recent years, significant efforts have been made to recognize robust tracers of sea surface temperature (SST) and sea surface salinity (SSS) in corals. Massive scleractinian corals are considered as the important archives of historical climate data. Because these corals are usually distributed throughout the tropical regions, they have a wide array of geochemical tracers, and can be accurately dated. These corals are useful specifically for times that go past instrumental climate recordings (Leder, Swart et al., 1996; Swart, Leder et al., 1996; Gagan, Ayliffe et al., 2000). Oxygen isotopic composition (δ^{18} O) and ratio of strontium to calcium (Sr/Ca) in coral skeletons are the most reliable SST tracers, in spite of the fact that variations in δ^{18} O of seawater can considerably alter SST reconstructed from δ^{18} O in corals. Because these changes in seawater δ^{18} O are linked to SSS variations, this primary complication can be turned into a benefit and give us a SSS tracer.

The SST component in the coral δ^{18} O signal can be evaluated by Sr/Ca measurements. Assuming that the Sr/Ca of the seawater is constant, the Sr/Ca in the coral varies inversely with temperature (Smith, Buddemeier *et al.*, 1979; Beck, Edwards *et al.*, 1992). Several studies, mostly in the Pacific, reconstructed SST by means of coral Sr/Ca as a proxy for temperature (Corrège, 2006). Investigations on Sr/Ca in Atlantic corals reported complications including growth rates, seawater Sr/Ca variations, sampling effects, light intensity, water chemistry, and other unknown factors (Cardinal, Hamelin *et al.*, 2001; Swart, Elderfield *et al.*, 2002; Saenger, Cohen *et al.*, 2008; Giry, Felis *et al.*, 2010). However, much uncertainty regarding the exact mode of incorporation of stable isotopes and trace elements into the coral skeleton has still remained.

The Persian Gulf is a semi-enclosed sea with a sub-tropical climate. It is under the influence of extreme environmental changes such as SST and SSS variations throughout a year. The corals in the Persian Gulf region are exposed to some of the most saline water bodies in the world (Karimi Mossadegh, Parker *et al.*, 2013). Despite of having a diverse ecosystem, the Persian Gulf has been devoid of the chronological climate records. To our knowledge, studies in this respect are limited to the work developed by Gischler and coworkers (Gischler, Lomando *et al.*, 2005). They reported the coral climate proxy data using a *Porites lutea* coral in the Persian Gulf for the first time.

Platygyra sinensis as a widespread coral in the Persian Gulf region, creates large colonies (Veron,

^{*}Corresponding author E-mail: fghazban@ut.ac.ir

1993; Dai and Horng, 2009). This species has not ever been used to generate climate records by trace element and isotopic variations. In the present study, we focus on developing a climate archive for the Persian Gulf region through reconstruction of SST variability using Sr/Ca ratio and δ^{18} O measurements in this species.

MATERIALS & METHODS

The Persian Gulf is located between Iran and the Arabian Peninsula. The depth range is varied with the western part being shallow and becoming deeper in the south east at the opening of the Strait of Hormuz. Through its narrowest part, the Persian Gulf is connected to the Gulf of Oman. Karun, Jarrahi, Zohreh, Mond, Hendijan, Kol, and Minab are the most watery rivers flow into the Persian Gulf from the Iranian Plateau. The western end is marked by the Arvand Rood which carries the water of the Euphrates, Tigris, and Karun rivers (UNGEGN, 2006). As shown in Fig. 1, the study area is located close to the Larak Island off the coast of Iran in the Persian Gulf. The waters around this island have one of the most diverse coral reef areas in the Persian Gulf. The Persian Gulf is in an arid area having evaporation mostly exceeding river runoff and precipitation (Johns and Olson, 1998). Water temperature in the Persian Gulf exhibits high seasonal fluctuations in the northwest. Water is more saline and cooler during the first half of the year than the second half (Johns and Olson, 1998; Bower, Hunt et al., 2000), and the evaporation rate is higher because of the south-western monsoon winds (Reynolds, 1993). Because the cool water coming from the Arvand Rood

flows to the south Arabian coasts and the warm oceanic water flows from the Indian Ocean toward the Persian Gulf, the water temperature in the Persian coasts is higher than the southern Arabian coasts (ROPME, 1999). The surface water salinity is variable in different areas in the Persian Gulf (Brewer, 1978).

We collected several hemispherical coral heads from the Persian Gulf around the Larak Island in late August 2012. Among all the samples, a colony of *Platygyra sinensis*, collected from the west marginal coast of the Larak Island at 26.84766N and 56.309883E in water depth of ~7 m was in a good condition and selected for detail analysis. This specimen, hereafter referred to as PSAUG2012, had a 25 cm diameter and a height of about 20 cm. The sample slab of 10-mm thickness was carefully cut from the head parallel to the axis of maximum coral growth. This slab was rinsed with seawater to remove the bulk of the organic material. Then, it was sun-dried and transferred to the laboratory. The slab was X-rayed by a Pro X-ray American Control Toshiba machine, exposed to 100 mA, 60 kV for 0.05 s to identify annual growth rate bands. Black-and-white print of the X-radiograph shows the skeletal low- and high-density pattern of the annual growth bands (Fig. 2). Despite the subtle changes in growth rate within coral, the annual growth rate of the PSAUG2012 varied between 19 to 24 mm with an average of about 22 mm/year. Sample preparation for the elemental and isotopic analyses was performed at the Rosenstiel School of Marine and Atmospheric Science (RSMAS), the University of



Fig. 1. Location map of the study area in the Strait of Hormuz. The Æ" symbol points to the Larak Island, where the coral sample was collected



Fig. 2. X-radiograph for the *Platygyra sinensis* coral (PSAUG2012) with age interpretation. Skeletal banding pattern of alternating low and high density bands can be seen.

Miami (USA). The x-radiograph was enhanced by "the Coral X-Radiograph Densitometry System" computer program for a better resolution. The powder samples of coral skeleton were milled out of the coral along the continuous polyp tracts by a 1.49 mm low speed hand held dental drill. The drilling was done in a direction perpendicular to the axis of growth at each step increment of 1 mm and progressed parallel to the axis of growth from step to step. After each sample collection, the drill and the coral slab were cleaned with pressurized air and brush to avoid sample contamination.

Oxygen (δ^{18} O) and carbon (δ^{13} C) isotopic measurements were performed at the Stable Isotope Laboratory (SIL) of RSMAS, using 80-100 µg of powdered sample by means of a Delta Plus mass spectrometer. Saturated ortho-phosphoric acid was reacted with samples at 70 °C in a vacuum system and produced gas. The evolved gases were analyzed by the mass spectrometer. Data was corrected for isobaric interference and expressed relative to the Vienna Pee Dee Belemnite (VPDB). Calibration to the VPDB standard was obtained by replicate measurements of NBS-19 standard. For both $\delta^{18}O$ and δ^{13} C, the internal analytical precision was 0.02‰. The long-term reproducibility of ±0.1‰ was derived from repeated measurements (6 standards to 40 samples) of Optically Clear Calcite (OCC) as the internal carbonate standard. The value of $\delta^{18}O$ was obtained using the equation 1:

$$\delta^{18}O = \{ [({}^{18}O/{}^{16}O)_{sample} / ({}^{18}O/{}^{16}O)_{standard}] - 1 \} \times 1000$$
 (1)

The analyses of Sr/Ca were performed by dissolving about 30-40 µg of the drilled sample in 5 mL 4% HNO,. Measurements of Sr/Ca ratios were performed by a Vista-Pro Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) housed at the SIL of RSMAS. Because the amount of sample was not always the same, the measurements were carried out twice. During the first analysis, the amount of Ca in each sample was estimated. Before the second measurements applied, based on the results of the first analysis, each sample was mixed with specific amount of 4% HNO₃ in order to have almost the same concentration for each sample solution. For simultaneous collection of all spectral lines within the analyzed wave range, the instrument was equipped with CCD photomultiplier tubes. CCD photomultiplier improves the overall analytical precision to better than 1% by decreasing the analytical uncertainty of the signal intensity fluctuation (Boss and Fredeen, 1997). Five samples of a standard solution prepared in the University of South Florida (hereafter referred to as USF standard) were analyzed in each set of analyses. The average corrected precision of the USF standard was 9.691 mM/M, based on batches of 60 consecutive measurements (1σ , n = 60 corrected values). For noise corrections and instrumental drift, after each 4 dissolved samples, a second standard consisting of a homogenized solution of a Porites lutea coral powder

from the Caribbean Sea in 2% HNO₃ was analyzed. The average precision of this second standard within instrument runs was 0.100 mM/M (1σ , n = 60).

The annual growth rate of the coral was measured along the major growth axes from the positive prints of the X-radiographs. Each consecutive low and high density bands represent summer and winter growth increments respectively. The annual extension rate of the coral was also measured from the δ^{18} O isotope curves as the distance between two consecutive minimum δ^{18} O. The coral δ^{18} O value depends inversely on the SST, as the lowest δ^{18} O values of each annual cycle shows the highest temperature value and the highest δ^{18} O values fixed to the lowest temperature values. To provide a monthly resolution for comparison with the SST data, the coral δ^{18} O and Sr/Ca values were linearly interpolated to equally spaced values per year. The samples were interpolated using a rectangular method to construct an age model for the coral isotope and element chronologies and convert the distance units into monthly time-scale units (Davis, 1974). The difference between two consecutive points shows the extension of one month relative to the annual total. Comparing the $\delta^{18}O$ interpolation, the Sr/Ca interpolation result has a better match with the monthly COADS data and was used for the age modeling. In a previous study (Swart, Elderfield and Greaves, 2002), the Sr/Ca data were compared with the temperature record. A least squares fit gave a linear relationship between Sr/Ca and SST. In the present study, this equation was used to calculate SST values.

For calibration and having a more precise result, a New Wave Microdrill was used to take samples at 400 μ m increments over a period of two years of 2009 and 2010. The number of samples per year was increased from 22 to 55 according to the average annual growth rate of ~22 mm for this period of time. The sampling was performed using a computer–controlled micro drill at SIL of RSMAS. Dense, clear, and wide thecal walls observed in the X-radiographs, presented an ideal target for μ m-scale sample drilling. Samples were milled along a line of about 50 μ m from the theca wall with an increment of 400 μ m to a depth of 50 μ m. A total of 110 Samples were taken from a continuous 44 mm-section of the coral. Each drilling provided ~100 μ g of powder, which were processed for δ^{18} O, δ^{13} C, and Sr/Ca analyses.

RESULTS & DISCUSSION

As shown in Fig. 2, the X-radiograph of the coral slab exhibited obvious skeletal density banding comprised of alternating low- and high-density bands. The variations along the isotopic profiles compared with the X-radiograph of the coral slab indicated that the high-density bands were enriched in the ¹⁸O values

(deposited during winter) and the low density bands were depleted in ¹⁸O values (deposited during summer). In this case, the upper part of a low-density band was being created at August 2012 as the time of collection. The average annual extension rate was ~22 (1 σ) mm/ year over the entire 7-year time series estimated from skeletal geochemistry. The minimum extension rates were in 2007, 2008, and 2009. The maximum growth rates were observed in 2005, 2006, and 2010. In addition, the lowest and highest extension rate were ~19 mm/ year in 2008 and ~24 mm/year in 2005 respectively.

Numerous scientists investigated variations in the δ^{13} C of coral skeletons and they believed that these variations represent changes in the δ^{13} C of the local waters which are driven by changes in the δ^{13} C of the global oceans (Swart, Greer *et al.*, 2010), local respiration and photosynthesis (Moses and Swart, 2006), respiration and photosynthesis of the coral (Goreau, 1977; Swart, 1983), growth rate, and changes in pH at the site of calcification (McConnaughey, 1989; Grottoli, 2000). In the present work, the total range of δ^{13} C was from 0.92‰ to -1.07% with an average of -0.09 % (N=86). In addition, an irregular variation as well as the average annual fluctuations of about 1.4‰ was observed (Fig. 3).

In recent years, the validity of Sr/Ca as a tracer of SST in corals has received considerable attention. Hence, some scientists have already verified a robust Sr/Ca-SST relationship and Sr/Ca reproducibility from corals (Swart, Elderfield and Greaves, 2002; Maupin, 2008; DeLong, Flannery et al., 2011). In this work, the overall mean and the average annual amplitude Sr/Ca values for the entire 7-year time series were $9.062 \pm$ $0.12 (1\sigma) \text{ mM/M}$ and $0.45 (1\sigma) \text{ mM/M}$, respectively. Because this species has corallites that tend to meander, we utilized careful micro-sampling technique in which the coral slabs were examined under a microscope. The mean amplitude of Sr/Ca values over the two years sampled was 0.3584 mM/M at 1.00 mm per sample and 0.4300 mM/M at 0.40 mm per sample, values that agreed within 2σ of instrumental precision for Sr/Ca measurements.

As shown in Fig. 3, in this work the δ^{18} O fluctuated from -3.45% to -2.24% with an average of -3.02%. The difference between the minimum and maximum of δ^{18} O value was used to calculate the seasonal amplitudes from the seasonal cycles of δ^{18} O. Strong seasonal variations which were on average of $\sim 0.78\%$ were shown in this coralline sample. A calendar year was assigned to a single pair of high- and low-density bands in the first step. Minimum and maximum δ^{18} O values in a given year were subsequently assigned to maximum and minimum SSTs derived from the Sr/Ca values for that year, respectively.

A pair of low- and high-density bands in the coral slab are generally known to form during a specific time of the year and correspond well with a single cycle in the elemental profile and skeletal isotopic of the coral (Flannery and Poore, 2013). However, this method assumes a linear growth between the growth bands and generally suffers from the problem that density bands do not always form during the same time period within each year. In addition, because of the problems relating the three-dimensional nature of the coral to a two-dimensional stain line, it is difficult to exactly correlate the instrumental SST with material drilled from the skeleton (Swart, Elderfield and Greaves, 2002). In the present study, a single pair of density bands in the Platygyra coral represented well the annual growth increments and showed that the high- and low-density bands formed in winter and summer, respectively. Nevertheless, some high-density micro-bands were observed inside a single annual band pair.

The skeletal δ^{13} C is controlled by numerous factors including the respiration, the photosynthetic activity of zooxanthellae, upwelling of water masses, feeding habits of corals, etc. In 1978, Erez (Erez, 1978) reported that increased photosynthetic activity results in isotopically depleted δ^{13} C in coral bands. Supportive evidence for this hypothesis was also suggested by Swart et al. (Swart, Leder, Szmant and Dodge, 1996). They demonstrated that an increase in photosynthesis causes a decrease in skeletal δ^{13} C. However, we believe that other local environmental factors might also be important in the Strait of Hormuz. As shown in Fig. 3, no significant seasonal trend in δ^{13} C was observed in this study. As mentioned before, because $\delta^{13}C$ variations are controlled by various environmental factors, their origins in coral skeletons are frequently very difficult to interpret (McConnaughey, 1989; Grottoli, 2000).



Fig. 3. Time series of monthly interpolated geochemical variations from 2005 to 2012

Although the most practical SST measurements are hourly in situ SST measurements next to the coral colony, these records are sparse and generally short in length. In theory, Sr/Ca is considered as a better SST tracer than δ^{18} O, because variability in seawater Sr/Ca is less than that of δ^{18} O. However, subtle changes in the seawater Sr/Ca through space and time can disturb the accuracy of reconstructed SST (Corrège, 2006). As shown in Fig. 3, the maxima in the Sr/Ca ratio were assigned to the coldest SST and the minima to the highest SST in order to constrain the chronology of the coral. The effect of increasing sampling resolution from 22 samples/year to 55 samples/year on the amplitude of the Sr/Ca signal recovered over two annual cycles of 2009 and 2010 was negligible and the anomalies noted in the Sr/Ca ratios were replicated (Fig. 4). In order to establish a geochemical thermometer for paleoclimate reconstructions, Sr/Ca variations in corals can be calibrated to local SST data. Unfortunately, local or in situ temperature measurements next to the coral colony were not available for this work. Instead, a relationship between the Sr/Ca ratio in the skeleton of the Montastraea annularis and SST in a previous work developed by Swart and coworkers (Swart, Elderfield and Greaves, 2002)was established:

 $Sr/Ca = 9.994(\pm 0.042) - 0.0377(\pm 0.0029)$

$$[SST(n = 95; r^2 = 0.62)]$$
(2)

For the equation (2), the slope was within the span of some previously published slopes. We used this

equation to reconstruct SST values because there was no calibration study for Platygyra sinensis. As a result, Sr/Ca-derived temperatures showed strong seasonal signal ranging from 17 to 30 °C. As shown in Fig. 5, when comparing Sr/Ca-SST signals from the coral time series with the Comprehensive Ocean-Atmosphere Data Set (COADS) SST signals in the study site, we found that both contained pronounced annual cycles and had significant correlation with each other (P<0.001, N=86). Therefore, we could conclude that the coral Sr/Ca variations are driven via SST variations. However, the COADS SST had a higher mean value (27.02) than that derived from the SST values reconstructed from the Platygyra sinensis coral sample (24.72) which could be due to differences in the calibration equation between Platygyra sinensis and Montastraea annularis.

Although variability in seawater δ^{18} O is much larger than that of Sr/Ca, δ^{18} O has been extensively used as a SST tracer. In coral skeletons, the δ^{18} O variations are controlled by the seawater δ^{18} O values and the temperature-induced fractionation. Apart from temperature and seawater δ^{18} O, the other factors such as growth rates, light levels, variation in pH, and feeding habits potentially affect δ^{18} O in coral skeleton (Corrège, 2006). The relation between δ^{18} O in coral and Sr/Ca-estimated SST data for 7 annual cycles was calibrated in this study. The regression equation for temperature dependence of δ^{18} O for *Platygyra sinensis* coral δ^{18} O was:

$$\delta^{18}O = -0.0565SST - 1.6242 (r = 0.6715)$$
(3)



Fig. 4. Effect of increasing sampling resolution from 1.0 mm/sample to 0.4 mm/sample on the amplitude of the coral δ¹³C, δ¹⁸O, and Sr/Ca signals over annual cycles of 2009 and 2010.



Fig. 5. Time series of the COADS database and the SST records extracted from the Sr/Ca values of coral.



Fig. 6. Monthly SSS (ppt) values based on the previously reported equations (Rosenheim, Swart, Thorrold, Eisenhauer and Willenz, 2005) calculated for the study area in the Persian Gulf over the period of 2005–2012

Based on the equation (3), the monthly δ^{18} O values were negatively correlated with Sr/Ca-estimated SST data. As shown in Fig. 4, the effect of increasing sampling resolution from 22 samples/year to approximately 55 samples/year on the amplitude of the δ^{18} O signal recovered over two annual cycles of 2009 and 2010 was negligible. Because δ^{18} O values vary with respect to SST and SSS in various places, seasonal variations in the δ^{18} O of the *Platygyra* coral and the annual density bands were also used to construct coral chronologies. Nevertheless, the relationship of SST and SSS with skeletal δ^{18} O depends on various parameters such as the location, species, rainfall, and water-depth of coral (Lough and Barnes, 1990). Calcification and extension rates are not constant throughout a year due to seasonal variations in skeletal thickening and in skeletal extension (Lough and Barnes, 1992; Taylor, Barnes et al., 1995).

In climate studies, the sea surface salinity (SSS) is an important physical factor. The SSS together with SST are the driving force of the thermohaline circulation. A trace of SSS has the potential to provide information of atmospheric components of climate, because changes in SSS can often be related to changes in precipitation/evaporation. The coral δ^{18} O is dependent on the SST and $\delta^{18}O_{water}$. Thus, it is possible to estimate past changes in SSS from δ^{18} O in coral only if the relationship between the $\delta^{18}O_{water}$ and SSS is known in the study area. In fact, by subtracting the Sr/Ca-based SST component from the δ^{18} O of the coral, the $\delta^{18}O_{water}$ can be calculated. This relationship is expressed by the modified equation (4) formulated by Leder et al. (Leder, Swart, Szmant and Dodge, 1996):

$$\delta^{18}O_{water} = \delta^{18}O_{coral} - \frac{5.18 - SST(^{\circ}C)}{4.523}$$
(4)



Fig. 7. Linear relationship between δ¹⁸O (‰VPDB) and Sr/Ca (top) and COADS SST (°C) and Sr/Ca (down) of the coral PSAUG2012

Using the equation (5) developed by Rosenheim et al. (Rosenheim, Swart *et al.*, 2005), we can estimate the SSS values:

SSS (ppt) =
$$\frac{\delta^{18} O_{water} + 19}{0.54}$$
 (5)

Based on the equation (5), the SSS values ranged from \sim 35.00 to \sim 39.73 ppt with an average of 37.60 ppt (Fig. 6).

We utilized an increased sampling resolution over two annual cycles to understand whether our sampling was capturing the entire range of environmental signal in the corals skeleton. The good agreement between low and high sampling resolutions demonstrated that our sampling was representative and reliable. Figure 7 shows significant correlation between Sr/Ca values and COADS data (R=0.8469), which proved that the Sr/Caderived temperatures were acceptable.

Corals are powerful archives of past oceanic conditions and their skeleton contains an array of tracers. In this work, the results are provided pertaining to the reconstruction of the SST and SSS as two main oceanic parameters. However, it is important to note that because of the relatively short length of the obtained time series, the relevance of our findings for reconstructing climatic processes in the Persian Gulf region is limited. Therefore, longer coral time series and in situ SST and SSS measurements from the Persian Gulf are needed in the future. The periodic burial of corals in sediment around the Larak Island could effect on the δ^{18} O, δ^{13} C, and Sr/Ca records and reduce the extension rate for the given time intervals. Finally, other tracers in corals such as barium, cadmium, manganese, boron, and osmium have been already used to infer past SST and SSS changes. However, little is known about the incorporation of these elements in the coral skeleton, and how they are bound to the aragonitic structure.

CONCLUSION

Ability of a climate proxy record within the Persian Gulf to reproduce variability within the region is an important issue when assessing the relevance of such records to the understanding of climate change. In this study, the oxygen isotopes variations and Sr/Ca ratios obtained from a massive *Platygyra sinensis* coral located offshore Larak Island agreed relatively well with COADS SST data from 2005 to 2012. Using the previously reported equations, Sr/Ca-derived SST ranged 17–30 °C, with an average of 24.7 °C. In addition, the SSS values ranged from 35.00 to 39.73 ppt with an average of 37.60 ppt. Our results showed that the *Platygyra sinensis* could be used to develop proxies of SST and SSS variability in the eastern part of the Persian Gulf.

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