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## Oxygen isotope fractionation in marine aragonite of coralline sponges

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**Abstract**—Oxygen isotope values of the extant Caribbean coralline sponge *Ceratoporella nicholsoni* are compared with published temperatures and  $\delta^{18}\text{O}$  of water calculated from salinities. The measured values from aragonitic sponge skeletons have a mean offset of  $1.0 \pm 0.1\%$  from calculated calcite equilibrium values ( $\alpha_{\text{aragonite-calcite}} = 1.0010$ ). This is in good agreement with published values from synthetic aragonite. They further agree with published near-equilibrium oxygen isotope values of temperate and cold water molluscs and foraminifera extrapolated to the temperature range of the coralline sponges. These results and the mode of skeleton formation of *Ceratoporella nicholsoni* suggest that these sponges precipitate aragonite close to isotopic equilibrium.

The temperature dependence of oxygen isotopic fractionation between the aragonite of *Ceratoporella nicholsoni* and water is only roughly constrained by the available data, due to the narrow temperature range of the Caribbean reef sites. However, as the data suggest oxygen isotopic equilibrium, we can calculate a well constrained temperature equation combining temperate and cold water equilibrium values from molluscs and foraminifera with our sponge data:

$$10^3 \ln \alpha_{\text{aragonite-water}} = (18.45 \pm 0.4) * 10^3/T \text{ (K)} - (32.54 \pm 1.5) \text{ and } T \text{ (}^\circ\text{C)} = (20.0 \pm 0.2) - (4.42 \pm 0.10) * (\delta_a - \delta_w); \text{ for } 3^\circ < T < 28^\circ. \text{ Copyright } \text{© } 2000 \text{ Elsevier Science Ltd}$$

### 1. INTRODUCTION

The oxygen isotopic composition of marine aragonite is a well established proxy for temperature and salinity variations of sea water (e.g., Aharon, 1991; Fairbanks et al., 1997; Halley et al., 1994). However, oxygen isotope values measured on coralline sponges have only recently come into focus of palaeoclimatologists (Dickson et al., 1996; Swart et al., 1998; Wörheide, 1998). It is assumed that many coralline sponge taxa precipitate a basal skeleton in oxygen and carbon isotopic equilibrium with ambient sea water (Reitner, 1992). With this and typical lifespans measuring in centuries (Swart et al., 1998; Wörheide, 1998) sponges appear well-suited as long-term climate recorders.

In this study we present data on the oxygen isotopic composition of aragonitic skeletons built by the coralline sponges *Ceratoporella nicholsoni* and *Astrosclera willeyana*. Both sponges build the bulk of their skeletons by extracellular, syn-vivo-diagenetic, epitactic precipitation of aragonite. This mode of skeleton formation and analyses of the carbon isotopic composition suggest isotopic equilibrium with the ambient seawater (Druffel and Benavides, 1986; Willenz and Hartman, 1989; Reitner, 1992; Böhm et al., 1996; Wörheide, 1998).

### 2. MATERIAL AND METHODS

Live sponges were collected in situ between 1993 and 1996 through scuba diving off the north Jamaican coast (Caribbean) and at the Great Barrier Reef (Coral Sea). They were taken from 20 mbsl (metres below sea level) at Montego Bay, 25 mbsl at Rio Bueno, 84 mbsl and 91 mbsl at Discovery Bay (Caribbean, 77.5°W, 18.5°N) and at 26 mbsl from Ribbon Reef #10 (Coral Sea, 145.7°E, 14.8°S). All sponges come from the reef fronts and slopes facing the open sea, away from the influence of lagoonal waters (Böhm et al., 1996; Wörheide, 1998). During cruise 35 of the research vessel Meteor (Spring, 1996) dives with the submersible Jago allowed collection of sponges from the NW slope (125 mbsl) of Pedro Bank (79.0°W, 17.5°N), a submerged carbonate bank about 200 km southwest of Jamaica. All Caribbean specimens are of the species *Ceratoporella nicholsoni* (Hickson). The Coral Sea specimen is an *Astrosclera willeyana* Lister.

Samples for carbon and oxygen isotope analyses were collected from the sectioned skeletons using a dental drill equipped with a 0.5 mm drill head. Samples were drilled along transects vertical to lamination. In one specimen we additionally sampled a transect along a well-visible lamina. Laminae are thought to represent isochronal layers, as they run parallel to the growth surface. The drill was operated at low speed to avoid possible aragonite-calcite conversion (Gill et al., 1995). Carbonate powder samples were reacted with "100%"  $\text{H}_3\text{PO}_4$  at 75°C in an online, automated carbonate reaction device (Kiel Device) connected to a Finnigan Mat 252 mass spectrometer at the University of Erlangen Geological Institute. Isotopic ratios are reported in permil relative to PDB (Peedee Belemnite) by assigning a  $\delta^{18}\text{O}$  value of  $-2.19\%$  (PDB) to standard NBS 19. All  $\delta^{18}\text{O}$  values of water are reported relative to SMOW (Standard Mean Ocean Water). External precision ( $2\sigma$ ) for  $\delta^{18}\text{O}$  is  $\pm 0.07\%$  (PDB) based on multiple analyses ( $N = 87$ ) of standards NBS 19 and IAEA CO1.

Only samples of growth layers that formed after about 1950 AD were used for this study. Sample ages were estimated from average growth rates (Böhm et al., 1996; Wörheide, 1998; Böhm et al., in prep.). Growth rates of the investigated sponges vary from 0.2 to 0.4 mm/year. Thus, samples were collected from the outer 8 to 16 mm of each specimen. With the given growth rates and mean sample diameter of 0.7 mm, each sample comprises an interval of 1.8 to 3.5 years.

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Table 1. Annual average temperatures and salinities at the sampling sites. Long-term averages and mean annual amplitudes. Data from Levitus and Boyer (1994) and Levitus et al. (1994), is available on the world wide web at: <http://ingrid.ldeo.columbia.edu/SOURCES/LEVITUS94/> "Annual amplitudes" are differences between coldest (least saline) and warmest (most saline) months, calculated from monthly averages. "Annual amplitude  $\delta^{18}\text{O}$ " is the variation in isotopic composition caused by these intra-annual temperature and salinity changes, calculated as given below. "Worst sample" is the size (years) of a sample that could produce the largest subannual bias. "Maximum deviation" is the biggest possible deviation from the annual mean produced by the "worst sample". "Maximum deviation in  $\delta^{18}\text{O}$ " is the biggest possible deviation caused by the "worst sample". It is calculated from the maximum deviations in temperature ( $\Delta T$ ) and salinity ( $\Delta S$ ), assuming  $\Delta\delta^{18}\text{O} = 0.25 * \Delta T$  (O'Neil et al., 1969, Grossman and Ku, 1986) and  $\Delta\delta^{18}\text{O} = 0.17 * \Delta S$  (Ferronsky and Brezgunov, 1989).

Locality Water depth	N' Jamaica 20 m		N' Jamaica 90 m		Pedro Bank 125 m		Ribbon Reef #10 25 m	
	Temp.	Salinity	Temp.	Salinity	Temp.	Salinity	Temp.	Salinity
Annual average	27.52°C	35.96	26.23°C	36.25	25.10°C	36.47	26.14°C	35.12
Ann. amplitude	2.98°C	0.38	0.88°C	0.31	0.95°C	0.32	4.07°C	0.61
Ann. ampl. $\delta^{18}\text{O}$	0.8‰	0.06‰	0.2‰	0.05‰	0.2‰	0.05‰	1.0‰	0.1‰
Worst sample	1.4 yr.	1.4 yr.	1.5 yr.	1.3 yr.	1.5 yr.	1.3 yr.	1.4 yr.	1.4 yr.
Max. deviation	$\pm 0.3^\circ\text{C}$	$\pm 0.04$	$\pm 0.09^\circ\text{C}$	$\pm 0.3$	$\pm 0.08^\circ\text{C}$	$\pm 0.03$	$\pm 0.43^\circ\text{C}$	$\pm 0.07$
Max. dev. $\delta^{18}\text{O}$	$\pm 0.07\text{‰}$	$\pm 0.006\text{‰}$	$\pm 0.02\text{‰}$	$\pm 0.005\text{‰}$	$\pm 0.02\text{‰}$	$\pm 0.004\text{‰}$	$\pm 0.11\text{‰}$	$\pm 0.01\text{‰}$

Consequently, subannual variations of temperature and salinity, which are small at the sampling sites anyway (Table 1), are barely represented in our samples.

For each specimen we calculated the average for the measured  $\delta^{18}\text{O}$  values (Table 2). We consider these averages to represent long-term means for the period 1950–1990. To calculate temperature dependences and expected equilibria we use the average water temperature, at the given depth, provided by Levitus and Boyer (1994) and estimate the  $\delta^{18}\text{O}$  for the ambient water ( $\delta_w$ ) from average salinity (S) (Levitus et al., 1994) (Fig. 1). For the Caribbean we use the salinity- $\delta_w$  relationship given by Fairbanks et al. (1992) for the Gulf Stream and Gulf of Mexico:

$$\delta_w = 0.11S - 3.15 \quad (1)$$

A  $\delta_w$  value of 0.8‰ (SMOW), measured by Land (1992) for Discovery Bay surface waters (Jamaica), agrees very well with the values calculated from salinity (Table 2). For the Coral Sea we use a  $\delta_w$  of 0.36‰ (SMOW) measured in water samples collected west of Ribbon Reef near Lizard Island in 1994 (Wörheide, 1998).

For the calculation of isotopic calcite-water equilibria we use the equation of Kim and O'Neil (1997), with a correction (+0.25) to keep compatibility with the conventional acid fractionation factor ( $\alpha = 1.01025$  at 25°C, Fig. 1 of Kim and O'Neil 1997):

$$10^3 \ln \alpha_{\text{calcite-water}} = (18.03 \pm 0.86) * 10^3/T - (32.17 \pm 2.9) \quad (2)$$

with  $\alpha_{\text{calcite-water}}$ : equilibrium fractionation factor between calcite and water, T: temperature in Kelvin. Errors are 95% confidence levels.

Table 2. Average  $\delta^{18}\text{O}$  and aragonite-water fractionation of coralline sponges for interval approximately 1950 to 1990. Annual temperature and salinity means from Levitus and Boyer (1994), Levitus et al. (1994), seawater  $\delta^{18}\text{O}$  calculated from salinity (Fairbanks et al., 1992). Equilibrium calcite  $\delta^{18}\text{O}_{\text{c,eq}}$  is calculated for temperature and  $\delta^{18}\text{O}_{\text{water}}$  for each site using the equation of Kim and O'Neil (1997) adjusted for conventional acid fractionation. Last column shows  $\epsilon_{\text{aragonite-calcite}} = (\alpha_{\text{aragonite-calcite}} - 1) * 1000 \approx \delta^{18}\text{O}_{\text{aragonite}} - \delta^{18}\text{O}_{\text{calcite}}$ . The mean  $\epsilon_{\text{aragonite-calcite}}$  is 1.0.

Locality, specimen	Mean $\delta^{18}\text{O}_{\text{aragonite}}$		Annual mean		$\delta^{18}\text{O}_{\text{water}}$ ‰ SMOW	$\alpha_{\text{arag.-water}}$	1000 ln $\alpha$ arag.-water	$\delta^{18}\text{O}_{\text{c,eq}}$ ‰ SMOW	$\epsilon$ aragonite- calcite
	‰ PDB	‰ SMOW	Temp. °C	Salinity psu					
Montego Bay 961	-0.83	30.00	27.5	35.96	0.81	1.02917	28.76	29.01	0.97
Montego Bay 952	-0.85	29.98	27.5	35.96	0.81	1.02915	28.73	29.01	0.95
Montego Bay 951	-0.79	30.05	27.5	35.96	0.81	1.02922	28.80	29.01	1.01
Rio Bueno	-0.71	30.12	27.5	35.98	0.81	1.02929	28.87	29.02	1.07
Discovery Bay 232	-0.48	30.37	26.2	36.25	0.84	1.02950	29.08	29.31	1.03
Discovery Bay 171	-0.47	30.37	26.4	36.21	0.83	1.02951	29.09	29.27	1.08
Pedro Bank	-0.38	30.47	25.1	36.47	0.86	1.02959	29.16	29.57	0.88
Ribbon Reef	-1.08	29.75	26.1	35.12	0.36	1.02938	28.95	28.84	0.89

SMOW to PDB conversions were calculated according to Friedman and O'Neil (1977).

### 3. RESULTS

The measured oxygen isotope values are shown in Figure 2 and Table 3. We measured three transects through a single specimen of *Ceratoporella* from the Rio Bueno site (Fig. 2a). This sponge grew in a cave at a water depth of 25 m (Böhm et al., 1996). The mean values of the individual transects are not significantly different (Table 3). The overall average is  $-0.71 \pm 0.14\text{‰}$  (PDB,  $\pm 2\sigma$ ,  $n = 40$ ). There is a minor shift of  $<0.1\text{‰}$  from isotope values around 8 mm to values between 0 and 5 mm. At Montego Bay (Fig. 2b) three specimens living in the same cave were investigated. The overall  $\delta^{18}\text{O}$  average is  $-0.83 \pm 0.12\text{‰}$  (PDB,  $\pm 2\sigma$ ,  $n = 37$ ). There is no significant long-term trend visible in the Montego Bay  $\delta^{18}\text{O}$  data.

The two specimens from the bottom of the mixed layer at Discovery Bay show very constant and significantly higher  $\delta^{18}\text{O}$  values (mean  $-0.48 \pm 0.06\text{‰}$ ,  $n = 18$ ; Fig. 2c) compared with the shallow water specimens (Fig. 2a,b). Within the limits of analytical precision the means for the two specimens are identical.

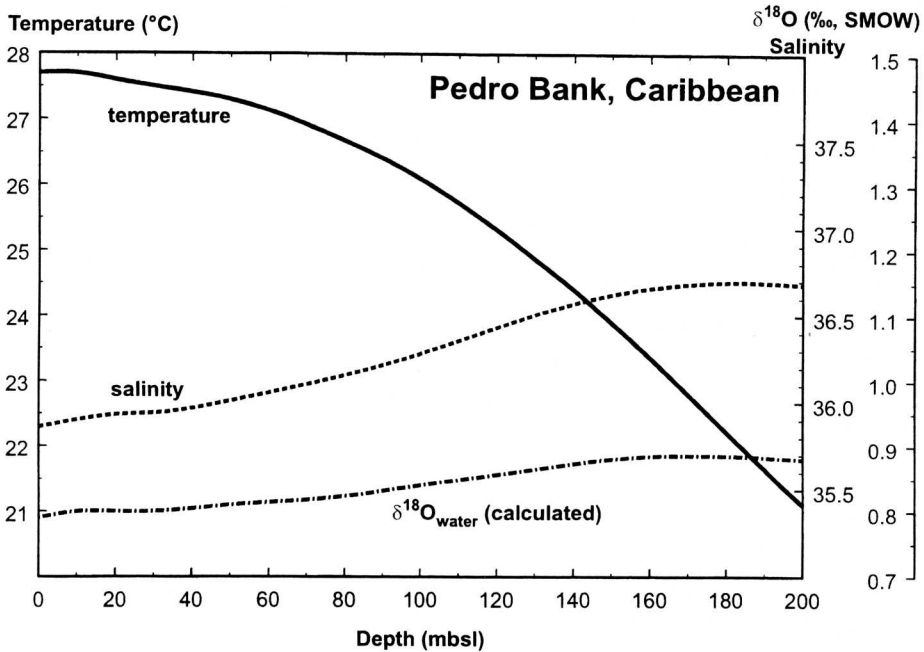


Fig. 1. Plot of water temperature (Levitus and Boyer, 1994), salinity (Levitus et al., 1994) and  $\delta^{18}\text{O}$  of water calculated from salinity (Fairbanks et al., 1992) for Pedro Bank.

The  $\delta^{18}\text{O}$  values of a specimen from the top of the thermocline at Pedro Bank (Fig. 2d,e) are similar to the Discovery Bay values, but show a slightly greater variability (mean  $-0.38 \pm 0.18\text{‰}$ ,  $n = 17$ ). Two parallel transects were sampled on the distinctly laminated specimen. The lamination allows approximate correlation between the transects (Fig. 3). Transect 2 shows consistently lower  $\delta^{18}\text{O}$  values, except for the two oldest samples (Fig. 2d). The mean offset is  $0.13\text{‰}$ . A third, "horizontal" transect was investigated to examine the variability within a single lamina (Fig. 2e). This growth layer is supposed to have formed "simultaneously" with respect to the time scale resolved by our sampling method (averaging about 3 yr per sample). Unexpectedly, the measured variability of  $\pm 0.12\text{‰}$  ( $2\sigma$ ,  $n = 6$ ) is of the same magnitude as the interlamina variability measured in Transects 1 and 2. The two values at the intersections with Transect 1 and 2 deviate significantly from the mean (Fig. 2e). Magnitude and sign of the deviations are consistent with the systematic offset between the values of Transect 1 and 2, where Transect 2 values are on average  $0.13\text{‰}$  lower.

Two transects through a specimen *Astrosclera willeyana* (Fig. 2f) from an outer reef at the Great Barrier Reef show significantly lower  $\delta^{18}\text{O}$  values (mean  $-1.08 \pm 0.18\text{‰}$ ,  $n = 13$ ) than the Caribbean sponges. This is expected, due to the lower  $\delta_w$  values seen at the Great Barrier Reef.

#### 4. DISCUSSION

##### 4.1. Reproducibility

The average oxygen isotope values (Table 3) measured on parallel transects through single specimens as well as on different specimens that lived in close proximity at the same site differ on average by  $0.05\text{‰}$  ( $n = 10$ ). This imprecision is

significantly smaller than the differences between average values from sponges that grew in different environments. However, the presence of systematic offsets in the three transects through the Pedro Bank specimen, however small, may indicate inhomogeneities in the oxygen isotopic composition of some skeletons. This could point to minor "vital effects" (McConaughy, 1989). These inhomogeneities may produce erroneous trends in climate proxy records derived from coralline sponges. We therefore recommend the use of multiple transects to verify palaeoclimatic interpretations.

##### 4.2. $^{18}\text{O}/^{16}\text{O}$ Equilibrium Fractionation of Aragonite

The equilibrium fractionation of oxygen isotopes between water and synthetic calcite is well studied (O'Neil et al., 1969; Kim and O'Neil, 1997), even though recent work points to previously overlooked complications (see discussion in Zeebe, 1999). On the other hand, there is still disagreement regarding the  $^{18}\text{O}/^{16}\text{O}$  equilibrium fractionation of aragonite (Kim and O'Neil, 1997). Experimental results for synthetic aragonite are available from the study of Tarutani et al. (1969), but only for a constant temperature of  $25^\circ\text{C}$ . Thus, equilibrium values for different temperatures are usually taken from the equation for biogenic aragonite of Grossman and Ku (1986) or calculated from the equilibrium values of calcite and the calcite-aragonite fractionation factor.

The  $^{18}\text{O}/^{16}\text{O}$  fractionation between synthetic calcite and aragonite was determined by Tarutani et al. (1969) from the difference of calcite-water and aragonite-water fractionations as  $0.6\text{‰}$ . However, since even the smallest calcite-water fractionation factors determined by Tarutani et al. are slightly higher than those reported in later studies (O'Neil et al., 1969, Kim and O'Neil, 1997), the calcite-water fractionation factors

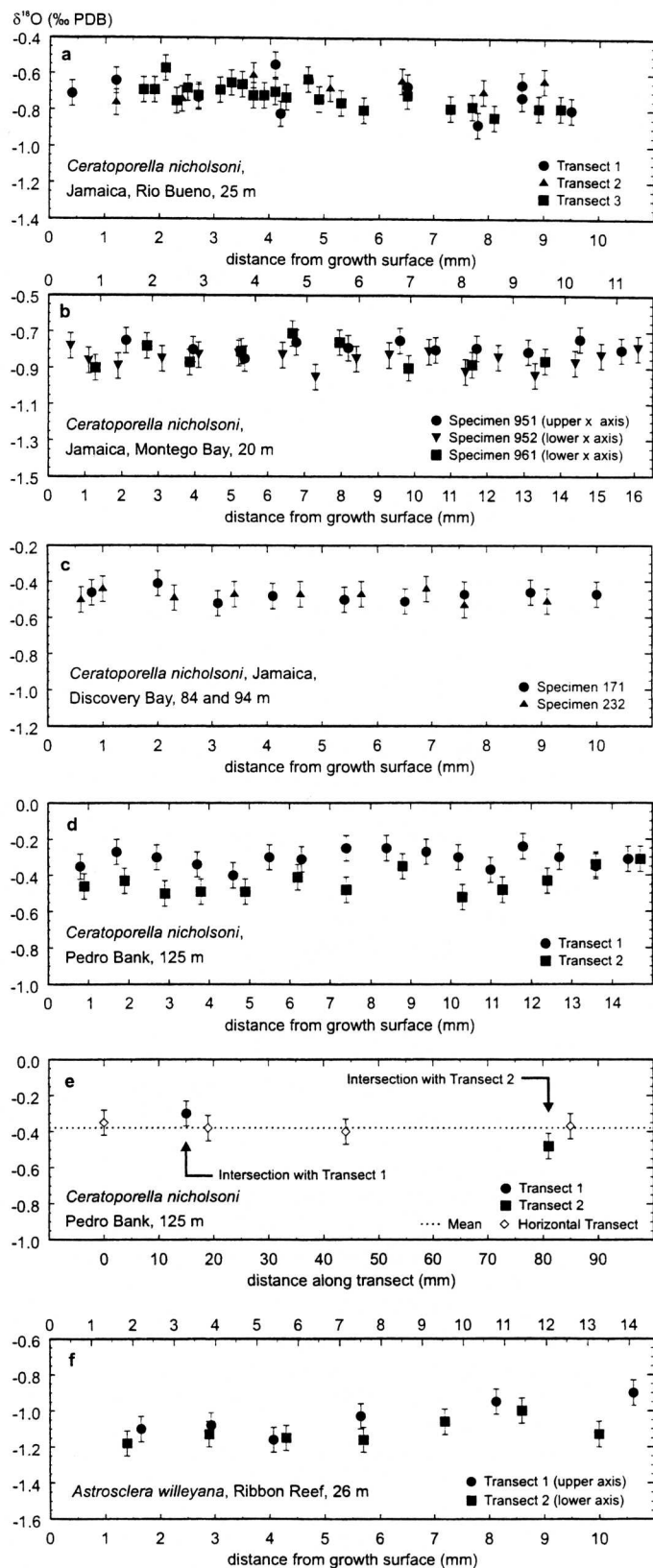


Fig. 2. Plots of measured  $\delta^{18}\text{O}_{\text{aragonitic}}$  values against distance from growth surface. Error bars represent external precision ( $\pm 2\sigma$ ). a. Specimen from Rio Bueno with three separate transects. b. Three specimens from a reef cave at Montego Bay. Horizontal axes are scaled to account for the different growth rates. Note, however, that single data points are not precisely dated as growth rates are not necessarily constant throughout the shown intervals. c. Specimens from Discovery Bay, bottom of the mixed layer. d. Two transects of a specimen from Pedro Bank, top of thermocline. The measured  $\delta^{18}\text{O}$  values of the two transects are systematically offset by about 0.13‰. The horizontal transect shown in e intersects with Transect 1 at 10.2 mm and with Transect 2 at 11.3 mm. e. Horizontal transect through the Pedro Bank specimen, following a distinct growth band. All samples of this transect are supposed to have formed simultaneously. Nevertheless, two values deviate significantly (about  $\pm 0.1\%$ ) from the mean (dotted line). The vertical transects 1 and 2 intersect this growth band at the points indicated by the arrows. f. Two transects through a specimen of *Astrosclera willeyana* from Great Barrier Reef. Transect 1 follows the major growth axis and is scaled to a higher growth rate.

Table 3. Oxygen isotope values measured on coralline sponges (in permil, PDB, deviations are given as  $1\sigma$ , standard deviation). a. Rio Bueno, Jamaica. Position of samples measured from growth surface, perpendicular to lamination. Data are from time intervals of approximately 40 years (1950–1990). Transect 1 is 4 cm from transect 2 and 3, the latter are 2 mm apart. Estimated growth rate 0.25 mm/year ( $^{14}\text{C}$  bomb spike”, Böhm et al., 1996). b. Montego Bay, Jamaica. Estimated growth rates (from Böhm et al., in prep.): Specimen 951 0.24 mm/year (U/Th age); specimen 952 0.34 mm/year (U/Th age); specimen 961 0.29 mm/year (U/Th age). c. Discovery Bay, Jamaica. Estimated growth rate: 0.25 mm/year ( $\delta^{13}\text{C}$  fit, Böhm et al., 1996). d. Pedro Bank. Vertical transects 1 and 2 are 6 cm apart. Transect 3 is parallel to lamination. Estimated growth rate 0.2 mm/year (U/Th age, Fig. 3). In addition, older data from 1900–1950 used for the reproducibility test are shown. e. Ribbon Reef #10, Great Barrier Reef. Two transects are 20 cm apart. Estimated average growth rate for transect 1: 0.38 mm/year, transect 2: 0.29 mm/year ( $^{14}\text{C}$  age, Wörheide, 1998).

Pos. mm	$\delta^{18}\text{O}$ ‰ PDB	Pos. mm	$\delta^{18}\text{O}$ ‰ PDB	Pos. mm	$\delta^{18}\text{O}$ ‰ PDB	Pos. mm	$\delta^{18}\text{O}$ ‰ PDB	Pos. mm	$\delta^{18}\text{O}$ ‰ PDB	Pos. mm	$\delta^{18}\text{O}$ ‰ PDB
<i>Ceratoporella nicholsoni</i>											
Rio Bueno, 25 m		3.9	-0.72	1.1	-0.86	2.0	-0.41	$\sigma$	0.05		
Transect 1		4.1	-0.70	1.9	-0.89	3.1	-0.52		pre-1950		Transect 3 (horizontal)
0.4	-0.71	4.3	-0.73	3.1	-0.85	4.1	-0.48	9.4	-0.27	0	-0.35
1.2	-0.64	4.7	-0.63	4.1	-0.83	5.4	-0.50	10.2	-0.30	4	-0.30
2.7	-0.73	4.9	-0.74	5.2	-0.82	6.5	-0.51	11.0	-0.37	41	-0.38
4.1	-0.55	5.3	-0.76	6.4	-0.83	7.6	-0.47	11.8	-0.24	66	-0.40
4.2	-0.82	5.7	-0.80	7.3	-0.95	8.8	-0.46	12.7	-0.30	70	-0.48
6.5	-0.67	6.5	-0.72	8.4	-0.85	10.0	-0.47	13.6	-0.35	85	-0.37
7.8	-0.88	7.3	-0.79	9.3	-0.83	Mean	-0.47	14.4	-0.31	Mean	-0.38
8.6	-0.66	7.7	-0.78	10.4	-0.81	$\sigma$	0.03	Mean	-0.33	$\sigma$	0.06
8.6	-0.73	8.1	-0.84	11.4	-0.92	Spec. 232, 94 m		$\sigma$	0.04		
9.5	-0.80	8.9	-0.79	12.3	-0.84	0.6	-0.50		Transect 2		Astroclera willeyana
Mean	-0.72	9.3	-0.79	13.3	-0.94	1.0	-0.44	0.9	-0.46		Ribbon Reef #10, 26 m
$\sigma$	0.10	Mean	-0.72	14.4	-0.87	2.3	-0.49	1.9	-0.43		Transect 1
Transect 2		$\sigma$	0.06	15.1	-0.83	3.4	-0.47	2.9	-0.50		
1.2	-0.76	Total mean		16.1	-0.79	4.6	-0.47	3.8	-0.49	2.2	-1.10
2.4	-0.74	-0.71 $\pm$ 0.07		Mean	-0.85	5.7	-0.47	4.9	-0.49	3.9	-1.08
3.7	-0.61	Montego Bay		$\sigma$	0.05	6.9	-0.44	6.2	-0.41	5.4	-1.16
5.1	-0.68	20 m		Specimen 961		7.6	-0.53	7.4	-0.48	7.5	-1.03
6.4	-0.64	Specimen 951		1.1	-0.90	9.1	-0.51	8.8	-0.35	10.8	-0.95
7.9	-0.70	1.5	-0.75	2.3	-0.78	Mean	-0.48	Mean	-0.45	14.1	-0.90
9.0	-0.64	2.8	-0.80	3.3	-0.87	$\sigma$	-0.33	$\sigma$	0.05	Mean	-1.04
Mean	-0.68	3.8	-0.85	4.5	-0.81	Pedro Bank			pre-1950	$\sigma$	0.10
$\sigma$	0.06	4.8	-0.76	5.7	-0.71	125 m		10.3	-0.52		Transect 2
Transect 3		5.8	-0.79	6.8	-0.76	Transect 1		11.3	-0.48	1.4	-1.18
1.7	-0.69	6.8	-0.75	8.4	-0.90	0.8	-0.35	12.4	-0.43	2.9	-1.13
1.9	-0.69	7.5	-0.80	9.9	-0.88	1.7	-0.27	13.6	-0.34	4.3	-1.15
2.1	-0.57	8.3	-0.79	11.6	-0.86	2.7	-0.30	14.7	-0.31	5.7	-1.16
2.3	-0.75	9.3	-0.81	Mean	-0.83	3.7	-0.34	Mean	-0.42	7.2	-1.06
2.5	-0.68	10.3	-0.74	$\sigma$	0.07	4.6	-0.40	$\sigma$	0.09	8.6	-1.00
2.7	-0.72	11.1	-0.80	Total Mean		5.5	-0.30	Total Mean		10.0	-1.13
3.1	-0.69	Mean	-0.79	-0.83 $\pm$ 0.06		6.3	-0.31	post-1950		Mean	-1.12
3.3	-0.65	$\sigma$	0.03	Discovery Bay		7.4	-0.25	-0.38 $\pm$ 0.09		$\sigma$	0.06
3.5	-0.66	Specimen 952		Spec. 171, 84 m		8.4	-0.25	pre-1950		Total Mean	
3.7	-0.72	0.6	-0.78	0.8	-0.46	Mean	-0.31	-0.35 $\pm$ 0.08		-1.08 $\pm$ 0.09	

given by Tarutani et al. are questionable (Table 4). The comparison of the Tarutani et al. (1969) aragonite-water fractionation values with the calcite-water values found by O'Neil et al. (1969) and Kim and O'Neil (1997) suggests an aragonite-calcite fractionation in the order of 0.7 to 0.9‰ (SMOW). The theoretical value is 0.79‰ (Tarutani et al., 1969).

Additional information for the aragonite-calcite-water fractionations comes from studies of biogenic aragonite shells that are precipitated very close to oxygen isotopic equilibrium. Grossman and Ku (1986) measured  $\delta^{18}\text{O}$  of extant aragonitic foraminifera, gastropoda and scaphopoda as well as calcitic foraminifera grown at temperatures between 2.6 and 22.0°C. They reported a  $\delta^{18}\text{O}$  difference between calcitic and aragonitic shells of  $0.6 \pm 0.3\text{‰}$ . This difference was constant throughout the investigated temperature range. A regression of the Grossman and Ku (1986) aragonite and calcite data, recast in terms of  $\ln\alpha$  versus  $1/T$  (Kelvin) shows an aragonite-calcite fraction-

ation of 1.05‰ at 25°C (Table 4), decreasing to 0.62‰ at 5°C. Essentially the same value for 25°C results when this aragonite data is compared with the experimental results of Kim and O'Neil (1997) (Fig. 4).

Barrera et al. (1994) compared calcitic and aragonitic bivalves from Antarctica and found an aragonite-calcite fractionation of 0.8‰ at -2°C. Recently, molluscs from the Australian Lapecede shelf were investigated by Rahimpour-Bonab et al. (1997). They compared calcitic bivalves and aragonitic gastropods that lived at temperatures of 12–16°C and found the aragonite to be enriched in  $^{18}\text{O}$  with respect to calcite by  $0.6 \pm 0.2\text{‰}$ . In all these studies fractionation was investigated in cold and temperate waters. In a study of the tropical bivalve *Tridacna gigas*, Aharon (1991) reports an aragonite-calcite fractionation of 0.9‰ from a warm water environment, calculated from measured aragonite values and the equation of O'Neil et al. (1969).



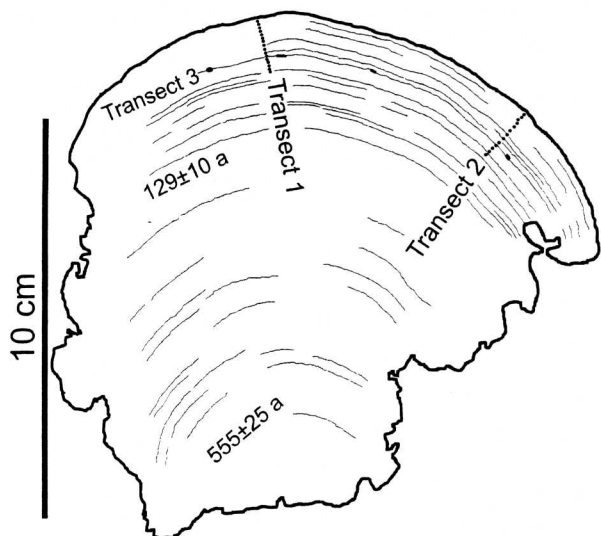


Fig. 3. Schematic line drawing of the Pedro Bank specimen of *Ceratoporella nicholsoni* showing the position of the three transects. The drawing shows a cross-section through the sponge with the smooth growth surface at the top. Note the bioeroded lateral surfaces. Only the most distinct laminae are shown. Samples of transect 3 were taken along the marked lamina (dark spots). Numbers are U/Th ages in years before collection (1996).

Table 4. Fractionation factors ( $10^3 \ln \alpha$ ) for calcite, aragonite and water from experimental and natural settings. Values of Tarutani et al. (1969) and O'Neil et al. (1969) are shown with the later redetermined  $H_2O-CO_2$  oxygen isotope fractionation (Friedman and O'Neil, 1977). The value of Kim and O'Neil (1997) has been recalculated for the conventional acid fractionation to make it comparable to other data. The aragonite and *Uvigerina* calcite values of Grossman and Ku (1986) are derived from fits of  $1/\text{temperature}$  regression lines to their original data, with both aragonite/calcite and water data adjusted to the SMOW scale. These regressions are extrapolated to  $25^\circ\text{C}$ . The resulting aragonite value is also compared to the calcite equilibrium values of O'Neil et al. (1969) and Kim and O'Neil (1997). The fourth row shows the directly measured average aragonite-calcite fractionation from Grossman and Ku (1986). The *Tridacna* (bivalve) aragonite value was calculated from the  $\delta^{18}O_{\text{aragonite}} - \delta^{18}O_{\text{water}}$  versus temperature equation of Aharon (1991).

Oxygen Isotope Fractionation Factors $1000 \ln \alpha$ for the system $H_2O - \text{Calcite} - \text{Aragonite}$ at $25^\circ\text{C}$			
$1000 \ln \alpha$ calcite- $H_2O$	$1000 \ln \alpha$ aragonite- $H_2O$	$1000 \ln \alpha$ aragonite-calcite	References Remarks
28.56	29.19	0.63	Tarutani et al., 1969 $\alpha(\text{CO}_2 - \text{H}_2\text{O}) = 1.0412$
28.46	29.19 <sup>a</sup>	0.73	O'Neil et al., 1969 $\alpha(\text{CO}_2 - \text{H}_2\text{O}) = 1.0412$
28.31	29.19 <sup>a</sup>	0.88	Kim and O'Neil, 1997 $\alpha(\text{CO}_2 - \text{H}_2\text{O}) = 1.0412$ acid fractionation = 1.01025
28.35 <sup>b</sup>		1.05	Grossman and Ku, 1986, recalculated; foraminifera,
28.46 <sup>d</sup>	29.40 <sup>c</sup>	0.94	molluscs
28.31 <sup>e</sup>		1.09	
		0.72 <sup>f</sup>	
28.46 <sup>d</sup>		1.00	Aharon 1991, <i>Tridacna</i> ,
28.31 <sup>e</sup>	29.46	1.15	calculated from equation
28.46 <sup>d</sup>		0.75	This study, <i>Ceratoporella</i>
28.31 <sup>e</sup>	29.21 <sup>g</sup>	0.90	<i>nicholsoni</i> , Caribbean

<sup>a</sup> Value from Tarutani et al., 1968.

<sup>b</sup> *Uvigerina* (calcitic foraminifer) data,  $1/T$  fit extrapolated from 19 to  $25^\circ\text{C}$ .

<sup>c</sup>  $1/T$  fit extrapolated from 22 to  $25^\circ\text{C}$ .

<sup>d</sup> value from O'Neil et al. 1969.

<sup>e</sup> value from Kim and O'Neil 1997.

<sup>f</sup> direct comparison of aragonitic and calcitic shells extrapolated to  $25^\circ\text{C}$ .

<sup>g</sup> extrapolated from  $25.1^\circ\text{C}$  to  $25.0^\circ\text{C}$ .

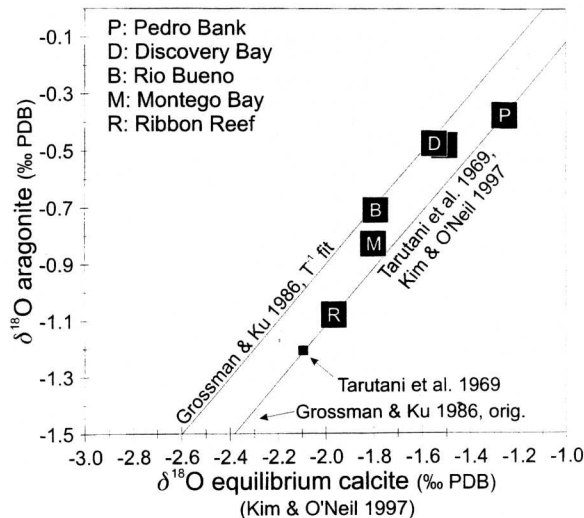


Fig. 4. Oxygen isotope fractionation between aragonite and calcite. Mean values of coralline sponges (Table 2, 3) are compared to relationships given in the literature. Equilibrium calcite values are calculated for the same temperature and  $\delta^{18}O_{\text{water}}$  as for the corresponding aragonite value (Table 2) with the modified  $1000 \ln \alpha$  - temperature relationship (Eqn. 2) of Kim and O'Neil (1997) and converted to the PDB scale. Aragonite values for the "Tarutani curve" are calculated analogously (Eqn. 2) adding a constant offset of  $0.88\text{‰}$  (Table 4). The "original Grossman and Ku line" was calculated with the equation of Grossman and Ku (1986) corrected for  $\delta_w$  expressed relative to SMOW (Hudson and Anderson, 1989). The corresponding  $T^{-1}$  fit is a linear regression of  $1000 \ln \alpha$  values calculated from the data given by Grossman and Ku (1986) after conversion to the SMOW scale.

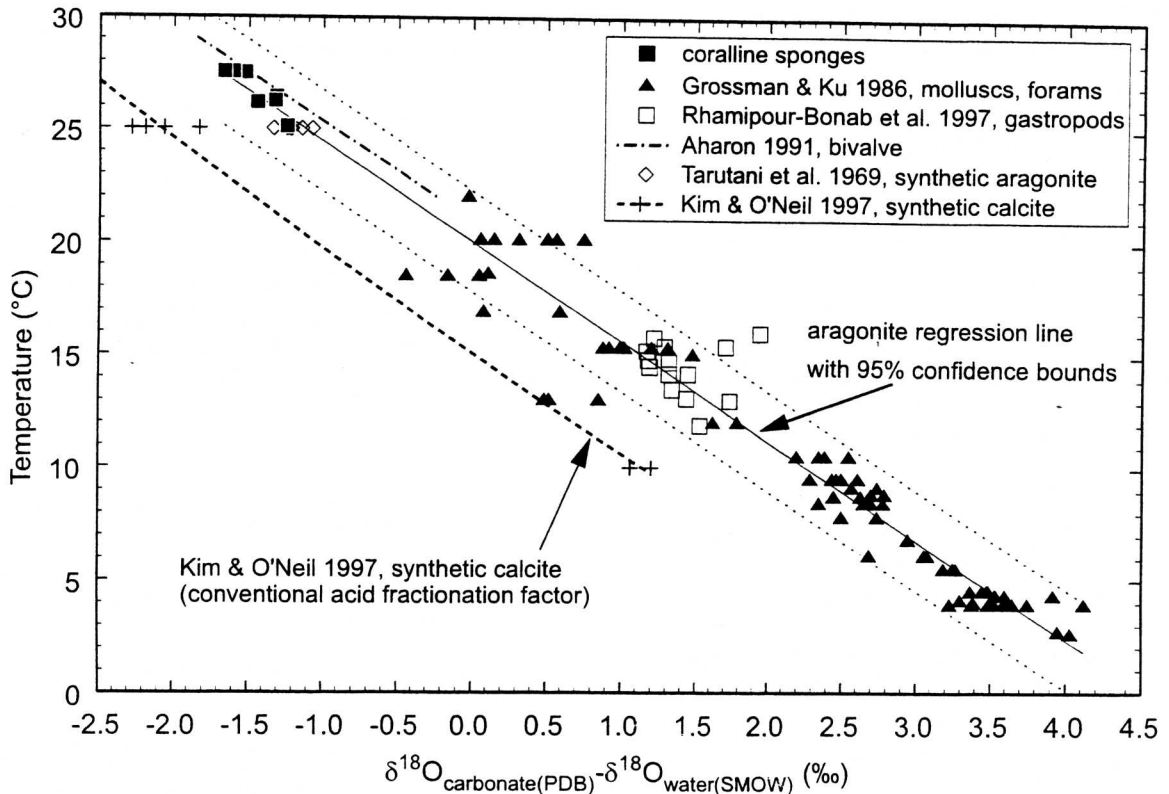


Fig. 5. Temperature dependence of oxygen isotope fractionation between aragonite and water. Mean values of coralline sponges as shown in Table 2 compared to published data for aragonite and calcite. Values of Tarutani et al. (1969) are corrected for fractionation between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  as given by Friedman and O'Neil (1977). Those of Kim and O'Neil (1997) are adjusted for a conventional acid fractionation factor. The aragonite regression line is a linear regression through all aragonite values. The calcite values are fitted by a second order polynome (dashed line). The relationship for *Tridacna* clams (Aharon, 1991) is shown for comparison.

Aragonite of *Ceratoporella nicholsoni* has  $\delta^{18}\text{O}$  values that differ from calculated calcite equilibrium values by 0.9 to 1.1‰ (Table 2) with a mean difference of 1.0‰. The difference is slightly larger than the 0.6 to 0.8‰ measured by Grossman and Ku (1986); Barrera et al. (1994); and Rahimpour-Bonab et al. (1997) in a temperature range of  $-2$  to  $22^\circ\text{C}$ , but agrees with the value of 0.9‰ of tropical bivalves (Aharon, 1991) and synthetic aragonite (Tarutani et al., 1969; Kim and O'Neil, 1997; see Table 4).

This comparison shows that the measured oxygen isotopic composition of *Ceratoporella nicholsoni* skeletons is compatible with the assumption that their aragonite is precipitated in oxygen isotopic equilibrium with the ambient water. The same is true for the investigated specimen of *Astrosclera willeyana* from Ribbon Reef (Table 2, Fig. 4).

The offset of 1‰ is close to the theoretical value for the aragonite-calcite fractionation of 0.8‰ (Tarutani et al., 1969). However, recently Kim and O'Neil (1997) found evidence for a difference between calcite and aragonite in the fractionation of oxygen isotopes during  $\text{CO}_2$  liberation by reaction with phosphoric acid. The difference was found to be on the order of 0.5‰ at  $25^\circ\text{C}$ . Thus, about half of the observed aragonite-calcite offset could be an artefact of acid fractionation. If this is the case, the remaining observed fractionation of about 0.5‰ is still close to the theoretical value.

### 4.3. Temperature Dependence of $^{18}\text{O}$ Fractionation

With the measured  $\delta^{18}\text{O}$  average values from *Ceratoporella nicholsoni* skeletons we can calculate the relationship between temperature and aragonite-water fractionation:

$$T (^{\circ}\text{C}) = (19.5 \pm 3.4) - (5.0 \pm 2.3) * (\delta_{\text{C.n.}} - \delta_{\text{w}}) \quad (3)$$

( $R^2 = 0.86$ ,  $n = 7$ ) for a temperature range from 25 to  $28^\circ\text{C}$ , where  $T$  is the water temperature,  $\delta_{\text{C.n.}}$  is the  $\delta^{18}\text{O}$  value of the aragonite sample from *Ceratoporella nicholsoni* versus PDB and  $\delta_{\text{w}}$  is the  $\delta^{18}\text{O}$  value of the ambient water versus SMOW. Errors are 95% confidence levels. The narrow temperature range of our data results in a relatively large uncertainty. However, as the skeletal aragonite of *Ceratoporella nicholsoni* is precipitated close to oxygen isotopic equilibrium, palaeotemperature determinations can be made with the common temperature equation of Grossman and Ku (1986). Therefore, we include the data of Grossman and Ku (1986); Rahimpour-Bonab et al. (1997); and Tarutani et al. (1969) in our calculation of the temperature-fractionation relationship (Fig. 5). For the Lapedede shelf we use annual mean temperatures from Levitus and Boyer (1994) (values at  $137.5^\circ\text{E}$ ,  $36.5^\circ\text{S}$ ). We fitted a second order polynomial to the data. The second order term was not significantly different from zero ( $-0.01 \pm 0.03$ ),

so we fit a linear regression, excluding 9 obvious outliers (values outside the 95% error bounds, Fig. 5):

$$T (^{\circ}\text{C}) = (20.0 \pm 0.2) - (4.42 \pm 0.10) * (\delta_a - \delta_w) \quad (4)$$

( $R^2 = 0.99$ ,  $n = 101$ ) were  $\delta_a$  is the  $\delta^{18}\text{O}$  value of the aragonite sample versus PDB. The relation for the fractionation factor  $10^3\ln\alpha_{\text{aragonite-water}}$  is:

$$10^3\ln\alpha_{\text{aragonite-water}} = (18.45 \pm 0.4) * 10^3/T (\text{K}) - (32.54 \pm 1.5) \quad (5)$$

( $R^2 = 0.99$ ,  $n = 101$ ) with the temperature given in kelvins. The combination of our data with the published cool water data resulting in Eqns. (4) and (5) reduces the error of the original Grossman and Ku (1986) equation

$$T (^{\circ}\text{C}) = (19.7 \pm 0.6) - (4.34 \pm 0.24) * (\delta_a - \delta_w) \quad (6)$$

( $R^2 = 0.94$ ,  $n = 80$ ) by about 50%.

The Kim and O'Neil (1997) data for synthetic calcite fits a very similar slope as Eqn. (4) over the temperature range of  $10^{\circ}$  to  $20^{\circ}\text{C}$  (Fig. 5). An aragonite-calcite offset  $1000\ln\alpha = 1.0$  is calculated from Eqns. (2) and (5) for  $28^{\circ}\text{C}$ . The respective value for  $10^{\circ}\text{C}$  is 1.1. The calcite-water relation of O'Neil et al. (1969), revised by Friedman and O'Neil (1977),

$$10^3\ln\alpha_{\text{calcite-water}} = 2.78 * 10^6/T^2 (\text{K}) - 2.89 \quad (7)$$

compared with Eqn. (5) again results in an aragonite-calcite offset  $1000\ln\alpha = 1.0$  at  $28^{\circ}\text{C}$ . However, the respective value for  $3^{\circ}\text{C}$  is only 0.7, reflecting the cool temperature divergence between the O'Neil et al. (1969) and the Kim and O'Neil (1997) equations. The latter value, nevertheless, is in good agreement with directly measured low temperature fractionation values of  $0.8\text{‰}$  at  $-2^{\circ}\text{C}$  (Barrera et al., 1994) and of  $0.7\text{‰}$  at  $3$  to  $5^{\circ}\text{C}$  (Grossman and Ku, 1986).

Thus, small discrepancies ( $<0.4\text{‰}$ ) exist between aragonite-calcite fractionations calculated from equilibrium equations and directly measured values. Nevertheless, within the limits given by the uncertainties of the available data, our results are compatible with a constant aragonite-calcite offset of about  $1\text{‰}$  in the temperature range of  $3^{\circ}$  to  $28^{\circ}\text{C}$ .

## 5. CONCLUSIONS

1. Comparison of the experimentally derived calcite fractionation equation of Kim and O'Neil (1997) and oxygen isotope values measured on aragonite of coralline sponges points to an aragonite-calcite fractionation of  $1.0 \pm 0.1\text{‰}$  ( $\alpha_{\text{aragonite-calcite}} = 1.0010$ ) at  $25^{\circ}\text{C}$ . This value is compatible with published data from molluscs, foraminifera and synthetic aragonite and is essentially constant for temperatures ranging from  $10^{\circ}$  to  $30^{\circ}\text{C}$ .
2. The oxygen isotopic composition of the skeletons of the coralline sponges *Ceratoporella nicholsoni* and *Astrosclera willeyana* is compatible with the assumption of isotopic equilibrium precipitation. Reproducibility is good. On average, means of  $\delta^{18}\text{O}$  measured on skeletons precipitated in the same environment differ by only  $0.05\text{‰}$ . However, a systematic offset of about  $0.13\text{‰}$  between two parallel transects in one specimen points to the possibility of inho-

mogeneities in the skeleton that could cause false trends in palaeotemperature reconstructions.

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