Chemical characterization of deep-sea corals from the continental slope of Santos Basin (southeastern Brazilian upper margin)

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ABSTRACT

Carbonate mounds and pockmarks are geologically and ecologically important features distributed worldwide in the world's oceans. In the present study, we present a chemical characterization of deep-sea scleractinian coral skeletons collected in these geomorphological areas at the southeastern continental margin of Brazil. Coral samples were collected from ten sampling stations during cruises aboard the R/V Alpha Crucis, in 2019. Three species of scleractinian corals were studied: *Enallopsammia rostrata, Solenosmilia variabilis*, and *Desmophyllum pertusum*. Stable isotopes of carbon and oxygen (δ^{13}C and δ^{18}O), metals, and phosphorus present in the coral carbonate skeletons were analyzed. Corals are recognized as archives of physical-chemical variations in the marine environment, and the Element/Ca ratios, δ^{13}C, and δ^{18}O allowed for the characterization of the studied areas. Chemical composition found in pockmark areas indicated affinity to terrigenous and particulate materials input (Ba/Ca, Fe/Ca, Mn/Ca, Li/Ca, and Mg/Ca). Greater availability of nutrients and anthropogenic materials (Pb/Ca, Cd/Ca, Zn/Ca, and P/Ca) is also likely to occur in this region, with some elemental ratios higher than those measured in other oceans. These mounds can act as barriers for metals from land flows. Also, corals benefit from a higher food supply due to stronger currents. The corals at the top of the Alpha Crucis Carbonate Ridge receive significant marine influence. Most coral samples have carbonate of aragonitic origin, except for a specimen of *D. pertusum*, which presented carbonate of biogenic calcite and aragonite. The results demonstrate the potential of scleractinian corals in the chemical characterization of the deep ocean and the need for further investigation of carbonate mound areas from the SW Atlantic.

Descriptors: Metals, Stable isotopes, *Enallopsammia rostrata*, *Solenosmilia variabilis*, Desmophyllum pertusum.

INTRODUCTION

Carbonate mounds are marine underwater geomorphological features found at depths between 300 and 1300 m, consisting of elongated carbonate ridges with extensions of up to tens of kilometers and heights ranging from meters to hundreds of meters (Lo Iacono et al., 2018). The formation of these carbonate mounds has been linked to long periods of growth (thousands to millions of years) and extinction of deep-sea corals (Henriet et al., 2014). Scleractinian corals are considered the most influential builders of deep-sea ecosystems, forming large carbonate mounds, together with sediments on slopes and continental shelves, seamounts, or ocean ridges

(Roberts et al., 2006; Raddatz et al., 2019). These structures have been studied in oceans worldwide (Raimundo et al., 2013; Fink et al., 2015; Montagna and Taviani, 2019). On the Brazilian continental margin, mounds of scleractinian deep-sea corals were first reported by Viana et al. (1998) and Sumida et al. (2004), with the species *Enallopsammia rostrata*, *Solenosmilia variabilis,* and *Desmophyllum pertusum* recognized as the main mound constructors (Pires, 2007; Freiwald et al., 2017; Raddatz et al., 2019).

In the southeast continental margin of Brazil, other geomorphological features also co-occur with carbonate mounds, such as saline diapirs and pockmarks. Recent studies have reported deep-sea carbonate mounds on the São Paulo Plateau and the Alpha Crucis Carbonate Ridge in the Santos Basin (Fujikura et al., 2017; Maly et al., 2019). These sites are significant for geological and biological reasons. Maly et al. (2019) found the coral species (*E. rostrata* and *D. pertusum*) at the top of the Alpha Crucis Carbonate Ridge together with a rich fauna of associated benthic invertebrates (e.g., sponges, echinoderms, and bryozoans). These corals serve as a refuge for several invertebrates that seek food, protection, and a place for reproduction; they are vital for the oceanic carbon cycle and are part of vulnerable marine ecosystems that require conservation due to their importance for the deep sea and global biodiversity (Roberts et al., 2006; Fink et al., 2015; Maly et al., 2019).

In addition to their great ecological importance, corals are widely used as archives of environmental changes due to their sensitivity to physical and chemical changes in the marine environment; they are excellent biomonitors (Anagnostou et al., 2011). Also known as recorders of climate variations, they are good tracers of changes in temperature, salinity, and contaminants (Smith et al., 2000; Rüggeberg et al., 2008; Spooner et al., 2016). Together with the properties of water masses, these environmental parameters may be related to geological records of these corals in deep water (Smith et al., 2000; Schröder-Ritzrau et al., 2005; Raimundo et al., 2013). These organisms preserve in their skeletons past physical-chemical changes and the properties of the seawater

in which they grew. Such information is stored as geochemical signals through changes in metal concentration and stable isotope ratios related to environmental parameters (Montagna and Taviani, 2019).

Stable isotopes, primarily carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$), are used as temperature proxies in corals which may be used in water mass identification (Rüggeberg et al., 2008; Raddatz et al., 2013). Further, the determination of metals in sediments and marine organisms, especially corals, has been used in paleoceanographic and paleoclimatic reconstruction studies (Raimundo et al., 2013). For example, ratios such as Sr/Ca, Mg/Ca, Li/Ca, and Li/Mg are used to assess variations in temperature and coral growth (Beck et al., 1992; Raddatz et al., 2013; Montagna and Taviani, 2019). The Cd/Ca and Mn/Ca ratios in skeletal matrices help detect upwelling processes, vertical mixing (particulate matter indicator), and coastal development (Carriquiry and Villaescusa, 2010). Ba/Ca, Cd/Ca, Fe/Ca, and P/Ca ratios can be used as nutrient and productivity change proxies (Montagna et al., 2006; Montagna and Taviani, 2019). Other ratios are used as tracers of anthropogenic input, such as Pb/Ca and Zn/Ca (Inoue et al., 2004; Saha et al., 2016). In addition to being influenced by environmental factors, stable isotopic fractionation and element ratios are affected by biological factors known as vital effects, widely studied and which will be considered in the interpretation of results (Montagna et al., 2005; Cohen et al., 2006; Rüggeberg et al., 2008; Raddatz et al., 2013).

When comparing corals to traditional sedimentary archives, the formers have the advantage of several geochemical tracer options, providing information on past conditions (Rüggeberg et al., 2008; Raddatz et al., 2013). In addition, few studies are dedicated to improving knowledge about biology, chemical characterization, and paleoceanographic reconstruction in deep-sea corals (Montagna et al., 2005; Raimundo et al., 2013). This work provides the first assessment of deep-sea corals composition in the Santos Basin (southwestern Atlantic margin). The corals were analyzed for metals, phosphorus, and stable isotopes to characterize and evaluate the predominant influences

and inputs on the carbonate mound areas on this sector of the continental margin.

METHODS

Study area and sampling procedures

The study area is comprised of two sectors of the continental slope of the Santos Basin (southeastern Brazilian upper margin; Figure 1). Area 1, corresponding to stations 681, 683, and 684, is associated with an alignment of carbonate mounds and pockmarks. Area 2, corresponding to stations 588, 591,592, 593, 685, and 687, is located in the Alpha Crucis Carbonate Ridge (Maly et al., 2019).

The sampling surveys were carried out onboard the R/V Alpha-Crucis, during February and November 2019. Samples from stations 588, 591, 592, and 593 were collected during the February 2019 survey, and stations 681, 683, 684, 685, and 687 were sampled during the November 2019 survey. The material was obtained at depths between 535 and 850 meters, totaling 15 box-core seafloor samples (Table 1). Among scleractinian corals, specimens were obtained from the families
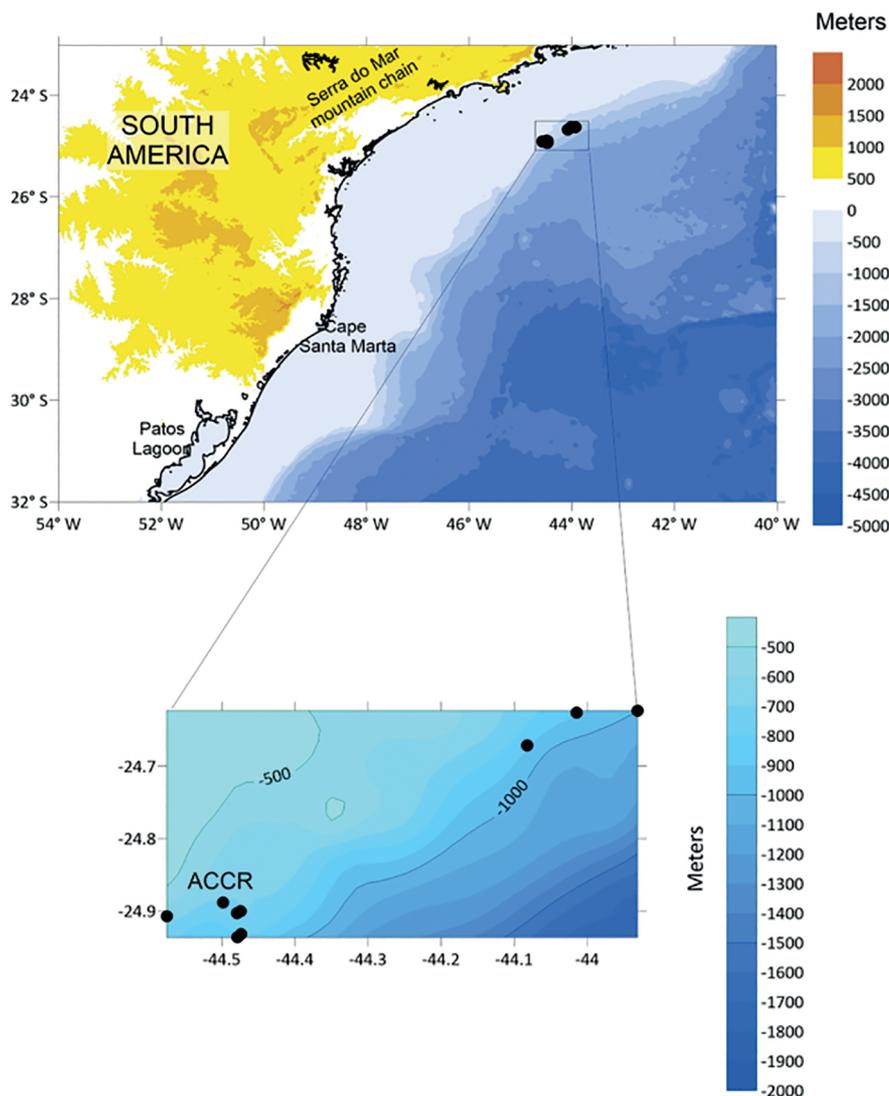
Figure 1. Study area in areas of cold exudation on the southeastern continental margin of Brazil and coral sampling stations: area 1 - stations 681, 683 and 684; and area 2 - stations 588, 591,592, 593, 685 and 687.

Table 1. Sampling stations of corals, latitude (Lat S), longitude (Long W), depth (m), date and time of the sample, sample number (n), species of coral (Spp), temperature (T °C) e salinity (Sal). *living coral.

Station	Lat (S)	Long (W)	Depth (m)	Date	Time	n	Spp	T°C	Sal
588	-24,9365	-44,4787	663	08/02/2019	16:07	1	*S. variabilis*	7.8	34.6
591	-24,9071	-44,5752	535	09/02/2019	15:13	1	*E. rostrata*	7.2	34.5
592	-24,8883	-44,4983	563	09/02/2019	16:50	1	*E. rostrata*	8.0	34.6
593	-24,9030	-44,4793	610	09/02/2019	18:00	1	*E. rostrata*	8.1	34.6
681	-24,6233	-43,9312	743	16/11/2019	18:09	4	*D. pertusum*	9.6	34.7
							D. pertusum		
							E. rostrata		
							S. variabilis		
683	-24,6257	-44,0146	850	18/11/2019	14:04	1	*D. pertusum*	4.8	34.3
684	-24,6714	-44,0824	829	18/11/2019	18:58	1	*D. pertusum*	4.7	34.3
685	-24,9320	-44,4737	591	19/11/2019	12:31	3	*S. variabilis*	7.6	34.5
							E. rostrata		
							*E. rostrata**		
687	-24,9002	-44,4745	567	20/11/2019		2	*S. variabilis*	6.8	34.5
							E. rostrata		

Dendrophylliidae (*Enallopsammia rostrata*, n = 7) and Caryophylliidae (*Solenosmilia variabilis*, n = 4 and *Desmophyllum pertusum*, n = 4). Coral specimens were dead, except for one *E. rostrata* specimen retrieved alive from sample 685, which reflects current chemical conditions. During collection, temperature and salinity data were obtained in situ using a Seabird SBE911 CTD (Conductivity, Temperature, Depth).

CHEMICAL ANALYSES

Individual coral samples underwent an initial treatment to remove interferents and contaminants. The cleaning process followed the method of Yu et al. (2005a), in which corals are soaked in hydrogen peroxide (H_2O_2 10%) for 24 hours, followed by washing with Milli-Q water for 5 to 10 minutes to remove organic matter. They are then ultrasonically cleaned in Milli-Q water for 30 minutes to eliminate surface contaminants. After cleaning, samples are dried in an oven at 60°C and macerated.

Carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotope ratio analyses were performed using Gasbench II & Thermo Fisher Delta V Advantage IRMS (Isotope Ratio Mass Spectrometry) from the Beta Analytic Laboratory (USA). The samples were treated with

He (helium) following the addition of five drops of phosphoric acid (H_3PO4) to stimulate the release of CO_2 in the headspace of the flask. The sample was then placed in a temperature-controlled tray at 72 °C for one hour until CO_2 equilibration was attained. A He + sample CO_2 mixture was injected for detection in a Gas Chromatography (GC) with the ISODAT software control. Reported results were calibrated using the International Vienna PDB (VPDB) standard. In addition, internal traceable standards (Supra and NaHCO3 - NIST IAEA-CO-8 e 8543 NBS 18) were used, showing recoveries of 106% for $\delta^{13}C$ and 100% for $\delta^{18}O$.

The extraction of metals (Ba, Ca, Cd, Fe, Li, Mg, Mn, Sr, Pb, and Zn) and phosphorus (P) from coral samples was performed in the Laboratory of Marine Inorganic Chemistry (LaQIMar) at the Oceanographic Institute of the University of São Paulo (IO-USP), following the method described by Trevizani et al. (2016). In this method, 0.35 g of dry coral sample is treated with 4 ml of ultrapure nitric acid (HNO_3). After eight hours, 1 ml of hydrogen peroxide (H_2O_2) is added and left to react for fifteen hours. Samples are then placed in a block digester at 90°C for three hours. The final solution is filtered (45μm) and completed up to 35 ml with Milli-Q water. The determination of the elements in

these extracts is performed using inductively coupled plasma optical emission spectrometry (ICP-OES – Varian, model 710ES). In some samples, metal concentrations were below the detection limit for the method, such as for Cd (LDM = 0.20 mg kg^{-1}) and Pb (LDM = 0.66 mg kg^{-1}), resulting in undetected elemental ratios (nd).

DATA ANALYSES

Elemental ratios, especially between metals and Ca, are frequently used as proxies to reconstitute oceanographic/environmental parameters. The mixture diagram between the Sr/Ca and Mg/Ca ratios, for example, allows us to verify the origin of the carbonate that forms the coral (Joseph et al., 2013).

The results were statistically analyzed using Statistica 13 (Statsoft), Microsoft Excel, and Past 3 (Hammer et al., 2001) software. Correlations were performed between the elementary ratios,

$\delta^{13}C$ and $\delta^{18}O$, with the environmental parameters depth, salinity, and temperature to verify the influence of specific proxies. The results of the correlations served as the basis for selecting the variables included in the principal component analysis (PCA). PCA, with standardized data through z-score, allowed for the integration of elementary ratios with $\delta^{13}C$ and $\delta^{18}O$. This, in turn, allowed for assessing the spatial distribution of these proxies, identifying distinctions between areas and coral species studied. Furthermore, the results obtained were compared with studies that involved the chemical characterization of corals worldwide.

RESULTS AND DISCUSSION

COLD-WATER CORALS $\delta^{13}C$ AND $\delta^{18}O$

The isotopic ratios of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) ranged between -6.88‰ and 0.85‰, and 0.36‰ and 3.18‰, respectively (Table 2).

Table 2. Element/element ratios (mmol mol^{-1}), and oxygen and carbon stable isotopic composition ($\delta^{13}C$ and $\delta^{18}O$ ‰) of coral species (Spp; Sv =$Solenosmilia\ variabilis$, Er = $Enallopsammia\ rostrata$ and Dp = $Desmophyllum\ pertusum$) analyzed at each sampling site (SS). minimum (Min), maximum (Max), average ($\bar{x}$) and SD (standard deviation). nd = not detected. *living coral.

SS	Spp	Ba/Ca	Cd/Ca	Fe/Ca	Li/Ca	Li/Mg	Mg/Ca	Mn/Ca	P/Ca	Pb/Ca	Sr/Ca	Zn/Ca	$\delta^{13}C$	$\delta^{18}O$
588	Sv	0.010	nd	1.69	0.019	7.64	2.43	0.208	0.45	0.002	13.18	0.01	-4.49	1.61
591	Er	0.009	nd	1.34	0.020	7.71	2.6	0.125	0.23	0.001	11.43	0.013	-2.28	0.86
592	Er	0.012	0.0002	1.48	0.022	8.27	2.6	0.161	0.35	0.001	11.81	0.01	-0.71	1.9
593	Er	0.011	nd	2.33	0.029	9.42	3.04	0.193	0.35	0.001	13.06	0.01	-0.45	2.08
681	Dp	0.015	0.0047	1.32	0.019	2.28	8.42	0.177	0.62	0.001	3.86	0.027	-5.03	1.27
681	Dp	0.027	0.0004	6.29	0.020	8.54	2.3	0.424	0.54	0.003	12.78	0.008	-0.36	2.97
681	Er	0.015	0.0002	6.18	0.017	6.97	2.43	0.398	0.57	0.003	13.15	0.011	-4.05	1.1
681	Sv	0.017	0.0003	0.40	0.009	4.06	2.17	0.038	0.27	0.0004	13.12	0.012	-2.16	2.06
683	Dp	0.016	nd	1.59	0.016	5.95	2.63	0.246	0.33	0.002	11.19	0.007	-6.88	0.39
684	Dp	0.018	0.0004	1.62	0.015	5.58	2.71	0.262	0.43	0.003	11.84	0.008	-5.95	0.36
685	Sv	0.013	nd	1.19	0.008	3.57	2.36	0.024	0.32	nd	12.64	0.004	-4.07	0.93
685	Er	0.014	nd	0.62	0.011	4.91	2.28	0.083	0.27	0.0004	14.37	0.004	-2.42	0.77
685	Er*	0.011	nd	0.02	0.005	2.57	2.03	0.003	0.54	nd	11.95	0.008	-3.2	1.08
687	Er	0.013	nd	0.64	0.013	5.34	2.37	0.177	0.33	0.001	12.67	0.005	-4.2	2.1
687	Sv	0.018	nd	2.66	0.018	6.88	2.57	0.483	0.53	0.004	13.37	0.011	0.85	3.18
	Min	0.009	0.0002	0.02	0.005	2.28	2.03	0.003	0.23	0.0004	3.86	0.004	-6.88	0.36
	Max	0.027	0.0047	6.29	0.029	9.42	8.42	0.483	0.62	0.004	14.37	0.027	0.85	3.18
	$\bar{x}$	0.015	0.0010	1.96	0.016	5.98	2.86	0.200	0.41	0.002	12.03	0.010	-3.02	1.51
	SD	0.004	0.0018	1.87	0.006	2.20	1.56	0.145	0.13	0.001	2.41	0.005	2.22	0.86

According to Rüggeberg et al. (2008), the existing data for stable carbon and oxygen isotopes for cold-water corals exhibit a wide range, with $\delta^{13}C$ ranging from -15‰ to −0.7‰ and $\delta^{18}O$ ranging from -4.2‰ to 4.4‰.

According to Rollion-Bard et al. (2010), isotope studies performed on corals show a considerable range of values, approximately 10‰ for carbon and 4 − 6‰ for oxygen, and there is a clear linear relationship between these isotopes. In the present study, the variation of $\delta^{13}C$ was 8‰ and $\delta^{18}O$ 4‰ between the coral samples studied; the correlation between isotopes was positive and significant (r= 0.78, p =0.0007; Table S1, Figure 2). Following Joseph et al. (2013), isotopic signatures found in the present study suggested cold water, gas hydrate dissociation, and clay mineral dehydration.

In the present study, $\delta^{18}O$ was not correlated with temperature (r= 0.41, p= 0.21), which was also noted by Stewart et al. (2020) in scleractinian corals due to the influence of ion pumping and the effects of the growth rate of these corals (Chen et al., 2018). $\delta^{13}C$ was significantly correlated with depth (r= -0.57, p= 0.03). This negative relationship was also observed in *Porites* related to photosynthesis, and at greater depths related to heterotrophic feeding (Linsley et al., 2019).

Ocean temperature is a crucial parameter to verify climatic variations, such as atmospheric humidity and temperature, extension of cloud cover, and oceanic and atmospheric circulation patterns (Beck et al., 1992). Nevertheless, the influence of vital and kinetic effects on $\delta^{18}O$ and $\delta^{13}C$ values makes this interpretation challenging (Montagna and Taviani, 2019).

Studies have proposed a method using the $\delta^{18}O$ and $\delta^{13}C$ relationship to estimate seawater paleotemperature (Smith et al., 2000; Smith et al., 2002). Due to the low number of samples, it was
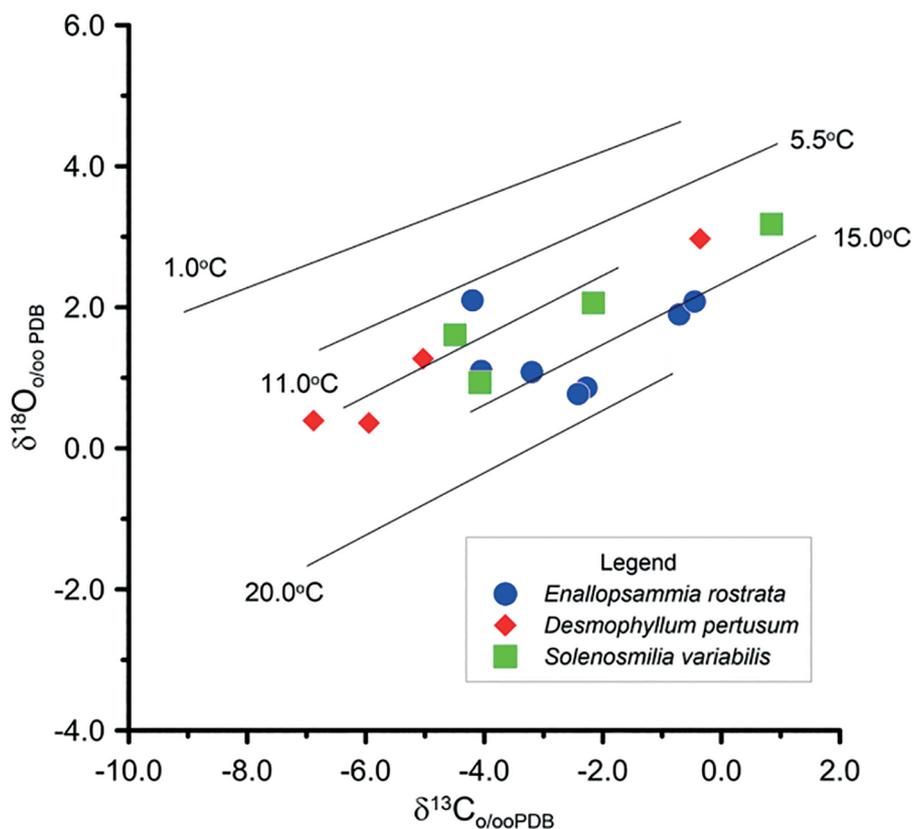
Figure 2. Carbon and oxygen stable isotopics composition ($\delta^{13}C$ and $\delta^{18}O$, ‰) by species of corals, and regression lines for temperature of formation of corals adapted from Smith et al. (2000).

impossible to estimate coral formation temperature. According to Smith et al. (2000), at least 27 specimens of each species studied are required for this estimate. Thus, we plotted isotope results obtained in the present study on the graph presented by Smith et al. (2000), who studied six species of corals from different parts of the world, from depths between 80–5220 m and temperatures between 1 to 15°C, to assess the possible temperature range in which the studied corals were formed. In Figure 2, it is observed that *D. pertusum* and *S. variabilis* showed a statistically significant linear trend around the 11°C isotherm, while *E. rostrata* did not show any tendency varying between 5.5 and 15°C. It is worth noting that the study area is located in the transition between the South Atlantic Central Waters (SACW) and the Antarctic Intermediate Water (AAIW) (Stramma and Schott, 1999), and that the turbulence caused by the presence of mounds (O'Reilly et al., 2003) may disrupt the stratification of water masses.

Cold-water corals elemental ratios

Coral elementary ratios were calculated using Ca, a major constituent element of skeletons, as the denominator (Table 2). Corals absorb dissolved Ca and carbonate ions from seawater during the growth process, incorporating them into their skeletons. Metals such as Sr, Mg, Mn, and Ba can replace Ca within the aragonite structure (Hanna and Muir, 1990; Saha et al., 2016; Jiang et al., 2017). In addition, metals can be absorbed by trapping particulate matter in the pores of corals, through adsorption by the skeletal surface, and through the formation of complexes with organic matter (Livingston and Thompson, 1971; Saha et al., 2016; Jiang et al., 2017).

The incorporation of metals into coral skeletons is well documented and can be influenced by several factors such as vital effects (including growth and calcification rates), symbiotic activities, mucus production, gamete development, weathering variations, and environmental factors such as temperature and salinity (Hanna and Muir, 1990; Saha et al., 2016). Although the difference in ratios between species was small, interspecific variations are reported in the literature and are attributed to differences in skeletal microstructure, metal

transfer efficiency between tissues and skeleton, metal tolerance, and feeding characteristics of the species (Anu et al., 2007; Saha et al., 2016).

The correlations between the elementary ratios and the environmental parameters depth, salinity, and temperature are shown in Table S1. In general, the Ba/Ca, Fe/Ca, and Mn/Ca ratios in corals are proxies for terrestrial fluxes (Jiang et al., 2017), and Pb/Ca is a tracer of anthropogenic input (Saha et al., 2016). These ratios correlated positively and significantly in the present study.

The Ba/Ca ratio in corals is related to the behavior of nutrients in seawater (Jiang et al., 2017). The main source of Ba in the seafloor sediments is Barite ($BaSO_4$), indicating the presence of methane fluxes (Joseph et al., 2013). Also, in seawater, this ratio makes it possible to trace other elements such as Silica, influenced by coastal river sources, with the concentration of Ba increasing with depth (LaVigne et al., 2010; Anagnostou et al., 2011). The Ba/Ca ratio ranged between 0.009 and 0.027 mmol mol^{-1}, similar to the values obtained by studies carried out in different coral species in the Atlantic and Pacific Oceans, the Mediterranean Sea, and the South China Sea (Anagnostou et al., 2011; Hasegawa et al., 2012; Jiang et al., 2017). Our values correlated positively and significantly with depth (r= 0.54, p= 0.04).

The Fe/Ca ratio ranged from 0.4 to 2.7 mmol mol^{-1} in *S. variabilis,* from 0.02 to 6.2 mmol mol^{-1} in *E. rostrata,* and from 1.3 to 6.3 mmol mol^{-1} in *D. pertusum*. Few studies with corals include this ratio, which is obtained only in *Porites* sp*.* and *Porites lutea* of the South China Sea and the Red Sea, with maximum values up to one fifth times smaller than those obtained in the present study (Hanna and Muir, 1990; Chen et al., 2010). Our values may indicate the importance of the terrigenous fraction in the buildup of carbonate mounds, as stated by Titschack et al. (2009) and Pirlet et al. (2011).

The Mn/Ca ratio in deep-sea corals is dependent on oceanographic processes such as advection, vertical mixing, and upwelling, used as suspended sediment proxies associated with river discharge, land-use changes, and coastal development (Carriquiry and Villaescusa, 2010; Chen et al., 2010). The values obtained for Mn/Ca in the

present study surpass those found in studies conducted in the Pacific Ocean and the South China Sea, but these were carried out on the species *Pavona gigantea*, *Pavona clivosa*, *Porites panamensis*, and *Porites lutea*, which are reef-building species (Jiang et al., 2017).

Lead (Pb) was used between 1940–1970 in gasoline and is a product of industrial pollution (Saha et al., 2016). Various studies use Pb records in corals to reconstruct the consequences of its use in industries and gasoline, such as with tetraethyl Pb which, through atmospheric transport, is deposited on the ocean surface, dissolved, and incorporated into the coral skeleton (Inoue et al., 2006; Kelly et al., 2009). The presence of iron and manganese oxides related to Pb concentrations was found in corals, which permitted the identification of polluted environmental conditions (Livingston and Thompson, 1971; Hanna and Muir, 1990). A study carried out on North Atlantic corals recorded the historical variation of the Pb/Ca ratio, with values of 5.0×10^{-6} mmol mol^{-1} in 1850, rising to 6.0×10^{-5} mmol mol^{-1} in the early 1970s, and decreasing to 25.0×10^{-6} mmol mol^{-1} after the ban on Pb in gasoline in the US (Kelly et al., 2009). Studies carried out in the Indian Ocean and the northern Pacific Ocean found an increase in the Pb/Ca ratio, reflecting the spatial differences and temporal variation of the anthropogenic input of Pb (Inoue et al., 2006; Lee et al., 2014). In the Indian Ocean, Pb/Ca ratios were 5.0×10^{-6} mmol mol^{-1} in the 1970s, increasing to 9.0×10^{-6} mmol mol^{-1} in the early 2000s (Lee et al., 2014). In the North Pacific, the concentration of Pb in *Porites* spp. was 0.0023 mg kg^{-1} in the 1950s, increasing to 0.063 mg kg^{-1} in the 2000s (Inoue et al., 2006). In a more recent study in the Indian Ocean, off the African coast, corals of the genus *Acropora*, *Fungia*, *Pocillopora*, and *Stylophora* presented Pb levels between 0.006 and 3.1 mg kg^{-1} (van der Schyff et al., 2020).

In the present study, Pb concentrations were from 0.7 to 7 mg kg^{-1}, while the Pb/Ca ratio was 0.0004 – 0.004 mmol mol^{-1} in the studied species, higher than the results reported in the studies performed in the Atlantic, North Pacific, and Indian Ocean (Inoue et al., 2006; Kelly et al., 2009; Lee et al., 2014; van der Schyff et al., 2020). This

suggests the existence of past sources providing Pb in the Southwest Atlantic, as Pb was not quantified in the living coral sample. This possibility corroborates a recent study carried out in mud depocenters in the same region of the Atlantic, in which the enrichment of Pb was related to the years 1923 to 1989, a period when leaded gasoline was used in Brazil (Kim et al., 2021). In addition, the presence of contaminant metals may be related to shipping, the input of ballast water, and wastewater from ships (Jägerbrand et al., 2019). A recent study in the Persian Gulf showed a reduction in Pb levels after implementing the ballast water convention (Tolian et al., 2020), demonstrating the contribution of waste dumping by cargo ships to Pb input, which may also have occurred in the SW Atlantic.

The P/Ca ratio was positively and significantly correlated with the Mn/Ca and Pb/Ca ratios, indicating a relationship between the nutrient source and anthropogenic activities (Chen et al., 2010). Phosphorus (P) is an essential nutrient in the global primary productivity process, its variations in seawater reflecting changes in cycling and biological production on the ocean surface (Montagna et al., 2006). Studies with the deep-sea coral *Desmophyllum dianthus* have shown that the P/Ca ratio is a linear function of the phosphate concentration in seawater, suggesting that this ratio can be used to reconstruct variations in biological productivity (Montagna et al., 2006; Anagnostou et al., 2011). The P/Ca ratio ranged from 0.2 to 0.6 mmol mol^{-1} in the studied corals, levels higher than those obtained in *D. dianthus* obtained in the northern Atlantic Ocean and the Pacific Ocean (0.02 – 0.11 mmol mol^{-1}; Anagnostou et al., 2011) and lower than those obtained in the Australian sector of the western Pacific Ocean (0.1 - 1.8 mmol mol^{-1}; Montagna et al., 2006). These variations may be related to nutrient input in these locations as well as different analytical techniques employed.

The Li/Ca ratio reveals the influence of temperature, pH, and coral growth rate (Raddatz et al., 2013). In the present study, the Li/Ca ratio ranged between 0.005 and 0.029 mmol mol^{-1}, while the Li/Mg ratio ranged between 2.3 to 9.4 mmol mol^{-1}. Both these values are higher than those obtained in studies with *D. pertusum* off the

European coast, in the Mediterranean Sea, and in the North Atlantic, which saw maximum values of 0.0016 mmol mol^{-1} for Li/Ca and 5.5 mmol mol^{-1} for Li/Mg. This suggests there is a Li source in the studied region of the Atlantic (Raddatz et al., 2013; Montagna et al., 2014).

While the Li/Mg ratio has recently been used as a temperature proxy in cold-water scleractinian corals, it has also been proposed as a normalizer of vital effects (Case et al., 2010; Raddatz et al., 2013; Robinson et al., 2014; Montagna and Taviani, 2019; Stewart et al., 2020). Extensive study with several species of scleractinian corals found a high correlation of the Li/Mg ratio with seawater temperature, suggesting that Li and Mg would be controlled by the same biological, physical, and chemical processes during coral growth, since both have a long residence time, minimizing vital effects (Montagna et al., 2014). However, in the present study, no correlation was found between Li/Ca (r= -0.07, p= 0.84) and Li/Mg (r= -0.08, p= 0.82) with temperature. This can be related to the measurement technique used, as studies that found this correlation used a larger number of samples analyzed by the ICP-MS Laser Ablation technique (Montagna et al., 2014; Montagna and Taviani, 2019).

The Cd/Ca, Mg/Ca, and Zn/Ca ratios correlated positively between themselves and negatively with Sr/Ca. Cd, a non-essential element for marine organisms, is generally related to the presence of essential elements such as Zn (Raimundo et al., 2013), as verified in the present study. The Cd/Ca ratio is a tracer of the distribution of nutrients in the ocean, in addition to an indicator of upwelling processes, vertical mixing (particulate matter indicator), and industrial pollution (Carriquiry and Villaescusa, 2010; Saha et al., 2016).

Although Cd was not detected in most samples, it was possible to verify the Cd/Ca ratio variation between the studied species: 0.0003 mmol mol^{-1} in *S. variabilis*, 0.0002 mmol mol^{-1} in *E. rostrata*, and 0.0004 – 0.0047 mmol mol^{-1} in *D. pertusum*. Similar results were obtained by the only previous study of corals in the Southwest Atlantic, with Cd/Ca values of 0.00032 mmol mol^{-1} in *D. pertusum* from mudbelts in the Campos Basin and 0.0002 mmol mol^{-1} in *D. pertusum* and *S. variabilis* in the Santos

Basin pockmarks (Mangini et al., 2010). Lower Cd/Ca ratios (0.00003 – 0.000018 mmol mol^{-1}) were obtained in corals from the Gulf of California, North Pacific (Carriquiry and Villaescusa, 2010).

The Zn/Ca ratio ranged from 0.004 – 0.027 mmol mol^{-1} in the studied species. Slightly higher values were verified in the coral species *Porites sp.* and *Porites lutea* in the Red Sea and bays of China and Japan; these studies report these Zn levels as coming from anthropogenic sources, including industrial and domestic sewage for an extended period (Hanna and Muir, 1990; Chen et al., 2010).

The Sr/Ca and Mg/Ca ratios have been used to verify the origin of carbonates in corals and sediments (Bayon et al., 2007; Joseph et al., 2013), with aragonite being related to higher Sr values and calcite rich in Mg. Observing the Sr/Ca and Mg/Ca mixture diagram (Figure 3), one infers that coral samples have carbonate of aragonitic origin with one exception, a specimen of *D. pertusum* from sampling station 681, which showed carbonate of mixed origin (biogenic calcite and aragonite) and low levels of Sr/Ca (3.9 mmol mol^{-1}).

The Mg/Ca ratio varied among the species studied, with values ranging from 2.2 to 2.4 mmol mol^{-1} in *S. variabilis*, 2.0 to 3.0 mmol mol^{-1} in *E. rostrata*, and 2.3 to 8.4 mmol mol^{-1} in *D. pertusum*. In general, the values obtained for Mg/Ca in the present study are similar to those obtained for the species *D. pertusum* in studies in the North Atlantic, Pacific, and Mediterranean Sea, and *P. lutea* in the South China Sea (Yu et al., 2005a; Raddatz et al., 2013; Montagna et al., 2014), except the high value of 8.4 mmol mol^{-1} in sample 681 (*D. pertusum*), due to its mixed carbonate origin.

As one of the significant elements in seawater, Mg would show constant Mg/Ca ratios. Its presence in coral skeletons is related to temperature and ocean depth, and its absorption is positively correlated with warm seasons (summer), which was primarily related to habitat rather than coral species (Hasegawa et al., 2012). In the present study, the Mg/Ca ratio did not correlate with temperature (r= 0.28, p= 0.41) and depth (r= 0.22, p= 0.43), as in the study by Raddatz et al. (2013) for *D. pertusum* along the European continental margin.
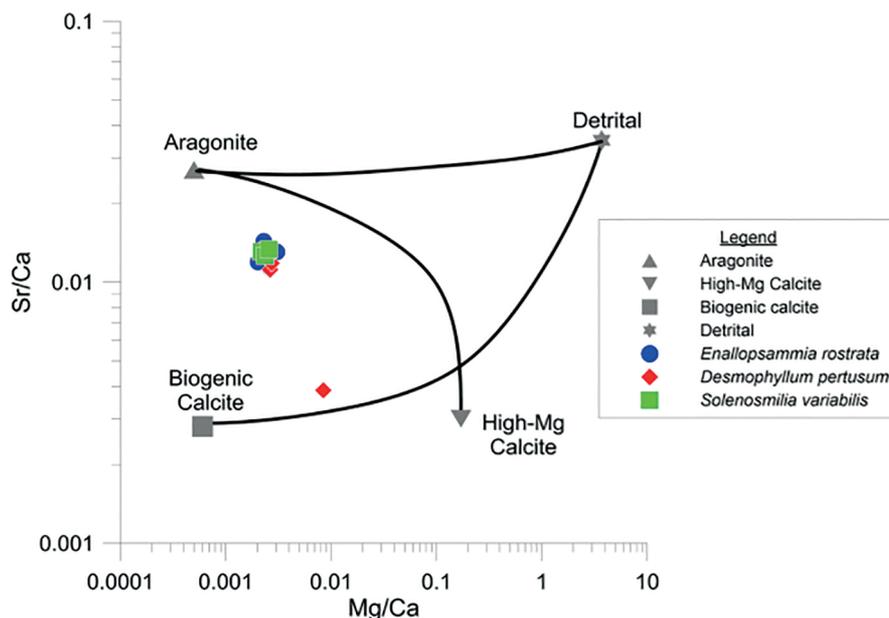
Figure 3. Mixing diagram of Sr/Ca and Mg/Ca for different types of carbonates, adapted from Joseph et al. (2013). (HMC = High Mg calcite).

It is noted that Mg/Ca is associated with the composition of the coral specimen, and that temperature and habitat conditions are not its dominant controls in scleractinian corals (Cohen et al., 2006; Case et al., 2010; Robinson et al., 2014), reinforcing the suggestion of Yu et al. (2005a) that it is not a reliable paleothermometer.

The Sr/Ca ratio ranged from 12.6 to 13.2 mmol mol^{-1} in *S. variabilis*, 11.4 to 14.4 mmol mol^{-1} in *E. rostrata*, and 3.9 to 12.8 mmol mol^{-1} in *D. pertusum* and *P. lutea*, from the European coast (North Atlantic and the Mediterranean Sea) and the South China Sea, respectively (Yu et al., 2005a; Yu et al., 2005b; Raddatz et al., 2013). The only exception is sample 681 (*D. pertusum*), with low Sr/Ca values, similar to those recorded in *Corallium* spp. from different locations in the Mediterranean Sea (Italy) and Pacific Ocean (Japan and Midway Island). These reef-forming corals show high-magnesium calcite in their skeletal formation (Hasegawa et al., 2012). This finding reinforces that the Sr/Ca ratio is related to the coral formation structure and varies according to the studied species (Cohen et al., 2006).

The Sr/Ca ratio in corals is widely used as a proxy for sea surface temperature (Beck et al., 1992). Concentrations of Sr and Ca in seawater are constant due to the long residence times, and the assimilation of Sr in scleractinian corals depends on temperature, inversely correlated and favored during the winter (Yu et al., 2005a; Raddatz et al., 2013). In the present study, Sr/Ca did not correlate with temperature (r = -0.17, p = 0.62), suggesting that this ratio is also influenced by vital effects, such as the origin of the carbonate in the skeleton and the physiology of the coral (Montagna et al., 2005; Montagna and Taviani, 2019; Stewart et al., 2020).

INTEGRATED ANALYSIS

The trends verified in the δ^{13}C and δ^{18}O and elemental ratios were confirmed in the PCA (Figure 4), allowing for a spatial and integrated analysis of the results. The first two principal components corresponded to 75% of the variance.

Principal component 1 (PC 1) formed two groups. Group 1 (PC 1) grouped the Mn/Ca, Pb/Ca, and δ^{18}O, with *E. rostrata* and *D. pertusum* (sample 681) and *S. variabilis* (sample 687). These are representative samples from Areas 1 and 2, in which stations 681 and 687 seem to be more susceptible to the input of terrigenous materials, including those from anthropogenic sources.
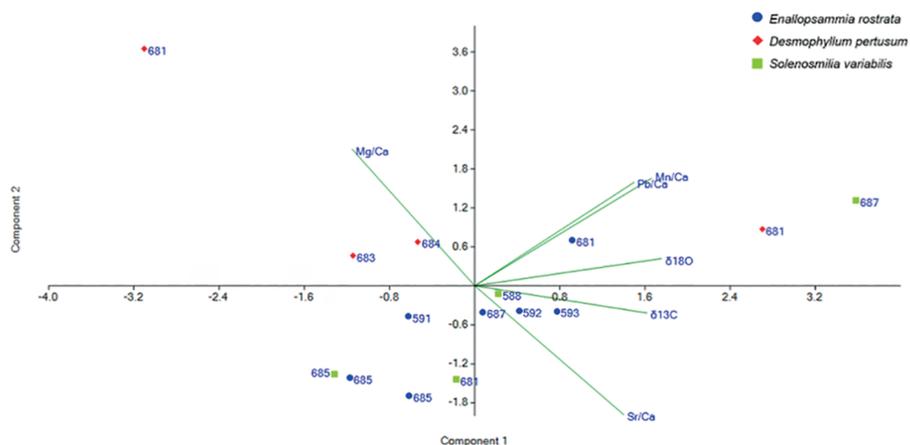
Figure 4. Principal component analysis for elemental ratios, $\delta^{13}C$ and $\delta^{18}O$ in coral samples from different locations (area 1 - stations 681, 683 and 684; and area 2 - stations 588, 591, 592, 593, 685 and 687) and species (*Solenosmilia variabilis*, *Enallopsammia rostrata* and *Desmophyllum pertusum*).

Group 2 (PC 1) grouped $\delta^{13}C$ and Sr/Ca ratio with samples obtained at stations 588 (*S. variabilis*), 592, 593, and 687 (*E. rostrata*), all from Area 2. These stations are located at the top of the Alpha Crucis Carbonate Ridge (Maly et al., 2019), which explains higher values of $\delta^{13}C$. These stations are linked to temperature proxies, coinciding with corals that possibly formed in warmer waters than today; the Sr/Ca ratio is related to the coral formation structure (Raddatz et al., 2013; Montagna and Taviani, 2019).

Principal component 2 (PC 2) grouped Mg/Ca with samples 681, 683, and 684 (*D. pertusum*). Mg/Ca correlates with Cd/Ca and P/Ca, demonstrating the nutrient enrichment in Area 1 associated with an alignment of carbonate mounds further north (pockmarks) and carbonate of mixed origin (Carriquiry and Villaescusa, 2010; LaVigne et al., 2010).

Samples 591 (*E. rostrata*), 681 (*S. variabilis*), 685 (*E. rostrata*, including living coral and *S. variabilis*) showed no association with any of the variables; these seemed to be related only to aragonitic carbonate.

The vital effects in the studied corals coincide with environmental changes, as reported in other studies. This is not fully understood, as the physiology of corals can control the geochemical signal and hinder the interpretation of paleoenvironmental reconstructions (Robinson et al., 2014; Montagna and Taviani, 2019). The elementary ratios and stable isotopes were indicators of the dominant spatial distribution and influence in the studied areas.

Area 1, containing pockmarks (681, 683, and 684) and station 687 (Area 2), showed an affinity for terrigenous material, nutrients, and compounds of anthropogenic origin. These seamounts are considered supports for marine biodiversity, including corals. Once the pockmarks and Alpha Crucis Carbonate Ridge had been formed, they acted as significant topographical obstacles; the corals there benefit from a higher food supply due to the strongest currents (Dorschel et al., 2007; Raimundo et al., 2013; Lo Iacono et al., 2018; Maly et al., 2019). It is possible that these mounds also became barriers for terrigenous sediments, and that there are deposited metals and nutrients associated with particulate material incorporated into corals, as observed in these samples. The corals at the top of the Alpha Crucis Carbonate Ridge in Area 2 (588, 591, 592, and 593) presented higher $\delta^{13}C$ values, showing changes in temperature formation and carbonate of aragonitic origin, receiving stronger marine influence.

CONCLUSIONS

The vital effects on the studied coral species (*E. rostrata*, *S. variabilis*, and *D. pertusum*) overlap with environmental changes, especially temperature proxies. Nonetheless, the results were indicators of the dominant spatial distribution and

influence in the studied areas. Area 1 (681, 683, and 684), which has pockmarks, and station 687 (Alpha Crucis Carbonate Ridge, Area 2), showed an affinity for terrigenous material, nutrients, and anthropogenic compounds. These seamounts can act as barriers for metals from land flows and are associated with particulate material incorporated into corals. These corals benefit from a higher food supply due to stronger currents and are biodiversity hot spots in the deep sea. The corals at the top of the Alpha Crucis Carbonate Ridge (Area 2; 588, 591, 592, and 593) show changes in temperature since their formation, receiving more significant marine influence. Coral samples have carbonate of aragonitic origin except for a specimen of *D. pertusum* from station 681, which showed carbonate of mixed origin (biogenic calcite and aragonite).

The formation temperature was estimated through the relationship between $\delta^{18}O$ and $\delta^{13}C$, allowing us to speculate that *S. variabilis* and *E. rostrata* were formed during periods of lower sea level due to the higher formation temperature compared to the current one. We recommend that future studies use isotopic ratios to predict the need for dating using the U/Th method.

The Ba/Ca, Mg/Ca, and Sr/Ca ratios showed levels similar to those found in corals around the world, but higher values of Cd/Ca, Fe/Ca, Pb/Ca, P/Ca, Li/Ca, Li/Mg, Zn/Ca than corals in other oceans, suggesting a higher supply of terrigenous compounds of anthropogenic origin and nutrients in the Southwest Atlantic. The results allowed for an assessment of the potential of coral species for chemical characterization, the first inventory of stable metals and isotopes in the Southwest Atlantic, providing a basis for future studies in areas of carbonate hills.

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AUTHOR CONTRIBUTIONS

T.H.T: Conceptualization; Methodology; Investigation; Formal Analysis; Writing - original draft

R.H.N.: Conceptualization; Investigation; Writing - original draft

R.C.L.F.: Investigation; Writing - original draft

P.Y.G.S.: Project Administration; Funding Acquisition; Writing - original draft;

M.M. de M.: Supervision; Resources; Conceptualization; Investigation; Writing - original draft.

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