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Interactive comment on "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)" *by* Anna Piwoni-Piórewicz et al.

Anonymous Referee #2

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Review of manuscript bg-2019-367

"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-Piorewicz, Stanislav Strekopytov, Emma Humphreys-Williams, and Piotr Kuklinski

This manuscript describes the elemental composition of aragonitic and bimeralic bi-

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valves, as well as a calcitic barnacle collected from the Gulf of Gdansk. The role of ontogeny is assessed by comparing elemental composition across four different size classes for each species. The authors conclude that differences in the elemental composition are dependent on the polymorph type i.e. calcitic vs. aragonitic, and that both environmental as well as ontogenetic controls strongly affect the elemental variabilities.

This is an interesting study, and in my opinion, could be a welcomed contribution for the community working on geochemistry of carbonates, biomineralisation and their potential application as recorders of past environmental and climatic reconstructions. I also welcome the authors approach by focusing the study on different calcifying groups and carbonate polymorphs from one region, which could potentially provide further insights on the underlying controls determining the elemental composition of the different biominerals. However, I have some serious issues when it comes to the analytical procedures, the data quality, the study design and interpretation of the data, as well as the manuscript focus and structure that, in my opinion, need to be carefully addressed before it may be considered for publication in Biogeosciences. I find the manuscript generally well written in terms of language, but given the diverse dataset with multiple variables, I strongly recommend to make the text as well as the figures more accessible to the readers and make the manuscript more clearly and systematically structured. I am missing critical information in the Methods part, and the Discussion section lacks several important aspects that need addressing and overall needs to be sharpened. The written and visual presentation of Results could also benefit from improvement, and, personally, I would advise the authors to better extract the principal findings of the study in the Abstract. All data from this manuscript should be provided in a Supplement, or other appropriate and accessible online data repository. In the following, I try to summarise my main concerns (as in my opinion the manuscript will need substantial modifications, I have not provided minor editorial comments at this stage; and neither have checked the referenced).

Fundamental information regarding the measurements and concentration calculations

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is missing or unclear, and the analytical uncertainties and repeatability based on appropriate reference materials are also lacking. In addition, in my opinion, the sample preparation and pre-cleaning procedures are questionable. The authors must prove the validity and explain their analytical procedures, and take into account analytical uncertainties when presenting or interpreting their data.

Furthermore, as detailed below, I have problems understanding how whole shell bulk measurements may be used to assess the role of ontogeny or even environmental variations. By using entire shells, the authors 'average' the composition of the growth lines precipitated during earlier and later stages of life, as well as the composition of growth lines built during different seasons or under different environmental conditions. Thus, I am not sure that by comparing bulk values from smaller vs. bigger (younger vs. older) individuals it is possible to determine whether environmental or ontogenetic controls drive the composition of the shell. Simply, the differences between the mean bulk values would depend on the elemental variability encompassed in the shell, which would depend on individuals' growth and environmental conditions experienced. ÂňThe mean bulk values from older individuals integrate large intra-shell variabilities, while in younger individuals smaller intra-shell variabilities, but I think that with this design it is difficult to disentangle the underlying controls on the elemental composition of the carbonates. In my opinion, the authors need take into account these problems, before any interpretations can be made. While a great deal of information is unfortunately lost by using average values, and I think the authors really have to reconsider the interpretations that can be made from this data and discuss their limits, I do acknowledge the authors' efforts for measuring numerous individuals, which I do not think is often done, and perhaps a point to that could be better taken advantage of. Just as a suggestion, maybe, this could be of use for defining the 'typical range' for each element for each species in the Gulf of Gdansk, which could be then compared to literature values from same / similar species in other parts of the world with very different settings. If possible, I think it would be interesting to see how the general elemental concentrations and variability compares between regions or not, and could be of use when constrain-

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ing environmental influences on the biomineral composition. In addition, I would also like to see a comparison between the different sampling sites within the Gulf of Gdansk. While on one hand it could be perhaps assumed that the differences between the sites are negligible, this is a very dynamic environment, and it might be that spatio-temporal variations account, at least partially, for some of the observed variabilities.

Moreover, the problem of using bulk also limits the interpretation of the data when it comes to the different polymorphs, and particularly this is the case for the bimineralic bivalve. Here, the authors may only conclude whether the composition of the mixture is different to other species building pure calcite vs. aragonite. However, it does not answer the question whether the composition of the calcitic part or aragonitic part within fundamentally differs and how much, which I think is the relevant question here. When discussing the composition of the bimeralic bivalves the authors could, at least, attempt to estimate the contribution from each polymorph to the mixture, and discuss the implications.

One thing that has surprised me the most about this study is that, despite the careful organism sampling strategy, the authors did not consider collecting and measuring water samples. In my opinion, this should come first in this kind of studies, and something I was expecting to see, and thus a real shame it was not done, especially since the authors had the opportunity to do so (and elemental analyses on water samples are relatively more straightforward that on carbonates). Data on seawater chemistry is critical for the calculation of partitioning coefficients, which could ease the interpretation of the results from different sites (in the case that the chemistry at the different sites strongly varies). While it may be a tall task to ask for the measurements at this stage, the authors should, at least, compile the available information on local concentrations of elements in seawater (including additional physico-chemical characteristics), and estimate the partitioning coefficients for each element for the different species.

Specific comments:

Line 1-2: I would suggest to reconsider the title language – 'composition' and 'composed', as well as 'different' twice in the same sentence, this is not orderly.

Line 32: 'Mg > Sr > Na' this needs a written definition first.

Line 195-197: Here, it would be particularly useful to provide concrete numbers on the local carbonate chemistry (other than Ω). Ideally, this should have been measured upon the collection of the specimens from in situ water samples, however, if this is not available the authors could at least summarize the information from the literature. An overview table with the physico-chemical characteristics of the local waters (including temperature and salinity trends etc., carbonate chemistry as well as the elemental composition), would be particularly useful.

Line 267: Why no water samples were collected?

Line 282-286: I have difficulties following this protocol and serious doubts on its effectivity and validity. Previously, the authors state that the periostracum was first physically removed. This is good and indeed important as it constitutes a large amount of organic material, which is difficult to treat chemically without having an impact on the carbonate. However, organic rests might still be present on the inside of the shell for example from the mantle, and foremostly in the pore spaces. Thus, physical cleaning is insufficient, and at least at a powder stage it is a generally established routine to apply a cleaning protocol step, consisting of oxidation of organics by buffered hydrogen peroxide (Barker et al., 2003 G3 4, 8407). As far as I am aware, this protocol or close adaptations are commonly applied to a wide range of calcifiers from forams to corals, bivalves and even brachiopods. In this sentence the authors indeed mention the use of H2O2, but only after the dissolution of the sample, which logic I cannot follow. All in all, I do not think that this is the correct way to treat carbonates samples, and would strongly recommend to first demonstrate the validity of this protocol (if the authors insist on using it, or follow a more broadly used protocol such as that of Barker et al., 2003).

Moreover, I am wondering why the entire shells were crushed? Surely, >100 mg is not

required for the analyses, as concentration measurements are typically done on <mg level. Why did the authors decide to measure the entire shell instead of e.g. a profile across the shell or different growth bands? Such approach, I believe, would be much better for defining an ontogenetic trend, and could also provide some insights into the intra-shell variability. The intra-shell variability, in particular, would be very meaningful to assess before any mean bulk values are used for interpretation of ontogenetic or environmental signals – i.e. how heterogenous are the shells, what is the driver, is it random or not, how big is the variation and what it reflects? I think it is really a shame this was not considered beforehand as a great amount of information from the shells is lost when measuring the whole shells rather than specific parts. Furthermore, I am not convinced that comparison of bulk large vs. small individuals, in this case, answers the question whether ontogenetic trend drives the elemental variability. For numerous calcifiers group, the partioning of elements between seawater and the carbonate is within a certain range band 'baseline' which is principally determined by their calcification mechanisms and mineralogy, and then this variability of the 'baseline' may be driven by environmental factors. In such case, simply by a probability, larger individuals would have lived longer vs. smaller individuals and thus likely witnessed during their life time more environmental fluctuations (e.g. temperature, nutrients, pH, O2, etc.). Thus, when using an average of an entire shell, it is reasonable to assume that the mean of the shell integrates larger intra-shell and therefore elemental variations in the older individuals in contrast to the younger, simply because they experienced more changes over their life. I believe that this is also quite apparent in Fig. 3. How may one, therefore, discriminate between ontogeny vs. environmental variability?

Also, when it comes to ontogenetic trends, let's take for example bivalves and specifically Mytilus, as far as I am aware, broadly speaking their shell growth follows von Bertalanffy growth curve (see e.g. ig. 3; Steffani & Branch, 2003; Mar Ecol Prog Ser 246, 197-209), which is common for many calcifiers. This means that during the very early shell formation the carbonate precipitation is relatively faster, which for the incorporation of numerous elements translates into kinetic effects. It is thus the geochemical

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composition of the umbo and the first growth lines vs. the latter growth lines (the ones at the growth 'plateau') that form the greater part of the valve that is commonly attributed to being driven by ontogeny. Potentially, in the case of the very small and thus very young individuals, their geochemical composition may reflect one environmental condition e.g. certain season and one ontogenetic stage i.e. the one dominated by kinetic factors, but I am not sure this can be directly compared to older individuals which mean elemental composition then reflects different ontogenetic stages (with potentially different contribution of each to the bulk), and broad range of seasons. Or am I missing something?

Line 294: What type of solutions? What do you mean by matrix-matched – one solution for each carbonate polymorph? Please provide more details.

Line 300: Why were the standards not treated the same way as samples? First, I do not think it is acceptable that the authors do not process the standards and the samples in the same way, and second, I do not think that the standards are representative and should be compared to these samples. The authors need to provide the measured absolute values (as well the relative standard deviation over the analysis period at least) of comparable biogenic standards such as JCp-1 or JCt-1, or similar internationally accepted alternatives.

Also, regarding the methodology, I am wondering how were the obtained counts converted into concentrations; e.g. did the authors use a calibration line for this or standard-bracketing? Did you normalise all measurements to a stable concentration of a selected element, e.g. Ca? What was the precision of the individual analyses, and the long-term reproducibility? How many times was each sample measured? Line 305 'most trace elements' – which elements were measured in He mode and which not? The authors must provide these details with rigour. Line 307 'periodic analyses' do you mean the standards were not measured along with the samples in a sequence? I have serious doubts on these analytical protocols, and especially do not consider it a good practice to not include standards along with samples in a run.

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Line 311: I would really welcome some visual representation for this – i.e. pictures of the different species, maybe with the different ontogenetic stages for each. It is really shame this is not provided; the authors study various interesting species, which offers an opportunity to include visually appealing picture figures, which is not used. Perhaps this is too much to ask, but given that the species build very different carbonate types and I assume microstructures, scanning electron microscope images could also be very relevant and interesting here.

Line 321: Throughout the Results section the figures are referred to very sporadically only, and there are several instances that a value is given and a statement is made, however the figure is not referred to afterwards. Foremostly, all individual panels of the figures need sub-categories (e.g. a, b, c, etc. please check the Biogeosciences format style), and need to be mentioned where the individuals results are being discussed.

Line 322: I am not sure what the authors mean here, please rephrase.

Line 327: I would say it is more appropriate to use μg/g rather than mg/kg.

Line 328: When concluding that some elements were 'generally present at higher concentration' or lower please also provide the concrete numbers in the text, here, but also in further parts of this section it is missing.

Line 334: What do you mean by 'lack of ontogenetic trend'?

Line 371: The entire Discussion section needs major revision, and foremostly substantial reorganisation in order to make it more suitable to the readers and a wider audience. I am aware that dealing with many different variables like several elements, size classes, species and carbonate polymorphs is not easy, but the authors really need to find a better way for presenting their findings and extracting their 'main message points' to the audience. At the moment I find the Discussion very broad and, to me, it does not provide clear answers to the research questions. I am afraid that often problems are addressed that cannot be resolved by the present dataset. I would say

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that it is better if one or two key points are discussed in-depth rather than touching on the surface many (these may still be mentioned, but the in a more concise form, with focus on the key points).

The structuring is also relevant for the other parts of the manuscript and especially the Results section. I would start with ensuring that were possible, the geochemical data is presented in a more systematic manner. The Discussion could benefit from being divided into different subsections, where different aspects are being discussed. The data quality and limitations need discussing, as well each of the different factors controlling the incorporation of the elements into the carbonate (preferably in different subsections), a comparison to other studies, and the implications of the presented findings (for e.g. biomineralisation, application as recorders of environmental conditions). At this stage, it is difficult for me to make a concrete suggestion on how to subdivide this, the authors need to see what works best when structuring the Discussion and the message they would like to convey. I would also suggest to separate the Results section, perhaps by species could work well for this part. Al

Line 372: There are numerous studies on Mg and Sr in carbonate, which uses and incorporation mechanisms, potential proxy-applications etc. need a better summary. Same for all other elements, the discussion of each element should be opened by the factors that control its incorporation into the carbonate. Also, as these are often not similar for calcite and aragonite, and especially since this study is focused on the incorporation of elements into different polymorphs, these two should be treated separately.

Line 375: The statistics should be provided in brackets. Also, please be specific, how much?

Line 378: 'Mg was the dominant impurity', please rephrase, what do you mean?

Line 383: Please be specific, what species?

Line 397: What is the origin of the high Sr in barnacles?

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Line 405: The concentrations are sometimes given in mg/kg and sometimes in wt%, which is confusing. Please be consistent throughout the manuscript in figures, and this should be preferably μg/g.

Line 414: Please explain, what do you mean?

Line 478: I wonder how would the data look if the metal concentrations are plotted as a function of the distance to the Vistula River mouth? Can you conclude that it is the contamination that controls the trace metal composition? A comparison to the species from non-contaminated water might help.

Line 481: Yes, and it is really necessary to add that the whole shells were measured. Therefore the mean values integrate these variations.

Line 486-489: Please rephrase. Also, of course, they varied but it is difficult to determine why.

Line 497: 'chemical profiles' please rephrase, as far as I am aware no chemical profiles were made.

Line 479-509: This sections contains many redundant parts, and the discussion could be sharpened.

Line 510: In addition to relative increase or decrease in concentrations, also the variability in the elemental concentration for a size class should be considered (although I am not sure if the differences between size classes will be significant).

Line 520: Please be specific, which trace elements (please provide in brackets; similar cases can also be found in other parts of manuscript).

Line 527: Yes, but as mentioned I doubt this has anything to do with the size / age.

Figure 1: Please provide the full site names in the figure caption to abbreviations. What are the grey lines in the big panel (bathymetry?), please specify in caption as well.

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Figure 2: This figure needs error bars. The analytical uncertainty should be shown here, as well as the variation of the mean i.e. the 2SD of the mean for each group and the respective n should be provided too. Also, what size classes were used for this? Is this the mean of a certain size class or the mean of all individuals, this needs definition in the caption. It may be more appropriate, too, instead of the mean of all individuals to depict the mean and the variation of each size class. I would also include information on the different polymorphs of each species. In general, I have no problems with the figures being black-and white only, but personally, I would try to improve the visual representation. In this case, maybe increasing the figure size to double and placing the legend within the top right corner could help separate a bit more out the different elements. Also, this is a detail, but to make it more intuitive, the grey filled symbols could be the aragonitic species, empty symbols the calcitic and half-filled for example bimineralic.

Figure 3: What is the x-axis? Please make the y-axis similar where possible, this is really difficult to read for me. Also, the information on the differences between size classes should be removed as at the moment there is too much information in this figure. The individual panels are missing sub-headings that should be also referred to in the manuscript text.

Figure 4: Please appropriately label all panels as 'a,b,c, etc.' What do you mean by 'raw data as black dots'? (I see blue dots.) Please include polymorphs, analytical uncertainty, indicate the sizes for each category. Maybe better to put each species in a separate row. Why some size classes have values in between the size class number categories?

Figure 5: I find this figure difficult to follow, maybe there is a better way to illustrate the message? Should be 'dashed line' instead of 'broken line'. Why are some panels darker? Please specify in the caption.

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