

1 Carbon stable isotope records in the coral species *Siderastrea stellata*: a 2 link to the Suess Effect in the tropical South Atlantic Ocean

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20 Abstract

21 Coral skeletons are natural archives whose geochemical signatures provide insights into
22 the tropical ocean history beyond the instrumental record. Carbon stable isotopes from
23 coral skeletons ($\delta^{13}\text{C}_{\text{coral}}$) have been used as a proxy for multiple variables on a seasonal
24 basis. Long-term changes in coral $\delta^{13}\text{C}$ relate to the changing isotopic composition of the
25 dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$). $\delta^{13}\text{C}_{\text{DIC}}$ in turn reflects changes in the $\delta^{13}\text{C}$ of
26 atmospheric CO_2 , which in the modern Earth system is governed primarily by
27 anthropogenic injection of CO_2 into the atmosphere – a process known as the Suess
28 Effect.

29 Here we report three $\delta^{13}\text{C}$ coral-based records of *Siderastrea stellata* from the tropical
30 South Atlantic. U-series dating for the colonies 12SFB-1, 13SS-1 and 13SS-2 suggests
31 these corals lived 13, 57 and 65 years, respectively. Short-term $\delta^{13}\text{C}$ variations in their
32 skeletal aragonite are dominated by inter-annual variation. All three $\delta^{13}\text{C}$ records
33 additionally exhibit an overall decreasing trend, with a depletion of about $-0.0243 \pm$
34 0.0057‰.yr^{-1} (12SFB-1), $-0.0208 \pm 0.0007 \text{‰.yr}^{-1}$ (13SS-1) and -0.0214 ± 0.0013
35 ‰.yr^{-1} (13SS-2). These rates of the coral records from Rocas Atoll are similar to the
36 reported trend for the $\delta^{13}\text{C}$ of atmospheric CO_2 over the years 1960-1990 (-0.023 to
37 -0.029‰.yr^{-1}), and to the estimated decreasing rates of global $\delta^{13}\text{C}_{\text{DIC}}$.

38 Our findings suggest that multiple $\delta^{13}\text{C}$ coral-based records are required for confidently
39 identifying local changes in the $\delta^{13}\text{C}_{\text{DIC}}$ of the ocean. This information, in turn, can be
40 used to infer changes in the $\delta^{13}\text{C}$ of the atmospheric CO_2 composition and provide
41 valuable information about recent changes on the carbon biogeochemical cycle during
42 the Anthropocene epoch.

43 **Keywords: Coral geochemistry; Climate changes; CO_2 ; Coral-based archives**

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46 **1. Introduction**

47 Scleractinian corals incorporate geochemical signatures in their exoskeleton that
48 can be used to reconstruct the environmental history of the tropical oceans (e.g., Weber
49 and Woodhead 1970; Weber 1973; Swart 1983; Swart and Grottoli 2003). The suitability
50 of corals to act as climate archives relies on high-quality calibrations of modern coral
51 skeletal chemistry (stable isotopes, as well as trace and minor elements) that can be
52 applied in ancient corals (e.g., Linsley et al. 1994; Corrège 2006; DeLong et al. 2007,
53 2013). Such environmental reconstructions in turn improve our knowledge about past
54 climate parameters beyond the instrumental record.

55 Some geochemical proxies are well established in coral records, such as $\delta^{18}\text{O}$ values
56 and Sr/Ca ratios for tracking sea surface temperature (SST) (e.g. Weber and Woodhead
57 1970, 1972; Weber 1973; Swart 1983b; Leder et al. 1996; Felis et al. 2000; Guilderson et
58 al. 2001; Swart et al. 2002; Moses et al. 2006; DeLong et al. 2011). The meaning of coral
59 $\delta^{13}\text{C}$, however, still remains incompletely understood due to the multitude of
60 physiological and environmental parameters involved (Swart 1983a; McConnaughey
61 1989a, 1989b, 2003; Swart et al. 1996; Al-Rousan and Felis 2013).

62 The C and O isotopic composition of corals is depleted compared aragonite formed
63 in isotopic equilibrium with seawater due to kinetic and metabolic fractionation (Weber
64 and Woodhead 1970). Carbon used corals for the secretion of their aragonite skeleton is
65 sourced from CO_2 which diffuses across the boundary membranes and ionizes to form
66 non-diffusible HCO_3^- and CO_3^{2-} . The latter combine with Ca^{2+} in the calcifying space to
67 form CaCO_3 . Depleted $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the resulting carbonate are a function of
68 kinetic fractionation during CO_2 hydration and hydroxylation (McConnaughey 1989a).

69 It has been suggested that the intra-annual variations of $\delta^{13}\text{C}$ are caused by
70 photosynthetic activity by the host symbionts (the zooxanthellae), which would change
71 the carbon isotopic composition of the internal dissolved inorganic carbon (DIC) pool
72 from which coral aragonite forms (e.g. Fairbanks and Dodge 1979; Pätzold 1984; Grottoli
73 and Wellington 1999). Increases in the rate of photosynthesis due to increased solar
74 irradiance have been observed to parallel increases in the coral $\delta^{13}\text{C}$, while a reduction in
75 solar irradiance led to depleted $\delta^{13}\text{C}$ values (Weber and Woodhead 1970). Consequently,
76 carbon isotope ratios in corals could be used as a proxy for solar irradiance or cloud
77 coverage (Fairbanks and Dodge 1979; Pätzold 1984; Grottoli and Wellington 1999; Sun
78 et al. 2008, among others).

79 However, many studies have shown a range of additional factors that may play
80 significant roles in the seasonal variations of coral $\delta^{13}\text{C}$. Amongst these are water depth
81 (e.g., Fairbanks and Dodge 1979; Swart et al. 1996; Grottoli and Wellington 1999),
82 heterotrophic level (Grottoli and Wellington 1999), kinetic isotope fractionation
83 (McConnaughey 1989b), reproduction (Gagan et al. 1994), bleaching (Leder et al. 1991),
84 spawning (Gagan et al. 1994) and the $\delta^{13}\text{C}$ of regional DIC (Swart et al. 2010; Al-Rousan
85 and Felis 2013; Dassié et al. 2013; Deng et al. 2017) .

86 Beyond the complicated short-term variations in coral $\delta^{13}\text{C}$, decadal- to centennial-
87 scale changes in coral $\delta^{13}\text{C}$ are observed and related to modifications of the $\delta^{13}\text{C}$ of the
88 surface water DIC (Swart et al. 1996, 2010; Al-Rousan and Felis 2013; Dassié et al. 2013;
89 Deng et al. 2017). Long-term decreases in coral $\delta^{13}\text{C}$ have first been reported as early as
90 the 1970s (Nozaki et al. 1978). This trend was first attributed to the Suess Effect by
91 Druffel and Benavides (1986) and has been since reported in coral-based records from
92 the Pacific ocean, Indian ocean, Red Sea, North Atlantic ocean and Caribbean Sea (Swart
93 et al. 2010; Al-Rousan and Felis 2013; Dassié et al. 2013 and references therein).

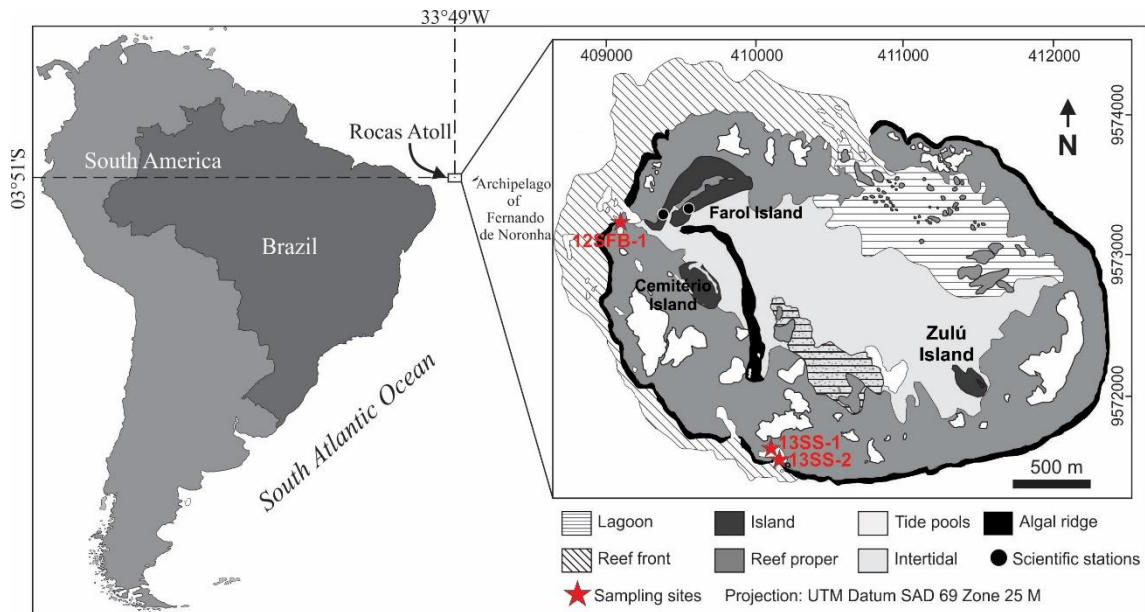
94 Changing $\delta^{13}\text{C}$ of atmospheric CO_2 since the industrial revolution caused by
95 anthropogenic CO_2 input to the atmosphere from fossil fuel burning and deforestation has
96 become widely known as the Suess Effect (Keeling 1979). Because anthropogenic CO_2
97 has a distinctly negative $\delta^{13}\text{C}$ signature of about -28‰ (Andres et al. 2013), this change
98 has been to progressively more negative atmospheric $\delta^{13}\text{C}$, amounting to about 1.14‰
99 since the beginning of the industrial revolution according to carbon isotopic data retrieved
100 from air bubbles trapped in ice cores (Friedli et al. 1986). 30 to 40% of the anthropogenic
101 CO_2 influx is currently taken-up by the oceans (Quay et al. 1992; Orr et al. 2001) which
102 caused $\delta^{13}\text{C}$ of the DIC reservoir to decrease in parallel to the atmosphere through the last
103 two centuries (Al-Rousan and Felis 2013).

104 Here we report three coral-based $\delta^{13}\text{C}$ records for the Tropical South Atlantic Ocean
105 retrieved from colonies of the hermatypic massive coral *Siderastrea stellata*. *S. stellata*
106 represents one the of the main reef builders of the Brazilian reefs, with a spatial
107 distribution from 0° to 23°S (Lins-de-Barros and Pires 2007). Evaluating the potential of
108 this species as a climate archive in the South Atlantic Ocean is important, because it is
109 widespread on Brazilian reefs and relatively abundant compared to other species. In this
110 study, we explore possible explanations for the short and long-term variability on the $\delta^{13}\text{C}$
111 signature on the *S. stellata* skeleton.

112 **2. Study area**

113 The Rocas Atoll ($3^\circ 51'\text{S}$, $33^\circ 49'\text{W}$) is the only atoll in the western part of the South
114 Atlantic, 266 km offshore from the city of Natal, northeastern Brazil (Fig. 1). Because of
115 its isolated location the Rocas Atoll receives no direct terrestrial input. This locality
116 constitutes a natural laboratory where ocean and atmospheric processes are the key
117 players, allowing for near-pristine geochemical signatures in biogenic carbonates. At this
118 peculiar atoll, most corals live in tidal pools which are under influence of a semi-diurnal

119 and mesotidal regime, with a maximum tidal range of 3.8 m (Gherardi and Bosence 2001).
120 The physicochemical, geologic and oceanographic conditions of the Rocas Atoll are
121 described by Kikuchi and Leão (1997) and Pereira et al. (2013).



123 **Figure 1. Location and geomorphological map of the reef complex of Rocas Atoll, with**
124 **indicated sampling site (red stars) for the colonies 12SFB-1, 13SS-1 and 13SS-2. Modified**
125 **from (Pereira et al 2010).**

126 3. Methodology

127 3.1. Studied colonies

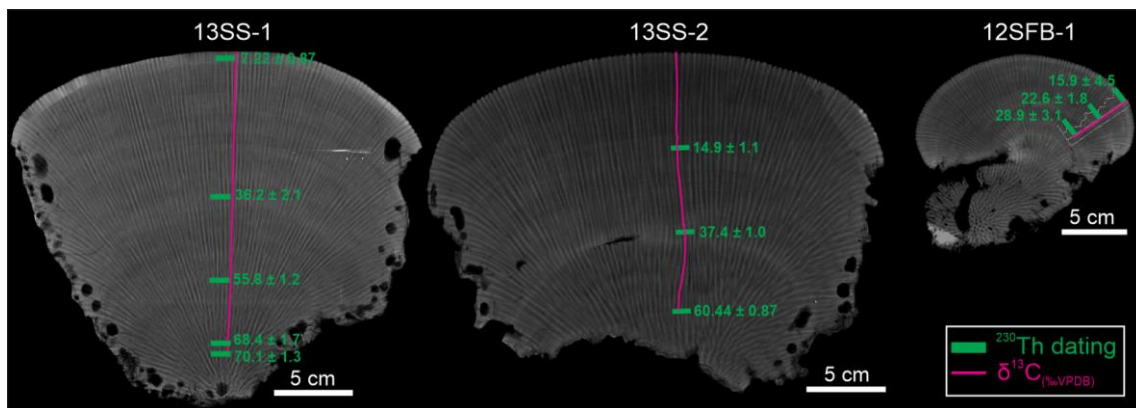
128 For this study, three colonies of *S. stellata* were used. Colonies 13SS-1 and 13SS-
129 2, both with approximately 50-cm diameter, were collected at the south portion of the
130 atoll (Fig. 1), from about 7 m depth, in July 2013. The colony 12SFB-1, a 15-cm diameter
131 colony, was collected dead, but still attached to the reef substrate, at the northwestern part
132 of the Rocas Atoll, at 3 m depth in January of 2012 (Fig. 1).

133 3.2. Sampling for geochemical analysis

134 The studied colonies were cut into halves, and one half was cut into 5-mm thick
135 slices, parallel to the growth axis of the whole colony. After cutting, these slices were
136 cleaned with deionized water, air-dried and then X-rayed at 50 kV and 320 mA, with an

137 exposure time of 3.2 s and distance from the equipment to the object of 108 cm. Carbonate
138 samples were collected at 0.5 mm intervals using a micromill (the section from 150-188
139 of coral 13SS-1 was sampled with 1 mm resolution). The coral powder was produced by
140 continuous, progressive grinding of the slab from the top towards the bottom, following
141 the thecal wall (Fig. 2).

142 Additional samples were collected along the growth axis of each colony (Fig. 2) for
143 dating by a high precision ^{230}Th method (Shen et al. 2008b, 2012). Eleven subsamples,
144 0.10-0.25 g each, were cut from three corals (Fig. 2) for U-Th dating. They were gently
145 crushed, physically cleaned with ultrasonic methods, and dried for U-Th chemistry.



146
147 **Figure 2. Radiographies of 5-mm-thick slices of the 13SS-1, 13SS-2 and 12SFB-1 coral**
148 **colonies. Density bands are not annual in the X-radiographs, inhibiting age assignment by**
149 **band counting alone. The sections analyzed for $\delta^{13}\text{C}$ (purple line) followed a single corallite**
150 **wall track. Subsamples along the coral slab of each colony were collected for U-Th dating**
151 **(green bars), numbers reported in green represent years before 11th July, 2016 for the**
152 **colonies 13SS-1 and 12SFB-1, and before 1st January, 2016.**

153 3.3. Geochemical analyses

154 3.3.1. Carbon and oxygen stable isotope

155 All coral $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data are reported in per mill relative to VPDB. Colony
156 13SS-2 and 12SFB-1 were measured at the Federal University of Pernambuco using a
157 Delta V Advantage coupled with a GasBench II device. Sets containing 56 coral samples

158 were analyzed against 16 samples of 4 different standards, 2 international, NBS-18 and
159 NBS-19 and 2 internal, REI and VICKS (n = 128). The precision of the analysis was
160 better than 0.1 ‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, except for $\delta^{18}\text{O}$ of colony 13SS-2, which are affected
161 by analytical issues and will not be presented here.

162 $\delta^{13}\text{C}$ values for coral carbonate samples of the colony 13SS-1 were analyzed at the
163 University of Copenhagen, using a Micromass IsoPrime mass spectrometer, employing
164 the protocols adopted from Spötl and Vennemann (2003) with modifications described in
165 Ullmann et al. (2013). The precision of the method was assessed by multiple
166 measurements of the laboratory reference material LEO (Carrara Marble) and was 0.09
167 ‰ for $\delta^{13}\text{C}$ and 0.10 ‰ for $\delta^{18}\text{O}$ (2σ , n = 129).

168 3.3.2. *Sr/Ca ratios*

169 Coral Sr/Ca ratios were measured using a Perkin Elmer Optima 7000 DV ICP-OES
170 at the University of Copenhagen. The samples were measured at a Ca concentration of
171 ~10 $\mu\text{g/g}$ against a synthetic calibration solution. The calibration solution contained only
172 Ca and Sr with a Sr/Ca ratio of 9.1289 mmol/mol. The measurements were done on the
173 317.933 nm line of Ca and the 407.771 nm line of Sr. Accuracy was controlled using JLs-
174 1, for which Sr/Ca ratios reproduced to 1.6 % (2 rsd) at a value of 0.345 mmol/mol (n =
175 83). All samples were analyzed at least twice and average repeatability of the Sr/Ca ratio
176 is 0.6 % (2 err). The measured values for Sr/Ca in JLs-1 are within 1 % of the values
177 computed from Imai et al. (1996).

178

179 **3.4. U/Th dating and age model**

180 Coral skeletal density patterns revealed by x-radiographies are often useful for
181 accurate chronologic control (Knutson et al. 1972). The density patterns of the *S. stellata*

182 specimens in this study, however, are not distinct. Thus, this methodology is not
183 appropriate for determining the age of these corals. To construct a reliable age model for
184 these colonies, we applied ^{230}Th dating through the profile section where $\delta^{13}\text{C}$ was
185 retrieved.

186 U-series dating was conducted in a class-10.000 metal-free clean room with class-
187 100 benches at the High-Precision Mass Spectrometry and Environment Change
188 Laboratory (HISPEC), Department of Geosciences, National Taiwan University (Shen et
189 al. 2008a). U-Th isotopic compositions and concentrations were determined on a multi-
190 collector inductively-coupled plasma mass spectrometer (MC-ICP-MS) in the HISPEC
191 (Shen et al. 2012). Half-lives of U-Th nuclides used for ^{230}Th age calculation are given
192 in (Cheng et al. 2013). Uncertainties in the U-Th isotopic data and ^{230}Th dates are
193 calculated at the 2σ level or two standard deviations of the mean ($2\sigma_m$) unless otherwise
194 noted.

195 An age model for each core was constructed based on linearly interpolating between
196 the uranium series dates and linearly extending the growth estimates in the short skeletal
197 sections not bounded by radiometric dates.

198 **3.5. Growth rate**

199 The U-series dates enable the calculation of average growth rates by dividing the
200 recorded time interval (years) by the total length (mm) of the coral record. Growth rate
201 was also determined for the various sub-sections bracketed by ^{230}Th date samples in each
202 coral record, by dividing the record span (years) by the extension (mm) of each of these
203 sub-section.

204 **3.6. Fourier transform analyses**

205 A Fourier transformation of the data was conducted on the depth series data before
206 age modeling to explore the variance of the data in frequency space. For the spectral
207 analysis, evenly sampled data (0.5 mm/sample) were de-trended before applying a
208 standard Blackman Tukey correlogram analysis with a Bartlet window using the SSA-
209 MTM toolkit (Dettinger et al. 1995; Ghil et al. 2002).

210 **4. Results**

211 **4.1. U/Th chronology**

212 Determined U-Th isotopic compositions and ^{230}Th dates are listed in Table 1. U-Th
213 dating of subsamples retrieved along the growth axis of the colony 13SS-1 ($n = 4$, Fig. 3)
214 constrained the geochemical record to the years 1948-2013. (Fig. 3). For the colony 13SS-
215 2 ($n = 3$), U-Th dating points to a recorded interval from 1956 to 2013 and for the colony
216 12SFB-1 ($n = 3$), a sampled interval from 1988 to 2001 (Fig. 3).

217 Many coral records have particularly clear seasonal $\delta^{13}\text{C}$ cycles, but no
218 straightforward evaluation of seasonal signals in the present specimens is possible.
219 Apparent cycles in the 13SS-1 and 13SS-2 records (Fig. 3) are demonstrated by the U-
220 series age not to be annual. In contrast to many other coral specimens, $\delta^{13}\text{C}$ cycles can
221 therefore not be used to refine the age model of this coral. In the coral 12SFB-1 on the
222 other hand the number of cycles agrees with the U-series age (Table 2). The contrasting
223 ages between ^{230}Th and the number of $\delta^{13}\text{C}$ cycles in 13SS-1 and 13SS-2 indicates: (i)
224 possible hiatus in coral growth, or (ii) that high frequency cycles of the $\delta^{13}\text{C}$ signal are
225 dominated by inter-annual variability rather than seasonal variability.

226 The number of $\delta^{13}\text{C}$ cycles (poorly defined) at the youngest part of the coral records
227 13SS-1 and 13SS-2 is compatible with U-series ages. Throughout ontogeny, however, the
228 number of $\delta^{13}\text{C}$ cycles increasingly disagree with U-series ages (table 2). Given that the

229 skeleton seems to show continuous growth (except in the coral 13SS-2 just before the
230 1979 date, where it is possible to see a slightly denser band and the die-off of a small
231 section of the coral; see Fig. 3), a likely explanation is that these are not seasonal cycles.
232 Rocas Atoll is close to the equator where there is very little seasonality, whereas inter-
233 annual variability of climate parameters may be more important.

234 **Table 1. U-Th isotopic compositions and ^{230}Th ages for coral samples by MC-ICPMS at HISPEC, NTU[†].**

Colony	Sample ID	Weight g	^{238}U ng/g ^a	^{232}Th pg/g	$\delta^{234}\text{U}$ measured ^a	$[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ activity ($\times 10^{-6}$) ^c	$[\text{}^{230}\text{Th}/\text{}^{232}\text{Th}]$ atomic ($\times 10^{-6}$)	Age uncorrected	Age corrected ^{c,d}	$\delta^{234}\text{U}_{\text{initial}}$ corrected ^b
13SS-1	SS1-1.1	0.13840	2918.4 ± 4.6	172.0 ± 3.4	143.0 ± 2.5	90.0 ± 5.6	25.2 ± 1.6	8.58 ± 0.54	7.22 ± 0.87	143.0 ± 2.5
	SS1-2.1	0.14800	2927.4 ± 5.6	478.9 ± 3.3	146.2 ± 2.5	419.8 ± 9.0	42.31 ± 0.95	39.94 ± 0.86	36.2 ± 2.1	146.3 ± 2.5
	SS1-3.1	0.17620	2832.2 ± 4.5	58.1 ± 2.6	143.1 ± 2.4	590 ± 13	474 ± 24	56.3 ± 1.2	55.8 ± 1.2	143.1 ± 2.4
	SS1-4.X	0.10780	2861.9 ± 5.2	289.1 ± 4.3	141.8 ± 2.5	741 ± 12	120.9 ± 2.7	70.7 ± 1.2	68.4 ± 1.7	141.8 ± 2.5
12SFB-1	SFB-1	0.18980	3299.1 ± 3.8	1260.4 ± 4.0	144.7 ± 1.9	259 ± 11	11.18 ± 0.46	24.7 ± 1.0	15.9 ± 4.5	144.7 ± 1.9
	SFB-2	0.13840	3173.7 ± 4.0	462.1 ± 3.4	145.1 ± 1.9	273.1 ± 7.2	30.92 ± 0.84	26.00 ± 0.68	22.6 ± 1.8	145.2 ± 1.9
	SFB-3	0.11500	3140.6 ± 4.0	812.6 ± 4.3	147.4 ± 1.8	367.3 ± 8.7	23.41 ± 0.56	34.92 ± 0.82	28.9 ± 3.1	147.4 ± 1.8
13SS-2	SS2-1	0.18150	2558.4 ± 2.4	224.8 ± 2.6	144.9 ± 1.7	177.5 ± 4.7	33.29 ± 0.97	16.90 ± 0.45	14.9 ± 1.1	144.9 ± 1.7
	SS2-2	0.22665	2649.9 ± 2.8	175.0 ± 2.1	144.7 ± 1.8	408.8 ± 6.7	102.1 ± 2.1	38.95 ± 0.64	37.4 ± 1.0	144.8 ± 1.8
	SS2-3	0.24368	2869.0 ± 2.6	152.1 ± 1.9	141.3 ± 1.6	645.2 ± 6.4	200.7 ± 3.2	61.67 ± 0.62	60.4 ± 0.9	141.3 ± 1.6

235 [†]Analytical errors are 2σ of the mean.

236 ^a $[\text{}^{238}\text{U}] = [\text{}^{235}\text{U}] \times 137.77 (\pm 0.11\%)$ (Hiess et al., 2012); $\delta^{234}\text{U} = ([\text{}^{234}\text{U}/\text{}^{238}\text{U}]_{\text{activity}} - 1) \times 1000$.

237 ^b $\delta^{234}\text{U}_{\text{initial}}$ corrected was calculated based on ^{230}Th age (T), i.e., $\delta^{234}\text{U}_{\text{initial}} = \delta^{234}\text{U}_{\text{measured}} \times e^{\lambda^{234}\text{Th} \times T}$, and T is corrected age.

238 ^c $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]_{\text{activity}} = 1 - e^{-\lambda^{230}\text{Th} T} + (\delta^{234}\text{U}_{\text{measured}}/1000)[\lambda_{230}/(\lambda_{230} - \lambda_{234})](1 - e^{-(\lambda_{230} - \lambda_{234}) T})$, where T is the age. Decay constants are $9.1705 \times 10^{-6} \text{ yr}^{-1}$ for ^{230}Th , $2.8221 \times 10^{-6} \text{ yr}^{-1}$

239 ¹ for ^{234}U (Cheng et al., 2013), and $1.55125 \times 10^{-10} \text{ yr}^{-1}$ for ^{238}U (Jaffey et al., 1971).

240 ^dThe degree of detrital ^{230}Th contamination is indicated by the $[\text{}^{230}\text{Th}/\text{}^{232}\text{Th}]$ atomic ratio instead of the activity ratio.

241 ^eAge corrections, relative to chemistry date on 1th, January, 2016 (colony 13SS-2) and 11th, July, 2016 (colonies 12SFB-1 and 13SS-1), were calculated using an estimated

242 atomic $^{230}\text{Th}/\text{}^{232}\text{Th}$ ratio of $4 \pm 2 \text{ ppm}$ (Shen et al., 2008)

243 **4.2. Growth rate**

244 The mean growth rates for the studied colonies estimated by U-series data revealed
 245 values of 2.75 ± 0.65 mm.year⁻¹ for 13SS-1, 3.18 ± 2.09 mm.year⁻¹ for 13SS-2 and 3.45
 246 ± 0.40 mm.year⁻¹ for 12SFB-1 (table 2). Therefore, the growth rate of these specimens
 247 are not constant through time but vary from 1.85 to 3.41 mm.year⁻¹ for colony 13SS-1,
 248 1.74 to 5.57 mm.year⁻¹ for colony 13SS-2, and 3.17 to 3.73 mm.year⁻¹ (Table 2).

249 The coral 13SS-2 showed the highest growth rate (5.57 mm.year⁻¹) that decreases
 250 to much slower rates (1.74 to 2.22 mm.year⁻¹) in older sections. An opposite behavior,
 251 however, is observed for colony 13SS-1, in which growth rate is higher (3.41 mm.year⁻¹)
 252 in older sections and decreases to slower rates at the youngest part (1.85 mm.year⁻¹).
 253 Colony 12SFB-1 presented constant values through the record.

254 **Table 2. Comparisons of age and growth based on $\delta^{13}\text{C}$ cycles and U-series dates.**

Colony	Sample ID	Depth range (mm)	Age interval (U-series)	Growth rate (mm.y ⁻¹)	$\delta^{13}\text{C}$ cycles	Years (U-series)
13SS-1	SS1-1.1	0-8	2009-2013*	1.85	1	4
	SS1-2.1	8 to 90	1980-2009	2.83	18	29
	SS1-3.1	90 to 147	1961-1980	2.91	14	20
	SS1-4.X	147 to 190	1948-1961	3.41	5	13
				**2.75 ± 0.65		
13SS-2	SA1	0 to 70	2001-2013*	5.57	15	13
	SA2	70 to 120	1979-2001	2.22	12	23
	SA3	120 to 160	1956-1979	1.74	11	23
				**3.18 ± 2.09		
12SFB-1	SFB2	5 to 30	1994-2001	3.73	7	7
	SFB3	30 to 50	1988-1994	3.17	6	6
				**3.45 ± 0.40		

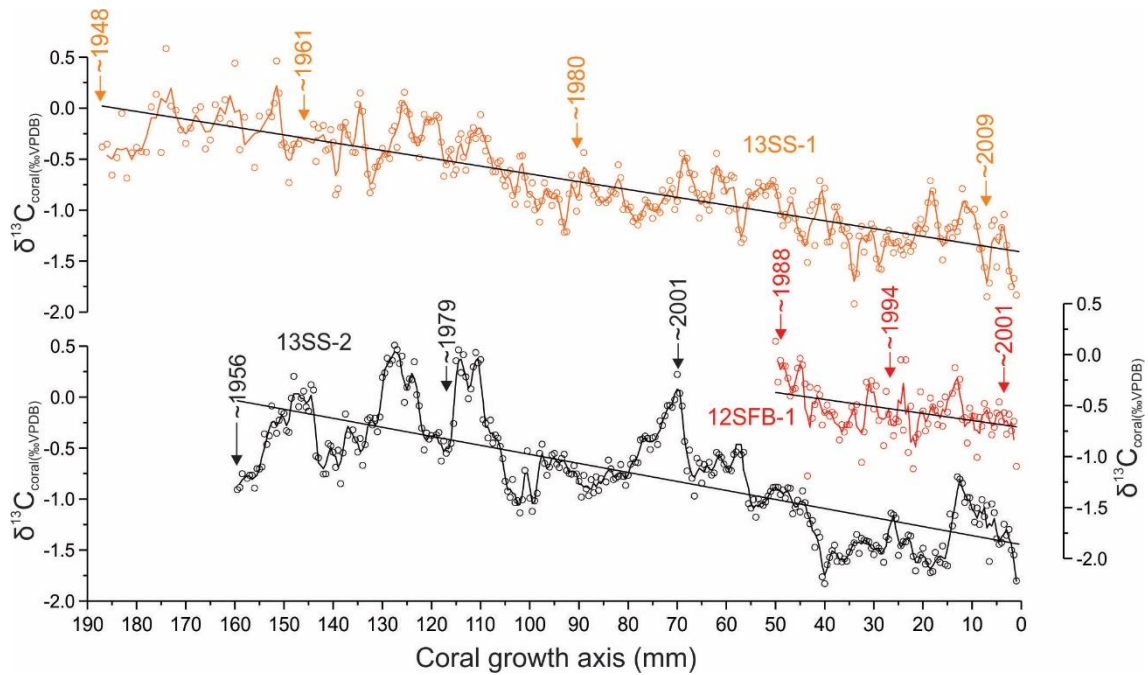
255 *Growth rate and calendar years calculated from October/2013. **Mean growth rate estimated
 256 on basis of U-series age for the total coral record.

257 **4.1. Carbon stable isotopes data ($\delta^{13}\text{C}$)**

258 The coral $\delta^{13}\text{C}$ values range from -1.92 to $+0.58\text{‰}$, with a mean value of $-0.76 \pm$
 259 0.45‰ and variance of 0.20‰ in colony 13SS-1 (n = 325). Colony 13SS-2 $\delta^{13}\text{C}$ values
 260 range from -2.06 to 0.51‰ , with a mean value of $-0.75 \pm 0.55\text{‰}$ and variance of 0.3‰

261 (n = 312). The carbon isotopic composition of colony 12SFB-1 varied from -1.19 to
262 +0.13‰, with a mean value of $-0.54 \pm 0.26\text{‰}$ and variance of 0.07‰ (n = 95).

263 All three $\delta^{13}\text{C}$ profiles are characterized by consistent decreasing trends from the
264 oldest towards more recently formed skeletal material (Fig. 3).

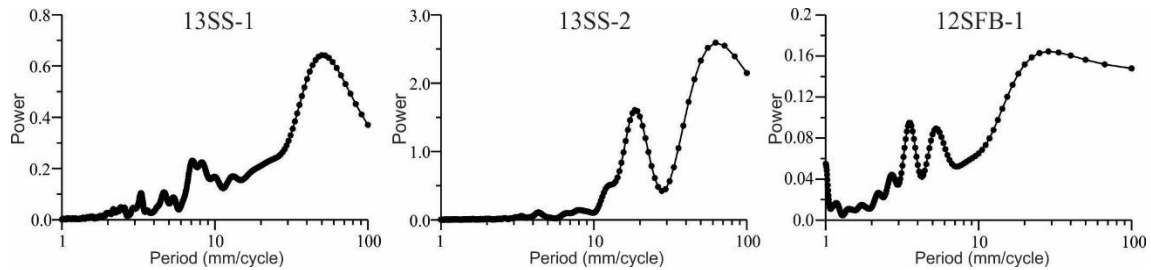


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266 **Figure 3. Skeletal $\delta^{13}\text{C}$ records for 13SS-1 (orange), 13SS-2 (black) and 12SFB-1 (red)**
267 **colonies from the Rocas Atoll, South Atlantic Ocean (running average window width = 3).**
268 **Arrows indicate values from ^{230}Th dating through sections of the coral growth axis.**

269 4.1.1. Inter-annual variability

270 We applied Fourier transform analysis to quantitatively assess seasonal frequencies
271 of the $\delta^{13}\text{C}$ time series of the three coral records (Fig. 4). Identification of frequencies
272 likely to be annual were then compare to the growth rate estimated according to U-series
273 ages and those available from the literature. Fourier transform analysis for coral 13SS-1
274 identified dominant peaks at the frequencies of 50, 8.2, 7.1 mm and weak peaks at the
275 frequencies of 4.7, 3.3 and 2.4 mm (most probable annual cycles), which is closer to the
276 estimated growth rate by U-series age. For colony 13SS-2, frequency peaks at intervals
277 of 62.5, 18.0 (strong) and a weak peak at 4.3 mm (most probable annual cycle). For the

278 colony 12SFB-1, strong frequency peaks are observed at the intervals of 28.6, 5.3 and 3.6
279 mm, the later peak is consistent with the growth rate of $3.45\text{year}\cdot\text{mm}^{-1}$, based on U-series
280 ages.



281

282 **Figure 4. Fourier transform analysis of the $\delta^{13}\text{C}$ time series of the coral records 13SS-1 (a),**
283 **13SS-2 (b) and 12SFB-1 (c).**

284 4.1.2. Long term variability

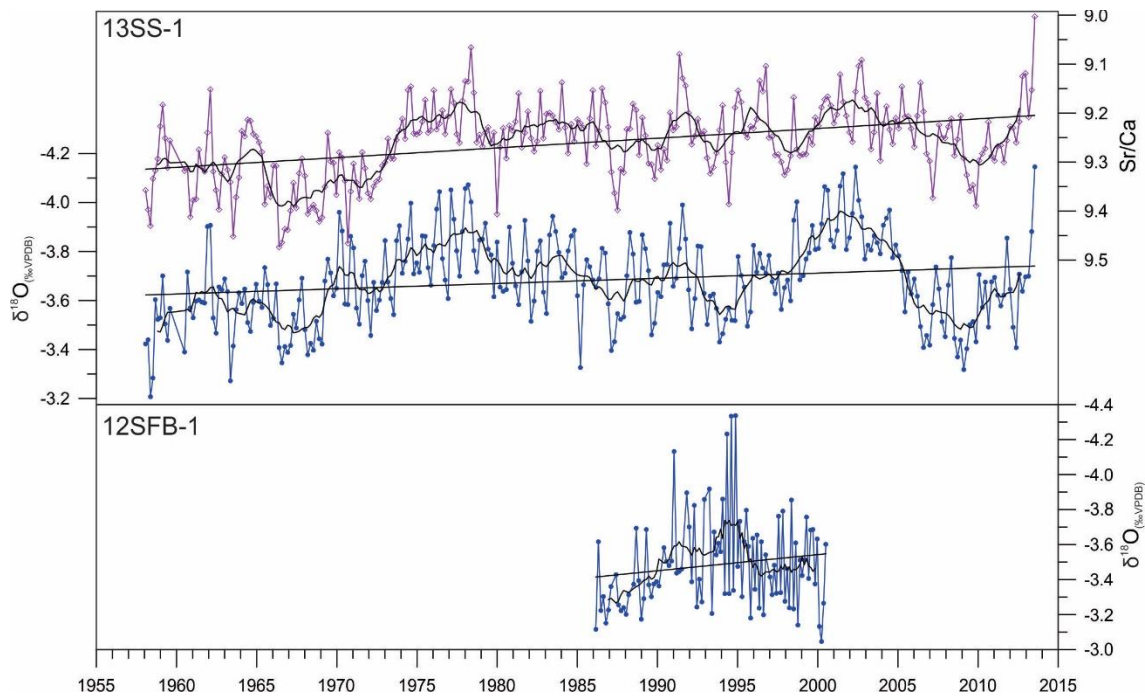
285 The decrease of the $\delta^{13}\text{C}$ in the three *S. stellata* records (Fig. 3) amounts to a
286 depletion rate of about $-0.0243 \pm 0.0057 \text{‰}\cdot\text{yr}^{-1}$ for 12SFB-1 ($r = -0.40$, $p < 0.001$),
287 $-0.0208 \pm 0.0007 \text{‰}\cdot\text{yr}^{-1}$ ($r = -0.83$, $p < 0.001$) for 13SS-1 and $-0.0214 \pm 0.0013 \text{‰}\cdot\text{yr}^{-1}$
288 ($r = -0.67$, $p < 0.001$) for 13SS-2.

289 4.2. Oxygen isotopes and Sr/Ca ratios

290 The coral $\delta^{18}\text{O}$ values range from -4.15 to -3.21‰ , with a mean value of $-3.68 \pm$
291 0.18‰ and variance of 0.03‰ in colony 13SS-1 ($n = 295$). Colony 12SFB-1 varied from
292 -4.34 to -3.05‰ , with mean value of $-3.49 \pm 0.26 \text{‰}$ and variance of 0.07‰ ($n = 94$).
293 Sr/Ca ratios for the colony 13SS-1 range from 9.00 to 9.47 mmol/mol with a mean value
294 of $9.26 \pm 0.08 \text{ mmol/mol}$ and variance of 0.006 mmol/mol ($n = 295$).

295 Both $\delta^{18}\text{O}$ and Sr/Ca ratios of 13SS-1 and $\delta^{18}\text{O}$ of 12SFB-1 lack coherent seasonal
296 cycles and are strongly dominated by an inter-annual signal (Fig. 5). In 13SS-1, $\delta^{18}\text{O}$ and
297 Sr/Ca are clearly correlated, but this covariation is dominated by multi-annual SST
298 variability rather than seasonal cycles which are developed weakly at best. Within the
299 resolution of the available age models no clear correlation of $\delta^{18}\text{O}$ data from the

300 specimens 13SS-1 and 12SFB-1 can be established, which might be associated to local
301 signals of different tidal ponds at the Rocas Atoll.



302

303 **Figure 5. $\delta^{18}\text{O}$ and Sr/Ca data of colony 13SS-1 (top) and $\delta^{18}\text{O}$ data of 12SFB-1 (bottom).**
304 **Sclerochronology based on the U-series age model. Running averages (11 data points**
305 **averaged) are shown as black lines for the geochemical cycles.**

306 5. Discussion

307 5.1. Seasonal variability of $\delta^{13}\text{C}$ and growth rate

308 Coral metabolism produces isotopic fractionation by respiration and photosynthetic
309 activity by symbiotic zooxanthellae (Swart 1983a; McConnaughey 1989a, 1989b, among
310 others). Since zooxanthellae photoactivity depends on light availability, $\delta^{13}\text{C}$ has been
311 conventionally used as proxy for cloud cover (e.g. Fairbanks and Dodge 1979; Swart
312 1983a; Pätzold 1984; Swart et al. 1996; Fairbanks et al. 1997; Grotoli and Wellington
313 1999; Reynaud-Vaganay et al. 2001; Reynaud and Saint-Martin 2010). During
314 photosynthesis zooxanthellae preferentially fix the ^{12}C , leading to ^{13}C enrichment in the

315 calcifying fluid and consequently higher $\delta^{13}\text{C}$ in coral aragonite (Swart 1983;
316 McConnaughey 1989).

317 The Fourier analysis indicated that the studied coral records have weak annual
318 variability and geochemical variance is dominated by lower frequency variance. The
319 equatorial location of the Rocas Atoll tends to be governed by stronger inter-annual
320 climate-related variability than seasonal variability compared to other sites. This is
321 evident in the three coral colonies that show weak peaks in the 4.7–2.5 mm/cycle range,
322 likely due to weak annual cycles, superimposed on stronger inter-annual variance (8.2
323 mm at the colony 13SS-1 and 18 mm at the colony 13SS-2). Even the colony 12SFB-1, in
324 which carbon isotope cycles are compatible with U-series age, shows a dominant inter-
325 annual variance in the $\delta^{13}\text{C}$ record.

326 The growth rate for *S. stellata* for the Rocas Atoll was previously estimated by
327 Pinheiro et al. (2017) to be on average $6.8 \pm 0.7 \text{ mm}\cdot\text{year}^{-1}$ using coralXDS software
328 (Helmle et al. 2002) – similar to the extension rate that can be deduced from some carbon
329 isotopic cycles in the coral records presented here. As discussed in section 4.1, the
330 comparison between the number of $\delta^{13}\text{C}$ cycles and U-series ages for colonies 13SS-1
331 and 13SS-2 (table 2) is compatible with die-off events in these colonies of *Siderastrea*,
332 probably associated environmental stress like SST anomalies. Multiple substantial growth
333 cessations through the coral life span, however, would be required to explain the gap in
334 time if the carbon isotope cycles were to be a reflection of seasonal environmental
335 variability. This seems unlikely given that there is little skeletal evidence of growth
336 cessation in the coral X-rays (except for the aforementioned growth anomaly in colony
337 13SS-2).

338 The weak signal revealed by the Fourier analysis at 2 to 4 mm is less than the annual
339 extension proposed by Pinheiro et al (2017), but similar to values of linear extension rates
340 ($2.73 \pm 0.35 \text{ mm}\cdot\text{year}^{-1}$) for the same species at the coast of Bahia, Brazil, reported by
341 Lins-de-Barros and Pires (2006), and specimens from this genus (*Siderastrea siderea*)
342 from the coast of Florida, U.S.A. (Maupin et al. 2008; DeLong et al. 2011). These smaller
343 extension rates (and carbon isotope fluctuations) underline that the seasonal $\delta^{13}\text{C}$ record
344 in *S. stellata* from the Rocas Atoll is poorly defined and overprinted by larger multi-
345 annual variability (Fig. 3). Consequently, the coral-based $\delta^{13}\text{C}$ records presented here do
346 not permit annual correlation and the generation of high-fidelity stacked records for this
347 species. However, the apparent non-linear growth of *S. stellata* seems to not obstruct the
348 long-term trends toward increasingly depleted $\delta^{13}\text{C}$, which is explored below.

349 **5.2. Potential sources of $\delta^{13}\text{C}$ variability at long term**

350 While the short-term (intra-annual) variability of the three colonies is not well
351 correlated, over multiple decades the $\delta^{13}\text{C}$ coral records show decreasing trends, which
352 indicates a common environmental forcing. Since coral $\delta^{13}\text{C}$ has been interpreted as
353 recording multiple environmental variables, we discuss each possibility below.

354 *5.2.1. Changes in solar irradiation*

355 As outlined in section 5.1., coral $\delta^{13}\text{C}$ is often associated with the photoactivity of
356 the zooxanthellae (Swart 1983a). To produce the observed long-term decreasing trend in
357 the coral $\delta^{13}\text{C}$ record, a reduction in solar irradiation would be expected.

358 Anthropogenic aerosols intensify the scattering and absorption of light
359 (Ramanathan et al. 2001) and could potentially cause a reduction in the amount of solar
360 irradiation reaching the coral. Measurements from 1960 to 1990 reported a decrease in
361 solar irradiation of about 4 to 6% (Gilgen et al. 1998; Wild et al. 2005), leading to a global

362 dimming phenomenon (Wild et al. 2005), which could potentially trigger the decreasing
363 trend in coral $\delta^{13}\text{C}$.

364 However, a reversal from dimming to brightening conditions occurred after 1985,
365 causing an increasing in solar irradiation, possibly associated with reduction of aerosol
366 burden as a result of more effective clean-air regulations (Wild et al. 2005). This reversal
367 is not seen in the coral $\delta^{13}\text{C}$ record, thus, solar irradiance by itself cannot be the main
368 force governing the long-term $\delta^{13}\text{C}$ trend.

369 The total solar irradiance (TSI) for the period A.D. 1945–2007 (Fig. 7) was
370 reconstructed by using a physical model ([http://vizier.cfa.harvard.edu/viz-bin/VizieR?-
371 source=J/A+A/531/A6](http://vizier.cfa.harvard.edu/viz-bin/VizieR?source=J/A+A/531/A6)) (Vieira et al., 2011) in which no decreasing trend was observed
372 ($r = -0.09$, $p < 0.001$), thus TSI could not explain the observed changes in coral $\delta^{13}\text{C}$
373 through time.

374 5.2.2. *Heterotrophy*

375 The influence of zooplankton ingestion to the coral $\delta^{13}\text{C}$ through time also should
376 be considered. If the negative trend was caused by changes in the level of heterotrophy,
377 it is expected that the three investigated colonies have continuously increased the
378 ingestion of zooplankton (Grottoli and Wellington 1999). Zooplankton is an important
379 dietary component of corals, because it supplies nitrogen, phosphorus and other nutrients
380 that are not provided by the zooxanthellae (Sebens et al. 1998).

381 Colonies 13SS-1 and 13SS-2 were collected at the southern part of Rocas Atoll and
382 12SFB-1-1 was collected at the northwestern part of the atoll (Fig. 1). It thus would be
383 necessary to explain why colonies from distinct locations are increasing zooplankton
384 ingestion continuously through time: changes in phototrophic-heterotrophic strategies?
385 Plankton rich upwelling events? Decrease in water transparency and concurrent

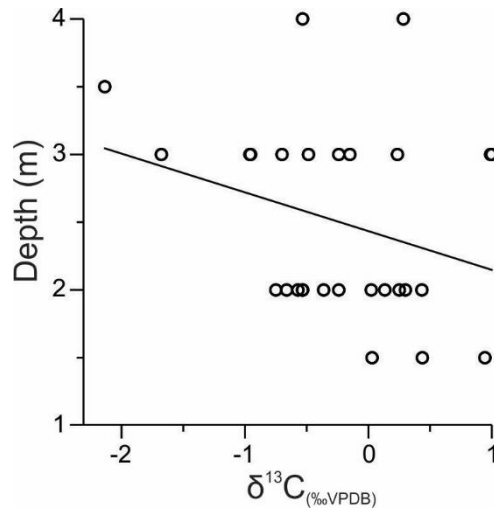
386 inefficiency of zooxanthellae in supplying coral nutrients, leading to higher level of
387 heterotrophy? These potential explanations require much more data than are available to
388 fully explore, but they require invoking coincident physical and biological process
389 changes and are therefore not the most parsimonious of explanations for the decrease in
390 $\delta^{13}\text{C}$ common to all three specimens.

391 5.2.3. *Water depth*

392 Average coral $\delta^{13}\text{C}$ could be affected by water depth (Weber and Woodhead 1970).
393 Light intensity decreases with depth, reducing the photosynthesis activity of
394 zooxanthellae, which decreases the $\delta^{13}\text{C}$ signal in coral aragonite through a decreased
395 removal of ^{12}C for photosynthesis, as discussed above (Weber and Woodhead 1970).
396 However, when this mechanism was tested with 25 specimens of *S. stellata* from this site
397 (Mayal et al., 2009), no correlation between depth and $\delta^{13}\text{C}$ ($r = -0.29$, $p(a) > 0.05$, $n =$
398 28) was observed over 1 to 4 m water depth (Fig. 6). Additionally, assuming a linear age
399 model between U-series dates, we calculated the mean $\delta^{13}\text{C}$ in our three corals over the
400 common growth period of 2000-1986 and get the values -0.93 (13SS-1, 7 m depth), -0.60
401 (13SS-2, 7 m depth) and -0.54 (12SFB-1, 3 m depth), with no depth related trend. Thus,
402 we conclude that depth is not a major factor controlling $\delta^{13}\text{C}$ in these corals.

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405

406 **Figure 6. Cross plot of depth against mean $\delta^{13}\text{C}$ of different colonies of *S. stellata* analyzed**
 407 **by Mayal et al. (2009), showing no evident correlation.**

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5.2.4. Suess Effect and $\delta^{13}\text{C}$ of DIC

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The decreasing rates observed in the corals of Rocas Atoll are similar to the reported trends for the $\delta^{13}\text{C}$ of atmospheric CO_2 over 1960-1990 (-0.023 to -0.029 ‰.yr^{-1}) (Keeling et al. 2010). Recently, decreasing trends on coral $\delta^{13}\text{C}$ for the Caribbean and North Atlantic (Swart et al. 2010; Hetzinger et al. 2016), Red Sea (Al-Rousan and Felis 2013) and Fiji (Swart et al. 2010; Dassié et al. 2013) have been reported. These authors attributed the decreasing trend to decreasing $\delta^{13}\text{C}$ values of the DIC, ultimately governed by changes in the carbon isotopic composition of atmospheric CO_2 , caused by increasing anthropogenic CO_2 emissions, known as the Suess Effect (Keeling 1979).

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Most of the coral records used to assess the Suess Effect date up to 1990 (Swart et al. 2010; Dassié et al. 2013) and these records show differences in detail, but generally exhibit a steepening downward slope between 1960-1990. The data presented for the $\delta^{13}\text{C}$ based on coral archives for the South Atlantic Ocean have $\delta^{13}\text{C}$ trends similar to those from the North Atlantic Ocean (-0.019 ‰.yr^{-1}) between 1960-1990 (Swart et al. 2010), which are comparatively higher than the coral $\delta^{13}\text{C}$ trends from the Pacific Ocean reported

423 by Swart et al. (2010) ($-0.0066 \text{ ‰}\cdot\text{yr}^{-1}$) and Dassié et al. (2013) ($-0.014 \text{ ‰}\cdot\text{yr}^{-1}$), and
 424 from the Indian Ocean ($-0.0057 \text{ ‰}\cdot\text{yr}^{-1}$ (Al-Rousan and Felis 2013)) for the same period.

425 Coral-based records of the same genus of this study (*Siderastrea*) were reported
 426 from Florida for the period of 1960-1994, with a decreasing rate for the $\delta^{13}\text{C}$ values
 427 varying from -0.0274 to $-0.0289 \text{ ‰}\cdot\text{yr}^{-1}$ (Swart et al. 2010) and Dominica, for the period
 428 between 1960-2000 and presented a $\delta^{13}\text{C}$ decreasing rate of $-0.0217 \text{ ‰}\cdot\text{yr}^{-1}$ (Swart et al.
 429 2010), equivalent to values reported for *S. stellata* from the Rocas Atoll. Table 2
 430 summarizes published coral $\delta^{13}\text{C}$ trends in different locations.

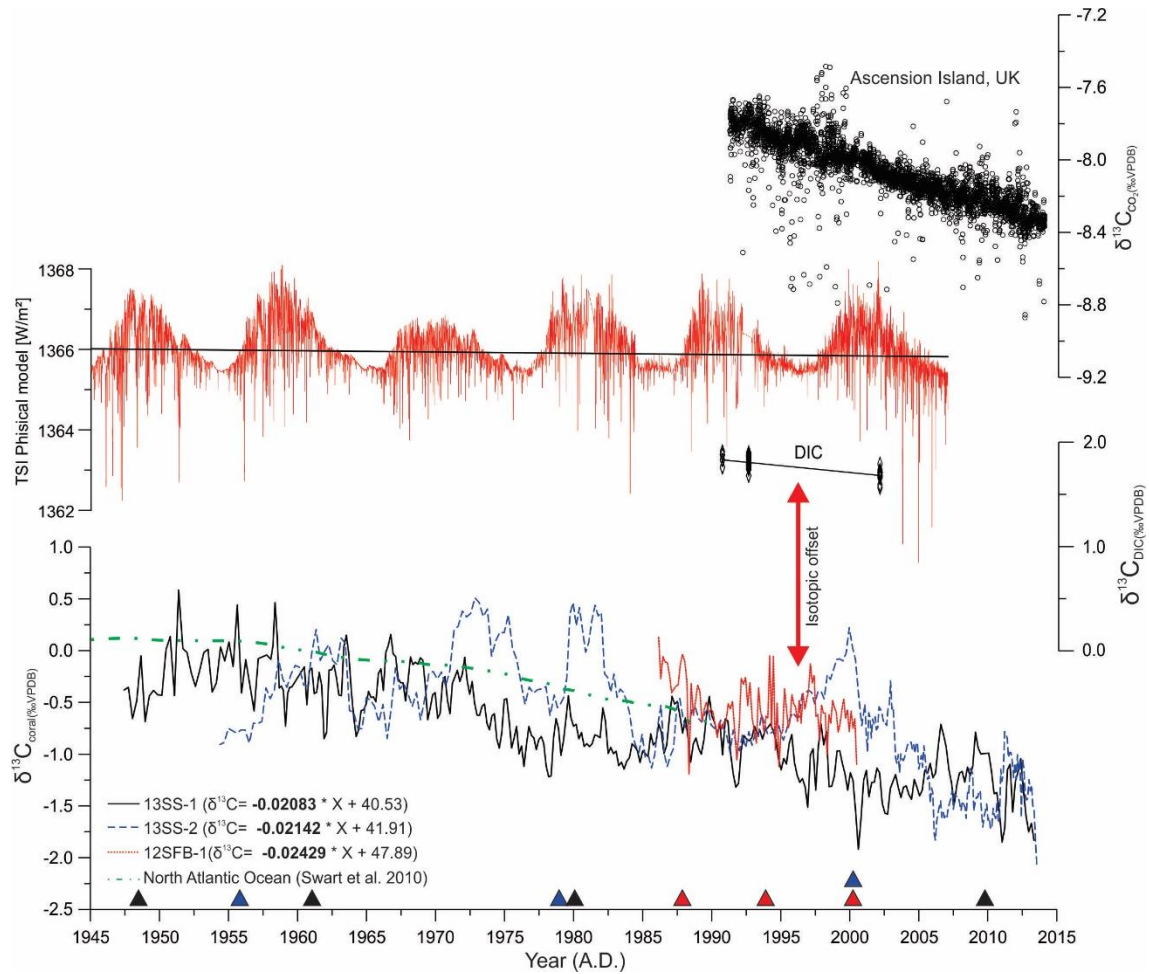
431 **Table 3. Comparison of coral $\delta^{13}\text{C}$ trends from Rocas Atoll and other regions.**

Data set	Location	Coral	Period	$\delta^{13}\text{C}_{(\text{‰VPDB})}$				Decreasing rate ($\text{‰}\cdot\text{yr}^{-1}$)
				average	max	min	range	
12SFB-1	South Atlantic	<i>S. stellata</i>	1988–2001	$-0.53 (\pm 0.26)$	0.13	-1.19	1.32	-0.0243
13SS-1	South Atlantic	<i>S. stellata</i>	1948–2013	$-0.76 (\pm 0.55)$	0.58	-2.76	3.34	-0.0208
13SS-2	South Atlantic	<i>S. stellata</i>	1956–2013	$-0.75 (\pm 0.47)$	0.51	-2.06	2.57	-0.0214
Dassié et al (2013)	Fiji	<i>Porites sp.</i>	1781–2001	–	–	–	–	-0.0052
Dassié et al (2013)	Fiji	<i>Porites sp.</i>	1960–1990	–	–	–	–	-0.014
Swart et al (2010)	Pacific Ocean	Multiple	1960–1999	–	–	–	–	-0.0066
Swart et al (2010)	Indian Ocean	Multiple	1900–1990	–	–	–	–	-0.0057
Wei et al. (2009)	GBR	<i>Porites sp.</i>	1950–2004	–	–	–	–	-0.028
Swart et al (2010)	North Atlantic	Multiple	1960–1990	–	–	–	–	-0.019
Al-Rousan and Felis (2013)	Gulf of Aqaba	<i>Porites</i>	1974–2004	–	–	–	–	-0.029
*CO ₂ Ascension Island	South Atlantic	–	1992-2014	$-8.08 (\pm 0.18)$	-7.48	-8.87	1.34	-0.027
**DIC	Tropical Atlantic	–	1991-2003	$1.77 (\pm 0.82)$	1.91	1.56	0.34	-0.013

432 *Measurements of carbon stable isotope for the atmospheric CO₂ from Ascension Island and
 433 **DIC from Tropical Atlantic is display for comparison.

434

435 $\delta^{13}\text{C}$ data of atmospheric CO₂ at the interval of 1992 to 2014 from the oceanic
 436 Ascension Island (Fig. 6), a location in the tropical South Atlantic Ocean with similar
 437 conditions to Rocas Atoll yielded a decreasing trend of $-0.027 \text{ ‰}\cdot\text{yr}^{-1}$, slightly higher
 438 than the coral records presented here (table 3).



439

440 **Figure 7. Evolution of the $\delta^{13}C$ of colonies 13SS-1, 13SS-2 and 12SFB-1 through time,**
 441 **together with the data of the coral $\delta^{13}C$ trend for the North Atlantic Ocean published by**
 442 **Swart et al. (2010). Time series of the CO_2 carbon isotope from Ascension Island, UK for the**
 443 **period from 1992 to 2014 and DIC from the Tropical Atlantic Ocean (data compiled from**
 444 **Schmittner et al. (2013)) and Total Solar Irradiance from 1945 to 2007 are plotted together**
 445 **for comparison. Colored triangles represent age tie points (U-series) used for age model of**
 446 **each colony, 13SS-1 (black); 13SS-2 (blue) and 12SFB-1 (red).**

447 Carbon stable isotope data for DIC from Tropical Atlantic (latitude varying from 8
 448 to -9), compiled from Schmittner et al. (2013) for the period of 1991 to 2003, show a
 449 decreasing trend of -0.013‰.yr^{-1} , whereas, for a global estimation, Gruber et al. (1999)
 450 proposed a $\delta^{13}C$ decrease rate of the surface oceanic DIC of approximately -0.018‰.yr^{-1}
 451 from 1985 to 1995.

452 The coral records presented here show slightly higher trends compared to
453 Schmittner et al (2013) but closer to the trend from the Gruber global compilation. The
454 carbon isotopic composition of DIC can be site specific (Quay et al 2003) which could
455 explain different trends between $\delta^{13}\text{C}$ of corals from Rocas and global DIC estimates.
456 This difference suggests that the coral record from the Rocas Atoll tracks changes in the
457 isotopic signature of local DIC.

458 The offset between the $\delta^{13}\text{C}$ from coral records and the surface DIC from this part
459 of the tropical Atlantic is approximately 2.3‰ (Fig. 7) which can be attributed to the
460 prevailing biological fractionation during coral biomineralisation. The primary long-term
461 signal from multiple records nevertheless is visible as a consistent $\delta^{13}\text{C}$ decreasing trend
462 thus imaging the Suess Effect. This successful detection of the Suess Effect highlights the
463 possibility of tracking changes in the $\delta^{13}\text{C}$ of the oceanic DIC and eventually, correlation
464 with $\delta^{13}\text{C}$ composition of the atmospheric CO_2 using *S. stellata*.

465 **6. Conclusions**

466 $\delta^{13}\text{C}$ time series of three colonies of *S. stellata* from the tropical South Atlantic
467 Ocean have been presented. The $\delta^{13}\text{C}$ signal is mostly dominated by inter-annual
468 variation, with weak annual signals. The latter are probably controlled by the solar
469 irradiation conditions at the tropical South Atlantic that influence zooxanthellae
470 photosynthesis activity.

471 $\delta^{13}\text{C}$ showed a consistent decadal trend toward negative values, with a decreasing
472 rate varying from -0.0208 to -0.0243 similar to rates expected from the Suess Effect.
473 These trends are also very similar to the global estimates for changes in carbon isotopic
474 composition of sea-surface DIC, suggesting that the $\delta^{13}\text{C}$ coral-based records from the

475 Rocas Atoll presented in this study are directly influenced by the $\delta^{13}\text{C}$ signature of local
476 DIC.

477 This study confirms that multiple $\delta^{13}\text{C}$ coral-based records can detect long-term
478 changes in the $\delta^{13}\text{C}_{\text{DIC}}$ of the ocean and, ultimately, identify changes in the $\delta^{13}\text{C}$ of the
479 atmospheric CO_2 , contributing to the understanding of the recent carbon cycle
480 disturbances within the atmosphere-ocean system during the Anthropocene epoch.

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