

Interactive comment on “Elemental composition of invertebrates shells composed of different CaCO₃ polymorphs at different ontogenetic stages: a case study from the brackish Gulf of Gdansk (the Baltic Sea)” by Anna Piwoni-Piórewicz et al.

Inge van Dijk (Referee)

inge.van.dijk@nioz.nl

Received and published: 14 October 2019

In the manuscript “Elemental composition of invertebrates shells composed of different CaCO₃ polymorphs at different ontogenetic stages: a case study from the brackish Gulf of Gdansk (the Baltic Sea)” by Piwoni-Piórewicz et al., the authors compare chemical composition of shells of bivalves and arthropods, which create their shell with (a mixture of) different polymorphs of CaCO₃. This is an interesting study which inves-

C1

tigates the effect of CaCO₃ characteristics on element incorporation, and also tries to disentangle the biological signal by studying different shell sizes and by comparison with data derived from inorganic CaCO₃ experiments. Although I am specialized in foraminiferal carbonate chemistry (and cannot truly judge the ecological side of the manuscript), I read the manuscript with interest. All in all, I am excited by studies which include the measurement of multiple elements on biogenic carbonates and I think it is an interesting study. However, I have some questions about the dataset and I am missing certain angles in the current discussion.

Major comments:

I was surprised to read about the cleaning methods used in this study. When investigate chemical composition of foraminiferal shells, we use a much more intense cleaning method with oxidation and reduction steps (especially when specimens are collected in the field), to remove any organics as well as diagenetic coating (like Mn-Fe-oxide coatings). I wonder if e.g. only mechanical removal of any organisms present on the shell is enough to remove any (organic or chemical) trace completely, and if coatings are present on the shell after the described cleaning protocol. Are there studies comparing different cleaning techniques?

Furthermore, the amount of organic inside the CaCO₃ might have a huge effect on the elemental composition of the shell, e.g. on Na, and the contribution of organics might differ between species and CaCO₃ polymorphs, as also acknowledge by the authors (in l.54: ‘species-specific organic matrix’). With the method described in this study, the organic matrix will also be analysed. I would like to see this issue discussed in the revised version of the manuscript. Has there been any study on the chemical composition of the organics in different species of bivalves, albeit on the compounds of the matrix or by microscale-analysis of the shell with e.g. nanoSIMS on cross-sections? This should be at least mentioned in the discussion as a potential reason for the offset between species, if not discussed in full detail.

C2

The authors are comparing small and big adults and use the obtained data to look at ontogenetic effects. However, the authors also state this is a very variable environment, with big seasonal (and maybe yearly) changes. Overprinted on the size effect, there is a time effect: the bigger specimens have recorded events that the smaller specimens did not experience. I'm missing the longevity of the different species in the discussion of the results. For example: The size effect observed for *A. improvisus* (life span = 1 year) might simply be a seasonal signal in food supply (and thus maybe growth rate) or physio- or chemical parameters like seawater temperature. If the samples are taken in end of summer (sample date not mentioned in the manuscript, should be added), it would explain why the Mg of the larger specimens is lower: lower temperatures lead to lower incorporation of Mg and these larger specimens likely experienced the winter period, while the smaller specimens maybe spawned in spring. As for the species with longer lifespans (of 10-12 years), could the decrease in element incorporation with size (thus, for older specimens) be due to increased heavy metal output of the Vistula river over the last years? Is there any (historical) data on this?

The authors see some difference between size classes, they conclude that in general smaller specimens have increased trace metal incorporation. Can this also be due to absorption of elements or diagenetic precipitation on the outside of the shell, compared to the more pristine CaCO₃ below the surface, leading to a surface/volume effect? E.g. larger specimens have thicker shells, and thus lower surface over area ratio?

I would also like to see habitat depth included in the discussion. The authors are assuming the shell chemistry of the different organisms tested are all reflecting either food or ambient seawater chemistry, but some organisms are living on hard substrates, while other live a few cm in the sediment, and the most extreme one (*Mya arenaria*) can live 20-30 cm in the sediment. The latter species would have a totally different "ambient seawater conditions", as it is exposed to interstitial water that is very likely to have totally different chemical signature than the overlying water. It would probably be in contact with e.g. much higher Mn concentrations. This is not reflected in the shell

C3

chemistry, so maybe this species does not take up elements from the seawater, but more from food intake?

For your purpose it would be best to have also some kind of idea of the (evolution) of trace metal concentrations in seawater over time. Is there any chemical data on the seawater available from this area? E.g. about the metal concentrations close to the Vistula river (l. 478)? Is there data showing that station GN is indeed increased in heavy metals compared to the other stations? These other stations are located in a bay area, making it possible the residence time of the water is higher, and there might be an actual increase in the metal concentration here.

In retrospect, for the main goal of the study, it maybe would have been better to not analyze full shells, but make small aliquots/subsamples by e.g. drilling the shell. Is there any data (in literature) on small-scale variation in the shells of (some of these) species?

In my opinion, at the moment, you have a combination of too many variables: CaCO₃ polymorph, different stations environmental variables (incl. unknown chemical compositions of the seawater), size effect and the vital effect (calcification pathway) of the organisms. It becomes very difficult to disentangle different drivers of shell chemistry, which means you have to be more careful in your conclusions, or at least convince readers which variables are minor/neglectable. I think some variables, like the different sampling stations, can be convinced as being minor, by showing chemical variability or the hydrological situations between the stations.

The authors often point out the strong seasonality in this region, section 2.1 and through the manuscript, e.g. l. 481-483. Maybe it is possible to add a (supplementary) figure to section 2.1, if needed compiled from literature data, about the environmental variability in this area, to show differences in physio-chemical parameters. This way, readers, like myself, that are not familiar with the study area can have a good overview of the (yearly) environmental variability in this area.

C4

Minor comments:

(Since I have a lot of major points for the discussion section, I give minimal textual changes, since I believe the manuscript, especially the discussion, will probably greatly change after revision.)

Throughout the manuscript:

-Change 'Mg/Ca ratio' to 'Mg/Ca'.

-Check manuscript for (double) bracketing issues, for instance in l.207: '(Darwin, 1854) (Arthropoda, Maxillopoda)' should be e.g. '(Arthropoda, Maxillopoda; Darwin, 1854)'. Also lines 217, 228, etc. For l.131 and l. 515: reference should not have brackets.

Abstract:

-The abstract as it reads a bit stiff. Please consider rewriting this section. For example, l. 28-29 on sample location can be merged with the first sentences, while line 29-30 is an explanation of the method, which should be either removed, or shortened, in my opinion.

-l. 26-27: 'The potential impact of environmental factors on the observed elemental concentrations in the studied shells is discussed': Is this really the case? Since there is no data on the environmental parameters presented, it is difficult to discuss the data in this framework.

Introduction:

-l.64-65: 'crystal layers are precipitated successively at regular periodicities,' is not true for all marine calcifiers, like Foraminifera. make it clear when you switch from all marine calcifiers to marine invertebrates.

-l.88-90: maybe add Stanley, 2008 , it is a nice overview paper. Stanley, S. M. (2008). "Effects of global seawater chemistry on biomineralization: past, present, and future." *Chemical reviews* 108(11): 4483-4498.

C5

-l.144: remove . after shells

Method section:

-l. 263: When were the samples taken?

-l. 295 What was the Ca concentrations in the sample solutions? 100ppm or varying?

-l.297: What were the accuracy and precision of the measured elements?

Discussion section:

-I would advise to divide the discussion session in smaller paragraphs to increase readability.

-I would like to see variables as life span, habitat depth and organic material in the shell (see above) included in the discussion.

-l. 372: You obtained specimens with the same polymorph from two contrasting temperatures: i.e. aragonite *Cerastoderma glaucum* (16.9°C), *Limecola balthica* (4.6°C), *Mya arenaria* (16.9°C), I would like to see a discussion on the (absence of) temperature effect Sr incorporation, which is currently lacking in the manuscript, while it is being discussed for Na and salinity.

-l. 478: ref? Are there any studies on this?

-l. 483: suggest to change 'animal' into 'organism'

-Fig 2 and 4: indicate which polymorph of CaCO₃ is used, like Fig. 3.

-Fig. 3: where possible, please use the same scaling for the y-axis for comparability, e.g. y axis of Mg for aragonitic species.

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2019-367>, 2019.

C6