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ORIGINAL PAPER

Carbonate mineralogy and geochemistry of bryozoans along the South African coast

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Abstract

The main aim of this study was to investigate whether environmental or biological factors predominantly influence bryozoan biomineralization along the South African coast (spanning from 29.263°S; 16.87°E to 27.540°S; 32.677°E), a region known for its diverse oceanographic conditions. New data into the mineralogical (calcite vs. aragonite) and geochemical (Mg content in calcite) composition of bryozoans are provided, enhancing the global database and understanding of biomineralization patterns. To date, there has been a notable scarcity of data on bryozoan skeletal composition in tropical and subtropical regions, representing a significant gap in our knowledge and understanding of the impacts of climate change on marine, calcifying organisms. Our research reveals a diverse array of carbonate skeletons across nearly half of the known bryozoan species in the region, with calcitic forms dominating, followed by bimineralic and aragonite-based forms. The prevalence of aragonite-containing skeletons, particularly within the Cheilostomatida, mirrors global patterns, indicating a correlation with sea temperature gradients. Significant mineralogy and magnesium calcite variability exists within the Flustrina and Membraniporina suborders (Cheilostomatida). Despite exploring various environmental parameters such as temperature, salinity, or impact of currents (Agulhas, Benguela, or mixed), no clear correlation with mineralogical patterns emerged. Instead, the study underscores the substantial influence of biological control on bryozoan skeletal carbonate mineralogy and geochemistry. These findings highlight the importance of comprehensive, multi-parametric analyses to unravel environmental signals in bryozoan biomineralization, contributing to a deeper understanding of the impacts of climate and local conditions on marine calcifiers.

Keywords Biomineralogy · Calcite · Aragonite · Calcifiers · Skeleton · Biomineralization · Marine invertebrates · Climate change

Introduction

Calcifying organisms, such as bryozoans, foraminifera, corals, and mollusks, serve as invaluable repositories of environmental information across past, present, and future contexts (Ram and Erez 2021). They record environmental information by incorporating macro, micro, and trace elements from the marine environment into their carbonate structures such as shells, skeletons, or stiffened mineralized tissues (Lowenstam and Weiner 1989). Despite drawing from external sources, the final composition of their carbonate structures may reflect or completely diverge from the surrounding environment due to biologically-induced or biologically-controlled regulations of the biomineralization process (Lowenstam and Weiner 1989). In biologically-controlled mineralization, the organism exerts a high degree

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of crystallochemical control over the nucleation and growth of the mineral particles. Mostly, the minerals are directly formed at a specific location within or on the cell and only under certain conditions (Lowenstam 1981). However, biologically-controlled biomineralization can also be affected by environmental factors such as temperature, pH, or salinity by modifying the mineralogy, structural organization, amount, and composition of skeletal organic components (Lowenstam and Weiner 1989; Weiner and Dove 2003; Addadi and Weiner 2014). Understanding the interplay between biological and environmental mechanisms over the biomineralization process is critical for explaining the responses of marine calcifying organisms to environmental changes and potential adaptations to climate change.

The biomineralization process is pivotal in the context of global climate change primarily due to its significant influence on carbon cycling. Calcifying organisms uptake carbon dioxide (CO_2) from the surrounding environment while forming their shells, exoskeletons, or mineralized tissues. This process effectively sequesters carbon in the form of calcium carbonate ($CaCO_3$). It is estimated that up to 90% of the carbon presently deposited in the seafloor results from the production of biogenic calcium carbonate (e.g., Feely et al. 2004; Sarmiento and Gruber 2006; Toyofuku et al. 2017; Snelgrove et al. 2018). However, the impacts of climate change, such as rising sea temperatures and ocean acidification, can disrupt the biomineralization process in marine calcifiers (Kroeker et al. 2010). Acidification, caused by the absorption of excess atmospheric CO_2 by seawater, can hinder the ability of calcifying organisms to build their calcium carbonate structures, leading to thinning and weakening shells or skeletons (Dove et al. 2020). Additionally, rising water temperatures can further stress these organisms, potentially impairing their growth and calcification rates (Kroeker et al. 2010). Therefore, understanding the intricate mechanisms of biomineralization and how they interact with environmental changes is critical for predicting the future role of marine calcifiers in carbon cycling and for developing strategies to mitigate the impacts of climate change on marine ecosystems and global carbon budgets.

Bryozoans are exceptional model organisms for studying mineralogical patterns due to their remarkable diversity (order Cyclostomatida – 648 extant species; order Cheilostomatida – 5511 extant species; WoRMS, accessed Aug 12, 2024), global distribution from intertidal to the deep sea, and complex mineralogy (Barnes and Kukliński 2010; Figuerola et al. 2012, 2018). Two classes, the Stenolaemata (order Cyclostomatida) and the Gymnolaemata (order Cheilostomatida), produce well-calcified, complex skeletons (Lowenstam 1954; Rucker and Carver 1969; Poluzzi and Sartori 1975; Lowenstam and Weiner 1989; Smith et al. 2006; Taylor et al. 2009). Calcium carbonate skeletons can be comprised of calcite with varying Mg content (ranging from 0 to 16 mol% $MgCO_3$), dual-calcite (occurrence of two distinct forms or compositions of calcite within a single sample; low-Mg calcite with up to 4 mol% $MgCO_3$, and subdominant calcite with more than 8 mol% $MgCO_3$), aragonite, or a combination of both minerals. Such mineralogical complexity offers opportunities for bryozoans to become indicators of global environmental changes (Smith and Girvan 2010; Smith 2014; Taylor et al. 2014).

Among marine invertebrates, calcium carbonate usually crystallizes in the form of two polymorphs: calcite and/or aragonite. Calcite's lower density and higher stability compared to aragonite make it energetically less demanding for organisms to produce. This, in turn, allows for more rapid calcification, which is advantageous in various biological contexts (e.g. Carter 1980). Aragonite, despite having the same chemical formula as calcite ($CaCO_3$), is thermodynamically metastable, and more soluble, but harder than calcite. In bryozoans, aragonite usually occurs as an admixture within bimineralic skeletons, and less commonly as purely aragonitic composition. The calcite/aragonite polymorphism is influenced by magnesium ion concentration in water, which inhibits calcite nucleation at the initial stages (Davis et al. 2000; Pan et al. 2021) and affects the thermodynamic stability and solubility of calcite (Stanienda-Pilecki 2018; Koskamp et al. 2021). Magnesium-bearing calcite crystals with over 8 mol% are less stable and more soluble than aragonite due to changes in surface structure (Morse et al. 2006; Koskamp et al. 2021). Factors like temperature, salinity, and pCO_2 influence Mg incorporation (Grenier et al. 2020; Alkhatib et al. 2022). The primary impact of temperature is manifested in the distribution of calcium carbonate polymorphs along latitudinal gradients, as illustrated by e.g. Smith et al. (2006); Figuerola et al. (2023) and Piwoni-Piórewicz et al. (2024). These results suggest that the major processes occurring in the ocean such as warming and acidification, may have a significant effect on the solubility of skeletons in marine calcifying organisms. Therefore, studying the composition of carbonate skeletons in marine taxa is particularly pertinent in the context of these rapidly changing environmental conditions.

South Africa provides an ideal environmental model system for investigating trends in the biomineralization and geochemistry of bryozoans. Firstly, there has been no prior examination of the carbonate composition of bryozoans from South Africa. Biodiversity assessments over the past decade have identified approximately 282 species of bryozoans in South African waters (Lombard et al. 2004; Florence et al. 2007; Sink et al. 2012; Boonzaaier-Davids et al. 2020, 2023). The marine biota in the study area demonstrates significant levels of diversity, with species exhibiting extensive ranges of environmental tolerance (Tittensor et al. 2010). South Africa is characterized by a notable degree of marine endemism, particularly among bryozoans (64%), and mollusks, with 56% (Griffiths et al. 2010). Furthermore, the marine ecosystem along the South African coast is shaped by distinct oceanographic conditions, creating an exceptional natural laboratory for examining how environmental factors influence mineralogical patterns.

South Africa's coastline spans latitudinally from 21°S to 35°S and longitudinally from 17°E to 33°E (Fig. 1). The southern tip of the continent is the convergence zone of the cold Atlantic Ocean influenced by the Benguela Current upwelling system, and warm waters of the Indian Ocean, carried by the Agulhas Current (Fig. 1). Coastal upwelling associated with the Benguela Current brings low aragonite saturation state (ΩAr) waters to the surface, especially between 29°S and 33°S (Tsanwani and de Villiers 2017), increasing the risk from ocean acidification exacerbated by anthropogenic CO_2. The mean annual primary productivity, reaching 1.25 kg of carbon per square meter annually, is approximately six times higher than in the North Sea, establishing the Benguela Current Large Marine Ecosystem (BCLME – Fig. 1) as one of the most productive ocean areas globally (Shannon and O'Tolle 2003; Shillington et al. 2006). At the southern end of the BCLME area lies the crucial oceanic region - the Agulhas Bank, where the warm Indian Ocean converges with the cold Atlantic Ocean, serving as the natural boundary between ocean currents from the Atlantic, Indian, and Southern oceans. Convergence of the currents gives rise to one of the world's most turbulent waters, fueling the nutrient cycle crucial for marine life. The Agulhas Current induces coastal dynamic upwelling in the vicinity of Port Alfred and Port Elizabeth, bringing nutrient-rich water to the surface (Lutjeharms et al. 2000). On a global scale, the Agulhas Current governs the exchange of heat and salt between the Indian and Atlantic Oceans and plays a role in the Atlantic meridional overturning circulation (Lutjeharms 2006; Guerra et al. 2018). Such an extraordinary system offers a great opportunity to enhance our understanding of how marine taxa regulate the mineralization process at various taxonomic levels and temperature ranges to ascertain the primary sources of biomineralization control. The presented research aims to investigate whether environmental or biological control is the major mechanism governing bryozoan mineralization along the South African coast, a region characterized by contrasting oceanographic conditions. We hypothesize that temperature

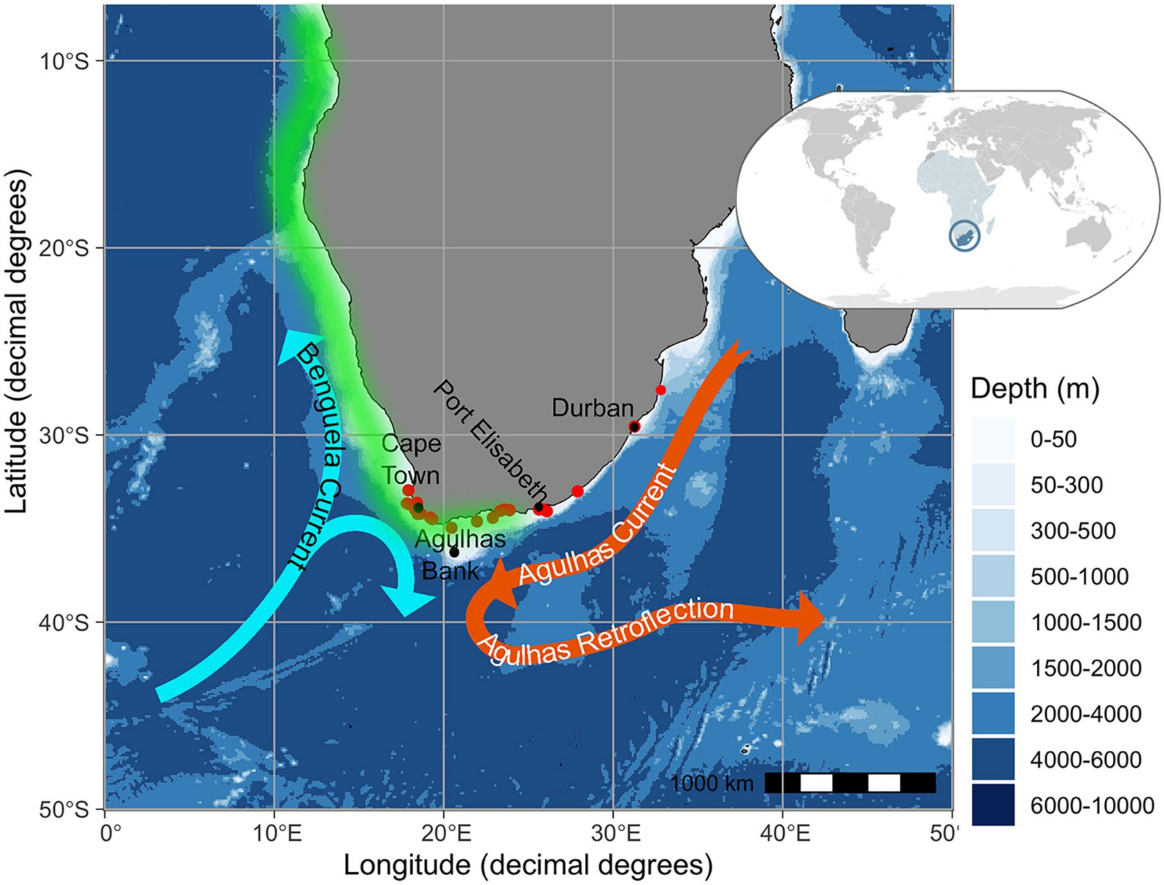


Fig. 1 Map of South African coast with sampling stations (red). The major Benguela (blue) and Agulhas currents (orange) converge at the Agulhas Retroflection; both are included in the Benguela Current Large Marine Ecosystem (BCLME, green)

gradients followed by biological factors are the strongest predictors of the mineralogical and geochemical composition of bryozoan skeletons along the South African coast. Additionally, this research provides new, lacking data on the mineralogical (calcite vs. aragonite) and geochemical (Mg content in calcite) composition of bryozoans from subtropical areas. These data significantly contribute to global trends in biomineralization patterns, particularly enhancing our understanding of the mechanisms behind bryozoan skeletal biomineralization.

Materials and methods

Collection of research material

Research material (388 analyzed samples) was systematically gathered during seven expeditions (03-04.1999; 01-10.2000; 06.2001; 04.2008; 10.2009; 04-05.2011; 09.2017) conducted along the South African coast, spanning from 29.263°S; 16.87°E to 27.540°S; 32.677°E (Fig. 1; Table 1). The sampling strategy encompassed a range of coastal environments, extending from shallow waters near the shore (by divers) to deeper regions (by dredge use) reaching 200 m. Whenever feasible, a substantial number of individuals belonging to a specific species were gathered from designated sampling locations or across regions, enhancing statistical robustness. Colonies were identified to the lowest taxonomic levels with the use of an optical microscope and referencing taxonomic guides (e.g. Hayward and Cook 1979, 1983; Florence et al. 2007). Taxonomic nomenclature was cross-checked with the World Register of Marine Species (WoRMS, 2023) to ensure accuracy and standardization. To preserve the integrity of skeletal mineralogy, specimens underwent no chemical cleaning or treatment, as such processes can potentially introduce analytical biases. In the case of encrusting bryozoans, preceding analytical procedures, colonies were dissected from their substrates (e.g. rocks, kelps, mussels) using a scalpel blade. Colonies were cleaned of any associated organisms, such as foraminifera and polychaete tubes, to prevent mineralogical contamination. Whenever possible, analyses were conducted on the unfouled tips of erect colonies. In the case of encrusting species with small colony sizes, the entire colony was used.

Table 1 Sampling station coordinates and environmental data (temperature, salinity, dominant current)

Sampling site	Latitude [decimal degrees]	Longitude [decimal degrees]	S [PSU]	T [°C]	Current
Sodwana Bay	– 26.83 to – 27.52	31.82 to 32.49	35.6	20.44	Agulhas
Durban Salt Rock	– 29.55	31.26	35.5	23.34	Agulhas
Nahoon Reef	– 33.02	27.90	35.5	22.64	Agulhas
Gqeberha	– 33.98	25.87	35.6	19.86	Agulhas
Nature’s Valley Tsitsikamma	– 33.98	23.56 to 23.88	35.5	19.25	Agulhas
Humewood beach	– 33.98	25.62	35.5	20.55	Agulhas
Plettenberg Bay	– 34.06	23.33	35.5	18.83	Agulhas
MKB27	– 34.08	26.99	35.5	17.17	Agulhas
SAM	– 34.43	22.89	35.5	13.57	Agulhas
SAM	– 34.62	21.95	35.4	14.03	Agulhas
AN0170	– 34.62	22.75	35.4	13.97	Agulhas
AN0172	– 34.93	23.28	35.7	12.46	Agulhas
AN0186	– 34.1	24.98	35.5	18.98	Agulhas
AN0190	– 34.12	26.03	35.5	17.10	Agulhas
AN0232	– 34.92	20.87	35.4	14.55	Agulhas
Saldanha Bay	– 32.96	17.91	35.3	16.37	Benguela
Paternoster Wreck	– 33.66	17.82	35.0	10.90	Benguela
Nahoon Reef	– 33.70	17.94	35.2	11.48	Benguela
Oudekraal	– 33.99	18.31	35.4	14.56	Benguela
Justin’s Caves	– 33.99	18.35	35.5	17.22	Benguela
Sandy Bay	– 34.02	18.33	35.5	16.69	Benguela
Bakoven	– 34.10	18.42	35.5	17.47	Benguela
Castle Rock	– 34.18	18.46	35.5	17.50	Benguela
AN0183	– 33.93	18.37	35.5	17.22	Benguela
False Bay	– 34.20 to – 34.21	18.46 to 18.64	35.5	16.48	Mixed
Hermanus	– 34.42 to – 34.43	19.21 to 19.22	35.5	17.43	Mixed
MB	– 34.5	19.33	35.5	17.33	Mixed

Mineralogical analyses

Mineralogical analyses were conducted at the Natural History Museum in London, using an Enraf-Nonius X-ray diffractometer (XRD), equipped with an INEL 120º-curved position-sensitive detector and a copper X-ray source. The copper source was operated under conditions of 40 kV and 30 mA, with a tilt angle of 4.7° between the source and the sample. A horizontal slit system, set to 0.14 mm, confined the X-ray beam to pure copper Kα1. To ensure accuracy, an internal standard (NaCl) was added to the samples for the correction of potential sample displacement. During measurements, the samples underwent rotation to enhance the randomness of grain orientations in the X-ray beam. The 2-theta linearity of the detector was calibrated using Y_2O_3 (yttrium (III) oxide) (99.9% BDH Laboratory Chemicals) and reference data from Mitric et al. (1997). The calibration curve was fitted using a least-squares cubic spline function. External standards of calcite (Iceland spar) and aragonite (BM53533) were collected for the mineral quantification. The proportion of calcite and aragonite of the bryozoan skeletons was derived by scaling the peak intensities of the standard patterns to the sample patterns. The mol percentage (mol%) of $MgCO_3$ in calcite was calculated by measuring the position of the d104 peak. There is a linear relationship between the position of d104 and the Mg content in calcite, as shown by Mackenzie et al. (1983), within the range of 0 to 20 mol% $MgCO_3$. The precision of this composition information is within 2%, verified on a well-calibrated instrument (Kukliński and Taylor 2009).

Integration of taxonomic and environmental data

Taxonomic and occurrence data for bryozoans from the current study were linked with environmental data. Marine data layers under present-day benthic conditions, including sea temperature and salinity, were extracted to R studio from Bio-ORACLE (Tyberghein et al. 2012; Assis et al. 2017). Bio-ORACLE is a set of GIS rasters available for global-scale applications at a spatial resolution of 5 arcmin (approximately 9.2 km at the equator; Tyberghein et al. 2012; Assis et al. 2017). In addition to the new data generated in this study, we incorporated relevant literature data on cheilostome and cyclostome bryozoans worldwide for comparative analysis (Cheetham et al. 1969; Sandberg 1971; Poluzzi and Sartori 1975; Borishenko and Gontar 1991; Bone and James 1993; Smith et al. 1998; Crowley and Taylor 2000; Steger and Smith 2005; Smith et al. 2006; Wejnert and Smith 2008; Kukliński and Taylor 2009; Smith and Clark 2010; Smith and Girvan 2010; Smith and Lawton 2010; Smith 2014; Krzemińska et al. 2016, 2022; Taylor et al. 2016; Loxton et al. 2018; Iglikowska et al. 2020; Piwoni-Piórewicz et al. 2020, 2024; Figuerola et al. 2023). To facilitate comparisons, data previously reported as weight% (wt%) $MgCO_3$ were converted to mol% $MgCO_3$.

Statistical analyses of mineralogical and geochemical data

The Shapiro–Wilk test was applied to assess the normality assumption of the data. Given the violation of parametric post-hoc testing criteria due to unequal sample sizes and heterogeneous variance among datasets, nonparametric methods were employed. To ascertain the significance of differences in mol%$MgCO_3$ across families and between suborders, a Kruskal–Wallis test was used, followed by Dunn-Bonferroni post-hoc tests. A correlation between mineralogy, Mg-calcite content, and environmental parameters such as temperature and salinity were tested with Spearman's rank correlation coefficients. Statistical significance was set at $p < 0.05$. All statistical procedures, data analyses, and figures were implemented and generated with R studio (Posit team 2023).

Results

Overall mineralogy and geochemistry of South African bryozoans

In the current study on South African bryozoans, 101 taxa (388 samples) were found to secrete all types of carbonate skeletons: fully calcitic, bimineralic, and aragonitic. The majority of specimens – 70% (Fig. 2a), including all cyclostomatids, was exclusively calcitic. The following four species were found to produce dual-calcite (presence of two distinct calcites within a sample: dominant low-Mg calcite and subdominant high-Mg calcite): *Escharoides contorta* ($n=2$; mean mol% $MgCO_3=4.5\pm3.54$ SD), *Margaretta levinseni* ($n=4$; 6.39 mol% $MgCO_3\pm4.76$), *Menipea triseriata* ($n=2$; 4.48 mol% $MgCO_3\pm4.06$), and *Cellaria* sp. ($n=4$; 5.64 mol% $MgCO_3\pm3.56$; Appendix 1). It is noteworthy to mention that the presence of the two distinct minerals was not ubiquitous across all specimens of the specific species, but rather sporadic in occurrence.

Bimineralic skeletons represent the second-largest category, comprising 25.9% of all specimens ($N=100$; 33 species) and contain only cheilostomatids. Specimens secreting monomineral aragonitic carbonate structures account for 4.28% ($N=17$, 13 species, Fig. 2a), e.g., individuals

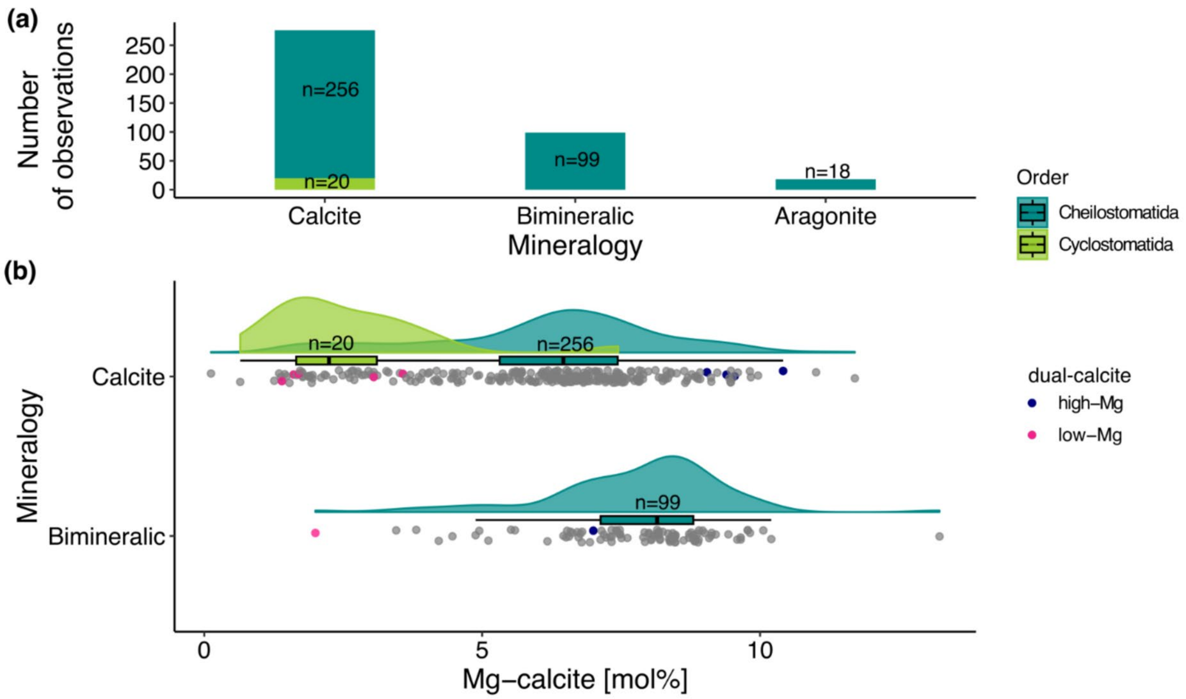


Fig. 2 Frequency distribution of mineral types in Cyclostomatida and Cheilostomatida **(a)**; Raincloud plot showing the distribution of Mg-calcite in calcitic and bimineralic skeletons. Dual-calcite data were marked with colors: - pink for low-Mg and dark blue for high-Mg calcite. The box plots show the first and third quartiles around the median, the tail indicates range **(b)**

belonging to *Adeonella* spp, *Adeonellopsis meandrina*, *Adeonellopsis* sp., and *Membranipora rustica*.

The distribution of magnesium content in bimineralic bryozoans exhibits a clear unimodal pattern (Fig. 2b), with a median of 8.2 mol% $MgCO_3 \pm 1.6$ SD (± standard deviation), significantly higher than in calcitic skeletons (6.4 mol% $MgCO_3 \pm 2.2$; Fig. 2b).

Distribution of Mg-calcite varied among cheilostomes, both within species (e.g., *Menipea triseriata*) and between species (Fig. 3). At higher taxonomic levels, such as between families, statistically significant differences in mol% $MgCO_3$ were observed (Kruskal-Wallis test, chi-squared = 168, df = 25, $p < 0.05$ post-hoc Dunn-Bonferroni test - Table 2a). Similarly, significant differences in mol% $MgCO_3$ were identified between suborders (Kruskal-Wallis chi-squared = 47, df = 5, $p < 0.05$, post-hoc Dunn-Bonferroni test - Table 2b).

Regional variability in bryozoan mineralogy with environmental parameters

We utilized heatmap plots to visualize the distribution of calcite (Fig. 4a) and Mg-calcite (Fig. 4b) across families and three ecological zones determined by the Benguela, Agulhas, and a mixture of both currents. The analysis revealed that there was no discernible pattern related to the currents or the environmental conditions associated with them, regarding the content of calcite and Mg-calcite. However, mineralogy and levels of Mg-calcite were specific to certain taxonomic groups. The family Adeonidae was found to be predominantly aragonitic with high Mg-calcite, regardless of the current and contemporary environmental conditions. The same pattern was consistent across most families (e.g., Thalamoporellidae, Calwellidae, Crisiidae) with certain exceptions in the Flustrina (e.g., Smittinidae, Lanceoporidae, Gigantoporidae, Cribrilinidae) and Membraniporina (Membraniporidae) sub-orders. Notably, all variability observed was found within these two sub-orders.

Regional variability of mineralogy and magnesium content was correlated with environmental variables, i.e., seawater temperature [°C] and salinity in practical salinity units [PSU]. The findings reveal low values of Spearman’s rank correlation coefficients across both examined parameters, as illustrated in the correlation matrices (Fig. 5). Notably, no significant correlation was observed between mineralogy and environmental factors.

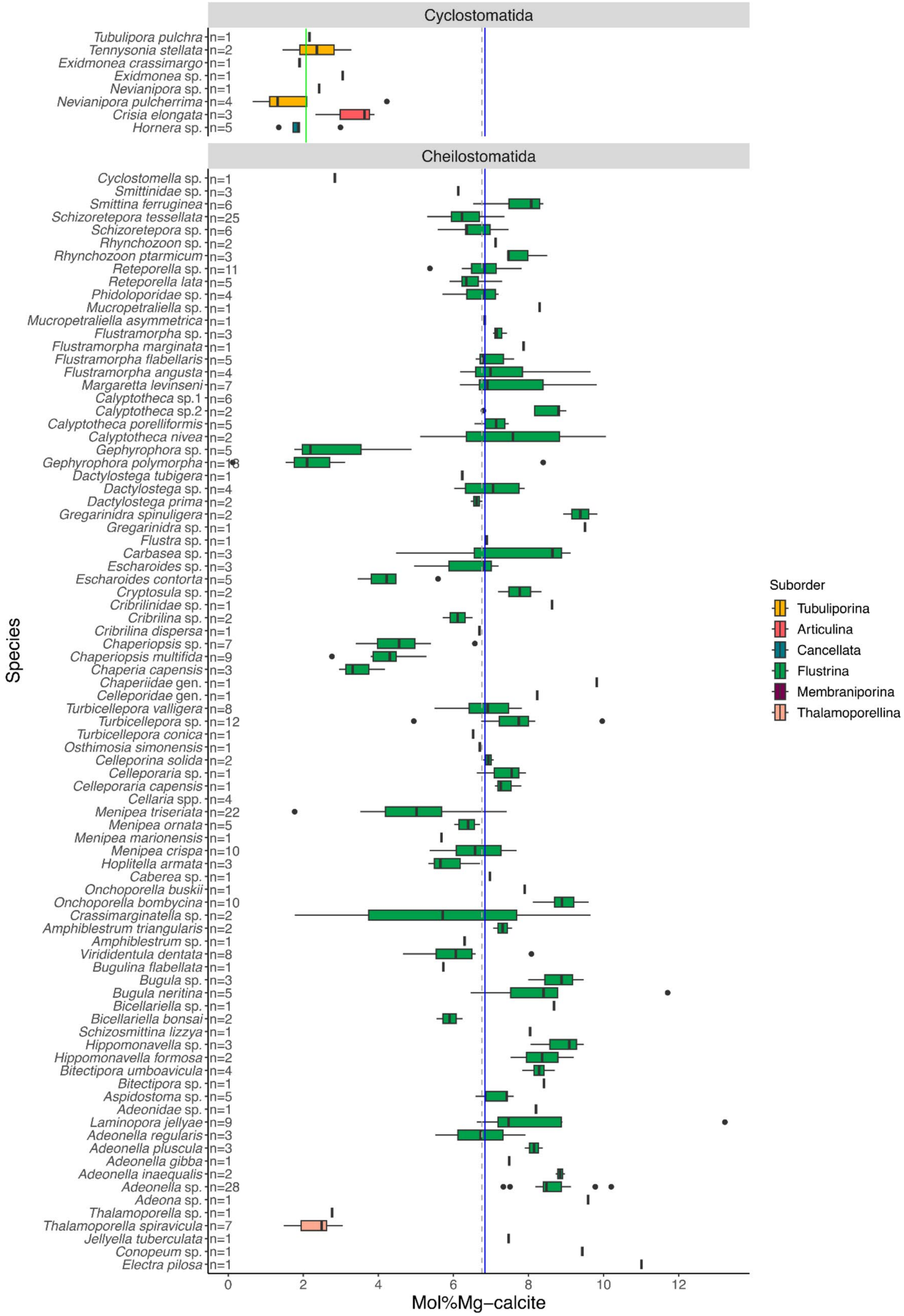


Fig. 3 Species-specific mol% $MgCO_3$ in skeletal calcite. Boxes show standard deviation around the median (mid-line), the tail indicates range and dots are outliers. The vertical grey dashed line indicates the median mol% $MgCO_3$ for all bryozoans, the blue line represents the median mol% $MgCO_3$ for cheilostomatids, while the green line shows the median value of mol% $MgCO_3$ for cyclostomatids

Table 2 Statistically significant differences in mol%$MgCO_3$ indicated by Dunn-Bonferroni post-hoc test, between pair of means of (a) families and (b) suborders. Z is a value of each pairwise comparison, p is a significance level (when $p < 0.05$)

a) Families	Z	*p*	a) Families (cont.)	Z	*p*
Adeonidae - Candidae	5.835	< 0.001	Calwelliidae - Gigantoporidae	6.730	< 0.001
Bitectiporidae - Candidae	4.909	< 0.001	Celleporidae - Gigantoporidae	5.201	< 0.001
Calwelliidae - Candidae	5.447	< 0.001	Electridae - Gigantoporidae	3.871	0.035
Adeonidae - Chaperiidae	5.943	< 0.001	Flustridae - Gigantoporidae	4.952	< 0.001
Calwelliidae - Chaperiidae	5.876	< 0.001	Adeonidae - Horneridae	4.439	0.003
Celleporidae - Chaperiidae	4.078	0.015	Bitectiporidae - Horneridae	4.654	0.001
Adeonidae - Diaperoeciidae	4.439	0.003	Calwelliidae - Horneridae	5.029	< 0.001
Bitectiporidae - Diaperoeciidae	4.712	0.001	Flustridae - Horneridae	3.857	0.037
Adeonidae - Exochellidae	3.891	0.032	Gigantoporidae - Margarettidae	-4.261	0.007
Chaperiidae - Flustridae	-4.181	0.009	Gigantoporidae - Microporellidae	-4.485	0.002
Diaperoeciidae - Flustridae	-4.017	0.019	Adeonidae - Phidoloporidae	4.160	0.010
Adeonidae - Gigantoporidae	7.073	< 0.001	Bitectiporidae - Phidoloporidae	3.827	0.042
Bitectiporidae - Gigantoporidae	6.257	< 0.001	Calwelliidae - Phidoloporidae	4.377	0.004
Bugulidae - Gigantoporidae	4.679	< 0.001	Gigantoporidae - Phidoloporidae	-4.179	0.009
b) Sub-orders	**Z**	**p**	**b: Sub-orders** (cont.)	**Z**	**p**
Cancellata - Flustrina	−3.022	0.038	Membraniporina - Thalamoporellina	3.032	0.036
Flustrina - Thalamoporellina	3.867	0.002	Flustrina - Tubuliporina	4.407	< 0.001
Membraniporina - Tubuliporina	3.190	0.021			

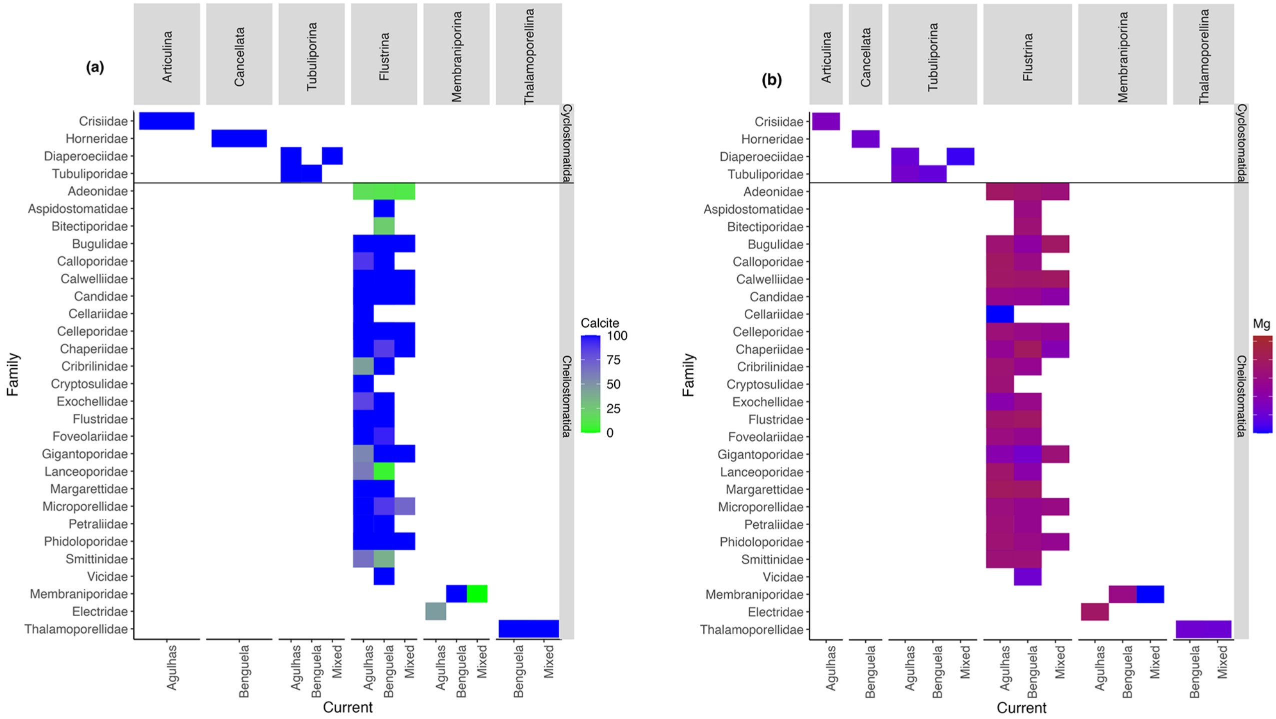
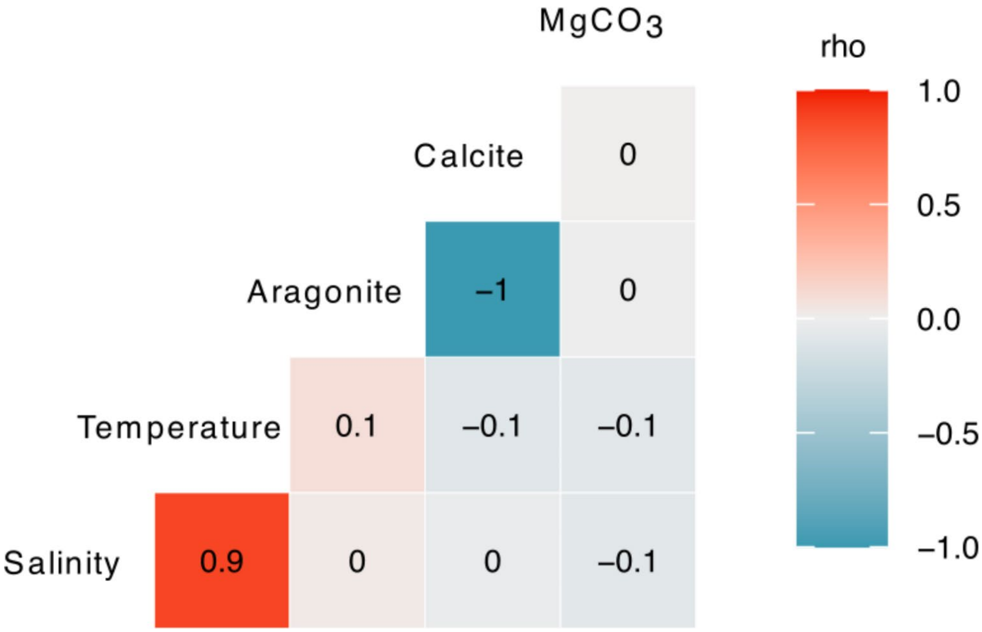


Fig. 4 Heatmap plots showing the distribution of (a) mineral forms from 100% for monomineralic-calcitic skeletons to 0% for fully aragonitic skeletons, through bimineral ones, and (b) the distribution of Mg-calcite between families and across Agulhas, Benguela and mix of both currents

Fig. 5 Correlation matrix showing the relationship between environmental variables (temperature, salinity), alongside skeletal mineralogy (calcite, aragonite content) and Mg-calcite in bryozoans



Discussion

Overall mineralogy and geochemistry of South African bryozoans

Bryozoan mineralogy from subtropical and moderate climates along South Africa's (SA) coast is one of the missing pieces in our knowledge about global patterns in skeletal mineralogy of this phylum. Newly presented data disclose the carbonate composition of approximately 40% of the known bryozoan species in South Africa (based on Florence et al. 2007). Within the bryozoan biota of South Africa, a diverse array of carbonate skeletons is produced, encompassing fully calcitic, bimineralic, and aragonite-based forms. Moreover, a limited number of species exhibit dual mineralogical compositions, characterized by both low-Mg and high-Mg calcite. Such variation is not consistently observed across all specimens of the same species; instead, it appears sporadically (Fig. 2b, Appendix 1). The presence of dual-calcite is likely related to astogeny (Smith et al. 1998; Smith and Lawton 2010). The low-Mg calcite constitutes the primary mineral phase and is deposited during the initial stages of biomineralization as the zooids grow (Smith et al. 1998, 2006; Smith and Lawton 2010). The high-Mg calcite is potentially added as a secondary strengthening layer in older zooids (secondary calcification), as in e.g. *Melicerita chathamensis* (Smith and Lawton 2010), to reinforce the structure or is deposited at newly formed branching internodes (Batson et al. 2020). Several *Cellaria* species also deposit secondary calcification later during biomineralization (Achilleos et al. 2020).

Notably, aragonite-containing skeletal frameworks, whether pure or as an admixture, constitute a minority (4–25%) and are confined to the cheilostomatids. About 70% of cheilostomatids and 100% cyclostomatids are fully calcitic (Fig. 2a). As suggested by Smith et al. (2006), the mineralogical complexity observed in cheilostomatids may be linked to the post-Coniacian evolution of the ascophoran frontal shield, frontal budding, secondary calcification, and robust colony growth (McKinney and Jackson 1991; Gordon and Voigt 1996; Gordon 2000). Alternatively, mineralogical diversification might be a by-product of the extensive radiation of cheilostomatids (Smith et al. 2006).

The distribution of individual minerals aligns with global data presented by Smith et al. (2006) (75% calcite – C; 20% bimineralic – B; 5% aragonite – A) and Figuerola et al. (2023) (72% – C; 22% – B; 5.5% – A). However, the addition of new data, particularly from the tropics and subtropics (65% – C; 19.5% – B; 14.8% – A; see Piwoni-Piórewicz et al. 2024), or a comparison of our results on a regional scale, such as with Scotland (64% – C; 32% – B; 4% – A; Loxton et al. 2018), reveals less congruence in the percentage distribution of specific mineral forms. This discrepancy underscores the influence of local environmental conditions, taxonomical composition variations, or disparities in the number of analyzed samples.

The presence of aragonite was expected among South African cheilostomatids, considering its prevalence at lower latitudes (Smith et al. 2006; Smith 2014; Krzemińska et al. 2016; Taylor et al. 2016; Piwoni-Piórewicz et al. 2020, 2024; Figuerola et al. 2023). Aragonite is less thermodynamically stable than calcite and more prone to dissolution particularly in cold water (e.g. Fabry et al. 2008), and thus appears more commonly as a skeletal component in bryozoans at low latitudes. Our results validate the existence of the latitudinal gradient. Consequently, sea temperature is a potential predictor of aragonite presence as well as higher magnesium content in bryozoan skeletons, particularly regarding the region of colony development (Piwoni-Piórewicz et al. 2024).

Our results revealed that all cyclostomatids exhibit a relatively narrow range of low-Mg calcite (Fig. 3), albeit acknowledging the limited number of cyclostomatid individuals in our samples. Cyclostomatids are known to consistently produce low-Mg calcites in South Africa and globally (Smith et al. 2006; Taylor et al. 2014), which is supported by our results. In contrast, most SA cheilostomatids build 'more soluble' skeletons with higher levels of $MgCO_3$ (> 7 mol% $MgCO_3$, Fig. 3). The variability of Mg-calcite among South African cheilostomatids is pronounced at all taxonomic levels, a phenomenon well-documented in the literature (Poluzzi and Sartori 1975; Smith et al. 1998). For instance, in *Menipea triseriata* (Candidae) Mg content ranged from 1.8 to 7.4 mol% $MgCO_3$, across 24 examined individuals. Contrary, the narrow Mg-calcite range was found in species such as *Schizoretepora tessellata* (5.3 to 7.4 mol% $MgCO_3$, $n=25$, family: Phidoloporidae) or *Onchoporella bombycina* (8.1 to 9.6 mol% $MgCO_3$, $n=10$, family: Calwelliidae). Although *Crassimarginatella* sp. showed one of the widest ranges of mol% $MgCO_3$, as illustrated in Fig. 3, the sample size of analyzed specimens ($n=2$) is insufficient to conclude about its true variability. The wide range of Mg content observed in cheilostomatids can be attributed to several factors, including astogeny (Smith and Lawton 2010), secondary calcification (Smith and Lawton 2010; Achilleos et al. 2020), wound repair (Batson et al. 2020), and environmental stress such as e.g. high CO_2 conditions (Swezey et al. 2017).

The suborder Flustrina ($n=361$), was characterized by significant differences in Mg-calcite between families (Table 2). Similarly, the suborder Membraniporina exhibits considerable variability in mol% $MgCO_3$ between and within families, albeit it is represented with a smaller sample size ($n=4$). Our results align with previous findings that both Flustrina and Membraniporina contain families and species with some of the highest degrees of mineralogical variability among cheilostomatids (Smith et al. 2006). Furthermore, Flustrina is recognized for its uniqueness and complexity in mineralogy, including free-living aragonitic families, dual-calcite skeletons, and within-genus mineralogical variability, features not found elsewhere (Smith et al. 2006). In South Africa, all types of mineralogy (calcite, bimineralic, aragonite) were found only in the Flustrina and Membraniporina suborders. According to Taylor et al. (2014), aragonite occurs in several major groups of cheilostomatids (Malacostegina - now Membraniporina, Flustrina, Umbonulomorpha, and Lepraliomorpha - two infraorders belonging to Flustrina), while being absent, or at least unrecorded, in some other groups (Inovicellina, Scrupariina, Acanthostegina, Hippothoomorpha). Based on literature data and our results, it can be indicated that mineralogy and taxonomic affiliation, are closely linked. Additionally, the median level of $MgCO_3$ in bimineralic skeletons was significantly higher than in purely calcitic skeletons. Magnesium is a prevalent impurity in calcite and exerts a non-linear impact on the solubility of Mg-calcites. It is also known to play a role in regulating the calcite/aragonite polymorphism (e.g., Koskamp et al. 2021). Dissolved Mg ions inhibit the nucleation of calcite, promoting aragonite deposition from supersaturated seawater. Therefore, the higher amount of Mg-calcite in bimineralic skeletons is likely related to such regulatory mechanisms. Our results, along with previous studies, confirm that taxonomic affiliation, and hence biological control have a substantial impact on skeletal carbonate mineralogy in marine bryozoans (Smith et al. 2006; Taylor et al. 2016; Loxton et al. 2018; Piwoni-Piórewicz et al. 2024). However, it is important to note that our comparisons were based on taxonomic affiliations rather than phylogenetic analysis, due to the lack of a well-sampled phylogeny.

Regional variability in bryozoan mineralogy with environmental parameters

The heat plot analysis revealed that the mineralogy (Fig. 4a) and levels of Mg-calcite (Fig. 4b) were specific to certain taxa or more specifically to certain taxonomic groups, rather than to the environmental parameters related to Benguela and Agulhas currents or a mixture of both. It was further confirmed by low correlation coefficients between mineralogy/magnesium content and temperature, or salinity, as shown in the correlation matrix (Fig. 5). The apparent lack of correlation between geochemistry, mineralogy, and temperature may be additionally influenced by the limited number of samples collected from the highest-temperature areas along the east seaboard of South Africa. The distribution of pure aragonite skeletons reveals that over half of these specimens (10 out of 17) originated from subtropical Sodwana Bay ($n=9$) and Durban ($n=1$), where water temperatures typically exceed 20 °C. The remaining single specimens were collected from several locations in cool temperate (14–15 °C; Paternoster and nearby Cape Town) or warm temperate areas with water temperatures between 16 and 18°C. Consequently, the potential influence of temperature on mineralogy, specifically aragonite content in bryozoan skeletons, cannot be ruled out. It is also possible that the variability among investigated environmental parameters in the study area was too small to generate any significant signal in mineralogical patterns. Previous studies, such as Figuerola et al. (2023) or Piwoni-Piórewicz et al. (2024) have indicated that seawater temperature significantly drives variations in bryozoan mineralogy on a global scale. These results suggest that to discern a strong signal in mineralogy, the temperature differences need to be substantial. Both cheilostome and cyclostome bryozoans typically precipitate their skeletons with organized, consistent, and highly complex ultrastructure (Taylor and Weedon 2000; Grenier et al. 2023, 2024), similar to brachiopods or corals (e.g. Simonet Roda et al. 2022). Additionally, the bryozoan skeleton is secreted beneath soft tissues and is not in direct contact with seawater (Smith et al. 2006), with the degree of control varying across species. Consequently, the results can yield remarkably sophisticated, species-specific products that provide specialized biological and ecological functions. Studies on other calcifiers, e.g., Arctic gastropods, speculated that differences in shell element concentrations can be driven by species-specific selective incorporation of elements into shells and the bioavailability of those elements in the ambient environment (Iglikowska et al. 2023). Among Arctic echinoderm skeletons, Mg concentration was characteristic for particular echinoderm classes or was even species-specific. These results strongly imply that biological factors play an important role in controlling the levels of Mg-calcite in the skeletons of the studied individuals (Iglikowska et al. 2017). Yet, due to contrasting results from several studies, understanding the extent of environmental influence on skeletal composition remains a puzzle. Thus, further investigations into the influence of environmental parameters (e.g., pCO_2, stable isotopes of oxygen $\delta^{18}O$ and carbon $\delta^{13}C$) are necessary to enhance our understanding of the range of environmental effects on mineralogy and geochemistry among calcifiers generally, and bryozoans specifically.

Overall, our results do not provide full support for the entire hypothesis that environmental factors (particularly temperature) influence the mineralogical composition of bryozoan skeletons along the South African coast. However, significant variability in the mineralogical composition of bryozoan skeletons within different taxonomic groups and suborders, suggests that biological factors may play a more significant role in modulating bryozoan skeletal carbonate mineralogy, aligning with the latter part of our hypothesis. Moreover, our results underscore the complexity of biomineralization processes and suggest a potential interplay between environmental and biological factors in shaping biomineralization patterns observed in marine calcifiers. The mechanisms driving bryozoan biomineralization and their response to changing environmental conditions are still unclear and need further research.

Conclusions

The newly presented data disclosed the carbonate composition of approximately 40% of the known bryozoan species in South Africa, revealing a prevalence of fully calcitic skeletons among cheilostomatids and cyclostomatids. Our results align with global trends, showing a predominance of calcite, followed by bimineralic and aragonite compositions. The presence of aragonite in South African cheilostomatids supports the latitudinal gradient hypothesis, wherein aragonite becomes more prevalent towards lower latitudes due to its stability in warmer waters. Furthermore, our study revealed significant variability in magnesium content among South African cheilostomatids, with cyclostomatids consistently producing low-Mg calcite. Our results indicated that biological control over the biomineralization process in bryozoans is substantial. Different bryozoan clades and species may exhibit unique responses to changing ocean parameters, reflecting their evolutionary history. Although our analyses failed to reveal any significant correlation between skeletal composition and environmental parameters, the influence of temperature cannot be completely neglected due to existing latitudinal patterns. Understanding the interplay between phylogeny, temperature, magnesium content, and mineralogy is crucial for predicting the response of bryozoans to changing oceanic conditions.

In conclusion, our study provides valuable insight into the mineralogical diversity of bryozoans in South Africa, highlighting the relationship between clade membership, environment, and skeletal composition in these important marine organisms.

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Data availability All data supporting the findings of our study are available within the paper and its Supplementary Information (Appendix 1).

Declarations

Competing interests The authors have no relevant financial or non-financial interests to disclose.

Ethics approval No approval of research ethics committees was required to accomplish the goals of this study because experimental work was conducted with an unregulated invertebrate species.

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