

# Evaluation of the effects of microscale chemical and isotopic heterogeneity of coral skeleton on conventional Sr/Ca and $\delta^{18}\text{O}$ paleothermometers

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Recent studies using secondary ion mass spectrometry revealed microscale heterogeneity of Sr/Ca and  $\delta^{18}\text{O}$  in shallow-water coral skeletons, i.e., Sr/Ca and  $\delta^{18}\text{O}$  differ significantly between two basic micro-features of the skeleton: the center of calcification (COC) and surrounding fibrous skeleton (SFS). The COC, in contrast with the SFS, consists of highly irregular crystals intermingled with significant amount of organic matter; therefore, analyzing the SFS only would probably be favourable for paleotemperature reconstruction. Conventional Sr/Ca and  $\delta^{18}\text{O}$  paleothermometers are, however, based on the analysis of the mixture of the COC and SFS, and thus may be significantly affected by the above-mentioned heterogeneity. In this study, I have evaluated the heterogeneity-induced effects on the conventional paleothermometers of *Porites* skeletons using published Sr/Ca,  $\delta^{18}\text{O}$  and volume-fraction data of the COC and SFS and published observations of seasonal variability of bulk skeletal density. Results indicate that the effects may yield significant or serious errors in paleotemperature reconstruction.

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## 1. Introduction

Sr/Ca and  $\delta^{18}\text{O}$  of shallow-water coral skeletons are important proxies for past sea-surface temperature (McConnaughey 1989; Beck *et al.* 1992). On the other hand, application of secondary ion microprobe mass spectrometry (SIMS) to the skeletons has revealed microscale heterogeneity in both Sr/Ca and  $\delta^{18}\text{O}$ , which is not due to temperature effects but by biological effects. The microscale heterogeneity is that the Sr/Ca and  $\delta^{18}\text{O}$  values differ significantly between two fundamental micro-features of the skeleton: the center of calcification (COC: generally less than tens of  $\mu\text{m}$  in diameter) and surrounding fibrous skeleton (SFS) (Allison 1996; Cohen *et al.* 2001; Allison and Finch 2004; Allison *et al.* 2005; Meibom *et al.* 2006; Juillet-Leclerc *et al.* 2009). Cohen *et al.* (2001) suggest

that the COC and SFS grow at night and during the day, respectively. The COC consists of submicron-sized granular crystals intermingled with significant amount of organic matter; the SFS is composed of bundles of larger acicular aragonite crystals and constitutes the bulk of the skeleton (Cohen *et al.* 2001; Meibom *et al.* 2007; Holcomb *et al.* 2009), indicating that highly irregular crystal growth occurs at the COC. It has been suggested that the COC has much larger amounts of crystal defects and crystal-organic interfaces into which various minor and trace elements are incorporated or adsorbed (Mitsuguchi *et al.* 2010; Mitsuguchi and Kawakami 2012) and that the COC may be more prone to diagenetic alteration than the SFS (Allison *et al.* 2005). Thus, avoiding the COC or analyzing the SFS only, would probably be favourable for paleotemperature reconstruction,

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although doing this for a long coral core (e.g., 2–3 m in length) using the present SIMS technique would be an extremely time-consuming work.

In conventional methods of coral-skeleton-based paleotemperature reconstruction, the skeleton is sampled along its growth direction at intervals of  $\geq 0.25$  mm (mostly 0.5–1.0 mm) using a tool such as a microdrill or needle, and the obtained samples are subjected to elemental/isotopic analyses. In this case, each sample is a mixture of the COC and SFS, which may yield significant differences in paleotemperature reconstruction compared with the case of analyzing the SFS only. Furthermore, the amount ratio of the COC to the SFS is seasonally variable within individual coral colonies, which is described as follows: the thickness of skeletal structures, which corresponds to the total thickness of the COC plus SFS, is generally seasonally variable (this process produces skeletal density banding), while the thickness of the COC is likely to be almost constant or less variable than the structural thickness. This idea was proposed by Mitsuguchi and Kawakami (2012). In addition, the amount ratio of the COC to the SFS may vary between coral colonies, if they are different species or if they are the same species but growing in quite different environments. These possible variations in the COC/SFS ratio may generate significant errors in the conventional paleotemperature reconstruction.

In this paper, I evaluate the effects of the COC–SFS mixing and seasonal COC/SFS variability on the conventional Sr/Ca and  $\delta^{18}\text{O}$  paleothermometers of *Porites* coral skeletons by calculation using published data and observations. The *Porites* skeletons are most widely used for coral-based paleostudies. Main structural elements of the skeletons vary from  $\sim 50$  to  $\sim 300$   $\mu\text{m}$  in thickness; this range covers not only within-colony seasonal variation but also inter-colony and inter-species variations.

It has been reported that the COC of the skeletons is generally 5–20  $\mu\text{m}$  in diameter (Allison 1996; Allison *et al.* 2005, 2007).

## 2. Calculation and data

All variables used in my calculation are listed and described in table 1. The effects of the COC–SFS mixing on the Sr/Ca and  $\delta^{18}\text{O}$  values are expressed by the following equations.

$$(\text{Sr/Ca})_{\text{MIX}} = \frac{V_{\text{SFS}}(\text{Sr/Ca})_{\text{SFS}} + \phi V_{\text{COC}}(\text{Sr/Ca})_{\text{COC}}}{V_{\text{SFS}} + \phi V_{\text{COC}}} \quad (1)$$

$$(\delta^{18}\text{O})_{\text{MIX}} = \frac{V_{\text{SFS}}(\delta^{18}\text{O})_{\text{SFS}} + \phi V_{\text{COC}}(\delta^{18}\text{O})_{\text{COC}}}{V_{\text{SFS}} + \phi V_{\text{COC}}} \quad (2)$$

It has been observed that the COC occupies 3–4 vol.% and 19 vol.% of modern and fossil *Porites* skeletons, respectively (Allison 1996; Allison *et al.* 2005). Thus, I adopt the following conditions:  $(V_{\text{COC}}, V_{\text{SFS}}) = (3, 97), (5, 95), (10, 90), (15, 85)$  and  $(20, 80)$ . Meibom *et al.* (2007) applied NanoSIMS analyses to a modern *Porites* skeleton and observed that the  $^{40}\text{Ca}^+$  signal near the COC was  $\sim 20\%$  lower than that of the SFS and that the  $^{12}\text{C}^-$  signal near the COC was  $\sim 50\%$  higher than that of the SFS, suggesting lower (higher) concentration of calcium-carbonate (organic) material at the COC. Thus, I set  $\phi=0.8$ . Published measurements of  $(\text{Sr/Ca})_{\text{COC}}$ ,  $(\text{Sr/Ca})_{\text{SFS}}$ ,  $(\delta^{18}\text{O})_{\text{COC}}$  and  $(\delta^{18}\text{O})_{\text{SFS}}$  for shallow-water corals (*Porites*, *Colpophyllia* and *Acropora*) are listed in table 2. Unfortunately, there seems to be no published data for *Porites*  $(\delta^{18}\text{O})_{\text{COC}}$  and  $(\delta^{18}\text{O})_{\text{SFS}}$ . Under these conditions, I calculate  $(\text{Sr/Ca})_{\text{MIX}}$  and  $(\delta^{18}\text{O})_{\text{MIX}}$ . Applying the slope of the linear Sr/Ca-temperature

Table 1. List of variables used in this study.

Variable	Description
$V_{\text{COC}}$	Volume of the COC
$V_{\text{SFS}}$	Volume of the SFS
$\phi$	Volume fraction of calcium-carbonate material in the COC
$(\text{Sr/Ca})_{\text{COC}}$	Sr/Ca (mmol/mol) of the COC
$(\text{Sr/Ca})_{\text{SFS}}$	Sr/Ca (mmol/mol) of the SFS
$(\text{Sr/Ca})_{\text{MIX}}$	Sr/Ca (mmol/mol) of the mixture of the COC and SFS
$(\delta^{18}\text{O})_{\text{COC}}$	$\delta^{18}\text{O}_{\text{VPDB}}$ (‰) of the COC
$(\delta^{18}\text{O})_{\text{SFS}}$	$\delta^{18}\text{O}_{\text{VPDB}}$ (‰) of the SFS
$(\delta^{18}\text{O})_{\text{MIX}}$	$\delta^{18}\text{O}_{\text{VPDB}}$ (‰) of the mixture of the COC and SFS
$\Delta t[\text{Sr/Ca}]$	COC–SFS mixing effect on conventional Sr/Ca paleothermometer ( $^{\circ}\text{C}$ )
$\Delta t[\delta^{18}\text{O}]$	COC–SFS mixing effect on conventional $\delta^{18}\text{O}$ paleothermometer ( $^{\circ}\text{C}$ )
$\Delta T[\text{Sr/Ca}]$	Effect of seasonal COC/SFS variability on conventional Sr/Ca paleothermometer ( $^{\circ}\text{C}$ )
$\Delta T[\delta^{18}\text{O}]$	Effect of seasonal COC/SFS variability on conventional $\delta^{18}\text{O}$ paleothermometer ( $^{\circ}\text{C}$ )

Table 2. Published measurements of Sr/Ca and  $\delta^{18}\text{O}$  in the center of calcification (COC) and surrounding fibrous skeleton (SFS) of shallow-water corals.

Reference	(Sr/Ca) <sub>COC</sub> <sup>a</sup>	(Sr/Ca) <sub>SFS</sub> <sup>a</sup>	( $\delta^{18}\text{O}$ ) <sub>COC</sub> <sup>b</sup>	( $\delta^{18}\text{O}$ ) <sub>SFS</sub> <sup>b</sup>	Sample
Allison and Finch (2004)	9.3	8.9	–	–	Modern <i>Porites</i>
Allison <i>et al.</i> (2005)	9.18	8.85	–	–	Modern <i>Porites</i>
Allison <i>et al.</i> (2005)	10.21	8.92	–	–	Fossil <i>Porites</i>
Meibom <i>et al.</i> (2006)	10.1 <sup>c</sup>	9.0 <sup>d</sup>	–3.9 <sup>e</sup>	–2.0 <sup>f</sup>	Modern <i>Colpophyllia</i>
Juillet-Leclerc <i>et al.</i> (2009)	–	–	–4.9	–2.6	Modern <i>Acropora</i>

<sup>a</sup>In mmol/mol.

<sup>b</sup>In ‰ (VPDB).

<sup>c</sup>Approx. mean of the data ranging from 9.8 to 10.4 mmol/mol.

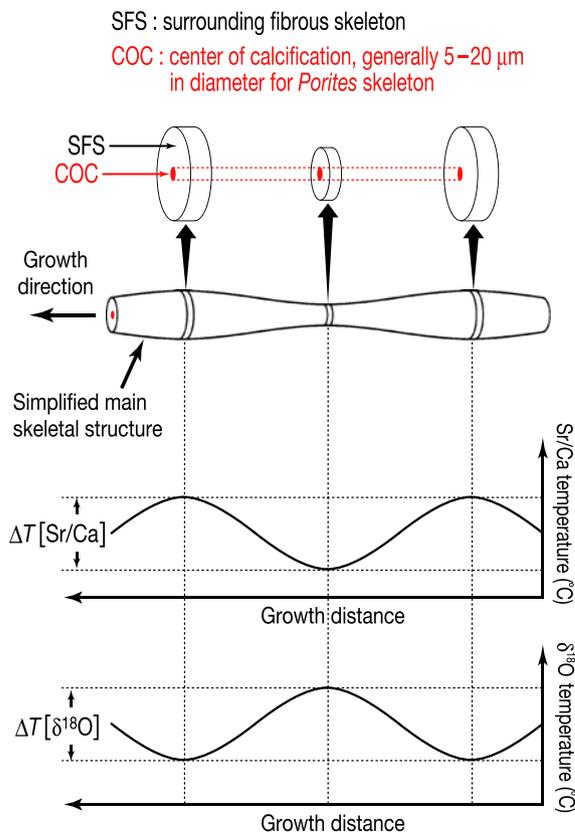
<sup>d</sup>Approx. mean of the data ranging from 8.6 to 10.0 mmol/mol.

<sup>e</sup>Approx. mean of the data ranging from –5.2 to –2.4‰.

<sup>f</sup>Approx. mean of the data ranging from –2.6 to –1.3‰.

relationship to the difference between  $(\text{Sr}/\text{Ca})_{\text{MIX}}$  and  $(\text{Sr}/\text{Ca})_{\text{SFS}}$  (i.e.,  $(\text{Sr}/\text{Ca})_{\text{MIX}} - (\text{Sr}/\text{Ca})_{\text{SFS}}$ ) allows me to evaluate the COC–SFS mixing effect on the Sr/Ca paleothermometer. Similarly, the COC–SFS mixing effect on the  $\delta^{18}\text{O}$  paleothermometer can be evaluated. In this study, I use the Sr/Ca-temperature and  $\delta^{18}\text{O}$ -temperature slopes of  $-0.0607$  mmol/mol/°C and  $-0.167$ ‰/°C, respectively, which are mean slopes for *Porites* skeletons (Corrège 2006; Gagan *et al.* 2012). As shown in table 2,  $(\text{Sr}/\text{Ca})_{\text{COC}}$  is higher than  $(\text{Sr}/\text{Ca})_{\text{SFS}}$ , and  $(\delta^{18}\text{O})_{\text{COC}}$  is lower than  $(\delta^{18}\text{O})_{\text{SFS}}$ . Consequently, the COC–SFS mixing effects on the two paleothermometers are in opposite directions.

In order to evaluate the effects of seasonal COC/SFS variability on the two paleothermometers, I set the following conditions: (1) the sum of  $V_{\text{SFS}}$  and  $V_{\text{COC}}$  varies seasonally (in a sinusoidal form) with its maximum 1.8 times its minimum; (2)  $V_{\text{COC}}$  is constant; (3)  $(\text{Sr}/\text{Ca})_{\text{COC}}$ ,  $(\text{Sr}/\text{Ca})_{\text{SFS}}$ ,  $(\delta^{18}\text{O})_{\text{COC}}$  and  $(\delta^{18}\text{O})_{\text{SFS}}$  are all constant (i.e., the values in table 2 are used). The first condition is based on the observation that, within individual *Porites* colonies, the highest bulk skeletal density is generally not more than 1.8 times the lowest bulk skeletal density (Buddemeier 1974; Lough and Barnes 1992). I use the following  $V_{\text{COC}}$  values and  $V_{\text{SFS}}$  ranges:  $(V_{\text{COC}}, V_{\text{SFS}}) = (3, 68.5\text{--}125.5)$ ,  $(5, 66.5\text{--}123.5)$ ,  $(10, 61.5\text{--}118.5)$ ,  $(15, 56.5\text{--}113.5)$  and  $(20, 51.5\text{--}108.5)$ . For each  $(V_{\text{COC}}, V_{\text{SFS}})$  pair, I calculate variabilities of  $(\text{Sr}/\text{Ca})_{\text{MIX}}$  and  $(\delta^{18}\text{O})_{\text{MIX}}$  and convert the variabilities into temperatures using the Sr/Ca-temperature and  $\delta^{18}\text{O}$ -temperature slopes. Thus, the effects of seasonal COC/SFS variability on the two paleothermometers are evaluated; a schematic illustration of the effects is presented in figure 1. It should be noted that I evaluate the ‘maximum effects’ of seasonal COC/SFS variability since I assume the maximum seasonality of bulk skeletal density.


 Figure 1. Schematic illustration of the effects of seasonal COC/SFS variability on conventional Sr/Ca and  $\delta^{18}\text{O}$  paleothermometers.

### 3. Results and discussion

Calculation results for the COC–SFS mixing effects ( $\Delta t[\text{Sr}/\text{Ca}]$  and  $\Delta t[\delta^{18}\text{O}]$ ) are shown in table 3 and those for the effects of seasonal COC/SFS variability ( $\Delta T[\text{Sr}/\text{Ca}]$  and  $\Delta T[\delta^{18}\text{O}]$ ) are shown in table 4. Results based on the Allison *et al.*'s (2005) and Meibom *et al.*'s (2006) modern Sr/Ca data are not shown in the tables, because they

Table 3. Calculation results for the COC-SFS mixing effects on conventional Sr/Ca and  $\delta^{18}\text{O}$  paleothermometers.

Condition no.	$V_{\text{COC}}$	$V_{\text{SFS}}$	$\phi$	$\Delta t[\text{Sr/Ca}]$ ( $^{\circ}\text{C}$ ) <sup>a</sup>	$\Delta t[\text{Sr/Ca}]$ ( $^{\circ}\text{C}$ ) <sup>b</sup>	$\Delta t[\delta^{18}\text{O}]$ ( $^{\circ}\text{C}$ ) <sup>c</sup>	$\Delta t[\delta^{18}\text{O}]$ ( $^{\circ}\text{C}$ ) <sup>d</sup>
1	3	97	0.8	-0.16	-0.51	0.27	0.33
2	5	95	0.8	-0.27	-0.86	0.46	0.56
3	10	90	0.8	-0.54	-1.73	0.93	1.12
4	15	85	0.8	-0.82	-2.63	1.41	1.70
5	20	80	0.8	-1.10	-3.54	1.90	2.30

<sup>a</sup>Calculation is based on the Allison and Finch's (2004) modern *Porites* Sr/Ca data (see table 2).

<sup>b</sup>Calculation is based on the Allison *et al.*'s (2005) fossil *Porites* Sr/Ca data (see table 2).

<sup>c</sup>Calculation is based on the Meibom *et al.*'s (2006) modern *Colpophyllia*  $\delta^{18}\text{O}$  data (see table 2).

<sup>d</sup>Calculation is based on the Juillet-Leclerc *et al.*'s (2009) modern *Acropora*  $\delta^{18}\text{O}$  data (see table 2).

Table 4. Calculation results for the effects of seasonal COC/SFS variability on conventional Sr/Ca and  $\delta^{18}\text{O}$  paleothermometers.

Condition no.	$V_{\text{COC}}$	$V_{\text{SFS}}$	$\phi$	$\Delta T[\text{Sr/Ca}]$ ( $^{\circ}\text{C}$ ) <sup>a</sup>	$\Delta T[\text{Sr/Ca}]$ ( $^{\circ}\text{C}$ ) <sup>b</sup>	$\Delta T[\delta^{18}\text{O}]$ ( $^{\circ}\text{C}$ ) <sup>c</sup>	$\Delta T[\delta^{18}\text{O}]$ ( $^{\circ}\text{C}$ ) <sup>d</sup>
1	3	68.5–125.5	0.8	0.10	0.32	0.17	0.21
2	5	66.5–123.5	0.8	0.17	0.54	0.29	0.35
3	10	61.5–118.5	0.8	0.34	1.10	0.59	0.71
4	15	56.5–113.5	0.8	0.52	1.69	0.91	1.10
5	20	51.5–108.5	0.8	0.72	2.31	1.23	1.49

<sup>a</sup>Calculation is based on the Allison and Finch's (2004) modern *Porites* Sr/Ca data (see table 2).

<sup>b</sup>Calculation is based on the Allison *et al.*'s (2005) fossil *Porites* Sr/Ca data (see table 2).

<sup>c</sup>Calculation is based on the Meibom *et al.*'s (2006) modern *Colpophyllia*  $\delta^{18}\text{O}$  data (see table 2).

<sup>d</sup>Calculation is based on the Juillet-Leclerc *et al.*'s (2009) modern *Acropora*  $\delta^{18}\text{O}$  data (see table 2).

are similar to the shown results based on the Allison and Finch's (2004) modern Sr/Ca data and Allison *et al.*'s (2005) fossil Sr/Ca data, respectively. In the case of the Allison and Finch's (2004) data (i.e.,  $(\text{Sr/Ca})_{\text{COC}} - (\text{Sr/Ca})_{\text{SFS}} = 0.4$  mmol/mol),  $|\Delta t[\text{Sr/Ca}]|$  varies from  $0.16^{\circ}\text{C}$  ( $V_{\text{COC}} = 3$  vol.%) to  $1.10^{\circ}\text{C}$  ( $V_{\text{COC}} = 20$  vol.%);  $|\Delta T[\text{Sr/Ca}]|$  ranges from  $0.10^{\circ}\text{C}$  ( $V_{\text{COC}} = 3$  vol.%) to  $0.72^{\circ}\text{C}$  ( $V_{\text{COC}} = 20$  vol.%), indicating that, when  $V_{\text{COC}} \geq \sim 15$  vol.%, both of the effects cause considerable errors in paleotemperature reconstruction. In the case of Allison *et al.*'s (2005) fossil data (i.e.,  $(\text{Sr/Ca})_{\text{COC}} - (\text{Sr/Ca})_{\text{SFS}} = 1.29$  mmol/mol), the above-calculated  $|\Delta t[\text{Sr/Ca}]|$  and  $|\Delta T[\text{Sr/Ca}]|$  values are approximately tripled:  $|\Delta t[\text{Sr/Ca}]| = 0.51^{\circ}\text{C}$ – $3.54^{\circ}\text{C}$  and  $|\Delta T[\text{Sr/Ca}]| = 0.32^{\circ}\text{C}$ – $2.31^{\circ}\text{C}$  for  $V_{\text{COC}} = 3$ – $20$  vol.%, mostly indicating significant or serious errors in paleotemperature reconstruction. Allison *et al.* (2005) did similar calculation for  $\Delta t[\text{Sr/Ca}]$ , using their estimation of  $V_{\text{COC}}$  for a modern and a fossil *Porites* skeleton (4 and 19 vol.%, respectively) and measurements of  $(\text{Sr/Ca})_{\text{COC}}$  and  $(\text{Sr/Ca})_{\text{SFS}}$  of the skeletons (shown in table 2). They suggest that the higher Sr enrichment at the COC and larger  $V_{\text{COC}}$  of the fossil skeleton are due to diagenetic alteration

(i.e., replacement of the original COC by secondary aragonite cement). If this is the case, then  $\phi \approx 1$ ,  $|\Delta t[\text{Sr/Ca}]| \approx 0.64^{\circ}\text{C}$ – $4.25^{\circ}\text{C}$ , and  $|\Delta T[\text{Sr/Ca}]| \approx 0.40^{\circ}\text{C}$ – $2.64^{\circ}\text{C}$  for  $V_{\text{COC}} = 3$ – $20$  vol.%. On the other hand, Meibom *et al.* (2006) observed a similarly high enrichment of Sr at the COC of a modern *Colpophyllia* skeleton (see table 2); the COC of the skeleton is exceptionally large ( $\sim 100$   $\mu\text{m}$  in diameter) and thus  $V_{\text{COC}}$  is likely to be relatively large, suggesting larger  $|\Delta t[\text{Sr/Ca}]|$  values for *Colpophyllia*. Cohen *et al.* (2001) observed, in a modern *Porites* coral, that  $(\text{Sr/Ca})_{\text{COC}}$  was  $\sim 0$ – $0.7$  mmol/mol higher than  $(\text{Sr/Ca})_{\text{SFS}}$ ; the  $\sim 0$  and  $\sim 0.7$  mmol/mol differences occur when the coral grows at the annual minimum and maximum seawater temperatures, respectively (data not shown in table 2). The  $(\text{Sr/Ca})_{\text{COC}} - (\text{Sr/Ca})_{\text{SFS}}$  difference of  $\sim 0.7$  mmol/mol is larger than the observation of Allison and Finch (2004) for a modern *Porites* coral (i.e., 0.4 mmol/mol) and smaller than that of Allison *et al.* (2005) for a fossil *Porites* coral (i.e., 1.29 mmol/mol) (see table 2).

If the Meibom *et al.*'s (2006)  $\delta^{18}\text{O}$  data is used,  $\Delta t[\delta^{18}\text{O}]$  varies from  $0.27^{\circ}\text{C}$  ( $V_{\text{COC}} = 3$  vol.%) to  $1.90^{\circ}\text{C}$  ( $V_{\text{COC}} = 20$  vol.%) and  $\Delta T[\delta^{18}\text{O}]$  ranges from  $0.17^{\circ}\text{C}$  ( $V_{\text{COC}} = 3$  vol.%) to  $1.23^{\circ}\text{C}$  ( $V_{\text{COC}} =$

20 vol.%); in the case of the Juillet-Leclerc *et al.*'s (2009) data,  $\Delta t[\delta^{18}\text{O}]$  varies from 0.33°C ( $V_{\text{COC}} = 3$  vol.%) to 2.30°C ( $V_{\text{COC}} = 20$  vol.%) and  $\Delta T[\delta^{18}\text{O}]$  ranges from 0.21°C ( $V_{\text{COC}} = 3$  vol.%) to 1.49°C ( $V_{\text{COC}} = 20$  vol.%), indicating significant or serious errors in paleotemperature reconstruction when  $V_{\text{COC}} \geq 5$  or 10 vol.%. The Meibom *et al.*'s (2006) and Juillet-Leclerc *et al.*'s (2009)  $\delta^{18}\text{O}$  data are derived from different genera: *Colpophyllia* and *Acropora*, respectively. Despite the difference in genus, the two datasets are similar for the difference between  $(\delta^{18}\text{O})_{\text{COC}}$  and  $(\delta^{18}\text{O})_{\text{SFS}}$ , i.e., the former indicates that  $(\delta^{18}\text{O})_{\text{COC}}$  is 1.9‰ lower than  $(\delta^{18}\text{O})_{\text{SFS}}$ , and the latter shows that  $(\delta^{18}\text{O})_{\text{COC}}$  is 2.3‰ lower than  $(\delta^{18}\text{O})_{\text{SFS}}$  (see table 2). Thus, I infer that the  $(\delta^{18}\text{O})_{\text{COC}} - (\delta^{18}\text{O})_{\text{SFS}}$  difference does not vary significantly between symbiotic coral genera, and that the two datasets are applicable to *Porites*.

The COC–SFS mixing effect and the effect of seasonal COC/SFS variability would generally combine to complicate the problem. The problem is further complicated by the fact that the formation of annual density bands in *Porites* skeletons greatly varies depending on individual colonies; for example, (1) some colonies form a high-density band in a warm season and others in a cool season even in the same region and (2) some colonies form distinct couplets of high- and low-density annual bands and others do not. This complication may be a cause of the fact that there are significant differences between conventional Sr/Ca-temperature (or  $\delta^{18}\text{O}$ -temperature) relationships for *Porites* skeletons (Corrège 2006; Gagan *et al.* 2012). In addition, the COC–SFS mixing effects on the two paleothermometers are in opposite directions (see table 3), and the effects of seasonal COC/SFS variability on the two are also in opposite directions (see figure 1), which may greatly perturb the paleosalinity reconstruction by the combination of conventional Sr/Ca and  $\delta^{18}\text{O}$  analyses (McCulloch *et al.* 1994; Gagan *et al.* 1998).

So far, only small amounts of data have been published for  $V_{\text{COC}}$ ,  $(\text{Sr}/\text{Ca})_{\text{COC}} - (\text{Sr}/\text{Ca})_{\text{SFS}}$  difference, and  $(\delta^{18}\text{O})_{\text{COC}} - (\delta^{18}\text{O})_{\text{SFS}}$  difference. Collection of these data will enable more accurate evaluation of the effects of the COC–SFS mixing and seasonal COC/SFS variability, and will probably lead to methodological improvements or changes for more accurate paleotemperature and paleosalinity reconstructions.

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