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REPORT

Effect of salinity on the skeletal chemistry of cultured scleractinian zooxanthellate corals: Cd/Ca ratio as a potential proxy for salinity reconstruction

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Abstract The effect of salinity on the elemental and isotopic skeletal composition of modern zooxanthellate scleractinian corals (*Acropora* sp., *Montipora verrucosa* and *Stylophora pistillata*) was investigated in order to evaluate potential salinity proxies. Corals were cultured in the laboratory at three salinities (36, 38 and 40). The other environmental parameters were kept constant. For all species analyzed, Sr/Ca, Mg/Ca, U/Ca and Li/Ca ratios were not influenced by salinity changes. The Ba/Ca ratio also lacks a systematic relationship with salinity and exhibits high inter-generic variations, up to one order of magnitude. On the

contrary, the Cd/Ca ratio decreases as a function of increasing salinity, and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ also presented a significant response, but with opposite trends to salinity variations. Since Cd/Ca is usually considered as an upwelling proxy, its salinity dependence could compromise the upwelling signal, unless some corrections can be carried out. Regardless, if the dependence found in the present dataset proved to be widespread and systematic, the Cd/Ca ratio could represent a promising salinometer awaiting further investigation. This study also confirmed the reliability of the well-established temperature proxies Sr/Ca, Mg/Ca and U/Ca, as these ratios were insensitive to salinity variations. Moreover, our results showed that $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ can be considered as reliable temperature recorders as far as the salinity effect is removed from the parameter reconstructed (e.g., temperature). Investigating the influence of salinity on the skeletal chemistry of scleractinian corals grown under controlled environmental conditions confirmed previous results, validated isotopic corrections, and identified a promising proxy of salinity.

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Introduction

Many reconstructions in the tropical realm have been performed using coral skeletons which are reliable marine archives providing proxies commonly used to track environmental changes (e.g., Weber and Woodhead 1970; Swart 1983; Druffel 1997; Gagan et al. 2000; Marshall and McCulloch 2002; Felis and Pätzold 2003; Corrège 2006). However, the geochemical signature recorded in coral

skeleton is often influenced by environmental or biological effects, which potentially may compromise paleoreconstruction (e.g., Druffel 1997; Adkins et al. 2003; Asami et al. 2004; Cohen and Hart 2004; Lough 2004; Delong et al. 2011). For accurate reconstruction, the external factors, which influenced the skeleton chemistry, need to be constrained and corrected for. For this purpose, a multi-proxy approach was commonly applied, combining several well-established proxies (Quinn and Sampson 2002). However, few studies focused on the influence of salinity on the elemental incorporation in aragonite coral skeleton (Reynaud-Vaganay 2000) or coral soft tissues (Muthiga and Szmant 1987; Downs et al. 2009).

Local salinity, coupled with sea-surface temperature (SST), is one of the most important oceanic parameters that drive water mass movement and heat repartition in the ocean and hence affect the global climate. Understanding the past sea-surface salinity (SSS) allows to better constrain the ocean and climate dynamics through time. In contrast to SST, which is overall well constrained, SSS reconstruction is currently less confident and relies on a multi-proxy approach combining $\delta^{18}\text{O}$ (McCulloch et al. 1994; Gagan et al. 1998; Le Bec et al. 2000; Ren et al. 2002; Kilbourne et al. 2004) along with Sr/Ca and U/Ca ratios (Felis et al. 2009). There is therefore a need to improve SSS reconstructions. Moreover, Sr/Ca and Mg/Ca ratios in coral skeleton are proxies widely used for paleotemperature reconstruction (e.g., Weber 1973; Smith et al. 1979; Beck et al. 1992; McCulloch et al. 1996; Alibert and McCulloch 1997; Gagan et al. 2000; Marshall and McCulloch 2001; Corrège et al. 2004; Corrège 2006; Delong et al. 2007). These ratios can be considered robust if they are unaffected by salinity changes.

Therefore, the present study focused on purpose of (1) evaluating the salinity influence on proxies used in oceanic paleoreconstruction and (2) exploring for a reliable salinity proxy. For the present study, three genera of corals (*Acropora* sp., *Montipora verrucosa* and *Stylophora pistillata*) were cultured in monitored aquaria where salinity was the unique variable (Reynaud-Vaganay 2000).

Materials and methods

Experimental design: cultured corals

Colonies of *Acropora* sp., *S. pistillata* and *M. verrucosa* were cultured in the laboratory under controlled environmental conditions at different salinities artificially obtained: 36.2 (36 in the following), 38 and 40. Three coral tips were sampled from the same parent colony, glued on glass slides with Epoxy (Devcon® UW) and randomly and equally distributed in 3

Table 1 Artificial salt (Instant Ocean, Aquarium systems®) element concentration compared with seawater

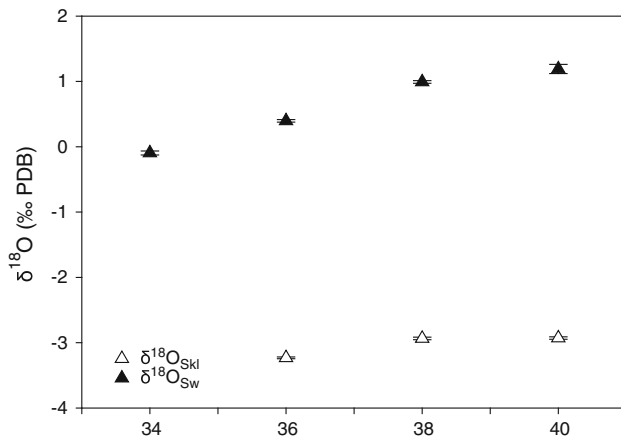
| Ion | Sea salt (ppm) | Seawater ^a (ppm) |
|--|----------------|-----------------------------|
| Salinity: around 35 ppt | | |
| Cl ⁻ | 19,290 | 19,353 |
| Na ⁺ | 10,780 | 10,781 |
| SO ₄ ²⁻ | 2,660 | 2,712 |
| Mg | 1,320 | 1,284 |
| K ⁺ | 420 | 399 |
| Ca ²⁺ | 400 | 412 |
| CO ₃ ²⁻ /HCO ₃ ⁻ | 200 | 126 |
| Br ⁻ | 56 | 67 |
| Sr ²⁺ | 8.8 | 7.9 |
| Li ⁺ | 0.3 | 0.173 |
| Ba ²⁺ | <0.04 | 0.014 |
| Mn ²⁺ | <0.025 | <0.001 |
| Cd ²⁺ | <0.002 | <0.001 |
| Salinity: around 32 ppt (sea salt) and 35 (seawater) | | |
| Concentration (g L ⁻¹) | 38 | 35.169 |
| Alkalinity (mEq L ⁻¹) | 3.0–4.0 | 2.32 |
| Calcium ion (mg L ⁻¹) | 349–392 | 411.9 |
| Magnesium ion (mg L ⁻¹) | 1,150–1,310 | 1,284 |

^a Data for seawater values are from Pilson (1998)

aquaria with salinities of 38, which is the normal salinity of the incoming water (Reynaud-Vaganay et al. 1999). Corals were fed three times a week with *Artemia salina* nauplii. The aquaria were supplied with Mediterranean seawater pumped from 50 m depth, renewed approximately five times per day and continuously mixed with a Rena® pump (6 L min⁻¹). To obtain artificial seawater at salinity 36, 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 natural Mediterranean seawater with artificial water of a salinity of 50 prepared with commercial salts (Instant Ocean, Aquarium Systems; cf. Table 1 for salt composition). The stability of the salinity was checked using a conductivity meter (Mettler LF196) and recorded continuously. Salinity in two out of the three aquaria was gradually increased to 40 or decreased to 36 at a rate of ca. 0.5 d⁻¹. The colonies were kept during 10 weeks under the three salinities. Seawater temperature was maintained at 27.1 ± 0.1 °C using a temperature controller (EW, PC 902/T) and recorded every 10 min with temperature recorders (Seamon®), at a resolution of 0.025 °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_{SW} 8.08 [measured with a combined

Table 2 $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ of seawater (data from Reynaud-Vaganay 2000) and coral skeleton, salinity and year of sampling for the cultured corals

| Sample | Coral species | Cultured year | Salinity | $\delta^{18}\text{O}$ | 2SD | <i>N</i> | $\delta^{13}\text{C}$ | 2SD |
|-------------|---------------------|---------------|----------|-----------------------|-------------------|----------|-----------------------|------|
| MC-Acr-36/1 | <i>Acropora</i> sp. | 1997 | 36 | −3.23 | 0.01 | | −0.84 | 0.01 |
| MC-Acr-38/1 | <i>Acropora</i> sp. | 1997 | 38 | −2.94 | 0.02 | | −1.88 | 0.01 |
| MC-Acr-40/1 | <i>Acropora</i> sp. | 1997 | 40 | −2.93 | 0.02 | | −2.09 | 0.01 |
| Sw-36 | Seawater | 1997 | 36 | 0.40 | 0.02 ^a | 7 | | |
| Sw-38 | Seawater | 1997 | 38 | 0.99 | 0.02 ^a | 11 | | |
| Sw-40 | Seawater | 1997 | 40 | 1.19 | 0.07 ^a | 5 | | |

^a SEM**Fig. 1** $\delta^{18}\text{O}$ composition of *Acropora* sp. skeleton (open triangle) and seawater (filled triangle) according to salinity

Ross[®] electrode (Orion 8102SC) on the Sea Water Scale], total alkalinity (2.6 mEq kg^{-1} : measured by potentiometric titration) and pCO_2 (adjusted in two buffer tanks using a pH controller; R305, Consort Inc[®]). More information is provided in Reynaud-Vaganay et al. (1999) and Reynaud-Vaganay (2000). The oxygen isotopic composition of seawater ($\delta^{18}\text{O}_{\text{sw}}$) was measured several times in the aquaria at salinities of 36, 38 and 40, respectively, to test the effect of dilution or artificial salt addition in seawater. Indeed, evaporation, which is the main natural process involved in salinity increase, induced a faster removal of lighter isotopes and thus increases $\delta^{18}\text{O}_{\text{sw}}$. The addition of salts could also induce a bias in the geochemical process. Moreover, the addition of freshwater decreased the $\delta^{18}\text{O}_{\text{sw}}$ of the aquaria (Table 2; Fig. 1).

A second set of samples comprised material from *Acropora* sp., *Stylophora* sp. and *Montipora* sp. cultured under controlled environmental conditions in 2010. Salinity was 38 and temperature 25°C ; all other parameters were identical to those of the first experiment. Coral tips were bleached during 24 h with NaClO (10 %), ultrasonicated and rinsed with Milli-Q water in order to remove organic matter. Sampling was made in coral tips using a drill tool. The elemental composition of seawater from this aquarium (Sw-38, 2010) is given in Table 3.

Laboratory analyses

Carbon and oxygen isotopes ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) were analyzed only for *Acropora* sp. cultured at different salinities. Isotopic measurements were performed in GeoZentrum Nordbayern, Erlangen, Germany. Analyses ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of organic carbon were performed with an elemental analyzer (Carlo-Erba 110) connected online to Thermo-Finnigan Delta Plus mass-spectrometer. Oxygen isotope values were corrected using the phosphoric acid fractionation factors given by Kim et al. (2007) and Rosenbaum and Sheppard (1986). All values are reported in permil relative to V-PDB by assigning a $\delta^{13}\text{C}$ value of $+1.95\text{‰}$ and a $\delta^{18}\text{O}$ value of -2.20‰ to NBS19. Reproducibility was checked by replicate analyses of laboratory standards and was better than $\pm 0.05\text{‰}$ (± 1 SD).

Major and trace element composition of the coral skeletons were determined by solution ICP-MS at Laurentian University following the general analytical protocol of Kamber (2009). Small amounts of coral (between 2 and 11 mg) were dissolved at room temperature in pre-cleaned 14 mL PP test tubes with 5 % triple sub-distilled HNO_3 . From this stock solution, one dilution was made (minimum dilution factor of 1,400) for the trace element run, whereas major elements were analyzed from a more diluted separate aliquot (dilution factor of 10,000–11,000). For both dilutions, a 4.4 ppb internal standard mixture of ^6Li , Rh, Re, Bi and ^{235}U was added to correct for drift. The instrument response was calibrated with two separate digestions of USGS standard W-2 diluted to 2,500 and 10,000, respectively. Our preferred W-2 concentrations are listed in Kamber (2009). Accuracy was checked by concomitant analyses of a selection of international rock standards (BIR-1, BCR-2, BHVO-1 BHVO-2, JA-2, and JA-3).

Of particular importance for this study is the analysis of Cd, which, in typical rock samples, occurs at the double digits ppb concentration. Values obtained in this study were calibrated against the W-2 concentration of 77 ppb determined by Sands and Rosman (1997) and agree very well with the most recent literature data. Figure 2 shows a comparison of the values obtained here with published data for the 6 above-mentioned

Table 3 Sample characteristics and elemental composition expressed in ppm (Mg and Ca) and ppb (Sr, Ba, Li, U) with absolute standard deviation

| Sample | Coral species | Cultured year | Salinity | Mg (ppm) | Ca (ppm) | Li (ppb) | Li abs. SD | Sr (ppb) | Sr abs. SD | Cd (ppb) | Cd abs. SD | Ba (ppb) | Ba abs. SD | U (ppb) | U abs. SD |
|--------------|----------------------|---------------|----------|-----------|----------|----------|------------|-----------|------------|----------|------------|----------|------------|---------|-----------|
| MC-Acr-40/5 | <i>Acropora</i> sp. | 1997 | 40 | 1,535 | 372,100 | 589.4 | 17.6 | 7,642,000 | 111,500 | 18.6 | 0.4 | 110,600 | 802 | 2,385 | 12 |
| MC-Acr-40/1 | <i>Acropora</i> sp. | 1997 | 40 | 985.7 | 240,500 | 1,053 | 228.3 | 7,143,000 | 19,860 | 4.4 | 2.4 | 13,650 | 262 | 2,726 | 25 |
| MC-Acr-38/1 | <i>Acropora</i> sp. | 1997 | 38 | 711.8 | 201,000 | 1,891 | 889.2 | 6,818,000 | 69,610 | 17.6 | 4.2 | 25,750 | 164 | 2,802 | 29 |
| MC-Acr-38/2 | <i>Acropora</i> sp. | 1997 | 38 | 1,417 | 369,100 | 530 | 6.1 | 7,189,000 | 37,240 | 17.6 | 1.0 | 35,300 | 93 | 2,816 | 13 |
| MC-Acr-36/4 | <i>Acropora</i> sp. | 1997 | 36 | 1,553 | 363,400 | 587.8 | 10.2 | 7,449,000 | 133,200 | 64.0 | 1.2 | 44,080 | 187 | 2,299 | 10 |
| MC-Acr-36/1 | <i>Acropora</i> sp. | 1997 | 36 | 1,541 | 369,000 | 628.6 | 26.1 | 6,932,000 | 79,230 | 51.1 | 0.7 | 48,330 | 248 | 2,439 | 8 |
| MC-Acr 1-1 | <i>Acropora</i> sp. | 2010 | 38 | 804.1 | 379,700 | 627.5 | 11.2 | 7,876,000 | 50,320 | 24.7 | 0.2 | 10,400 | 29 | 3,446 | 21 |
| MC-Mon-40/2 | <i>M. verrucosa</i> | 1997 | 40 | 2,791 | 336,600 | 846.2 | 4.5 | 6,958,000 | 57,340 | 18.1 | 0.3 | 287,900 | 2,243 | 1,799 | 9 |
| MC-Mon-38/2 | <i>M. verrucosa</i> | 1997 | 38 | 2,257 | 354,100 | 734.6 | 19.1 | 7,202,000 | 81,380 | 5.2 | 0.5 | 78,030 | 50 | 2,281 | 13 |
| MC-Mon-36/1 | <i>M. verrucosa</i> | 1997 | 36 | 3,002 | 330,400 | 765.8 | 4.4 | 6,632,000 | 44,170 | 62.0 | 0.5 | 120,300 | 644 | 2,269 | 13 |
| MC-Sty-40/4 | <i>S. pistillata</i> | 1997 | 40 | 1,484 | 335,900 | 557.9 | 17.4 | 6,855,000 | 72,390 | 8.0 | 0.6 | 13,770 | 41 | 1,960 | 5 |
| MC-Sty-38/6 | <i>S. pistillata</i> | 1997 | 38 | 1,434 | 331,200 | 533.6 | 12.5 | 6,986,000 | 66,080 | 10.2 | 0.3 | 7,146 | 44 | 2,494 | 5 |
| MC-Sty-36/5a | <i>S. pistillata</i> | 1997 | 36 | 1,947 | 342,600 | 640.3 | 17.5 | 7,284,000 | 68,980 | 37.5 | 0.8 | 8,553 | 49 | 2,917 | 13 |
| MC-Sty 1-1 | <i>S. pistillata</i> | 2010 | 38 | 1,248 | 377,600 | 696.5 | 13.6 | 7,149,000 | 8,293 | 4.4 | 0.3 | 8,741 | 53 | 2,583 | 40 |
| MC-Mon 1-1 | <i>M. verrucosa</i> | 2010 | 38 | 951.7 | 383,900 | 750.6 | 9.6 | 7,325,000 | 79,040 | 53.6 | 1.2 | 59,170 | 484 | 3,303 | 25 |
| Average | | | | 1,578 | 339,100 | 762.2 | 85.8 | 7,163,000 | 65,240 | 26.5 | 1.0 | 58,120 | 360 | 2,568 | 16 |
| Sw-38 | Seawater | 2010 | 38 | 1,562,000 | 521,800 | 205.8 | 1.4 | 8,484 | 45.3 | 0.012 | 0.002 | 7.9 | 0.1 | 3.7 | 0.02 |

standards. Within 1 sigma standard deviation, all values agree and fall on a tight regression line ($r^2 = 0.974$, not shown in Fig. 2) and are compatible with a 1:1 correlation. The standards for which the best agreement in literature Cd data exists are JA-2 and JA-3. The average of the three measured Cd referred to in the literature values for JA-2 is 74 ± 4 ppb (see caption of Fig. 2 for references), comparing well with this study's value of 75 ± 3 ppb (22 analyses from 9 digestions over 4 yr). The average of the four measured Cd values for JA-3 referred to in the literature is 89 ± 3 ppb (see caption of Fig. 2 for references), comparing well with this study's value of 89 ± 2 ppb (20 analyses from 7 digestions over 4 yr). The agreement of values given in the literature and USGS standards is not as good, but our values agree well with the overall averages. The long-term laboratory Cd average concentrations relevant to this study are BHVO-1 (44 analyses from 11 digestions over 2 yr): 117 ± 4 ppb; BHVO-2 (70 analyses from 14 digestions over 4 yr): 116 ± 6 ppb; BIR-1 (37 analyses from 14 digestions over 4 yr): 64 ± 4 ppb; and BCR-2 (29 analyses from 9 digestions over 4 yr): 219 ± 25 ppb.

Results

Elemental ratios

The elemental composition and ratios for all samples are compiled in Tables 3 and 4, respectively. Sr/Ca, Mg/Ca, Li/Ca and U/Ca ratios do not vary with salinity changes, independently of the coral genus (Fig. 3, Analysis of variance (ANOVA), $p = 0.56, 0.10, 0.92$ and 0.19 for Sr/Ca, Mg/Ca, Li/Ca and U/Ca, respectively). Normal distribution failed but ANOVA on ranks shows no significant difference with salinity. Mean values of Sr/Ca, Mg/Ca, Li/Ca and U/Ca are 2.2×10^{-2} , 4.7×10^{-3} , 2.5×10^{-6} , 7.8×10^{-6} , respectively. Ba/Ca (mean: 1.7×10^{-4}) and Cd/Ca (mean: 7.7×10^{-8}) show more variations between genera, up to one order of magnitude (Fig. 3). Ba/Ca ratio exhibits significant inter-generic differences (ANOVA p value: 0.005), particularly between *M. verrucosa* and *S. pistillata*. Cd/Ca ratio decreases with increasing salinity values (ANOVA p value = 0.002). The p value of the correlation coefficient is 1.7×10^{-3} , which confirms the negative correlation between Cd/Ca and salinity.

Isotope fractionation

Isotope fractionation of oxygen ($\delta^{18}\text{O}$) and carbon ($\delta^{13}\text{C}$) measured on the same aliquots originating from *Acropora* sp. coral skeleton powder, as those used for elemental analyses (Table 2) show two opposite relationships with salinity (Fig. 4). Trends are negatively correlated (Corr. coef. = -0.99): $\delta^{18}\text{O}_{\text{skel}}$ increases with salinity, whereas

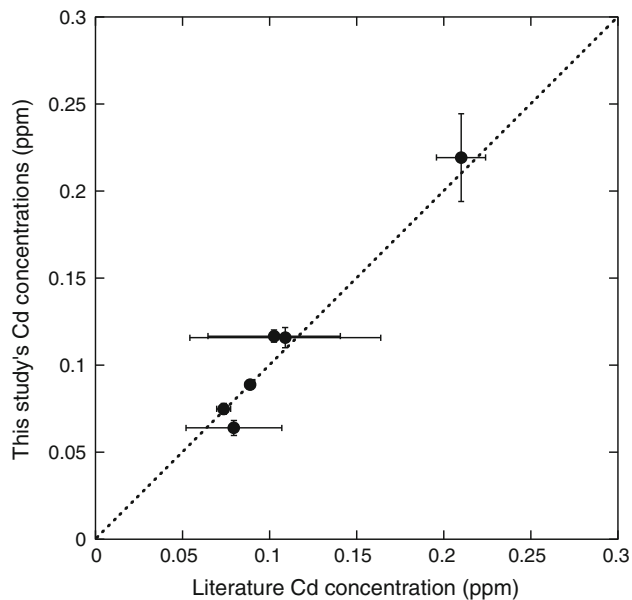


Fig. 2 Comparison of literature data for Cd concentrations in international rock standards with long-term averages (4 yr) obtained in the Laurentian University laboratory. *Error bars* represent one sigma standard deviations. *Stippled line* is theoretical 1:1 correlation. Literature data sources: Imai et al. (1995; JA-2, JA-3); Sands and Rosman (1997; BIR-1, BHVO-1); Govindaraju (1994; JA-2, JA-3, BIR-1, BHVO-1); Eggins et al. (1997; BIR-1, BHVO-1); Godard et al. (2009; BIR-1); Yi et al. (1998; BIR-1); Cotta and Enzweiler (2012; BIR-1, BHVO-2); Hu and Gao (2008; BIR-1, BHVO-2, BCR-2); Hergt et al. (2007; BHVO-1); Makishima et al. (2011; JA-2, JA-3, BHVO-1); Weis et al. (2005; BHVO-1 and 2); Matthews et al. (2006; BHVO-1); Moune et al. (2006; BHVO-1); Bouman et al. (2004; BHVO-2); van der Straaten et al. (2008; BHVO-2); He et al. (2010; BHVO-2); Adam and Green (2011; BHVO-2, BCR-2); Norman et al. (2010; BCR-2); Hanano et al. (2010; BCR-2)

$\delta^{13}\text{C}$ decreases. Values are comparable with those reported in previous studies (e.g., Juillet-Leclerc and Reynaud 2010), ranging from -2.1 to -0.8 ‰ and from -3.2 to -2.9 ‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively. However, both trends are not linear: the isotopic composition of the skeleton grown at 38 and 40 of salinity are similar (Fig. 4).

$\delta^{18}\text{O}_{\text{sw}}$ and $\delta^{18}\text{O}_{\text{skl}}$ exhibit positive trends with increasing salinity (Table 2; Fig. 1). The coefficient of determination for $\delta^{18}\text{O}_{\text{sw}}$ is 0.9667 whereas it is 0.7648 for $\delta^{18}\text{O}_{\text{skl}}$, which means that salinity influence explains more than seventy percent of the variation of $\delta^{18}\text{O}_{\text{skl}}$.

Discussion

Influence of salinity on skeletal chemistry

Cd/Ca: a promising salinity proxy?

The results of the present study revealed a positive correlation between Cd/Ca and salinity for each coral genus

studied (Fig. 3). Our results showed that salinity dependence could compromise Cd/Ca as upwelling proxy, unless corrected for using an independent salinity proxy. Regardless, if the dependence found in the dataset proves to be systematic, the Cd/Ca ratio represents a promising salinometer awaiting detailed investigation, especially the comparison between areas exhibiting differences in salinity at the regional scale, e.g., as reported in Delaney et al. (1993) between eastern and western Galapagos.

In previous studies, Cd/Ca ratio in coral skeleton has been proposed to reconstruct upwelling dynamics (van Geen et al. 1992; van Geen and Husby 1996; Matthews et al. 2008; Carriquiry and Villaescusa 2010). These previous studies reported a positive correlation between Cd/Ca ratio and upwelling. These results are not in agreement with those of the present study given that upwelling periods were characterized by higher salinities (upwelling period: 34.9 ± 0.2 ; non-upwelling period: 30.8 ± 0.4 ; Matthews et al. 2008). Matthews et al. (2008) further showed that the relationship between Cd/Ca ratio and upwelling varies depending on species, which is not revealed by the species used in the present study (Fig. 3).

In addition, the results of the present study revealed a positive correlation between Cd/Ca and $\delta^{13}\text{C}$ and an inverse correlation between Cd/Ca and $\delta^{18}\text{O}$ for each coral genus studied (Fig. 4). These results do not agree with those of Matthews et al. (2008). These authors reported a lack of relationship between Cd/Ca, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ which led to the conclusion that at seasonal resolution, Cd/Ca ratio was independent of growth rate, coral metabolism, SST and SSS. One should notice that the genera used in the present study (*Acropora* sp., *M. verrucosa* and *S. pistillata*) are different from those in Matthews et al. (2008) who used *Pavona clavus*, *Pavona gigantea* and *Porites lobata*. Moreover, processes which lead to Cd incorporation into coral skeleton are not fully constrained (Matthews et al. 2008).

Nevertheless, one should keep in mind that artificial conditions in monitored aquaria can lead to different responses to salinity increase: the salinity of 40 was obtained artificially by salt addition (Reynaud-Vaganay 2000), meaning that the same elemental ratios were introduced to the solution, which differed from upwelling that enriched surface water in nutrients. Moreover, upwellings are controlled by several environmental parameters including light, temperature or salinity whereas only one parameter varied during our experiment. In addition, salinity can fluctuate during upwelling period and the Cd concentration in seawater can increase, e.g., from 0.2 (non-upwelling) to 0.6 (upwelling) nmol kg^{-1} (van Geen and Husby 1996).

The relationship between Cd/Ca and salinity has not been evaluated on natural samples so far. Therefore, more studies and a larger database are required. Our results have

Table 4 Sample characteristics and elemental to calcium ratio composition with absolute standard deviation

| Sample | Coral species | Cultured year | Salinity | Mg/Ca | Li/Ca | Li abs. SD | Sr/Ca | Sr abs. SD | Cd/Ca | Cd abs. SD | Ba/Ca | Ba abs. SD | U/Ca | U abs. SD |
|--------------|----------------------|---------------|----------|----------|----------|------------|----------|------------|----------|------------|----------|------------|----------|-----------|
| MC-Acr-40/5 | <i>Acropora</i> sp. | 1997 | 40 | 4.12E-03 | 1.58E-06 | 4.73E-08 | 0.0205 | 3.00E-04 | 5.01E-08 | 1.19E-09 | 2.97E-04 | 2.16E-06 | 6.41E-06 | 3.11E-08 |
| MC-Acr-40/1 | <i>Acropora</i> sp. | 1997 | 40 | 4.10E-03 | 4.38E-06 | 9.49E-07 | 0.0297 | 8.26E-05 | 1.83E-08 | 9.87E-09 | 5.68E-05 | 1.09E-06 | 1.13E-05 | 1.05E-07 |
| MC-Acr-38/1 | <i>Acropora</i> sp. | 1997 | 38 | 3.54E-03 | 9.41E-06 | 4.42E-06 | 0.0339 | 3.46E-04 | 8.76E-08 | 2.09E-08 | 1.28E-04 | 8.17E-07 | 1.39E-05 | 1.42E-07 |
| MC-Acr-38/2 | <i>Acropora</i> sp. | 1997 | 38 | 3.84E-03 | 1.44E-06 | 1.64E-08 | 0.0195 | 1.01E-04 | 4.77E-08 | 2.60E-09 | 9.56E-05 | 2.53E-07 | 7.63E-06 | 3.40E-08 |
| MC-Acr-36/4 | <i>Acropora</i> sp. | 1997 | 36 | 4.27E-03 | 1.62E-06 | 2.81E-08 | 0.0205 | 3.67E-04 | 1.76E-07 | 3.25E-09 | 1.21E-04 | 5.16E-07 | 6.33E-06 | 2.71E-08 |
| MC-Acr-36/1 | <i>Acropora</i> sp. | 1997 | 36 | 4.18E-03 | 1.70E-06 | 7.08E-08 | 0.0188 | 2.15E-04 | 1.39E-07 | 2.03E-09 | 1.31E-04 | 6.71E-07 | 6.61E-06 | 2.05E-08 |
| MC-Acr 1-1 | <i>Acropora</i> sp. | 2010 | 38 | 2.12E-03 | 1.65E-06 | 2.96E-08 | 0.0207 | 1.33E-04 | 6.51E-08 | 4.85E-10 | 2.74E-05 | 7.75E-08 | 9.08E-06 | 5.52E-08 |
| MC-Mon-40/2 | <i>M. verrucosa</i> | 1997 | 40 | 8.29E-03 | 2.51E-06 | 1.32E-08 | 0.0207 | 1.70E-04 | 5.39E-08 | 9.51E-10 | 8.55E-04 | 6.66E-06 | 5.35E-06 | 2.74E-08 |
| MC-Mon-38/2 | <i>M. verrucosa</i> | 1997 | 38 | 6.37E-03 | 2.07E-06 | 5.39E-08 | 0.0203 | 2.30E-04 | 1.48E-08 | 1.35E-09 | 2.20E-04 | 1.41E-07 | 6.44E-06 | 3.77E-08 |
| MC-Mon-36/1 | <i>M. verrucosa</i> | 1997 | 36 | 9.09E-03 | 2.32E-06 | 1.34E-08 | 0.0201 | 1.34E-04 | 1.88E-07 | 1.40E-09 | 3.64E-04 | 1.95E-06 | 6.87E-06 | 3.78E-08 |
| MC-Mon 1-1 | <i>M. verrucosa</i> | 2010 | 38 | 2.48E-03 | 1.96E-06 | 2.50E-08 | 0.0191 | 2.06E-04 | 1.40E-07 | 3.18E-09 | 1.54E-04 | 1.26E-06 | 8.60E-06 | 6.50E-08 |
| MC-Sty-40/4 | <i>S. pistillata</i> | 1997 | 40 | 4.42E-03 | 1.66E-06 | 5.17E-08 | 0.0211 | 2.16E-04 | 2.37E-08 | 1.82E-09 | 4.10E-05 | 1.23E-07 | 5.83E-06 | 1.59E-08 |
| MC-Sty-38/6 | <i>S. pistillata</i> | 1997 | 38 | 4.33E-03 | 1.61E-06 | 3.79E-08 | 0.0211 | 2.00E-04 | 3.07E-08 | 1.03E-09 | 2.16E-05 | 1.32E-07 | 7.53E-06 | 1.52E-08 |
| MC-Sty-36/5a | <i>S. pistillata</i> | 1997 | 36 | 5.68E-03 | 1.87E-06 | 5.11E-08 | 0.0213 | 2.01E-04 | 1.10E-07 | 2.29E-09 | 2.50E-05 | 1.44E-07 | 8.51E-06 | 3.76E-08 |
| MC-Sty 1-1 | <i>S. pistillata</i> | 2010 | 38 | 3.31E-03 | 1.84E-06 | 3.59E-08 | 0.0189 | 2.20E-05 | 1.16E-08 | 7.67E-10 | 2.32E-05 | 1.41E-07 | 6.84E-06 | 1.06E-07 |
| Average | | | | 4.68E-03 | 2.51E-06 | | 2.17E-02 | | 7.70E-08 | | 1.71E-04 | | 7.82E-06 | |
| Sw-38 | Seawater | 2010 | 38 | 2.99E+00 | 3.94E-04 | | 1.63E-02 | | 2.28E-08 | | 1.51E-05 | | 7.07E-06 | |

two major implications for the use of Cd/Ca: (1) this ratio is a promising salinometer awaiting confirmation by future experiments and ideally on samples originating from corals grown in natural environments, and (2) the salinity dependence of Cd/Ca can compromise the use of this ratio as an exclusive upwelling proxy, unless corrected for using an independent salinity proxy.

Salinity and isotope fractionation

The oxygen isotopic composition of coral skeleton ($\delta^{18}O_{skl}$) is usually linked with SST, evaporation and salinity (Delaney et al. 1993; Druffel 1997; Gagan et al. 2000; Henderson 2002). The correction coefficient for skeletal growth, applied to $\delta^{18}O_{skl}$ record prior to its use as temperature proxy (Maier et al. 2004), and the approach in combining $\delta^{18}O_{skl}$ and Sr/Ca to reconstruct SSS (McCulloch et al. 1994; Gagan et al. 1998; Le Bec et al. 2000; Ren et al. 2002) are confirmed by the results of the present study. Indeed, the $\delta^{18}O_{skl}$ is a function of temperature and seawater oxygen isotopic composition ($\delta^{18}O_{sw}$), which is mainly controlled by SST and evaporation/SSS (McConnaughey 1989). Thus, by removing SST signal using Sr/Ca ratio, SSS signal can be discriminated and reconstructed. Moreover, this method can be used to identify ENSO periods (Kilbourne et al. 2004). However, Cahyarini et al. (2008) were not able to reconstruct SSS in locations where analytical uncertainties of reconstructed $\delta^{18}O_{sw}$ were equal to the magnitude of seasonal variations in $\delta^{18}O$, e.g., in Tahiti. Moreover, one should notice that light could affect the $\delta^{18}O_{skl}$, a factor that should be taken into account in paleoreconstructions (Reynaud-Vaganay et al. 2001).

Low productivity and light availability are commonly accepted as parameters which modify the $\delta^{13}C$ signature in coral skeleton (Weber and Woodhead 1972; Fairbanks and Dodge 1979; McConnaughey 1989; Reynaud-Vaganay et al. 2001). The results of the present study showed that salinity could affect and distort $\delta^{13}C$ record in coral skeleton as well (Fig. 4). However, further investigations and measurements must supplement our current data to confirm the salinity influence on $\delta^{13}C$ signature in other coral genera at a global scale.

Thus, this study showed a salinity influence on both $\delta^{18}O$ and $\delta^{13}C$, which should be taken into account when reconstructing environmental parameters. This influence on $\delta^{18}O$ was already used as SSS proxy, which is currently the only well-constrained salinometer despite temperature and environmental influences. However, the salinity influence was usually not considered in $\delta^{13}C$ application.

Nevertheless, further investigations should be performed to confirm the present results. Indeed, corals were grown in artificial conditions and salt addition can introduce chemical

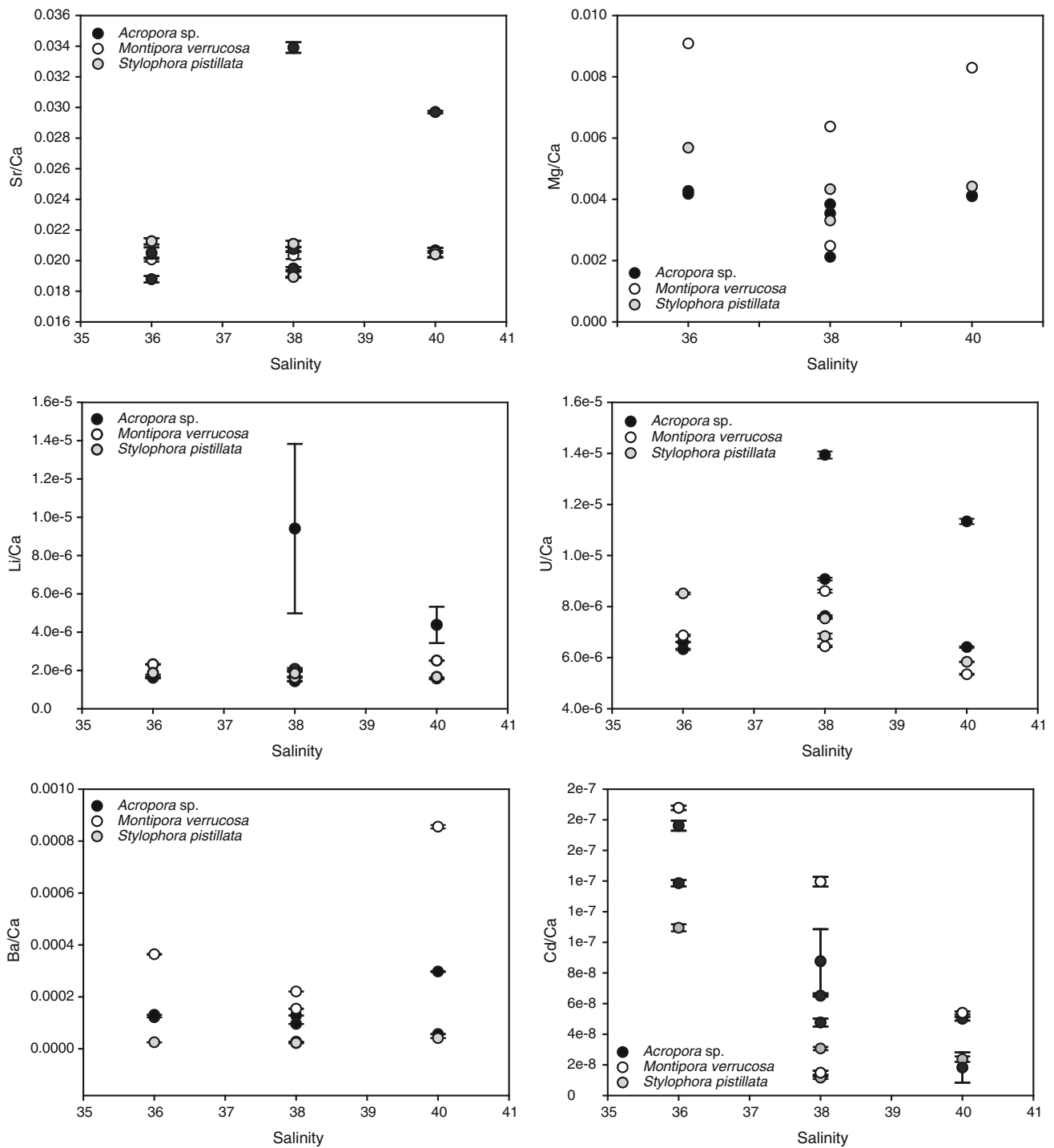
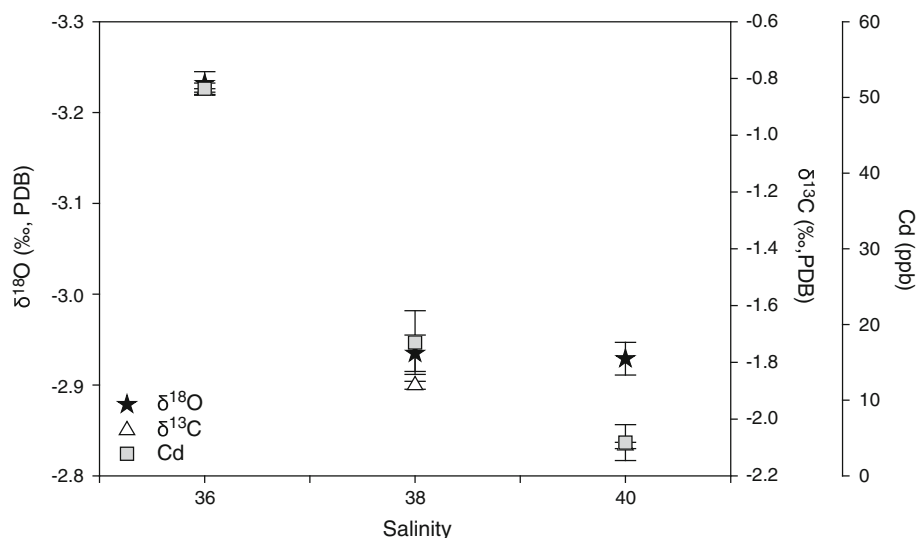


Fig. 3 Sr/Ca, Mg/Ca, Li/Ca, U/Ca, Ba/Ca and Cd/Ca according to salinity for *Acropora sp.* (filled circles), *M. verrucosa* (open circles) and *S. pistillata* (gray circles). Absolute standard deviation is represented with bars

differences compared with natural seawater. This bias is revealed by the nonlinearity of the trends due to similar $\delta^{18}\text{O}_{\text{sw}}$, $\delta^{18}\text{O}_{\text{skl}}$, $\delta^{13}\text{C}_{\text{skl}}$ and Cd/Ca values at 38 and 40 of salinity (Figs. 1, 4). However, $\delta^{18}\text{O}_{\text{sw}}$ measured at 34, 36, 38 and 40 (Fig. 1) was compared with values from literature

(Reynaud-Vaganay 2000). The trend of the values obtained in the present study is close to that of GEOSECS values (tropical and equatorial areas, <http://iridl.ldeo.columbia.edu/SOURCES/GEOSECS/>) for the same salinities (Reynaud-Vaganay 2000). Thus, variations in the isotopic composition

Fig. 4 $\delta^{13}\text{C}$ (filled star), $\delta^{18}\text{O}$ (open triangle) and Cd/Ca (gray square) in *Acropora* sp. skeleton according to salinity



of artificial seawater at different salinities are close to that of natural seawater. Therefore, we consider coral skeleton isotopic composition unaffected by salt addition.

It is worth noting that salinity does not influence all the isotopic systems and fractionation in coral skeleton: e.g., calcium isotope fractionation ($\delta^{44/40}\text{Ca}$), measured in the same sample set used in the present study, was found to be immune from salinity changes (except for *S. pistillata*) (Pretet et al. 2013).

Elemental ratios in coral skeleton immune from salinity influence

Sr/Ca and Mg/Ca: reliable temperature proxies?

Since the Sr/Ca ratio was independent from salinity variations in the present dataset (Fig. 3), and all parameters in the aquaria were monitored during the experiment, this ratio can be considered as reliable temperature proxy.

However, previous studies have shown the limits of using Sr/Ca ratio as paleothermometer, notably because it is influenced by other factors such as nutrient supply, water composition, ecology and sexual reproduction. These parameters can interfere with temperature influence when elements (and thus elemental ratios) were incorporated in coral skeleton (e.g., de Villiers et al. 1995; Enmar et al. 2000; Cohen et al. 2001; Marshall and McCulloch 2002; Fallon et al. 2003; Reynaud et al. 2007; Delong et al. 2011). Nevertheless, most studies focused on Sr/Ca as temperature proxy and showed its reliability to be used in environmental paleoreconstructions despite some external or intrinsic minor influences. The present study supports the current use of Sr/Ca as temperature proxy and shows that salinity does not affect this ratio, whichever the genus.

Although Mg/Ca ratio was considered less reliable than Sr/Ca ratio (Inoue et al. 2007), it has been used as temperature proxy when Sr/Ca failed to record temperature variations, as shown by previous studies based on this proxy (Mitsuguchi et al. 1996; Wei et al. 2000). Despite these studies which use Mg/Ca as SST proxy, other analyses showed the variability of Mg concentration in coral skeleton due to microstructure and skeletal growth rate (Meibom et al. 2004; Inoue et al. 2007; Reynaud et al. 2007). The present study confirms the biological influence on Mg incorporation into the coral skeleton due to the strong species-specific variation in Mg/Ca ratio measured in three different genera (Fig. 3). Thus, biological effects should be considered when using Mg/Ca as SST proxy (Sinclair et al. 2006). However, according to the results of the present study, Mg/Ca ratio is immune from salinity influences (Fig. 3). One should notice that Mg (as Li) is not preferentially incorporated into the coral skeleton due to seawater Mg/Ca (and Li/Ca) composition (Table 4).

Li/Ca and U/Ca: non-traditional proxies

In the present study, no variability in the Li/Ca ratio between species is observed (Fig. 3). This result is at odds with those of a previous study, which reported variability among species (Rollion-Bard et al. 2009). Also, our results show that Li/Ca ratio and, subsequently, Li incorporation in coral skeleton was not influenced by salinity changes (Fig. 3). This is consistent with the results obtained from cold-water corals (Case et al. 2010). Being not affected by salinity, this proxy can thus be used to trace paleotemperatures, as suggested by Marriott et al. (2004a, b), who showed a strong temperature dependence in the coefficient of distribution ($D(\text{Li}/\text{Ca})$) (inverse correlation between temperature and $D(\text{Li}/\text{Ca})$)

coral skeleton aragonite). Marriott et al. (2004a) further showed a clear correlation between $D(\text{Li}/\text{Ca})$ and salinity in inorganic calcite, whereas no correlation is observed for inorganic aragonite. According to these authors, the difference between calcite and aragonite reflects differences in the mechanism of Li incorporation into carbonates: substitution to Ca in inorganic aragonite and interstitial incorporation in inorganic calcite.

Previous studies reported an inverse correlation between U/Ca and SST in coral skeleton (Min et al. 1995; Shen and Dunbar 1995). Subsequent studies combined U/Ca with proxies such as $\delta^{18}\text{O}$ and Sr/Ca to remove environmental parameters other than SST (Cardinal et al. 2001; Hendy et al. 2002). This combination was specifically used in locations characterized by a wide salinity range, even if alkalinity might have a weak influence on the record (Shen and Dunbar 1995). However, Shen and Dunbar (1995) did not exclude that large salinity changes may affect the U/Ca ratio in coral skeleton. Nevertheless, data from the present study showed that the U/Ca ratio is immune from salinity variations, at least in the ranges used in our experiment (Fig. 3). Thus, U/Ca ratio can be confidently used in a multi-proxy approach involving Sr/Ca and $\delta^{18}\text{O}$ as shown in Felis et al. (2009).

Ba/Ca: genus-specific Ba incorporation?

Ba/Ca composition in coral skeleton is commonly used as proxy for upwelling, nutrient tracer or river discharge (e.g., Lea et al. 1989; Fallon et al. 1999; Alibert et al. 2003; Reuer et al. 2003; Montaggioni et al. 2006). A previous study (Sinclair and McCulloch 2004), which used Ba/Ca ratio as river discharge tracer revealed that Ba supply in the ocean varies according to Ba weathering from rivers. Ba was desorbed from the dissolved sediment in low-salinity area (Sinclair and McCulloch 2004). Therefore, the increase in Ba content was thought to be linked with Ba weathering rather than river salinity. The present study confirms that Ba/Ca ratio is not linked with salinity, independently of the coral genus concerned (Fig. 3).

Inter-generic differences in Ba/Ca ratios were statistically significant, up to one order of magnitude for coral skeleton grown in the same environment. However, values of Ba/Ca ratio ranging between 2 and $6 \mu\text{mol mol}^{-1}$ reported in previous studies (e.g., Fallon et al. 1999, Montaggioni et al. 2006) are not reflected in data obtained in the present study (Fig. 3). However, Ba incorporation in coral skeleton is not yet fully understood and other mechanisms, such as Ba-rich particle incorporation in the crystal lattice, can influence the Ba concentration (Chen et al. 2011). Previous studies showed that elemental incorporation in coral skeleton (especially Ba or Mg) varies upon the species or skeletal structure (e.g., Allison and

Tudhope 1992; Allison 1996). These mechanisms showed that the wide inter-generic difference in Ba/Ca skeletal composition in this study was not linked with environmental factor, but eventually related to Ba-rich impurities trapped in skeletal pores, which distort the Ba/Ca ratio. If so, the coral skeleton-cleaning procedures applied before analyses were not able to remove all the particles that can lead to these differences. Admittedly, previous studies pointed out that Ba/Ca in coral skeleton is tricky to interpret (Quinn and Sampson 2002). Nonetheless, the results of the present study suggest that Ba/Ca ratio in coral skeleton is immune from salinity changes.

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