Coral-based climate records from tropical South Atlantic: 2009/2010 ENSO event in C and O isotopes from *Porites* corals (Rocas Atoll, Brazil)

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ABSTRACT

Coral skeletons contain records of past environmental conditions due to their long life span and well calibrated geochemical signatures. C and O isotope records of corals are especially interesting, because they can highlight multidecadal variability of local climate conditions beyond the instrumental record, with high fidelity and sub-annual resolution. Although, in order to get an optimal geochemical signal in coral skeleton, sampling strategies must be followed. Here we report one of the first coral-based isotopic record from the Equatorial South Atlantic from two colonies of *Porites astreoides* from the Rocas Atoll (offshore Brazil), a new location for climate reconstruction. We present time series of isotopic variation from profiles along the corallite valley of one colony and the apex of the corallite fan of the other colony. Significant differences in the isotopic values between the two colonies are observed, yet both record the 2009/2010 El Niño event - a period of widespread coral bleaching - as anomalously negative $\delta^{18}O$ values (up to -1 permil). $\delta^{13}C$ is found to be measurably affected by the El Niño event in one colony, by more positive values ($+0.39$ ‰), and together with a bloom of endolithic algae, may indicate physiological alteration of this colony. Our findings indicate that corals from the Rocas Atoll can be used for monitoring climate oscillations in the tropical South Atlantic Ocean.

Key words: coral, climate change, Rocas Atoll, carbon and oxygen isotopes, South Atlantic Ocean.

INTRODUCTION

Geochemical information from massive, boulder-like corals has long been used to reconstruct climate oscillations through time (Corrège 2006, DeLong et al. 2013, Felis and Rimbu 2010, Felis et al. 2000, Hereid et al. 2012, Kilbourne et al. 2008, Linsley et al. 1994, Moses and Swart 2006, Swart et al. 2010). These corals can live for hundreds of years and are natural archives with annual density bands, visible in X-ray images of cross-sections of their aragonite skeleton (Buddemeier et al. 1974, Knutson et al. 1972). These bands allow dating and assessing

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the duration of environmental perturbations in the shallow-marine tropical environment, ranging from a few years to centuries and before the instrumental record.

Such coral-based climate records have been reported for different tropical localities in the Pacific Ocean (Alibert and Kinsley 2008, Asami et al. 2004, Beck et al. 1992, Cobb et al. 2003, Dunbar et al. 1994, Guilderson and Schrag 1998, 1999, Hereid et al. 2012), Indian Ocean (Kuhnert et al. 1999), Caribbean (Kilbourne et al. 2008, Medina-Elizalde et al. 2002, Moses and Swart 2006, Winter et al. 1991), Red Sea (Al-Rousan et al. 2003, Felis and Rimbu 2010, Felis et al. 2000, Klein and Loya 1991), but there is a lack of records for the Tropical South Atlantic Ocean.

The analysis of the geochemical composition along the coral growth axis, allows the reconstruction of environmental parameters at the sea-surface. Such geochemical investigations provide a better understanding of climate oscillations, which can be used as a background for paleoceanographic models (Gagan et al. 2000, Kilbourne et al. 2008, Schrag and Linsley 2002).

Oxygen and carbon isotope ratios are extensively used as proxies to identify environmental and physiological factors in hermatypic corals (Weber and Woodhead 1970, 1972). For decades, oxygen isotopes of coral skeletons have been used for climatic reconstructions (Dunbar et al. 1994, Gagan et al. 1994, Kuhnert et al. 1999, Wei et al. 2000, Corrège 2006, Moses and Swart 2006, Moses et al. 2006, Hereid et al. 2012, Chen et al. 2013 among others). Depending on local conditions, $\delta^{18}O$ in corals reflects sea-surface temperature (SST) (Dunbar et al. 1994, Fairbanks and Dodge 1979, McConnaughey 1989, Pätzold 1984, Weber and Woodhead 1970, 1972, Wefer and Berger 1991) and sea-surface salinity (SSS) (Cole and Fairbanks 1990, Linsley et al. 1994). Carbon isotopes, in turn, are more complicated to interpret due to a multitude of physiological controls (Swart 1983).

The signal of the $\delta^{18}O$ in corals can be used as a proxy for climatic disturbances like the El Niño Southern Oscillation (ENSO). Pacific coral-based ENSO reconstructions have been used by researchers to understand the range of natural variability of the ENSO in modern and Pre-historical time (Cobb et al. 2003, 2013, Dunbar et al. 1994, Hereid et al. 2012, 2013).

The year 2010 was marked by anomalously high sea-surface temperatures that led to a bleaching event throughout coral reefs of the tropical oceans (Krishnan et al. 2011). At Rocas Atoll, Ferreira et al. (2013) reported anomalous temperatures during the years of 2009 and 2010 which caused coral bleaching. Those authors pointed out the susceptibility of the Rocas Atoll to El Niño events and their potential detrimental effects on this reef. In this study, we report on a coral-based record of oxygen and carbon isotopes from two *Porites* colonies. We relate anomalous isotope signals observed in contemporaneous parts of the corals, to thermal stress triggered by the 2009/2010 ENSO event.

STUDY SITE

The Rocas Atoll is the only atoll located in the western part of the South Atlantic (3°51′S, 33°49′W), 266 km from the coastal city of Natal, northeastern Brazil (Fig. 1). The equatorial location of Rocas Atoll leads to minimal SST seasonal variability (26 to 29 °C) with larger inter-annual variability, analogous to the study sites in the equatorial Pacific, where the same genus *Porites* was investigated (McConnaughey 1989, Omata et al. 2006).

The Rocas Atoll offers a great opportunity to investigate the influence of ENSO at a location practically devoid of human influence. The atoll receives no direct terrestrial runoff and ocean and atmosphere are the key players determining the environmental conditions at the locality. Therefore,
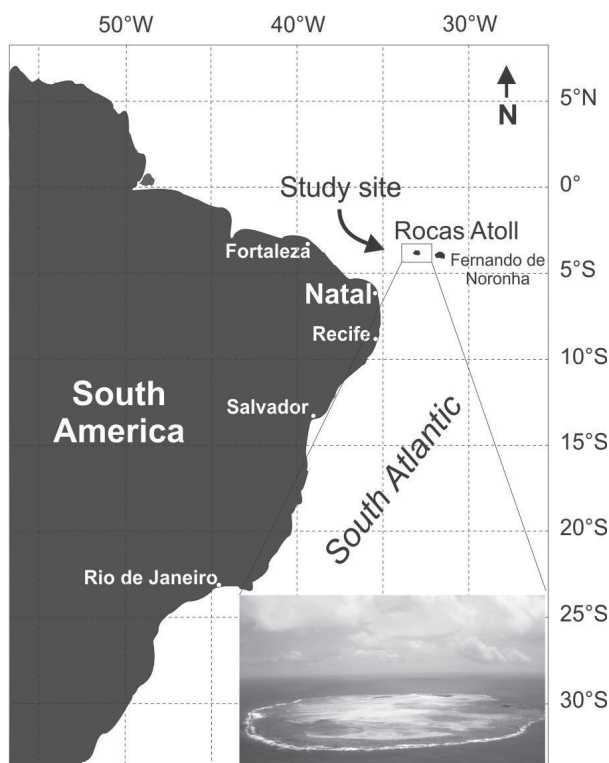
Figure 1 - Location and aerial southward view of the Rocas Atoll.

coral-based records from this atoll might prove to be useful in the understanding of the frequency of ENSO events and their influence in the Tropical South Atlantic.

This atoll is located within the South Equatorial Current (SEC), with a consistent westerly flow (Goes 2005). The mean speed of this current in the 4° parallel (which crosses Rocas Atoll) is 30 cm per second (Richardson and Walsh 1986). The tidal regime on this atoll is semi-diurnal and meso-tidal, with a maximum tidal range of 3.8 m (Gherardi and Bosence 2001). The monthly mean temperatures of the surface water vary from 26.3 °C in September to 28.5 °C in April, while the salinity varies from 36 to 37 psu (Gherardi and Bosence 1999).

The reef grows in the western portion of a submarine volcanic mountain with a flattened top

(Guyot type) rising up from depths of 4,000 m (Kikuchi and Leão 1997, Pereira et al. 2013). The evolution of this complex reef included colonization by coralline algae, coral reefs, molluscs, and crustaceans on the guyot. The accumulation of marine carbonate provided the basis for the ring ellipsoid reef (Gherardi and Bosence 2001).

Based on core drilling combined with a shallow seismic refraction survey, Kikuchi and Leão (1997) identified three units comprising the Rocas Atoll. The topmost unit is a 12 m-thick Holocene sequence with seismic velocity of 0.33 km/s. This Holocene sequence is mainly composed of encrusting coralline algae, vermetid gastropods, encrusting foraminifera (*Homotrema rubrum*) and corals. The second and third unit have seismic-velocities of 2.50 km/s (Pleistocene?) and 4.70 km/s, respectively, the latter corresponding to velocities typical for basaltic rocks.

The oldest ^{14}C radiometric age for coral skeletons of drill holes was 4.86 ± 0.21 ky BP at the depth of 11.2 m (Kikuchi and Leão 1997). Nevertheless, this age may not correspond to the beginning of the reef development. Thus, it is assumed that the initiation of reef growth began before 4.86 ka, with a build-up rate ranging from 1.5 to 3.2 m/kyr (Kikuchi and Leão 1997).

MATERIALS AND METHODS

CORAL COLLECTION

Two small colonies (~15 cm of diameter) of the massive coral *Porites astreoides* were collected from a depth of about 3 m at the Cemitério (PC2 colony) and Tartaruga (PT2 colony) tide pools from the reef complex in July 2012 (Fig. 2).

ANNUAL EXTENSION RATE

The two colonies were cut into halves, and one half was cut into 5-mm thick slices parallel to the vertical growth axis of the whole colony. After cutting, these slices were air-dried and X-ray images were
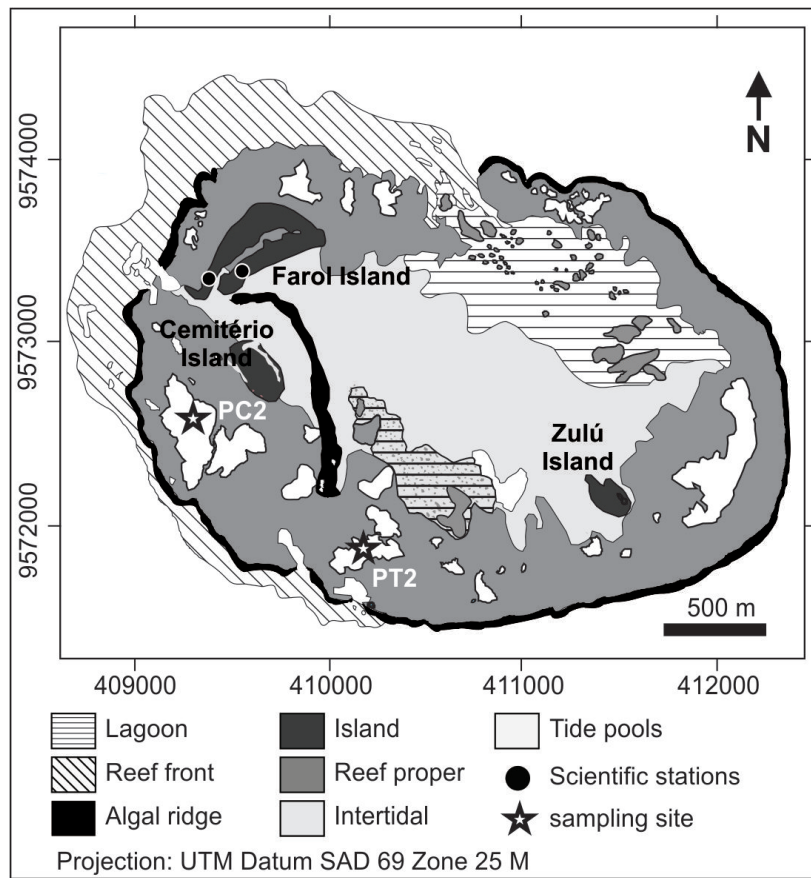
Figure 2 - Geomorphological map of the Rocas Atoll and locations of the collected
Porites colonies. (Modified from Pereira et al. 2013).

taken. X-ray positives were used to select a track for extension rate measurement as well as sampling path for C and O isotopic analyses. The coral slabs were sampled along ontogenic profiles, considering the skeletal architecture. The PC2 coral slab was sampled in the valley between corallites (Fig. 3a), whereas the PT2 coral slab was sampled following the central axis of a corallite fan (Fig. 3c). This method improves the knowledge of sampling methods in *Porites* coral skeletal architecture for geochemical analysis, thus expanding upon some previous studies (Alibert and McCulloch 1997, Cohen and Hart 1997, DeLong et al. 2013, Gagan et al. 2012, Marshall and McCulloch 2002). The tracks were located where the banding density presented the least disturbed pattern, avoiding

imperfections in the skeleton architecture such as bore holes or encrusting organisms. In order to derive information about the depth extent of the coral tissue at the time of coral collection, no bleaching was applied to the slices.

Annual extension rates were determined from sclerochronology data using CoralXDS Software 3.0. To this end, several transects in the digital image of the coral X-radiography were analyzed. Transects that showed clear banding patterns were chosen for C- and O-isotope investigation.

CARBON AND OXYGEN ISOTOPE ANALYSES

Analyses of C and O isotopes of carbonates were performed at the Stable Isotope Laboratory
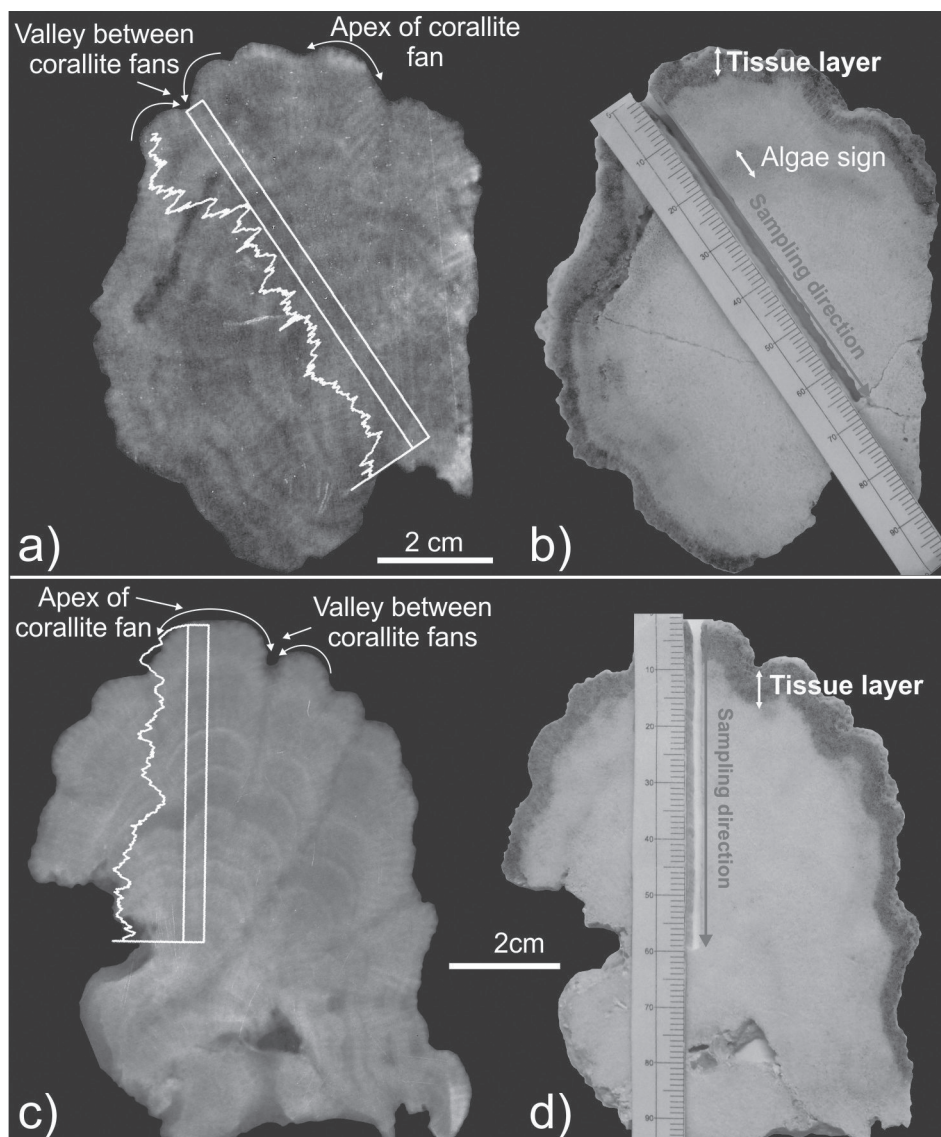
Figure 3 - PC2 and PT2 corals collected from the Cemitério and Tartarugas tide pool in the Rocas Atoll. (**a**) X-ray of a 5-mm-thick slice from the PC2 colony with a transect generated using the software CoralXDS; (**b**) Coral slice indicating location of points analyzed for O and C isotopes, tissue layer and the endolithic sign; (**c**) X-ray of a 5-mm-thick slice from the PT2 colony with transect generated using the software CoralXDS; (**d**) Coral slice indicating the location of points analyzed for O and C isotopes and tissue layer.

(LABISE) of the Department of Geology, Federal University of Pernambuco, Brazil. Carbonate samples (aragonite; 4−20 mg) were collected using a modified hand held dental drill at intervals of 1 mm (or 2 mm, in a few cases) for both colonies. CO_2 gas from micro-drilled powder was extracted in a high-vacuum line after reaction with 100% orthophosphoric acid at 25 °C for one day. Released CO_2 was analyzed after cryogenic cleaning in a VG Isotech, double inlet, triple-collector SIRA II or Thermofinnigan Delta V Advantage mass spectrometer and results are reported in δ notation in permil (‰) relative to the Vienna Pee Dee Belemnite (VPDB) standard. Borborema Skarn

Calcite (BSC), calibrated against international standards, was used as the reference gas and reproducibility of the measurements was better than ±0.1 ‰ (1 sd) for both, carbon and oxygen isotope ratios. The values obtained for the standard NBS-20 in separate runs against BSC, yielded $\delta^{13}C_{V\text{-PDB}}$ = -1.05 ‰, and $\delta^{18}O_{V\text{-PDB}}$= -4.22 ‰. These results are in close agreement with the values reported by the US National Bureau of Standards (-1.06 ‰ and -4.14 ‰, respectively).

RESULTS

ANNUAL EXTENSION RATE AND SCLEROCRONOLOGY

The X-radiograph of the PC2 colony shows relatively clear banding (Fig. 3a). Extension rate analysis and sampling for C- and O-isotope determination were preformed along a corallite valley through almost the entire PC2 slab (Fig. 3b). The number of banding pairs indicates an age of 11 years for specimen PC2 (Fig. 7). The extension rate for this section ranged from 4.0 to 8.9 mm/a with an average of 5.8 ± 1.5 mm/a (1 sd, n= 11). This colony exhibits a significant reduction in the extension rate between the years of 2008 - 2010 (Table I), coinciding with the pronounced El Niño Southern Oscillation (ENSO) pointed out by Ferreira et al. (2013) who reported strong sea-surface temperature anomalies from Rocas locality in 2009-2010 (ENSO).

The X-ray radiography of the PT2 colony shows a clear banding pattern (Fig. 3c). The extension rate analysis and sampling for C and O isotope measurements on this colony were preformed along the central axis of a corallite fan (Fig. 3d). The PT2 colony is interpreted to have reached an age of 7 years according to the number of banding pairs (Fig. 7). The extension rate for the investigated section ranges from 6.3 to 9.5 mm/a, with an average of 8.1 ± 1.3 mm/a (1 sd, n= 7).

STABLE ISOTOPES

The total data of $\delta^{13}C$ and $\delta^{18}O$ analysis are presented in Table II. The $\delta^{13}C$ values for the PC2 colony range from -0.90 to +0.47 ‰, with median value of -0.13 ‰ (±0.30, 1 sd, n = 61) and a total range of 1.37 ‰. The $\delta^{13}C$ values for the PT2 colony skeletal, range from -1.88 to -0.13 ‰ with median value of -0.75 ‰ (±0.45, 1 sd, n = 56) and a total range of 1.75 ‰ (Fig. 4).

Skeletal $\delta^{18}O$ values range from -5.16 to -3.63 ‰ VPDB, with median value of -4.05 ‰ (±0.25 VPDB, 1 sd, n = 61) and a total range of 1.53 ‰ at the PC2 colony and from -5.52 to -3.88 ‰, with median value of -4.24 ‰ (±0.26 VPDB, 1 sd, n = 56) and a total range of 1.64 ‰ at the PT2 colony (Fig. 4).

The average values from the two colonies investigated here differ from each other in $\delta^{18}O$ and a more pronounced difference exists in $\delta^{13}C$ (t test, confidence level< 0.05) (Fig. 4). The colonies can be distinguished from each other in a cross plot of $\delta^{18}O$ and $\delta^{13}C$ values (Fig. 5). This offset might result from sampling in different skeletal architecture (i.e. corallite valley in PC2 and apex of bump in PT2) or may be an indication that environmental and/or physiological controls operate in different ways in the Cemitério and Tartarugas tide pools.

DISCUSSION

ANNUAL EXTENSION RATE AND ENSO

Several studies have attempted to explain the influence of ENSO events on coral-growth rates, but have reched contrasting conclusions. Glynn et al. (1996) reported decreasing extension rates of *Porites lobata* at the Clipperton Atoll during the 1987 ENSO event. Gischler et al. (2009) and Dunbar et al. (1994) also reported lower skeletal growth-rates during ENSO events in Pleistocene corals from Southern Florida and in recent *Pavona ssp*. from the Galapagos Islands. Evangelista et
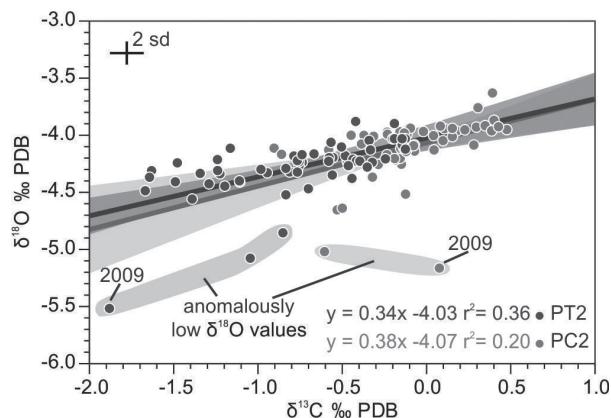
TABLE I

Annual growth rate (AGR) in cm/a and O and C isotope analyses for coral sections of the PC2 and PT2 colonies. $\delta^{18}O$ and $\delta^{13}C$ values are expressed as mean values for analyses from each annual band pair.

	PC2			PT2		
Year	Mean AGR	Mean $\delta^{18}O$ (‰VPDB)	Mean $\delta^{13}C$ (‰VPDB)	Mean AGR	Mean $\delta^{18}O$ (‰VPDB)	Mean $\delta^{13}C$ (‰VPDB)
2002	-	-4.10	-0.14	-	-	-
2003	0.89	-4.03	-0.01	-	-	-
2004	0.44	-4.07	-0.08	-	-	-
2005	0.65	-4.12	-0.16	-	-	-
2006	0.55	-4.12	-0.60	0.95	-4.31	-0.95
2007	0.67	-4.22	-0.28	0.63	-4.32	-0.62
2008	0.43	-4.16	-0.12	0.84	-4.34	-0.84
2009	0.51	-4.25	0.10	0.95	-4.39	-0.76
2010	0.4	-3.97	0.04	0.71	-4.21	-0.67
2011	0.64	-4.19	-0.11	0.68	-4.30	-1.05
2012	0.64	-3.88	0.34	0.9	-4.18	-0.50
Mean	0.58 ± 0.15	-4.10 ± 0.1	-0.09 ± 0.24	0.81 ± 0.13	-4.29 ± 0.07	-0.77 ± 0.19
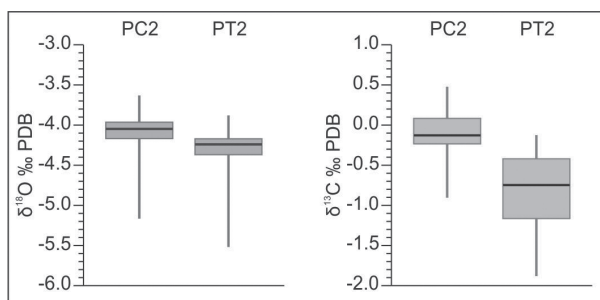
Figure 4 - Boxplot of $\delta^{13}C$ and $\delta^{18}O$ analysis of PC2 and PT2 colonies.

Figure 5 - $\delta^{18}O$ and $\delta^{13}C$ correlation from PC2 colony ANOVA $F_{1, 58}= 14.6$, $p< 0.001$; and PT2 colony ANOVA $F_{1, 54}= 30.8$, $p< 0.001$; and anomalous values related to ENSO.

al. (2007) , in contrast, noted a positive feedback of coral-growth rates with ENSO events in *Favia leptophylla* at the Abrolhos Coral Reef Bank (ACRB) on the Brazilian coast. These authors suggested that during ENSO events, ACRB experienced favorable conditions (i.e. increases in light abundance and lower sediment influx) to coral growth. At Rocas Atoll, the growth rate of the PC2 coral colony seems to be reduced during ENSO events, as indicated by the slower growth of specimen PC2 during such an interval.

In the PC2 colony, endolithic microorganisms generated a green band over the distance of 2 cm from the top (Fig. 3b). Endolithic algae can inhabit the skeleton of several coral species (Shashar and Stambler 1992), frequently forming green dense bands (Highsmith 1981). Hartmann et al. (2010) relate characteristic green bands in coral skeletons, to stress events that could lead to the complete loss
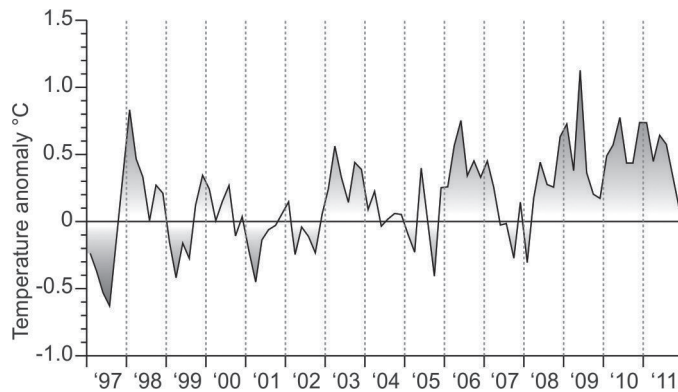
TABLE II
O and C isotope results for the transects through the PC2 and PT2 colonies (see Figs. 3b and 3c).

	PC2				PT2		
Sample	Distance (mm)	$\delta^{18}O_{PDB}$	$\delta^{13}C^{13}_{PDB}$	Sample	Distance (mm)	$\delta^{18}O_{PDB}$	$\delta^{13}C_{PDB}$
PC2.2	2	-3.87	0.401	PT2.3	2	-4.523	-0.834
PC2.4	4	-3.631	0.392	PT2.4	4	-4.238	-0.737
PC2.6	6	-4.087	0.281	PT2.5	5	-4.181	-0.481
PC2.7	7	-3.93	0.296	PT2.6	6	-4.063	-0.566
PC2.8	8	-3.76	0.306	PT2.7	7	-4.032	-0.19
PC2.9	9	-3.996	-0.116	PT2.8	8	-4.032	-0.126
PC2.10	10	-4.14	-0.07	PT2.9	9	-4.085	-0.143
PC2.11	11	-5.02	-0.605	PT2.10	10	-4.165	-0.667
PC2.12	12	-4.255	-0.148	PT2.11	11	-4.267	-0.756
PC2.13	13	-3.968	-0.018	PT2.12	12	-4.338	-1.225
PC2.14	14	-4.067	-0.122	PT2.13	13	-4.411	-1.107
PC2.15	15	-3.917	0.348	PT2.14	14	-4.311	-1.631
PC2.16	16	-	-	PT2.15	15	-4.323	-0.811
PC2.17	17	-3.939	-0.104	PT2.16	16	-4.232	-0.756
PC2.18	18	-4.218	-0.184	PT2.17	17	-4.183	-0.786
PC2.19	19	-3.974	-0.233	PT2.18	18	-4.223	-0.766
PC2.20	20	-5.165	0.077	PT2.19	19	-4.196	-0.554
PC2.21	21	-3.963	0.387	PT2.20	20	-4.197	-0.577
PC2.22	22	-3.951	0.477	PT2.21	21	-4.115	-1.164
PC2.23	23	-3.927	0.427	PT2.22	22	-4.329	-0.944
PC2.24	24	-4.655	-0.53	PT2.23	23	-4.208	-0.243
PC2.25	25	-3.992	-0.231	PT2.24	24	-4.211	-0.436
PC2.26	26	-4.052	-0.141	PT2.25	25	-4.227	-0.416
PC2.27	27	-4.002	-0.371	PT2.26	26	-4.267	-0.463
PC2.28	28	-4.64	-0.499	PT2.27	27	-4.238	-0.321
PC2.29	29	-4.046	-0.154	PT2.28	28	-4.31	-1.239
PC2.30	30	-	-	PT2.29	29	-5.518	-1.881
PC2.31	31	-4.517	-0.124	PT2.30	30	-4.447	-1.196
PC2.32	32	-4.028	-0.158	PT2.31	31	-4.856	-0.851
PC2.33	33	-4.078	-0.385	PT2.32	32	-4.104	-0.504
PC2.34	34	-4.001	-0.447	PT2.33	33	-3.88	-0.42
PC2.35	35	-4.114	-0.904	PT2.34	34	-4.046	-0.34

Table II (continuation)

	PC2				PT2		
Sample	**Distance (mm)**	**δ¹⁸O$_{PDB}$**	**δ¹³C¹³$_{PDB}$**	**Sample**	**Distance (mm)**	**δ¹⁸O$_{PDB}$**	**δ¹³C$_{PDB}$**
PC2.36	36	-4.168	-0.859	PT2.35	35	-4.123	-0.125
PC2.37	37	-4.13	-0.58	PT2.36	36	-4.13	-0.332
PC2.38	38	-4.172	-0.234	PT2.37	37	-5.078	-1.045
PC2.39	39	-4.257	-0.286	PT2.38	38	-4.335	-1.342
PC2.40	40	-4.272	-0.456	PT2.39	39	-4.369	-1.643
PC2.41	41	-3.964	-0.154	PT2.40	40	-4.409	-1.489
PC2.42	42	-4.368	-0.32	PT2.41	41	-4.35	-0.558
PC2.43	43	-4.085	-0.071	PT2.42	42	-3.898	-0.19
PC2.44	44	-3.944	0.106	PT2.43	43	-4.228	-0.395
PC2.45	45	-3.921	0.083	PT2.44	44	-4.469	-0.7
PC2.46	46	-4.004	0.042	PT2.45	45	-4.032	-0.144
PC2.47	47	-4.202	-0.155	PT2.46	46	-4.28	-0.351
PC2.48	48	-4.117	-0.113	PT2.47	47	-	-
PC2.49	49	-3.939	-0.095	PT2.48	48	-4.56	-1.39
PC2.50	50	-4.049	0.099	PT2.49	49	-4.324	-0.766
PC2.51	51	-3.964	0.178	PT2.50	50	-4.379	-0.442
PC2.52	52	-3.954	0.228	PT2.51	51	-4.229	-0.58
PC2.53	53	-3.971	-0.157	PT2.52	52	-4.3	-0.982
PC2.54	54	-4.013	0.154	PT2.53	53	-	-
PC2.55	55	-4.143	-0.121	PT2.54	54	-4.291	-0.834
PC2.56	56	-4.116	-0.152	PT2.55	55	-4.171	-0.738
PC2.57	57	-4.033	-0.201	PT2.56	56	-4.401	-1.109
PC2.58	58	-3.982	-0.132	PT2.57	57	-4.214	-1.24
PC2.59	59	-4.205	-0.189	PT2.58	58	-4.488	-1.668
PC2.60	6	-4.115	-0.135	PT2.59	59	-4.243	-1.478
PC2.61	61	-3.941	0.154	PT2.60	60	-4.427	-1.29
PC2.62	62	-4.13	0.045				
PC2.63	63	-	-				
PC2.64	64	-4.092	-0.076				
PC2.65	65	-4.01	-0.313				
PC2.66	66	-4.232	-0.469				

Figure 6 - Sea-surface temperature anomalies recorded at the Rocas Atoll. Values over ± 0.5 are considered anomalous (data from Ferreira et al. 2013).
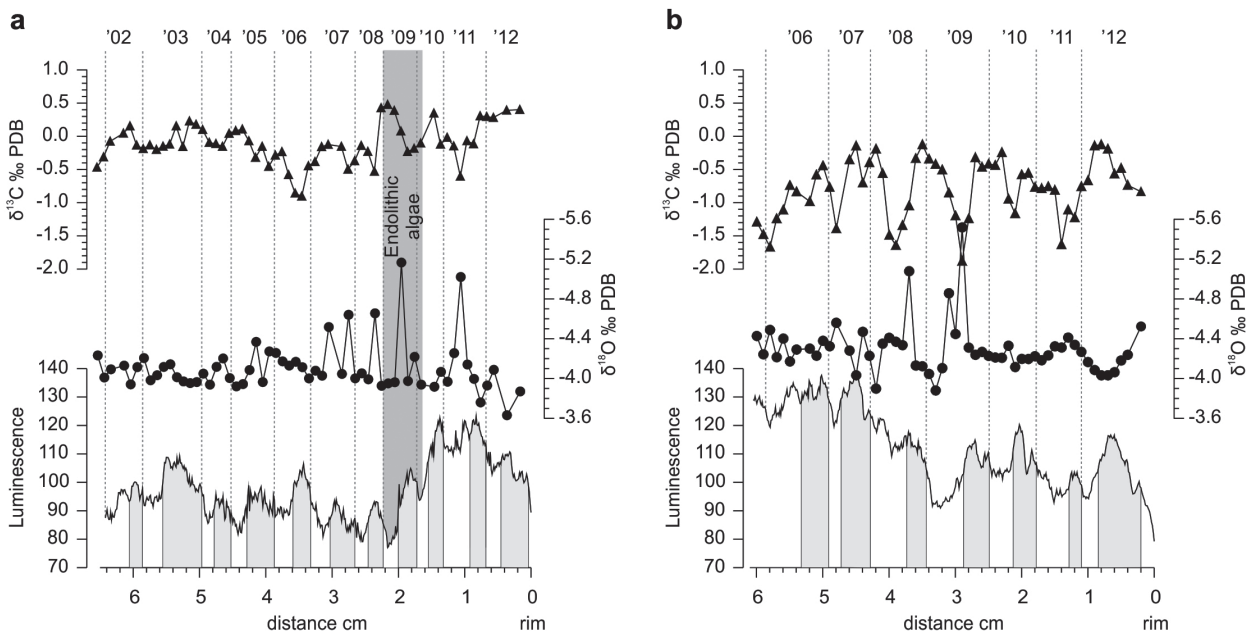
Figure 7 - (a) O and C isotope analyses and high- and low-density bands from PC2 coral. The position of the transect is indicated in Fig. 3a and 3b. **(b)** Oxygen and carbon stable isotopes and high- and low-density bands from PT2 coral. The position of the transect is indicated in Figure 3c and 3d.

of the dinoflagellate symbionts (zooxanthellae) or to a drastic reduction in the symbiont population. The colonization of the coral skeleton by endolithic microorganisms might therefore indicate a stress event suffered by the colony. The sea-surface temperature anomalies at Rocas Atoll (Fig. 6) during the 2009-2010 ENSO event (Ferreira et

al. 2013) is a probable trigger of the bloom of endolithic algae in the PC2 colony.

The PT2 colony grew faster than PC2 and did not show any marked endolithic algae bloom (Fig. 3d). There is no clear relationship between the growth recorded in the PT2 colony and an ENSO event. The absence of a microalgal bloom

suggests that this coral may not have suffered from bleaching, even though $\delta^{18}O$ data (Fig. 7) point to thermal stress during the year of 2009. Corals seem to respond differently to stress events. Even among individuals of a single species at the same place in the reef, some colonies can be damaged by stress, whereas others are not (Brown et al. 1986, Lough and Barnes 1990, Winter et al. 1991).

The depth extent of coral tissue at the time of extraction differs between the two studied colonies, PT2 (~8 mm) and PC2 (~5 mm). The skeleton space occupied by the tissue layer (i.e. the polyp body) varies according to the environmental conditions, presenting a wider layer where conditions to coral development are better (Barnes and Lough 1992). In unfavorable conditions (i.e. wave action, higher sedimentation rate etc.) abrasion of coral tissue may happen (Cruz-Piñón et al. 2003), leading to negative effects on the formation of the coral skeleton (Cortés and Risk 1985, Scoffin et al. 1992). The difference in the tissue layer observed in these two colonies could be used as a parameter for unravelling environmental conditions that influenced the coral development. Here, a wider tissue layer coincides with faster coral growth rate underlining that colonies from the same species can have different extension rates in the same reef complex. Moreover, the disparity in $\delta^{18}O$ and $\delta^{13}C$ behavior (discussed later) complements the array of information on the environmental and physiological patterns for each colony.

Although no strong correlation between ENSO phases and coral growth rates at Rocas Atoll was found, different extension rates and tissue layer thicknesses between the two specimens indicate different susceptibility of colonies to environmental stress (recorded as endolithic algae blooms). The complexity of the atoll environment, including hydrodynamics, tide regime and size of tide pool, for example, exerts strong control on the geochemical signals recorded in coral skeleton and its morphology.

STABLE ISOTOPES

$\delta^{13}C$ fluctuations in the coral skeleton have been discussed for over 40 years (McConnaughey 1989, Swart 1983, Swart et al. 1996, Weber and Woodhead 1970). Currently, the common interpretation is that this variation has been governed by the fractionation of carbon isotopes in the internal inorganic carbon pool (Erez 1978, Goreau 1963, 1977). Bicarbonate derived from the surrounding sea water is modified by the fractionation during CO_2 respiration (Furla et al. 2000) and, more strongly, during photosynthetic reactions (McConnaughey 2003, Swart 1983).

In the photosynthetic processes, ^{12}C is preferentially processed by the symbionts, resulting in metabolic fractionation (McConnaughey 1989, Swart 1983). Alternatively, Erez (1978) proposed that photosynthesis leads to lowering of $\delta^{13}C$ in the coral carbonate by adding ^{13}C-depleted CO_2 into coral skeletons. Later findings of Swart et al. (1996) in the Florida Reefs, support Erez's hypothesis that photosynthesis causes decrease in $\delta^{13}C$. The true mechanism, by mean of which $\delta^{13}C$ values are influenced in the coral skeleton, however, is still a matter of debate.

From the abovementioned, $\delta^{13}C$ changes in the coral skeleton would be expected during a stress event leading to coral bleaching (i.e. loss of zooxanthellae). Changes in carbon isotope values would be expected because the metabolic fractionation by photosynthesis would drop drastically during a bleaching event, unless another symbiont assumes the main role of the photosynthetic process. In this case, the endolithic algae bloom could lead to a more intense metabolic fractionation.

Higher values of $\delta^{13}C$ at the onset of the bloom of endolithic algae (Fig. 7a) are recorded in the PC2 colony. The $\delta^{13}C$ enrichment across the endolithic bands might be a response of metabolic fractionation governed by increasing photosynthetic activity during the algae bloom (Hartmann et al. 2010).

There are two $\delta^{13}C$ trends separated by the endolithic mark in the PC2 coral skeleton: the first, after the ENSO event embracing 4 years (2009-2012), shows more positive values of $\delta^{13}C$ (mean= +0.09 ‰) and the second, prior to the event (2002-2008), presents a seasonal cycle with lighter $\delta^{13}C$ values (mean= -0.20 ‰).

Other authors credited enriched $\delta^{13}C$ in *Porites* corals, to slow skeletogenesis during bleaching events, due to kinetic effects in the period of carbonate precipitation (Allison et al. 1996, Suzuki et al. 2003). This could generate $\delta^{13}C$ enrichment during slow calcification, according to the McConnaughey model (McConnaughey 1989). In contrast, Leder et al. (1991) found different behaviors of isotopes in response to bleaching event in 1987 on *Montastrea annularis* corals in the Caribbean, casting doubts to the reliability on isotopic composition, which might not always be a useful tool.

At the PT2 colony, $\delta^{13}C$ values follow a very consistent seasonal cycle (Fig. 7b). Contrary to this, in the PC2 colony neither a disturbance in the $\delta^{13}C$ curve after the ENSO event nor any apparent endolithic algae signal in its skeletal structure are present. It seems that this colony, even though having experienced a stress episode during the 2009/2010 ENSO (depicted by depleted $\delta^{18}O$ values), did not undergo bleaching. The steady cycle of $\delta^{13}C$ through the section (Fig. 7b) could be interpreted as a normal or healthy condition between the coral and its symbionts, since no evident disruption in this symbiosis is displayed by the $\delta^{13}C$ behavior.

Moreover, the PT2 colony shows a more pronounced variability in C isotopes and generally lighter values. This could be explained by two features: (i) a negative correlation of growth rate with isotope ratios would be expected, pointing to a relation where faster growth, indicated by tissue layer and growth rate analysis (Table III), leads to more disequilibrium $\delta^{13}C$ due to kinetic effects

TABLE III
Mean values of C and O isotope values, mean coral growth rate and tissue layer of the PC2 and PT2 colonies.

	PC2	PT2
Mean $\delta^{18}O$ (‰VPDB)	-4.10 ± 0.25	-4.29 ± 0.26
Mean $\delta^{13}C$ (‰VPDB)	-0.10 ± 0.3	-0.78 ± 0.45
Mean growth rate (cm/a)	0.58 ± 0.15	0.81 ± 0.13
Tissue layer (cm)	0.5	0.8

during skeletogenesis (Allison et al. 1996, Suzuki et al. 2003); or (ii) the fact that the PT2 colony was sampled in the corallite apex (Fig. 3c), considered by DeLong et al. (2013) as optimal sampling track, truly reflecting the isotopic composition (Fig. 7b).

The $\delta^{18}O$ curve for the PC2 colony (Fig. 7a) is marked by anomalously low values, which, according to the sclerochronology, were recorded in the years of 2009 and 2011, whereas the $\delta^{18}O$ curve for the PT2 colony (Fig. 7a) displays a pronounced anomalously negative value in the year of 2009 and a less pronounced one in 2008. Although different $\delta^{18}O$ excursions were respectively recorded just before and after 2009 in the PT2 and PC2 colonies, both are in agreement with anomalous values in the year of 2009 that exhibited maximum positive temperature anomalies of 1.61 °C at the Rocas site (Fig. 6). This temperature spike is larger than the ENSO 1997/1998 anomaly of 1.21 °C for Rocas Atoll, responsible for one of the most severe, worldwide bleaching events (Ferreira et al. 2013).

One of the $\delta^{18}O$ excursion of the PC2 colony matches the signal of endolithic microorganisms in the coral skeleton (Fig. 7a), indicative of bleaching event, as discussed before, and coincides with the temperature anomalies during the 2009-2010 El Niño-Southern Oscillation event (ENSO) mentioned by Ferreira et al. (2013).

$\delta^{18}O$ is controlled by the interplay of temperature and the seawater isotopic composition,

where the latter is controlled by changes in precipitation, evaporation and local upwelling (Suzuki et al. 2003). The observed rapid shifts (> 1.0 ‰) towards negative values might express the response to higher SST and are supported by the anomalous temperature at Rocas Atoll during this time (Ferreira et al. 2013). The oxygen isotope curve up to 2009 does not exhibit any similarly low value as observed during and after the ENSO event (except for the year of 2008 in PT2 coral).

Clearly the O isotope spikes in the corals cannot really be true temperature spikes but rather represent disequilibrium aragonite formation related to thermal stress (otherwise we would be speaking about a 4 degree temperature anomaly, which we didn't observe). It seems that while the timing of such events might be faithfully recorded by the corals, the magnitude might be misestimated due to the stressing effect on the corals during skeletogenesis.

In a tide-pool environment, tide regime is expected to generate noise in the isotopic signal leading to problems in the identification of an ENSO event. Changes in the seawater isotopic composition are unlikely to produce these signals, because the phenomenon behind these changes (i.e. evaporation, precipitation and upwelling) occur at higher frequency and are expected to be recorded in coral skeleton multiple times. We therefore conclude that the isotope signals are controlled by changes in SST, despite apparent disequilibrium effects during mineralization of the coral skeleton.

Linear regressions between $\delta^{18}O$ and $\delta^{13}C$ (Fig. 6) display a weak positive relationship (PC2, $r^2 = 0.20$; $p < 0.0001$; PT2, $r^2 = 0.36$; $p < 0.0001$). If $\delta^{13}C$ expresses kinetic fractionation by physiological activity (photosynthesis and respiration) and if $\delta^{18}O$ responds to SST fluctuation (i.e. more negative values mean higher SST), increases in SST lead to depletion in $\delta^{13}C$, which means lower photosynthetic activity and higher respiration (Coles and Jokiel 1977).

Positive correlations of oxygen and carbon isotope values are common in ahermatypic coral, whose metabolic activity and respiration are the only processes directly influencing the isotopic fractionation. In hermatypic corals, photosynthesis affects the O − C isotope relationship that, occasionally, presents a completely random pattern (Swart 1983).

McConnaughey (1989) has ascribed positive correlations between $\delta^{13}C$ and $\delta^{18}O$ to carbonates showing kinetic isotopic fractionation patterns, which implies isotopic fractionation in carbonates being controlled mainly by kinetics rather than by physiological processes. Alternatively, Fairbanks and Dodge (1979) pointed out that the relationship between insolation and temperature, controls the degree of correlation between oxygen and carbon isotopes.

Although Swart et al. (1996) have found inverse correlation between photosynthesis/respiration rates (P/R), based on Coles and Jokiel (1977) we believe that at higher temperatures, when photosynthesis/respiration rates are reduced, the contribution of ^{12}C from respiration to the internal carbon pool increases, thereby generating the observed positive correlation.

Moreover, the hottest and coldest months at Rocas Atoll are respectively April and September while the maximum and minimum peaks of insolation are in January and July, respectively. This out-of-phase relationship of temperature and insolation supports the Fairbanks and Dodge (1979) ^{13}C-insolation model.

The observed positive correlation of C and O isotopes is ambiguous and might be related to kinetic fractionation (McConnaughey´s proposal) or be the product of changing photosynthesis/respiration rates (Fairbanks and Dodge´s proposal).

Here we prefer the suggestion of Fairbanks and Dodge, indicating a fractionation mainly governed by temperature and respiration processes. This conclusion is based on two observations: (1)

Temperature at the inner reef can reach higher levels in the tide pools during low tides potentially favoring a lower photosynthesis/respiration rate; and (2) the $\delta^{13}C$ shift during algae bloom in specimen PC2 indicates that the colony responded to a physiological turnover, thus the carbon-isotope signal seems to be governed mainly by coral physiology, are not by kinetic effects.

CORALLITE APEX X CORALLITE VALLEY

The importance of investigating the variability of $\delta^{18}O$ and $\delta^{13}C$ values for different colonies in similar environments is well known (Guilderson and Schrag 1999, Leder et al. 1991, 1996). The mean $\delta^{18}O$ for the PC2 colony is 0.19 ‰ higher than that for the PT2 one, which is in the range of inter-colony variability in $\delta^{18}O$ of 0.15–0.40 ‰ reported for *Porites* from some tropical Pacific Islands (Guilderson and Schrag 1999, Linsley et al. 1999, Stephans 2004). The average difference of 0.68 ‰ in $\delta^{13}C$ between the PC2 and PT2 colonies (Fig. 5) is probably due to physiological controls, as $\delta^{13}C$ is believed to be partly and variably influenced by photosynthesis/respiration processes (Swart 1983).

The influence of skeletal architecture on the isotopic signal cannot be neglected. DeLong et al. (2013) provided new insights on sampling methods to improve coral-based reconstructions mainly by appraisal of the skeletal architecture, where the optimal geochemical signal can be obtained at the central axis of a corallite fan, whereas suboptimal signals, as the ones derived from corallite valleys, can result in loss of geochemical information. Moreover, geochemical determinations in the valley between corallites have yielded higher $\delta^{18}O$ and Sr/Ca values than the apex bump, implying colder temperatures of about 1 to 2 °C (Alibert and McCulloch 1997, Cohen and Hart 1997).

Our data seems to support results reported by Alibert and McCulloch (1997) and Cohen and Hart (1997), who stated that suboptimal sampling,

in case of corallite valleys, can yield colder temperatures. In our study, we found differences in $\delta^{18}O$ values between PC2 (corallite valley) and PT2 (corallite fan) colonies, with PT2 being depleted in relation to PC2 by an average of 0.19 ‰, and in the maximum and minimum values by 0.25 and 0.36 ‰, respectively. These offsets suggest a bias of approximately 1 °C (using the mean value), based on different *Porites* calibrations that yielded slopes varying from −0.134 (‰/°C) to −0.262 (Omata et al. 2006) and for Galapagos Islands (which has a latitude similar to Rocas Atoll but is situated in the Pacific Ocean), calibrations yielded 0.209 ‰/°C (McConnaughey 1989).

Even though the skeletal architecture issues are still a matter of concern when considering highly accurate and precise coral-based climate reconstructions (DeLong et al. 2013), geochemical signals of the ENSO of 2009/2010 can be detected with high fidelity.

ENSO AND STABLE-ISOTOPE SIGNAL

The effect of the El Niño-Southern Oscillation in South America was investigated by Ropelewski and Halpert (1987, 1996). According to these authors, the South American continent has two areas of precipitation patterns associated to ENSO events, one in the Northeastern of South America (NSA) and another in the Southeastern of South America (SSA).

At the NSA, where Rocas Atoll is located, Ropelewski and Halpert (1987) highlighted a consistent relationship between ENSO and precipitation, with dry seasons in the area during ENSO events. Such ENSO-related droughts had been previously described by Hastenrath and Heller (1977), who pointed out the strong pattern between extremely dry season in the Northeast Brazil and El Niño phases. Kousky et al. (1984) suggested that this low precipitation may be related to increasing atmospheric subsidence over Northern South

America which perturbs the Walker and Hadley circulations over South America, in turn causing a westward displacement of the Atlantic Walker circulation during ENSO events.

Such perturbation would cause physical, chemical and biological changes in the marine system via atmospheric-ocean interaction. This feedback might be imprinted in the isotopic composition of the coral skeleton, as a response of SST changes affecting coral $\delta^{18}O$ and, more indirectly, by coral physiological factors, affecting $\delta^{13}C$.

The negative $\delta^{18}O$ excursion observed in the present study might be a response to the severe thermal stress caused by the ENSO of 2009/2010. Thermal stress on coral reefs has been reported also for the year 2005 in the 1000 km long Mesoamerican reef system. The reef systems in the Southern Tropical America region experienced severe coral bleaching during this year, causing a severe crisis from the oceanic reefs of Colombia in the Southwestern Caribbean to Brazilian reefs in the Western Atlantic. However, the severity of bleaching varied greatly and bleaching mortality was generally low (Wilkinson and Souter 2008).

Although the isotopic record of coral colony PC2 reaches back to 2002, and a geochemical signal from the ENSO of 2005 might have be expected, no corresponding excursion was observed. The fact that PC2 was sampled in a valley between corallites might account for the loss of geochemical signal. Nevertheless, in Brazil, the HotSpots of 2005 affected reefs from South Bahia (Itacolomis and Abrolhos reefs) with a rise in temperature of 0.75 °C above maximum summer averages. The National Oceanic and Atmospheric Administration (NOAA) has not detected a major Hotspot in the satellite images, suggesting this to be a doldrum-like event (Wilkinson and Souter 2008). Approximately 25 % of the coral cover was affected by bleaching during the 2005 ENSO for the two areas (Leão et al. 2010). The Hotspot at Rocas Atoll during 2005

barely exceeded 0.5 °C (Ferreira et al. 2013) and no bleaching event was reported for this site, and this might also explains the lack of oxygen isotopic excursion recorded in the PC2 colony.

CONCLUSIONS

We presented one of the first coral-based isotopic records in *Porites* of a remote atoll in the South Atlantic, the Rocas Atoll. Such coral-based record seems to be a good proxy in the search for anomalous climatic fluctuations. Here we recognized anomalous $\delta^{18}O$ and $\delta^{13}C$ linked to the 2009/2010 ENSO event.

$\delta^{18}O$ negative excursions were recorded in both colonies investigated here. The magnitude of the geochemical record apparently misestimates (up to 4 °C) the true temperature observed at the place (1.6 °C) and a calibration would be necessary to assure accurate temperature values inferred via $\delta^{18}O$.

We investigated differences in the geochemical signal by sampling in the corallite valley and corallite fan. $\delta^{18}O$ recorded on the corallite valley was depleted compared to the corallite fan by 0.19 ‰. Nevertheless, both corallite valley and the corallite fan seemed to faithfully record the 2009/2010 ENSO event.

Changes in $\delta^{13}C$ after the ENSO event at the PC2 colony were interpreted as a consequence of coral bleaching (inferred via endolithic algae bloom) leading also to changes in the $\delta^{13}C$ values. Depleted $\delta^{13}C$ values in the PT2 colony might have been a consequence of disequilibrium conditions due to faster growth rates or an effect of sampling in the corallite fan.

The coral-based records in this study assure that the Rocas Atoll is a vital site in the record of climate oscillations in the Tropical South Atlantic Ocean. Moreover, it warns us that the current global climate changes threaten coral reefs in the

South Atlantic Ocean, even in pristine places as Rocas Atoll.

RESUMO

Esqueletos de corais contêm excelentes registros de condições ambientais passada, devido à sua longevidade e assinaturas geoquímicas bem calibradas. Registros de isótopos estáveis de C e O de isótopos em corais são especialmente interessantes, porque eles podem destacar a variabilidade multidecadal das condições climáticas locais além do registro instrumental com alta fidelidade e resolução sub-anual. Aqui nós relatamos um dos primeiros registros climáticos com base em coral do Atlântico Sul Equatorial, através de perfis isotópicos de duas colônias de *Porites* sp. do Atol das Rocas, um local-chave para reconstruções climáticas e anteriormente não estudada. Aqui são apresentados dados de perfis ao longo do vale entre coralitos de uma colônia e na parte central do leque de coralitos de outra colônia. Embora exista diferenças significativas nos valores isotópicos entre as duas colônias, ainda são observados em ambas o registro do evento do ENSO 2009/2010 - um episódio de branqueamento do coral mundial – através de valores anômalos de $\delta^{18}O$ negativos (até 1 permil mais negativo do que os valores de base). Valores de isótopos estáveis de C também aparentam ser afetada pelo evento do ENSO. Nossos resultados indicam que os corais do Atol das Rocas são substratos ideais para monitorar grandes oscilações climáticas no Oceano Atlântico tropical Sul.

Palavras-chave: coral, mudanças climáticas, Atol das Rocas, isótopos estáveis de carbono e oxigênio, Oceano Atlântico Sul.

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