Coral Sr thermometer simplified from Sr/Ca thermometer *

SUN Min(孙 敏)[1], LEE Typhoon(李太枫)[2], CHIU Chin-Hsin(邱景星)[2], SHEN Chuan-Chou(沈川洲)[2], SUN Yali(孙亚莉)[1,3] and NIE Baofu(聂宝符)[4]

(1. Department of Earth Sciences, The University of Hong Kong, Hong Kong, China; 2. Institute of Earth Sciences, Academia Sinica, Taipei, China; 3. Institute of Rock and Mineral Analysis, Beijing 100037, China; 4. South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510310, China)

Received March 9, 2000; revised April 10, 2000

Abstract Cubic sub-samples obtained from a Porites coral slice collected from Xisha Islands, South China Sea, were weighed with precise micro-balance. The Sr and Ca concentrations were analyzed with isotope dilution thermal ionization mass spectrometry. Our results demonstrate that Ca concentrations in all samples are very uniform (mean = 9.52mmol/g, 2σ = 0.02mmol/g); Sr concentrations and Sr/Ca ratios are well correlated (correlation coefficient r = 0.9968). It implies that the Sr thermometer can replace Sr/Ca thermometer and the determination of Ca can be omitted. This can save up to 50% time and cost, and more importantly, paleoclimate study using coral proxy can now be carried out in routine Sr isotope laboratories.

Keywords: coral, Sr content, Ca content, thermometer.

The reconstruction of paleoclimate is important in understanding the causes of past climate fluctuations. The relationship between temperature and natural isotopic fractionation was identified by Urey[1] about fifty years ago. Then oxygen isotope compositions of biogenic marine carbonates played an important role in the reconstruction of sea surface temperature (SST). The Deep Sea Drilling Program (DSDP) of 1968 and the following Ocean Drilling Program (ODP) have provided considerable systematic and continuous oxygen isotope data from foraminifera, which greatly enhanced our understanding of the temperature change in the Mesozoic and Cenozoic[2].

However, there are some limitations on using oxygen isotopic compositions to reconstruct climatic changes. Firstly, the recovered temperatures from oxygen isotope compositions of the foraminifera samples (fossils) do not have high temporal resolution. Secondly, the foraminifera oxygen isotope compositions are affected by the seawater $^{18}O/^{16}O$ ratio and we do not know the history of the $^{18}O/^{16}O$ fluctuations in seawater.

It is crucial to search other natural archives which can be more directly used to reconstruct environmental parameters. Porites corals have continuous growth history of more than one century so their contents of trace elements can indicate their living environments. Smith et al.[3] firstly found a quantitative relationship between coral skeletal Sr/Ca ratios and SST. Atomic absorption spectroscopy (AAS) was used but this technique cannot offer accurate Sr/Ca ratios because the precision (2%—3%) is similar to the seasonal Sr/Ca variation (2%—4%) in corals. More precise determinations of

* Project supported by the Research Grants Council of Hong Kong (Grant No. NKU510/96P).

Sr and Ca were developed by Beck et al.[4] in 1992 with triple isotope dilution-thermal ionization mass spectrometry (IDTIMS), the precision of Sr/Ca ratios is 0.03%. The uncertainty of Sr/Ca-SST calibration with monthly or even weekly resolution is better than 0.5℃. This technique has attracted many researchers[5—9] to explore its applications to the reconstruction of SST for tropical oceans. However, the traditional sampling method is to drill off a very small amount of powder for each sub-sample to approach higher resolution (more than 10 or even 50 samples per year), the quantity of powder is too little (12.5—25 μg) to weigh accurately. Therefore, the previous studies only provide accurate Sr/Ca ratios, but not Sr or Ca contents, since the weights can be cancelled in Sr/Ca ratio calculation. This technique is costly and time-consuming. Because of the high mass fractionation of Ca isotopes during TIMS measurement, only several laboratories in the world can analyze Ca using IDTIMS. This has greatly hindered the development in the study of this interesting area.

In this work, we used a micro-surgical machine to cut coral slice. Cubic sub-samples were obtained and precisely weighed. Sr and Ca concentrations were determined by IDTIMS, which allows us to investigate Ca variation in the coral skeleton.

1 Sample preparation and results

The Porites coral was collected from Xisha Islands, South China Sea. Sub-sampling, weighing and TIMS analyzing were carried out in the Institute of Earth Sciences, Academia Sinica, Taipei. The coral slices were cut using a micro-surgical machine, China-2, to get cubic sub-samples. The sub-samples were weighed accurately with a Cahn C-31 micro-balance and dissolved in 1mol/L HCl. A small aliquot was mixed with ^{42}Ca-^{44}Ca-^{84}Sr triple spike. The mixture was dried on a hot plate. Concentrations of Sr and Ca were determined by VG 354 mass spectrometry. The results of 49 samples are presented in table 1. The mean of all Ca data is 9.52/mmolg^{-1} with 0.21% relative standard devi-

Table 1 Sr and Ca concentrations and Sr/Ca ratios from 49 coral sub-samples

Sample	Sr/μmolg^{-1}	Ca/mmolg^{-1}	Sr/Ca/mmolmol^{-1}	Sample	Sr/μmolg^{-1}	Ca/mmolg^{-1}	Sr/Ca/mmolmol^{-1}
1	86.4	9.53	9.07	26	83.1	9.53	8.71
2	85.9	9.51	9.03	27	85.8	9.51	9.02
3	83.1	9.52	8.73	28	83.1	9.53	8.71
4	86.1	9.5	9.06	29	85.9	9.52	9.02
5	83.1	9.53	8.72	30	85.9	9.52	9.02
6	84.0	9.52	8.82	31	85.6	9.52	8.99
7	85.9	9.52	9.03	32	83.8	9.53	8.78
8	84.8	9.51	8.92	33	86.0	9.53	9.03
9	85.7	9.50	9.02	34	85.4	9.52	8.97
10	83.3	9.52	8.75	35	83.6	9.53	8.77
11	85.4	9.50	8.98	36	83.5	9.53	8.76
12	83.4	9.52	8.76	37	83.5	9.53	8.76
13	86.2	9.52	9.06	38	84.4	9.53	8.86
14	83.4	9.53	8.75	39	85.2	9.51	8.96
15	84.9	9.52	8.92	40	85.8	9.50	9.03
16	85.6	9.50	9.01	41	84.9	9.51	8.93
17	85.5	9.50	9.00	42	84.9	9.51	8.93
18	83.2	9.52	8.74	43	84.3	9.51	8.87
19	83.2	9.53	8.72	44	83.9	9.52	8.82
20	84.9	9.52	8.92	45	83.3	9.52	8.75
21	85.7	9.51	9.01	46	83.6	9.53	8.77
22	82.7	9.52	8.69	47	86.0	9.52	9.04
23	84.4	9.52	8.89	48	86.0	9.50	9.05
24	83.0	9.51	8.73	49	83.7	9.51	8.80
25	85.9	9.52	9.01				

ation (2σ).

2 Discussion

Sr/Ca ratios and Sr concentrations show a linear relationship (fig. 1). The regression of these data gives an equation, Sr/Ca = 0.1095Sr − 0.3731, with high correlation coefficient, r = 0.9968.

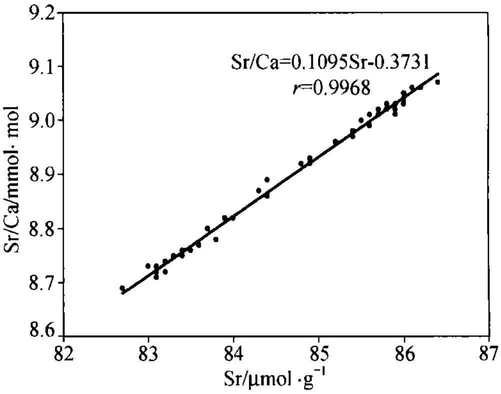

Fig. 1. Relationship between Sr concentration and Sr/Ca ratio of 49 sub-samples from a *Porites* coral from Xisha Island, South China Sea.

Our results show that Ca variation is 0.21%, about the level of 0.16% uncertainty[10] of the Ca determination by IDTIMS. Using the Sr/Ca-SST calibration of Beck et al.[4], the 0.21% variation of Ca corresponds to ±0.4℃, less than ±0.5℃ uncertainty of the Sr/Ca thermometer. Our 49 sub-samples cover a period of 18 years (1976—1994), and 14 sub-samples cover a continuous year, the rest sub-samples are those with maximum and minimum Sr concentrations (two samples per year). During this period, four El Nino events (90—94, 86—87, 82—83 and 76—77) occurred, but the Ca content is still uniform in the coral skeleton. Our results suggest that the Sr concentration can replace Sr/Ca ratio in Sr/Ca thermometer. Without Ca determination, much time and cost can be saved; Sr thermometer can become a routine work in many laboratories.

References

1 Urey, H. C., The thermodynamic properties of isotopic substance, *J. Chem. Soc.*, 1947, 11: 562.

2 Miller, K. G., Fairbanks, R. G., Mountain, G. S., Tertiary oxygen isotope synthesis, sealevel history, and continental margin erosion, *Paleoceanography*, 1987, 2(1): 1.

3 Smith, S. V., Buddemeier, R. W., Redalje, R. C. et al., Strontium-calcium thermometer in coral skeletons, *Science*, 1979, 204: 404.

4 Beck, J. W., Edwards, R. L., Ito, E. et al., Sea surface temperature from coral skeletal strontium/calcium ratios, *Science*, 1992, 257: 644.

5 Guilderson, T. P., Fairbanks, R. G., Rubenstone, J. L., Tropical temperature variation since 20000 years ago: Modulating inter-hemispheric climate change, *Science*, 1994, 263: 663.

6 de Villiers, S., Shen, G. T., Nelson, B. K., The Sr/Ca temperature relationship in coralline aragonite: influence of variability in (Sr/Ca) seawater and skeletal growth parameters, *Geochim. Cosmochim. Acta*, 1994, 58: 197.

7 McCulloch, M. T., Gagan, M. T., Mortimer, G. E. et al., A high-resolution Sr/Ca and $\delta^{18}O$ coral record from the Great Barrier Reef, Australia, and the 1982—1983 El Nino, *Geochim. Cosmochim. Acta*, 1994a, 58: 2747.

8 McCulloch, M. T., Mortimer, G. E., Esat, T. et al., High resolution windows into early Holocene climate: Sr/Ca coral records from the Huon Peninsula, *Earth Planet. Sci. Lett.*, 1996, 138: 168.

9 Robert, B. D., Julia, E. C., Annual records of tropical systems (ARTS), *PAGES Workshop Report*, Series 99-1, 1999, 22—27.

10 Min, G. R., Edwards, R. L., Taylor, F. W. et al., Annual cycles of U/Ca in coral skeletons and U/Ca thermometer, *Geochim. Cosmochim. Acta*, 1995, 59: 2025.