

LETTER

Sr thermometer for *Porites* corals: Little need to measure Ca?

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Cubic sub-samples of 1 mm³ (about 0.5 mg) were obtained from a *Porites* coral slice collected from Xisha Island, South China Sea, and analysed for Sr and Ca concentrations by ID-TIMS after precise weighing. Ca contents in the coral are quite uniform (mean = 38.16 wt%, $2\sigma = 0.11$ wt%). The variation corresponds to $\pm 0.4^\circ\text{C}$, about the level of uncertainty of the Sr/Ca-SST calibration. Sr concentrations and Sr/Ca ratios covary linearly, and the line can be defined by the equation $\text{Sr}/\text{Ca} \times 10^3 = 0.111\text{Sr} - 0.5061$ (correlation coefficient $r = 0.9955$), where Sr is in $\mu\text{mol}/\text{gm}$. Consequently, our results demonstrate that the previously established coral Sr/Ca thermometer, $\text{Sr}/\text{Ca} \times 10^3 = A + B \times T$, can be simplified as a Sr thermometer, $0.111\text{Sr} - 0.5061 = A + B \times T$, where Sr is in $\mu\text{mol}/\text{gm}$. Therefore, measurement of Ca in corals could be unnecessary. If different levels of impurity exist in different corals, a few Ca measurements in each coral may be needed, but definitely there is no need to measure every sub-sample.

INTRODUCTION

Trace elements in corals, the natural archives, have been widely used in reconstructing variations of environmental parameters and anthropogenic contaminations around coastal and pelagic zones in past tropical oceans (e.g., Shen and Boyle, 1987; Beck *et al.*, 1992, 1997; Guilderson *et al.*, 1994; Gagan *et al.*, 1998). About two decades ago, Sr/Ca ratios in coral aragonite skeletons were proven to be directly related to Sea Surface Temperature (SST). Smith *et al.* (1979) suggested that Sr/Ca ratios in coral skeletons can be used as a proxy for SST. However, because of small seasonal variations (about 2–4%) in coral Sr/Ca ratios, precision of data was not satisfactory until recent years. A high precision Sr/Ca coral thermometer was first established by Beck *et al.* (1992), and further calibrated by de Villiers *et al.* (1994), Shen *et al.* (1996a), Alibert and McCulloch (1997), and

Gagan *et al.* (1998). These recent studies employed isotope dilution-thermal ionization mass spectrometer (ID-TIMS) technique. This technique provides high quality data, so SST in the past can be reconstructed with an accuracy better than 0.5°C . In addition, ID-TIMS requires only very small quantities of sub-samples for the measurements. Consequently, reconstruction of SST with high resolution (monthly or even weekly) is now possible. However, a vital obstacle exists for reconstruction of long time period SST with such high resolution (monthly or weekly), by using this method. Since too many sub-samples need to be analyzed for Sr and Ca, it will be time consuming and very costly.

Calcium is a major constituent element in coral skeletons. Obviously if its variation in a coral sample is negligible at the level of ID-TIMS Sr analytical error, or Ca concentrations can be determined by a fast method, we can greatly speed up

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studies in this important field. Unfortunately, Ca variations in corals have not yet been investigated, because previous ID-TIMS studies only provide precise Sr/Ca ratios, but often not accurate Sr or Ca concentrations. The reason is that the Sr/Ca thermometer does not require precise weighing each of the sub-sample, since weights will be cancelled in the calculation of Sr/Ca ratios. Moreover, in order to achieve monthly or even weekly resolution, the quantity of each coral sub-sample is extremely small, which makes precise weighing difficult. So precise weighing is not common in coral Sr/Ca studies.

In this study, with the help of a special sub-sampling technique and using a high precision micro-balance, we obtained accurate data for both Sr/Ca ratios and concentrations of Sr and Ca in a *Porites* coral collected from Xisha Island, South China Sea. The results enable us to examine Ca variation in the coral sample, and we found that the Sr/Ca thermometer can be simplified to a Sr thermometer.

METHODOLOGY

A specially-designed micro-surgical machine, CHINA-2 (Shen *et al.*, 1996b), was used in this study. The sample slice was placed on a micrometer-controlled 3-D stage, a high speed fine circular diamond saw fixed over the stage can cut the sample in any direction. Cubic sub-samples of 1

mm³ (about 0.5 mg) were obtained along the maximum growth direction of the *Porites* coral slice from Xisha Island. This sampling technique allows us to clean each sub-sample after cutting, and makes precise weighing easier. A CAHN C-31 micro-balance was utilized for sample weighing (precision 0.1 μ g).

Sub-samples were dissolved in 1 N HCl, and then small aliquots were mixed with ⁴²Ca-⁴⁴Ca-⁸⁴Sr triple spike. Concentrations of Sr and Ca were measured on a VG-354 mass spectrometer at the Institute of Earth Sciences, Academia Sinica, following the method described by Shen (1996) and Shen *et al.* (1996a).

RESULTS AND DISCUSSION

High precision monthly coral Ca variation

Two hundred and one *Porites* coral sub-samples from Xisha were measured for Sr concentrations. They cover a time-interval of 18 years (1977–1994). After obtaining Sr data, 61 remaining aliquots of these sub-samples were carefully chosen for Ca determination so that at least those with maximum and minimum Sr concentrations for each year would also have Ca data. Fourteen continuous sub-samples show trivial seasonal Ca variations (<0.22%) in the coral skeleton (Fig. 1). Our overall results also indicate that Ca contents in the coral are quite uniform (mean = 38.16 wt%, $2\sigma = 0.11$ wt%). The variation corresponds to

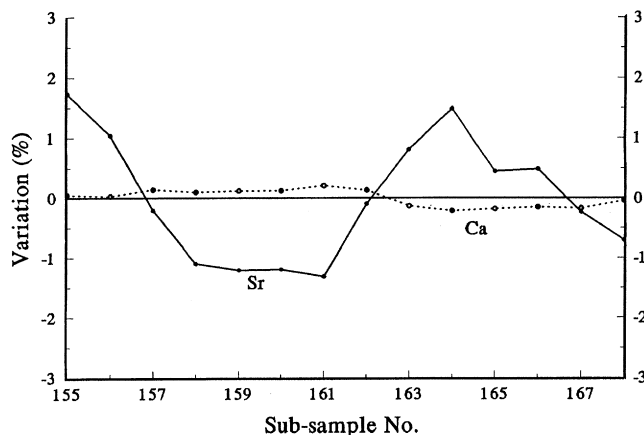


Fig. 1. Variation of Sr and Ca contents in 14 continuous sub-samples from Xisha *Porites* coral.

$\pm 0.4^\circ\text{C}$, about the level of uncertainty of the Sr/Ca-SST calibration (e.g., Shen *et al.*, 1996a). Therefore, measurement of Ca in corals may not be necessary.

In order to investigate the consistency of variations of Ca in coral samples from different localities, the same laboratory also measured a modern *Porites* coral sampled from Lutao offshore, southeastern Taiwan and a *Porites* fossil coral from Shi-Zu Profile in Kenting, southern Taiwan. The modern coral from Lutao possesses Ca contents identical to that from Xisha (38.18 wt%, $2\sigma = 0.14$ wt%). However the 3050 ± 70 year fossil coral has higher Ca contents (38.47 wt%, $2\sigma = 0.05$ wt%). This difference is either due to very small degree of recrystallization of the coral aragonite, which is difficult to detect by X-ray diffraction analysis, or can be attributed to different levels of impurities in different corals. If the former is the reason, the sample would not be suitable for SST study, no matter how the Ca varies; if the latter is true, some Ca measurements are required for each coral sample. This question can be addressed by future studies. Nevertheless, even a few Ca measurements in each coral may be needed, but definitely there is no need to measure every sub-sample.

Sr thermometry

Mainly because the Ca concentrations are uni-

form, Sr data from the Xisha coral co-vary with Sr/Ca ratios with a correlation coefficient $r = 0.9955$. The linear equation is $\text{Sr/Ca} \times 10^3 = 0.111\text{Sr} - 0.5061$, where Sr is in $\mu\text{mol/gm}$ (Fig. 2). Consequently, our results demonstrate that the previously established Sr/Ca thermometer, $\text{Sr/Ca} \times 10^3 = A + B \times T$ (e.g., Beck *et al.*, 1992), can be simplified to a Sr thermometer, $0.111\text{Sr} - 0.5061 = A + B \times T$, where Sr is in $\mu\text{mol/gm}$. Because of the trivial seasonal Ca variation in the coral skeleton (Fig. 1), this equation should be more precise than simply substituting the average Ca content into the Sr/Ca thermometer.

Because ID-TIMS can provide precise analysis for small quantities of each sub-sample, past SST records can be reconstructed for monthly or even weekly resolution by coral Sr/Ca proxy. However, this means thousands of sub-samples need to be analyzed for a hundred-year record, using this time-consuming and high-cost technique. Our study indicates that it is now possible to save many (if not all) instrumental analyses for Ca concentrations. Therefore the total number of analyses can be reduced up to 50%. More significantly, Sr ID-TIMS analysis is routine work in numerous laboratories, whereas mainly because of the serious mass fractionation during mass spectrometer measurement, only a few isotope laboratories in the world can analyze Ca. This has greatly hampered coral paleo-climate studies. If

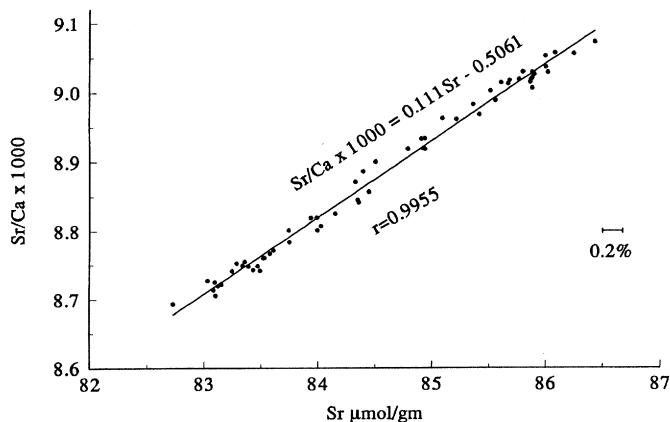


Fig. 2. Sr vs. Sr/Ca diagram for 61 subsamples from a *Porites* coral from Xisha Island. The Sr/Ca ratio of a sub-sample can be calculated from its Sr concentration within analytical error.

it is possible to avoid most, or all, Ca analyses, many more studies can be carried out, and this will definitely speed up our understanding of global change in the past.

Furthermore, Ca measurements can also be saved in other trace element studies on corals. For example, seasonal variations of Mn/Ca ratios in corals are about 30% (Shen *et al.*, 1991), those of Mg/Ca ratios are 25% (Mitsuguchi *et al.*, 1996), U/Ca ratios vary 17% (Min *et al.*, 1995), and Ba/Ca ratios vary 15% (Lea *et al.*, 1989). We suggest that these variations are also almost entirely caused by the intrinsic differences in concentrations of the trace elements. Therefore we should be able to keep the similar precision in the trace element to Ca ratio studies, but save time and cost if Ca measurement is omitted.

CONCLUSIONS

The Ca concentrations in the *Porites* coral from Xisha Island are nearly uniform, and the Sr concentrations covary linearly with the Sr/Ca ratios. The Sr/Ca coral thermometer can be simplified to a Sr thermometer. Therefore Ca measurements are not always necessary in coral studies.

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REFERENCES

- Alibert, C. and 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**, 345–363.
- Beck, J. W., Edwards, R. L., Ito, E., Taylor, F. W., Recy, J., Rougerie, F., Joannot, P. and Henin, C. (1992) Sea-surface temperature from coral skeletal strontium/calcium ratios. *Science* **257**, 644–647.
- Beck, J. W., Recy, J., Taylor, F., Edwards, R. L. and Cabioch, G. (1997) Abrupt changes in early Holocene tropical sea surface temperature derived from coral records. *Nature* **385**, 705–707.
- de Villiers, S., Shen, G. T. and Nelson, B. K. (1994) Sr/Ca thermometry in corals: method calibration and evaluation of (Sr/Ca) seawater and interspecies: variability. *Geochim. Cosmochim. Acta* **58**, 197–208.
- Gagan, M. K., Ayliffe, L. K., Hopley, D., Cali, J. A., Mortimer, G. E., Chappell, J., McCulloch, M. T. and Head, M. J. (1998) Temperature and surface-ocean water balance of the mid-Holocene tropical western Pacific. *Science* **279**, 1014–1018.
- Guilderson, T. P., Fairbanks, R. G. and Rubenstone, J. L. (1994) Tropical temperature variations since 20,000 years ago: Modulating interhemispheric climate change. *Science* **263**, 663–665.
- Lea, D. W., Shen, G. T. and Boyle, E. A. (1989) Coralline barium records temporal variability in equatorial Pacific upwelling. *Nature* **340**, 373–376.
- Min, G. R., Edwards, R. L., Taylor, F. W., Recy, J., Gallup, C. D. and Beck, J. W. (1995) Annual cycles of U/Ca in coral skeletons and U/Ca thermometry. *Geochim. Cosmochim. Acta* **59**, 2025–2042.
- Mitsugushi, T., Matsumoto, E., Abe, O., Uchida, T. and Isdale, P. J. (1996) Mg/Ca thermometry in coral skeletons. *Science* **274**, 961–963.
- Shen, C. C. (1996) High precision analysis of Sr/Ca ratio and its environmental application. Ph.D. Dissertation, Tsing Hwa University.
- Shen, C. C., Lee, T., Chen, C. Y., Wang, C. H., Dai, C. F. and Li, L. A. (1996a) The calibration of D[Sr/Ca] versus sea surface temperature relationship for porites corals. *Geochim. Cosmochim. Acta* **60**, 3849–3858.
- Shen, C. C., Lee, L. A., Dai, C. F. and Lee, T. (1996b) Improved subsampling method for biogenic skeletons and detailed growth pattern of porites coral. *Proc. 4th Taiwan Conference of Coral Reef Biology*, 246–255.
- Shen, G. T. and Boyle, E. A. (1987) Lead in corals: Reconstruction of historical industrial fluxes to the surface ocean. *Earth Planet. Sci. Lett.* **82**, 289–304.
- Shen, G. T. and Dunbar, R. B. (1995) Environmental controls on uranium in reef corals. *Geochim. Cosmochim. Acta* **59**, 2009–2024.
- Shen, G. T., Campbell, T. M., Dunbar, R. B., Willington, G. M., Colgan, M. W. and Glynn, P. W. (1991) Paleochemistry of manganese in corals from the Galapagos Islands. *Coral Reefs* **10**, 91–101.
- Smith, S. V., Buddemeier, R. W., Redalje, R. C. and Houck, J. E. (1979) Strontium-calcium thermometry in coral skeletons. *Science* **204**, 404–407.