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Polar Biology

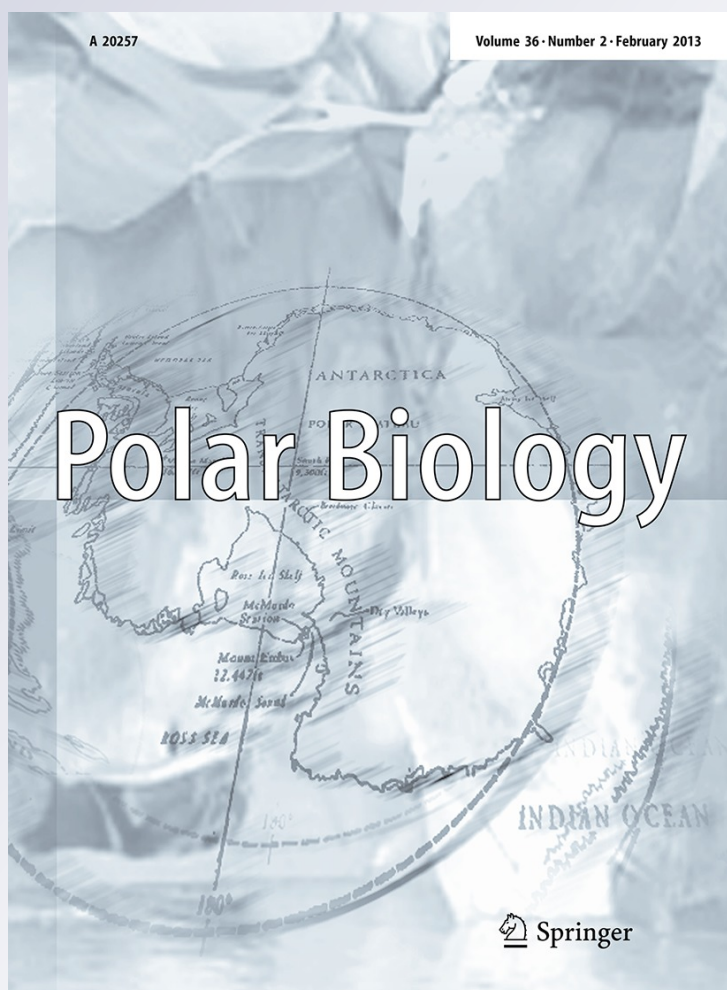
ISSN 0722-4060

Volume 36

Number 2

Polar Biol (2013) 36:193-200

DOI 10.1007/s00300-012-1250-z



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Patterns of magnesium content in Arctic bryozoan skeletons along a depth gradient

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Received: 6 December 2011 / Revised: 11 September 2012 / Accepted: 20 September 2012 / Published online: 14 October 2012
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Abstract A growing body of evidence suggests that ocean acidification acting synergistically with ocean warming alters carbonate biomineralization in a variety of marine biota. Magnesium often substitutes for Ca in the calcite skeletons of marine invertebrates, increasing their solubility. The spatio-environmental distribution of Mg in marine invertebrates has seldom been studied, despite its importance for assessing vulnerabilities to ocean acidification. Because pH decreases with water depth, it is predicted that levels of Mg in calcite skeletons should also decrease to counteract dissolution. Such a pattern has been suggested by evidence from echinoderms. Data on magnesium content and depth in Arctic bryozoans (52 species, 103 individuals, 150 samples) are here used to test this prediction, aided by comparison with six conceptual models explaining all possible scenarios. Analyses were based on a uniform dataset spanning more than 200 m of coastal water depth. No significant relationship was found between depth and Mg content; indeed, the highest Mg content among the analyzed taxa (8.7 % mol MgCO₃) was recorded from the deepest settings (>200 m). Our findings contrast with previously published results from echinoderms in which Mg was found to decrease with depth. The bryozoan results suggest that ocean acidification may have less impact on the studied bryozoans than is generally assumed. In the broad context, our study exemplifies quantitative testing of

spatial patterns of skeletal geochemistry for predicting the biological effects of environmental change in the oceans.

Keywords Magnesium · Depth · Bryozoans · Ocean acidification · Ocean warming · Arctic

Introduction

Ocean acidification is a decrease in pH in the oceans caused by the uptake of anthropogenic CO₂ from the atmosphere (e.g., Orr et al. 2005) and is recognized to have negative effects on many groups of planktonic and benthic marine invertebrates with calcareous skeletons (for reviews see Hoegh-Guldberg et al. 2007; Fabry 2008; Pörtner 2008; Fabry et al. 2008; Rost et al. 2008; Doney et al. 2009; Pelejero et al. 2010). It may have a biotic impact at various levels, from cells to larvae, mature individuals, populations and entire ecosystems/regions. These effects may be expressed as decreases or increases in calcification rate, skeletal thinning and dissolution, decrease in abundance, recruitment and survival rates, and alteration in reproductive, metabolic, growth or physiological traits (e.g., Kleypas et al. 1999; Riebesell et al. 2000; Gazeau et al. 2007; Dupont et al. 2008, 2010; Kurihara 2008; Kuffner et al. 2008; Wood et al. 2008, 2011; Clark et al. 2009; de Moel et al. 2009; Findlay et al. 2010a).

Ruttimann (2006) predicted that a decline in coccolithophore production caused by ocean acidification could affect climate, contributing to global climate warming by decreasing the Earth's albedo. There are indications that the processes of ocean acidification and ocean warming are closely linked and even synergistic (e.g., Rodolfo-Metalpa et al. 2010). However, the effect of elevated CO₂ on marine biota is still being assessed and debated (e.g., Martin et al.

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2008; Nienhuis et al. 2010). A number of studies using short-term experimental conditions to simulate long-term effects have lacked acclimatization time and multigenerational adaptations to the environment (as has recently been shown to occur in a species of coccolithophore, Lohbeck et al. 2012), causing ‘shock responses’ that may not apply in nature. Therefore, it is necessary to search for ‘natural proxies’ to test predictions related to ocean acidification and warming.

Most previous studies of the effects of ocean acidification on invertebrates have concerned corals, molluscs, echinoderms or crustaceans, with relatively few focusing on bryozoans (cf. Martin et al. 2008; Smith 2009; Rodolfo-Metalpa et al. 2010; Lombardi et al. 2011a, b; Loxton et al. 2013). Like echinoderms, corals and pteropods, bryozoans have calcareous skeletons potentially vulnerable to dissolution (e.g., Kukliński and Taylor 2009; Smith 2009; and literature cited therein). Their diversity (at least 6,000 species), abundance, habitat-creating abilities and significant contribution to the carbonate budget since the Ordovician (e.g., Taylor and Allison 1998) underline the importance of bryozoans among benthic organisms (Gordon et al. 2009).

Magnesium in the form of magnesium carbonate (magnesite) is a common component of many marine invertebrates producing shells and skeletons of calcite, including echinoderms, corals, molluscs and bryozoans (e.g., Lowenstam and Weiner 1989; Ries 2004; Stolarski et al. 2007; Lombardi et al. 2008; Ries et al. 2009; Taylor et al. 2009). The solubility of calcite increases with increase in mol% MgCO_3 (e.g., Morse et al. 2006; Andersson et al. 2009), to the extent that calcite containing a high proportion of MgCO_3 is even more soluble than aragonite (e.g., Andersson et al. 2009), the other common calcium carbonate biomineral which is generally regarded as being especially prone to dissolution. Quantitative spatial patterns of Mg contents in calcium carbonate biomineralizers, including bryozoans, have seldom been investigated (but see, for example, Smith et al. 2006; Kukliński and Taylor 2008, 2009).

With respect to carbonate minerals, seawater saturation state is lower in polar than in temperate and tropical latitudes (e.g., Andersson et al. 2008) because calcium carbonate is more soluble in cold water. It is also recognized worldwide that pH and CO_2 levels change with water depth (e.g., Bathurst 1975; Palmer et al. 1998; Palmer 2009, fig. P25). For example, Anderson et al. (2010) noted a decrease in pH of about 0.4 to a minimum of 7.6 in the upper 200 m of Arctic shelf depths, which is equivalent to the global changes in oceanic pH projected by the year 2100 (Caldeira and Wickett 2003, fig. 1), and undersaturation with respect to aragonite at greater depths. Thus, depth gradients in skeletal magnesium content might be anticipated, with Mg declining with depth in order to counteract the threat of

dissolution. By comparing skeletal magnesium content and depth, it should be possible to investigate mineralogical responses of organisms living in different pH regimes.

Among echinoderms, a bathymetric gradient has been recognized in crinoids that matched the prediction of declining Mg with depth (Roux et al. 1995; Kroh and Nebelsick 2010, fig. 9), while Sewell and Hofmann (2011) examined the effect of depth-related processes on the skeletal magnesium content of echinoids and their test thickness. Although the echinoid study focused only on the deep environments of the Antarctic region, the crinoid data came from two sources (Clarke and Wheeler 1922; Roux et al. 1995), both showing a trend of decreasing Mg with depth down to over 1,000 m. Additionally, Lowenstam and Rossman (1975) found a decrease in silica and phosphate content with water depth in holothurian dermal sclerites, clearly marked even at shelf depths. Amini and Rao (1998) found a decrease in Mg content within carbonate bulk samples along a depth gradient on the Tasmanian temperate shelf. On the other hand, Ponder and Glendinning (1974) suggested that one foraminifera species responded to depth increase by slightly decreasing the Mg content of its test, whereas others showed no trend.

Sea ice retreat in the central Arctic Ocean due to warming will lead to higher $p\text{CO}_2$ values in the surface waters and reduced CaCO_3 saturation states on the shelf zone (see Fabry et al. 2009). Therefore, we here focus on the shelf biota of the Arctic, which is particularly susceptible to rising atmospheric CO_2 . We evaluate the potential vulnerability of Arctic marine benthic communities to acidification and warming using the carbonate skeletons of bryozoans as a model. Bryozoans represent one of the best model groups in the Arctic due to their richness, high abundance, wide distribution and diverse spectrum of mineralogical and geochemical compositions. Our main goals are to (1) test the prediction that Mg content in bryozoan skeletons decreases along a depth gradient, (2) propose a conceptual model of the relationship between depth and Mg content and (3) demonstrate the utility of statistical treatments of biogeochemical and biomineralogical data for investigating important issues of ocean change.

Materials and methods

Models

Six models summarizing possible relationships between magnesium content and depth (Fig. 1) were developed. These are similar in concept to the models proposed by Fabry (2008) and Ries (2011) and are inspired by some evolutionary models (e.g., Jablonski 1997; Trammer and

Kaim 1999). The models show the following patterns: in model A, Mg remains constant with depth; model B predicts variations in Mg at each depth; model C suggests constant Mg across depths; model D assumes Mg varying in parallel with depth; model E considers Mg decreasing with depth; and model F demonstrates Mg increasing with depth.

Data

The data used to test the relationship between depth and Mg content in bryozoan skeletons were obtained from Kukliński and Taylor (2009). There are several advantages of this dataset: (1) taxonomic identifications were made by one scientist, (2) uniform analytical methods of magnesium content were obtained using standard XRD methods (for details see Kukliński and Taylor 2009), (3) precise depth values and high sampling resolution were available, (4) replicates of the same species were analyzed, (5) a large number of samples (>100) were available, (6) the environmental context and ecological distributional patterns of Arctic bryozoans are quite well known, (7) the quality of the specimens (e.g., for contaminant epibionts) was carefully controlled and (8) sampling was essentially random. Other published datasets, for example on bryozoans (e.g., Borisenko and Gontar 1991; Smith et al. 2006; Kukliński and Taylor 2008; Smith and Clark 2010), lack sampling depth data, focus on areas other than the Arctic, employ a smaller number of samples or used destructive mineralogical/geochemical analysis techniques excluding further specimen verification causing taxonomic inconsistencies. The bryozoans studied by Kukliński and Taylor (2009) came from numerous localities (see Fig. 2), ranging from

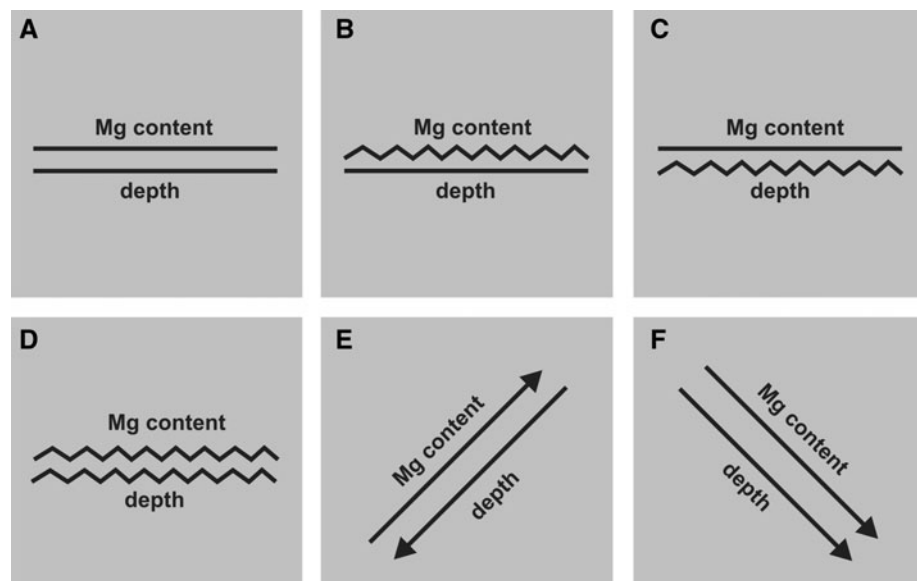
northern Norway to Greenland, Spitsbergen and the Siberian coast (Laptev Sea), and can be regarded as fairly representative for the Arctic as a whole. Bryozoan classification followed the Bryozoa Home Page (2010).

A total of 150 analyses were undertaken of 76 bryozoan species exhibiting various colony forms. Mg content was expressed as mole percentage (% mol) of magnesite (MgCO_3 ; here referred to simply as magnesium; see also Tucker and Wright 1990). The error associated with this method is estimated to be 2 % (see Kukliński and Taylor 2009). Mean values were calculated for species with more than one analysis, such as some erect species where Mg was measured at the tips and bases of the colonies. Exclusion of analyses from samples for which no depth information was available reduced the dataset to 103 points. This comprised 52 species from 40 genera classified in 29 families within two bryozoan orders (see Table 1). When sample collection depth was expressed as a range (e.g., ‘11–36 m’), median depth was used.

Applied indexes

Few publications have studied statistical patterns in the mineralogy and geochemistry of skeletons (e.g., Ries 2004; Stanley et al. 2005; Kukliński and Taylor 2009; and literature cited therein). Thus, there are no established standard protocols for data analysis and interpretation. Therefore, we here propose several additional metrics to supplement those previously used for analytical purposes, for example, minimum, maximum or average Mg content values. For each depth bin, we recorded maximum, minimum and mean values of MgCO_3 , maximum variance of MgCO_3 in a single species within the bin, ABC index, magnesium ratio,

Fig. 1 Conceptual models for theoretically possible depth and magnesium content relationships. **a** Mg remains constant with depth, **b** variations in Mg content at each depth, **c** constant Mg across depths, **d** Mg varying in parallel with depth, **e** Mg decreasing with depth, **f** Mg increasing with depth



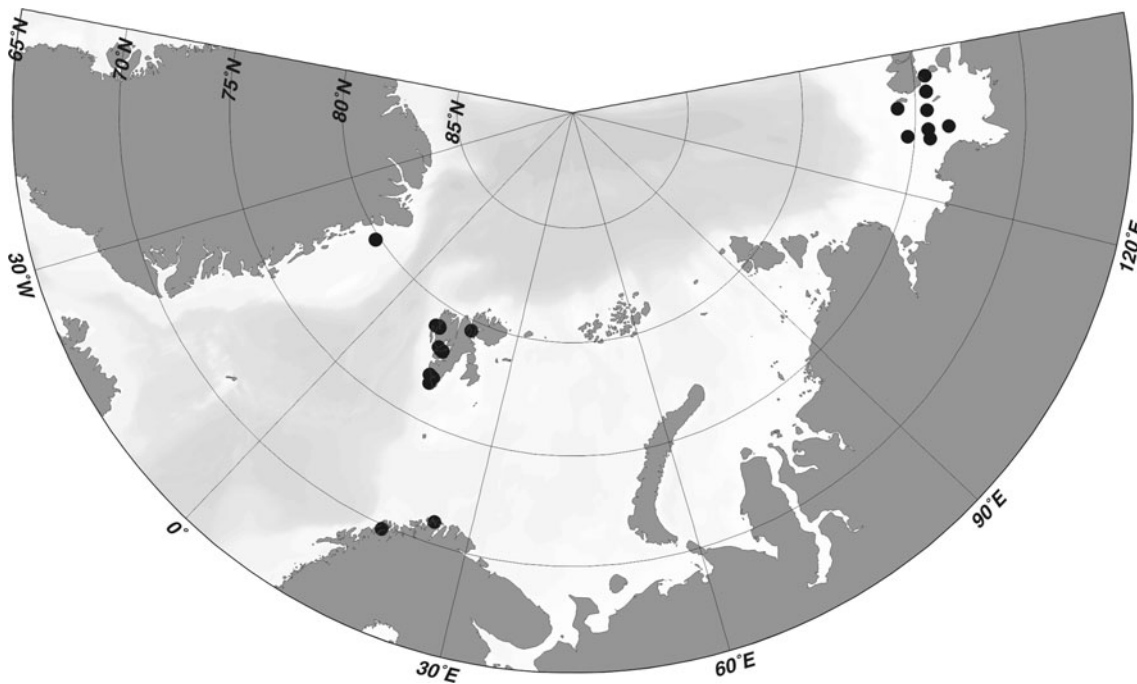


Fig. 2 Map of bryozoan localities (black dots) from this study of the relationship between skeletal Mg content and depth. The map was generated using Ocean Data View Software (Schlitzer 2012) based on

presence/absence of MgCO_3 bearing taxa within the bin and number of overlaps (see Table 1). The ABC (aragonite, bimineralic and calcite) index is a measure of the ratio of bryozoan taxa of particular mineralogy within each bin and is expressed as number of samples per bin and also as number of genera per bin (as a proxy for species). The presence or absence of species with skeletons containing MgCO_3 was also determined. Finally, a ‘number of overlaps’ metric was calculated to provide an index of similar Mg contents in taxa from the same depth. Species with calcitic skeletons were divided into low-Mg calcite (<4 mol% MgCO_3), intermediate-Mg calcite (4–8 mol% MgCO_3) and high-Mg calcite (>8 mol% MgCO_3) categories, following Rucker and Carver (1969).

Statistical analyses

Linear regression was used to explore the relationship between depth and magnesium content. Statistical analyses were performed using mean values for given depth in cases of two, three or more Mg content replicates from the same depth. We performed analyses on datasets that included zero values as well as those without zero values. Based on depth distributions of Arctic bryozoan communities (for details see Kukliński et al. 2005), samples were divided into three depth bins: <50, ~100 and ≥ 200 m. In addition, data were also analysed at higher sampling resolutions based on depth points available in our dataset (see Fig. 3).

sampling localities of Kukliński and Taylor (2009). Note that due to map scale a single dot may represent several neighboring localities

Although all data were transformed, this did not improve normality; therefore, differences in Mg content between depth bins were identified using one-way nonparametric Kruskal–Wallis tests. The same procedure was performed on all available Arctic data and separately only on data obtained from Spitsbergen. This allowed us to test whether the broad pattern of Mg distribution in bryozoan skeletons from the Arctic is similar to that observed locally, helping when drawing conclusions about the influence of environmental factors and scale on observed patterns. All statistical analyses were performed using Statistica 8 software.

Results

Maximum values of Mg in our dataset were unexpectedly found in the bryozoans from the deepest depth bin (below 200 m), while the lowest values were found in the shallowest bin (<50 m) (Table 1). Mean values of Mg increased with water depth, as did their variance (Table 1). However, there was no significant relationship between depth and skeletal Mg content for all samples ($R^2 = 0.02$, $p = 0.121$; without zero values $R^2 = 0.04$, $p = 0.037$), or for mean values from given depths ($R^2 = 0.03$, $p = 0.591$ see also Fig. 3; without zero values $R^2 = 0.08$, $p = 0.390$). A Kruskal–Wallis test showed no differences among the three depth bins ($H_{(2,103)} = 4.58$, $p = 0.101$).

Table 1 Values for tested indices grouped in three operational depth bins

Indexes	Depth bin		
	<50 m	~ 100 m	≥200 m
Maximum MgCO ₃ content (% mol)	7.4	5.7	8.7
Minimum MgCO ₃ content (% mol) ^a	0.1	3.3	0.5
Mean MgCO ₃ content ± SD (% mol)	3.5 ± 2.23	4.1 ± 0.75	4.7 ± 2.41
Maximum variance of MgCO ₃ content in single species within bin (% mol) ^b	5	0.8	1.2
ABC ratio (aragonite/bimineralic/calcite ratio)			
Number of samples	0/1/77	0/0/9	0/2/16
Number of genera	0/1/31	0/0/5	0/2/9
Bin diversity (ord/fam/gen/sp)	2/24/32/38	1/5/5/5	2/11/11/14
Magnesium ratio (number of samples) (low-Mg/intermediate-Mg/high-Mg calcite)	43/34/0	4/5/0	4/12/2
Presence/absence of MgCO ₃ content			
Present/absent	Present	Absent	Present
Number of samples	6	–	2
No. of taxa (ord/fam/gen/sp)	1/2/3/3	–	1/1/1/1
Number of overlaps ^{a,b} (similar Mg content within bin in various taxa/the same species/total number of overlaps)	24/2/26	1/0/1	1/0/1
Number of samples (total)	78	9	18
Total number of taxa (ord/fam/gen/sp)	2/29/40/52		

All data are from Kukliński and Taylor (2009). Each depth bin records commonly used metrics such as maximum, minimum and mean values of MgCO₃, together with some newly proposed metrics. The ABC (aragonitic, bimineralic, calcitic) index quantifies the ratio of bryozoan taxa with particular mineralogies within each bin. In addition, the presence or absence of species with skeletons containing MgCO₃ was also determined. The ‘number of overlaps’ metric provides an index of similar Mg contents in taxa from the same depth. For more details see ‘Materials and methods’ section

ord Orders, fam families, gen genera, sp species

^a Samples with zero values of MgCO₃ were excluded

^b Tips and bases measurements were excluded

Similar patterns were found when data from Spitsbergen were analyzed separately: no significant relationship was found between depth and Mg for the full data or for mean values ($R^2 = 0.01$, $p = 0.284$; $R^2 = 0.09$, $p = 0.547$, respectively). A one-way Kruskal–Wallis test revealed no difference between depth bins ($H_{(2,71)} = 2.81$, $p = 0.244$). The fact that there is a lack of pattern locally as well as for the entire area covered by this study demonstrates that local differences in environmental conditions (e.g., within-region temperature differences observed within the Arctic) have no appreciable influence on the pattern of skeletal Mg with depth.

Analysis of mean values (Fig. 3) for given depths revealed some trends in skeletal Mg between certain depths: Mg decreased between 1 and 24 m depth, and again between 25 and 44 m, but increased between 100 and 210 m depth. However, there was very weak or no statistical relationship within these bins between depth and skeletal Mg content (1–24 m: $R^2 = 0.29$, $p < 0.001$; 25–44 m: $R^2 = 0.05$, $p = 0.467$; 100–210 m: $R^2 = 0.01$, $p = 0.504$).

Discussion

Our findings do not support the prediction based on solubility that Mg should decrease with depth in bryozoan skeletons. The results from bryozoans contrast with those from crinoids summarized by Kroh and Nebelsick (2010), one of the few published studies dealing with skeletal Mg content in relation to depth. Using data from two literature sources, Kroh and Nebelsick found a linear relationship between skeletal Mg and depth (see also Roux et al. 1995). The contrast between the bryozoan and crinoid patterns may reflect a different degree of biological control (Lowenstam and Weiner 1989) of skeletal chemistry in these two groups. In addition, our bryozoan data were gathered only from the Arctic, whereas the crinoid data of Kroh and Nebelsick (2010) came from all around the world and included tropical sites and fewer polar sites. Borremans et al. (2009) among others have noted that patterns of ocean chemistry are spatially homogenous, and geographical factors can be ruled out as the cause of the observed differences. However, the crinoid data ranged down to

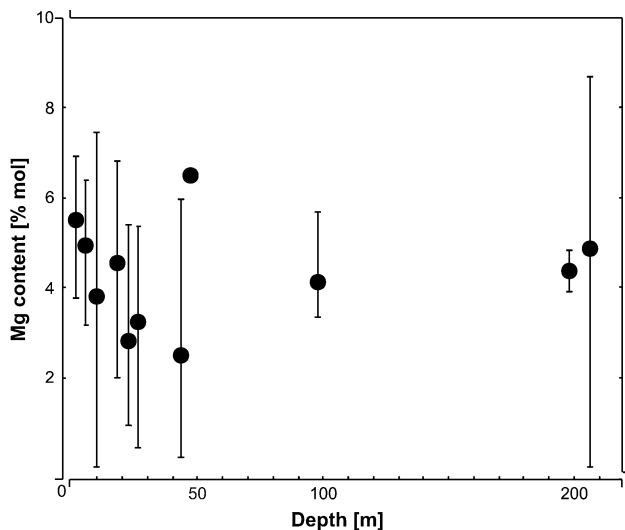


Fig. 3 Mean (circles), minimum and maximum (whiskers) values of magnesium content in Arctic bryozoans along a depth gradient. Note that only a single data point is available from a depth of 50 m. Original data from Kukliński and Taylor (2009, appendix)

depths of more than 2,000 m, an order of magnitude greater than our bryozoan data. This is congruent with the study of Schlager and James (1978) which demonstrated that a large depth gradient might be responsible for decreasing Mg content in abiogenic sea floor precipitates such as cold water calcite cements. However, for the depth range covered by our bryozoan analysis, crinoids show a clear pattern of decreasing Mg, contrasting with the lack of correlation in the bryozoans. Salinity should also be considered as a potential factor explaining the difference between the crinoid and bryozoan patterns, due to the known influence of salinity on magnesium content in skeletons such as those of echinoids (e.g., Borremans et al. 2009). In the case of the analyzed bryozoans, salinity is rather unimportant because our material came from a region where salinity showed little geographical variation (e.g., Karnovsky et al. 2003; Walkusz et al. 2009), while at the global scale of the crinoid data salinity is expected to vary more greatly.

Following the study of Chave (1954), temperature-related variations in Mg content in skeletal carbonate have been documented in various groups, for example, molluscs (Taylor and Reid 1990) and bryozoans (Kukliński and Taylor 2009; Taylor et al. 2009). More recently, Findlay et al. (2010b) showed a change in the Mg content of barnacle shells with latitude (and thus temperature), comparing temperate and Arctic representatives. In higher latitudes (colder waters), the rate of temperature change with water depth is generally lower than close to the equator. For example, Kwaśniewski et al. (2010, fig. 2) showed for Spitsbergen that temperature declines by only 2–3 °C, maximally 4 °C, over 150 m of depth. These and

other authors (e.g., Karnovsky et al. 2003; Walkusz et al. 2009) have also noted that temperatures here are spatially heterogeneous, but differ only by up to a few degrees over distances of several kilometers. Such slight variability in temperature may make any changes related to Mg level undetectable above the ‘noise’ of background factors.

Kukliński et al. (2005) identified several depth-specific bryozoan assemblages and dominants clustered as ‘shallow’ or ‘deeper’ over the coastal range encompassed by this study. They found that a major change in assemblages occurs at depths between 35 and 50 m. In contrast, the current study found no patterns in Mg content correlated with this ecological boundary (see also Fig. 3).

Variance of Mg content in single species within a bin is highest in the shallowest depth bin, lowest in the intermediate bin and of intermediate level in the deepest bin. The ABC ratio on the other hand shows that the diversity of bryozoan mineralogies lacks a relationship with depth. The number of genera decreases with depth but this is not associated with changes in the number of genera with particular mineralogies and is not the result of a sampling artifact (see Table 1). Kukliński et al. (2005) found, for example, a higher bryozoan diversity in deeper than shallower assemblages. In contrast to mineralogical diversity, the magnesium ratio index shows significant changes between depths (see Table 1). In the deepest depth bin, bryozoans lacking magnesium are restricted to a single genus, while in the shallowest depth bin skeletons lacking a detectable Mg content occur in three species distributed between three genera and two families (more sensitive analytical methods will be required in future to check whether these bryozoans, unlike previously reported calcitic skeletons, really possess no trace of Mg in their skeletons). This pattern contrasts with the expected increase in taxa lacking magnesium with water depth due to the greater solubility of Mg-rich calcite with depth.

We may predict that with respect to skeletal mineralogy, bryozoans will be adapted, preadapted or ecophenotypically responsive for inhabiting particular depths, leading to a strong Mg signature for each depth bin. For example, Kukliński and Taylor (2009) explained latitudinal patterns of bryozoan mineralogy in terms of ecophenotypic responses and genetic adaptations/preadaptations. The present study on patterns of Mg with depth has failed to find support for a correlation of Mg with depth, possibly reflecting the fact that Arctic communities may be too young to have developed genetic adaptations/preadaptations in skeletal mineralogy. This hypothesis could be tested using mineralogical data from other groups, and by more thorough sampling, ideally in polar, temperate and tropical regions.

The lack of any depth-related changes in skeletal Mg could indicate a high degree of biological control of skeletal mineralogy in Arctic bryozoans. The observed pattern of skeletal Mg seems to fit best with the ‘disequilibrium’ model (Fig. 2),

with Mg varying irregularly at particular depths without any predictive linear trends. Our results may imply that bryozoans will show some resilience to the effects of ocean acidification and warming, at least with respect to the Mg content of their calcitic skeletons. However, this issue will require further investigations, ideally utilizing other groups of Mg calcite calcifiers as well as focusing on geographical areas other than the Arctic.

Acknowledgments We would like to thank Caroline Kirk and Gordon Cressey (both formerly of the Department of Mineralogy, NHM, London) for help with previous XRD and mineralogical data analyses. TB is grateful to Dr Grażyna Bzowska, Tomasz Krzykawski M.Sc. (both University of Silesia, Sosnowiec) and Przemysław Gorzelak M.Sc. (Institute of Paleobiology, Warszawa) for fruitful discussions about invertebrate skeletal mineralogy and geochemistry. The journal Editor, Prof. Dieter Piepenburg, and his assistants, as well as Prof. Abigail Smith and four anonymous reviewers provided helpful suggestions on earlier versions of this paper. We are grateful to Prof. Noel P. James (Queen's University, Ontario) for help with the literature and Emilia Trudnowska (Institute of Oceanology, Sopot) for assistance with map preparation. This study was completed thanks to a grant from the Polish Ministry of Science and Higher Education (No. N N304 404038).

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