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The cold-water coral *Solenosmilia variabilis* as a paleoceanographic archive for the reconstruction of intermediate water mass temperature variability on the Brazilian continental margin

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Recent oceanographic observations have identified significant changes of intermediate water masses characterized by increased temperatures, lowered pH and deoxygenation. In order to improve our understanding as to how these changes may impact deep-sea ecosystems one important strategy is to reconstruct past oceanic conditions. Here we examine the applicability of the scleractinian cold-water coral *Solenosmilia variabilis* as a marine archive for the reconstructions of past intermediate water mass temperatures by using Lithium (Li)/Magnesium (Mg) ratios. In particular, our study addresses 1) the calibration of Li/Mg ratios against *in-situ* temperature data, 2) the reconstruction of past intermediate water mass temperatures using scleractinian coral fossil samples from the Brazilian continental margin and 3) the identification of intraspecies variability within the coral microstructure. Results showed that Li/Mg ratios measured in the skeletons of *S. variabilis* fit into existing Li/Mg-T calibrations of other cold-water scleractinian. Furthermore, the coral microstructure exhibits interspecies variability of Li/Ca and Mg/Ca ratios were also similar to what has been observed in other cold-water scleractinian corals, suggesting a similar biomineralization control on the incorporation of Li and Mg into the skeleton. However, the Li/Mg based temperature reconstruction using fossil samples resulted in unexpectedly high variations >10°C, which might not be solely related to temperature variations of the intermediate water mass over the last 160 ka on the Brazilian continental margin. We speculate that such temperature variability may be caused by vertical movements of the aragonite saturation horizon and the associated seawater pH changes, which in turn influence the incorporation of Li and Mg into the coral skeleton. Based on these results it is recommended

that future studies investigating past oceanic conditions need to consider the carbonate system parameters and how they might impact the mechanisms of Li and Mg being incorporated into skeletons of cold-water coral species such as *S. variabilis*.

KEYWORDS

cold water coral (CWC), south atlantic, *solenosmilia variabilis*, Li/Mg, intermediate water mass

1 Introduction

The reconstruction of past oceanic and environmental conditions is one important application to help predict the impact of the current climate change on ocean circulation, ocean chemistry and deep-sea ecosystems. Seawater temperature is a particularly important parameter to assess as temperature influences various physical and chemical processes within the oceanic system (Weyl, 1959). For decades, the Antarctic Intermediate water (AAIW) has experienced warming off the coast off Brazil. From 1958 to 2009, the temperature has increased to about 0.23°C (McCarthy et al., 2011).

To accurately predict how anthropogenic climate change will affect the mid-depth of the South Atlantic, it is crucial to study the sensitivity of physiochemical properties in marine systems to changes in atmospheric greenhouse gases such as CO₂, as well as rising atmospheric temperatures. Already, it is known how much deep ocean waters in certain regions have changed in terms of temperature. During the last ice age and the deglacial period (about 20,000-10,000 years ago), high-resolution records from ice cores from polar regions showed rapid (centennial to decadal) changes in ocean climate (Barnola et al., 1987; Indermühle et al., 1999; Petit et al., 1999; Augustin et al., 2004). Conventional paleoceanographic reconstructions are often made from marine sediment cores (e.g. Charles et al., 1996; Raddatz et al., 2017) but these have the disadvantage of being intermixed with marine organisms, thus blurring rapid signals (e.g. Leuschner et al., 2002). In addition, the timing of deposition is difficult to determine from the sediment cores, leading to inaccurate age models. As such, there is an urgent need to combine both atmospheric and oceanic records to understand the various coupling mechanisms involved during times of rapid climate change.

In this study cold-water scleractinian stony corals present a promising new tool to reconstruct past ocean properties. In comparison to other marine proxy archives in use, this group have the advantage that they, 1) commonly occur in almost all oceans, 2) are located in great depths, living far from sunlight inn

well over 1000 m depth, 3) incorporate the isotopic and element composition of the surrounding seawater in equilibrium with various ocean parameters such as temperature and pH, 4) can live for decades to millennia, and lastly 5) their skeletons can be accurately dated using radioactive isotope decay methods (Cheng et al., 2000; Houlbrèque et al., 2010; Frank et al., 2011; Montagna et al., 2014; Raddatz et al., 2014a; Robinson et al., 2014; Wefing et al., 2017; Freiwald et al., 2021).

For instance, U/Ca and boron isotope systematics are commonly used for reconstruction of parameters of the carbonate system (Sinclair et al., 2006; Blamart et al., 2007; Anagnostou et al., 2011; Anagnostou et al., 2012; McCulloch et al., 2012; Raddatz et al., 2014a; Raddatz et al., 2014b; Raddatz et al., 2016). Element ratios such as P/Ca, B/Ca and Cd/Ca in scleractinian corals are known for the nutrient concentration (Adkins et al., 1998; Montagna et al., 2006; Mangini et al., 2010; Anagnostou et al., 2011; Hemsing et al., 2018; Spooner et al., 2018). Biological processes however, need to be considered in the development of proxies in coral skeletons, as the incorporation of the elements can be affected by different pathways. The most pronounced geochemical and mineralogical variations occur in corals between the center of calcification (COC) and the theca wall (e.g. Gladfeiter, 1982; Cohen et al., 2006; Meibom et al., 2006; Sinclair et al., 2006; Gladfeiter, 2007; Meibom et al., 2008; Rollion-Bard et al., 2010; Raddatz et al., 2013; Schleinkofer et al., 2019). The COC is composed of small granular crystals and the fibrous aragonite of organic mineral compounds forming long aragonite needles (Gladfeiter, 1982; Constantz, 1989; Gladfeiter, 2007). Various vital effects influence geochemical properties within the calcification process, both on the pathway itself as well as in the formation of the skeletal structure (Adkins et al., 2003; Gagnon et al., 2007). It is postulated that there are several ways that the elements enter the calcifying fluid. According to Holcomb et al. (2009) and Gagnon et al. (2007) the increase of the pH in the extracellular calcifying fluid causes a higher saturation of the Element/Ca (E/Ca) ratio in the COC than in the fibrous aragonite. In contrast Rollion-Bard et al. (2010) assumes the fibrous aragonite and COC to be formed independently and therefore have different E/Ca composition.

Other changes that may cause a difference in the coral chemistry and calcification process are Rayleigh fractionation and kinetic effects (Cohen et al., 2006; Montagna et al., 2006; Sinclair et al., 2006; Gagnon et al., 2007).

Recent studies developed a method to overcome such “vital effects”, by implementing Li/Mg ratio of aragonitic marine carbonates (Bryan and Marchitto, 2008; Case et al., 2010; Hathorne et al., 2013; Raddatz et al., 2013). A positive correlation between Li/Ca and Mg/Ca suggest that the uptake mechanism and the biological and physicochemical factors are in fact the same for both E/Ca (Case et al., 2010; Raddatz et al., 2013; Montagna et al., 2014). By combining Li/Ca and Mg/Ca ratios the effect of the biological processes is reduced, resulting in temperature being the primary factor to influence the coral’s Li/Mg composition. Hence, the Li/Mg ratios exhibits a strong inverse exponential relationship with temperature across both warm and cold-water corals of 0–30°C (Case et al., 2010; Hathorne et al., 2013; Raddatz et al., 2013; Montagna et al., 2014). This is also seen in benthic foraminifera (Stewart et al., 2020). Very few studies to date have applied this proxy for the reconstruction of past seawater temperatures (e.g. Montero-Serrano et al., 2013; Raddatz et al., 2014b; Fowell et al., 2016; Raddatz et al., 2016; Cuny-Guirriec et al., 2019).

The cold-water coral (CWC) *Solenosmilia variabilis* is one of the six most important reef building corals located in the deep sea but thus far, this group has not been the focus of paleoceanographic studies. *S. variabilis* occurs primarily in depths of 220–2,165 m and is often found below the dominant depths of the cold-water corals *Desmophyllum pertusum* (also known as *Lophelia pertusa*) and *Madrepora oculata*. The distribution of *S. variabilis* extends over mostly all oceans of the world however no occurrences have been recorded from the Antarctic Ocean nor in the North and East Pacific regions (Cairns, 1995; Freiwald et al., 2004; Davies and Guinotte, 2011). A possible reason for this distribution pattern is the appearance of *S. variabilis* in the aragonite undersaturated zones or close to the aragonite saturation horizon (Davies and Guinotte, 2011; Bostock et al., 2015), which in the North Pacific is in > 2000 m at greater depths than in the Northeast Atlantic (50–600 m) (Guinotte et al., 2006). Suitable growth areas are predicted in the Atlantic at continental slopes and the Mid ocean ridge (Davies and Guinotte, 2011). Today live and dead *S. variabilis* colonies are located primarily on underwater features such as seamounts in the New Zealand (NZ) region (Tracey et al., 2011) as well as in the Drake passage in the southwestern part of the Atlantic Ocean, southeastern Pacific Ocean. While the reef-like colonies in NZ do survive in waters that are deeper than 2000 m, they thrive in depths from ~800 to 1000 m (Davies and Guinotte, 2011; Tracey et al., 2011; Bostock et al., 2015; Freiwald et al., 2021).

Here we study the applicability of the scleractinian cold-water coral *S. variabilis* as a geochemical proxy archive for the reconstructions of past intermediate water masses in the

Brazilian Continental margin, South Atlantic and in the South Pacific region. In particular, we address 1) the calibration of Li/Mg ratios against *in-situ* temperature, 2) the reconstruction of past intermediate water mass temperature using fossil samples and 3) discuss the intraspecies variability of Li/Mg ratios.

1.1 Study area

1.1.1 SW Pacific

Live collected *S. variabilis* were provided from the National Institute for Water and Atmosphere (NIWA), Wellington, New Zealand. The sampling area is restricted to offshore deep waters the NZ Exclusive Economic Zone in the Southwest Pacific (Figure 1A; Table 1). Two samples were collected from a ridge-like feature on, the Chatham Rise, an area that stretches about 1400 km to the east of New Zealand (Clark and Rowden, 2009) and one sample was gathered north of New Zealand, in the southern area of the Kermadec Ridge. All samples were located in the Antarctic intermediate water (AAIW) at a water depth of 1000–1300 m and a temperature range of 3.7–5.4°C (Locarnini

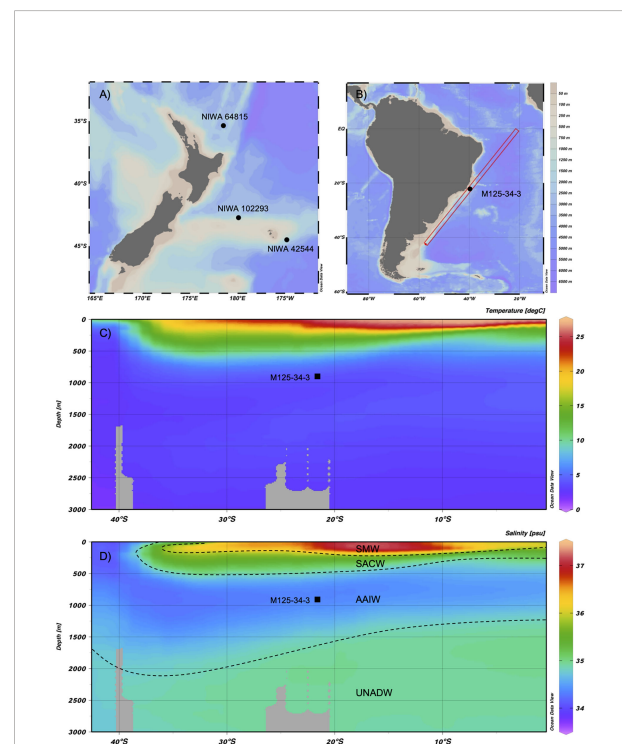


FIGURE 1

Map of the sampling locations: (A) live samples locations off New Zealand and (B) the location of the sediment core M125-34-3 off the coast of Brazil. (C) Temperature profile and (D) salinity profile of marked area in B, the black squares mark the position of the Bowie Mound (Schlitzer, 2021). The dashed lines show the boundary of the water masses from shallow to deep. These are: the salinity maximum waters (SMW), South Atlantic Central waters (SACW), Antarctic intermediate waters (AAIW) and Upper North Atlantic deep waters (UNADW).

TABLE 1 Coordinates of the analyzed samples in the Pacific (NIWA 102293; NIWA 42544; NIWA 64815) and the gravity core (M125-34-2) in the South Atlantic.

	NIWA 102293	NIWA 42544	NIWA 64815	M125-34-2
Latitude	42°43.62'S	44°29.88'S	35°21.18'S	21°56, 957'S
Longitude	179°53'49"W	174°49.02'W	178°30.66'E	39°35,117"W
Depth [m]	1020	1386	1382	866
Temp. [°C]	5.4 ± 0.2	3.8 ± 0.1	3.7 ± 0.2	4.3

et al., 2009). The samples are all located in the lower part of the AAIW, characterized by a low salinity of 34.4 g/kg (Antonov et al., 2009).

1.1.2 South Atlantic

The modern hydrography around the Bowie Mound, in the South Atlantic, to the east of Brazil is shown in Figure 1. The top water mass is the Salinity maximum water and reaches depth of up to 200 m (Mémery et al., 2000). In deeper waters, the north flowing South Atlantic Central Water (SACW) is characterized by lower temperatures and salinities. At the depth of the Bowie Mound (866 m) the AAIW follows with a transport direction to the north and low salinity (< 34.4 g/kg). At 900 m the Ω_{Ar} is ~1.2, the pH of the seawater ~7.97, the CO_2 concentration 79 μ mol/kg and temperatures are about 4.3°C (Raddatz et al., 2020). Beneath AAIW the Upper North Atlantic Deep Water (UNADW) flows in the southward direction with higher salinity (Antonov et al., 2009).

2 Material and methods

Three live collected samples of *S. variabilis* came from various research surveys in New Zealand waters, Southwest Pacific region. Sample depth and temperature details are as follows: NIWA 102293 was collected at a depth of 1020 m in 5.4 ± 0.2°C; NIWA 42544 in 1386 m at 3.8 ± 0.1°C; and NIWA 64815 in a depth of 1382 m at 3.7 ± 0.2°C (Figures 1A, 2A; Table 1).

Fossil *S. variabilis* (Figure 2B) samples were retrieved during cruise M125 with the German research vessel METEOR and originate from the Bowie Mound, east of Brazil in a depth of 866 m and in 4.3°C (Figure 1; Table 1; Bahr et al., 2016).

The 5.86 m gravity core retrieved from Bowie Mound covered 160 ka and was characterized by non-coral-bearing and coral-bearing intervals. The coral-bearing intervals mainly comprised fossil forms of *S. variabilis* cold-water corals (Raddatz et al., 2020), and these were bedded in silty clay and clay-like

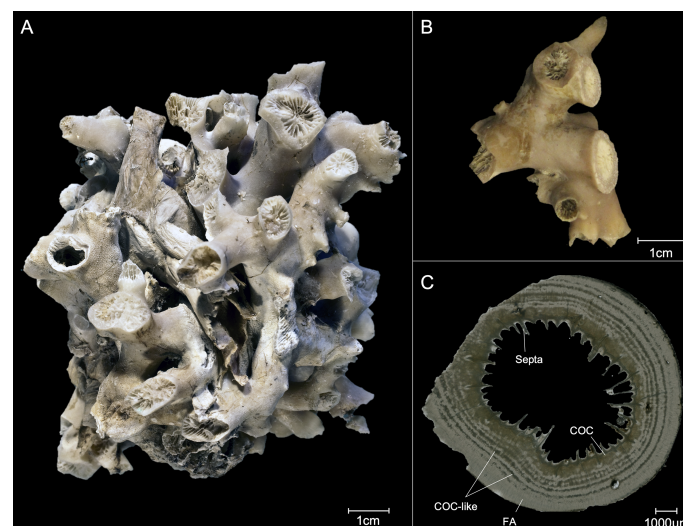


FIGURE 2

Different representations of the coral samples of *S. variabilis*: (A) Live picked sample in the Pacific near New Zealand. (B) Fossil sample of the Bowie Mound in AAIW and (C) cross section of a fossil sample; COC, center of Calcification; FA, Fibrous aragonite.

sand sediment (Bahr et al., 2020), providing very good preservation of the coral fragments.

The coral fragments were dated by using the $^{230}\text{Th}/\text{U}$ method (seen in Raddatz et al., 2020). Further information on the structure of the sediment core can be obtained from the studies by Raddatz et al. (2020) and Bahr et al. (2020). For this study a total of 27 samples were analyzed.

2.1 Element/Ca measurements

About 1 mg of calcium-carbonate was taken from the uppermost calices extracted with a Proxxon IBS/E dremel tool out of the theca wall. Samples have been drilled by avoiding visible lines of calcification (COC), as they display different element compositions compared to the surrounding theca wall (Gagnon et al., 2007; Montagna et al., 2014). Subsequently, samples were cleaned by weak acid leach in 5 % HNO_3 for 5 sec. Samples for the heterogeneity profiles (Figure 2C; $N = 5-6$) did not avoid COCs and were extracted using a Micromill.

Elemental ratios of CWCs were measured with an Inductively-Coupled-Plasma-Mass-Spectrometer (ICP-MS) ThermoScientific Element 2 at Fierce, Institute of Geoscience, Goethe University Frankfurt. Approximately 150 μg of homogenized carbonate powder was dissolved in 1.8 ml 2% HNO_3 containing 1.2 ppm Yttrium (Y) used as an internal standard. The measured intensities were background subtracted and standardized internally to Y and normalized to Ca. External standards were made from single-element solutions to match typical element compositions of cold-water scleractinian corals (Rosenthal, 1999). The coral standard JCP-1 was measured after every fifth sample in order to allow for any drift corrections. The measured JCP-1 ($N = 15$) are consistent with the recommended values by Hathorne et al. (2013): Li/Ca $6.185 \pm 0.107 \mu\text{mol/mol}$, Mg/Ca $4.199 \pm 0.065 \text{ mmol/mol}$ and this study Li/Ca $6.036 \pm 0.701 \mu\text{mol/mol}$ (97.6 %), Mg/Ca $4.153 \pm 0.374 \text{ mmol/mol}$ (98.9 %).

3 Results and discussion

3.1 *S. variabilis* as a geochemical archive for Li/Mg based temperature reconstructions

3.1.1 Adding *S. variabilis* to the Li/Mg-T calibration

In previous studies, elemental ratios (e.g. Li/Ca, Sr/Ca, Mg/Li) have been identified to be temperature depended in scleractinian cold-water corals (Case et al., 2010; Raddatz et al., 2013; Raddatz et al., 2014a). The most robust temperature proxy, including aragonitic zooxanthellate (shallow) and azooxanthellate (deep) scleractinian, appears to

be Li/Mg ratio (Case et al., 2010; Montagna et al., 2014; Cuny-Guirriec et al., 2019; Stewart et al., 2020).

To test the cold-water coral *S. variabilis* as a suitable archive for reconstructions of intermediate water temperatures, the Li/Mg-temperature calibration by Montagna et al. (2014), was applied:

$$\text{Li/Mg (mmol/mol)} = 5.41 \exp(-0.049 \pm 0.002 \times T (^{\circ}\text{C})), R^2 = 0.975. \quad (1)$$

This calibration includes a temperature range of 0-30°C for cold- temperate- and warm-water scleractinian corals. In addition, the study by Stewart et al. (2020) extended this calibration to cover other aragonitic corals, including stylasterid hydrocorals, scleractinian (including Zooxanthellate) corals, as well as foraminifera:

$$\text{Li/Mg (mmol/mol)} = 5.42 \pm 0.04 \exp(-0.050 \pm 0.0004 \times T (^{\circ}\text{C})), R^2 = 0.97 \quad (2)$$

within uncertainty similar to the original calibration by Montagna et al. (2014).

Using the *in-situ* temperature data, extracted from World Ocean Atlas 2009 (Locarnini et al., 2009), the live collected samples from the SW Pacific produced expected Li/Mg ratios of $2.74 \pm 0.14 \text{ mmol/mol}$ (2SD) at $5.4 \pm 0.5^{\circ}\text{C}$, $4.52 \pm 0.78 \text{ mmol/mol}$ at $3.8 \pm 0.1^{\circ}\text{C}$ and $3.74 \pm 0.61 \text{ mmol/mol}$ at $3.7 \pm 0.2^{\circ}\text{C}$ (Figure 3). Combining these data with published data from Case et al. (2010) and Montagna et al. (2014) results in the following empirical Li/Mg-T calibration:

$$\text{Li/Mg (mmol/mol)} = 5.23 \exp(-0.46 \times T (^{\circ}\text{C})), R^2 = 0.94. \quad (3)$$

The new samples and calibration are consistent with the original exponential function by Montagna et al. (2014), considering the confidence interval (Figure 3).

3.2 Li/Mg based temperatures using fossil *S. variabilis* from Bowie Mound, off Brazil

The Li/Mg measurements obtained from the Bowie Mound samples produced a variability of $2.55-5.55 \pm 0.11 \text{ mmol/mol}$ (Figure 4), resulting in a large temperature range of -0.53 to $15.34 \pm 1.55^{\circ}\text{C}$, when applying the Li/Mg-Temperature calibration by Montagna et al. (2014). In particular, four samples plot outside the expected temperature range of 4-15.2°C (Mienis et al., 2014; Raddatz and Rüggeberg, 2021). AAIW temperatures of up to 15°C appear very high considering the water depth of almost 900 m (Figure 5). However, Mg/Ca data based temperature reconstruction using the endobenthic foraminiferal species *Uvigerina* spp. also show reconstructed temperature variations of $8-9^{\circ}\text{C}$ ($\pm 1^{\circ}\text{C}$ 2σ) in the intermediate water (IW) (852 m water

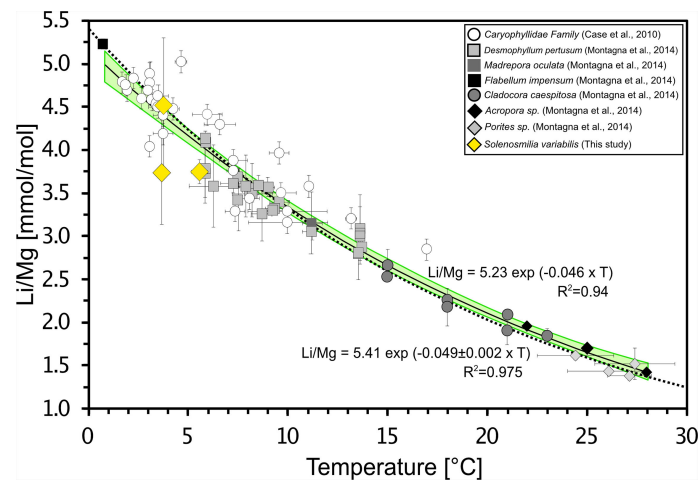


FIGURE 3

Li/Mg. ratio vs. seawater temperature for the published data Case et al. (2010); Montagna et al. (2014) and new data from current study (yellow diamond). The temperature range of cold-water, temperate, and warm-water corals is 0–30°C with a range of the Li/Mg of 1–5.5 mmol/mol measured by laser and solution ICP-MS. The additional measurements are 2.74 ± 0.14 mmol/mol (2SD) at $5.4 \pm 0.2^\circ\text{C}$, 4.52 ± 0.78 mmol/mol at $3.8 \pm 0.1^\circ\text{C}$ and 3.74 ± 0.61 mmol/mol at $3.7 \pm 0.2^\circ\text{C}$. The calibration of Montagna et al. (2014) is shown as black dashed line ($R^2 = 0.975$). The black solid line indicates the new function with additional data of this study ($R^2 = 0.94$). Light green shaded band show the 95% confidence interval.

depth) in the SW Atlantic (M78/1-235-1; $11^\circ36.53'\text{N}$, $60^\circ57.86'\text{W}$) over the last 24 ka (Poggemann et al., 2018).

The Bowie Mound represent five distinct coral growth periods (C_1 – C_5) according to their occurrence between 0–160 ka (Raddatz et al., 2020) (Table 2). The calculated average Li/Mg temperature are with 7.71°C ($\pm 1.55^\circ\text{C}$, 2SD), by 3.4°C higher than the present day ambient AAIW (Raddatz et al., 2020).

At about 16.5 ka, Poggemann et al. (2018) recorded an IW temperature of 4.4°C based on the Mg/Ca ratios of benthic foraminifera, which is consistent with the average temperature of 3.2°C in this study in C_1 (Table 2). The cold temperatures of $< 4^\circ\text{C}$ retrieved from one of the two coral fragments in C_1 and the one sample from C_2 cannot be treated as outliers, since Roberts et al. (2016) also reconstructed temperatures below 0°C in the IW at a depth of 598 m 2–20 ka BP. Accordingly, we assume here that the cold temperatures are part of the ecological niche of *S. variabilis*, as they live in the South Pacific Region of New Zealand at 2 – 3°C (Davies and Guinotte, 2011).

Compared to average temperature of the last 160 ka, *S. variabilis* occurred in colder temperature periods (Figure 5A), in times when both, global sea level and atmospheric CO_2 concentration were lower than they are today (Figures 5B, F; Petit et al., 1999; Grant et al., 2012). The occurrence of *S. variabilis* during these periods correlates with the cold events in the northern hemisphere, in particular the Heinrich stadial (HS) 1 before 14.6–18 ka, the HS4 before approx. 40 ka and the HS6 before 60 ka, as reported in the study by (Raddatz et al., 2020). During HS's large amounts of ice collapsed from the northern ice sheets (Toggweiler and Lea, 2010), thereby reduced

the temperature gradient between the two hemispheres (Toggweiler and Lea, 2010). There is an ongoing discussion as to whether the Atlantic meridional overturning circulation (AMOC) was significantly weakened during such periods or possibly completely ceased and therefore inhibited North Atlantic deep-water formation (NADW) (Böhm et al., 2014; Lund et al., 2015; Lynch-Stieglitz 2017; Poggemann et al., 2017). The conditions for a collapse scenario could only have been fulfilled in HS1, HS2 and HS11; HS3 to HS10 resulted only to a weakening of NADW formation (Böhm et al., 2015). Poggemann et al. (2018) postulated three possible explanations for the heating of IW in HS1: (1) the exchange of the AAIW with warm water, (2) a heating of the surface water, which is transferred to the intermediate water, or (3) a warming of the AAIW itself. In the first scenario, warmer water masses from the north would have had to replace the IW or at least be involved in their warming (Poggemann et al., 2018). However, the influence of overlying or northerly water masses could not be detected by using different proxies (Poggemann et al., 2018). The second scenario can be excluded here as the SST in the South Atlantic (Figures 5D, E; Santos et al., 2017; Hou et al., 2020) was quite constant and do not correlate with the temperature at *S. variabilis* locations in the IW. Therefore, the present data set supports the hypothesis of the third scenario, in which the AAIW warmed by itself. Poggemann et al. (2018) demonstrated a warming of the IW in HS1 of about 1.6 – 10.9°C , which is consistent with the temperature ranges of 1.4 – 3.3°C obtained in this study. The apparently weakened or even ceased southward flowing NADW no longer influenced the

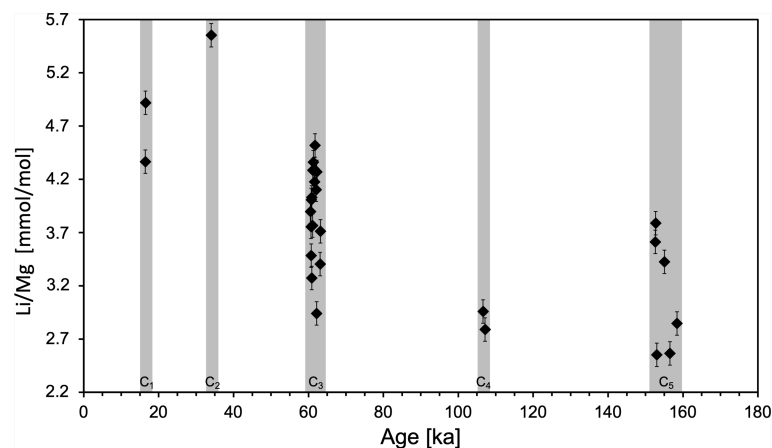


FIGURE 4
Li/Mg [mmol/mol] (± 0.11 2SD) measurements of fossil *S. variabilis* of the past 180 ka, subdivided in intervals C1-C5.

formation of the AAIW in the HS1 (Böhm et al., 2015; Poggemann et al., 2017). Additionally, this contributed to an intense upwelling and release of CO_2 from the Circumpolar Deepwater (CPDW) in the SO (e.g. Broecker, 1998; Burke and Robinson, 2012; Poggemann et al., 2017). The resulting increase in nutrient concentration in the SO could not be metabolized due to an insufficient iron content (e.g. Martínez-García et al., 2014). Subsequently, these excessive nutrients were transported northwards via AAIW to the tropical West Atlantic (Poggemann et al., 2017). This may have increased primary production and enhanced the biological pump, leading to a deglacial CO_2 plateau in the atmosphere and an elevated export of organic matter to the deep sea (Archer et al., 2000; Sigman and Boyle, 2000; Marcott et al., 2014). The resulting higher respiration outputs of CO_2 in the AAIW has the potential to lower seawater pH and drive aragonite dissolution, thereby shift the aragonite compensation depth. The study by Allen et al. (2015) presents such an effect of CO_3^{2-} decrease in the deep water and a lowering in atmospheric CO_2 in the southwest Pacific during the onset of HS1 (18-20 ka). In contrast Lynch-Stieglitz et al. (2019) suggests that the high nutrient content in the water masses is not the source of the high CO_2 content in the deglacial. The study assumes a direct atmosphere CO_2 uptake direct by the surface and intermediate water masses in the Southern and North Atlantic.

It is typical for *S. variabilis* to grow in a temperature range of 3-4°C, which differs by 3°C from *D. pertusum* (Fallon et al., 2014; Flögel et al., 2014; Gammon et al., 2018). As *D. pertusum* exhibits temperature fluctuations of more than 6°C in Tisler Reef (Guihen et al., 2012), we also suggest a large tolerance range of temperature (> 8°C) and possibly other environmental parameters for *S. variabilis*. While *D. pertusum* occurs primarily in interglacial periods at higher latitudes at shallower

depths, *S. variabilis* has already been documented to prefer more extreme environmental conditions at lower latitudes, greater depths and thus less aragonite-saturated water masses (Schröder-Ritzrau et al., 2005; Thresher et al., 2011; Flögel et al., 2014; Bostock et al., 2015; Gammon et al., 2018).

Considering the high temperature tolerance, we assume, that a secondary factor influences the incorporation of Li and Mg into the coral skeleton. Regarding the lower aragonite saturation within the occurrence of *S. variabilis*, we propose the aragonite saturation here as a secondary controller of Li/Mg. At a aragonite saturation ($\Omega_{\text{Ar}} = ([\text{Ca}^{2+}] \times [\text{CO}_3^{2-}])/K_{\text{sp}}$; K_{sp} is the solubility product of aragonite) $\Omega_{\text{Ar}} > 1$ precipitation is induced, whereas at $\Omega_{\text{Ar}} < 1$ dissolution of aragonite is preferred (Mucci, 1983; Doney et al., 2009).

Aragonite dissolution in the late Pleistocene South Atlantic has been reconstructed using the pteropod *Limacina inflata* dissolution index (LDX) (Gerhardt et al., 2000; Gerhardt and Henrich, 2001). In particular, in the western South Atlantic, LDX traced undersaturated AAIW and Upper Circumpolar Deep Water (UCDW; Henrich et al., 2003). The coral periods (C1-C4) mostly occur during such phases of low aragonite saturation (Henrich et al., 2003). Since aragonite saturation influences the calcification rate, this could also have an impact on the elemental composition of the Li/Mg. Such an effect has been demonstrated in foraminifera on Mg/Ca-temperature proxy (Gray et al., 2018; Gray and Evans, 2019). Several pathways of element incorporation into foraminifera shells have been postulated as well as vital effects that control the incorporation of Mg during calcification (Bentov and Erez, 2006). Furthermore it has been shown that also salinity and pH influence the Mg/Ca the shell composition (Gray and Evans, 2019). In addition to the temperature sensitivity, the study conducted by Gray and Evans (2019) on foraminifera revealed

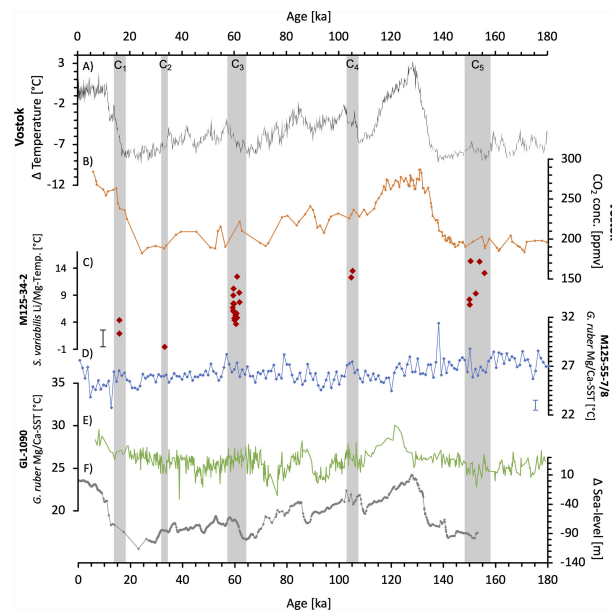


FIGURE 5

Evolution of environmental parameters over the last 180 ka before present. (A) The temperature fluctuations, averaged over the last 1,000 years, from the Vostok ice core (Petit et al., 1999). (B) CO₂ concentration in ppmv reconstructed from the Vostok ice core (Petit et al., 1999). (C) Temperature reconstruction of the SAIW from sediment core M125-34-2, using the Li/Mg in the CWC *S. variabilis* (this study). With a 2SD of 1.55°C calculated from the JCp-1 measurements. (D) Temperature reconstruction of surface water from the southwestern tropical Atlantic (M125-55-7/8) based on the Mg/Ca of Globigerinoides ruber (*G. ruber*) (pink). The standard deviation is $\pm 0.5^\circ\text{C}$ (Hou et al., 2020). (E) Surface water temperatures of the subtropical western South Atlantic reconstructed from sediment core GL-1090 of the Mg/Ca of *G. ruber* (Santos et al., 2017). (F) Global sea level variations referenced to present-day sea level (Grant et al., 2012). The gray bars mark the intervals (C₁₋₅) of *S. variabilis*.

a salinity sensitivity of $3.6 \pm 0.01\%$ (2SD) per g/kg and a carbonate chemistry sensitivity of -5 to -9% per 0.1 pH unit. This may also be valid for Li/Mg with respect to aragonite saturation. To follow this up, further studies should investigate the dependence of Li/Mg on aragonite saturation using boron isotopes and U/Ca (Anagnostou et al., 2011; Anagnostou et al., 2012; McCulloch et al., 2012).

3.3 Heterogeneity profiles of Li/Ca and Mg/Ca in *S. variabilis*

Different fluctuations on the cross-sectional axis, with almost uniform changes are reflected in the elemental ratios of the coral skeleton (Figure 6). Here the change of E/Ca ratios are prominent in the COC and fibrous aragonite (theca wall) (Figure 2). In three of four samples, the Mg/Ca and Li/Ca ratios exhibits a decreasing trend following the direction of the COC structure to the theca-wall (Figures 6A–C), at the fourth sample (Figure 6D) the Li/Ca and Mg/Ca increase. The Mg/Ca shows a range of $0.75\text{--}4.71 \pm 0.25$ mmol/mol (2SD). Within the coral structure the variability is about $0.75\text{--}2.27$ mmol/mol, with an average variation factor of 1.5. The Li/Ca varies between 8.48 and 19.31 ± 0.77 $\mu\text{mol/mol}$ (2SD), with an internal fluctuation of ~ 5 $\mu\text{mol/mol}$ and an average

variation factor of 1.5. The corresponding Li/Mg ratios indicate an increase in the direction of the theca-wall in three samples, in the fourth sample the trend is opposite. The measured range is $2.93\text{--}5.15 \pm 0.11$ mmol/mol (2SD).

Previous studies also indicated internal fluctuations of Mg/Ca and Li/Ca up to a variation factor of 3 (e.g. Case et al., 2010; Raddatz et al., 2013; Montagna et al., 2014). Here we compare the *S. variabilis* measurements with the additional scleractinian cold-water corals: *D. pertusum*, *Balanophyllia* sp., *Desmophyllum cristagalli* (*D. cristagalli*) and *Desmophyllum dianthus* (*D. dianthus*) (Figure 7). *D. pertusum* exhibits a Mg/Ca range of $1.5\text{--}4.6$ mmol/mol and Li/Ca about $8.0\text{--}25.3$ $\mu\text{mol/mol}$ with a variation factor of 1.48–2.4 and 1.68–1.8 (Raddatz et al., 2013; Rollion-Bard and Blamart, 2015 and Schleinkofer et al., 2019). *Balanophyllia* reveals Mg/Ca variations of $1.2\text{--}2.8$ mmol/mol and $6.0\text{--}13.5$ $\mu\text{mol/mol}$ Li/Ca, with a variation factor over 2 on both E/Ca (Case et al., 2010). The Mg/Ca is about $2.0\text{--}3.7$ mmol/mol and Li/Ca is $7.7\text{--}13.8$ $\mu\text{mol/mol}$ in the internal coral structure of *D. cristagalli*, the variation factor for both ratios is 1.8 (Rollion-Bard and Blamart, 2015). Recorded Mg/Ca in *D. dianthus* indicate a range of $0.9\text{--}4.0$ mmol/mol and Li/Ca of $6.0\text{--}15.0$ $\mu\text{mol/mol}$, with a variation factor of 2–3 and 2 (Gagnon et al., 2007; Case et al., 2010), which is higher than in *S. variabilis*.

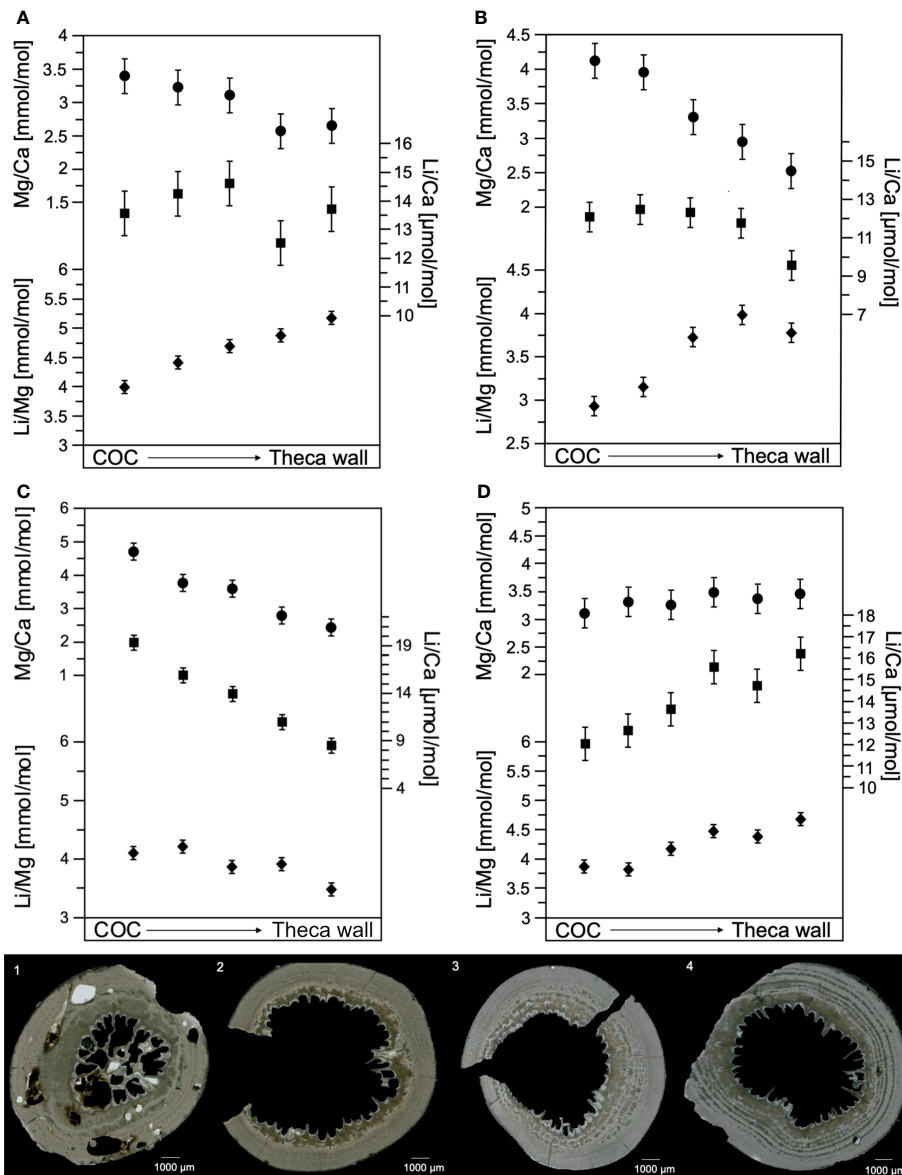


FIGURE 6 Elemental ratios Mg/Ca [mmol/mol], Li/Ca [μ mol/mol], and Li/Mg [mmol/mol], of four samples from the South Atlantic. The doubled standard variation for Mg/Ca ± 0.25 mmol/mol, Li/Ca ± 0.77 μ mol/mol and Li/Mg ± 0.11 mmol/mol was determined by JCp-1 measurements. **Figures 1–4** below, show the cross-section of the analyzed sample with an allocation of **1-A**, **2-B**, **3-C** and **4-D**. Samples were collected by micromill starting at the COC structure ongoing until the theca wall.

TABLE 2 Coral periods C₁-C₅, their time range, temperature range and average temperature.

Coral periods	C ₁	C ₂	C ₃	C ₄	C ₅
Time range [ka]	16.443-16.476	34.03	60.53-63.19	106.62-107.14	152.61-158.40
Temp. range [°C]	1.9-4.3	-0.5	3.6-12.4	12.3-13.5	7.2-15.3
Average Temp. [°C]	3.2	-0.5	6.81	12.9	11.4

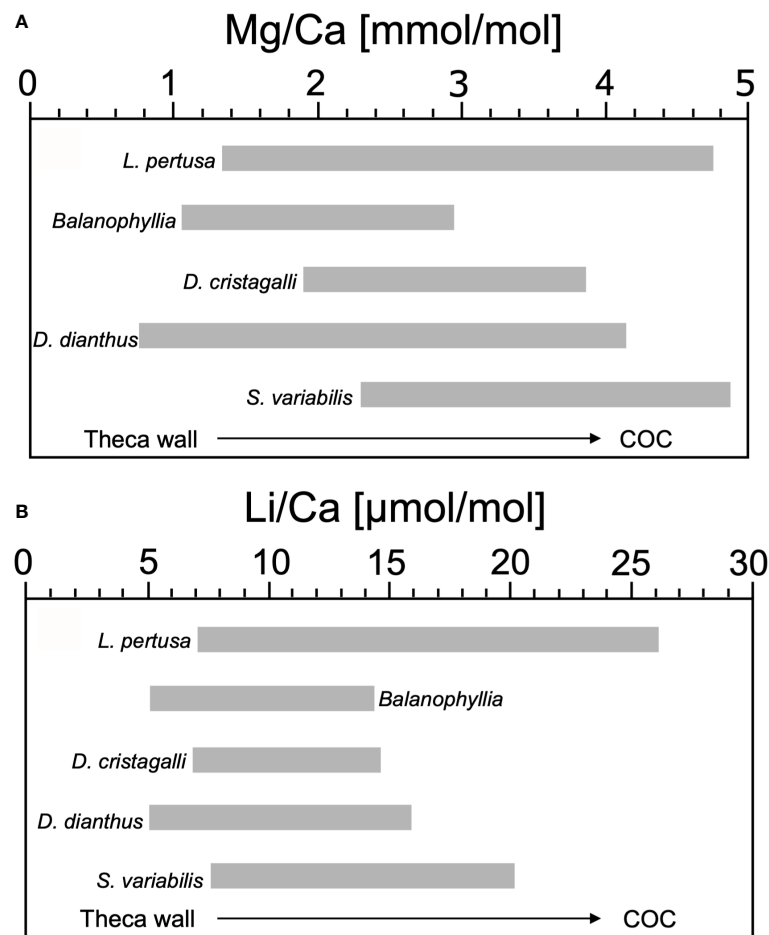


FIGURE 7

Comparison of the Mg/Ca [mmol/mol] and Li/Ca [$\mu\text{mol/mol}$] in the internal skeleton structure of different CWC's: *L. pertusa*, *Balanophyllia*, *D. cristagalli*, *D. dianthus* and *S. variabilis*. (A) In *L. pertusa*, Mg/Ca vary in a range of 1.5–4.6 mmol/mol (Raddatz et al., 2013; Rollion-Bard and Blamart, 2015; Schleinkofer et al., 2019), in *Balanophyllia* 1.2–2.8 mmol/mol (Case et al., 2010), in *D. cristagalli* 2.0–3.7 mmol/mol (Rollion-Bard and Blamart, 2015), in *D. dianthus* the range of values extends of 0.9–4.0 mmol/mol (Gagnon et al., 2007; Case et al., 2010), and in *S. variabilis* between 2.4–4.7 mmol/mol (this study). (B) Li/Ca range from 8.0–25.3 $\mu\text{mol/mol}$ in *L. pertusa* (Raddatz et al., 2013; Rollion-Bard and Blamart, 2015), 6.0–13.5 $\mu\text{mol/mol}$ in *Balanophyllia* (Case et al., 2010), in *D. cristagalli* 7.7–13.8 $\mu\text{mol/mol}$ (Rollion-Bard and Blamart, 2015), in *D. dianthus* 6.0–15.0 $\mu\text{mol/mol}$ (Case et al., 2010), and in *S. variabilis* 8.5–19.3 $\mu\text{mol/mol}$ (this study).

The internal correlation of the Mg/Ca and Li/Ca ratios is apparent in all measurements, especially in sample D (Figure 6D). These internal variations are suspected to be induced by another factor than temperature. Based on the positive correlation between Mg/Ca and Li/Ca (Figure 8) ($R^2 = 0.48$; $P = 1.66 \times 10^{-8}$), it is most likely that both ratios are controlled by similar mechanism (Case et al., 2010; Raddatz et al., 2013) and diagenetic overprints appear to be unlikely. The increase in element ratios from the COC to the outer part of theca wall in sample D (Figure 6) can be explained by the occurrence of several COC-like structures within the fibrous aragonite (shown in Figure 2C). Hence, the internal fluctuations in the remaining samples can also be explained by the presence of COC-like structures.

Finally, *S. variabilis* exhibits the same fluctuation in E/Ca ratios as other scleractinian corals that are likely induced by vital effects. We assume here that Li/Ca and Mg/Ca in *S. variabilis* also mainly follows the Rayleigh-fractionation model, as this is the primary model in warm, temperate and cold-water corals (Montagna et al., 2014). However, the variation factor is still smaller compared to other CWC's, possibly due to the slow growth rate of *S. variabilis* (Fallon et al., 2014; Gammon et al., 2018). The E/Ca ratios of *S. variabilis* are most consistent with measured E/Ca ratios of *D. pertusum* in the North Atlantic, Mediterranean Sea and Red Sea (Figure 8; Raddatz et al., 2013; Rollion-Bard and Blamart, 2015; Schleinkofer et al., 2019). *S. variabilis* growth rate is about 0.8–1.25 mm/yr in natural habitats (Fallon et al., 2014) and in cultivation experiments

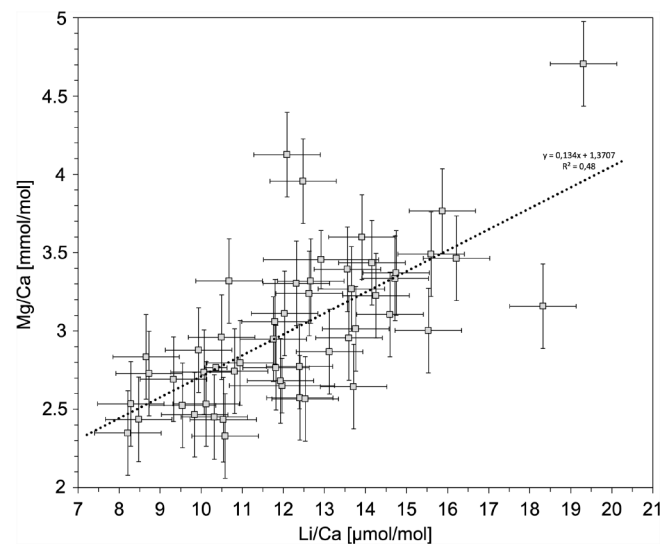


FIGURE 8

All samples exhibit a correlation of Mg/Ca and Li/Ca in *S. variabilis*, which is shown by the dotted line. Uncertainties are indicated in 2SD.

about 0.5–3.968 mm/yr (Gammon et al., 2018) with a similar growth rate as *D. pertusum* about 2.44–3.77 mm/yr in the Gulf of Mexico (Brooke and Young 2009). The gradual growth rate of *S. variabilis* could result in an increased variability of the element concentrations and formation of COC-like structures due to the reflection of longer time scales of elemental incorporation.

The large internal fluctuation within the coral structure represents an inaccuracy in the proxy application. Here we used bulk samples for solution-based chemistry, which might contain COC-like structures and could affect the resulting Li/Mg. However, Mg/Ca and Li/Ca show larger fluctuations, which are already reduced by using Li/Mg. To avoid a possible bias, alternative sampling strategies can be applied. Since COC-like structures can be visually identified in the skeleton of the coral, they could be excluded if sampled by a micromill. Another approach are *in situ* techniques using laser ICP-MS, EPMA (electron probe microanalyzer) or NanoSIMS (secondary ion mass spectrometry) to directly detect and reject variations induced by the COC or COC-like structures. High Mg/Ca ratios could be caused by high organic material content in the COC/COC-like structures as shown in other scleractinian corals (Cuif et al., 2003, Stolarski 2003).

4 Conclusion

This study provides the first application of using *S. variabilis* as a geochemical archive using the Li/Mg-T paleothermometer.

Our analysis of live collected samples from the South Pacific Region of New Zealand fit in the existing Li/Mg-Temperature calibrations, indicating that a species-specific calibration is not needed.

However, the reconstructed Li/Mg bases paleotemperatures of intermediate water masses from the fossil *S. variabilis* coral from sediment cores exhibit relatively large temperature fluctuations of up to 15°C in the AAIW off Brazil. We propose that such high temperature fluctuations can be, to a certain degree, related to intermediate water mass warming during Heinrich Stadials, but are possibly also related to change in the aragonite saturation state.

Nevertheless, the internal variation of Li/Ca and Mg/Ca in the coral microstructure is consistent with previous studies of e.g. Case et al. (2010); Raddatz et al. (2013) and Schleinkofer et al. (2019). Compared to other scleractinian CWCs, the variation factor is assumed to be related to the slow growth rate.

For more accurate reconstructions of temperature future studies should investigate other secondary factors, such as pH, aragonite saturation and salinity that might influence the Li and Mg incorporation in *S. variabilis*. We encourage further investigation on cold-water corals for their suitability as archives for their use in multiproxy studies. Especially with regard to studies on climate change, it is important to understand and recognize to which environmental conditions different species can adapt to and which future changes in their marine environment they can cope with.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

ES, SN and RJ contributed to conception and design of the study. ES, SA and RJ organized the database. ES wrote the first draft of the manuscript. SN, RJ, TD, FN wrote sections of the manuscript. RJ cruise participation. All authors contributed to manuscript revision, read, and approved the submitted version.

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