Chemical composition of two mineralogically contrasting Arctic bivalves' shells and their relationships to environmental variables

A. Iglikowska [a,*], J. Bełdowski [b], M. Chełchowski [a], M. Chierici [c,d], M. Kędra [a], J. Przytarska [a], A. Sowa [a], P. Kukliński [a]

[a] Marine Ecology Department, Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81-712 Sopot, Poland
[b] Marine Chemistry and Biochemistry Department, Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81-712 Sopot, Poland
[c] Institute of Marine Research, Sykehusveien 23, 9294 Tromsø, Norway
[d] University Centre in Svalbard, Longyearbyen, Norway

A B S T R A C T

The main goal of this study was to determine the concentrations of trace elements in the mineralogically contrasting shells of two Arctic bivalves: *Chlamys islandica* and *Ciliatocardium ciliatum*. Aragonite shells seem to be more susceptible to the binding of metal ions, which is most likely a result of their crystal lattice structure. We suggest that less biologically controlled aragonite mineralization tends to incorporate more metal impurities into the crystal lattice in waters with a lower pH, where metal ions are more available. Higher concentrations of impurities may further increase the lattice distortion causing lower crystal lattice stability and higher susceptibility to dissolution. Calcitic shells seem to be less prone to bind metal ions than aragonite shells most likely because under strict biological control, the uptake of ions from ambient seawater is more selective; thus, the final crystal lattice is less contaminated by other metals and is more resistant to dissolution.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

In the ocean, organisms and their habitats are linked and influence each other (Piepenburg et al., 1997; Ambrose et al., 2006; Carroll et al., 2008). The distribution of all chemical elements in seawater and sediment is strongly dependent on both biological and geochemical processes (Broecker and Peng, 1982; Stumm and Morgan, 2012). Global cycles of carbon (C), nitrogen (N), sulfur (S) and phosphorus (P) are linked with each other and are now strongly affected by human activities. Atmospheric carbon dioxide (CO_2) concentration has increased over the past 250 years by nearly 40%. Approximately one-third of the anthropogenic CO_2 has been absorbed by the oceans, resulting in a rapid change in the carbonate chemistry towards a shift to a lower pH and carbonate ion availability, so called ocean acidification (OA). Acidification has been shown to alter the chemical speciation in the seawater, thus affecting the biogeochemical cycles of elements and compounds (Millero et al., 2009). Additionally, minor element cycles have been substantially affected (Stumm and Morgan, 2012). Most metal complexes

in water increase with a decreasing pH, but the biosorption of metals declines along with the pH (Vijayaraghavan et al., 2006).

The Arctic is currently changing at a faster rate than any other place on earth (IPCC, 2013). Not only is the sea ice cover retreating and opening large areas for potential direct oceanic CO_2 uptake, the colder waters themselves have increased CO_2 solubility and thus have created a larger potential for further CO_2 uptake (ACIA, 2004; AMAP, 2013). Both processes result in higher susceptibility of the Arctic Ocean to chemical changes in the water masses compared to the other areas of the world's ocean. The environmental conditions of the Arctic seas are changing rapidly, and as a result of human activity, in each subsequent decade, these changes are progressing faster. The Arctic Ocean is the region projected to undergo substantial changes in the near future (IPCC, 2013; AMAP, 2013); therefore, all possible shifts and alterations in the biogeochemistry, physiology, biodiversity and ecology of Arctic organisms should be detected and tracked. This approach enables us to predict future problems and will provide possibilities to develop management strategies for the mitigation of or the adaptation to future environmental conditions.

Calcifying marine invertebrates are important ecological groups in many marine ecosystems; they provide food and thus have commercial value. More importantly, these invertebrates often create biological structures that maintain and increase local biodiversity and/or provide nursery grounds for other organisms. However, these invertebrates are predicted to be the most vulnerable to the effects of ocean

* Corresponding author.
  E-mail addresses: iglikowska@iopan.gda.pl (A. Iglikowska), hyron@iopan.gda.pl (J. Bełdowski), maciej.chelchowski@op.pl (M. Chełchowski), melissa.chierici@imr.no (M. Chierici), kedra@iopan.gda.pl (M. Kędra), jprzytarska@iopan.gda.pl (J. Przytarska), glanna23@wp.pl (A. Sowa), kuki@iopan.pl (P. Kukliński).

acidification because the rate of calcification may decrease with reduced carbonate-ion availability (Findlay et al., 2009; AMAP, 2013). Moreover, the formation of calcified shell, composed of different minerals and chemical elements, is an important part of global elemental and mineral cycles (Lowenstam and Weiner, 1989; Weiner and Dove, 2003). Biogenic calcium carbonate ($CaCO_3$) consists of carbonate ions and calcium (Ca) as a major element, whereas trace elements are incorporated into skeletons in significantly lower concentrations (≈ 0.1 wt.%) (Dalbeck, 2008). Minor and trace elements are not typical components of calcite and aragonite, although their presence in biogenic carbonate systems is common and can alter crystal morphologies. Trace element composition may provide information on how these 'impurities' affect crystal growth and thus yield a better understanding of biomineralization processes. Additionally, trace metals concentrations can provide insight into the conditions in which calcification occurred. Further, some minor and trace elements, such as copper (Cu), zinc (Zn), iron (Fe), and cobalt (Co), are important micro-nutrients that play important roles in biological production – for example – as cofactors in enzymes or as structural elements in proteins (Harris, 1992; Sharma and Sahni, 1993). Benthic organisms are most likely able to control which elements they build into their tissues and thus influence the cycle of biologically important metals. In contrast, these metals partly control the growth of organisms and thus the cycling of major elements. This mutual interdependence results from the complex coevolution of benthic organisms, sediment, and seawater chemistry (Stumm and Morgan, 2012).

The uptake of trace metals is likely linked to feeding strategy, life history and traits, as well as habitat depth, although it is still unknown to what extent the incorporation of metals is physiologically controlled by the organism. Similarly, there are large unknowns with regards to the extent and influence of the physical and chemical processes that govern the uptake of elements into the calcified shell. After the death of an organism, calcareous non-living skeletons undergo destruction and dissolution. As a result, the shell components are released into the surrounding environment, thus supplying both the seawater and sediment with major, minor and trace elements. Investigating and determining the chemical composition of the $CaCO_3$ shells and skeletons will provide increased knowledge regarding which elements are involved in the biomineralization process. Consequently, we will understand which elements will be transferred to the environment after the death of an organism. The process of shell dissolution usually occurs at the highest rates near the sediment-water layer, where the seawater is typically undersaturated with respect to aragonite ($\Omega Ar < 1$) and calcite ($\Omega Ca < 1$), the main minerals forming carbonates in the ocean (Davies et al., 1989). The $CaCO_3$ dissolution is controlled by the saturation state of the mineral such that when the waters are undersaturated $\Omega < 1$, dissolution of $CaCO_3$ will occur. In this process, CO_2 is consumed, bicarbonate (HCO_3^-) is produced, and the bottom waters with high CO_2 content from the degradation from organic matter influence the dissolution rate (Davies et al., 1989). Since ocean acidification results in decreased carbonate ion concentration (CO_3^{2-}) and shoaling of the saturation horizon, larger areas of bottom waters are exposed to undersaturation. Ocean acidification enhances the dissolution of calcareous shells, further increasing the release rate of chemical components to the environment (Findlay et al., 2009; Waldbusser et al., 2011). However, it is still poorly understood which elements and compounds are delivered to the ambient environment after shell dissolution and the processes that control it.

Bivalves have been successfully employed in the biomonitoring of metals in the Arctic seawaters; however, most studies have focused on bioaccumulation by soft body parts (Zauke et al., 2003), with poorer and less complete data on calcareous shells. The majority of shell studies have dealt with various aspects of bivalve growth in the Arctic environment (Tallqvist and Sundet, 2000; Sejr et al., 2009; Carroll et al., 2011, 2014); however, there are scarce data on shell chemical composition and mineralogy. In mature molluscs, the shell is usually aragonitic, calcitic or, in certain taxa, bimineralic, consisting of both calcite and

aragonite layers (Lowenstam and Weiner, 1989; Falini et al., 1996; Addadi et al., 2006). Chemical analysis of calcareous skeletons can provide vital information regarding the process of calcification, as well as the interrelationships between the mineralizing system and the ambient environment. However, our knowledge of the differences in binding minor and trace elements by particular $CaCO_3$ polymorph types is still limited.

In this study, we examined two species, *Chlamys islandica* (O.F. Müller, 1776) and *Ciliatocardium ciliatum* (Fabricius, 1780), which are common bivalves in the Arctic seas. These two species were used as model organisms representing two mineralogical systems: calcitic and aragonitic. By collating the results on bivalve shell mineralogy and chemistry with abiotic environmental parameters of the surrounding seawater, we aimed to reveal the factors that can either influence or regulate the process of trace metal incorporation into calcareous skeletons. Therefore, the main goals of this study were as follows: 1. to determine skeletal and trace element concentrations in the mineralogically different shells of the two Arctic bivalve species, 2. to examine the interdependence between the elemental composition and size class of the bivalve shells, 3. to evaluate the possible relationships between shell chemistry and factors related to depth, and finally, 4. to detect possible influences of the physical and chemical properties of ambient seawater on shell chemistry.

2. Material & methods

2.1. Study area

The study area was located in three fjords in western and southern Spitsbergen (Svalbard Archipelago). The climate of Svalbard is mostly shaped by its high latitude geographical position. Located most southwards in Spitsbergen, the Hornsund fjord (76°58′N, 15°34′E) is directly connected with the open sea by a wide outlet. The maximum depth of Hornsund is 280 m, and the bottom is diverse with a rocky and stony hard bottom in the northern and southern coasts, and muddy soft sediment with varying contributions of sand and gravel in the deeper parts of the fjord (Różycki, 1992). Hydrologically, Hornsund is influenced by the mixing of warm and more saline Atlantic waters transported in the West Spitsbergen Current (WSC) with the colder and fresher Arctic waters from the Barents Sea transported by the Cape Current (CC). At the outlet and in the central part of the fjord, the relatively warm West Spitsbergen Current (1.6–2.0 °C) penetrates to a depth of 70–100 m (Swerpel, 1985), and near the bottom, cooler waters are found (≈ 1.2 °C) with a salinity of 34.5 (Drewnik et al., 2016). In the inner part of Hornsund, Brepollen Bay, cold bottom seawater temperatures are observed (0.0 °C) with a salinity of approximately 34.2 (Drewnik et al., 2016). Generally, cold Arctic waters penetrate Hornsund and thus make the waters of this fjord colder than the more northerly located Kongsfjorden (78°55′N, 11°56′E) (Svendsen et al., 2002, personal observations). Kongsfjorden is mainly influenced by the warm, saline Atlantic water masses (>3 °C, sal. >34.89) of the WSC (Svendsen et al., 2002; Cottier et al., 2005). In the summer, the bottom water temperature in Kongsfjorden is approximately 2 °C with a salinity of >34.8 (Fransson et al., 2016). At the same time, the local benthic fauna is strongly affected by three tidal glaciers, with Kongsbreen as the most active glacier in the Svalbard Archipelago (Lefauconnier et al., 1994). In some years, the bottom water at the glacier front is considerably colder and can reach temperatures of <− 1 °C (Fransson et al., 2016). Kongsfjorden is deeper than Hornsund, with a maximum depth of 400 m. The shores of the fjord consist of a steep and rocky hard bottom, which becomes weakly declining slopes with soft glacial sediments in the deeper parts (Ito and Kudoch, 1997).

Storfjorden (77°33′N, 19°05′E) is a large semi-enclosed fjord, widely open to the Barents Sea bay, and situated between the islands of Spitsbergen, Barentsøya and Edgeøya. The fjord is approximately 190 m deep at its maximum depth, and its bottom temperatures remain