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Skeletal Mg content in common echinoderm species from Deception and Livingston Islands (South Shetland Islands, Antarctica) in the context of global change

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ABSTRACT

Echinoderms with high levels of magnesium (Mg) in their skeletons may be especially sensitive to ocean acidification, as the solubility of calcite increases with its Mg content. However, other structural characteristics and environmental/biological factors may affect skeletal solubility. To better understand which factors can influence skeletal mineralogy, we analyzed the Mg content of Antarctic echinoderms from Deception Island, an active volcano with reduced pH and relatively warm water temperatures, and Livingston Island. We found significant interclass and inter- and intraspecific differences in the Mg content, with asteroids exhibiting the highest levels, followed by ophiuroids and echinoids. Specimens exposed to hydrothermal fluids showed lower Mg levels, which may indicate local environmental effects. These patterns suggest that environmental factors such as seawater Mg^{2+}/Ca^{2+} ratio and temperature may influence the Mg content of some echinoderms and affect their susceptibility to future environmental changes.

1. Introduction

About 30 % of the anthropogenic carbon dioxide (CO_2) released to the atmosphere is absorbed by the oceans, leading changes in seawater CO_2 chemistry, in a process known as ocean acidification (OA) (Feely et al., 2004; Doney et al., 2009). Ocean acidification results in the lowering of seawater pH and carbonate ion (CO_3^{2}) concentration, which reduces the calcium carbonate ($CaCO_3$) saturation state (Ω), likely limiting biomineralization and promoting skeletal dissolution of many marine calcifiers ($CaCO_3$ shell and skeleton-building organisms) (Orr et al., 2005; Kroeker et al., 2010, 2013). This effect may be even exacerbated in Southern Ocean (SO) due to its increased $CaCO_3$ solubility at low temperatures (Fabry et al., 2009). These environmental conditions together with the historical absence of shell-crushing predators in Antarctica probably led to several SO calcifiers to develop thinner shells and skeletons and these species could thus show early OA negative impacts (Aronson and Blake, 2001; McClintock et al., 2008, 2009).

Carbonate shells and skeletons are mainly made of two $CaCO_3$ minerals (calcite and aragonite), with magnesium (Mg) frequently replacing some of the Ca^{2+} ions in calcite (Weiner and Dove, 2003). The skeletal Mg content is commonly categorized as low (LMC; <4 mol% $MgCO_3$), intermediate (IMC; 4–8 mol%), and high (HMC; >8 mol%) (Rucker and Carver, 1969). These minerals have different physical and chemical properties. Aragonite and HMC are more soluble than calcite and HMC may be even more soluble than aragonite. It is thus expected that some taxa secreting aragonitic and HMC shells or skeletons may be vulnerable to future carbonate chemistry changes (Andersson et al., 2008; Figuerola et al., 2021, 2023). However, structural characteristics such as crystal size, mineral stability and presence of impurities may also affect their skeletal solubility (Morse et al., 2007; Dery et al., 2014).

The skeletal Mg content may be controlled by environmental (e.g., temperature, salinity, pH, seawater Mg^{2+}/Ca^{2+} ratio and seawater saturation state) and biological factors (e.g., diet, growth rate and life span) (Mackenzie et al., 1983; Andersson et al., 2008; Borremans et al., 2009; Asnaghi et al., 2014; Kołbuk et al., 2020, 2021). Previous studies showed a general trend of increasing aragonite and Mg toward lower

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latitudes in different marine calcifying taxa (e.g., Lowenstam, 1954; Taylor et al., 2009; McClintock et al., 2011). Similarly, Smith et al. (2016) observed this trend in different life stages (i.e., juveniles and larvae vs. adults) and skeletal elements (i.e., spines and tooth) of echinoids. This pattern is generally attributed to an increase in Mg content with seawater temperature but has yet to be rigorously tested in most taxonomic groups (Chave, 1954; Mackenzie et al., 1983). In the case of bryozoans, Figuerola et al. (2023) recently showed that these patterns are consistent with the hypothesis that seawater temperature is likely a significant driver of variations in bryozoan mineralogy at a global scale. These results suggest that ocean warming could further accelerate skeletal solubility in different marine calcifiers. However, this still remains unclear at local scale as it is expected that responses will be distinct according to local environmental factors and taxa (Kroeker et al., 2010, 2013; Figuerola et al., 2021).

Among marine calcifiers, echinoderms are a phylum divided into the classes Asteroidea, Ophiuroidea, Echinoidea, Crinoidea and Holothuroidea and can be found in a variety of ecosystems and depths (Dubois, 2014). As one of the main marine carbonate producers, echinoderms play a key role in the global carbon cycle (Lebrato et al., 2010). They also play an important ecosystemic role, often being keystone predators in Antarctic benthic ecosystems (e.g., *Odontaster validus* (Koehler, 1906)) (Dayton et al., 1974). Their skeletons show large interspecific variations in their Mg content, ranging from 3 to 43 mol% $MgCO_3$, although most species have HMC skeletons (Chave, 1954; Schroeder et al., 1969). While their HMC skeletons may make echinoderm species more sensitive to skeletal dissolution than other marine calcifiers, the ability of some echinoderms to regulate their calcification rates may also enable them to cope with dissolution due to acidification stress (Wood et al., 2010; Dubois, 2014). Nevertheless, SO species, which inhabit more affected regions by OA, could be less resilient to this climate-related stressor (Fabry et al., 2009; Hancock et al., 2020; Figuerola et al., 2021). In addition, the knowledge about the mineralogical composition of many echinoderm species at SO and how it varies with the environment is still limited (i.e., McClintock et al., 2011; Duquette et al., 2018; Di Giglio et al., 2021).

Therefore, to better understand which factors may influence skeletal mineralogy in Antarctic echinoderms, we analyzed and compared the Mg content in different skeletal body components of nine common Antarctic echinoderm species collected from different sampling stations at Deception Island, an active volcano with fumarolic emissions, reduced pH levels and relatively warm temperatures, and Livingston Island, an adjacent island with no presence of fumarolic emissions and ambient pH levels and temperatures, both from the South Shetland Islands. The specific objectives of this study were: (i) to generate new mineralogical data, (ii) to determine interclass and interspecific variability in the skeletal Mg content among common Antarctic echinoderms species from these islands and (iii) to examine intraspecific differences among populations inhabiting under different environmental conditions, including lower pH and higher temperatures, ambient pH and higher temperatures and ambient pH and temperatures. Additionally, the presence of fumarolic emissions was considered. We hypothesize that we will observe intraclass and intraspecific variations in the Mg content, and interspecific differences in the Mg content among stations due to different local environmental conditions.

2. Material and methods

2.1. Study area

The South Shetland Islands form an archipelago located at the northwest of the Antarctic Peninsula, separated from it by the Bransfield Strait (Bastías et al., 2023). They support a high biodiversity of echinoderm species, with representatives from all five classes (Arnaud et al., 1986). Deception Island is an active volcano characterized by the presence of fumarolic emissions, a low water exchange from outer waters to the inner bay and mainly volcanic sandy sediments (Lenn et al., 2003). Its special environmental features resulting from the volcanic activity, such as low pH levels (decreasing from 7.9–8.0 to 7.4–7.6 in certain areas) or relatively warm water temperatures (2–3 °C), are likely the main drivers that influence the benthic populations of this island (Lovell and Trego, 2003; Angulo-Preckler et al., 2018). Its bottoms are dominated by echinoderms, with the sea star *Odontaster validus*, the brittle star *Ophionotus victoriae* (Bell, 1902) and the sea urchin *Sterechinus neumayeri* (Meissner, 1900) as the most abundant echinoderms species (Arnaud et al., 1998; Barnes et al., 2008). Due to the low pH conditions at Deception Island, a previous study evaluated the acidification effects on physiology, mechanical properties of the skeleton and metal contamination in two echinoderm species (i.e., *O. validus* and *S. neumayeri*) (Di Giglio et al., 2021). However, no studies are available on the low pH effects on their mineralogy in this island. Livingston Island's marine bottoms are composed by diverse substrate types (i.e., mud, rocks, sand and mixed), with high densities of echinoderms on all substrate types (Arnaud et al., 1998; Manjón-Cabeza et al., 2001). Although less studied, Livingston Island also hosts a rich biodiversity of echinoderm species, with *O. validus* and *O. victoriae* as the dominant species (Manjón-Cabeza et al., 2001; Moya et al., 2003). The reduced number of observations of *S. neumayeri* populations is remarkable on this island (*authors' observations*).

2.2. Sample collection and preparation

Antarctic echinoderms from the most representative classes (i.e., Asteroidea, Ophiuroidea and Echinoidea) were collected by SCUBA diving at depths ranging from 4 to 25 m depth (n = 5 per sampling station when possible; Supplementary Material Tables S1 and S2) at different sampling stations from Deception and Livingston Islands (South Shetland Islands, Antarctica; Fig. 1) from January to March 2016 (only 3 specimens of *Odontaster meridionalis* (E.A. Smith, 1876)), 2017 and 2018 and from January to March 2022, respectively (Supplementary Material Table S3). Individuals were then placed into plastic bottles filled with seawater and transported to the laboratory. Once in the lab, the samples were taxonomically identified and then frozen and stored at −20 °C until dissection was conducted.

Different skeletal body components of collected species were dissected following the previous methodology applied by McClintock et al. (2011). For asteroid species (i.e., *O. validus*, *O. meridionalis*, *Diplasterias* sp. 1 and sp. 2, *Lysasterias* sp. and *Perknaster* sp.), one arm was excised and the pyloric ceca and gonads were removed from each specimen. For the ophiuroid species (i.e., *O. victoriae*), one arm and one segment of the central disk were excised. For the regular echinoid species (i.e., *S. neumayeri*), a segment of the test was excised, spines were collected by scraping with a dissection blade and the Aristotle's lantern was extracted. For the irregular echinoid species (i.e., *Abatus* sp.), a segment of the test was excised and spines were collected. Dissected skeletal body components were then dried at 60 °C for 48 h and stored until mineralogical analyses were conducted.

2.3. Environmental descriptors

Seawater pH was quantified (n = 3–10) using a pH–meter (Metrohm 826 pH mobile) from 1 m above the benthos at each sampling station at Livingston Island during austral summer 2022 (Supplementary Material Table S1). Existing environmental data (temperature, pH and sediment data) were compiled from Angulo-Preckler et al. (2017, 2018). These data were measured when the samples used in the present study were collected in 2017 and 2018 in Deception Island. Additionally, temperature data of Livingston Island were extracted from ERDAP (https://coastwatch.pfeg.noaa.gov/erddap/index.html), which correspond to sea surface temperature (SST; °C).

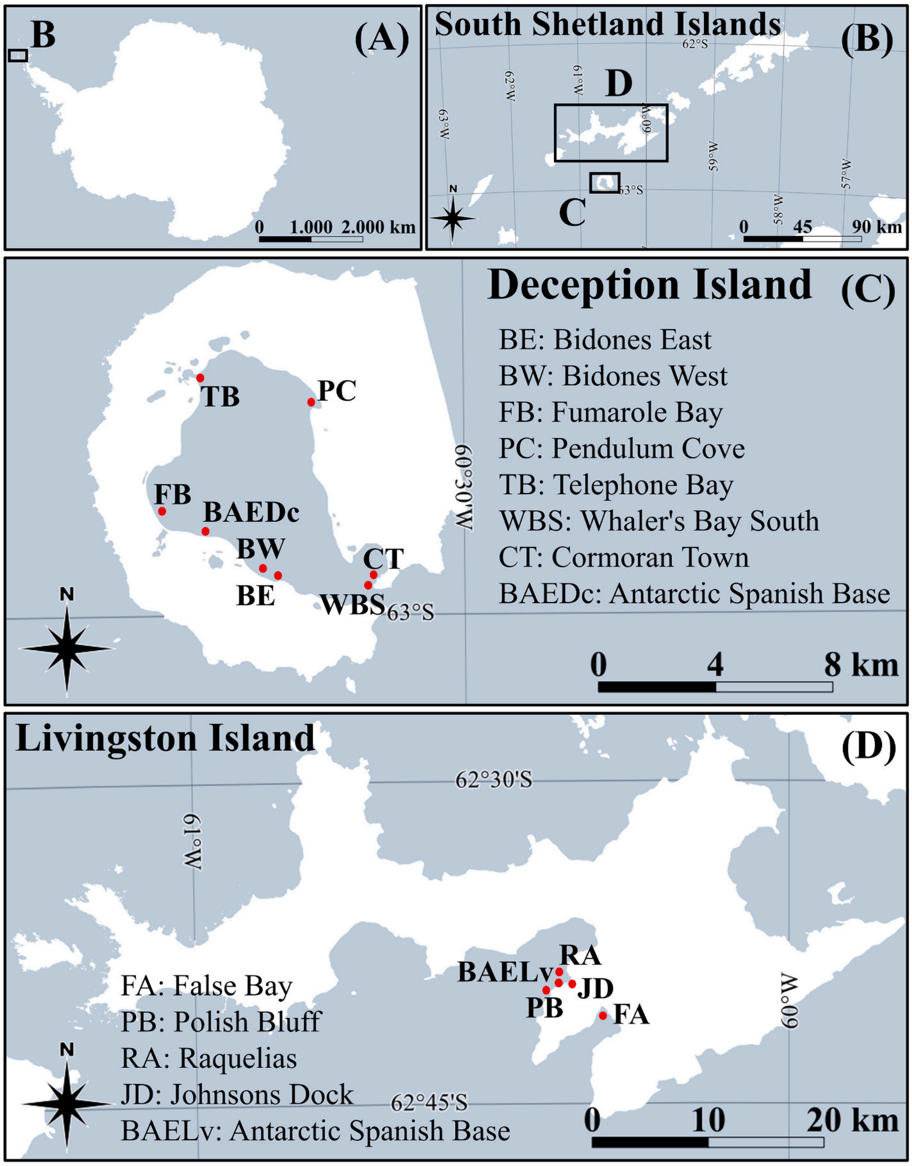

Fig. 1. Map of Antarctica indicating the location of the South Shetland Islands (black square) (A); map of the South Shetland Islands (B); and maps of Deception (C) and Livingston Islands (D) showing sampling stations (solid circles). Maps were made using QGIS software and the Quantarctica package (Matsuoka et al., 2018).

2.4. Mineralogical analyses

Mineralogical analyses were conducted following the previously described methodology (Figuerola et al., 2015). Dry skeletal body components of the echinoderms were powdered in an agate mortar and dispersed in ethanol. Then the sample was transferred at the centre of a 25 × 25 × 2 mm quartz glass slid and left drying at room temperature. The slid was then mounted on a standard sample holder for bulk samples (PW1812/00). The Mg content present in the skeletal calcite of each sample was measured using a *PANalytical X'Pert PRO MPD Alpha1* powder diffractometer in reflection Bragg-Brentano θ/2θ geometry equipped with a X'Celerator detector and a copper X-ray source. Operating conditions of the copper source were 45 kV and 40 mA. Finally, the Mg content (mol% $MgCO_3$; Supplementary Material Table S3) in the skeletal body components of the echinoderm species were calculated obtaining the d104 peak of the calcite and assuming a linear interpolation between $CaCO_3$ and $MgCO_3$ (Chave, 1952). The analytical error obtained from replicate measurements was 0.1 mol% $MgCO_3$.

2.5. Statistical analyses

For statistical analyses, normality (Shapiro-Wilk test) and homogeneity of variances (Levene's test) of the data were tested. When data met the criteria, analyses of variance (ANOVA) and multiple post-hoc comparisons (Tukey's pairwise test) were conducted (Supplementary Material Table S4). Otherwise, a non-parametric Kruskal-Wallis test and multiple post-hoc comparisons (Dunn test) were applied. Firstly, to study differences in the pH and the temperature among islands and stations, two two-way ANOVAs with island (Is) and station (St) nested in Is as factors were conducted. To assess interclass variations in the Mg content among echinoderm classes, a one-way Kruskal-Wallis test with class (Cl) as a single factor, with the levels Asteroidea, Ophiuroidea (arms) and Echinoidea (test), was carried out. Then, to determine interspecific variations among species of the same class, a one-way ANOVA with species (Sp) as a single factor was then carried out within Asteroidea and Echinoidea (test) species (ophiuroids were excluded from this analysis as only one species was collected; i.e., *O. victoriae*). To assess variations among skeletal body components within brittle stars and sea urchins, a one-way ANOVA with skeletal component (Sc) as a single factor was carried out for *O. victoriae*, *S. neumayeri* and *Abatus* species. Lastly, to assess intraspecific differences among islands (Is) and stations (St), two-way ANOVAs with Is and St nested in Is as factors were conducted for *O. validus*, *Lysasterias* sp., *Diplasterias* sp. 2, *O. victoriae* and *S. neumayeri*. Finally, to visualize differences in environmental variables among islands and stations and Mg content among stations, various principal component analyses (PCAs) were conducted (Fig. 2 and Supplementary Material Fig. S1). Prior conducting PCA analyses, data were normalized. Statistical analyses were conducted using the statistical software Rstudio and PRIMER & PERMANOVA 6.

3. Results

3.1. Environmental variables

Deception Island displayed significantly lower pH levels compared to Livingston Island (ANOVA, $p < 0.05$). Furthermore, significant differences in the pH levels were also observed among stations (ANOVA, $p < 0.05$), with Pendulum Cove and Fumarole Bay recording the lowest pH levels. Deception Island also exhibited significantly higher temperatures when compared to Livingston Island (ANOVA, $p < 0.05$). In addition, the PCA results (Fig. 2) of the environmental variables separated the studied stations into four groups: (i) stations with the lowest pH levels and high temperatures (Pendulum Cove and Fumarole Bay), (ii) stations with low pH levels and high temperatures (Bidones (East and West) and Telephone Bay), (iii) stations with ambient pH levels and high temperatures (BAEDc, Whaler's Bay South and Cormoran Town) and (iv) stations with ambient pH levels and temperatures (False Bay, Polish Bluff, BAELv, Johnsons Dock and Raquelias).

3.2. Mineralogical analyses

Our results showed significant differences in the Mg content among the studied echinoderm classes (Kruskal-Wallis, df: 2, sum of ranks: 8.73E+05, *Chi-square*: 133.68, $p < 0.05$). Asteroids showed the highest Mg levels (17.8 ± 0.3 mol% $MgCO_3$; $n = 79$), followed by ophiuroids (arms and central disk: 16.8 ± 0.2 mol%; $n = 70$) and echinoids (test: 11.7 ± 1.4 mol%; $n = 45$; spines: 4.2 ± 0.7 mol%; $n = 45$).

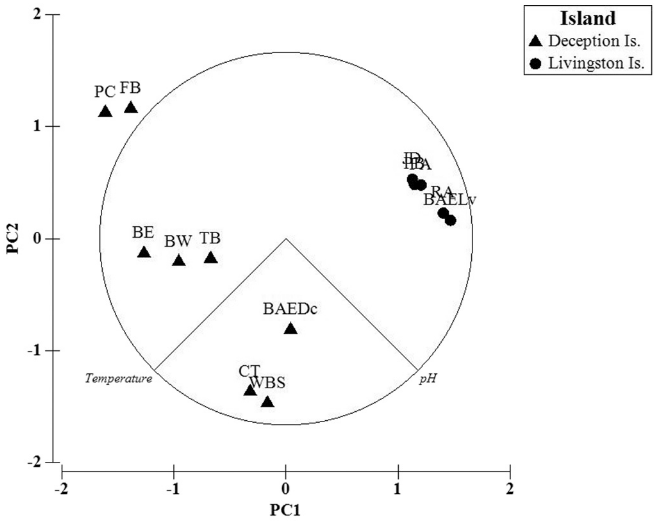

Fig. 2. Principal component analyses (PCA) results grouping the studied stations of Deception and Livingston Islands based on their environmental characteristics, specifically pH levels and temperature (°C). BAEDc: Antarctic Spanish Base of Deception Island; BAELv: Antarctic Spanish Base of Livingston Island; BE: Bidones East; BW: Bidones West; CT: Cormoran Town; FA: False Bay; FB: Fumarole Bay; JD: Johnsons Dock; PB: Polish Bluff; PC: Pendulum Cove; RA: Raquelias; TB: Telephone Bay; WBS: Whaler's Bay South.

Significant differences in the Mg content among the asteroid species analyzed were observed (Kruskal-Wallis, df: 5, sum of ranks: 8.24E+04, *Chi-square*: 15.94, $p < 0.05$). In particular, the sea star *Odontaster validus* showed a mean Mg concentration of 17.7 ± 0.2 mol% $MgCO_3$ ($n = 45$), showing significant differences in the Mg content among stations (ANOVA, $p < 0.05$). However, similar concentrations of Mg were observed in samples from Deception (17.8 ± 0.2 mol%; $n = 30$) and Livingston Islands (17.7 ± 0.2 mol%; $n = 15$) (ANOVA, $p > 0.05$). In Deception Island, the highest Mg levels were registered in Bidones West (18.0 ± 0.1 mol%; $n = 5$; Fig. 3) and Whaler's Bay South (17.9 ± 0.1 mol%, $n = 5$), being significantly lower than in Pendulum Cove (17.5 ± 0.1 mol%; $n = 5$), where the minimum Mg content was observed in this species. Although no significant differences among islands were observed, significantly higher Mg levels were registered in Bidones West from Deception Island than in False Bay (17.6 ± 0.1 mol%; $n = 5$) and BAELv (17.6 ± 0.1 mol%; $n = 5$) from Livingston Island. The Mg levels observed at the rest of stations in Deception Island (Telephone Bay: 17.7 ± 0.1 mol%; Bidones East: 17.7 ± 0.1 mol%; BAEDc: 17.7 ± 0.1 mol%; $n = 5$ for each station) and in Livingston Island (Polish Bluff: 17.8 ± 0.2 mol%; $n = 5$) showed similar results. The sea star *O. meridionalis* (Cormoran Town, Deception Island) showed a mean Mg content of 17.9 ± 0.1 mol% ($n = 3$).

The sea star *Lysasterias* sp. collected in Livingston Island showed a mean Mg concentration of 17.9 ± 0.2 mol% $MgCO_3$ ($n = 11$), revealing similar concentrations at False Bay (18.0 ± 0.2 mol%; $n = 2$), Polish Bluff (17.9 ± 0.3 mol%; $n = 5$) and BAELv (17.9 ± 0.1 mol%; $n = 4$). No significant differences among these sample stations were observed for this species (ANOVA, $p > 0.05$).

The sea stars of the genus *Diplasterias* and *Perknaster* collected at Livingston Island showed relatively high Mg levels compared to the other species in this study. Specifically, *Diplasterias* sp. 1 from False Bay showed a mean concentration of 18.3 ± 0.3 mol% ($n = 5$) and *Diplasterias* sp. 2 from Raquelias, False Bay and Polish Bluff displayed mean values of 17.9 ± 0.2 ($n = 5$), 17.8 ± 0.2 ($n = 3$) and 17.6 ± 0.2 mol% ($n = 5$), respectively. No significant differences in the Mg content among stations were also observed in this species (ANOVA, $p > 0.05$). *Perknaster* sp. from Polish Bluff showed a mean value of 18.3 ± 0.4 mol% ($n = 2$), exhibiting the highest Mg concentration of this study.

The brittle star *Ophionotus victoriae* showed no significant differences in the Mg levels among arms (16.8 ± 0.2 mol% $MgCO_3$; $n = 35$) and the central disk (16.8 ± 0.2 mol%; $n = 35$) (ANOVA, $p > 0.05$). Similar Mg levels were also observed in the arms of this species at Deception (16.9 ± 0.2 mol%; $n = 25$) and Livingston Islands (16.8 ± 0.1 mol%; $n = 10$) (ANOVA, $p > 0.05$). However, significant differences among stations were observed at Deception Island (ANOVA, $p < 0.05$), particularly among Cormoran Town (17.1 ± 0.1 mol%; $n = 5$; Fig. 4) and Pendulum Cove (16.6 ± 0.2 mol%; $n = 5$), coinciding with the maximum and minimum levels observed in the arms of this species, respectively. Contrary, the central disk of *O. victoriae* showed significantly lower Mg levels in Deception Island (16.7 ± 0.2 mol%; $n = 25$) than in Livingston Island (16.9 ± 0.2 mol%; $n = 10$) (ANOVA, $p < 0.05$), but with no significant differences among stations (ANOVA, $p > 0.05$).

The Mg content observed in the different skeletal body components of echinoid species were the lowest of this study. Significant differences in the Mg content among the two echinoid species were observed (ANOVA, $p < 0.05$). The regular sea urchin *S. neumayeri* showed significant differences in the Mg content among skeletal body components (ANOVA, $p < 0.05$), displaying the highest levels in the Aristotles's lantern (11.9 ± 1.1 mol% $MgCO_3$; $n = 39$), followed by the test (11.4 ± 1.1 mol%; $n = 40$) and the spines (4.3 ± 0.7 mol%; $n = 40$). Significant differences in the Mg levels of the test of *S. neumayeri* were observed among sampling stations (ANOVA, $p < 0.05$), revealing significantly higher values in Whaler's Bay South (12.8 ± 0.4 mol%; $n = 5$; Fig. 5) than in Fumarole Bay (10.9 ± 0.5 mol%; $n = 5$), Telephone Bay (10.8 ± 0.5 mol%; $n = 5$) and Pendulum Cove (10.6 ± 0.8 mol%; $n = 5$), where

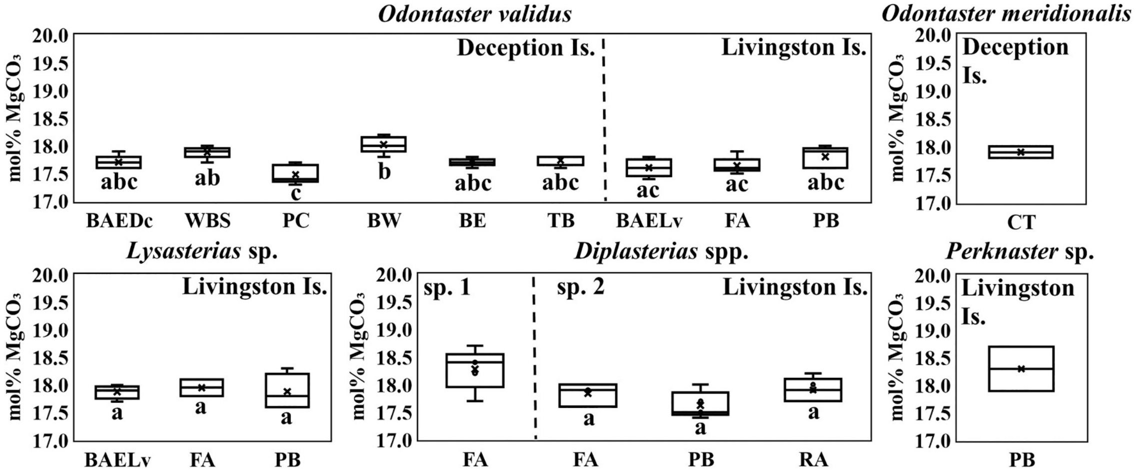

Fig. 3. Mean values (± SD) of Mg (mol% $MgCO_3$) in the six asteroid species collected at Deception and Livingston Islands. Differences in one letter within each species indicate significative differences among stations. Sampling stations: Antarctic Spanish Base of Deception Island (BAEDc); Whaler's Bay South (WBS); Pendulum Cove (PC); Bidones West (BW); Bidones East (BE); Telephone Bay (TB); Cormoran Town (CT); Antarctic Spanish Base of Livingston Island (BAELv); False Bay (FA); Polish Bluff (PB) and Raquelias (RA).

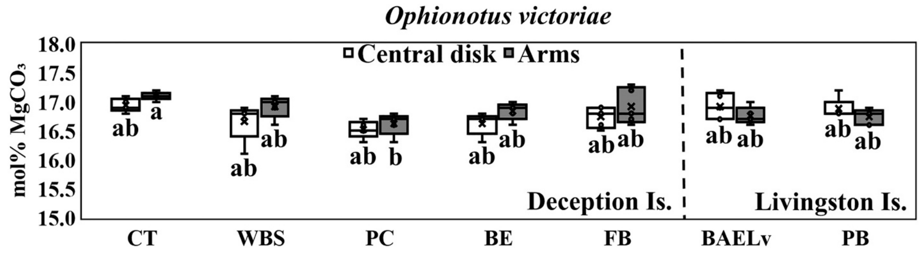

Fig. 4. Mean values (± SD) of Mg (mol% $MgCO_3$) in the central disk and arms of the ophiuroid species collected at Deception and Livingston Islands. Differences in one letter indicate significative differences among stations. Sampling stations: Cormoran Town (CT); Whaler's Bay South (WBS); Pendulum Cove (PC); Bidones East (BE); Fumarole Bay (FB); Antarctic Spanish Base of Livingston Island (BAELv); and Polish Bluff (PB).

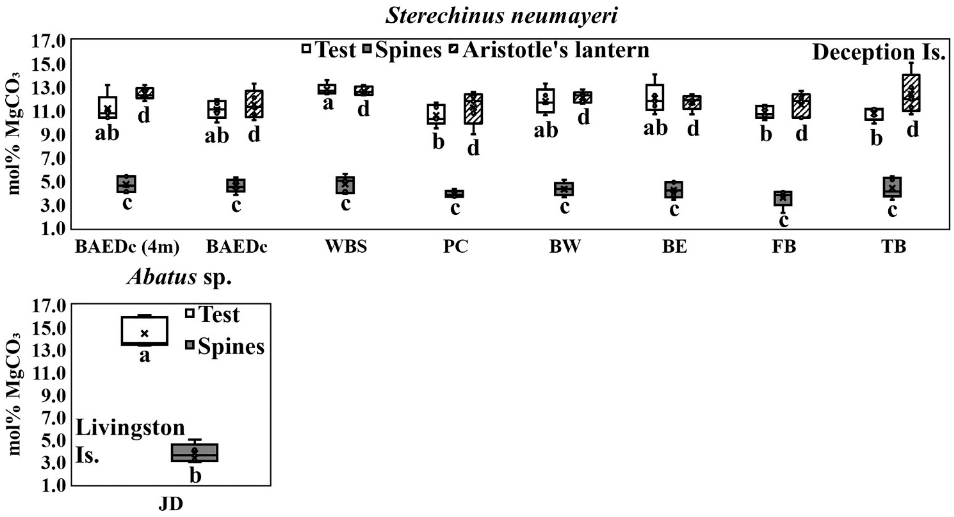

Fig. 5. Mean values (±SD) of Mg (mol% $MgCO_3$) in the test, spines and Aristotle's lantern of the two echinoid species collected at Deception and Livingston Islands. Differences in one letter within each species indicate significative differences among stations. Sampling stations: Antarctic Spanish Base of Deception Island (BAEDc); Whaler's Bay South (WBS); Pendulum Cove (PC); Bidones West (BW); Bidones East (BE); Fumarole Bay (FB); Telephone Bay (TB) and Johnsons Dock (JD).

the minimum value for this species was recorded. In contrast, no significant differences in the Mg content of the Aristotle's lantern and spines among stations were observed (ANOVA, $p > 0.05$). The irregular sea urchin *Abatus* sp. also showed significantly higher Mg levels in the test (14.5 ± 1.2 mol%; $n = 5$) than in the spines (3.8 ± 0.7 mol%; $n = 5$).

4. Discussion

This is the first assessment of the Mg content in common Antarctic echinoderm species conducted in Deception and Livingston Islands, and the first for *Odontaster validus* and *Abatus* sp. in Antarctica. All species analyzed were found to secrete calcitic skeletons with HMC, which is consistent with previous results in Antarctic echinoderm species (McClintock et al., 2011). Therefore, these species are potentially more vulnerable to dissolution than IMC or LMC species from the SO, which is likely to be one of the first, and most severely affected regions by global change (Orr et al., 2005; Fabry et al., 2009).

Interclass differences in the Mg content among echinoderm classes were observed, thus supporting findings from previous studies which have reported recent and fossil Antarctic and Arctic echinoderm skeletons to show variations in the skeletal Mg content (Dickson, 2002; McClintock et al., 2011; Iglikowska et al., 2017). These differences could be attributed to physiological differences, such as morphology, growth rates or organic matter concentration (Iglikowska et al., 2017). For instance, asteroids and ophiuroids may have evolutionary developed ossicles with higher Mg concentrations than echinoid tests because their skeletal body structures are covered by thicker tissues layers and thus are more protected from ambient conditions (Duquette et al., 2018). We also reported intraspecific significant differences in the Mg content for species belonging to the three studied classes (*O. validus*, *Ophionotus victoriae* and *Sterechinus neumayeri*), which may suggest that their skeletal Mg levels are both biologically and environmentally controlled.

In asteroids, interspecific differences were detected, with the highest Mg content observed in the genera *Perknaster*, followed by *Diplasterias*, *Lysasterias*, and with *Odontaster* showing the lowest levels. However, this pattern contrasts with that observed in previous studies on specimens of the same species and/or genera (i.e., McClintock et al., 2011; Duquette et al., 2018) and may reflect a kinetic effect (e.g., growth rate) and/or the influence of local environmental conditions at Deception and Livingston Islands (e.g., Mg^{2+}/Ca^{2+} ratio, temperature or pH) (Mackenzie et al., 1983; Borremans et al., 2009; Kołbuk et al., 2021). In addition, it should be noted that these differences may also be influenced by latitudinal deviations among studies, as Mg content in echinoderms is negatively correlated with the latitude due to changes in environmental conditions (e.g., temperature or $CaCO_3\Omega$) or physiological characteristics (e.g., growth rates) (Chave, 1954; Mackenzie et al., 1983; McClintock et al., 2011). The differences in the depth at which the organisms were collected among studies (>120 m depth) could also influence the Mg content as solubility of $CaCO_3$ minerals increases with depth due to the increased pressure and lower temperature (Millero, 1979; Catarino et al., 2013). Other local environmental variation from sources such as freshwater inputs can also affect seawater chemistry and consequently the mineralogy as suggested for other marine calcifiers (Figuerola et al., 2019).

Among asteroid species, only *O. validus* showed intraspecific differences in the Mg content. Individuals from Bidones West, situated near to the entrance of the bay (Fig. 1), had higher Mg concentrations, differing significantly from Pendulum Cove in Deception Island, and from BAELv and False Bay in Livingston Island. The combination of particular environmental conditions such as a higher influence of the open water, the absence of shallow fumarolic emissions (Rey et al., 1995), higher temperatures, the proximity of a glacier and a higher percentage of organic matter (2.71 ± 1.82 %) at Bidones West could account for the differences found here. In particular, skeletal Mg content positively correlate with higher skeletal growth rate, which may thus lead to a higher skeletal Mg content (Ford et al., 2010). In contrast, the lowest Mg levels were recorded at Pendulum Cove, being significantly lower than in Bidones West and Whaler's Bay South. Pendulum Cove is characterized by a pH of 7.39 ± 0.32, the presence of several fumaroles along the coast and low renovation rate of the water (Rey et al., 1995; Vidal et al., 2011; Flexas et al., 2017). We thus suggest that the lower Mg content found in Pendulum Cove may be attributed to an environmental influence from warm acidic hydrothermal water exposure. These hydrothermal fluids also have lower Mg^{2+}/Ca^{2+} ratios, particularly those from stations with poor seawater recirculation of this island (i.e., Pendulum Cove, Telephone Bay and Fumarole Bay; Somoza et al., 2004; Kusakabe et al., 2009), which may have also contributed to lower Mg concentrations. Consistent with this, low pH levels together with high temperatures have been previously proven to influence the skeletal Mg content of asteroid species (Khalil et al., 2022). The PCA results (Supplementary Material Fig. S1) also support our hypothesis, grouping the populations exposed to similar environmental conditions. However, it is still unclear how this species will cope with simultaneous environmental changes. Previous studies reported negative effects on the reproductive fitness and maintenance of early stages of *O. validus* when were experimentally exposed to low pH conditions (Gonzalez-Bernat et al., 2013; Karelitz et al., 2017). In contrast, Di Giglio et al. (2021) did not observe any effect of low pH levels on the mechanical properties of the skeleton of *O. validus*. This sea star also seems to be more resistant to low pH conditions than other echinoderm species as Dell'Acqua et al. (2019) did not observe the degradation of the gonads of *O. validus* under low pH conditions, contrary to other echinoderm species. Furthermore, low pH conditions may even benefit these species as may affect the capacity to scape of their preys, thus promoting changes on the food chain (Jellison et al., 2016).

For the ophiuroid *O. victoriae*, no differences were observed among the central disk and the arms as previously found in this and other ophiuroid species (Duquette et al., 2018). However, we found intraspecific differences in the Mg content of the arms of this species among sampling stations. The specimens from Pendulum Cove also showed a lower Mg concentration, which could also indicate a local effect of environmental variables as previously observed in ophiuroids which seem to be more sensitive to seawater chemistry (Kołbuk et al., 2021). Brittle star species exposed to low pH conditions previously showed compensatory mechanisms to dissolution such as an increase of the metabolism and calcification rates (Wood et al., 2008), which may explain how this species can survive in such conditions in Deception Island. However, the expected future increased temperatures could lead to adverse effects on this species due to a higher energy demand as previously showed in Arctic and temperate ophiuroid species when exposed to low pH levels and high temperatures (Wood et al., 2010, 2011).

We also found interspecific differences in echinoids. For instance, higher Mg levels in the test of the irregular sea urchin *Abatus* sp. compared with the regular sea urchin *S. neumayeri* were observed. Differences among distinct skeletal body components were also observed in both species. The lower Mg concentrations found in the spines of both echinoids compared to other skeletal body components may be a response to cold Antarctic waters as spines are only covered by a thinner epidermis and are thus more exposed to surrounding seawater (Dubois, 2014; Iglikowska et al., 2018). In agreement, Chave (1954) observed a positive correlation among the temperature and the Mg content in the spines of echinoids. In the case of *S. neumayeri*, the Aristotle's lantern showed significant higher Mg content, followed by the test and the spines. This pattern is consistent with previous reports on echinoids species, suggesting the Aristotle's lantern requires higher robustness due to its biological functions, such as feeding and rock scratching (Smith et al., 2016; Duquette et al., 2018; Iglikowska et al., 2018).

Intraspecific differences on the Mg content of the test of *S. neumayeri* were also observed, specifically among the stations from the northern region of Deception Island (i.e., Telephone Bay, Fumarole Bay and Pendulum Cove) and those of the southern region of the island (i.e., Whaler's Bay South). These differences may also indicate a local environmental influence due to the presence of fumarolic emissions as suggested for *O. validus* and *O. victoriae*. Other echinoid species, for instance, also exhibit lower Mg content when exposed to low Mg^{2+}/Ca^{2+} ratios (Kołbuk et al., 2019). Previous studies have also described a wide variety of responses to reduced pH in this species. In particular, sea urchins are able to maintain homeostasis between their celomic fluid and the surrounding environment under low pH conditions (Collard et al., 2015). By contrast, the degradation of its gonads or a poorer larval development has been reported under low pH conditions (Byrne et al., 2013; Dell'Acqua et al., 2019). While previous experiments studying the effect of low pH levels on the embryo development, fertilisation and sperm concentration of *S. neumayeri* reported only a negative effect on the latter, acidic conditions combined with higher temperatures seem to cause also negative effects on the fertilisation and embryo development (Ericson et al., 2010, 2012). Additionally, more corrosive conditions may increase the pressure that some predators (e.g., *O. validus*) may exert on sea urchins as the thickness of their skeletons may be reduced, especially at juvenile stages (McClintock, 1994; Rodríguez et al., 2017). Contrastingly, we did not observe a lower Mg content in the spines or the Aristotle's lantern of sea urchins from the stations of the northern region of the island. Finally, we did not observe any effect of the depth range (4 and 15 m depth at BAEDc) in the Mg content of *S. neumayeri*. While other studies found a negative correlation between the Mg content and depth in diverse echinoderms (Lowenstam, 1973; Catarino et al., 2013), further studies should consider a wider depth range to test the effect of the lower $CaCO_3$ Ω as previously suggested for bryozoans (Figuerola et al., 2015).

5. Conclusions

Knowledge about the mineralogical composition of most echinoderm species at the SO and their response to environmental conditions is still limited. These data are essential to predict the potential effects of future ocean acidification and warming on marine calcifiers. This study provides new mineralogical data from common echinoderm species, which are ecologically important marine invertebrates in Antarctic benthic ecosystems. We found that the studied echinoderms species presented HMC skeletons, displaying interclass differences among asteroids, ophiuroids and echinoids. We also observed the existence of inter- and intraspecific differences in the mineralogy of echinoderms in both studied islands. The differences in the Mg content observed here may reflect the influence of the local environmental conditions of Deception Island, such as temperature, lower Mg^{2+}/Ca^{2+} ratio in the thermal fluids from the fumarolic emissions, pH and lower water renovation rate as well as a biological control (e.g., modulation of calcification rates) on the skeletal mineralogy. Since these species with HMC skeletons, a priori, could be potentially more vulnerable to OA, more field and laboratory studies exposing diverse species under future environmental conditions are needed to obtain a clearer picture of how they will respond to global change.

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CRediT authorship contribution statement

Tomás Azcárate-García: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Conxita Avila:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **Blanca Figuerola:** Conceptualization, Formal analysis, Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data have been included in the supplemental material.

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Appendix A. Supplementary material

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