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Elemental composition of invertebrates shells composed of different $CaCO_3$ polymorphs at different ontogenetic stages: a case study from the brackish Gulf of Gdansk (the Baltic Sea)

Anna Piwoni-Piórewicz[1*], Stanislav Strekopytov[2†], Emma Humphreys-Williams[2], Piotr Kukliński[1, 3]

[1]Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81-712 Sopot, Poland
[2]Imaging and Analysis Centre, Natural History Museum, Cromwell Road, London SW7 5BD, United Kingdom
[3]Department of Life Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, United Kingdom

[*]Corresponding author
E-mail: apiwoni@iopan.pl
Tel.: (+ 48 58) 731 16 96
[†] Present address: Inorganic Analysis, LGC Ltd, Queens Road, Teddington, United Kingdom

Abstract

In this study, the concentrations of 12 metals: Ca, Na, Sr, Mg, Ba, Mn, Cu, Pb, V, Y, U and Cd in shells of bivalve molluscs (aragonitic: *Cerastoderma glaucum*, *Mya arenaria* and *Limecola balthica* and bimineralic: *Mytilus trossulus*) and arthropods (calcitic: *Amphibalanus improvisus*) were obtained. The main goal was to determine the incorporation patterns of shells built with different calcium carbonate polymorphs. The role of potential biological control on the shell chemistry was assessed by comparing the concentrations of trace elements between younger and older individuals (different size classes). The potential impact of environmental factors on the observed elemental concentrations in the studied shells is discussed. Specimens were collected from brackish waters of the Baltic Sea (the Gulf of Gdansk). For every species, 40 individuals (ten in each size class) were selected. Pre-cleaned shells were analysed by ICP-OES and ICP-MS to determine the concentrations of metals.

The distributions of elements both differ between species and exhibit high intraspecific variability. Calcitic shells preferentially incorporated Mg > Sr > Na, aragonitic shells incorporated Na > Sr > Mg, and bimineralic shells accumulated Na approximately two times more intensively, than Mg and Sr which remained at similar levels. Among all species, the calcitic shells of *A. improvisus* most effectively concentrated the majority of the studied elements, especially Mg > Mn > Ba, which was contrary to the shells of aragonitic molluscs that contained the lowest levels of trace elements. The size-dependent distributions of elements in shells did not exhibit a consistent pattern. The highest significant differences were found for the bimineralic shells of *M. trossulus*, while the smallest were found for aragonitic shells; if any variability occurred, it was observed in heavy metals (Pb, Cd).

Our results indicate that elemental variability, especially that of Mg and Sr, is dominated by the properties of the crystal lattice. The inconsistent variability of trace element concentrations between species and within single populations supports the important role of species-specific biological control of the biomineralization process and indicates that environmental factors have a significant influence on the incorporation of trace elements into the shells.

Key words: calcite, aragonite, trace metals, ontogeny, shell, ICP-MS, ICP-OES

1. Introduction

Marine invertebrates such as molluscs (bivalves, gastropods), brachiopods, corals, echinoderms, bryozoans and some groups of protozoa (foraminifera) are able to precipitate shells and skeletons as composite materials consisting of calcium carbonate ($CaCO_3$) crystallised on a species-specific organic matrix (Cusack and Freer, 2008). In a living organism, $CaCO_3$ is deposited mainly in the form of two polymorphs, calcite and aragonite, which are commonly found co-existing in the same specimens and appear to be precipitated in the same environments (Morse et al., 2007; Taylor et al., 2008). Trace elements are incorporated into the crystal lattice from both the ambient seawater and ingested food particles (Cubadda et al., 2001). Biological carbonates determine the largest component of the hydrosphere's carbon reservoir, and the biogenic production of $CaCO_3$ has a strong interdependence on the ocean composition, biogeochemistry and the carbon cycle (Cohen and McConnaughey, 2003). In the last few decades, increasing attention has been paid to the relationship between the elemental compositions of shells and external environmental factors. It has been repeatedly observed that the crystal layers are precipitated successively at regular periodicities, recording the conditions in which the calcification occurred (Marchitto et al., 2000; Rodland et al., 2006). The elemental composition of the crystal lattice can provide records of seawater chemistry and has great potential for use in the interpretation of patterns of ocean history (Freitas et al., 2006; Gillikin et al., 2006; Khim et al., 2003; Ponnurangam et al., 2016; Vander Putten et al., 2000). However, as recent studies have indicated (Dove, 2010), the influence of environmental parameters on shell precipitation could be very complex. The mineralogy and chemistry of shells are likely to be not only linked to environmental conditions but are also simultaneously controlled by the organism itself. Even a single population or closely related species within the same habitat may exhibit different accumulation strategies (Rainbow et al. 2000).

Calcite and aragonite differ in structure, symmetry and properties. The calcium ion has 9-fold coordination in aragonite and 6-fold coordination in calcite, and its coordination creates hexagonal and cubic packing (Putnis, 1992). Due to the spatial structure, larger cations, such as Sr, fit better in aragonite, while smaller cations, such as Mg, are energetically favoured in calcite. In natural systems, calcite commonly incorporates Mg (Morse et al., 2007; Reeder, 1983; Wang and Xu, 2001), and increasing Mg concentrations are known to increase the calcite solubility (Kuklinski and Taylor, 2009; Smith et al., 2006). At the temperatures and pressures of the Earth's surface, low-Mg calcite is the most stable form of $CaCO_3$ (de Boer, 1977). Nevertheless, in many marine organisms, aragonite and high-Mg calcite are the dominant phases precipitated from seawater (Dickson, 2004). The solution chemistry (Cusack and Freer, 2008), temperature (Balthasar and Cusack, 2015), pressure (Allison et al., 2001), $CaCO_3$ saturation state (Watson et al., 2012), pCO_2 (Lee and Morse, 2010) and phylogenesis (Kuklinski and Taylor, 2009; Smith et al., 1998; Smith and Girvan, 2010) are known to influence shell mineralogy. The main driving force controlling the mineralogy of precipitated $CaCO_3$ is the ratio of Mg to Ca ions in seawater (Cusack and Freer, 2008; Morse et al., 2007).. A Mg/Ca > 2 favours the precipitation of aragonite and high-Mg calcite. At high Mg/Ca ratios, such as those in modern seawater (Mg/Ca = 5.2), calcitic structures incorporate Mg, which is observed to inhibit calcite nucleation and growth, whereas aragonite nucleation is not affected by magnesium in solution (De ChoudensSanchez and Gonzalez, 2009; Morse et al., 2007). Most low-Mg calcite-producing taxa are known to actively control the amount of magnesium incorporated. Since the Mg/Ca ratio of the calcifying fluid is dissimilar to that of ambient seawater, organisms might be unaffected by changes in the environmental Mg/Ca ratio (Bentov and Erez, 2005; De Nooijer et al., 2014). Several studies of organisms that secrete calcareous skeletons have shown that lower seawater temperatures are correlated with the secretion of calcite skeletons with low Mg contents, rather than more soluble high-Mg calcite or aragonite skeletons (Taylor and Reid, 1990). The mineralogy of many calcareous structures changes with latitude, likely as a result of the temperature gradient from the poles to the equator (Kuklinski and Taylor, 2009; Loxton et al., 2014; Taylor et al., 2014). However, the secretion of calcite by marine organisms inhabiting low-temperature areas and aragonite in warmer waters is not an absolute rule, as many polar molluscs form fully aragonitic shells (Cairns and Macintyre, 1992). Thermodynamics predicts that aragonite is the stable phase at pressures higher than 5000 hPa (roughly 40 m depth), and calcite is the stable phase at lower pressures. However, aragonite is the major constituent of shells or pearls, indicating its metastable formation in shallow waters (Sunagawa et al., 2007). The incorporation of Sr was suggested to play a significant role in the biomineralogical precipitation of aragonite (Allison et al., 2001). Many studies have demonstrated a clear correlation between the concentration of Sr in the hard parts and precipitation of the aragonite layer (Iglikowska et al., 2016; Reeder, 1983). The ionic radius of Sr is larger than that of Ca; thus, Sr is more likely to form 9-fold coordination, which triggers metastable aragonite nucleation (Sunagawa et al., 2007).

Although many studies have demonstrated that the biological control of shell composition is often more important than the environmental control (Carré et al., 2006; Freitas et al., 2005, 2006; Gillikin et al., 2005), there is evidence to the opposite trend (Klein et al., 1996; Pearce and Mann, 2006). In biologically controlled mineralization, the organism drives the process of nucleation and growth of the minerals independently from the environmental conditions. Basically, endogenous factors manifest through co-regulation of all the structures and functions of the organism, including its sex, growth rate, metabolism, and feeding strategy (Lowenstam and Weiner, 1989). Throughout the lifespan, the biogenic system experiences ontogenetic trends and seasonal variations in physiology, determining metabolic expenses on the basis of life's needs. Biological effects have been repeatedly used to explain any shifts of elemental concentrations in shells from a theoretical equilibrium (Davis et al., 2000; Watson et al., 1995). Ontogenetic fluctuations of the growth rate and metabolic activity affect the intensity of the metal uptake (Lee et al., 1998). Vander Putten et al. (2000) concluded that the seasonality of the accumulation of Mg, Sr and Pb in *Mytilus edulis* shells shows significant similarity across individuals, with a maximum during spring and early summer, and profiles cannot be explained by seasonal variations in the seawater composition. (Carré et al., 2006) developed a model of ion transport in bivalve shells that shows that Ca channels are less ion-selective when Ca^{2+} fluxes are higher. Other studies have found that trace metal uptake rate increases as mussel filtration rate increases (Janssen and Scholtz, 1979).

It is still difficult to separate the degree to which the organism itself controls the composition of the carbonate shell and how much this process is affected by the environment (Casella et al., 2017; Schöne and Krause, 2016; Weiner et al., 2001). Although calcareous parts serve as a powerful tool for the interpretation of the environmental conditions, detailed insight into the different factors controlling the composition of biological $CaCO_3$ is fundamental for understanding the chemical profiles. Tracking potential sources of variation within calcifying organisms of many species with diverse mineralogy should provide valuable insight into the patterns driving the biomineralization process (Smith et al., 1998).

The aim of this study is, by examining the trace element concentrations in calcitic, aragonitic and bimineralic shells. to assess the potential differences in free ion binding in two crystalline polymorphs in the low-salinity environmental system using the example of the southern Baltic Sea. Brackish waters influence the activities of metal ions, enhancing their bioavailability (Fritioff et al., 2005) and contributing to lower Ca^{2+} concentrations, $CaCO_3$ saturation states, alkalinity and buffering capacity compared to those of more saline waters (Beldowski et al., 2010; Cai et al., 2010; Findlay et al., 2007). The seasonal changes (mainly the surface temperature variability, periodic lowering of salinity, irregular inflow of pollutants and intensity of biological processes) were found to affect both the metal concentration and the physiological processes of living organisms (Urey et al., 1951). For this study we selected dominant species of the calcifying benthic fauna in this region. This includes the bivalve molluscs: aragonitic *Cerastoderma glaucum*, *Mya arenaria*, and *Limecola balthica* and bimineralic *Mytilus trossulus*, as well as an arthopod, *Amphibalanus improvisus,* with a fully calcitic shell. The investigated species are deposit and filter feeders and have sessile or semi-sessile lifestyles. Their lifespan is long enough to include various seasons and years covering therefore a range of environmental conditions during their existence. The potential influence of local environmental conditions on the observed trace element concentrations in the shells of the studied organisms is discussed. A comparison of concentration levels between size classes is also performed, to demonstrate any potential biological control of the shell chemistry (assuming that the larger specimens were older than the smaller specimens of the same species).

2. Material and methods

2.1. Study area

The study area is located in the Gulf of Gdansk in the southern region of the Baltic Sea (Fig. 1). The Gulf is partially sheltered from the northwest by the Hel Peninsula and from the west and south by the Polish coastline (Kruk-Dowgiałło and Szaniawska, 2008; Rainbow et al.,

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2004). This location makes the seawater the most turbulent in January and the calmest in June, with weak bottom currents and minimal tidal amplitudes. The hydrophysical parameters of the Gulf are mostly driven by the temperate climate and the following seasonal changes. Differences in air temperature and water mixing cause seasonal fluctuations of the surface water temperature, ranging from approximately 4 to 22°C (Uścinowicz, 2011). The Gulf of Gdansk is a low-salinity system under the influence of brackish water from the open southern Baltic Sea and fresh waters from rivers, mainly the Vistula River; the Vistula is the largest river in Poland and has an average annual inflow in the estuary of 1080 $m^3\ s^{-1}$, which varies seasonally from 250 to 8000 $m^3\ s^{-1}$ and has a maximum in spring (Cyberski et al., 2006). Thus, the average water salinity in the gulf is 7, varying from approximately 5.5 in summer to 8.4 in winter (Bulnheim and Gosling, 1988; Szefer et al., 2002).

The Gulf is known as an area highly exposed to human impact. This is due to intensive usage of its resources and to anthropogenic emissions originating from various coastal sources, river inflows and atmospheric deposition. The most significant input of industrial and municipal pollution into the Gulf of Gdansk is derived from the Vistula River, which transports pollutants from a catchment area of 194,000 km^2 (Pruszak et al., 2005). Both the water discharge and sediment load into the Gulf are strongly seasonally dependent. The maximum river flow typically occurs in spring, with the minimum in autumn and winter, mainly due to periods of snow and ice melting (Cyberski et al., 2006; Pruszak et al., 2005; Szefer et al., 1996). Winter storms cause the re-deposition of sediments further into the Gulf of Gdansk (Damrat et al., 2013). Because of the natural conditions, mainly, the limited water exchange, contaminants brought by the river remain in the ecosystem for decades, accumulating in the sediments and in living organisms (Glasby et al. 2004; Szumiło-Pilarska et al. 2016).

The benthic community of the Gulf of Gdansk is characterized by the dominance of calcifying filter feeders and deposit feeders (Kruk-Dowgiałło and Dubrawski, 1998). The low salinity (~7) and alkalinity, which, in most regions of the Baltic Sea, are lower than those in oceanic surface waters, cause reduced CO_3^{2-} and Ca^{2+} concentrations in seawater, thus lowering the $CaCO_3$ saturation state (Ω). Furthermore, due to the seasonality of the temperature and water chemistry, the amplitude of Ω in the Baltic Sea is high in comparison to that in the open ocean. It alternates between approximately 1 to 5 for calcite and 0.5 to 2.5 for aragonite (Findlay et al., 2007). Seasonal changes also affect the feeding behaviour. The capacity for food processing is evolutionarily adapted to the concentrations of suspended matter, primarily phytoplankton, that prevail in the biotope during the productive seasons of the year. During these periods, organisms exploit their growth potential (Pierscieniak et al., 2010; Staniszewska et al., 2016).

2.2. Species

The barnacle *Amphibalanus improvisus* (Darwin, 1854) (Arthopoda, Maxillopoda), commonly named the bay barnacle, is a small sessile crustacean that typically exists in shallow coastal zones that are less than 10 m deep. It is widespread around the Atlantic and has been dispersed by shipping to many parts of the world, now having a worldwide distribution. It is a euryhaline and eurythermal species that is absent only from the Arctic and Antarctic seas (Kerckhof, 2002). *A. improvisus* is a filter feeder that inhabits hard substrates. In the Baltic Sea, the reproduction of barnacles starts in spring with temperatures over 10°C and ends in autumn. The species grows to approximately 10 mm in diameter with a maximum height of approximately 6 mm, and generally, it has longevity of one year (Żmudziński, 1990). It has a conical shell composed of six fused calcite plates (Weidema, 2000).

The clam *Cerastoderma glaucum* (Bruguière, 1789) (Mollusca, Bivalvia), commonly known as the lagoon cockle, is a saltwater clam found along the coasts of Europe and North Africa, including in the Mediterranean and Black Seas, the Caspian Lake, and the low-salinity Baltic Sea. It is a euryhaline species living in salinities of 4–84. *C. glaucum* can tolerate habitats with wide range of temperatures, from periodically freezing to above 30°C. It is a filter feeder that burrows 2–4 cm below the surface in soft sediments at shallow depths of secluded bays. It actively lives near the sediment surface, acting as a biodiffuser (Urban-Malinga et al., 2013). The clam is surrounded by a ribbed aragonite shell, which is externally yellowish to greenish brown (Jelnes et al., 1971). In the brackish environment of the Gulf of Gdansk, *C. glaucum* spawns in May-July and typically lives up to 4 years, achieving a height of 27 mm (Żmudziński, 1990).

The soft-shell clam *Mya arenaria* (Linnaeus, 1758) (Mollusca, Bivalvia) is a marine invasive species introduced into European waters from the Atlantic coasts of North America (Behrends et al., 2005). It has a wide global distribution, mainly due to its adaptability to varying environments with salinities between 4 and 35 and temperatures between –2 and 28°C (Gofas, 2004; Strasser et al., 1999). *M. arenaria* burrows into the sediment up to 20–30 cm below the surface of the sea floor. *M. arenaria* is a filter feeder, filtering organic particles and microinvertabrates using long fused siphons, and a deposit feeder. In the Gulf of Gdansk, *M. arenaria* is a common inhabitant of shallow waters up to a depth of 30 m. It spawns once

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or twice a year in spring or summer, at temperatures of 10 – 15°C. Individuals live 10 – 12 years. They have aragonitic shells and grow up to 70 mm (Żmudziński, 1990).

The clam *Limecola balthica* (Linnaeus, 1758) (Mollusca, Bivalvia) lives in the northern parts of the Atlantic and Pacific oceans, in Subarctic and European waters from southern France to the White Sea and Pechora Sea, including the Baltic Sea (Strelkov et al., 2007). It is a euryhaline clam capable of living in a wide range of water salinities from 3 to 40 and at temperatures from –2 to more than 30°C (Sartori and Gofas, 2016). *L. balthica* is a filter feeder and deposit feeder that lives buried a few centimetres below the surface. It has a semi-sessile lifestyle, with the ability to undertake periodic migrations (Hiddink et al., 2002). In the Baltic Sea, *L. balthica* lives at depths of up to 40 m and grows to 24 mm. Adults reproduce in spring when the water temperature reaches 10°C and live 12 years (Żmudziński, 1990). They have aragonitic shells varying in colour between individuals and locations, mainly exhibiting white, pink, yellow and orange (Sartori and Gofas, 2016).

The mussel *Mytilus trossulus* (Gould, 1850) (Mollusca, Bivalvia) is one of three closely related taxa in the *Mytilus edulis* complex of blue mussels, which, collectively, are widely distributed in the temperate and cold-water coasts of the Northern Hemisphere and are often dominant organisms on hard substrates of shallow nearshore habitats (Rainbow et al., 1999; Wenne et al., 2016). Generally, *M. trossulus* has a life span of approximately 12 years and grows to 100 mm, yet in the estuarine environment of the Gulf of Gdansk, it reaches a maximum length of approximately 50 mm (Gofas, 2004; Żmudziński, 1990). Mussels are sessile filter feeders, mainly depending on phytoplankton. They reproduce from late spring to early autumn, depending on the temperature and food abundance (Larsson et al., 2017; Lauringson et al., 2014; Rainbow et al., 2004). The shell of *M. trossulus* is bimineralic and consists of two calcium carbonate layers: an outer calcite and inner aragonite layer in variable proportions between individuals (Dalbeck, 2008; Piwoni-Piórewicz et al., 2017).

2.3. Sample collection and preparation

Samples of shells were gathered by a Van Veen grab sampler from four stations, GN, MA, M2 and MW, located in the Gulf of Gdansk (Table 1, Fig. 1). No single location that would be a source of several species presenting different forms of $CaCO_3$ was found. Three species were found at MA, M2 and MW (one at each station), while two species were collected at station GN (see Table 1). To ensure that the samples were not contaminated or modified by solutions of preservatives, the collected material was transported alive in tanks filled with seawater to the laboratory, where sample preparation took place.

By measuring the shell heights of clams and shell diameters of barnacles using a calliper with an accuracy of ±1 mm, the shells were classified into four size classes. The division into size classes was performed on the basis of the size reached by each species in the southern Baltic Sea environment (Table 2). Forty shells (ten in each class) were selected for *A. improvisus*, *C. glaucum*, *M. arenaria* and *L. balthica*. For *M. trossulus*, 20 shells were selected, with five in each class, while the results for the rest were obtained from Piwoni-Piorewicz et al. (2017). After the removal of soft tissues, each shell was viewed under a stereoscopic microscope to examine the epibiotic flora and fauna, which could contaminate the sample and bias the chemical analysis. If any organisms were present on the shell, they were carefully removed. To remove the biofilm, the periostracum was scraped with a scalpel, and pre-cleaned shells were placed in an ultrasonic bath (InterSonic IS-7S) in ultra-pure water for 30 minutes and then dried at 70°C for 24 hours. The shells were then crushed and ground into a fine powder with an agate mortar and pestle. Aliquots (2.8 − 849 mg, mean = 132 mg) of the powdered samples were weighed using a 5-digit analytical balance, placed into a 15 ml plastic tube (Sarstedt®) and dissolved in a mixture of 1.5 ml concentrated nitric acid (HNO_3, Sigma Aldrich®, Trace SELECT for trace analysis), 1.5 ml ultra-pure water and 0.3 ml 30% hydrogen peroxide (H_2O_2, Merck® Suprapure grade). After 24 hours at 70°C, the liquid samples were diluted to c. 15 ml by weight with ultra-pure water.

2.4. Elemental analysis

Concentrations of chemical elements in the digested samples were determined at the Natural History Museum, London, using a Thermo iCap 6500 Duo inductively coupled plasma optical emission spectrometer (ICP-OES) for Ca, Mg, Na and Sr and an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS) for Ba, Cd, Cu, Pb, U, V, Mn and Y. Calibration of the ICP-OES analysis was performed using solutions that were matrix-matched to the high calcium concentrations in the samples. Multiple wavelengths for each element were recorded, and line selection was performed by accounting for the suitability of the wavelength to the concentrations in the samples. The accuracy and reproducibility of the analyses were checked using two calcium-rich certified reference materials (CRMs), JLs-1 Limestone and JDo-1 Dolomite (both from the Geological Survey of Japan), which were dissolved by the total digestion method using hydrofluoric acid. The reference materials were diluted to match the concentrations of Ca in the sample solutions (Imai et al., 1996).

The limits of quantification (LOQ) of the ICP-MS analysis were generally determined as the concentration corresponding to ten times the standard deviation of the signal obtained

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by analysing 5% HNO_3 solution (6–7 times) in each individual run. ICP-MS was run in helium (He) mode (5 ml min^{-1} He, 99.9995% purity) for most trace elements to minimize the molecular interference from plasma and solution components and Ca from the samples. The accuracy and reproducibility was checked by periodic analyses of JLs-1 and JDo-1 (Imai et al., 1996).

2.5. Statistical analyses

To evaluate the effect of the shell size (ontogenesis stage) on the concentrations of trace elements in calcareous parts of *A. improvisus*, *C. glaucum*, *M. arenaria L. balthica* and *M. trossulus*, the concentrations of Ca, Na, Sr, Mg, Ba, Mn, Cu, Pb, V, Y, U and Cd were examined in the four size classes separately for each species. The data were not normally distributed (Shapiro-Wilk test); therefore, significant differences between the mean concentrations of the selected elements in the size classes were identified by one-way Kruskal-Wallis nonparametric ANOVA (*p*-value = 0.05) and post-hoc Dunn's tests for multiple independent groups. Statistical computing and graphical visualizations were performed in RStudio.

3. Results

The species exhibited similar accumulation orders since they had the highest concentration of Na, Sr and Mg and the lowest concentrations of U and Cd (Table 3, Fig. 2). However, the concentrations of metals were different between the calcitic shells of *A. improvisus*, the aragonitic shells of *C. glaucum*, *M. arenaria*, *L. balthica* and the bimineralic shells of *M. trossulus*, showing high variability (Fig. 3). Manganese was the most variable and increased from 1.4 ± 1.0 mg kg^{-1} in aragonitic *M. arenaria* to 620 ± 155 mg kg^{-1} in calcitic *A. improvisus*. Trace elements (V, Cu, Y, Cd, Ba, Pb, U) were generally present at higher concentrations in calcitic shells than in aragonitic ones. Shells of *M. arenaria* had the lowest concentrations of impurities. The smallest variability between species was found for Sr, Na and Ca (Fig. 3).

The results of the Kruskal-Wallis nonparametric ANOVA test, which was used to compare the shell chemistry between the four size classes in each population, revealed the lack of ontogenetic changes within aragonitic *M. arenaria*. The smallest variability was found in aragonitic *L. balthica*, for which only the concentration of Na (p = 0.014) decreased with shell growth. The third of the aragonite species, *C. glaucum*, showed high variability of the four elements. Throughout the lifespan, shells were built with increasing concentrations of Sr

($p = 0.002$), which was contrary to the decreasing concentration of Na ($p = 0.015$), Mn ($p = 0.014$) and Cd ($p = 0.009$). Similarly, the calcitic shells of *A. improvisus* also showed variability of four elements between size classes, namely, Mg ($p = 0.007$), V ($p = 0.011$), Cu ($p = 0.027$) and Pb ($p = 0.004$). However, in this case, the sequences of the ontogenetic changes were not straightforward but, rather, had a tendency to fluctuate between the youngest and the oldest individuals. The highest variability was found within the bimineralic shells of *M. trossulus*. The size classes differed in terms of five elements. The incorporation of V ($p < 0.001$), Cu ($p < 0.001$), Y ($p = 0.013$), Cd ($p = 0.002$) and U ($p < 0.001$) into the crystal lattice decreased in larger mussels (Fig. 3, Fig. 4).

Detailed analyses of the significant differences in the studied elements between the size classes based on post-hoc Dunn's tests for multiple independent groups indicated that the variations were not linear (Fig. 5). In *L. balthica* aragonitic shells, sodium concentration decreased with ageing, showing differences between the size classes I and III and I and IV. In the shells of *C. glaucum*, Sr concentration increased gradually, reaching a peak in the size class IV, while statistically significant differences were observed between the size classes I and IV and the III and IV. An inverse pattern was observed for sodium, yet its concentration differed only between the youngest and oldest individuals. The aragonitic shells were characterized by a common trend of the Mn and Cd concentrations, which decreased from I size class and later reached a plateau. In the calcitic shells of *A. improvisus,* the concentrations of Mg, V, Cu and Pb decreased in larger individuals. The levels of magnesium in shells statically differed between the size classes III and IV; likewise, shells from the size class III had the highest concentrations. Vanadium and lead occurred at the highest concentrations in the shells of the youngest individuals, and later, they oscillated around a similar average. Co decreased in growing shells of barnacles, reaching the minimum in the size class III. There were no statistically significant differences between the classes III and IV, and the oldest half of the group maintained the downward trend. However, it is worth noting that Cu concentrations in many of the oldest shells are several times higher. The bimineralic shells of *M. trossulus* were characterized by the highest variability of trace element concentrations between size classes. The trend of decreasing concentrations was clearly marked for V, Co, Cd and U. The concentration of Y decreased in larger shells, but the oldest shells showed an upward trend; therefore, significant differences were found between the size classes I and III (Fig. 5).

4. Discussion

Magnesium and strontium are some of the most commonly studied elements in the skeletons of marine calcifiers due to their important role in the biological precipitation of $CaCO_3$ (Allison et al., 2001; De Choudens¯Sanchez and Gonzalez, 2009; Morse et al., 2007). We found statistically significant differences in the concentrations of Mg and Sr between the calcitic, aragonitic and bimineralic species. This confirms that the crystal structure of the shell plays a key role in the incorporation of major elements. In the calcitic *A. improvisus,* Mg was the dominant impurity, while aragonitic *C. glaucum*, *M. arenaria* and *L. balthica* had concentrations of Sr over 15 times higher than those of Mg. The shell of *M. trossulus* contains layers of calcite and aragonite, thus favouring both Mg and Sr. Not surprisingly, in this study, mussels were characterized by similar concentrations of Mg and Sr, reaching 0.106 ± 0.017 mg kg^{-1} and 0.117 ± 0.010 mg kg^{-1}, respectively (Table 3, Fig. 3). These observations are in agreement with results obtained by other authors for different calcareous species (Iglikowska et al., 2016; Morse et al., 1997; Reeder, 1983; Wang and Xu, 2001). Such results confirm the importance of the Mg and Sr ionic radius in terms of the aragonite and calcite lattice properties (England, 2005). The studied calcitic *A. improvisus*, without a doubt, has the highest Mg concentration in its shells (0.394 ± 0.032 mg kg^{-1}); however, the Sr concentration was also higher in barnacles (0.225 ± 0.019 mg kg^{-1}) compared to that in aragonitic clams (0.170 − 0.216 mg kg^{-1}) (Table 3, Fig. 3). Kinetic and biological effects (Urey et al., 1951) influence the partitioning of Sr between the shell and seawater, and Sr in shells is known to significantly exceed its concentration expected at the thermodynamic equilibrium (Schöne et al., 2010). An important consideration for Sr concentrations in calcite is that Mg incorporation into the shells may increase the Sr affinity through changes in the calcite crystal morphology (Carpenter and Arbor, 1992). Greater inclusion of minor ions into the shell structure may result in crystal defects, contributing to a higher incorporation rate of less compatible ions into the crystal lattice (Dalbeck, 2008; Davis et al., 2000). Furthermore, it was found that barnacles differ from other calcitic species, having an uncommonly high Sr level (Carpenter and Arbor, 1992; Ullmann et al., 2018), and the highest concentration in *A. improvisus* in the Gulf of Gdansk could act as species-specific adaptation (Fig. 3).

Sodium belongs to the group of proxies used in the robust reconstruction of salinity, and this relationship seems to be related mainly to the increase of Na activity in seawater with increasing salinity (Findlater et al., 2014; Wit et al., 2013). Although we observe that for invertebrates collected from stations with similar salinities between 6.9 and 7.3, the aragonitic species incorporated more Na than did the calcitic and bimineralic species (Figs. 3 and 4). The concentration of Na ranged, on average, from 0.2 wt% in *M. trossulus* to 0.32 wt% in *C.*

glaucum (Table 3). This finding could mean that the polymorph orientation affects Na concentration in shells. Following the orientation of the crystal lattice, Na, as a cation larger than Ca, performs better in the aragonite structure (Davis et al., 2000). Dalbeck (2008) compared the minor element variations between the polymorphs of *Mytilus edulis* bimineralic shells, and faound that Na occurred in higher concentrations in the aragonitic layer. Although the Na/Ca ratio is frequently discussed as a climate proxy, the degree to which Na concentration in biogenic carbonate represents the environmental salinity varies from one species to another (Vander Putten et al., 2000; Schöne and Krause Jr, 2016). This study shows lack of pattern in the distribution of Na between individuals from one population and between species.

The concentrations of manganese and barium in the calcitic shells of *A. improvisus* were several orders of magnitude larger than those in other species, reaching 625 ± 160 mg kg^{-1} and 73.2 ± 19.3 mg kg^{-1}, respectively (Table 3). The bimineralic shells of the mussel *M. trossulus* collected from the same location as *A. improvisus* (GN) contained 56.6 ± 20.0 mg kg^{-1} of Mn and 17.0 ± 6.7 mg kg^{-1} of Ba, while the aragonitic shells of clams incorporated from 1.419 ± 1.01 mg kg^{-1} to 11.933 ± 10.47 mg kg^{-1} of Mn and from 2.63 ± 1.58 mg kg^{-1} to 15.12 ± 10.15 mg kg^{-1} of Ba (Table 4, Fig. 3). This trend does not seem to be strongly linked to the crystal lattice orientation because smaller Mn cations are energetically favoured in calcitic species, while larger cations, such as Ba, better fit into aragonite (Dalbeck, 2008; Davis et al., 2000; Wang and Xu, 2001). It was expected that aragonite shells would incorporate Ba more intensively than would calcitic shells (Findlater et al., 2014; Gillikin et al., 2006), yet this trend was not observed (Figs. 3 and 4). The organisms derive metal ions from both the surrounding water and food (Freitas et al. 2006; Gillikin et al. 2005; Poulain et al. 2015). It is highly probable that intra-species variabilities reflect the seasonal variability of Mn and Ba concentrations in seawater, while differences between species partly depend on feeding strategies. Findlater et al. (2014), based on shells of fossil freshwater bivalves and gastropods from the same location, concluded that a clear biochemical vital effect was evident for Mn and Ba. Dissolved Mn is intensively delivered to the oceans by riverine input, and in the Gulf of Gdansk, the geographical range of the Vistula River inflow plays a very important role in the Mn distribution (Uścinowicz, 2011). However, much lower concentrations of Mn were found in the shells of molluscs than in barnacles from the same location (Figs. 3 and 4). A similar relationship was found in the soft tissues of *M. trossulus* and *A. improvisus* collected from different locations in the Gulf of Gdansk in May 1998 (Rainbow et al., 2000). The range of Mn in the soft tissues of *M. trossulus* varied from 19.0 to 41.0, while that in *A.*

improvisus ranged from 187 to 307 mg kg^{-1}. Therefore, *A. improvisus* is a very effective accumulator of Mn. The disproportionality of Mn and Ba concentrations between molluscs and barnacles could reflect the ability of molluscs to limit vital processes and to reduce the calcification rate during stressful conditions (Berge et al., 2006; Hiebenthal et al., 2012). A limited food base, low temperatures, saturation states during colder months and even the high river inflow in early spring (Cyberski et al., 2006; Pruszak et al., 2005; Szefer et al., 1996) can reduce the precipitation rates of *C. glaucum*, *M. arenaria*, *L. balthica* and *M. trossulus*. In contrast, the calcified shells of barnacles grow more or less continuously (Bourget and Crisp, 1975) and represent yearly calcification. The Mn and Ba incorporation from seawater into calcite and aragonite has been shown to correlate with changes in primary production and phytoplankton blooms (Freitas et al., 2006; Lazareth et al., 2003; Vander Putten et al., 2000). As many clams and barnacles are filter-feeding organisms, Mn- or Ba-rich particles are ingested with food and from the water column. Schoemann et al. (1998) recorded a seasonal increase of dissolved Mn in the water column after peaks in phytoplankton blooms. This partly explains why *M. arenaria* had the smallest concentrations of Mn and Ba. This clam represents a deposit-feeding mode and thus may have limited access to suspended particles. Uptake and accumulation in filter-feeders correlates with metal concentrations in seawater, whereas accumulation in deposit-feeders most likely reflects the metal concentrations in the sediments (Newman and McIntosh, 1982). Luoma and Jenne (1976) concluded that the degree of metal accumulation by deposit-feeders was directly related to the characteristic rate of metal desorption from a particular type of sediment.

Shells of *A. improvisus*, characterized by the highest concentrations of Mg, Sr, Mn and Ba, were simultaneously the richest in most other trace metals, which were likewise more concentrated in bimineralic *M. trossulus* than in aragonitic clams (Table 3, Fig. 2). It was mentioned previously that impurities arise in deformed crystal lattices (Dalbeck, 2008; Davis et al., 2000), and these lattices could be changed through the intensive incorporation of Ca substitutions. However, it is also important to mention that the ionic radii of smaller cations, such as V, Cd, Y, Pb, U and Cu, are more energetically favoured in calcite than in aragonite (Morse et al., 1997; Reeder, 1983; Wang and Xu, 2001).

Trace metal concentrations in shells are usually linked to local environmental conditions. If heavy metals in the shells of calcifying invertebrates reflect the environmental levels of bioavailable ions, the highest concentrations of most trace metals in the shells of *A. improvisus* and *M. trossulus* from GN station (Table 4, Fig. 3) are probably related to local contamination. Rainbow et al. (2004) compared the differences between the bioavailabilities

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of seven metals (Cu, Zn, Fe, Pb, Ni, Cd and Mn) to *A. improvisus* and *M. trossulus* across five localities in the Gulf of Gdansk, including GN station, which was often the richest metal source for marine organisms. Among the stations selected in this study, GN is closer than MA, MW and M2 to the mouth of the Vistula River, which is a major source of metal contaminants in the marine system (Fig. 1).

In this study, individuals were collected over a wide range of sizes from each station (Table 2), representing different ages and various periods of time, living under the influence of seasonal changes. The southern Baltic Sea is driven by cyclical environmental dynamics, which evoke physiological stress, reduce the food base and determine the biogeochemical cycle (Elder and Collins, 1991). It is certain that the biological processes of an animal precipitating carbonate complicate the calcification course (Vander Putten et al., 2000; Zacherl et al., 2003). However, the physiology of an organism is likely dependent on the environmental conditions it experiences (Gillikin et al., 2005). The recorded concentrations of metals in all populations exhibited marked variability among individuals within a single location (Table 3, Fig. 3), an attribute which was previously noticed by several researchers (Gillikin et al., 2005; Vander Putten et al., 2000). The wide range of inter-species variability suggests that the uptake of metals, and the subsequent bioavailability, are highly dependent on biological factors such as the growth rate, feeding strategy, genotype and phylogeny. Within species, organisms from juveniles to adults experience morphological and functional changes related to sex, metabolic rate or reproductive stage, which affect the biomineralization process (Carré et al., 2006; Freitas et al., 2006; Gillikin et al., 2005; Schöne et al., 2010, 2011; Warter et al., 2018). In shells of the studied *A. improvisus*, *C. glaucum*, *M. arenaria*, *L. balthica* and *M. trossulus*, differences in elemental concentrations over the lifespan did not produce a consistent pattern. From the chemical profiles, it is evident that the size-dependent distributions of elements in the shells were only marked in a few cases (Figs. 5 and 6). The studied *A. improvisus* and *M. trossulus* showed the greatest chemical variability between size classes (Fig. 4). However, in this case, the varied elements were not uniform for *A. improvisus* and *M. trossulus*, even though the organisms came from one location (Table 1). No size-related trend was observed for Y, U, and Cd in barnacles or for Pb in molluscs (Fig. 3). It was previously found that different species in the same habitat might show different patterns of metal accumulation, which are caused by specific routes of uptake or differences in the physiological pathway of metals (Rainbow, 2002, 1995). Rainbow et al. (1999) tested *A. improvisus* and *M. trossulus* from the Gulf of Gdansk as environmental biomonitors by measuring the concentrations of Co, Zn, Fe, Cd, Pb, Mn and Ni in soft tissues. They revealed that the mussels and barnacles gathered at one location did not show the same variation in metal bioavailabilities.

In this study, generally, when statistical differences between size classes were recorded, the concentrations of metals decreased with the size of the shell. The reverse trend was found only for Sr in the shells of *C. glaucum*, in which the concentration of Sr increased with size (Fig. 4). It is possible that the younger specimens had a greater calcium carbonate precipitation rate and uptake of trace elements due to a higher metabolism in the earlier stages of the animal life (Dalbeck, 2008). Rosenberg and Hughes (1991) suggested that areas of higher shell curvature, such as the umbo, require greater metabolic expenditure, resulting in an increase of metals uptake. This supports the idea of a higher metabolic rate and metal concentrations in younger specimens (Szefer et al., 2002). This study also indicates that the smallest individuals seem to be the most efficient accumulators of trace elements. This is mostly expressed in the cases of a few trace elements, in which the concentration decreased across the four size classes in the shells of *A. improvisus*, *M. trossulus* and *C. glaucum* (Fig. 4). There are several studies confirming a negative relationship between metal concentrations and shell size (Martincic et al., 1992; Piwoni-Piórewicz et al., 2017; Ritz et al., 1982). Catsiki and Gialamas (1994) suggested that apart from metabolic processes, an active detoxification mechanism is responsible for this trend, and its efficiency is higher in older and larger individuals.

Nevertheless, many of the elements studied herein showed a lack of statistically significant relationships between the shell sizes. Few trace metals in the shells of *A. improvisus* (Y, U, Cd), *C. glaucum* (V, Cu, Y, Pb, U) and *M. trussulus* (Pb) and all trace metals in the shells of *L. balthica* and *M. arenaria* (V, Cu, Y, Pb, U, Cd) showed no significant variability related with the growth of organisms (Fig. 3). This is not unusual in biomineralization studies. Saavedra et al. (2004) observed no differences between Cd, Pb, Cr, Ni, As, Cu and Zn concentrations for different shell lengths of the raft *Mytilus galloprovincialis* separated into four size classes. Protasowicki, Dural, & Jaremek (2008) similarly found that the concentrations of Hg, Pb, Cd, Cu, Zn, Cr, Ni, Fe, Mn, V, Li and Al in the shells of the mussel *Mytilus edulis* from the Polish coast of the Baltic Sea did not vary between shell sizes. This inconsistent pattern proves that biological effects modify the way in which environmental data are recorded in the biogenic hard parts.

5. Summary

The shells of the calcitic *A. improvisus*, the aragonitic *C. glaucum*, *L. balthica*, *M. arenaria* and the bimineralic *M. trossulus* from the Gulf of Gdansk are accumulators of a wide spectrum of metals from the surrounding environment. The selected taxa differed in terms of the chemical compositions of shells, both between taxa and within a single population. Elemental variability is strongly associated with the properties of the crystal lattice, which are different between calcite and aragonite. Remarkably high variability of elemental concentrations between species, especially for manganese, supports the importance of species-specific biological control of the biomineralization process. The high variability of elemental values within a single population indicates that both physiological and environmental factors have an influence on the incorporation of these trace elements into the shell. Given that the species were obtained from various sites, an impact from local environmental factors cannot be excluded.

This study has shown that interpreting the chemical profiles of calcium carbonate shells to determine the marine environment conditions is recommended to investigate how metal concentrations vary among large numbers of species from contrasting habitats. Nevertheless, we recommend using shells of similar sizes to reduce the ontogenetic variability.

Author contribution

Anna Piwoni-Piórewicz and Piotr Kukliński designed the study and carried them out. Stanislav Strekopytov and Emma Humphreys-Williams conducted elemental analysis. Anna Piwoni-Piórewicz prepared the manuscript with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

Data availability

The underlying research data can be accessed at Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81-712 Sopot, Poland.

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Tables and Figures

Table 1 Details of the research stations utilized for the collection of organisms. The environmental parameters T (temperature) and salinity were measured near the bottom during sample collection

Station	Latitude N	Longitude E	Collected species	Depth (m)	T (°C)	Salinity	Date
GN	54°32.0'	18°48.1'	*Amphibalanus improvisus*	36	3.1	7.3	May 2013
GN	54°32.0'	18°48.1'	*Mytilus trossulus*	36	3.1	7.3	May 2013
M2	54°38.9'	18°33.0'	*Cerastoderma glaucum*	10	16.9	6.9	June 2014
MA	54°37.2'	18°32.8'	*Mya arenaria*	10	19.8	6.9	June 2014
MW	54°37.4'	18°37.5'	*Limecola balthica*	31	4.7	7.0	June 2014

Table 2 The range of shell sizes for each studied species within a given size class

Species	Mineral type	Size classes (mm)				Maximum size in the Gulf of Gdansk (mm)*
		1	2	3	4	
Amphibalanus improvisus	Calcite	3–4	5–6	7–8	9–10	10
Mytilus trossulus	Bimineralic	6–5	16–25	26–35	36–44	50
Cerastoderma glaucum	Aragonite	4–8	9–12	12–16	16–20	27
Mya arenaria	Aragonite	10–20	20–30	30–40	40–49	70
Limecola balhtica	Aragonite	4–7	8–11	12–15	15–18	24

*Based on the literature data (Żmudziński, 1990)

Table 3 The concentrations of the studied elements in shells of the collected organisms

Amphibalanus improvisus

Elements	Mineral type	Unit	N	Mean	±1 SD	Min	Max
Ca	Calcite	wt %	37	31.6	2.60	27.6	39.0
Mg			37	0.394	0.032	0.337	0.472
Na			37	0.285	0.047	0.222	0.508
Sr			37	0.225	0.019	0.198	0.283
V		mg kg^{-1}	36	0.466	0.156	0.155	0.78
Mn			37	625	160	414	1161
Cu			37	3.90	2.20	1.20	8.30
Y			37	0.21	0.12	0.070	0.78
Cd			37	0.062	0.020	0.029	0.125
Ba			37	73.0	20.1	59.0	145
Pb			37	1.34	0.79	0.456	3.86
U			37	0.108	0.043	0.035	0.220

Cerastoderma glaucum

Elements	Mineral type	Unit	N	Mean	±1 SD	Min	Max
Ca	ragonit	t	40	34.8	1.60	30.4	38.1

Mg			40	0.008	0.003	0.005	0.023
Na			40	0.322	0.021	0.277	0.361
Sr			40	0.170	0.014	0.143	0.199
V		mg kg^{-1}	37	0.069	0.061	0.003	0.239
Mn			40	11.9	10.5	0.614	48.8
Cu			40	4.08	6.29	0.188	30.6
Y			40	0.070	0.074	0.006	0.401
Cd			37	0.011	0.009	0.001	0.043
Ba			40	15.0	10.0	1.22	35.4
Pb			34	0.14	0.10	0.006	0.298
U			40	0.096	0.084	0.003	0.339

Limecola balthica

Elements	Mineral type	Unit	N	Mean	±1 SD	Min	Max
Ca	Aragonite	wt %	40	34.5	1.70	29.0	37.5
Mg			40	0.008	0.003	0.003	0.018
Na			40	0.31	0.03	0.25	0.367
Sr			40	0.177	0.021	0.135	0.244
V		mg kg^{-1}	35	0.035	0.031	0.002	0.102
Mn			40	7.90	7.10	0.264	28.5
Cu			40	3.00	3.40	0.047	11.5
Y			40	0.08	0.11	0.002	0.421
Cd			37	0.007	0.008	0.0004	0.031
Ba			40	13.0	10.0	0.638	27.6
Pb			39	0.14	0.16	0.007	0.585
U			40	0.034	0.024	0.004	0.088

Mya arenaria

Elements	Mineral type	Unit	N	Mean	±1 SD	Min	Max
Ca	Aragonite	wt %	40	36.3	1.8	30.5	39.1
Mg			40	0.015	0.002	0.011	0.021
Na			40	0.308	0.021	0.26	0.345
Sr			40	0.216	0.028	0.168	0.295
V		mg kg^{-1}	40	0.016	0.014	0.001	0.062
Mn			40	1.40	1.00	0.276	5.32
Cu			40	0.031	0.024	0.006	0.114
Y			40	0.020	0.018	0.003	0.089
Cd			37	0.002	0.003	0.0002	0.016
Ba			40	2.60	1.60	0.574	6.26
Pb			40	0.015	0.014	0.002	0.077
U			40	0.006	0.005	0.001	0.022

Mytilus trossulus

Elements	Mineral type	Unit	N	Mean	±1 SD	Min	Max
Ca	Bimineralic	wt %	40	34.4	2.8	25.2	39.7
Mg			40	0.106	0.017	0.061	0.14
Na			21	0.201	0.031	0.147	0.291
Sr			41	0.117	0.01	0.101	0.143
V		mg kg^{-1}	40	0.78	0.52	0.206	2.30
Mn			35	54.0	15.0	31.8	92.6
Cu			40	14.0	10.0	3.36	58.3
Y			40	0.70	1.20	0.040	4.86
Cd			40	0.091	0.11	0.022	0.689

Ba			38	17.0	6.70	8.97	38.7
Pb			32	1.00	1.40	0.143	6.26
U			40	0.053	0.033	0.018	0.129

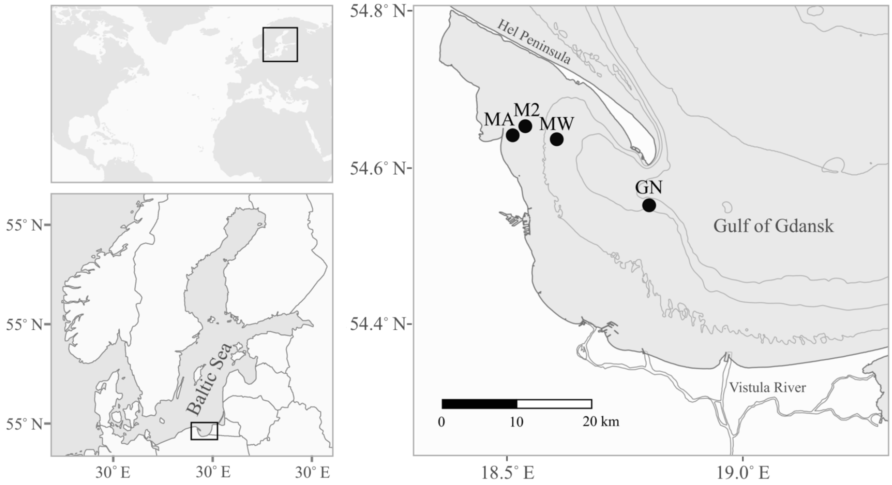

Fig. 1 The study area, with sampling stations indicated by black dots (stations details see Table 1)

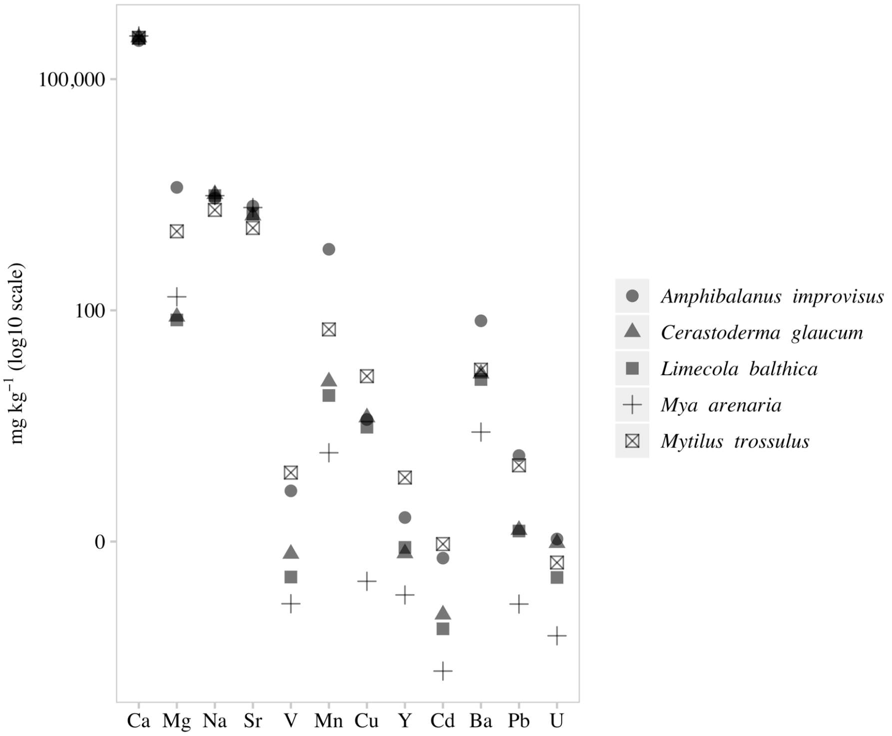

Fig. 2 The distribution of logarithmically transformed mean metal concentrations in shells of *Amphibalanus improvisus, Cerastoderma glaucum*, *Limecola balthica*, *Mya arenaria* and *Mytilus trossulus*

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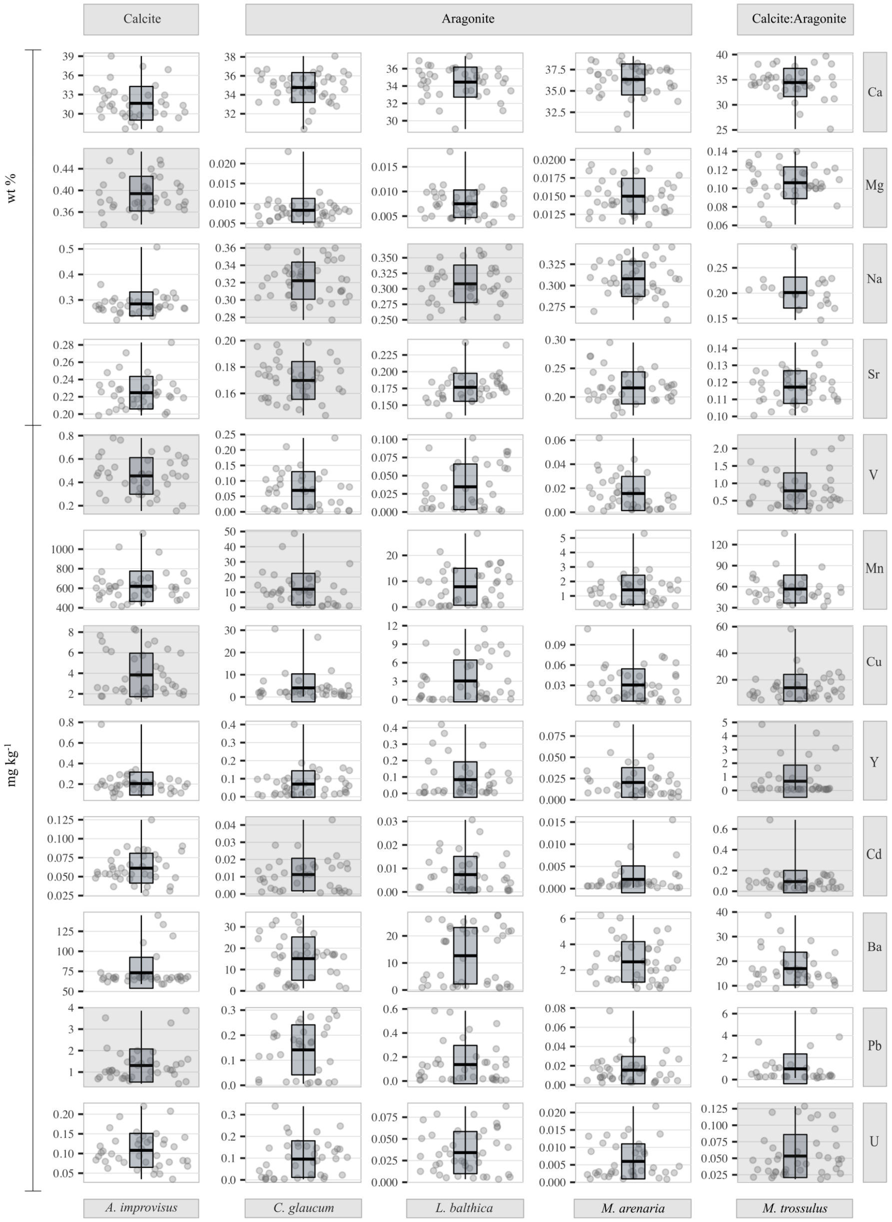

Fig. 3 Metal concentrations in analysed shells of *Amphibalanus improvisus, Cerastoderma glaucum*, *Limecola balthica*, *Mya arenaria* and *Mytilus trossulus*. The figure shows the raw data as grey dots, with boxplots representing a ±1 standard deviation around the means and whiskers indicating the minimum and maximum concentrations. The grey areas show elements with statistically significant differences between size classes

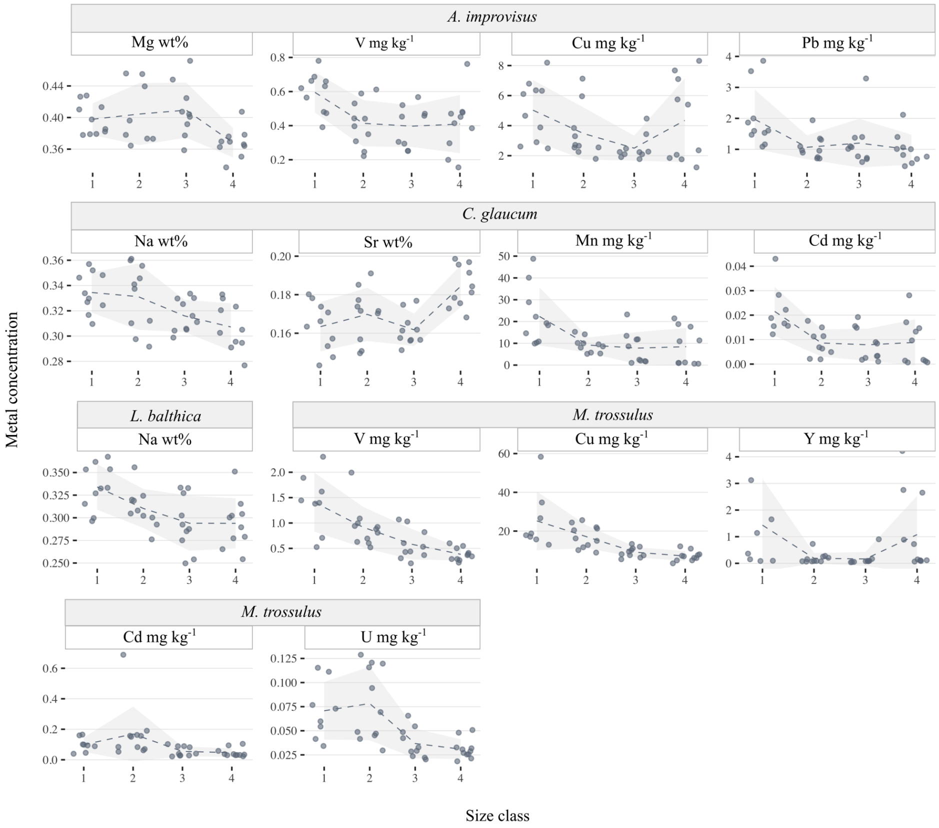

Fig. 4 Concentrations of elements with statistically significant differences between the four size classes (for size class details see Table 2) in the shells of *Amphibalanus improvisus, Cerastoderma glaucum*, *Limecola balthica* and *Mytilus trossulus*. The figure shows the raw data as black dots, with the light grey areas representing the standard deviations around the means (middle line)

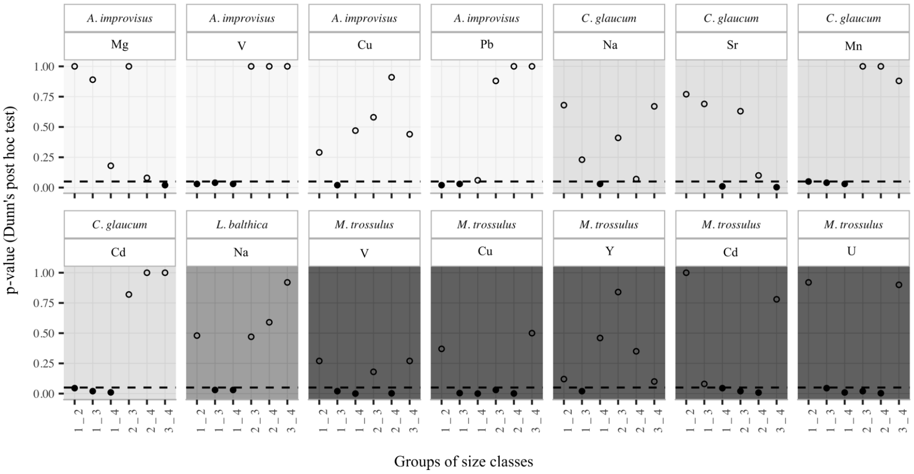

Fig. 5 Pairwise comparisons of metal concentrations between size classes (for size class details see Table 2) in the shells of *Amphibalanus improvisus, Cerastoderma glaucum*, *Limecola balthica* and *Mytilus trossulus*. The broken line separates statistically significant dependence (black points) from statistically non-significant dependence (empty points)