Light and temperature effects on Sr/Ca and Mg/Ca ratios in a scleractinian coral

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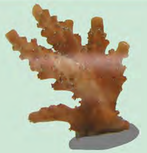

INTRODUCTION

Reconstruction of climatic data from the geologic record is important for validating global climate models. To this end, scleractinian coral skeletal (that contain minor elements such as Sr and Mg) have been used extensively to reconstruct the climatic variability of the recent past.
Correlations have been observed between Sr/Ca or Mg/Ca and SST (Beck et al., 1992; Alibert & McCulloch, 1997; McCulloch et al., 1999). However, recent studies 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, and because of discrepancies between or within different coral species (Allison, 1996). Local variations in the Sr/Ca or Mg/Ca ratios of the seawater have been considered to be the major cause of theses discrepancies. However, micro-analytical studies found the distribution of Sr to be heterogeneously distributed in the coral at the millimeter and micrometer length scales (Allison et al., 2004). Dramatic Sr concentration variations have been found to correspond to individual skeletal components and ultra-structure (Allison, 1996; Hart & 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.
Correlations have also been observed between Sr/Ca or Mg/Ca, and coral extension rates (De Villiers et al., 1994). Previous studies therefore suggest 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 (Hart & Cohen, 1996; Cohen et al., 2001; Allison et al., 2004). Environmental and biological factors are clearly linked and it is therefore difficult to discriminate between the two types of control in the field. This study was set up with the aim to investigate, in a highly controlled laboratory environment, the relative importance of environmental and biological factors for the trace element concentration in the coral skeleton. Specifically, we investigate the effects of light level and water temperature, on the Sr/Ca and Mg/Ca ratio of the skeleton of a sleractinian coral: *Acropora* sp.

MATERIALS & METHODS

Biological material
"Nubbins" (small, live coral samples) of *Acropora* sp. were obtained by cutting terminal portions of branches of a single parent colony and then glued onto glass slides (Reynaud-Vaganay et al., 1999).

Experimental set up
Tanks (30 l) were continuously supplied with Mediterranean seawater (salinity = 38.5) pumped from a depth of 50 m and heated. The water renewal rate was 5 times per day. Light was provided by metal halide lamps (Phillips HPIT, 400 W), photoperiod was 12:12. The duration of the experiments was 12 weeks. During this period, nubbins were fed once a week with *Artemia salina* nauplii.

* For the "light experiment", nubbins were cultivated under 3 light intensities (100, 200 and 400 µmol m^{-2} s^{-1}) and the water temperature was kept constant at 27°C.
* For the "temperature experiment" nubbins were distributed into 5 tanks heated to 21, 23, 25, 27 and 29°C, and the light intensity was kept constant (400 µmol photons m^{-2} s^{-1}).

At the end of each experiment, 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.

Calcification rates: corals were weighed once a week following the buoyant weight technique (Jokiel et al., 1978).

Sr/Ca and Mg/Ca analysis
These ratios were determined 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 matter, coral samples were placed in 30% hydrogen peroxide in plastic vials and sonicated (60 min). The peroxide was replaced and the process was repeated 3 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, 100 mg of the prepared sample was taken up in 2 ml of 2% ultra-pure nitric acid to achieve a dissolved Ca concentration in the range of 15-35 ppm. All samples were run in replicates. External precision of a laboratory standard was ± 0.8% for Sr/Ca and ± 2% for Mg/Ca. The average difference between replicate samples was about 0.05 and 0.07 mmol/mol for Sr/Ca and Mg/Ca respectively.

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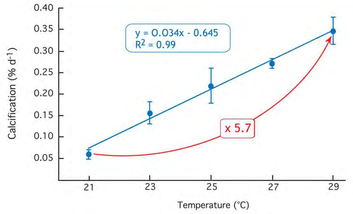

Fig. 1- Calcification rates of nubbins of *Acropora* sp. *vs.* culture seawater temperature (mean ± SE)

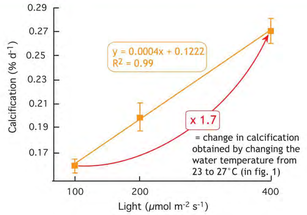

Fig. 2 - Calcification rates of nubbins of *Acropora* sp. *vs.* light level (mean ± SE)

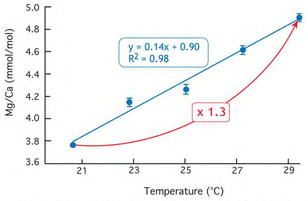

Fig. 3 - Mg/Ca measured in the skeleton of *Acropora* sp. as a function of culture seawater temperature (mean ± SE)

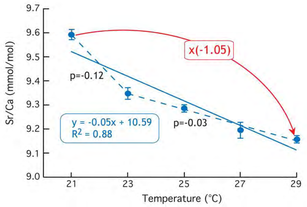

Fig. 6 - Sr/Ca measured in the skeleton of *Acropora* sp. as a function of culture seawater temperature (mean ± SE)

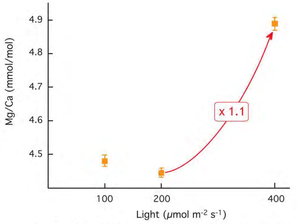

Fig. 4 - Mg/Ca measured in the skeleton of *Acropora* sp. as a function of culture light level (mean ± SE)

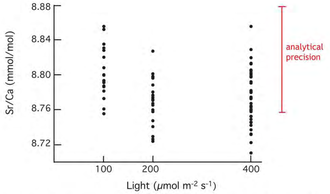

Fig. 7 - Sr/Ca measured in the skeleton of *Acropora* sp. as a function of culture light level (mean ± SE)

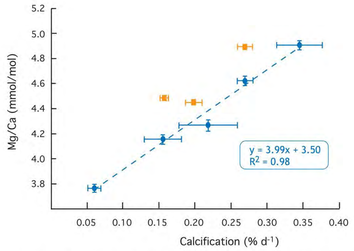

Fig. 5 - Mg/Ca measured in the skeleton of *Acropora* sp. as a function of calcification rate wich varied by changing either the temperature (blue circles) or light (orange squares). The regression was calculated using data from temperature experiment only.

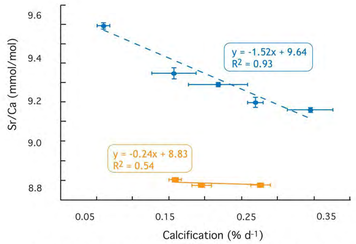

Fig. 8 - Sr/Ca measured in the skeleton of *Acropora* sp. as a function of calcification rate measured by changing either the temperature (blue circles).

RESULTS & DISCUSSION

Presently, the Sr/Ca and the Mg/Ca ratios of coral skeletons are considered to be good proxies for the paleo-temperature of the shallow tropical waters. However, several studies have suggested that biological processes ('vital effects'), modify any thermodynamic relationship between water temperature and the skeletal concentrations of these trace elements. The majority of previous studies have assessed the effect of skeletal growth on SST proxies. Results obtained with Sr/Ca are controversial, with either a good inverse relationship between the two parameters (De Villiers et al., 1994, 1995) or no correlation (Shen et al., 1996; Mitsuguchi et al., 2003). The same lack of clarity exists for Mg/Ca measurements, with 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 & McCulloch, 1997; Mitsuguchi et al., 2003). In contrast to our study, these workers did not find 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 (from estimates of linear extension rates and skeletal density derived from measurements on drilled cores).

Relationships between Mg/Ca and light-level, water temperature and calcification rate

Because of the strong correlation between temperature and calcification rate, there was also a strong correlation between Mg/Ca and temperature-induced calcification rate. In contrast, by increasing the light level by a factor of four, the rate of calcification was increased only by a factor of 1.7, 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 with the corresponding relative change in Mg/Ca ratio (30% vs. 9%). It is concluded that the **primary control over the Mg/Ca ratio in the coral skeleton is the rate of calcification.** Therefore, the seasonal variations of Mg/Ca observed in several coral species (Hart & Cohen, 1996; Mitsuguchi et al., 1996; Alibert et al., 2003) are likely driven by the seasonal changes in calcification rate. The 30% change in Mg/Ca observed here is within the range of 26% to 55% change in Mg/Ca ratio observed by Mitsuguchi et al. (1996) and Hart & Cohen (1996) over several seasonal cycles.
Recently, high spatial resolution ion microprobe imaging has demonstrated that the distribution of Mg in the coral skeleton corresponds exactly to the layered ultra-structural organization of the fibrous skeleton and displays corresponding Mg/Ca variations (Meibom et al., 2004).
Microscale observations point to a very important 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 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). Furthermore, the Mg/Ca ratio of seawater (~5000 mmol/mol) is significantly different from that of the skeleton (3.8 - 4.9 mmol/mol). Together, these observations forces the conclusion that there is a very high degree of biological control of the coral during calcification process. This strong biological control on the incorporation of Mg has also be shown for forminifera shells (Eggins et al., 2004; Bentov & Erez, 2006).

Relationships between Sr/Ca and light-level, water temperature and calcification rate

A temperature-induced 5.7 fold increase in the calcification rate only induces a 5% decrease in the Sr/Ca ratio. 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.
The regression lines calculated for Sr/Ca *vs.* water temperature can be divided into two parts. The slope measured between 21°C and 23°C is four times higher than the slope measured between 23°C and 29°C. 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, but quite different from some Sr/Ca *vs.* SST calibrations obtained from corals living under natural conditions. These data indicate that the level of 'biological' control on Sr/Ca ratio, was weaker than for Mg. Again, these observations are consistent with micro-analytical observations. Meibom et al. (2004) found that the distribution of Sr was less variable than the Mg and not strongly correlated with the ultra-structure of the fibrous aragonite. These results indicate that Sr is transported from the ambient seawater and incorporated into the skeleton in a manner different from that of Mg; a conclusion strongly supported by the fact that the temperature-induced change in the Sr/Ca ratio is only 5%, compared with the 30% for Mg/Ca.
Laboratory experiments indicate that transport of Sr and Ca to the surface of the growing skeleton involves Ca^{2+}-ATPase membrane pumps in the calicoblastic endodermal cell layer. If a significant fraction of Sr and Ca are transported along such similar pathways, increasing the fluxes can lead to a competition in the transport of these two cations. Under such conditions, less Sr will be incorporate into skeleton, leading to a decrease of the ratio.

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