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The significance of geochemical proxies in corals, does size (age) matter?

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Abstract. The main goal of this paper is to determine how size (small vs. large coral heads) and age (juvenile vs. adult) potentially affect geochemical proxies in coral skeleton, widely used in paleoclimate studies. After ensuring that corals are not diagenetically altered, we analyse Sr/Ca, Mg/Ca, $\delta^{18}O$ and $\delta^{13}C$ on 3 cores from two study areas. We compare two different size corals from similar environmental setting in Vanuatu. The smaller coral head, despite presenting a similar seasonal shape pattern that its larger counterpart, presents higher Sr/Ca, potentially interpreted as cooler temperatures. We also study the top and the basement of a ~7m-high massive *Porites* sp. core from New Caledonia that reveal both modern and post-settlement periods. A sharp evolution of the geochemical proxies is seen during the post-settlement period. The differences in between the cores seem unlikely to be caused by environmental factors alone and we argue for biological differences. The implications are important for fossil studies where coral cores are often recovered in small pieces with no age indices (adult or young). Geochemical reconstructions should then be carefully interpreted as ontogenic effects could easily bias the results.

Key words: coral, geochemical proxies, paleoclimate reconstruction

Introduction

Massive coral have received growing attention in paleoclimate studies over the years. Coral carbonate skeletons are useful archives containing multiple proxies that could help reconstructing environmental history. In most coral studies, a calibration phase linking geochemical signals to environmental parameters is achieved on the modern part of a core. Calibration equations are then applied to the whole core (Ourbak 2006) or to a fossil piece (Corrège et al. 2004) to evaluate paleoclimate variability. Calibration studies often invokes thermodynamic laws predicting a temperature-related incorporation of trace elements (Sr/Ca for example) and oxygen isotopes ($\delta^{18}O$) in calcium carbonate (Kinsman and Holland 1969; Weber and Woodhead 1972). Calcification in bioconstructed minerals such as coral aragonite have complex incorporation processes and a “vital” effect is invoked to account for biological effects perturbing the pure thermodynamic relationship (Erez 1978).

Several studies have been conducted on biological effects, but only a few indirectly address the potential impact of coral size or age (different growth stages) on the geochemical signals. However, geochemical composition of several marine carbonate species such as benthic and planktonic foraminifera (Bijma et al. 1998; Hintz et al. 2006), or bivalves (Gillikin et al. 2007) present ontogenic effect. Concerning corals, a potential size-effect on the accuracy of Sr/Ca=f (SST) calibration has been published (Marshall and McCulloch 2002); SST stands for sea surface temperature. A comparison of several coral heads along the Great Barrier Reef produced different calibrations. Marshall and McCulloch (2002) suggested that younger corals are less reliable than larger/older corals because of some physiological difference.

Fossil corals are often recovered out of growth position or as fragments. Thus, it is important to study the potential effect of size/age on skeleton geochemical composition as a potential bias to environmental reconstructions. After ensuring that the cores present pristine aragonite, we interpret geochemical results (Sr/Ca, Mg/Ca, $\delta^{18}O$, $\delta^{13}C$).

First, we address the importance of the size of coral heads. We selected two Vanuatu coral heads of different sizes and compare their Sr/Ca composition. Small coral heads capture temperature signal as well as their larger counterparts but the two series present a systematic difference.

Second, we test the age-effect by determining how reliable are the geochemical signals at the basement of a coral core, corresponding to the post-settlement period. We use a ~7m-high massive colony from New Caledonia. At the bottom of the core, 23-years of distinct banding patterns give crucial information on coral post-settlement period.

Material and Methods

Material

All the cores were recovered by SCUBA, sliced, cleaned in deionized water ultrasonic bath and then air-dried.

Two *Porites lutea* cores from Espiritu Santo, Republic of Vanuatu were sampled. A large (~140 cm long) coral head was cored in 1992 within Malo Channel (15.7ºS, 167.2ºE) and described by Kilbourne et al. (2004a; 2004b). The second colony (22 cm high) was collected by hand in July 1979 offshore of Tasmaloum, 34 km away. Chronology established by band counting on X-rays give ages of 65 years and 11 years, respectively, based on a 2cm/year growth rate for both cores. Even though the two sites are situated in similar oceanic settings, episodic terrestrial inputs during the rainy season (May to September) could be important at Tasmaloum site (F. Taylor, pers communication). These episodes affect salinity signal but are usually hours to daylong and should not affect our monthly sampling resolution.

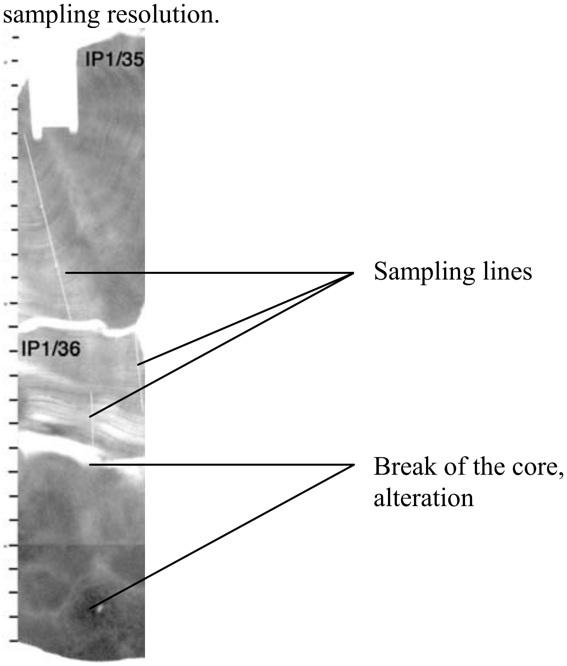

Figure 1: X-Ray of IP1/35 and IP1/36 slices at the very bottom of the New Caledonia coral. Scale on the left: 1 cm in between two ticks. The last 8 cm have been discarded due to absence of clear growth bands and presence of alteration features at the very bottom of the core.

A ~7m-high *Porites sp*. core was collected in 2003 on the outer reef of Ile des Pins, New Caledonia (22.31ºS, 167.25ºE). Results of the more recent 567 cm are discussed in Ourbak (2006). Deeper than 567 cm, about a meter of the core was discarded due to erratic growth patterns. This study focuses on the last two bottom slices (Fig. 1), undated, at the basement of the core, which we expect to correspond to the post-settlement period and the initial growth period of the colony. We chose a constant 0.5 cm per sample (corresponding to a pseudo-half year resolution). A narrow zone of preferential dissolution and complex growth band patterns at the bottom position of the core led us to stop sampling 8 cm before the bottom of the core (slice named IP1/36, Fig. 1).

Methods

Vanuatu Sr/Ca measurements were made using a PerkinElmer Optima 4300 DV ICP-OES (CMS, University of South Florida), following the method for drift corrected from Schrag (1999). An Optima mass spectrometer was used to produce New Caledonia δ^{18}O and δ^{13}C data (UMR EPOC, Université Bordeaux 1). New Caledonia Sr/Ca and Mg/Ca ratio were determined with a PerkinElmer Optima 3000 DV ICP-AES (IRD Nouméa). A Siemens D500 diffractometer and a Cambridge Stereoscan 200 scanning electron microscope were used for XRD analysis and SEM images, respectively, at IRD Bondy Ile de France center.

Results and Discussion

Potential diagenetic alteration

Diagenetic features in corals such as secondary deposition of aragonite needles and dissolution processes alter Sr/Ca, Mg/Ca, δ^{18}O and δ^{13}C values in fossil cores and even in the very recent part of modern cores (Bar-Matthews et al. 1993; Hendy et al. 2007). This could bias paleothermometers by cooling the temperature as much as 5 ºC (Muller et al. 2001).

XRD (not shown here) does not detect calcite and confirms that New Caledonia coral is made of aragonite. Moreover, SEM image (Fig. 2) presents unaltered primary aragonitic needles with no indications of dissolution. In addition, level of correlation between geochemical tracers increase for altered crystals compared to pristine ones (see Quinn and Taylor (2006), for example). We computed correlation coefficients and did not find any increase of the correlation over the bottom samples (Table 1), ruling out any diagenesis impact on New Caledonia coral. Similarly, The Malo channel Vanuatu core has been previously checked (SEM and petrographic microscope) and do not present diagenetic alteration (Kilbourne et al. 2004a).

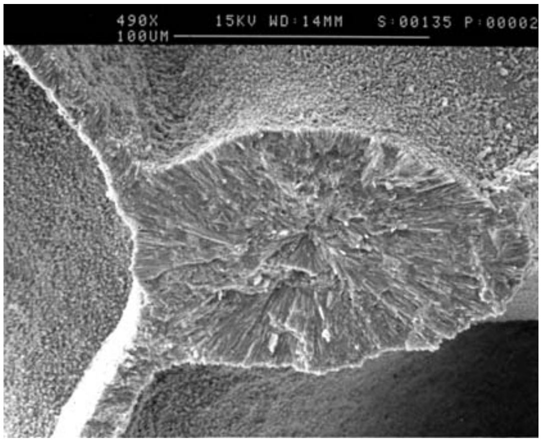

Figure 2: IP1/35 SEM image presents well-preserved dissepiments, broken septa and aragonite needles arguing for a pristine skeletal material, without alteration.

Sr/Ca	*-0.45*	*0.47*	*-0.42*	*-0.60*
-0.04	**Mg/Ca**	*-0.49*	*-0.28*	*-0.14*
0.40	0.07	**δ^{18}O**	*-0.09*	*-0.74*
-0.69	0.07	-0.17	**δ^{13}C**	*0.74*
-0.72	-0.001	-0.77	0.76	**δ^{13}Ct**

Table 1: Correlation coefficients (r) between the different geochemical proxies measured in New Caledonia core ($r > 0.38$, $p < 0.5$, $n = 25$). δ^{13}Ct stands for $\delta^{13}C_{transformed}$, see text for details. Top (modern) samples are on the right side, in italic while bottom (older) are on the left.

Does size matter? The Vanuatu corals

Marshall and McCulloch (2002) found large differences in Sr/Ca=f (SST) calibration equations from the Great Barrier Reef modern coral heads. They suggest that smaller corals produce less reliable calibrations than larger ones and point that "immature or juvenile coral heads are somehow physiologically different from their more mature counterparts, and this is reflected in their intake of trace elements and isotopes." To our knowledge, no other study dealt with the size of coral heads and its potential influence on geochemical signature over the biomineralized inorganic skeleton.

We tested Marshall and McCulloch's hypothesis on the Vanuatu corals. Kilbourne et al. (2004b) published a modern Vanuatu coral record with 65 years of monthly Sr/Ca data that varied with temperature. We sampled a small coral head (26 cm in diameter, 22 cm high) that was removed from the same island (assuming that Sr/Ca is spatially and temporally constant at the timescales studied). The difference between the mean is 0.096 mmol/mol for 3 years (Fig. 4). Reconstructing the SST based on the Kilbourne et al. (2004b) equation (0.05 mmol/mol of Sr/Ca per 1°C), the SST difference between the cores is 1.9°C, with the smaller head recording cooler temperatures. This is the opposite to what one can expect from the coral locations, as the small coral head lived in a more confine environment than the large coral head (bay vs. open water pass). This study tends to agree with Marshall and McCulloch's (2002) hypothesis regarding size effect on coral Sr/Ca composition.

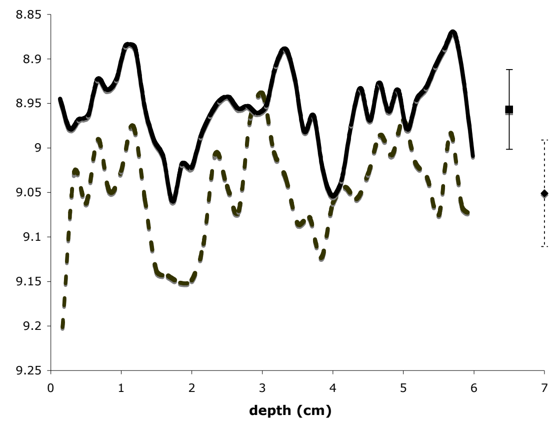

Figure 4: Comparison between Sr/Ca series from a small (dotted line) and a larger Vanuatu coral heads. Mean values are shown with one standard deviation. Sr/Ca scale is inverted to mimic SST.

Does age matter? The New Caledonia coral

Fig. 3 presents geochemical composition (Mg/Ca, Sr/Ca, δ^{13}C and δ^{18}O) of 25 samples from New Caledonia coral. The modern part (top slice) is compared to the basement (bottom slices).

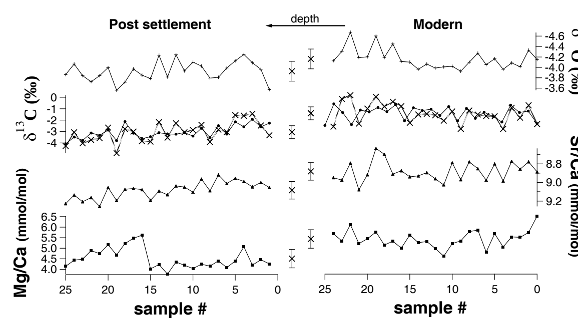

Figure 3: Geochemical data. From bottom to top: Mg/Ca, Sr/Ca, δ^{13}C and $\delta^{13}C_{transformed}$ to remove kinetic effect (crosses, see text for details) and δ^{18}O. The post-settlement period (bottom slices) is on the left and the modern period (top slice) is on the right side. Average values for each series are also shown with one standard deviation, in the center of the figure. 25 samples with half yearly resolution, i.e. ~12.5 years in total, are presented. Sr/Ca and δ^{18}O scales are inverted to mimic sea surface temperature variations.

Concerning the modern period, correlation coefficients between proxies (Table 1) are consistent with previous studies from New Caledonia (Stephans et al. 2004; Ourbak et al. 2006). Sr/Ca and δ^{18}O, anti-correlated to SST, are commonly used as paleothermometers in corals. Mg/Ca varies with temperature (e.g. Mitsuguchi et al. 1996) which explains the negative correlation with Sr/Ca and $\delta^{18}O$ in Table 1.

The post-settlement period has a different geochemistry than the modern section (Fig. 3 and Table 1). For example, the post-settlement period records the Sr/Ca maximum and the $\delta^{13}C$ minimum of the New Caledonia data presented in Fig. 3 but also of the whole core (over 1000 samples), implying that this period was very different from the rest of the coral history. During the post-settlement period, Mg/Ca show no correlation with Sr/Ca and $\delta^{18}O$. Mg/Ca are on average lower during the post-settlement period vs. modern period (4.50 vs. 5.44 mmol/mol). On the contrary, Sr/Ca and $\delta^{18}O$ show higher averages during the post-settlement period (9.08 vs. 8.88 mmol/mol and -3.92 vs. -4.16‰, respectively). All these proxies vary principally with sea surface temperature and reveal cooler values for the bottom of the core. The average Mg/Ca difference between top and bottom, 0.94 mmol/mol, corresponds to a 4.3°C difference (using 0.218 mmol/mol per °C, Ourbak et al. (2006)). A 3.8°C SST variation is recorded in Sr/Ca (using a -0.0528 mmol/mol per °C (Ourbak 2006)) and $\delta^{18}O$ records a 1.5°C difference but this value could be subdued by the salinity influence on $\delta^{18}O$.

Although undated, based on extension rate and the total length of the core, we project the post settlement period ~7 centuries ago. A ~4°C is cooler than any similar record for the last millennium and would equate to the Younger Dryas 4.5°C cooling recorded in a Vanuatu coral (Corrège et al. 2004) (to compare with 1.4°C cooling during the Little Ice Age (1701-1761) period in New Caledonia (Corrège et al. 2001)). This would imply that temperature doesn't have the same effect on Sr, Mg and oxygen isotopes incorporation at the early stage of life of this coral compare to nowadays or that other parameters affect Sr/Ca, Mg/Ca and $\delta^{18}O$.

$\delta^{13}C$ is on average lower during the post-settlement period than the modern period (-3.05 vs. -1.4‰). One plausible factors causing $\delta^{13}C$ difference between New Caledonia slices could be the light-effect and its potential metabolic shift associated. According to several studies (see Ourbak et al submitted, and references therein) the ~7m difference between top and bottom slices could be sufficient to affect $\delta^{13}C$ signal by a 1.4‰ range as shown here (see depth-effects in the $\delta^{13}C$ composition e.g. McConnaughey 1989). This hypothesis alone is appealing but one should keep in mind that $\delta^{13}C$ in coral skeleton is difficult to interpret due to multiple affecting factors (Dissolved Inorganic Carbon, Photosynthesis/ Respiration rate, kinetic and metabolic factors etc). We also present $\delta^{13}C_{transformed}$. A mixture of kinetic isotope effects (resulting in isotopic depletion of carbon relative to isotopic equilibrium) and an equilibrium process control isotopic composition of corals. We applied a simple data transformation to correct for disequilibrium kinetic influences and to emphasize $\delta^{13}C$ metabolic signals only ($\delta^{13}C_{transformed} = \delta^{13}C_{original} - 3*(\delta^{18}O_{original} - \delta^{18}O_{average})$), see Heikoop et al. 2000). $\delta^{13}C_{transformed}$ show that kinetic effects at the early stage of life had the same range of effect on $\delta^{13}C$ signal than later in life (Fig. 3).

An explanation of the results presented here could be that ontogenic effects affect coral geochemical composition. Only a few studies have reported geochemical signature of the time of post-settlement of corals. In a very high resolution study (50 samples per year), Gagan et al. (1996) report on spawning events of two coral heads from two different reefs. A reproductively mature colony from Pandora Reef (6 years of growth at the top of a ~300 years old massive *Porites*) "revealed sharp ^{13}C enrichments closely corresponding to the time of the annual synchronized coral spawning event" and $\delta^{13}C$ and $\delta^{18}O$ signals are in phase. On the contrary, a small colony ~15 years old from Ningaloo Reef present no $\delta^{13}C$ annual variations for the first 6 years and when variations happen, $\delta^{13}C$ is out of phase with $\delta^{18}O$ signal. Gagan et al. (1996) suggest, "$\delta^{13}C$ signature is linked to the chemistry of the early reproductive patterns typical of juvenile massive corals". Thus monotonous $\delta^{13}C$ signature would correspond to years without reproduction, and subsequent shift to greater $\delta^{13}C$ variability would reflect the onset of "adolescence" of the coral, punctuated by brief annual reproductive cycles.

Even if our study misses the very first years of the post-settlement and our sampling resolution does not capture reproductive cycles, the ~2‰ $\delta^{13}C$ increase over the first 25 samples is similar to the one observed by Gagan et al (see Gagan et al 1996, Fig. 1B) concerning the differences between non-reproductive and reproductive years. Based on our preliminary results, we can anticipate that slice IP1/36 does not reflect environmental variability but rather is geochemically affected by early stage of growth and that Sr/Ca, Mg/Ca and $\delta^{18}O$, commonly used as SST proxy reveal erroneous reconstructed temperature.

Preliminary conclusions and implications for coral research.

We compared coral skeleton geochemical composition recorded by two different size Vanuatu corals and by the top and the basement of a New Caledonia core and find in both case large variations.

Mean Sr/Ca show a systematic shift in between small and larger Vanuatu corals. The Sr/Ca, Mg/Ca, $\delta^{18}O$ and $\delta^{13}C$ reveal anomalous values between New Caledonia core sections that are not due to diagenetic perturbations. We propose they are the results of ontogenic effects.

If one apply a calibration equation initiated from a large coral head to a small coral head, as it is often the case in fossils studies, the absolute temperature reconstruction could be biased by as much as 1.9°C based on Vanuatu example. Moreover, in a best-case scenario, when calibration is from the same core, ontogenic effects could alter the geochemistry at the youngest portions, thus introduce a bias in SST reconstruction, as demonstrated in the New Caledonia core.

These findings have important implications for paleoenvironmental studies, as in small coral colonies, as well as juvenile parts, one should be aware of the potential size/age effect and interpret Sr/Ca results in terms of relative changes rather than absolute temperature value. In other words, temperatures reconstructed from a fossil coral not collected in growth position, i.e. without indices of total length or age of the specimen could be biased if the coral has not reached maturity. Could we find a size threshold corresponding to sexual maturity for commonly used coral species? Can we quantify the ontogenic effect to discriminate against climatic factors affecting coral proxies? Numerous questions remain and further studies are needed to better understand biomineralization processes and how ontogenic factors affect the geochemical composition of coral skeleton.

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