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Pretet Chloé[1], Samankassou Elias[1], Felis Thomas[2], Reynaud Stéphanie[3], Böhm Florian[4], Eisenhauer Anton[4], Ferrier-Pagès Christine[3], Gattuso Jean-Pierre[5], Camoin Gilbert[6]

1: Section of Earth and Environmental Sciences, University of Geneva, Rue des Maraîchers 13, CH-1205 Geneva, Switzerland
2: MARUM, Center for Marine Environmental Sciences, University of Bremen, 28359 Bremen, Germany
3: Centre Scientifique de Monaco, Avenue Saint-Martin, 98000, Monaco
4: Helmholtz Zentrum für Ozeanforschung (GEOMAR), Wischhofstr. 1-3, 24148 Kiel, Germany
5: Université Pierre et Marie Curie-Paris 6, Observatoire Océanologique de Villefranche, 06230 Villefranche-sur-Mer, France / CNRS-INSU, Laboratoire d'Océanographie de Villefranche, BP 28, 06234 Villefranche sur-Mer Cedex, France
6 : CEREGE, UMR 6635, CNRS, BP 80, F-13545 Aix en Provence cedex 4, France

Abstract

The present study investigates the influence of environmental (temperature, salinity) and biological (growth rate, inter-generic variations) parameters on calcium isotope fractionation ($\delta^{44/40}Ca$) in scleractinian coral skeleton to better constrain this record. Previous studies focused on the $\delta^{44/40}Ca$ record in different marine organisms to reconstruct seawater composition or temperature, but only few studies investigated corals.

This study presents measurements performed on modern corals from natural environments (from the Maldives for modern and from Tahiti for fossil corals) as well as from laboratory cultures (Centre scientifique de Monaco). Measurements on *Porites* sp., *Acropora* sp., *Montipora verrucosa* and *Stylophora pistillata* allow constraining inter-generic variability.

Our results show that the fractionation of $\delta^{44/40}Ca$ ranges from 0.6 to 0.1‰, independent of the genus or the environmental conditions. No significant relationship between the rate of calcification and $\delta^{44/40}Ca$ was found. The weak temperature dependence reported in earlier studies is most probably not the only parameter that is responsible for the fractionation. Indeed, sub-seasonal temperature variations reconstructed by $\delta^{18}O$ and Sr/Ca ratio using a multi-proxy approach, are not mirrored in the coral's $\delta^{44/40}Ca$ variations. The intergeneric and intrageneric variability among the studied samples are weak except for *S. pistillata*, which shows calcium isotopic values increasing with salinity. The variability between samples cultured at a salinity of 40 is higher than those cultured at a salinity of 36 for this species.

The present study reveals a strong biological control of the skeletal calcium isotope composition by the polyp and a weak influence of environmental factors, specifically temperature and salinity (except for *S. pistillata*). Vital effects have to be investigated in situ to better constrain their influence on the calcium isotopic signal. If vital effects could be extracted from the isotopic signal, the calcium isotopic composition of coral skeletons could provide reliable information on the calcium composition and budget in ocean.

Keywords

Calcium isotopes, Modern/fossil scleractinian corals, Sea surface salinity, Sea surface temperature, Biomineralization

1. Introduction

Calcium is an essential element in many geological and biological processes (see review in DePaolo, 2004). Calcium isotopic fractionation ($\delta^{44/40}Ca$) was studied in various marine organisms including foraminifera (Gussone et *al*., 2003, 2009, 2010; Griffith et *al*., 2008; Hippler et *al*., 2009), coccoliths (Gussone et *al*., 2007; Langer et *al*., 2007), rudists (Immenhauser et *al*., 2005), brachiopods (von Allmen et *al*., 2010), dinoflagellate (Gussone et *al*., 2010) and bivalves (Heinemann et *al*., 2008). These studies revealed a significant relationship between calcium isotopic fractionation and temperature (Nägler et *al*., 2000; Gussone et *al*., 2003), mineralogy (Gussone et *al*., 2005) and inter-generic differences (Gussone et *al*., 2006, 2007). These studies on biogenic calcite or aragonite were extended to experimental precipitates (e.g. Lemarchand et *al*., 2004; Tang et *al*., 2008). Differences in calcium isotopic composition between inorganic and biogenic precipitates were reported (Gussone et *al*., 2006). Calcium isotopic fractionation was used to reconstruct seawater composition and calcium balance in ocean through time (DelaRocha and DePaolo, 2000) but some uncertainties remain. Some studies argue for disequilibrium between outputs and inputs (Zhu and McDougall, 1998), whereas other studies suggest a balanced budget (e.g. Schmitt et *al*., 2003; Fantle & DePaolo 2005). Some modeling studies have proposed that variations of $\delta^{44/40}Ca$ are influenced by secular variations in seawater composition, specifically by shifts from aragonitic to calcitic seas, or carbonate precipitation (Farkas et *al*., 2007a, b). Thus, many uncertainties about calcium isotopic fractionation in biogenic carbonates remain.

Zooxanthellate scleractinian corals are widely used to reconstruct paleoenvironmental changes (e.g. Weber and Woodhead, 1970; Swart, 1983; Gagan et *al*., 2000; Felis and Pätzold, 2003; Corrège, 2006): the oxygen isotopic composition of the skeleton is a proxy for sea surface temperature (SST) and seawater isotopic composition ($\delta^{18}O_{sw}$) (e.g. Cole et *al*., 1993; Linsley et *al*., 1994; Quinn et *al*., 1998; Felis et *al*., 2009); the carbon isotopic composition is used to understand coral physiology ($\delta^{13}C$: e.g. Felis et *al*., 1998; Heikoop et *al*., 2000; Juillet-Leclerc and Reynaud, 2010); in addition, boron isotopic composition appears to be an indicator for pH (e.g. Hönisch et *al*., 2004; Reynaud et *al*., 2004; Pelejero et *al*., 2005; Taubner et *al*., 2010). However the calcium isotopic composition of corals, particularly with respect to inter-specific variations and influences of environmental parameters is poorly constrained (Halicz et *al*., 1999; Chang et *al*., 2004; Böhm et *al*., 2006).

Furthermore, coral skeletons are prone to diagenetic alteration (McGregor and Gagan, 2003; Allison et *al*., 2007; Hathorne et *al*., 2011). Thus, along with potential vital effects that could

affect the isotopic signals recorded in the skeleton, a careful screening for alteration using techniques such as microscopy, powder X-ray diffraction (XRD) and laser ablation ICP-MS is required prior to any analysis or data interpretation (Hathorne et *al*., 2011; Felis et *al.*, 2012). The evaluation of vital effects requires a detailed knowledge of polyp biology and biomechanics including calcification (Cohen and McConnaughey, 2003; Allemand et *al*., 2004; Tambutté et *al*., 2011), calcium pathway through the organism (Wright and Marshall, 1991; Allemand et *al*., 2011), growth rate and other parameters that may influence the isotopic fractionation in the skeleton. Processes involved in coral skeleton calcification are still under debate and there is no consensus regarding the ion pathway from seawater to calcification area (Tambutté et *al*., 1996; Gaetani et *al*., 2011; Tambutté et *al*., 2011). The understanding and quantification of biomineralization require discriminating the influence of environmental factors.

The present study focuses on the biological and environmental parameters that are fundamental in interpreting calcium isotopic signals in coral skeletons, specifically (1) linear extension rate and inter- and intra-generic variations; and (2) sea surface temperature (SST) and sea surface salinity (SSS). The interpretation is based on a systematic investigation of these parameters using coral sample sets from various locations, different ages and genera.

2. Material and methods

2.1. Fossil corals from Tahiti

The fossil coral material was recovered by the Integrated Ocean Drilling Program (IODP) Expedition 310 off Tahiti, French Polynesia, in the central tropical South Pacific Ocean (Fig.1) (Camoin et *al*., 2007). The modern sea surface temperature mean is 27.5 ± 0.2°C and varies between 26.2°C (August) and 28.8°C (March). The modern sea surface salinity mean is around 36. [1982 - 1995. Salinity and temperature data derived from Integrated Global Ocean Services System (IGOSS) Products bulletin; http://iridl.ldeo.columbia.edu/SOURCES/.IGOSS/; Asami et *al*., 2009]. The massive *Porites* sp. coral investigated in the present study (310-M0018A-19R-1W 29-45) was recovered from 115 m below present sea level (33 m below sea floor) at the outer shelf of Maraa located on the south side of the island of Tahiti (Hole M0018A; 17°46.0124'S, 149°32.8433'W, Fig.1). X-radiography of the slabbed coral revealed skeletal density banding with no evidence for

diagenetic cements (Fig. 2). Furthermore, XRD analyses confirmed that the coral skeleton in all samples is pristine (See Felis et *al*., 2012; Deschamps et *al*., 2012). Using a 0.8 mm diameter drill bit, samples were obtained from the coral slab by continuous spot-sampling along the major growth axis, following a single fan of corallites.

2.2. Modern corals from the Maldives

Modern corals from natural environment were collected on 2010 in Maghoodoo Island, the Maldives (Faafu, Nilandhoo atoll, 3°04'49°76"N; 72°57'55°98"E; Fig. 1), northern Indian Ocean. The modern sea surface temperature varies between 28 and 31°C (2005 - 2011 data: area average time series 72°E-73°E, 3°N-3°N (MTMO_SST_9km.CR, Modis Terra, http://disc.sci.gsfc.nasa.gov/giovanni/overview/index.html). Monthly SST was lowest in December-January and highest in April-May (Edwards et *al*., 2001; Ministry of Environment, Energy and Water, 2007). The modern sea surface salinity mean is 35 ± 0.4 (data from 1958-1997, Woodworth, 2005). Coral samples of *Porites* sp., *Acropora* sp., and an unidentified massive coral species were collected at the same date and location along a transect from the lagoon to the open ocean (Fig. 1). Corals were ultrasonicated and rinsed several times, cut in slabs parallel to the growth axis and sampled on the tips using a drill tool and agate mortar. Thin-sections from slab counterparts were checked qualitatively for diagenesis. Microscopic analysis revealed a well-preserved aragonitic skeleton, without diagenetic cements, that was confirmed by the X-radiograph image. Powder XRD analysis performed at the Department of Geosciences, University of Fribourg (Switzerland), indicates that the coral skeleton is 100 % aragonite (authors' unpublished data).

2.3. Cultured corals from Monaco

Colonies of *Acropora* sp., *Stylophora pistillata* and *Montipora verrucosa* were cultured in the laboratory under controlled environmental conditions at different salinities obtained artificially: 36.2 ("36" in the following), 38 and 40 (Table 3). Coral tips were sampled from the same parent colony, glued on glass slides with Epoxy glue (Devcon® UW) and randomly distributed in aquaria with salinities of 38 during ten weeks (Reynaud-Vaganay et *al*., 1999). The corals were fed three times a week with *Artemia salina* nauplii. The aquaria were supplied with Mediterranean seawater pumped from 50 m depth. The seawater renewal rate

was approximately five times per day and the seawater was continuously mixed with a Rena® pump (6 l.min^{-1}). To obtain artificial seawater at salinity 36 from the Mediterranean seawater originally at a salinity of 38, the natural seawater was mixed with distilled water and added with a peristaltic pump in an extra tank before reaching the experimental aquarium. Seawater at salinity 40 was obtained by mixing the Mediterranean seawater and the artificial water prepared with artificial salts to obtain a salinity of 50 (Instant Ocean, Aquarium Systems). The stability of the salinity was checked using a conductivity meter (Mettler LF 196) and recorded continuously. Some of the tips from aquaria maintained at a salinity of 38 were transferred to another aquarium at a salinity of 40 and 36 after ten weeks. All transfers of coral tips were gradual (+ 0.5 salinity units per day) to avoid stress.

$\delta^{18}O_{sw}$ was measured 7, 11 and 5 times in the aquaria at a salinity of 36, 38 and 40, respectively, to test the effect of dilution or artificial salt addition in seawater. Evaporation, which is the main natural process involved in salinity increase, induces a faster removal of lighter isotopes and thus increases $\delta^{18}O_{sw}$. Indeed, the addition of artificial salts, which is the method to increase salinity in the present study, could induce a bias in the geochemical process. Moreover, the addition of freshwater influences the $\delta^{18}O_{sw}$ of the aquaria. However, in experimental setting, these biases cannot be avoided. Seawater was maintained at 27.1 ± 0.1°C using a temperature controller (EW, PC 902/T), and recorded each 10 min with Seamon® recorders (resolution: 0.025°C, precision: ± 0.1°C). Metal halide lamps (Philips HPIT, 400 W) provided irradiance of 204 ± 3 µmol.m^{-2}.s^{-1} on a 12:12 photoperiod. Seawater was continuously aerated with outside air. All parameters were kept constant during the experiment: nutrition, irradiance, pH [8.08: measured with a combined Ross® electrode (Orion 8102SC) according to the Sea Water Scale], total alkalinity (2.6 mEq.kg^{-10}: measured by potentiometric titration) and pCO_2 (adjusted in two buffer tanks using a pH controller (R305, Consort Inc.) (Reynaud-Vaganay et *al*., 1999; Reynaud-Vaganay, 2000).

At the end of the experiment, the skeleton deposited on the glass slide was removed with a scalpel (Reynaud–Vaganay et *al*., 1999), dried overnight at room temperature and stored in glass containers.

2.4. Measurement

Calcium isotopic analysis was conducted at GEOMAR (Kiel, Germany), using thermal ionization mass spectrometer (TIMS Finnigan Triton TI) and double spike (^{43}Ca-^{48}Ca), following the method described in Heuser et *al*. (2002). Samples of about 300 ng Ca,

dissolved in 2 N HCl, were loaded with $TaCl_5$ activator after addition of a ^{43}Ca–^{48}Ca double spike on zone-refined Re single filament. Measurements were made in dynamic mode with $^{40}Ca/^{43}Ca$, $^{42}Ca/^{43}Ca$, and $^{44}Ca/^{43}Ca$ measured in the main cycle and $^{43}Ca/^{48}Ca$ in the second cycle. Five samples and six standards (of which four are NIST SRM 915a and two are CaF_2) were loaded on a turret for 25h duration and each sample was measured three times. Signal intensity during acquisition was typically 4–5 V for ^{40}Ca. The isotope values were expressed relative to NIST SRM 915a as $\delta^{44/40}Ca = ((^{44}Ca/^{40}Ca)_{sample} / (^{44}Ca/^{40}Ca)_{NIST\ SRM\ 915a} - 1) \cdot 1000$ (Eisenhauer et *al*., 2004). $\delta^{44/40}Ca$ values of each session were calculated with the session mean value of the standard NIST SRM 915a. The average precision for NIST SRM 915a during a session was ± 0.08 ‰ (2SEM, N = 4). The long-term (2008-2012) mean $^{44}Ca/^{40}Ca$ of NIST SRM 915a was 0.0211842 ± 0.0000078 (2SD, N = 1006).

$\delta^{18}O$ analyses of the fossil Tahiti coral were carried out at the University of Bremen following established methods (Felis et *al*., 2000; 2004; 2009). Sr/Ca analyses were carried out at the University of Bremen following the methods described in Felis et *al*. (2012) and Giry et *al.* (2012). A 0.20-0.32 mg split of the sample powder that was used for $\delta^{18}O$ analyses was dissolved in 7 mL 2% suprapure HNO_3, containing 1 ppm Sc as internal standard. The calcium concentration of dissolved samples was 5-15 ppm. Measurements were performed on a Perkin-Elmer Optima 3300R simultaneous radial ICP-OES using a CETAC U5000-AT ultrasonic nebulizer. Element wavelengths were detected simultaneously in 3 replicates (Ca 317.933 nm, Ca 422.673 nm, Sr 421.552 nm, Sc 361.383 nm, Mg 280.271 nm). Calcium concentrations measured on an atomic line (422.673 nm) were averaged with the concentrations from an ionic line (317.933 nm) to compensate for possible sensitivity drift in a radial ICP-OES. Calibration standards were diluted from a master standard with a Sr/Ca ratio of 9.099 $mmol.mol^{-1}$. A control standard set had calcium concentrations of 15 ppm and varying Sr concentrations yielding Sr/Ca ratios of 8.6-10 $mmol.mol^{-1}$. Measurements of a laboratory coral standard after each sample allowed offline correction for instrumental drift. Relative standard deviation of the Sr/Ca determinations was better than 0.2%.

$\delta^{18}O$ of cultured coral skeleton from Monaco was measured by gas source mass spectrometer VG-OPTIMA®, using bracketing technique in CEA-CNRS (Laboratoire des Sciences du Climat et de l'Environnement, Gif-sur-Yvette, France) as described by Reynaud-Vaganay (2000). The measurements were expressed relative to PDB standard and the analytical precision was 0.16‰. The oxygen isotopic composition of aquaria seawater samples was measured on a Finnigan MAT 252 and the results expressed relative to SMOW standard. The reproducibility of the seawater $\delta^{18}O$ measurements was 0.05 ‰ (SD).

Aliquots of the same samples were used for both analyses of isotopic ratios and elemental composition ($\delta^{18}O$, $\delta^{44/40}Ca$, Sr/Ca).

3. Results and discussion

$\delta^{44/40}Ca$, standard error of the mean (SEM) and repeats of all sample sets are listed in Table 1 (fossil coral from Tahiti), Table 2 (modern corals from the Maldives) and Table 3 (cultured corals from Monaco). The $\delta^{44/40}Ca$ values ranged between 0.6 and 0.1‰ (Fig. 3); the overall mean $\delta^{44/40}Ca$ was 0.81 ± 0.18 ‰ (2SD), in good agreement with results from previous studies (Böhm et *al*., 2006: 0.81 ± 0.05 ‰).
According to several studies, the calcium isotopic composition of many biogenic carbonates differs from that expected for equilibrium precipitation in the ambient seawater. The result is an offset in isotopic values referred to as "vital effect". Such biologically induced isotope offsets may correlate with growth rate or reflect inter-generic variability as documented in several studies (e.g. McConnaughey, 1989; Cardinal et *al*., 2001; Felis et *al*., 2003; Maier et *al*., 2004). These offsets must be taken into account to extract the environmental signals recorded in coral skeletons. We discuss below the biological effects and environmental parameters likely to influence the calcium isotopic record in corals.

3.1. Linear extension rate and inter-generic comparison of the geochemical record

The seasonal linear extension rate of the fossil *Porites* sp. colony from Tahiti along the micro-sampled transect ranged from 3.4 $mm.yr^{-1}$ (dry and cool season) to 9 $mm.yr^{-1}$ (wet and hot season) and the average linear extension rate was 5.3 $mm.yr^{-1}$. The $\delta^{18}O$ and Sr/Ca analyses of the fossil *Porites* sp. revealed a continuous record of three years of skeletal growth. The seasonal linear extension rate was calculated using the clear seasonal cycles documented in $\delta^{18}O$ and Sr/Ca (Fig. 4). The range of the linear extension rate was comparable to that obtained from previous studies (Lough and Barnes, 2000; Böhm et *al*., 2006; Asami et *al*., 2009). However, the relationship with total skeletal weight and calcification rate, which is related to density, was not investigated in the present study.
The linear extension rate of the fossil Tahiti *Porites* sp. varied by a factor of 2 to 3 depending on the season, but the calcium isotopic composition showed no correlated variation (Fig. 5). This result confirms previous assumptions that growth rate may not explain variations in

$\delta^{44/40}$Ca aragonite of coral skeletons (Böhm et *al*., 2006). This is not in agreement with results obtained from inorganic calcite precipitation experiments, which showed that the precipitation rate strongly influenced the calcium isotopic fractionation, although the trend of the slope remained controversial (Lemarchand et *al*., 2004, Tang et *al*., 2008). Moreover, in the experiments on calcite precipitates, precipitation rate seemed to be controlled by temperature (Tang et *al*., 2008).

Felis et *al*. (2003) have shown that the oxygen isotopic composition in skeletons of *Porites* sp. may be influenced by low extension rate (< 0.6 cm.yr^{-1}). In the present study, no such threshold was found for $\delta^{44/40}$Ca (Fig. 5).

For all genera considered, the $\delta^{44/40}$Ca range was wide and nearly identical, between 0.6 and 0.1 ‰, and no inter-generic difference in calcium isotopic composition among the three different genera studied here was observed (Fig. 3), in agreement with previous results (Böhm et *al*., 2006). However, *Acropora* sp. showed intra-generic differences between different localities. The $\delta^{44/40}$Ca values of *Acropora* sp. from the Maldives (0.95 ± 0.02‰) were significantly higher than those of cultured *Acropora* sp. from Monaco (0.78 ± 0.05‰ in the present study; 0.81 ± 0.05‰ in Böhm et *al*., 2006; ANOVA: p = 0.022, Fig. 3). Such differences can be originated from the different species of *Acropora*. Even though the calcium isotope ratio is higher in samples from the Maldives than in the cultured *Acropora* sp., this difference cannot be explained by morphological differences, as the samples did not exhibit any specific morphological difference according to macroscopic observations. The ultrastructure was not investigated in this study.

However, at different salinities, *S. pistillata* is the only species that shows a distinguishable geochemical signal ($\delta^{44/40}$Ca) between samples subject to same conditions, as discussed below (section 3.2.3, Fig. 9).

3.2. Environmental parameters

3.2.1. Location across the platform: depositional settings

The average $\delta^{44/40}$Ca values of samples for each genus across the platform transect were not significantly different (Kruskal-Wallis H test: H(2) = 3.079, p = 0.214; Fig. 6). However, inter-genera variability was smaller in the reef crest compared to that in the lagoon or the forereef (SD: lagoon = 0.09, reef crest = 0.02 and forereef = 0.11).

Physical and chemical factors, e.g. light, water motion and/or suspended sediments, are known to vary across a carbonate platform (Rex et *al*., 1995; Flügel, 2004). Some of these variations can be recorded in isotopic systems including O and C (e.g. Reynaud-Vaganay et *al*., 2001). However, in the present study, even though the environmental parameters were not monitored quantitatively, the samples were collected in different locations which correspond to different depositional settings (lagoon, reef crest and forereef) exhibiting different environmental conditions (Chester, 2000). Our results show that, in natural conditions, the calcium isotopic composition of the coral skeleton is immune from the environmental variations such as light, sedimentation rate or hydrodynamism across the platform. Therefore, if other parameters such as temperature or salinity influence the composition of coral skeleton, the isotopic record is likely to preserve signals linked to these parameters.
This finding is important for the fossil record because past environmental depositional conditions are difficult to reconstruct with accuracy, possible lateral variations in calcium isotopes across platforms can be excluded, allowing for trustful correlation of sections.

3.2.2. $\delta^{44/40}$Ca record and sea surface temperature

Paleo-SST (°C) was reconstructed from skeletal $\delta^{18}O$ values (‰) and Sr/Ca ratio (mmol.mol^{-1}). The equations used were those applied in previous studies, choosing those currently used for the coral genera analyses and/or the settings studied. For $\delta^{18}O$ proxy, we used the equation of Gagan et *al*. (1998):

(1) $SST = (\delta^{18}O - 0.146) / -0.18$

for the Sr/Ca ratio, the equation of Corrège et *al*. (2006):

(2) $SST = (Sr/Ca - 10.553) / (-0.061)$

The equation of Böhm et *al*. (2006) was applied to reconstruct SST using $\delta^{44/40}$Ca record:

(3) $SST = (\delta 44/40Ca - 0.3) / 0.022$

Although the relationship between SST and $\delta^{44/40}$Ca is widely studied for marine organisms including foraminifera, brachiopods, bivalves and coccoliths, only few previous studies examined this relationship in coral skeleton (Halicz et *al*., 1999; Chang et *al*., 2004; Böhm et *al*., 2006). One of these studies reported a weak but significant positive trend (+0.02 ‰/°C, Böhm et *al*., 2006) although the authors did not recommend the methodology unless the

precision was significantly improved or the temperature variations to be reconstructed exceed 5°C. Since our fossil sample set from Tahiti revealed a pristine skeleton, without evidence of diagenetic cements, and accurate $\delta^{18}O$ and Sr/Ca records, it was interesting to compare these well-constrained proxies with the $\delta^{44/40}Ca$ record.

In the present study, the aim was to compare the reliability of different proxies ($\delta^{18}O$, Sr/Ca and $\delta^{44/40}Ca$) used to reconstruct SST variability. Thus, we considered only the amplitude and not the absolute SST. Indeed, the amplitude of reconstructed $SST_{\delta44/40Ca}$ (15.5°C) was significantly higher than that of $SST_{\delta18O}$ (3°C) and $SST_{Sr/Ca}$ (3°C), from the SST anomaly (deviation from the mean, Fig. 7). Moreover, $SST_{\delta44/40Ca}$ did not reveal the seasonal cycle shown by the other proxies (Fig. 7).

The $SST_{\delta18O}$ and $SST_{Sr/Ca}$ anomalies (Fig. 7), reconstructed from the fossil Tahiti *Porites* sp. are consistent with values from previous studies of modern and fossil Tahiti corals (Cahyarini et *al*., 2008; Asami et *al*., 2009; Felis et al., 2012). The seasonal SST cycles reconstructed in Tahiti by Asami et *al*. (2009) have similar amplitudes at 14.2 (3.0 ± 0.3°C) and 12.4 ka relative to the present (3.3 ± 0.6°C) as the values recorded today by instrumental measurements between 1982 and 1995 (2.8 ± 0.6°C) [Data derived from Integrated Global Ocean Services System (IGOSS) Products bulletin – http://iridl.ldeo.columbia.edu/SOURCES/.IGOSS/; Asami et *al*., 2009]. Our results however show that $SST_{\delta44/40Ca}$ did not correlate with the amplitude of the SST reconstructed from $\delta^{18}O$ and Sr/Ca (Fig. 7). Such large $SST_{\delta44/40Ca}$ variations (15.5°C) appear non-realistic, compared to the SST variations derived from $\delta^{18}O$ (3°C) and Sr/Ca (3°C). Furthermore, Tahiti is located in a tropical area characterized by weak (2.8 ± 0.6°C, 1σ) seasonal average amplitude of SST. The unrealistic SST variations obtained using $\delta^{44/40}Ca$ records (equation 3) confirm that temperature is not the main parameter controlling calcium isotopic fractionation in coral skeleton.

3.2.3. $\delta^{44/40}$Ca record and sea surface salinity

According to the results from Reynaud-Vaganay (2000), *S. pistillata* showed lighter $\delta^{18}O$ than other cultured genera (*Acropora* sp. and *M. verrucosa*) for salinities of 36 and 40. For $\delta^{13}C$, *S. pistillata* showed also lighter values than the other genera. At a salinity of 38, which is the cultured salinity of the parent colonies, these inter-generic differences were minor for $\delta^{13}C$, and nonexistent for $\delta^{18}O$. There was no relationship between salinity and $\delta^{44/40}Ca$ in the cultured corals from Monaco (Fig. 8, ANOVA: p-value = 0.5). Nevertheless, $\delta^{44/40}Ca$ values

of *S. pistillata* samples plotted against salinity reveal a positive trend which was, however, not statistically significant (p-value = 0.14) (Fig. 9). Moreover, the observed ranges of $\delta^{44/40}Ca$ values of the *S. pistillata* colonies increased in parallel with salinity: the range was from 0.68 ± 0.09 to 0.7 ± 0.07 at 36 of salinity and from 0.62 ± 0.04 to 0.98 ± 0.06 at 40 of salinity (Fig. 9). The variability was significantly different at a salinity of 36 compared with 38 or 40, as shown by the F-test (Table 4). Measurement artifacts can be excluded because each measurement was repeated three times and standard errors are smaller at 40, confirming the precision of the measurements (Table 3).

Many studies have used coral $\delta^{18}O$ in combination with Sr/Ca to reconstruct $\delta^{18}O_{sw}$ and SST simultaneously (McCulloch et *al*., 1994; Gagan et *al*., 1998; Le Bec et *al*., 2000; Ren et *al*., 2002; Felis et *al*., 2009). However, in a previous study of modern corals from Tahiti (Cahyarini et *al*., 2008), it was shown that the analytical uncertainties of coral $\delta^{18}O$ (±0.07 ‰) equal the amplitude of the seasonal cycle of $\delta^{18}O_{sw}$ (±0.08 ‰); thereof it was not possible to resolve the seasonal SSS in this area. On the other hand, combining coral $\delta^{18}O$ and Sr/Ca was successfully applied for SSS and SST reconstructions in other tropical locations, e.g. Timor (Cahyarini et *al*., 2008), where the analytical error of $\delta^{18}O_{sw}$ (±0.07 ‰) was smaller than the mean seasonal cycle of $\delta^{18}O_{sw}$ (±0.16 ‰). To avoid potential analytical bias noted in natural conditions, in the present study we examined the influence of salinity on calcium isotopes using cultured corals grown under monitored conditions.

In this study, the coral response to salinity changes as been evaluated by measuring physiological responses, e.g. net photosynthesis, respiration, amount of chlorophyll a (Reynaud-Vaganay, 2000) and geochemical parameters: $\delta^{18}O$, $\delta^{13}C$ and $\delta^{44/40}Ca$. The results reveal that neither the amount of chlorophyll a, nor respiration and photosynthesis were affected by salinity (Reynaud-Vaganay, 2000). This result is in agreement with a previous study, which has shown that corals may be more tolerant than expected to salinity changes (Muthiga and Szmant, 1987). On the contrary, other studies (Moberg et *al*., 1997; Porter et *al*., 1999) showed that the amount of chlorophyll increase and the photosynthesis decrease when salinity reaches 40. However, these studies were conducted on a short time period. During the experimental protocol of the present study, the gradual modification of salinity (+0.5 units per day) did not induce stress to the coral and no abnormal metabolic response was recorded. In the present study, only the effect of hyper-salinity (salinity: 40) could be investigated because the lower salinity level (salinity: 36) was high compared with the values

used in previous studies, e.g. 20 (Downs et *al*., 2009). Furthermore, no gross modifications in the polyp induced by hypo-salinity were recorded.

Nevertheless, the geochemical analyses revealed a noticeable difference in the calcium isotopic composition of *S. pistillata* compared to the other genera (Figs. 8 and 9). Such difference might be due to the fact that *S. pistillata* belongs to the *Pocilloporidae* family whereas *Acropora* sp. and *M. verrucosa* belong to another family (*Acroporidae*). It is worth noting that Ferrier-Pagès et al. (1999) measured a maximal net photosynthesis at 38 of salinity whereas the minimum was reached at 40 of salinity for *S. Pistillata*. In the present study, $\delta^{44/40}$Ca record of *S. pistillata* only showed the least variability at a salinity of 36. The reproducibility of the measurements showed that this feature is not related to an analytical artifact. Since physiological parameters were not affected by salinity changes (Reynaud-Vaganay, 2000) and the other conditions were kept constant, this special geochemical signature revealed in *S. pistillata* may be linked to calcium pathway in the polyp, as calcium isotopic fractionation during the calcium pathway across the polyp may vary upon species or family. Differences in calcium isotopic fractionation between families could reveal different biological sensitivities to salinity, but further investigations are needed, using other genera. As discussed by Tambutté et *al*. (2012) the calcium ion flux from the external seawater across the coral tissue to the site of calcification is controlled by the coral. The ion flux likely follows both a passive paracellular and an active transcellular transport route. The importance of the two routes may depend on physiological conditions, e.g. the permeability of the coral tissue. Böhm et *al*. (2006) suggested that calcium isotope fractionation in scleractinian corals occurs during the transepithelial transport to the calcification site. If this is the case, calcium isotope fractionation may be influenced by the permeability of the coral tissue. However, in the present study, the salinity variation appears not significant enough to influence the permeability.

A better knowledge of calcification processes is, thus, necessary to better constrain which isotope fractionation processes are affected by salinity variations and how sensitivities to salinity changes vary among different scleractinian species. More species could be cultured at a wider range of salinity. Moreover, additional experiments with different duration or with greater variations in steps of salinity changes can be carried out to evaluate the potential influence of stress on coral growth.

4. Biological processes and calcification

Different environmental parameters were tested in this study: SSS, SST and depositional settings across the platform. None of these revealed any unequivocal relationship with $\delta^{44/40}$Ca. Nevertheless, calcium isotopic fractionation was not always constant, as shown by the variations in the *Porites* sp. record from Tahiti (Fig. 4) and the variability in the *S. pistillata* samples grown at different salinities (Fig. 9). Such variations are likely due to intrinsic factors influencing the polyp. Although the processes involved in coral calcification are still under debate, two models reached a consensus. Based on the compartmental model of coral polyp (Tambutté et *al*., 1996), various studies argued for a confined calcifying space, connected periodically with seawater and invoked Rayleigh fractionation to explain the chemical composition of coral skeleton (Cohen and Holcomb, 2009; Gaetani et *al*., 2011). Other studies demonstrated, however, that this calicoblastic space is isolated from seawater and that calcium ions pass through the polyp tissue (Böhm et *al*., 2006; Tambutté, 2010, Allemand et *al*., 2011). The "semi-open calicoblastic space" theory agrees upon the elemental ratio (Mg/Ca, Ba/Ca and Sr/Ca) composition of coral skeleton (Gaetani et *al*., 2011), whereas the "isolated compartment" theory may explain the isotopic composition. Previous experiments to evaluate the influence of pH on calcium isotopic composition in coral skeleton indicate that calcium is not influenced by Rayleigh fractionation (Taubner et *al*., 2010 and pers. comm.) and tended to favour the "isolated compartment" theory.

In the present study, the $\delta^{44/40}$Ca record of *S. pistillata* was increasingly variable between specimens when salinity increases. Such variability argues for a strong influence of the polyp on fractionation during the calcification processes because the colonies grew under identical external conditions. *S. pistillata* seems to be more sensitive to salinity than other genera analyzed and could adapt to these variations without influence on vital processes (e.g. respiration).

To better constrain the causes of the calcium isotope fractionation in coral skeleton, investigations on living corals are needed to locate the site of fractionation and the calcium pathway in the polyp and to evaluate these processes. New methods such the labeling techniques recently used to locate calcein pathways in corals (Tambutté et *al*., 2012) combined with measurement of isotope ratios can be used for this purpose.

5. Conclusion

Coral skeleton composition is widely used for environmental reconstruction and represents a privileged chemical proxy for temperature. However, unlike other biogenic component such as foraminifera, $\delta^{44/40}$Ca signature in coral skeleton was not investigated systematically. By the diversity of parameters and species investigated, this study contributes to improve significantly current knowledge. The main result shows that $\delta^{44/40}$Ca of coral skeleton is immune from any environmental influence whichever the species and the location. However, the variability between colonies cultured under identical conditions increases with salinity for *S. pistillata*. This behavior attests for the importance of biological influences on isotopic fractionation during the calcification process. Once calcium isotopic fractionation behavior on coral is constrained using in situ measurements, the signal can be trustfully used to reconstruct seawater composition and the calcium budget in the ancient ocean. Therefore, additional studies are crucial to better evaluate the contribution of biological processes in calcium isotopic composition of coral skeleton. If the biological influence can be quantified and proves to be a constant factor, the latter can be discriminated and the calcium isotope fractionation can be applied for reconstructions.

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References

Allemand, D., Tambutté, E., Zoccola, D., Tambutté, S., 2011. Coral calcification, cells to reefs, in: Dubinsky, Z., Stambler, N., (Eds.), Coral reefs: an ecosystem in transition. Springer, pp. 119-150

Allemand, D., Ferrier-Pagès, C., Furla, P., Houlbrèque, F., Puverel, S., Reynaud, S., Tambutté, E., Tambutté, S., Zoccola, D., 2004. Biomineralisation in reef-building corals: from molecular mechanisms to environmental control. Palevol 3, 453-467

Allison, N., Finch, A.A., Webster, J.M., Clague, D.A., 2007. Palaeoenvironmental records from fossil corals: the effects of submarine diagenesis on temperature and climate estimates. Geochim. Cosmochim. Acta 71(19), 4693-4703

Asami, R., Felis, T., Deschamps, P., Hanawa, K., Iryu, Y., Bard, E., Durand, N., Murayama, M., 2009. Evidence for tropical South Pacific climate change during the Younger Dryas and the Bølling-Allerød from geochemical records of fossil Tahiti corals. Earth Planet. Sci. Lett. 288(1-2), 96-107

Böhm, F., Gussone, N., Eisenhauer, A., Dullo, W., Reynaud, S., Paytan, A., 2006. Calcium isotope fractionation in modern scleractinian corals, Geochim. Cosmochim. Acta 70(17), 4452-4462

Cahyarini, S.Y., Pfeiffer, M., Timm, O., Dullo, W.C., Schönberg, D.G., 2008. Reconstructing seawater $\delta^{18}O$ from paired coral $\delta^{18}O$ and Sr/Ca ratios: Methods, error analysis and problems, with examples from Tahiti (French Polynesia) and Timor (Indonesia). Geochim. Cosmochim. Acta 72, 2841-2853

Camoin, G.F., Iryu, Y., McInroy, D.B., and the Expedition 310 Scientists, 2007. Proc. IODP, 310: Washington, DC (Integrated Ocean Drilling Program Management International, Inc.), doi:10.2204/iodp.proc.310.2007

Cardinal, D., Hamelin, B., Bard, E., Patzold, J., 2001. Sr/Ca, U/Ca and $\delta^{18}O$ records in recent massive corals from Bermuda: relationships with sea surface temperature. Chem. Geol. 176, 213-233

Chang, V.T.C., Williams, R.J.P., Makishima, A., Belshawl, N.S., O'Nions, R.K., 2004. Mg and Ca isotope fractionation during $CaCO_3$ biomineralisation. Biochem. Biophys. Res. Com. 323(1), 79-85

Chester, R., 2000. Marine geochemistry. Oxford, Blakwell Science, 506p

Cohen, A., Holcomb, M., 2009. Why corals care about ocean acidification? Uncovering the mechanism. Oceanography 22(4), 118-127

Cohen, A., McConnaughey, T., 2003. Geochemical perspectives on coral mineralization, Rev. Miner. Geochem. 54(1), 151-187, doi:10.2113/0540151

Cole, J.E., Fairbanks, R.G., Shen, G.T., 1993. Recent variability in the southern oscillation: Isotopic results from a Tarawa Atoll Coral, Science 260(5115), 1790-1793

Corrège, T., 2006. Sea surface temperature and salinity reconstruction from coral geochemical tracers. Palaeogeogr. Palaeoclim. Palaeoeco. 232(2-4), 408-428, doi:10.1016/j.palaeo.2005.10.014

De La Rocha, C., DePaolo D., 2000. Isotopic evidence for variations in the marine calcium cycle over the Cenozoic. Science 289, 1176-1178

DePaolo, D., 2004. Calcium isotopic variations produces by biological, kinetic, radiogenic and nucleosynthetic processes. Rev. Miner. Geochem. 55, 255-288

Deschamps, P., Durand, N., Bard, E., Hamelin, B., Camoin, G., Thomas, A.L., Henderson, G.M., Okuno, J.i., Yokoyama, Y., 2012. Ice-sheet collapse and sea-level rise at the Bolling warming 14,600 years ago. Nature 483(7391), 559-564

Downs, C.A., Kramarsky-Winter, E., Woodley, C.M., Downs, A., Winters, G., Loya, Y., Ostrander, G.K., 2009. Cellular pathology and histopatology of hypo-salinity exposure on the coral *Stylophora pistillata*. Science Tot. Enviro. 407 (17), 4838-4851

Edwards, A.J., Clark, S., Zahir, H., Rajasuriya, A., Naseer, A., Rubens, J., 2001. Coral bleaching and mortality on artificial and natural reefs in Maldives in 1998, sea surface temperature anomalies and initial recovery. Mar. Poll. Bull. 42(1), 7-15

Eisenhauer, A., Nägler, T., Stille, P., Kramers, J., Gussone, N., Bock, B., Fietzke, J., Hippler, D., Schmitt, A., 2004. Proposal for international agreement on Ca notation resulting from discussions at workshops on stable isotope measurements held in Davos (Goldschmidt 2002) and Nice (EGS-AGU-EUG 2003). Geostand. Geoanal. Res. 28 (1), 149-151

Fantle, M.S., DePaolo, D.J., 2005. Variations in the marine Ca cycle over the past 20 million years. Earth Planet. Sc. Lett 237(1-2), 102-117

Farkas, J., Böhm, F., Wallmann, K., Blenkinsop, J., Eisenhauer, A., Van Geldern, R., Munnecke, A., Voigt, S., Veizer, J., 2007a. Calcium isotope record of Phanerozoic oceans: Implications for chemical evolution of seawater and its causative mechanisms. Geochim. Cosmochim. Acta 71, 5117-5134, doi:10.1016/j.gca.2007.09.004

Farkas, J., Buhl, D., Blenkinsop. J., Veizer. J., 2007b. Evolution of the oceanic calcium cycle during the late Mesozoic: Evidence from $\delta^{44/40}$Ca of marine skeletal carbonates. Earth Planet. Sc. Lett. 253(1-2), 96-111, doi:10.1016/j.epsl.2006.10.015

Felis, T., Pätzold, J., Loya, Y., Wefer, G., 1998. Vertical water mass mixing and plankton blooms recorded in skeletal stable carbon isotopes of a Red Sea coral. J. Geophys. Res. 103(C13), 30731-30739

Felis, T., Pätzold, J., Loya, Y., Fine, M., Nawar, A.H., Wefer, G., 2000. A coral oxygen isotope record from the northern Red Sea documenting NAO, ENSO, and North Pacific teleconnections on Middle East climate variability since the year 1750. Paleoceanography 15, 679-694

Felis, T., Pätzold, J., Loya, Y., 2003. Mean oxygen-isotope signatures in *Porites* spp. corals: inter-colony variability and correction for extension-rate effects. Coral Reefs 22, 328-336

Felis, T., Pätzold, J., 2003. Climate records from corals, in: Wefer, G., Lamy, F., Mantoura, F. (Eds.), Marine science frontiers for Europe. Springer-Verlag Berlin Heidelberg New York Tokyo, pp. 11-27

Felis, T., Lohmann, G., Kuhnert, H., Lorenz, S.J., Scholz, D., Pätzold, J., Al-Rousan, S.A., Al-Moghrabi, S.M., 2004. Increased seasonality in Middle East temperatures during the last interglacial period. Nature 429, 164-168

Felis, T., Suzuki, A., Kuhnert, H., Dima, M., Lohmann, G., Kawahata, H., 2009. Subtropical coral reveals abrupt early-twentieth-century freshening in the western North Pacific Ocean. Geology 37(6), 527-530

Felis, T., Merkel, U., Asami, R., Deschamps, P., Hathorne, E.C., Kölling, M., Bard, E., Cabioch, G., Durand, N., Prange, M., Schulz, M., Cahyarini, S.Y., Pfeiffer, M., 2012. Pronounced interannual variability in tropical South Pacific temperatures during Heinrich Stadial 1. Nat. Commun. 3:965, DOI: 10.1038/ncomms1973

Ferrier-Pagès, C., Gattuso, J.-P., Jaubert, J., 1999. Effect of small variations in salinity on the rates of photosynthesis and respiration of the zooxanthellate coral *Stylophora pistillata*. Mar. Ecol. Prog. Ser. 181, 309-314

Flügel, E., 2004. Microfacies of carbonates rocks: analysis, interpretation and application. Springer, p 976

Gaetani, G.A., Cohen, A.L., Wang, Z., Crusius, J., 2011. Rayleigh-Based, Multi-Element coral thermometry: a biomineralization approach to developing climate proxies. Geochim. Cosmochim. Acta 75 (7), 1920-1932

Gagan, M.K., Ayliffe, L.K., Hopley, D., Cali, J.A., Mortimer, G.E., Chappel, J., McCulloch, M.T., Head, M.J., 1998. Temperature and surface ocean water balance of mid-Holocene tropical western Pacific. Science 279, 1014–1018

Gagan, M.K., Ayliffe. L.K., Beck. J.W., Cole. J.E., Druffel. E.R.M., Dunbar. R.B., Schrag. D.P., 2000. New views of tropical paleoclimates from corals. Quaternary Sci. Rev. 19(1-5), 45-64

Giry, C. Felis, T., Kölling, M., Scholz, D., Wei, W., Lohmann, G., Scheffers, S., 2012. Mid- to late Holocene changes in tropical Atlantic temperature seasonality and interannual to multidecadal variability documented in southern Caribbean corals. *Earth Planet. Sci. Lett.* 331–332, 187-200

Griffith, E.M., Paytan, A., Kozdon, R., Eisenhauer, A., Ravelo, A.C., 2008. Influences on the fractionation of calcium isotopes in planktonic foraminifera. Earth Planet. Sci. Lett. 268 (1-2), 124-136, doi:10.1016/j.epsl.2008.01.006

Gussone, N., Eisenhauer, A., Heuser, A., Dietzel, M., Bock, B., Böhm, F., Spero, H. J., Lea, D. W., Bijma, J., Nägler, T., 2003. Model for kinetic effects on calcium isotope fractionation (δ^{44}Ca) in inorganic aragonite and cultured planktonic foraminifera. Geochim. Cosmochim. Acta 67(7), 1375-1382, doi:10.1016/S0016-7037(02)01296-6

Gussone, N., Böhm, F., Eisenhauer, A., Dietzel, M., Heuser, A., Teichert, B. M., Reitner, J., Wörheide, G., Dullo, W., 2005. Calcium isotope fractionation in calcite and aragonite. Geochim. Cosmochim. Acta 69(18), 4485-4494, doi:10.1016/j.gca.2005.06.003

Gussone, N., Langer, G., Thoms, S., Nehrke, G., Eisenhauer, A., Riebesell, U., Wefer, G., 2006. Cellular calcium pathways and isotope fractionation in *Emiliania huxleyi*. Geology 34(8), 625-628, doi:10.1130/G22733.1

Gussone, N., Langer, G., Geisen, M., Steel, B.A., Riebesell, U., 2007. Calcium isotope fractionation in coccoliths of cultured *Calcidiscus leptoporus*, *Helicosphaera carteri*, *Syracosphaera pulchra* and *Umbilicosphaera foliosa*. Earth Planet. Sci. Lett. 260(3-4), 505-515, doi:10.1016/j.epsl.2007.06.001

Gussone, N., Hönisch, B., Heuser, A., Eisenhauer, A., Spindler, M., Hemleben, C., 2009. A critical evaluation of calcium isotope ratios in tests of planktonic foraminifers. Geochim. Cosmochim. Acta 73, 7241-7255

Gussone, N., Zonneveld, K., Kuhnert, H., 2010b. Minor element and Ca isotope composition of calcareous dinoflagellate cysts of cultured *Thoracosphaera heimii*. Earth Planet. Sci. Lett. 289(1-2), 180-188

Halicz, L., Galy, A., Belshawl, N.S., O'Nions, R.K., 1999. High-precision measurement of calcium isotopes in carbonates and related materials by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). J. Anal. Atom. Spectrom. 14, 1835-1838

Hathorne, E.C., Felis, T., James, R.H., Thomas, A., 2011. Laser ablation ICP-MS screening of corals for diagenetically affected areas applied to Tahiti corals from the last deglaciation. Geochim. Cosmochim. Acta 75(6), 1490-1506

Heikoop, J.M., Dunn, J.J., Risk, M.J., Schwarcz, H.P., McConnaughey, T.A., Sandeman, I.M., 2000. Separation of kinetic and metabolic isotope effects in carbon-13 records preserved in reef coral skeletons. Geochim. Cosmochim. Acta 64(6), 975-987

Heinemann, A., Fietzke, J., Eisenhauer, A., Zumholz, K., 2008. Modification of Ca isotope and trace metal composition of the major matrices involved in shell formation of *Mytilus eduli*. Geochem. Geophy. Geosy. 9(1), Q01006

Heuser, A., Eisenhauer, A., Gussone, N., Bock, B., Hansen, B. T., Nägler, T., 2002. Measurement of calcium isotopes ($\delta^{44}Ca$) using a multicollector TIMS technique. Int. J. Mass. Spectrom. 220, 387–399

Hippler, D., Kozdon, R., Darling, K., Eisenhauer, A., Nägler, T., 2009. Calcium isotopic composition of high-latitude proxy carrier *Neogloboquadrina pachyderma* (sin.). Biogeosciences 6(1), 1-14

Hönisch, B., Hemming, N.G., Grottoli, A.G., Amat, A., Hanson, G.N., Bijma, J., 2004. Assessing scleractinian corals as recorders for paleo-pH: Empirical calibration and vital effects. Geochim. Cosmochim. Acta 68(18), 3675-3685

Immenhauser, A., Nägler, T., Steuber, T., Hippler, D., 2005. A critical assessment of mollusk $^{18}O/^{16}O$, Mg/Ca, and $^{44}Ca/^{40}Ca$ ratios as proxies for Cretaceous seawater temperature seasonality. Palaeogeogr. Palaeoclim. Palaeoeco. 215, 221-237

Juillet-Leclerc, A., Reynaud, S., 2010. Light effects on the isotopic fractionation of skeletal oxygen and carbon in the cultured zooxanthellate coral, *Acropora*: implications for coral-growth rates. Biogeosciences 7, 893-906

Langer, G., Gussone, N., Nehrke, G., Riebesell, U., Eisenhauer, A., Thoms, S., 2007. Calcium isotope fractionation during coccolith formation in *Emiliania huxleyi*: Independence of growth and calcification rate. Geochem. Geophy. Geosy. 8(5), Q05007

Le Bec, N., Juillet-Leclerc, A., Corrège, T., Blamart, D., Delcroix, T., 2000. A coral $\delta^{18}O$ record of ENSO driven sea surface salinity variability in Fiji (south-western tropical Pacific). Geophy. Res. Lett. 27(23), 3897-3900

Lemarchand, D., Wasserburg, G., Papanastassiou, D., 2004. Rate-controlled calcium isotope fractionation in synthetic calcite. Geochim. Cosmochim. Acta 68(22), 4665-4678, doi:10.1016/j.gca.2004.05.029

Linsley, B.K., Dunbar, R., Wellington, G.M., Mucciarone, D.A., 1994. A coral-based reconstruction of Intertropical Convergence Zone variability over Central America since 1707. J. Geophys. Res. 99(C5), 9977-9994

Lough, J.M., Barnes, D.J., 2000. Environmental controls on growth of the massive coral *Porites*. J. Exp. Mar. Biol. Ecol. 245, 225-243

Maier, C., Felis, T., Pätzold, J., Bak, R.P.M., 2004. Effect of skeletal growth and lack of species effects in the skeletal oxygen isotope climate signal within the coral genus *Porites*. Mar. Geol. 207(1-4), 193-208

McConnaughey, T., 1989. ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns. Geochim. Cosmochim. Acta 53,151-162

McCulloch, M.T., Gagan, M.K., Mortimer, G.E., Chivas, A.R., Isdale, P.J., 1994. A high-resolution Sr/Ca and $\delta^{18}O$ coral record from the Great Barrier Reef, Australia and the 1982–1983 El Nino. Geochim. Cosmochim. Acta 58, 2747–2754

McGregor, H.V., Gagan, M.K., 2003. Diagenesis and geochemistry of Porites corals from Papua New Guinea: Implications for paleoclimate reconstruction Geochim. Cosmochim. Acta 67(12), 2147-2156

Ministry of Environment, Energy and Water, 2007. http://unfccc.int/resource/docs/napa/mdv01.pdf

Moberg, F., Nyström, M., Kautsky, N., Tedengren, M., Jarayabhand, P., 1997. Effect of reduced salinity on the rates of photosynthesis and respiration in the hermatypic corals *Porites lutea* and *Pocillopora damicornis*. Mar. Ecol. Prog. Ser. 157, 53-59

Muthiga, N.A., Szmant, A.M., 1987. The effects of salinity stress on the rates of aerobic respiration and photosynthesis in the hermatypic coral *Siderastrea siderea*. Biol. Bull. 173(3), 539-551

Nägler, T., Eisenhauer, A., Müller, A., Hemleben, C., Kramers,, J., 2000. The $\delta^{44}Ca$-temperature calibration on fossil and cultured *Globigerinoides sacculifer* : new tool for reconstruction of past sea surface temperatures. Geochem. Geophy. Geosy. 1(9), 1052, 9pp

Pelejero, C., Calvo, E., McCulloch, M., Marshall, J.F., Gagan, M.K., Lough, J.M., Opdyke, B.N., 2005. Preindustrial to modern interdecadal variability in coral Reef pH. Science 309, 2204-2207

Porter, J.W., Lewis, S.K., Porter, K.G., 1999. The effect of multiple stressors on the Florida Keys coral reef ecosystem: A landscape hypothesis and a physiological test. Limnol. Oceanogr. 44(3, part 2), 941-949

Quinn, T.M., Crowley, T.J., Taylor, F.W., Henin, C., Joannot, P., Join, Y., 1998. A multicentury stable isotope record from a New Caledonia coral: interannual and decadal sea surface temperature variability in the Southwest Pacific since 1657 AD. Paleoceanography 13(4), 412–426

Ren, L., Linsley, B.K., Wellington, G.M., Schrag, D.P., Hugh-Guldberg, O., 2002. Deconvolving the $\delta^{18}O$ seawater component from subseasonal coral $\delta^{18}O$ and Sr/Ca at Rarotonga in the southwestern subtropical Pacific for the period 1726 to 1997. Geochim. Cosmochim. Acta 67, 1609–1621

Rex, A., Montebon, F., Yap, H.T., 1995. Metabolic responses of the scleractinian coral *Porites cylindrica Dana* to water motion: I. Oxygen flux studies. J. Exp. Mar. Biol. Ecol. 186(1), 33-52

Reynaud, S., Ferrier-Pagès, C., Boisson, F., Allemand, D., Fairbanks, R.G., 2004. Effect of light and temperature on calcification and strontium uptake in the scleractinian coral *Acropora verweyi*. Mar. Ecol. Progr. Ser. 279, 105-112

Reynaud-Vaganay, S., Gattuso, J.P., Cuif, J.P., Jaubert, J., Juillet-Leclerc, A., 1999. A novel culture technique for scleractinian corals: application to investigate changes in skeletal $\delta^{18}O$ as a function of temperature. Mar. Ecol. Progr. Ser. 180, 121-130

Reynaud-Vaganay, S., 2000. Contrôle environnemental de la physiologie et de la composition isotopique du squelette des Scléractiniaires à zooxanthelles : approche expérimentale. Thèse de Doctorat, Université de Nice-Sophia Antipolis, 215 p.

Reynaud-Vaganay, S., Juillet-Leclerc, A., Jaubert, J., Gattuso, J.P., 2001. Effect of light on skeletal $\delta^{13}C$ and $\delta^{18}O$, and interaction with photosynthesis, respiration and calcification in two zooxanthellate scleractinian corals. Palaeogeogr. Palaeoclim. Palaeoecol. 175, 393-404

Schmitt, A., Chabaux, F., Stille, P., 2003. The calcium riverine and hydrothermal isotopic fluxes and the oceanic calcium mass balance. Earth Planet. Sci. Lett. 213(3-4), 503-518, doi:10.1016/S0012-821X(03)00341-8

Swart, P.K., 1983. Carbon and oxygen isotope fractionation in scleractinian corals: a review. Earth Sci. Rev. 19, 51-80.

Tambutté, E., Allemand, D., Mueller, E., Jaubert, J., 1996. A compartimental approach to the mecanism of calcification in hermatypic corals. J. Exp. Biol. 199, 1029-1041

Tambutté, S., 2010. How is biomineralization controlled in corals? An open question… Euro ISRS Symposium, Wageningen, P.KL-5, 29

Tambutté, S., Holcomb, M., Ferrier-Pagès, C., Reynaud, S., Tambutté, E., Zoccola, D., Allemand, D., 2011. Coral biomineralization: from the gene to the environment. J. Exp. Mar. Bio. Ecol. 408, 58-78

Tambutté, E., Tambutté, S., Segonds N., Zoccola D., Venn A., Erez J., Allemand D., 2012. Calcein labelling and electrophysiology: insights on coral tissue permeability and calcification. Proc. R. Soc. B. 279, 19-27

Tang, J., Dietzel, M., Böhm, F., Köhler, S., Eisenhauer, A., 2008. Sr^{2+}/Ca^{2+} and $^{44}Ca/^{40}Ca$ fractionation during inorganic calcite formation: II. Ca isotopes. Geochim. Cosmochim. Acta 72(15), 3733-3745, doi:10.1016/j.gca.2008.05.033

Taubner, I., Böhm, F., Fietzke, J., Eisenhauer, A., Garbe-Schoenberg, C., Erez, J., 2010. Influence of pH and temperature on elemental and isotopic composition of cultured scleractinian corals AGU, San Francisco, #PP11C-1450

Von Allmen, K., Nägler, T.F., Pettke, T., Hippler, D., Griesshaber, E., Logan, A., Eisenhauer, A., Samankassou, E., 2010. Stable isotope profiles (Ca, O, C) through modern brachiopod shells of *T. septemtrionalis* and *G. vitreus*: implications for Ca isotope paleo-ocean chemistry. Chem. Geol. 269 (3-4), 210-219

Weber, J.N., Woodhead, P.M.J., 1970. Carbon and oxygen isotope fractionation in the skeletal carbonate of reef-building corals. Chem. Geol. 6, 93-117

Woodworth, P.L., 2005. Have there been large recent sea level changes in the Maldives Islands? Glo. Pla. Cha. 49, 1-18

Wright, O., Marshall, A.T., 1991. Calcium transport across the isolated oral epithelium of scleractinian corals. Coral reefs 10(1), 37-40

Zhu, P., MacDougall, J.D., 1998. Calcium isotopes in the marine environment and the oceanic calcium cycle. Geochim. Cosmochim. Acta 62(10), 1691-1698

Figure captions:

Fig. 1: Geographic location of the samples studied (A.): The Maldives (B.1), Maghoodoo Island (B.2), along with the sampled transect (C.) and Tahiti (D.1) along with the location of IODP Hole M0018A (D.2, E) that coral samples originated from.

Fig. 2: Fossil *Porites* sp. from Tahiti (310-M0018A-19R-1W 29-45), X-radiograph positive image and location of the samples on the slab [black dots, from number 1 (bottom) to 25 (top)].

Fig. 3: $\delta^{44/40}$Ca (± 2SEM) data from different genera and different data sets. Stars: fossil corals from Tahiti (this study), filled circles: modern corals from the Maldives (this study), open circles and triangles: corals cultured in monitored conditions in Monaco (respectively: this study and Böhm et *al*., 2006), cross: modern corals from the Red Sea (Böhm et *al*., 2006), diamonds: modern corals from Galapagos (Böhm et *al*., 2006; N=1).

Fig. 4: δ^{18}O (open circles), $\delta^{44/40}$Ca (± 2SEM) (stars) and Sr/Ca (filled circles) records of fossil *Porites* sp. plotted as the samples according to their position in the coral slab (cf. Fig. 2).

Fig. 5: $\delta^{44/40}$Ca (± 2SEM) of the fossil coral *Porites* sp. from Tahiti plotted against the seasonal linear extension rate.

Fig. 6: $\delta^{44/40}$Ca (± 2SEM) of the modern corals from the Maldives plotted against the location of the samples across the platform.

Fig. 7: Reconstructed Tahiti coral SST anomaly (deviation from the mean) reconstructed using δ^{18}O, $\delta^{44/40}$Ca and Sr/Ca. Open circles represent the SST anomaly reconstructed using the equation from Gagan et *al*. (1998); filled squares, using the equation from Corrège et *al*. (2006) and stars, using equation from Böhm et *al*. (2006).

Fig. 8: $\delta^{44/40}$Ca (± 2SEM) of the cultured corals from Monaco: *Acropora* sp. (squares), *S. pistillata* (circles), *M. verrucosa* (diamonds) plotted against salinity 36, 38, 40.

Fig. 9: $\delta^{44/40}$Ca (± 2SEM) of *S. pistillata* cultured in Monaco plotted against salinity 36, 38, 40 (stars symbols). Circles represent the mean of the sample for each salinity.

Table caption :

Table 1 : Calcium isotope values of fossil *Porites* sp. from Tahiti

Table 2: Location on transect and calcium isotope values of modern corals from the Maldives

Table 3: Salinity and calcium isotope values of cultured corals from Monaco

Table 4: Results of the F-test that reveal the variability between $\delta^{44/40}$Ca of the samples when salinity increases for *S. pistillata*

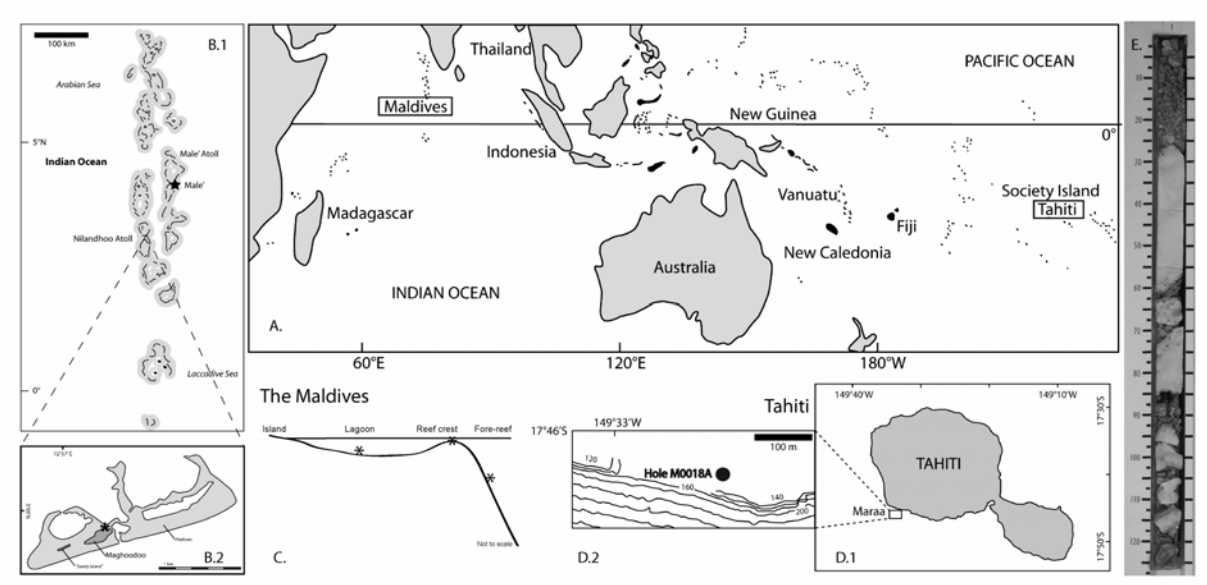
B.1
100 km
Arabian Sea
5°N
Indian Ocean
Male' Atoll
Male'
Nilandhoo Atoll
Laccadive Sea
0°
B.2
Maghoodoo
A.
Thailand
Maldives
Indonesia
New Guinea
PACIFIC OCEAN
0°
Madagascar
Vanuatu
Fiji
Society Island
Tahiti
New Caledonia
Australia
INDIAN OCEAN
60°E
120°E
180°W
E.
The Maldives
Island
Lagoon
Reef crest
Fore-reef
Not to scale
C.
Tahiti
149°33'W
17°46'S
100 m
Hole M0018A
120
160
140
200
D.2
149°40'W
149°10'W
17°30'S
17°50'S
TAHITI
Maraa
D.1

Fig. 1

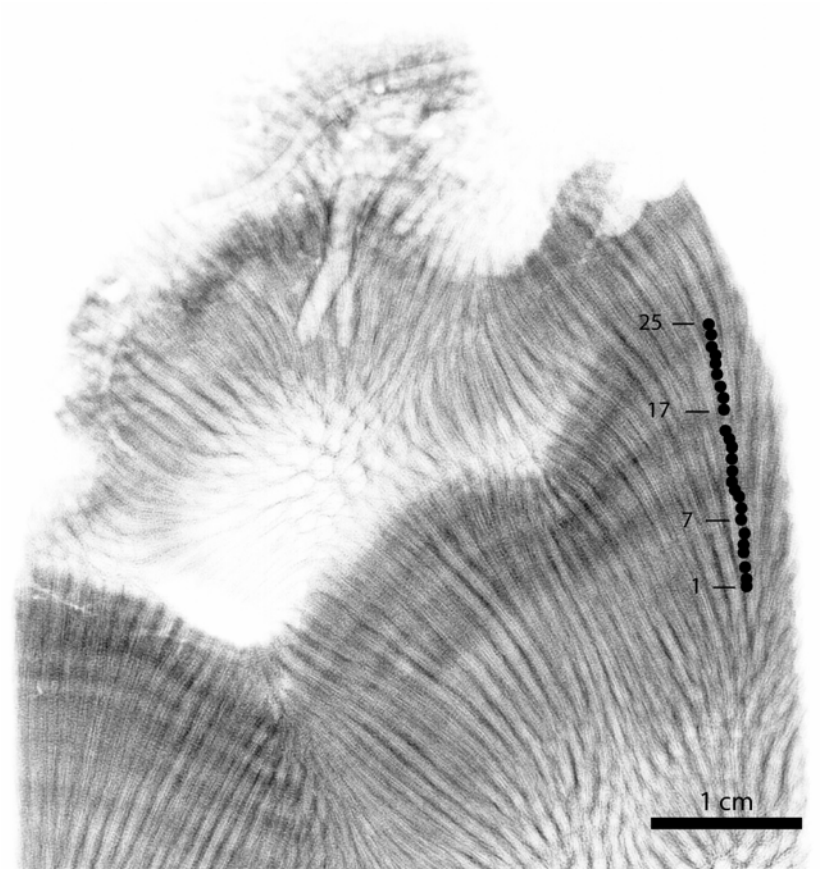

Fig. 2

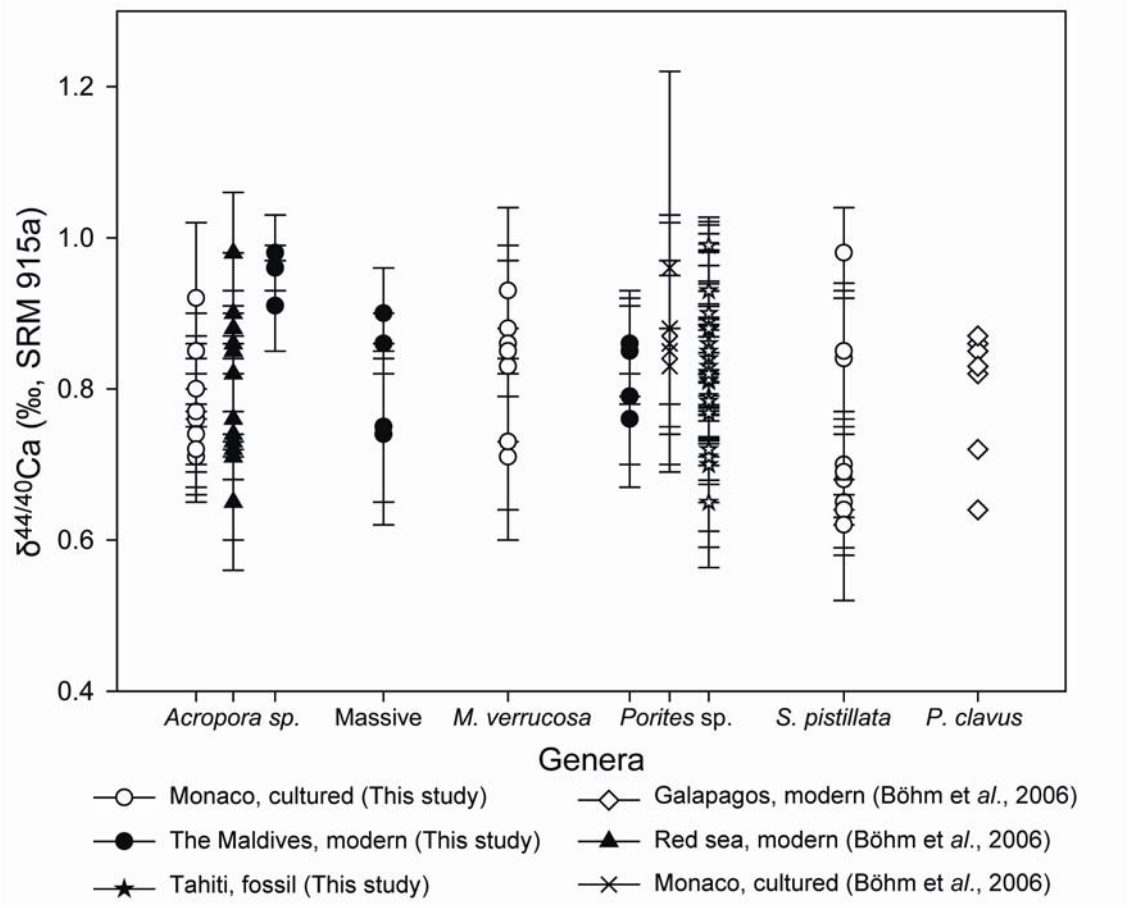
1.2
1.0
0.8
0.6
0.4
δ44/40Ca (‰, SRM 915a)
Acropora sp.
Massive
M. verrucosa
Porites sp.
S. pistillata
P. clavus
Genera
Monaco, cultured (This study)
The Maldives, modern (This study)
Tahiti, fossil (This study)
Galapagos, modern (Böhm et al., 2006)
Red sea, modern (Böhm et al., 2006)
Monaco, cultured (Böhm et al., 2006)

Fig. 3

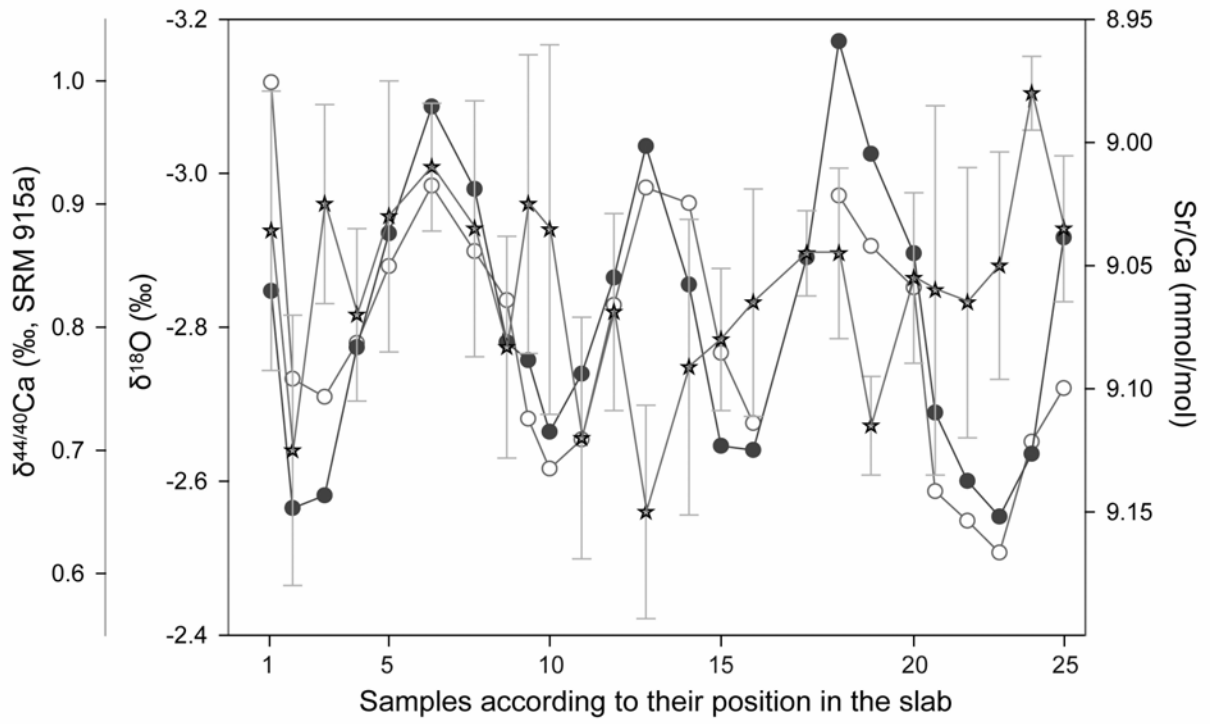
δ44/40Ca (‰, SRM 915a)
δ18O (‰)
Sr/Ca (mmol/mol)
Samples according to their position in the slab
1.0
0.9
0.8
0.7
0.6
-3.2
-3.0
-2.8
-2.6
-2.4
8.95
9.00
9.05
9.10
9.15
1
5
10
15
20
25

Fig. 4

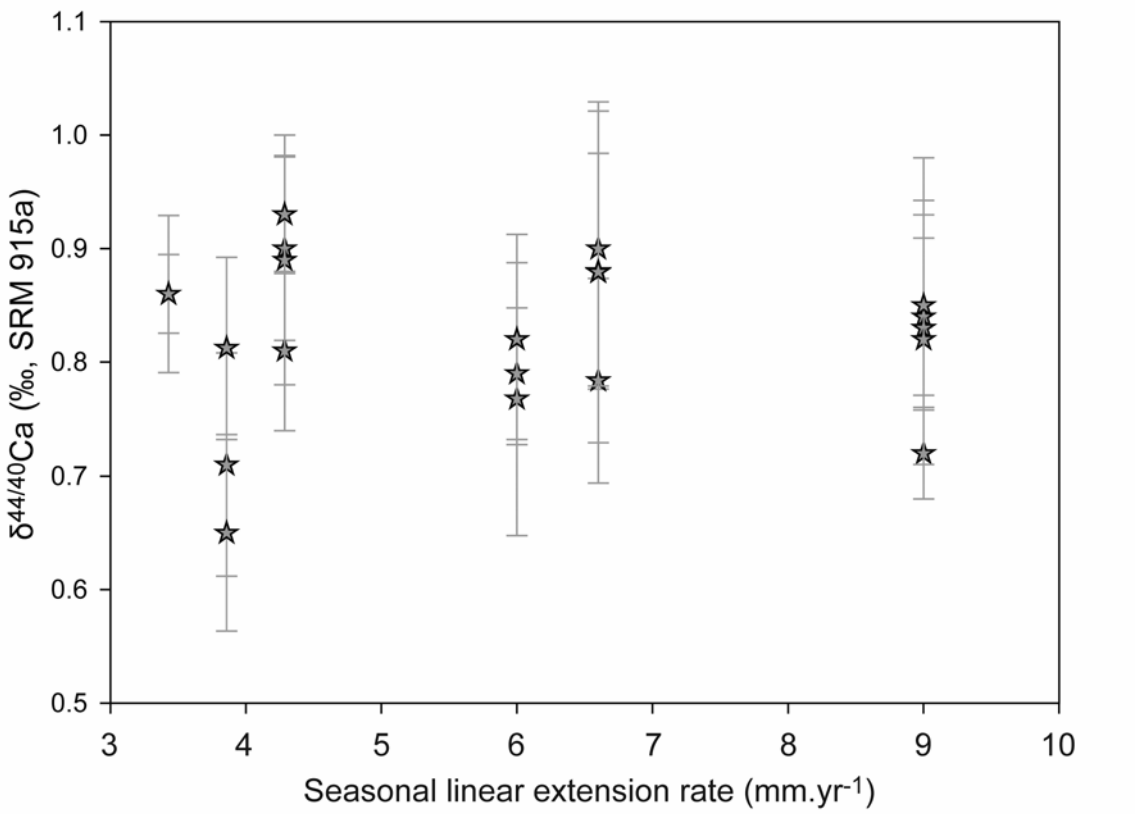
1.1
1.0
0.9
0.8
0.7
0.6
0.5
δ44/40Ca (‰, SRM 915a)
3
4
5
6
7
8
9
10
Seasonal linear extension rate (mm.yr-1)

Fig. 5

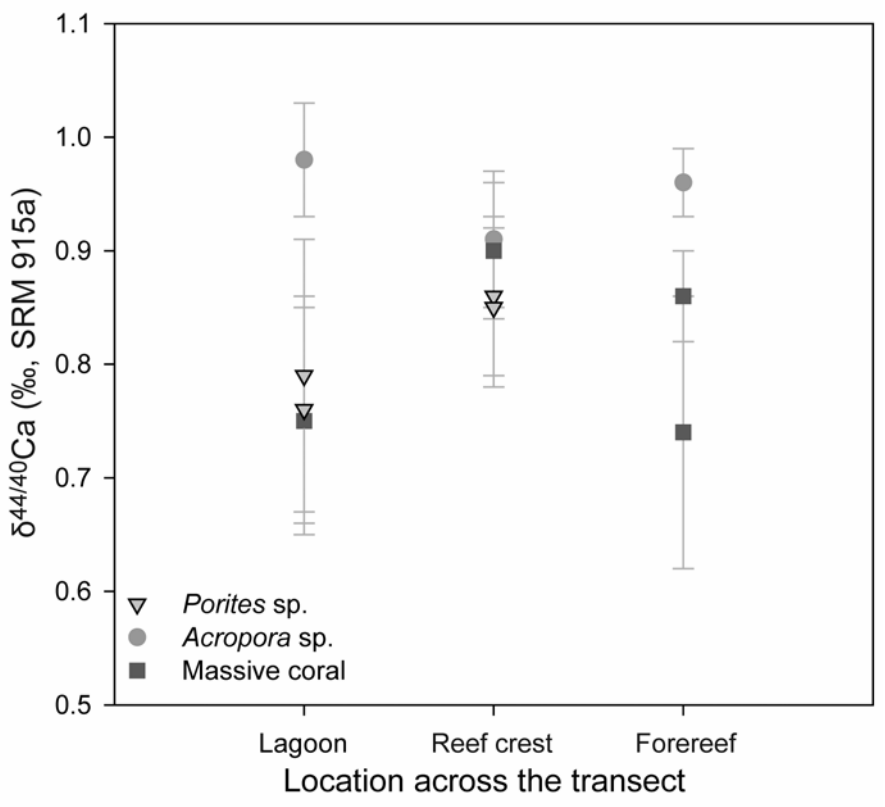
1.1
1.0
0.9
0.8
0.7
0.6
0.5
δ44/40Ca (‰, SRM 915a)
Porites sp.
Acropora sp.
Massive coral
Lagoon
Reef crest
Forereef
Location across the transect

Fig. 6

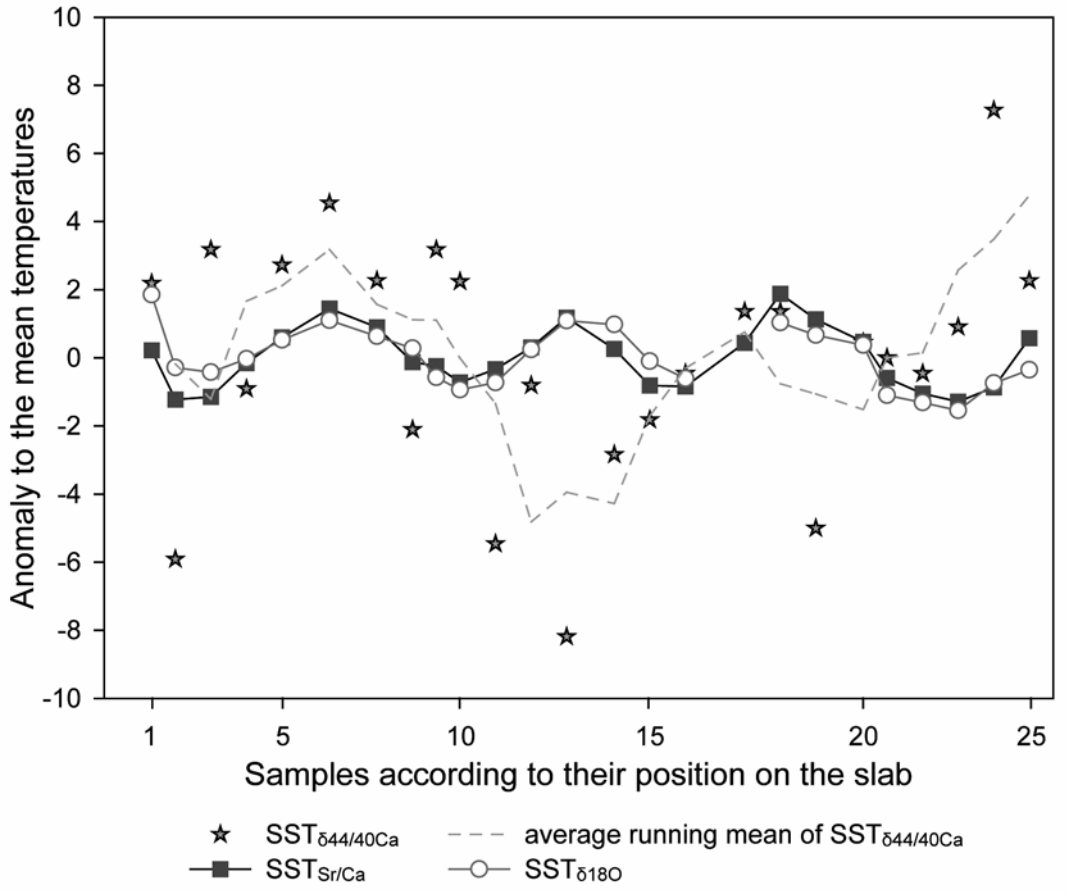
Anomaly to the mean temperatures
10
8
6
4
2
0
-2
-4
-6
-8
-10
1
5
10
15
20
25
Samples according to their position on the slab
SST δ44/40Ca
average running mean of SST δ44/40Ca
SST Sr/Ca
SST δ18O

Fig. 7

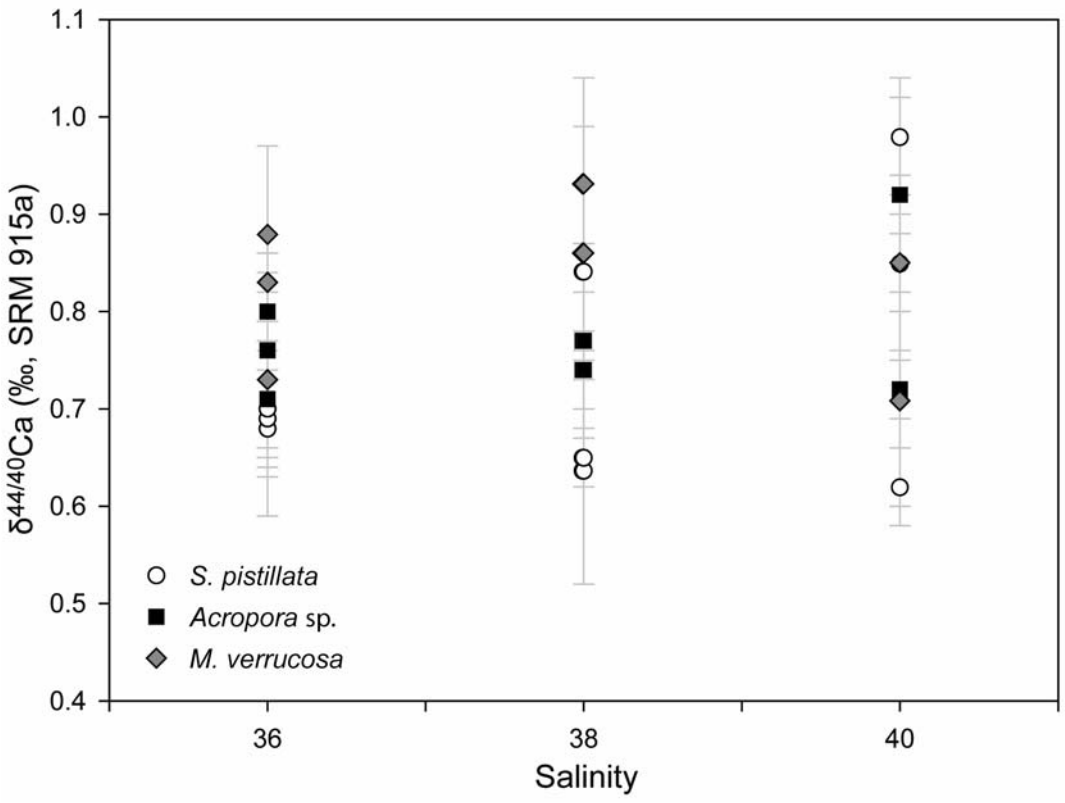
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
δ44/40Ca (‰, SRM 915a)
S. pistillata
Acropora sp.
M. verrucosa
36
38
40
Salinity

Fig. 8

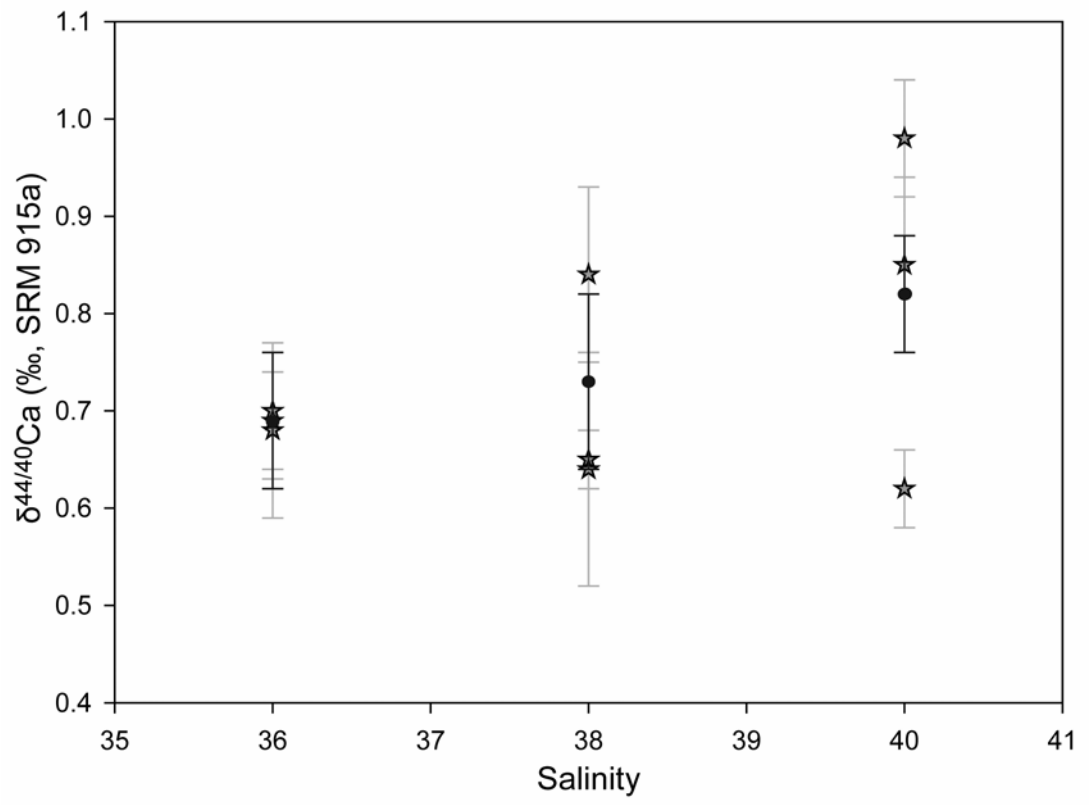
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
δ44/40Ca (‰, SRM 915a)
35
36
37
38
39
40
41
Salinity

Fig. 9

Sample name	Sample number	$\delta^{44/40}$Ca (‰)	2SEM (‰)	N
224	1	0.88	0.11	3
225	2	0.70	0.11	3
226	3	0.90	0.08	3
227	4	0.81	0.07	3
228	5	0.89	0.11	3
229	6	0.93	0.05	3
230	7	0.88	0.11	3
231	8	0.78	0.09	3
232	9	0.90	0.12	3
233	10	0.88	0.15	5
234	11	0.71	0.10	3
235	12	0.81	0.08	5
236	13	0.65	0.09	3
237	14	0.77	0.12	5
238	15	0.79	0.06	3
239	16	0.82	0.09	3
240	17	0.86	0.03	3
241	18	0.86	0.07	3
242	19	0.72	0.04	5
243	20	0.84	0.07	3
244	21	0.83	0.15	5
245	22	0.82	0.11	3
246	23	0.85	0.09	3
247	24	0.99	0.03	5
248	25	0.88	0.06	4

Table 1

Sample	Genus	Location on the transect	Distance from the beach (m)	Water depth (m)	$\delta^{44/40}$Ca (‰)	2SEM (‰)	N
MAL-Por1-2	Porites sp.	Lagoon	35	1	0.79	0.12	5
MAL-Por1-3	Porites sp.	Lagoon	35	1	0.76	0.06	6
MAL-Por2-1	Porites sp.	Reef flat	90	0.7	0.85	0.07	6
MAL-Por2-2	Porites sp.	Reef flat	90	0.7	0.86	0.07	6
MAL-Acr1-1	Acropora sp.	Lagoon	40	0.9	0.98	0.05	3
MAL-Acr2-1	Acropora sp.	Reef flat	100	1	0.91	0.06	3
MAL-Acr3-1	Acropora sp.	Forereef	150	3	0.96	0.03	4
MAL-XX1-1	Massive unidentify	Lagoon	50	0.8	0.75	0.10	6
MAL-XX2-1	Massive unidentify	Reef flat	150	1	0.90	0.06	5
MAL-XX3-1	Massive unidentify	Forereef	155	3.5	0.86	0.04	3
MAL-XX3-2	Massive unidentify	Forereef	155	3.5	0.74	0.12	5

Table 2

Sample	Salinity	Genus	$\delta^{44/40}$Ca (‰)	2SEM (‰)	N
MC-Acr-36/1	36	*Acropora* sp.	0.71	0.06	3
MC-Acr-36/2	36	*Acropora* sp.	0.8	0.04	3
MC-Acr-36/4	36	*Acropora* sp.	0.76	0.1	3
MC-Acr-38/1	38	*Acropora* sp.	0.77	0.10	3
MC-Acr-38/2	38	*Acropora* sp.	0.74	0.04	3
MC-Acr-40/1	40	*Acropora* sp.	0.72	0.03	3
MC-Acr-40/5	40	*Acropora* sp.	0.85	0.05	3
MC-Acr-40/6	40	*Acropora sp.*	0.92	0.10	3
MC-Mon-36/1	36	*M. verrucosa*	0.73	0.09	3
MC-Mon-36/2	36	*M. verrucosa*	0.83	0.01	3
MC-Mon-36/3	36	*M. verrucosa*	0.88	0.09	3
MC-Mon-38/1	38	*M. verrucosa*	0.93	0.11	5
MC-Mon-38/2	38	*M. verrucosa*	0.86	0.13	3
MC-Mon-40/1	40	*M. verrucosa*	0.71	0.11	3
MC-Mon-40/4	40	*M. verrucosa*	0.85	0.03	3
MC-Sty-36/1	36	*S. pistillata*	0.68	0.09	3
MC-Sty-36/3	36	*S. pistillata*	0.7	0.07	3
MC-Sty-36/5a	36	*S. pistillata*	0.69	0.05	3
MC-Sty-38/1	38	*S. pistillata*	0.65	0.03	3
MC-Sty-38/3	38	*S. pistillata*	0.84	0.09	3
MC-Sty-38/5	38	*S. pistillata*	0.64	0.12	3
MC-Sty-40/1	40	*S. pistillata*	0.85	0.09	3
MC-Sty-40/4	40	*S. pistillata*	0.98	0.06	3
MC-Sty-40/5	40	*S. pistillata*	0.62	0.04	3

Table 3

F-test between two salinities	p-values
36-38	0.016
36-40	0.006
38-40	0.553

Table 4