

## Light and temperature effects on Sr/Ca and Mg/Ca ratios in the scleractinian coral *Acropora* sp.

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### Abstract

This study was designed to investigate the effect of light and temperature on Sr/Ca and Mg/Ca ratios in the skeleton of the coral *Acropora* sp. for the purpose of evaluating temperature proxies for paleoceanographic applications. In the first experiment, corals were cultivated under three light levels (100, 200, 400  $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ ) and constant temperature (27 °C). In the second experiment, corals were cultivated at five temperatures (21, 23, 25, 27, 29 °C) and constant light (400  $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ ). Increasing the water temperature from 21 to 29 °C, induced a 5.7-fold increase in the rate of calcification, which induced a 30% increase in the Mg/Ca ratio. In contrast, by increasing the light level by a factor of 4, the rate of calcification was increased only by a factor of 1.7, with a corresponding 9% increase in the Mg/Ca ratio. Thus, the relative change in the calcification rate in the two experiments (5.7 vs. 1.7) scales with the corresponding relative change in Mg/Ca ratio (30% vs. 9%). We conclude that there is a strong biological control on the incorporation of Mg.

For Sr/Ca, good correlations were also observed with water temperature and the calcification rate induced by temperature changes. However, in sharp contrast with the Mg/Ca ratio, a temperature-induced 5.7-fold increase in the calcification rate only induced a 4.5% change (decrease) in the Sr/Ca ratio. An important finding for paleoceanographic applications is that the Sr/Ca ratio did not appear to be sensitive to changes in the light level, or to changes in calcification rate induced by changes in the light level. Thus, in this study, water temperature was found to be the dominant parameter controlling the skeletal Sr/Ca ratio.

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### 1. Introduction

Retrieval of climatic and oceanographic data from a wide range of archives is important for reconstructing climatic changes and for evaluating their causes by comparison with global climate models. To this end, coral skeletal chemistry and isotopic composition have been used extensively to reconstruct the climatic variability of the recent past. Scleractinian corals form aragonitic carbonate skele-

tons that contain minor elements such as Sr and Mg (Milliman et al., 1974). Both Sr and Mg concentrations have been explored as a tool for reconstructing sea surface temperature (SST) (Weber, 1973; Beck et al., 1992). Both of these minor elements have long residence times that result in relatively constant Sr/Ca and Mg/Ca ratios of the oceans (Carpenter and Manella, 1973; Broecker and Peng, 1982) and provide a good basis for paleo-thermometry (de Villiers et al., 1994; McCulloch et al., 1994). Good correlations have been observed between Sr/Ca and/or Mg/Ca ratios in coral skeletons and SST (Beck et al., 1992; Alibert and McCulloch, 1997; McCulloch et al., 1999).

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Recent studies, however, have highlighted problems with these thermometers because of the observation of large shifts in the coral-based estimates of SST compared with *in situ* measurements of SST and because of discrepancies between or within different coral species (Allison, 1996). At some sites, local variations in the Sr/Ca or Mg/Ca ratios of the seawater have been assumed to be the major cause of the discrepancies in inferred SST between different corals. However, micro-analytical studies found the distribution of Sr (which is in solid solution in the aragonite crystal structure (Allison et al., 2005)) to be highly heterogeneous in the coral at the micrometer length scales, with dramatic Sr concentration variations corresponding to skeletal components and ultra-structure (Allison, 1996; Hart and Cohen, 1996; Allison et al., 2001; Cohen et al., 2002; Meibom et al., 2003). Additionally, Meibom et al. (2004), using Nano-SIMS ion microprobe imaging, observed that the distribution of Mg is strongly correlated with the fine-scale structure of the skeleton. Furthermore, correlation has also been observed between Sr/Ca or Mg/Ca and coral extension rates (de Villiers et al., 1994) or the specifics of the calcification process (Allison, 1996; Alibert and McCulloch, 1997; Allison et al., 2001). Swart (1981), for example, observed higher Mg contents associated with faster extension rates. This suggests that temperature is not the only factor controlling the distribution of Sr and Mg in coral skeletons, and that biological factors might be very important in establishing the trace element composition of the coral skeleton (Weber, 1973; Hart and Cohen, 1996; Baer et al., 2000; Cohen et al., 2001; Allison et al., 2005). A similar conclusion has been reached for the skeletal oxygen isotope composition (Rollion-Bard et al., 2003). However, experiments designed to disentangle the relationship between environmental variability and biological factors, such as the calcification rate and the concentration of trace elements in the coral skeleton, have only rarely been attempted. Environment and biological factors are clearly linked together and it is therefore difficult to discriminate between the two types of control in natural and largely uncontrolled settings.

This study was therefore set up with the aim to investigate, in a controlled laboratory environment, the relative importance of environmental and biological factors for the trace element concentration in the *Acropora* coral skeleton. We investigate the correlations between changes in environmental factors (light-level and water temperature) and a biological factor (calcification rate) and the Sr and Mg concentration of the *Acropora* skeleton, which is arguably one of the most useful coral genera for paleo SST and radiocarbon calibration studies.

## 2. Material and methods

### 2.1. Biological material

The experiment was performed using a single colony of the branching zooxanthellate scleractinian coral, *Acropora* sp. maintained under controlled condition in aquaria at the Centre Scientifique de Monaco. "Nubbins" (small, live coral samples) were obtained by cutting terminal

portions of branches of a parent colony and were then glued onto glass slides following the procedures described by Reynaud-Vaganay et al. (1999).

### 2.2. Experimental set up

The experimental tanks were continuously supplied with Mediterranean seawater (salinity = 38.5) pumped from a water depth of 50 m. This seawater was heated using a temperature controller (EW, PC 902/T) and continuously circulated and mixed by a Rena® pump (6 l min<sup>-1</sup>). The water renewal rate in each tank was approximately five times per day. The duration of the experiments was 12 weeks. During this period, nubbins were fed once a week with *Artemia salina* nauplii. Light was provided by metal halide lamps (Phillips HPIT, 400 W) with a light:dark ratio of 1 (12 h of light:12 h of darkness).

For the "Light experiment", 38 nubbins were first cultivated for 4 weeks under a light intensity of 400 μmol photons m<sup>-2</sup> s<sup>-1</sup> (referred to as the high-light "HL" condition). After this period, a ring of ca. 1 cm radius of new skeleton had grown on the glass slide. This skeleton was sampled as described in Reynaud-Vaganay et al. (1999) for chemical analysis. Nubbins were then divided into two tanks (30 l), receiving two different light intensities (100 or 200 μmol photons m<sup>-2</sup> s<sup>-1</sup> (referred to as the low-light "LL", and the medium-light "ML" conditions, respectively) and maintained under these culture conditions for 4 weeks. At the end of this culture period, the new skeleton grown on the glass slide was sampled for chemical analysis. Light intensities used in this experiment (100, 200, 400 μmoles photons m<sup>-2</sup> s<sup>-1</sup>) correspond to 4.3, 8.6 and 17.3 mol m<sup>-2</sup> d<sup>-1</sup>, respectively. Davies (1991) estimated that, during a typical sunny day on a tropical reef, a coral receives about 14.4 mol m<sup>-2</sup> d<sup>-1</sup> of sunlight at a depth of 3 m in turbid water. On a cloudy day the coral receives about 6.2 mol m<sup>-2</sup> d<sup>-1</sup> of sunlight. Thus the light intensities in our experiments imitate a range from quite low natural illumination levels to very strong natural illumination levels. In these light experiments, the water temperature was kept constant at 27 °C.

For the determination of the calcification rates, corals were weighed once a week following the buoyant weight technique (Jokiel et al., 1978) and using a Mettler AT 261 balance (accuracy ± 0.01 mg). The calcification rate was measured using the following formula:

$$G = \sqrt[n]{\frac{P_n}{P_0}} - 1$$

Where  $G$  is the calcification rate,  $n$  is the number of the culture days,  $P_n$  is the dry weight after  $n$  days of culture,  $P_0$  is the initial dry weight.

For the temperature experiments, 50 nubbins were distributed in five tanks (30 l) heated to 21, 23, 25, 27 and 29 °C (10 nubbins per tank). The light intensity was constant at 400 μmol photons m<sup>-2</sup> s<sup>-1</sup> and the light:dark ratio was 1 (12 h light:12 h darkness). Nubbins were maintained for 4 weeks under these conditions and their weight was measured once a week (Jokiel et al., 1978) for the determination of the calcification rate. At the end of the 4 weeks, new skeleton grown on the glass slide was sampled for analysis as described below.

### 2.3. Measurement of environmental variables

Temperature (accuracy: ±0.05 °C) was logged at 10 min intervals using a Seamon® temperature recorder. Salinity and irradiance were measured using a conductivity meter (Meter LF196) and a 4π quantum sensor (Li-Cor, LI-193SA), respectively.

### 2.4. Sr/Ca and Mg/Ca ratios

Sr/Ca and Mg/Ca ratios in coral samples were determined at Lamont-Doherty Earth Observatory by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) using a Jobin-Yvon Panorama 2000 ICP-OES equipped with a Model AS421 autosampler. In order to remove organic material, coral samples were placed in 30% hydrogen peroxide in plastic vials and sonicated for 60 min. The peroxide was replaced and the

process was repeated until no additional whitening of sample was observed (a total of two to three times). Coral fragments were rinsed with double deionized water, dried at 60 °C and then crushed to a granular powder. For measurement of trace element ratios the sample uptake rate was about 0.5 ml per minute 2% ultra pure nitric acid to achieve a dissolved Ca concentration in the range of 20 to 30 ppm Ca. Raw elemental concentration data (Ca, Mg, and Sr) were drift-corrected using the sample-standard correction method described by Schrag (1999). All samples were run in replicate. Samples found to have dissolved Ca concentrations exceeding 40 ppm Ca were repeated. External precision of a laboratory standard was  $\pm 0.8\%$  for Sr/Ca and about  $\pm 2\%$  for Mg/Ca, respectively. The average difference between replicate samples was about 0.05 and 0.07 mmol/mol for Sr/Ca and Mg/Ca, respectively.

Chemical analyses at ultra-structural length scales (Fig. 10) were performed on a *Porites* sp. coral from coastal Kenya (Meibom et al., 2003) with the Cameca NanoSIMS N50 ion microprobe at the Muséum National d'Histoire Naturelle in Paris. Using a primary beam of  $O^-$ , secondary ions of  $^{24}Mg^+$ ,  $^{40}Ca^+$  and  $^{88}Sr^+$  were sputtered from sample surface and detected simultaneously in electron multipliers at a mass resolving power of  $\sim 4000$ . At this mass-resolving power,  $^{24}Mg^+$  is resolved from  $^{23}NaH^+$ . Data were obtained from a pre-sputtered region of the polished and gold-coated sample surface in a series of line-scans with the primary ions focused to a spot-size of  $\sim 150$  nm. The primary beam was stepped across the sample surface with a step-size of about 100 nm. Magnesium and Strontium concentrations were calibrated against carbonate standards of known composition.

### 2.5. $\delta^{18}O$

Stable isotopes were measured on a FISON Optima Mass Spectrometer equipped with Multiprep sample introduction device. External precision is about  $0.05\%$  (1 SD) for  $^{18}O$  based on repeated analysis of Lamont-Doherty laboratory carbonate standard. All values are reported relative to the V-PDB standard.

### 2.6. Statistical analysis

All statistical analyses were carried out using the statistical package JMP IN version 5 (SAS Institute, Cary, USA). Results are reported as the mean  $\pm$  standard error of the mean (SE), and  $N$  is the sample size.

## 3. Results

### 3.1. Calcification rates

Files of raw data are available on the journal web site in electronic annex as EA-2.

The rates of calcification were significantly different for corals grown at different temperatures (ANOVA,  $P < 0.0001$ , Fig 1). There is a clear positive linear correlation, which can be parameterized as: Rate of Calcification ( $\% \text{ day}^{-1}$ ) =  $0.034 \times T$  (°C) - 0.645 ( $R^2 = 0.99$ ). Calcification rates ranged from  $0.061 \pm 0.009\% \text{ day}^{-1}$  to  $0.346 \pm 0.032\% \text{ day}^{-1}$  at 21 and 29 °C, respectively. This corresponds to a 5.7-fold increase in calcification rate from the lowest to the highest water temperature.

The rate of calcification was also found to be significantly different for different light levels (ANOVA,  $P < 0.0001$ , Fig 2) with a significant, but positive correlation parameterized as: Rate of Calcification ( $\% \text{ day}^{-1}$ ) =  $0.0004 \times \text{light} + 0.1222$  ( $R^2 = 0.99$ ). Under different light levels the rates of calcification ranged from  $0.158 \pm 0.006\% \text{ d}^{-1}$  to

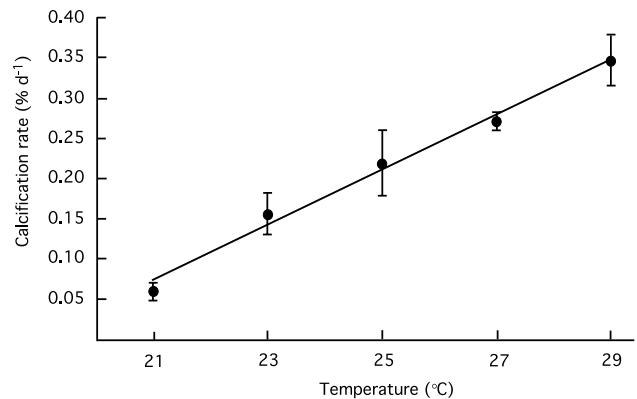


Fig. 1. Calcification rates of nubbins of *Acropora* sp. vs. seawater temperature.

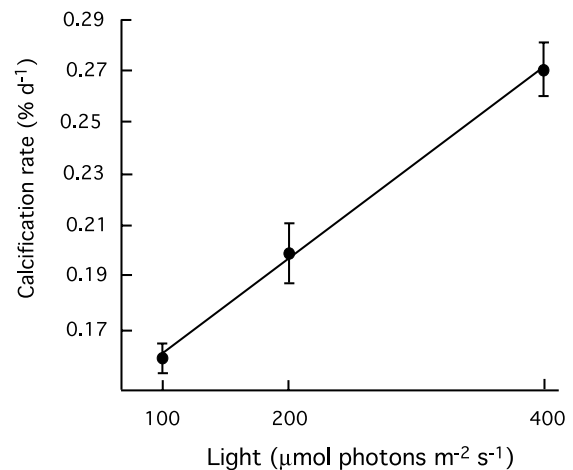


Fig. 2. Calcification rates of nubbins of *Acropora* sp. vs. light level.

$0.270 \pm 0.010\% \text{ day}^{-1}$  at 100, and  $400 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ , respectively, corresponding only to a 1.7-fold increase. Therefore, the change in calcification rate obtained during a  $300 \mu\text{mol photon m}^{-2} \text{ s}^{-1}$  increase (from 100 to  $400 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ ) is equivalent to that obtained by changing the water temperature from 23 to 27 °C.

### 3.2. Mg/Ca

Files of raw data are available on the journal web site in electronic annexes as EA-1 (for temperature experiment) and EA-3 (for light experiment).

Skeletal Mg/Ca ratios showed a positive linear correlation with temperature: Mg/Ca (mmol/mol) =  $0.138 \times T$  (°C) + 0.898,  $R^2 = 0.98$ , (Fig. 3) and increased from  $3.759 \pm 0.029$  mmol/mol at 21 °C to  $4.901 \pm 0.037$  mmol/mol at 29 °C (i.e. 30% increase). In contrast, the relationship between Mg/Ca and light was not linear (Fig. 4). There was indeed no significant variation in the Mg/Ca ratio between 100 and  $200 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ . However, when the light intensity was increased to  $400 \mu\text{mol photons}$

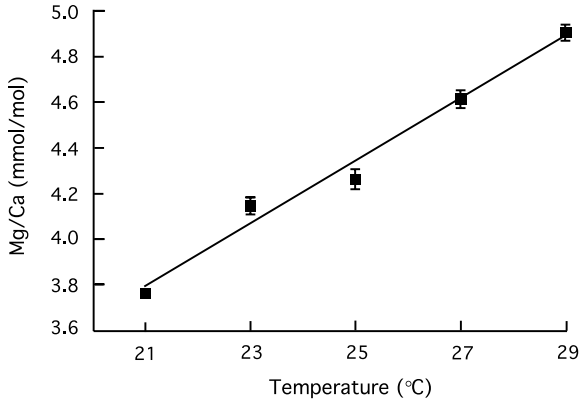


Fig. 3. Mg/Ca measured in the skeleton of *Acropora* sp. as a function of water temperature (mean  $\pm$  SE,  $N = 10$  for each condition).

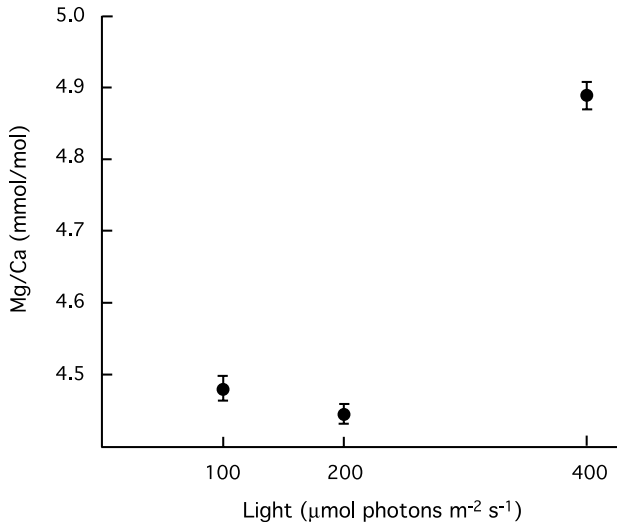


Fig. 4. Mg/Ca measured in the skeleton of *Acropora* sp. as a function of light level ( $N = 19, 19$  and  $38$  for  $100, 200$  and  $400 \mu\text{mol m}^{-2} \text{s}^{-1}$ , respectively).

$\text{m}^{-2} \text{s}^{-1}$ , the Mg/Ca ratio significantly increased (ANOVA,  $P < 0.0001$ ) by 9% (from 4.48 to 4.89 mmol/mol).

Fig. 5 shows the plot of Mg/Ca ratio vs. the calcification rate, obtained by changing the water temperature (circles), or the light level (squares). A significant relationship can only be calculated between Mg/Ca and calcification rate obtained during the temperature experiment. It is interesting to note that the Mg/Ca ratios from the light experiment are systematically higher than for the temperature experiment.

### 3.3. Sr/Ca

There is a significant negative correlation between water temperature and the Sr/Ca of the coral skeleton that can be parameterized as follows (Fig. 6):

$$\text{Sr/Ca} = 0.007 \times T^2 - 0.393 \times T + 14.807 (R^2 = 0.97).$$

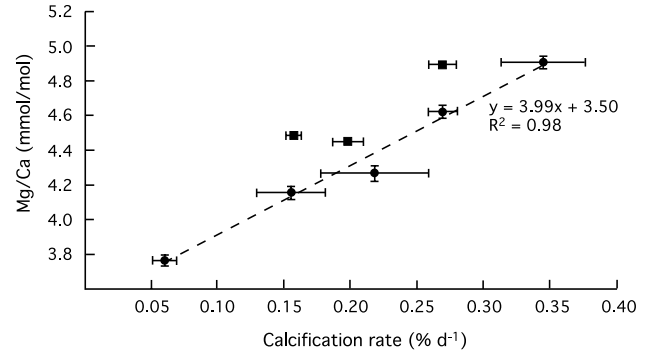


Fig. 5. Mg/Ca measured in the skeleton of *Acropora* sp. as a function of calcification rate. The calcification rate varied when changing either the temperature (circles) or the light level (squares). A linear regression was calculated using data from temperature experiment only.

Sr/Ca varies from  $9.592 \pm 0.018$  mmol/mol to  $9.157 \pm 0.011$  mmol/mol between 21 and 29 °C (equivalent to a 4.5% change in the Sr/Ca ratio).

There was no significant difference in the Sr/Ca ratio of corals cultured at different light levels (Fig. 7). Mean values

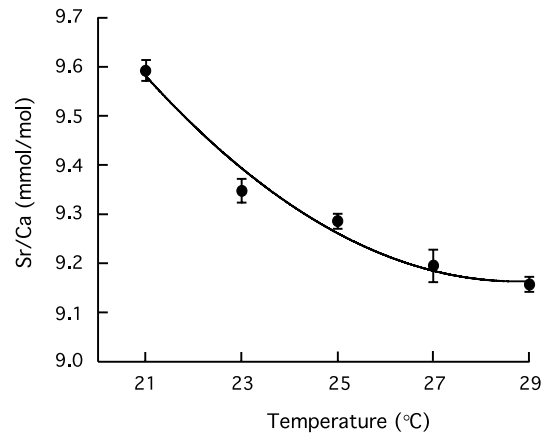


Fig. 6. Sr/Ca ratios measured in the skeleton of *Acropora* sp. as a function of water temperature (mean  $\pm$  SE,  $N = 10$  for each condition).

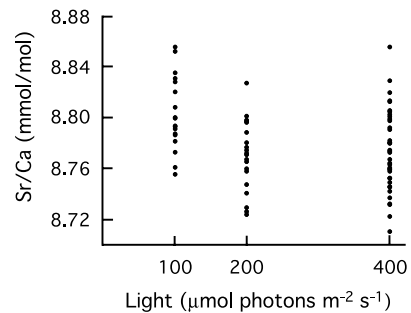


Fig. 7. Sr/Ca measured in the skeleton of *Acropora* sp. as a function of light level ( $N = 19, 19$  and  $38$ , respectively for  $100, 200$  and  $400 \mu\text{mol m}^{-2} \text{s}^{-1}$ ).

of Sr/Ca (mmol/mol) were  $8.803 \pm 0.007$ ,  $8.770 \pm 0.007$ , and  $8.772 \pm 0.005$  for light levels of 100, 200 and 400  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , respectively. The standard error associated with the analysis of the Sr/Ca ratios ( $1\sigma \pm 0.08$ ) is therefore larger than the ‘differences’ between the three light regimes.

As a result, when plotting Sr/Ca ratio vs. the calcification rate, two different relationships are obtained depending on whether the growth rate changes were induced by changing the water temperature or by changing the light levels (Fig. 8).

### 3.4. $\delta^{18}\text{O}$

There is a positive correlation between  $\delta^{18}\text{O}$  and temperature (Fig. 9), with the following parameterization:  $\delta^{18}\text{O} = -0.34 \times T (\text{°C}) + 6.35$  ( $R^2 = 0.99$ ).

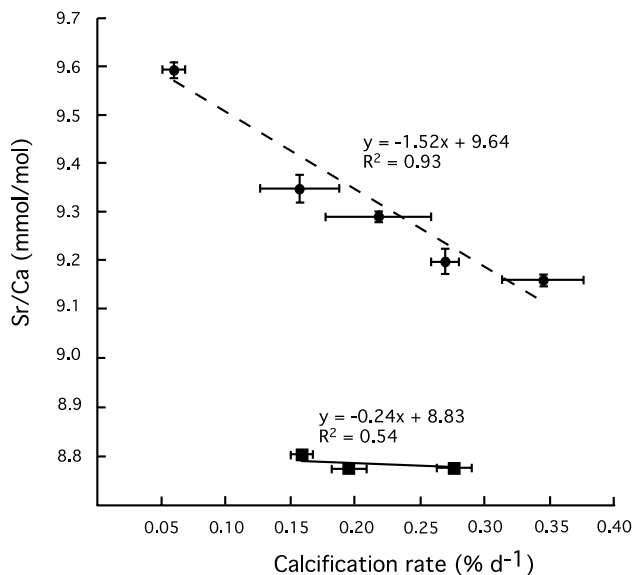


Fig. 8. Sr/Ca measured in the skeleton of *Acropora* sp. as a function of calcification rate. The calcification rate varied when changing either the temperature (circles) or the light level (squares).

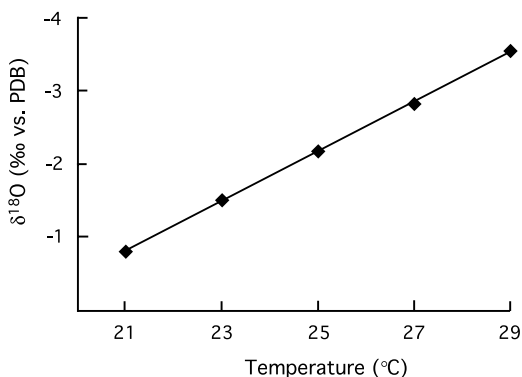


Fig. 9.  $\delta^{18}\text{O}$  measured in the skeleton of *Acropora* sp. as a function of seawater temperature (SE are inside symbols).

## 4. Discussion

The Sr/Ca ratio (Swart, 1981; Aharon, 1991; Beck et al., 1992; de Villiers et al., 1995; Hughen et al., 1999; McCulloch et al., 1999) and the Mg/Ca ratio of coral skeletons (Weber, 1973; Oomori et al., 1982; Oomori et al., 1987) are widely used as proxies for the paleo-SST of the shallow tropical and sub-tropical waters. However, a number of studies have suggested that biological processes (so-called vital effects) modify any straightforward thermodynamic relationship between water temperature and the skeletal concentrations of these trace elements. Indeed, a strong link between the measured Sr/Ca and Mg/Ca ratios and coral growth rate or rate of calcification have been suggested by a number of authors (Weber, 1973; de Villiers et al., 1994; de Villiers et al., 1995; Fallon et al., 1999; Schrag, 1999). Two parameters have been used to quantify the skeletal growth rate: the calcification rate and the linear extension rate. Calcification rate, which is the product of the linear extension rate and the skeletal density (Alibert and McCulloch, 1997) is the most appropriate measure with respect to geochemical proxies because it represents the mass increment of carbonate deposited per unit of time. The calcification rate is known to vary with several environmental factors, such as water temperature and light level (Lough and Barnes, 1997, 2000; Reynaud-Vaganay et al., 2001; Howe and Marshall, 2002; Grottoli et al., 2005), composition of particulate feeding (Grottoli, 2002; Houlbrèque et al., 2003; Houlbrèque et al., 2004), inorganic nutrient input (Ferrier-Pagès et al., 1998; Ferrier-Pagès and Gattuso, 1998) and  $\text{CO}_2$  partial pressure (Reynaud et al., 2004). The majority of previous studies have assessed the effect of skeletal growth on SST proxies by evaluating their data in the context of the linear extension rate (Oomori et al., 1982; de Villiers et al., 1994; de Villiers et al., 1995; Shen et al., 1996; Mitsuguchi et al., 2003). Results obtained with Sr/Ca are controversial, with either a good inverse relationship between the two parameters (de Villiers et al., 1994; de Villiers et al., 1995) or no real correlation observed (Shen et al., 1996; Mitsuguchi et al., 2003). The same lack of clarity exists for Mg/Ca measurements, which have yielded either a negative (Oomori et al., 1982) or no correlation (Mitsuguchi et al., 2003) with linear extension rate. Only two studies have considered directly the effect of calcification rates on SST proxies (Alibert and McCulloch, 1997; Mitsuguchi et al., 2003). In contrast to the present study, these authors did not find a good correlation between calcification rate and the Sr/Ca or the Mg/Ca ratio. This might be due to differences in the way the calcification rate was measured. In these previous studies, the calcification rates were calculated from estimates of linear extension rates and skeletal density derived from measurements on drilled cores. In our experiment, calcification was measured directly from the skeleton deposited during the incubation period and we used the same skeleton for subsequent trace element analyses. In our study, the calcification rate changed by factors of 1.7- and 5.7-fold by changing the light level and the water temperature, respectively.

#### 4.1. Relationships between Mg/Ca, light level, water temperature and calcification rate

Results obtained in this study for Mg/Ca ratio show that there was a good correlation between Mg/Ca and water temperature (Fig. 3). Because of the strong correlation between temperature and calcification rate (Fig. 1), there was also a strong correlation between Mg/Ca and temperature-induced calcification rate (Fig. 5). Increasing the water temperature from 21 to 29 °C, induces a 5.7-fold increase in the rate of calcification (Fig. 1), which induces a 30% increase in the Mg/Ca ratio (Fig. 3). In contrast, by increasing the light level by a factor of 4, the rate of calcification was increased only by a factor of 1.7 (Fig. 2), with a corresponding increase of only a 9% in the Mg/Ca ratio. Thus, the relative change in the calcification rate in the two experiments (5.7 vs. 1.7) scales well with the corresponding relative change in Mg/Ca ratio (30% vs. 9%). It is concluded that the rate of calcification may exert a strong control on the Mg/Ca ratio in the coral skeleton. The calcification rate itself is most strongly controlled by the water temperature (Fig. 1), but the light level experiments (Fig. 2) show that temperature is not the only environmental factor that controls the calcification rate. This is, from a perspective of paleo-environmental applications, unfortunate. The seasonal variations of Mg/Ca observed in several coral species (Hart and Cohen, 1996; Mitsuguchi et al., 1996; Fallon et al., 1999; Schrag, 1999; Alibert et al., 2003) are likely driven by the seasonal changes in calcification rate, but the effect and variability of other environmental parameters have not been evaluated. The 30% change in Mg/Ca observed in this study (driven by the temperature-induced change in calcification rate) is within the range of 26% to 55% change in Mg/Ca ratio observed by Mitsuguchi et al. (1996) and Hart and Cohen (1996) over several seasonal cycles.

Recently, high spatial resolution ion microprobe imaging has demonstrated that the distribution of Mg in the coral skeleton is directly related to the ultra-structural organization of the coral skeleton (Meibom et al., 2004). Fibrous aragonite, which constitutes the bulk of the coral skeleton, is characterized by a layered organization that is the result of the cyclic biomineralization process by which the coral skeleton is formed (Cuif and Dauphin, 2005). The Mg distribution in the skeleton corresponds exactly to this layered organization of the fibrous skeleton and displays corresponding Mg/Ca variations on the order of 50–100% over length scales of a few micrometers (Fig. 10). Certainly, Mg is not incorporated into the skeleton as a passively transported element that simply partitions into the carbonate structure following temperature-driven shifts in a thermodynamic equilibrium between the skeleton and the ambient seawater. In contrast, the micro-scale observations point to a very important and active role of Mg in the skeletal biomineralization process and it has been suggested that Mg is transported actively by the coral, in conjunction with a broad spectrum of mainly acidic

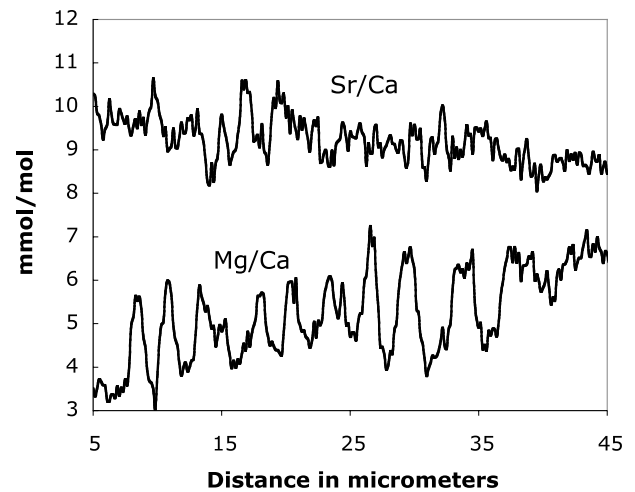


Fig. 10. NanoSIMS analyses of the Mg/Ca and Sr/Ca variations in a *Porites* sp. skeleton (Meibom et al., 2003). The Mg/Ca ratio displays dramatic oscillations (50–100%) that are strongly correlated with the layered organization of the fibrous aragonite skeletal component. In contrast, although the Sr/Ca ratio does display significant variations, it is less variable than the Mg/Ca and not strongly correlated with the skeletal ultra-structure. See Meibom et al. (2004) for analytical details.

organic molecules (Cuif et al., 2004), in order for the coral to control the skeletal growth process, perhaps by temporarily stabilizing amorphous carbonate phases that are suspected to be involved in the calcification process (Meibom et al., 2004). Similarly, a strong biological control on the incorporation of Mg has recently been shown for foraminifera shells (Eggins et al., 2004; Bentov and Erez, 2006), and for estuarine ostracodes (Ito et al., 2003).

#### 4.2. Relationships between Sr/Ca, light level, water temperature and calcification rate

There are several important observations to be made from the Sr/Ca data in Figs. 6–8. A good correlation is observed between Sr/Ca and water temperature (Fig. 6) and, consequently, with the calcification rate induced by temperature changes (Fig. 8). In sharp contrast with the Mg/Ca ratio, a temperature-induced 5.7-fold increase in the calcification rate only induces a 4.5% decrease in the Sr/Ca ratio (as opposed to the 30% increase induced in the Mg/Ca ratio). Furthermore, and also in contrast with the Mg/Ca observations, the Sr/Ca ratio does not change measurably in the light level experiments (Fig. 7). The Sr/Ca ratio does not appear to be sensitive to the light level, or to changes in calcification rate induced by changes in the light level.

For water temperatures above 23 °C the Sr/Ca ratio changes by about -0.03 mmol/mol per °C. This is fairly close to the value obtained from inorganic precipitation experiments (Kinsman and Holland, 1969), but quite different from some Sr/Ca vs. SST calibrations obtained for corals living under natural conditions (Table 1). Table 1 indicates that the apparent temperature sensitivity of the skeletal Sr/Ca ratio might simply be specific to different coral species. From Table 1 it can be seen that *Porites* corals

Table 1  
Calibrations of the Sr/Ca paleo-SST proxy from the literature

Reference	Coral species	<i>b</i>	<i>a</i>
Kinsman and Holland (1969)	Inorganique aragonite	−0.039	10.66
Smith et al. (1979)	<i>Montipora verrucosa</i>	−0.089	11.64
	<i>Porites</i> sp.	−0.070	10.94
	<i>Pocillopora damicornis</i>	−0.071	11.01
	<i>Porites lobata</i>	−0.062	10.48
Beck et al. (1992); Beck et al. (1994)	<i>Porites lobata</i>	−0.080	10.96
de Villiers et al. (1994)	<i>Pocillopora eydouxi</i>	−0.076	11.00
	<i>Pavona clavus</i>	−0.067	10.65
Alibert et al. (1994)	<i>Porites mayeri</i>	−0.075	10.80
de Villiers et al. (1995)	<i>Pavona clavus</i> (6 mm y <sup>−1</sup> )	−0.042	10.25
	<i>Pavona clavus</i> (12 mm y <sup>−1</sup> )	−0.039	10.11
	<i>Pavona clavus</i> (14 mm y <sup>−1</sup> )	−0.033	9.92
	<i>Porites lutea</i>	−0.061	10.50
Mitsuguchi et al. (1996)	<i>Porites lobata</i> , <i>Porites lutea</i>	−0.05	10.29
Shen et al. (1996)	<i>Diploria labyrinthiformis</i>	−0.045	10.10
Cardinal (1996)	<i>Porites</i> sp.	−0.062	10.48
Alibert and McCulloch (1997)	<i>Acropora nobilis</i>	−0.33	18.20
Boiseau et al. (1997)	<i>Porites lutea</i>	−0.061	10.58
Heiss et al. (1997)	<i>Porites lutea</i>	−0.066	10.78
Gagan et al. (1998)	<i>Porites</i> sp.	−0.062	10.70
McCulloch et al. (1994)	<i>Porites lobata</i>	−0.063	10.76
Fallon et al. (1999)	<i>Montastraea annularis</i>	−0.038	9.99
Swart et al. (2002)	<i>Porites</i> sp.	−0.058	10.41
Fallon et al. (2003)			

$$\text{Sr/Ca (mmol/mol)} = b \times T (\text{°C}) + a.$$

generally have Sr/Ca temperature sensitivities greater than about −0.06 mmol/mol per °C, whereas the numbers are generally below −0.04 mmol/mol per °C for *Pavona*. (de Villiers et al., 1995). Katz et al. (1972) conducted experiments with inorganic precipitation of aragonite and found a drop in the solid-liquid partition coefficient for Sr of 10% between 21 and 30 °C. In our study, the Sr/Ca ratio decreases by only 4.5% for an equivalent change in temperature. Assuming that the temperature sensitivity of the Ca solid-liquid partition coefficient cannot make up for the difference, our data indicate that Sr partition coefficients inferred from inorganically precipitated aragonites are not of direct relevance to the composition of the coral skeleton and that there is some level of ‘biological’ control on Sr/Ca ratio in coral skeleton, but that this control is weaker than for Mg. Again, these observations are consistent with micro-analytical observations. Meibom et al. (2004) found that while the Mg distribution is strongly correlated with the skeletal ultra-structure and highly variable, the corresponding Sr distribution is less variable and not strongly correlated with the ultra-structure of the fibrous aragonite (Fig. 10). These observations indicate that Sr is transported from the ambient seawater and incorporated into the skeleton in a manner very different from that of Mg; a conclusion strongly supported by the fact that the temperature-induced change in the Sr/Ca ratio is only 4.5% (Fig. 6), compared with the 30% for Mg/Ca (Fig. 3).

#### 4.3. Sr/Ca and Mg/Ca as paleothermometers

Tables 1 and 2 present a literature survey of Sr/Ca and Mg/Ca calibrations against SST, respectively. Slopes from

these calibrations show large variations, equivalent to 2.5 °C temperature shifts. These variations were explained by differences in the minor-elemental seawater composition (Fallon et al., 2003), or in sampling protocols, or also in coral species. However, different calibrations of Sr/Ca vs. SST are also obtained for the same coral species sampled in different locations of the same reef (Stoll and Schrag, 1998; Crowley, 2000; Enmar et al., 2000). McCulloch and Esat (2000) reported two different Sr/Ca vs. SST calibrations for the same coral species sampled from inshore or mid- to outer-reef sites in the Great Barrier Reef, Australia; it is unlikely that the SST and light levels change much between these two sites. It is therefore clear from Table 1 that factors other than SST affect the Sr/Ca ratio. Nutrient levels and nutrient quality (inorganic vs. organic), water currents and local reef ecology can vary significantly on a local scale and induce biological responses that were not triggered in the present study, but which might have indeed affected the Sr/Ca ratio of the formed skeleton. For example, Meibom et al. (2003) found evidence for large amplitude, monthly cycles in the Sr/Ca ratio of a *Porites* coral from coastal Kenya. Such findings indicate that, besides

Table 2  
Calibrations of the Mg/Ca paleo-SST proxy from the literature

Reference	Coral species	<i>b</i>	<i>a</i>
Mitsuguchi et al. (1996)	<i>Porites</i> sp.	0.129	1.15
Fallon et al. (1999)	<i>Porites lobata</i>	0.088	1.38
Wei et al. (2000)	<i>Porites</i> sp.	0.113	1.60
Fallon et al. (2003)	<i>Porites</i> sp.	0.098	1.54
This study	<i>Acropora</i> sp.	0.138	0.90

$$\text{Mg/Ca (mmol/mol)} = b \times T (\text{°C}) + a.$$

the water temperature, a number of other environmental parameters and cyclic biological processes, such as metabolism and sexual reproduction, can affect the Sr/Ca ratio of the skeleton in a manner that is poorly understood at the moment. The results of our study indicate that bulk Sr/Ca measurements are correlated with water temperature and that the high level of microscale Sr/Ca variability (Fig. 10) measured by ion-probe does not suppress this first-order correlation.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2006.09.009](https://doi.org/10.1016/j.gca.2006.09.009).

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