Mg/Ca Thermometry in Coral Skeletons

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The magnesium-to-calcium (Mg/Ca) ratio of coral skeletons from Ishigaki Island, Ryukyu Islands, Japan, closely tracked sea surface temperature (SST) over an 8-year period. Measurements were made with the fast technique of inductively coupled plasma–atomic emission spectrometry. The variation of the coral Mg/Ca ratio with SST change is about four times that of the current, widely used coral strontium-to-calcium ratio. The temporal and geographic variation of the seawater Mg^{2+}/Ca^{2+} ratio probably has little influence on coral Mg/Ca variation. Results indicate that the coral Mg/Ca ratio has the potential to provide fast, precise, high-resolution proxies for past tropical SSTs.

Tropical ocean temperature is one of the key parameters in paleoclimatic analysis, because of its interaction with other climate variables. Hermatypic corals are particularly suited for high-resolution studies of tropical paleoceanic environments, because most grow annual growth bands at rates of millimeters to centimeters per year. The Sr/Ca ratio and $\delta^{18}O$ values of coral skeletons (*1*) are already used to extract high-quality information about past tropical SSTs. These SST tracers, however, have some problems. Coral Sr/Ca variation with SST change is small (~7 per mil/°C), and time-consuming isotopic dilution mass spectrometry (IDMS) is required for precise measurements (*2*). This method is unfit for the survey of SST change over a series of centuries. Variations in the $\delta^{18}O$ value of seawater with rainfall, evaporation, or runoff can also affect coral $\delta^{18}O$ values in some locations. Recently, the annual variation of coral U/Ca ratio was found, by use of IDMS, to correlate well with that of the Sr/Ca ratio, and its potential as a paleothermometer has been proposed (*3*). The use of complementary SST tracers such as these and the technique we report here will provide clearer understanding of paleoclimatic variability.

Several investigators have studied the skeletal Mg content of calcareous marine organisms and its controlling factors. Chave (*4*) showed that skeletal Mg content increased with seawater temperature for both calcitic organisms and aragonitic corals, whereas Weber (*5*) reported negative results concerning this relation in aragonitic corals. However, they both measured Mg content, using bulk skeletons of various genera and species collected from various regions of the world, and compared the values with SST averages at each sampling site; therefore, their results seem to be perturbed by the rough method and interspecies or intergeneric differences. Subsequently, Oomori *et al.* (*6*) showed, by measuring along the skeletal growth axis, that coral Mg/Ca ratio exhibits a seasonal pattern of variability. Through use of ion microprobe technique, which shows promise for rapid and microscale analysis, Hart and Cohen (*7*) found that the annual variations of coral Mg/Ca, B/Ca, and F/Ca ratios correlated well with that of the Sr/Ca ratio. Here, we develop and extend the use and understanding of coral Mg/Ca ratio as an SST proxy, with a simple, speedy analytical technique, inductively coupled plasma–atomic emission spectrometry (ICP-AES).

We determined the Mg/Ca and Sr/Ca ratios and $\delta^{18}O$ of coral skeleton with a sampling resolution corresponding to ~3 weeks of growth. A vertical core (1.8 m in length and 9 cm in diameter) of the massive coral species *Porites lutea* was drilled by using a method of the Australian Institute of Marine Science (*8*) on 20 September 1993 from Yasurazaki, Ishigaki Island, Ryukyu Islands, Japan. The Ryukyu Islands are suitable for studying coral skeletal composition as a thermometric indicator, because the annual SST range is ~10°C. The sampling site lies near the fringing reef opening, with continuous flow of ocean water and no adjacent river discharge; therefore, salinity and seawater composition are almost constant at this site throughout the year, which indicates that coral $\delta^{18}O$ should be mostly controlled by SST. The coral core was sliced longitudinally to a thickness of 7 mm and x-ray–radiographed. A count of the annual bands showed that the coral colony grew at ~16 mm/year. We obtained subsamples of ~2 mg at 1-mm increments along the growth axis of the sliced core. Typically, 0.5 mg of each subsample was used for oxygen isotope measurement (*9*). The remainder was cleaned (*10*) and used for measurements of Mg, Sr, and Ca with ICP-AES (*11*). No other minerals but aragonite were detected by x-ray analysis (*12*).

The Mg/Ca and Sr/Ca ratios and $\delta^{18}O$ all exhibit clear synchronous seasonal variation (Fig. 1). These variations have in common an anomaly described as a shallower trough ~88 mm from the top of the coral core. The variation of the Mg/Ca ratio is ~26% relative to its average, which is about four times that of the Sr/Ca ratio. The relationship between the variations of Mg/Ca and Sr/Ca ratios is in excellent agreement with that reported by Hart and Cohen (*7*). We compared the variations of the Mg/Ca and Sr/Ca ratios and $\delta^{18}O$ with SST data observed at the tidal station at Ishigaki Port, 30 km south of the sampling site (Fig. 2). All of the tracers exhibit a strong dependence on SST, and the common anomaly also coincides with the SST anomaly early in 1988. As a further test, we calculated the anomalies of coral Mg/Ca ratio and SST for annual maxima and minima (Fig. 3) (*13*). All SST anomalies larger than ±0.5°C are in agreement with those of coral Mg/Ca ratio except for that during the summer of 1986. Thus, it seems that coral Mg/Ca ratio is controlled by SST and has about four times the sensitivity of the Sr/Ca ratio. The equation of a best fit line through all of the Mg/Ca–SST points in Fig. 2A is

$$10^3\ \mathrm{Mg/Ca(molar\ ratio)} = 1.15 + 0.129(\mathrm{SST}) \quad (1)$$

for *P. lutea*. The analytical error (2σ) on the measurement of the Mg/Ca ratio (*14*) corresponds to an uncertainty of ±0.5°C in SST. In addition to SST, other possible factors affecting coral Mg/Ca ratio are seawater Mg/Ca ratio and salinity. Seawater Mg/Ca ratio probably varies by less than 1% in most circumstances (*15*). The common salinity change makes no appreciable difference in the

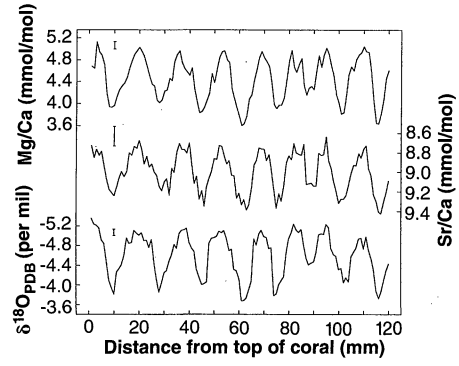

Fig. 1. Profiles of the Mg/Ca and Sr/Ca ratios and $\delta^{18}O$ along the growth axis of coral (*P. lutea*) collected from Yasurazaki, Ishigaki Island, Ryukyu Islands, Japan. Average growth rate of this specimen is 16 mm/year. The time resolution of these data is ~3 weeks. Error bar for each result represents average external analytical error (2σ). External analytical error includes all uncertainties from sample pretreatment and measurement. The estimation of the analytical errors is as described for the Mg/Ca and Sr/Ca ratios (*14*) and for $\delta^{18}O$ (*9*).

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activity coefficient ratio of Mg^{2+} to Ca^{2+}. These effects yield an uncertainty of only ~±0.3°C in SST reconstruction, assuming that skeletogenesis of Mg is similar to inorganic aragonite precipitation. Thus, coral Mg/Ca ratio seems to be an excellent SST proxy with resistance to oceanic chemical changes, because it has such a high sensitivity to SST change and the ocean residence times of Mg and Ca are so long [1.3×10^7 years and 1.1×10^6 years, respectively (*16*)].

Delaney *et al.* (*17*) reported no change in Mg/Ca and Sr/Ca ratios after a cleaning sequence, which is very similar to ours (*10*), for both aragonitic green alga and *Porites* sp. coral. Thus, it seems that the amount of Mg associated with labile organic and adsorbed phases is negligible relative to skeletal Mg content, and that laborious sample cleaning is not necessary.

Although the Mg/Ca ratio of synthesized calcite shows clear temperature dependency, the behavior and thermodynamics of the Mg^{2+} ion in aragonite synthesis remain unsolved (*18*). The $CaCO_3$-$MgCO_3$ solid solution series have a rhombohedral calcite-type structure, rather than an orthorhombic aragonite-type structure, because of the small ionic radius of Mg^{2+}. Therefore, the location of Mg^{2+} ion in aragonite crystal lattice is unclear, and its bonding in the lattice might be weak. Amiel *et al.* (*19*) reported that Mg was preferentially released from coral aragonite to distilled water. Cross and Cross (*20*) reported the decrease in coral skeletal Mg concentration with diagenesis. Consequently, the Mg/Ca thermometer may be susceptible to diagenesis, such as by freshwater.

Mg/Ca thermometry may be affected by biological variations in growth rate and interspecies differences. This has been suggested in both Sr/Ca and $\delta^{18}O$ thermometry (*21*). Swart (*22*) observed that higher Mg content is associated with faster extension rate, whereas Oomori *et al.* (*6*) reported a contrary result. Although the effects of diagenesis, growth rate, and interspecies differences on coral Mg/Ca thermometry require careful evaluation, our results indicate that the combination of coral Mg/Ca ratio and ICP-AES has the potential to provide fast, precise, high-resolution proxies for past tropical SSTs.

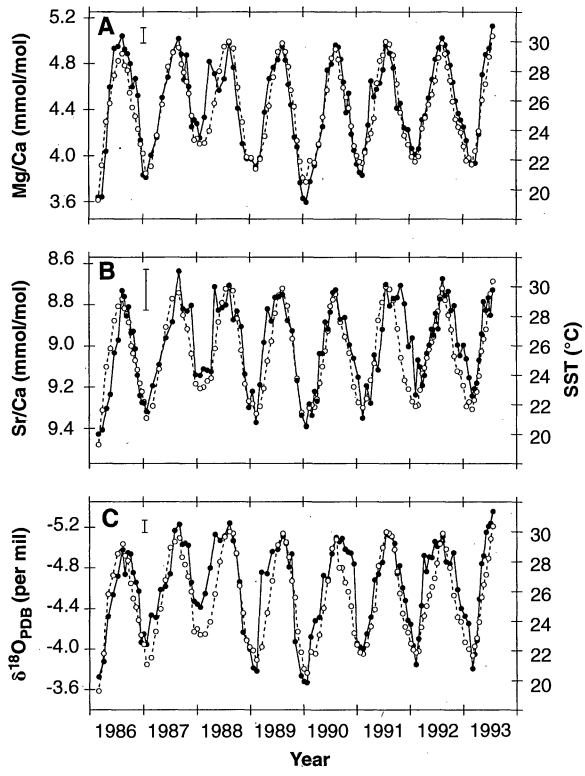

Fig. 2. Comparisons between the SST record (dashed line, ○) observed at tidal station at Ishigaki Port, 30 km south of the sampling site, and the variations of the Mg/Ca and Sr/Ca ratios and $\delta^{18}O$ (solid lines, ●) of coral (*P. lutea*) collected from Yasurazaki, Ishigaki Island, Ryukyu Islands, Japan over the period 1986–93. The time resolution of the data points for these tracers is ~3 weeks. The SST data points represent 3-week averages of daily SST measurements (*23*). (**A**) The Mg/Ca–SST linear calibration is given in Eq. 1 ($r = 0.923$). Analytical error bar (2σ) (*14*) corresponds to an uncertainty of ±0.5°C. (**B**) The Sr/Ca–SST linear calibration is 10^3 Sr/Ca (molar ratio) = 10.5 − 0.0608(SST) ($r = 0.853$). Analytical error bar (2σ) (*14*) corresponds to an uncertainty of ±1.6°C. (**C**) The $\delta^{18}O$–SST linear calibration is $\delta^{18}O_{PDB}$(per mil) = −1.21 − 0.134(SST) ($r = 0.877$). Analytical error bar (2σ) (*9*) corresponds to an uncertainty of ±0.4°C.

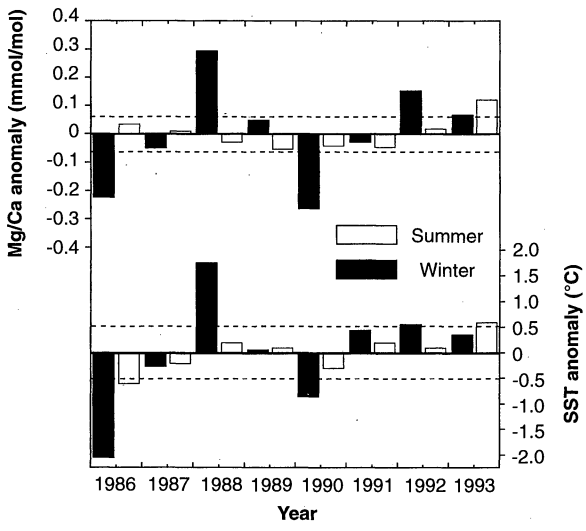

Fig. 3. Comparison between Mg/Ca anomalies and SST anomalies for annual maxima and minima over the period 1986–1993. Open bars indicate the anomalies for annual maxima (summer). Dark bars indicate the anomalies for annual minima (winter). The range between the two dashed lines corresponds to the analytical error (2σ), which can be translated as the SST uncertainty of ±0.5°C (*14*).

REFERENCES AND NOTES

1. $\delta^{18}O$ is the normalized deviation, in parts per thousand, of the sample $^{18}O/^{16}O$ ratio relative to the reference standard. For coralline aragonite $\delta^{18}O$, the conventional reference standard is the Pee Dee belemnite (PDB).
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9. The fraction was treated with 100% phosphoric acid at 60°C in a CO_2 extraction line for sequential replicate (n = 5) measurements with a Finnigan MAT251 mass spectrometer. We used the reference carbonate standardized by NBS-19. Average analytical error for $\delta^{18}O$ was estimated at 0.06 per mil (2σ) after 20 runs of 0.5 mg reference carbonate.
10. First, we cleaned the samples with 1 ml of distilled (deionized) water at room temperature, followed by addition of 1 ml of 4 mM nitric acid at room temperature and then 2 ml of 30% hydrogen peroxide at 60°C, all in an ultrasonic cleaner for 15 min.
11. Typically, 1 mg of the washed subsample finally obtained was dissolved in 4 g of 0.5 M nitric acid for sequential triplicate measurements of Mg, Sr, and Ca by ICP-AES with Seiko SPS-7000A.
12. The sample for x-ray diffraction was taken from adjacent parts of the transect and homogenized in an agate mortar. We used copper Kα radiation. A scan was made at the rate of 1 degree (2θ) per minute between 20 and 60 degrees (2θ).
13. Anomalies for annual maxima and minima are differences from the mean values for annual maxima and minima, respectively, over the period 1986–1993.
14. We estimated the analytical errors (2σ) for the Mg/Ca and Sr/Ca ratios with the following method. We crushed and homogenized 10 g of coral sample cut from other parts of the sliced core in an agate mortar. Twenty-five coral powder fractions of 1.5 mg each were taken from the whole and cleaned and used for measurements (*10, 11*). The average analytical errors (2σ) for the Mg/Ca and Sr/Ca ratios were 0.068 and 0.10 mmol/mol, respectively.
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23. The comparison is based on the following: The annual extrema of each tracer are assigned to the corresponding annual extrema of the SST record, and coral growth rate is assumed to be constant between the extrema.
24. We thank B. Parker of the Australian Institute of Marine Science for drilling the coral core and R. G. Fairbanks of the Lamont-Doherty Earth Observatory of Columbia University for helpful comments.

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Anisotropy in the Inner Core: Could It Be Due To Low-Order Convection?

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A recently assembled data set of inner core–sensitive free oscillation splitting measurements and body wave differential travel times provides constraints on the patterns of anisotropy in the Earth's inner core. Applying a formalism that allows departures from radial symmetry and cylindrical anisotropy results in models with *P*-wave velocity distributions whose strength and pattern are incompatible with frozen-in anisotropy, but rather suggest a simple large-scale convection regime in the inner core.

Inner core anisotropy was proposed to explain faster propagation of inner core sensitive *P* waves (*1*) on paths parallel to the Earth's rotation axis than on equatorial paths (*2*), as well as anomalous splitting of inner core–sensitive free oscillations (*3*). A model of constant cylindrical anisotropy with the fast axis parallel to the Earth's rotation axis was proposed (*4–10*). There has been disagreement on the strength of this anisotropy until recently (*1*, *4*, *8*, *9*), but consensus has now been reached on a strength of about 3 to 3.5%, in order to explain travel times of shallow and deep turning rays in the inner core (*10*). The debate is now focused on the physical process responsible for this anisotropy. Two classes of mechanisms have been proposed: (i) fluid inclusions in an inner core close to the melting point of its constituents (*11*), and (ii) preferential orientation of anisotropic crystals (*12*, *13*). Recent results that favor the latter interpretation include the following: (i) the expected variations in *P* wave velocity for hexagonal close packed (hcp) iron at inner core conditions match the average seismic travel time observations (*13*); (ii) recently documented existence of anisotropy in attenuation from differential PKP (BC-DF) measurements (*14*) indicates a correlation of fast velocities with high attenuation in the inner core, confirming earlier observations (*5*, *8*, *15*) and ruling out models based on fluid inclusions.

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To determine whether it is convection (*12*, *16*) or freezing governed by the magnetic field (*17*) that causes the crystal alignment, we must investigate its variations in three dimensions. Most studies have only considered one-dimensional models. Departures from such models have been limited to (i) a slight tilt (~10° to 15°) of the axis of symmetry with respect to the Earth's rotation axis (*6*–*8*) and (ii) possible depth dependence of the transversely isotropic elastic tensor, resulting in a middle zone of reduced anisotropy in the inner core (*7*).

Although there is evidence for three-dimensional effects (*6*, *7*), we cannot resolve them in detail because of (i) the large number of parameters necessary to describe the most general form of anisotropy; (ii) the inadequate illumination of the inner core by body waves, due to the limited distribution of sources and receivers at the Earth's surface; and (iii) the difficulty of estimating and eliminating the effect of mantle heterogeneity. As shown in studies of mode splitting (*1*, *18*), anomalous mode splitting is dominated by zonal terms (terms that do not depend on the longitude), which are comparatively weak in the mantle (*19*, *20*). This leads us to consider, as a first approximation, models of inner core anisotropy that are three-dimensional but axisymmetric with respect to the Earth's rotation axis (or the best fitting slightly tilted axis of symmetry), thus limiting the number of free parameters.

A formalism for the inversion of normal mode splitting data for inner core anisotropy—cast in terms of general, low-degree, axisymmetric models—has been previously applied to an existing data set of inner core–sensitive modes (*21*). The resulting model, based on data for only eight modes, featured significant depth dependence but failed to provide an adequate fit to subsequent mode measurements (*22*). The occurrence of two very large, deep earthquakes in 1994 [Bolivia and Kurile Islands (*23*)] has since provided mode observations of unprecedented quality at more than 50 broadband digital stations distributed around the world. These data are being analyzed to constrain various properties of the deep Earth (*23*). We have measured the splitting of inner core–sensitive modes with the use of data from these earthquakes. Combining data for 19 such modes with differential time measurements from digital broadband stations (*24*) allows us to better constrain the deeper parts of the inner core that mode data are unable to resolve.

We applied the axisymmetric formalism (*22*) to obtain models of inner core anisotropy with various degrees of complexity. This formalism is cast in terms of spherical harmonics expansion of the anisotropic elastic tensor in the geographical coordinates (θ, ϕ) and polynomial representation as a function of radius r with further constraints that the elastic tensor must be analytical at the center of the Earth and that there are no lateral variations of Lamé parameters (*21*). The mode data are represented in terms of splitting function coefficients as defined in (*25*). The depth parameterization is quantified by ν, which is the maximum power in r of the depth dependence (ν = 0 to 4), whereas the spatial characteristics depend on n (n = 0, 2, or 4), which is related to the maximum degree of the spherical harmonics expansion. The value n = 0

Table 1. Model parameterizations for inner core anisotropy (*26*). In model #1, the transverse isotropy is constant. In models #2 and #3, it varies radially. Models #4 and #5 have an axisymmetric anistropy. X indicates that data are included in the model. Tr. times, travel times.

Data	Model number									
	1a	1b	2a	2b	3a	3b	4a	4b	5a	5b
Modes	X	X	X	X	X	X	X	X	X	X
Tr. times		X		X		X		X		X
n	0		0		0		2		4	
ν	0		2		4		4		4	