Reef coral $\delta^{18}O$ thermometer in Hainan island waters, South China Sea

HE Xue-Xian, PENG Zi-Cheng, WANG Zhao-Rong
(Department of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026)

HUO Wei-Guo, TAN Jun
(The Research Center of Mineral Resources Exploration, the Chinese Academy of Sciences, Bejing 100101)

NIE Bao-Fu, CHEN Te-Gu, ZHONG Jin-Liang
(South China Sea Institute of Oceanography, the Chinese Academy of Science, Guangzhou 510310)

Abstract An 18-year-long (1981-1998) study was conducted in Hainan Island waters (22°20'N, 110°39'E) to determine the relationship between $\delta^{18}O$ in skeletal aragonite carbonate and sea surface temperature (SST) in *porites lutea* of reef-building corals. $\delta^{18}O$ values in skeletal aragonite carbonate were measured by means of mass spectrometry. Coral samples grew at 5 m depth at Longwan Bay. Monthly measurements of the SST from 1960 to 1998 were taken at Qinglan Bay adjacent to the place of the collected samples. The thermometer shows that SST=–4.16 $\delta^{18}O_{PDB}$ + 4.9 (r=0.80) and $d\delta^{18}O/dT$=–0.24 permil/°C. The $\delta^{18}O$ thermometer is strongly influenced by the rainfall and runoff. Using the thermometer, the SST in the past hundred years with monthly resolution will be reconstructed and the climatic change in the northern area of South China Sea will be hindcasted

Keywords Reef-building coral, Oxygen isotope, Thermometer, Mass spectrometry

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1 INTRODUCTION

Forecasting the global change trend in the future is a hot point in environmental study. Devising prediction models need a lot of data on past environmental conditions. The best way to reconstruct environmental records is to analyze proxy materials preserving environmental information in nature (e.g., ice core, loess and tree ring, etc.). The coral is useful for the proxy materials. The coral skeleton is made from aragonite ($CaCO_3$). The elements and their isotopes fixed in the skeleton would no more exchange with those in the sea water. The system is closed. A lot of published articles expressed that oxygen isotope composition in coral skeleton was controlled by oxygen isotopic fractionation coefficient between the sea water and coral skeleton, and also the oxygen isotope composition in sea water.[1~4] The oxygen isotopic fractionation coefficient was

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mainly dominated by temperature in surrounding sea water. So when the oxygen isotopic composition in the sea water was relatively stable, the oxygen isotope composition in coral skeleton could trace sea surface temperature (SST).It is possible to set up the $\delta^{18}O$ thermometer when oxygen isotopic composition in the coral is determined by mass spectrometry.

Reef-building corals are particularly well suitable for high-precision and high-resolution reconstruction of sea surface temperature in tropic ocean because coral skeletal aragonite is deposited at rapid but variable rates (e.g. several millimeters to several centimeters per year) and so its precise age can be determined.[1~5] Up to now, there are about 70 coral $\delta^{18}O$ thermometers constructed to study global climatic change (e.g. ENSO, ocean current, typhoon, etc.).[1~3]

We measured oxygen isotopic compositions in the reef-building coral *porites lutea* collected in Hainan Island, in the northern area of South China Sea, studied the relationship between the SST and $\delta^{18}O$ in coral skeleton and created the $\delta^{18}O$ thermometer for the further study on hindcasting the monthly SST for the past 100 years, and on monsoon and typhoon.

2 METHODS

A ~2.5 m long and 4.5 cm diameter core was drilled nearly down the vertical axis of maximum growth of the *Porites lutea* coral in August 1998, near Longwan bay, Qionghai city, Hainan province. The sample coral collected grew at about 5 m water depth, about 25 kilometers away from the Wanquan River. The sample was slabbed to a thickness of 5 mm. X-ray photographs of the coral slabs were taken with a medical X-radiograph set. The X-ray photographs revealed annual density bands[5]. We can get precise age by counting the number of density bands.

We sampled the coral slab using a steel saw rasp by hand, at a resolution of 0.5 mm/sample relative to half a month growth increment. We choose one sample for every mm skeletal length to perform the oxygen isotope experiment, because we have only monthly SST measurement records.

Oxygen isotopic analyses were performed in The Research Center of Mineral Resources Exploration of the Chinese Academy of Sciences. The testing method is the normal phosphoric acid method. Prior to isotopic analysis, powdered coral aragonite samples were roasted in vacuum for 2.5 hours at 350°C to eliminate organization. The samples were reacted with anhydrous phosphoric acid at 50°C. The CO_2 produced was put into a MAT 252 Mass Spectrometer. Standard reference CO_2 gas was produced by Chinese national standard calcite sample GBW 04405 ($\delta^{18}O_{PDB}$=−8.49 ‰) in the same reaction system and the same reaction condition, which could eliminated the systematic error. Precision ($\pm\sigma$) was monitored by daily analyses of a powdered GBW 04405 and a mixed coral sample made of half a year growth increment. Values are reported in standard δ notation relative to the Chicago Pee Dee belemnite (PDB) standard.

$$\delta^{18}O=(R_{sample}/R_{standard} - 1)\times 1000$$

where R_{sample} and $R_{standard}$ are the ratios of $^{12}C^{16}O^{18}O$ to $^{12}C^{16}O_2$ for the sample and standard reference gas, respectively.

We determined $\delta^{18}O_{PDB}$ of GBW 04405 samples, which was –8.57 ‰, with only 0.08 ‰ difference from its quoted value. That means our experiment is credible.

3 RESULTS AND DISCUSSION

The oscillation of $\delta^{18}O_{PDB}$ values measured in the coral skeleton seemed to be a sine curve (See Fig.1). This kind sine oscillation means that the changes of $\delta^{18}O_{PDB}$ values in coral core are characteristic of periodicity with the coral growth. Oxygen isotopic values were converted from the length domain to the time domain in two steps. First, a calendar year was assigned to each density-band couplet according to the coral X-ray photography, and hence to every twelve samples assuming linear sub-annual skeletal extension. Secondly, systematic variations in oxygen isotopic composition were correlated with monthly SST values using visual curve matching between the minimum peaks of SST and the maximum values of oxygen isotopic composition and vice versa. The length of coral growth each year can be modulated. The SST records measured by instruments are from Qinglan Ocean Station near the collecting location. In studying sea area, the rainfall and runoff occur more often in summer than in winter and so, the oxygen composition in coral was contributed from rain more greatly in summer than in winter, because $\delta^{18}O_{SMOW}$ in rain is –5 ‰ ~ -6 ‰, equal to $\delta^{18}O_{PDB}$ –34.8 ‰ ~ –35.8 ‰, [6] more negative than that in mean sea water. Since the probability of minimum peaks of the SST in January is 70%, it is easier to make curve matching using the minimum peaks of SST corresponding to maximum $\delta^{18}O$ values than using maximum peaks of SST corresponding to minimum $\delta^{18}O$ values. Fig.1 shows the curve matching, in which part of $\delta^{18}O$ values lack in the experiment were compensated by using linear increment. The number of compensated values were less than 3 per year. The compensated data were not peak values.

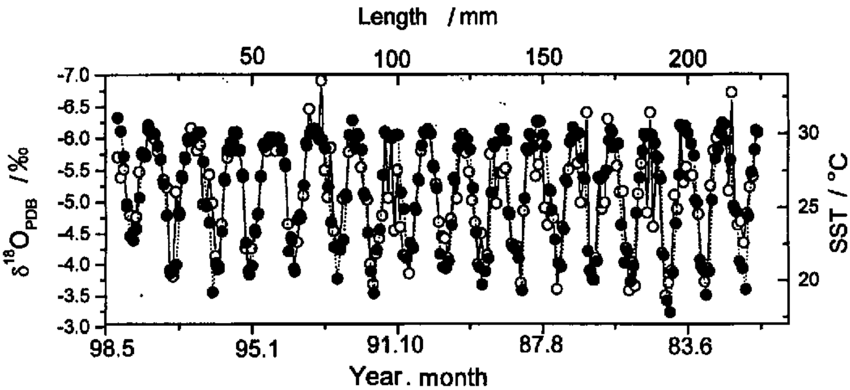

Fig.1 Relationship between the SST and coral skeleton $\delta^{18}O$

—o— $\delta^{18}O$, ···•··· SST

Refer to corresponding relationship between $\delta^{18}O_{PDB}$ in the coral skeletal and SST (see Fig.2a), linear correlation was performed, and obtained the following equation.

$$SST = -3.87\,\delta^{18}O_{PDB} + 6.4,$$

$$r = 0.70, \quad (1)$$

$$d\delta^{18}O/dT = -0.26\ ‰\ /°C$$

The slope of equation (1) (−3.87°C per 1 ‰) is consistent with what observed in coral studies, values ranging from −3.5 to −6.0 are more typical[7~9]. Empirical and laboratory experiments refine the slop term to be ∼ −4.5, a value that produces the widely recognized $\delta^{18}O$-temperature calibration of −0.22 ‰ /°C[5]. The correlation coefficient of equation (1), r=0.7, is not high. That means that oxygen isotopic composition in coral skeleton was effected by other factors and equation (1) must be corrected to some extent. In the studied sea area, the oxygen isotopic composition in sea water varies greatly in Autumn, because rainfall in September maximizes in most of years and runoff in Wanquan river affects hysteretically. We picked out the $\delta^{18}O$ values in September, October and November every year (see Fig.2b), performed a linear correlation again, and got the following equation.

$$SST = -4.16\,\delta^{18}O_{PDB} + 4.9,$$

$$r = 0.80, \quad (2)$$

$$d\delta^{18}O/dT = -0.24\ ‰\ /°C$$

The slope of equation (2) (−4.16°C per 1 ‰) is close to the universal value (−0.22 ‰ /°C). If we use only the peak $\delta^{18}O$ values and peak SST, we got the following relation.

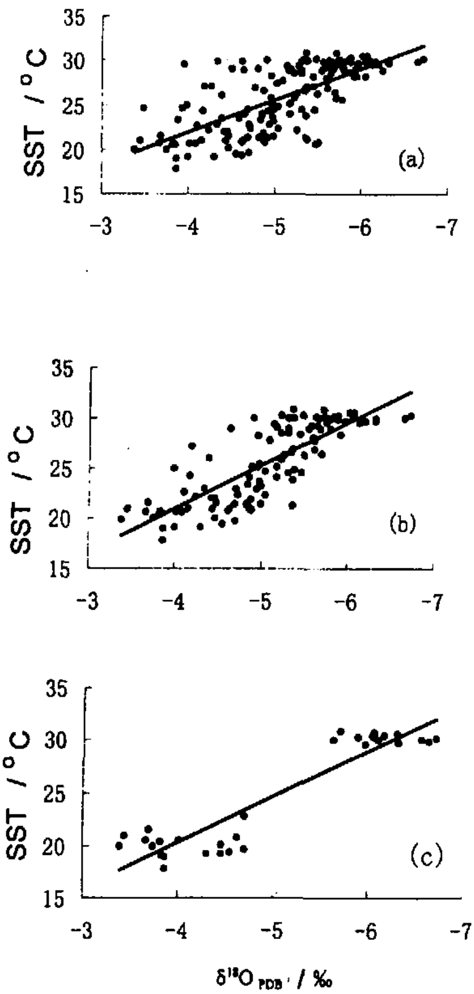

Fig.2 Correlation of the oxygen isotope and the monthly SST variations at Longwan with each of the records sampled monthly.
(a) is the relation between all the coral skeleton $\delta^{18}O$ and all the monthly SST;
(b) is the relation between the coral skeleton $\delta^{18}O$ and monthly SST except the data in September, October and November;
(c) is the relation between the peak coral skeleton $\delta^{18}O$ and the peak monthly SST each year

$$SST = -4.2\,\delta^{18}\mathrm{O}_{\mathrm{PDB}} + 4.2, \qquad r = 0.95, \tag{3}$$

$$\mathrm{d}\delta^{18}\mathrm{O}/\mathrm{d}T = -0.24‰/°\mathrm{C}$$

The slope of equation (3) (–4.2°C per 1 ‰) is the same as the slope of equation (2) and $\mathrm{d}\delta^{18}\mathrm{O}/\mathrm{d}T$= –0.24 ‰ /°C is close to the universal value (–0.22 ‰ /°C) too. Due to the fact that equation (3) reflects the relation of the peak data, the slope of equation (3) is representative. It means $\mathrm{d}\delta^{18}\mathrm{O}/\mathrm{d}T$= –0.24 ‰ /°C is suitable for this kind of coral in 1981~1998.

The differences between the peak temperature that we calculate using equation (2) and the peak SST measured per year are less than 0.5°C, which is consistent with most of published results.[3~5] So we recognize equation (2) that is suitable for the high precise and high resolution δ^{18}O thermometer.

4 CONCLUSIONS

The article set up the δ^{18}O thermometer of 1981~1998 in the reef-building coral *porites lutea* collected in Hainan Island, in the northern area of South Chinese Sea. The absolute differences between the peak temperature that we calculated using the δ^{18}O thermometer and the peak SST measured by the equipment per year are less than 0.5°C. It means that the δ^{18}O thermometer is reliable for reflecting the change of ancient sea surface temperature. Using the δ^{18}O thermometer, we can reconstruct the past monthly SST records for studying sea area later. It is of special significance for the area where there is lack of instrumental SST records and great interference from rainfall or runoff (e.g. monsoon affected area, typhoon affected area).

The present results show that the normal phosphoric acid method may be used in analyzing only several milligram carbonate samples. The slope of the thermometer is the same as the slope of the equation calculated using only peak δ^{18}O values and peak SST per year, and their formula are similar. It means the number of samples to be analyzed may be decreased later if only the peak δ^{18}O values per year are obtained.

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