



EGUsphere, referee comment RC1
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Comment on egusphere-2022-1144

Anonymous Referee #1

Referee comment on "Multi-proxy assessment of brachiopod shell calcite as a potential archive of seawater temperature and oxygen isotope composition" by Thomas Letulle et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-1144-RC1>, 2022

Review comments **egusphere-2022-1144** (Letulle et al.)

Dear EGU sphere, dear authors,

Thank you for inviting me to review the manuscript titled "Multi-proxy assessment of brachiopod shell calcite as a potential archive of seawater temperature and oxygen isotope composition" by Letulle et al. In their manuscript, the authors present a dataset consisting of various geochemical proxies measured in brachiopods grown at known temperatures. The goal of the study is to compare and assess the temperature dependence of various geochemical proxies in brachiopod shell calcite.

The authors describe a very comprehensive dataset, and their analyses has clear implications for paleoclimate studies. I would commend the authors on their coverage of the literature background required to follow the discussion in the study. This is not straightforward since the dataset describes various proxies and techniques, but I think they did this well. The description of the methods and results of this study and the line of reasoning put forward in the discussion also mostly makes sense to me.

My only major disagreement with the author's assessment is the need for a taxon-specific calibration for clumped isotope-temperature reconstructions in brachiopods. In my opinion, the authors arrive at this conclusion a bit too hastily, only comparing their findings to one pre-existing clumped isotope-temperature calibration (by Anderson et al., 2021), even though previous studies have noted that this equation tends to underestimate temperatures (see detailed comments below). This conclusion of a brachiopod-specific

paleotemperature equation is, in my opinion, also in disagreement with the conclusions of disequilibrium fractionation in brachiopods put forward by papers by David Bajnai (which are cited and discussed in the manuscript). I do not agree with the approach of circumventing this disequilibrium issue by inventing a new empirical temperature equation for using clumped isotopes for temperature reconstructions from brachiopod calcite. I therefore think the authors should revise this conclusion before the paper becomes acceptable.

Besides this point, I think this is a well written manuscript about a well-thought-out study which will be of interest to the paleoclimate community and merits publication. Below I provide some line-by-line feedback which I hope will help the authors to improve their manuscript.

Major comments

In the Introduction (lines 49-89), several potential temperature proxies in brachiopod calcite are introduced one by one. While these introductions are important and well-written, the individual paragraphs are quite detached from each other and disrupt the flow of the manuscript somewhat. I suggest the authors either tie the paragraph a bit better into the rest of the manuscript or place them in a separate "Background" paragraph.

Lines 124-129: Perhaps the authors can provide a citation or reason for why they used this pre-treatment method. There is some literature suggesting that pre-treatment with oxidizing agents might influence the (clumped) isotope or trace element composition of the carbonate. Personally, I am of the opinion that excess pre-treatment with such substances should be avoided in these types of studies. However, if the authors have convincing evidence (either by their own research or from the literature) that this treatment is warranted in this case, I am happy to support it.

Section 3.1: It is not clear from this section how the authors dealt with uncertainty on the temperature and salinity/d18Ow value associated with the samples. Since brachiopod samples are large and do not always represent mean annual averages (i.e. due to sampling of less than a full year, see lines 144-146, or due to variations in growth rate over the year) I think the authors should take into account the seasonal cycle in temperature and d18Ow (or salinity) at the sampling locality as uncertainty on their regression. I assume from the text in this section that the authors used a normal linear regression (not including errors on measurements or on the independent variables). To incorporate uncertainty on the independent variable, the authors could use a Deming regression which takes into account measurement error as well as errors on the "known" variable (in this case temperature and d18Ow). Judging from Figure 1 (which I assume shows uncertainties on temperature), these uncertainties are significant.

Line 348-351: I suggest the authors also compare the clumped isotope-temperature relationship in brachiopod calcite with the values obtained by applying the Meinicke et al. (2020) calibration, which was recently updated to the I-CDES scale (Meinicke et al., 2021). A recent study by de Winter et al. (2022) demonstrated that the Anderson et al. equation likely induces a cold bias on shallow water carbonates which might explain part of the observed offset in clumped isotope values in this study. I wonder if the brachiopod-specific clumped isotope equation proposed by the authors is significantly different from Meinicke et al. if projected on the I-CDES scale. If so, it might not be warranted to propose a new clumped isotope calibration as brachiopods might be calibrated with general calcite calibrations.

Meinicke, N., Ho, S. L., Hannisdal, B., Nürnberg, D., Tripathi, A., Schiebel, R., and Meckler, A. N.: A robust calibration of the clumped isotopes to temperature relationship for foraminifers, *Geochimica et Cosmochimica Acta*, 270, 160–183, <https://doi.org/10.1016/j.gca.2019.11.022>, 2020.

Meinicke, N., Reimi, M. A., Ravelo, A. C., and Meckler, A. N.: Coupled Mg/Ca and Clumped Isotope Measurements Indicate Lack of Substantial Mixed Layer Cooling in the Western Pacific Warm Pool During the Last 5 Million Years, *Paleoceanography and Paleoclimatology*, 36, e2020PA004115, <https://doi.org/10.1029/2020PA004115>, 2021.

de Winter, N. J., Witbaard, R., Kocken, I. J., Müller, I. A., Guo, J., Goudsmit, B., and Ziegler, M.: Temperature Dependence of Clumped Isotopes (δ^{47}) in Aragonite, *Geophysical Research Letters*, 49, e2022GL099479, <https://doi.org/10.1029/2022GL099479>, 2022.

Minor comments

Line 29: “but is significantly offset” rephrase to “are significantly offset” (“D47 values” is plural)

Line 85-87: Perhaps the authors could add here that current empirical clumped isotope-temperature calibrations also show good agreement with *ab initio* models of the carbonate isotope system, as was demonstrated in Jautzy et al. (2020). This is another argument in favor of the use of common clumped isotope thermometers in a variety of carbonate materials.

Jautzy, J. J., Savard, M. M., Dhillon, R. S., Bernasconi, S. M., and Smirnov, A.: Clumped

isotope temperature calibration for calcite: Bridging theory and experimentation, *Geochemical Perspectives Letters*, 14, 36–41, 2020.

Line 142: "graving bit" should this read "engraving bit"?

Line 262-263: "At temperate and polar temperatures (20 to 0°C) our equation has a steeper slope than that of Brand et al. (2019)" The authors need to explain this in more detail and/or refer to a figure where the reader can spot this effect. The authors refer to figure 2A later, but it is not clear which line in this figure represents the equation by Brand. I do not understand how the slope can be different with temperature if a linear equation (with a constant slope) is compared, but I might misunderstand what the authors are trying to say. Later on, the authors mention that the Brand et al. equation is non-linear, but I still have trouble following the description of the comparison in this section.

Line 342: "In consequence" rephrase to "As a consequence"

Line 415: "constrain" should read "constraint"

Line 416: "should be privileged for trace-element-based paleotemperatures reconstructions" consider rephrasing to "should be selected/prioritized for trace element-based paleotemperature reconstructions"

Line 443-466: This clear grouping based on trace element content is an interesting observation. I wonder if the authors considered whether there might be a relationship with growth rate. Does the "high" or the "low" group show significantly faster growth than the other? If so, this could be an explanation for the difference in shell composition, as trace element concentrations in calcifiers often show a correlation with growth rate. In addition, in this section about grouping of specimens based on trace element content, adding a figure showing the differences in concentration would be helpful.

Line 475: The authors might consider rephrasing the title of this section to: "Precipitation of brachiopod shell calcite out of equilibrium with seawater"

Line 493-495: The authors might consider citing the recent study by Garbelli et al. (2022) here who also interpret changes in isotopic composition of (fossil) brachiopod shells as seasonal variability.

Garbelli, C., Angiolini, L., Posenato, R., Harper, E. M., Lamare, M. D., Shi, G. R., and Shen, S.: Isotopic time-series ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) obtained from the columnar layer of Permian brachiopod shells are a reliable archive of seasonal variations, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 607, 111264, <https://doi.org/10.1016/j.palaeo.2022.111264>, 2022.

Lines 516-531: It seems that some of the discussion of kinetic (growth rate-related) effects in trace element composition could be a useful addition to the section above where the observation of differences in trace element composition between brachiopod groups is discussed (see my comment on lines 443-466).

Line 532: "isotopic" should read "isotopic"

Line 539-540: "Given the highly...may be coincidental." I think the authors should explain this line of reasoning in a bit more detail.

Line 582: Please add the missing "delta" before " $^{18}\text{O}_{\text{sw}}$ ".

Line 586: "central values" is a bit of a cryptic term, perhaps the authors mean median or mean/average values?

Lines 556-610: I think the addition of a fossil case study is nice, but it is not essential for the study. If the authors would like to keep their manuscript more concise, this is a section that could be significantly shortened or removed in my opinion.

Table 4: As mentioned in one of my previous comments, it might be worthwhile to add the clumped isotope-based temperature reconstructions based on the Meinicke et al. calibration, since these are likely more accurate and more closely in line with the modern brachiopod data in this study as well.

Line 623-624: The temperature underestimation by ~ 3 degrees is very similar to the offset found in de Winter et al. (2022; see comment above) and this nice corroboration between multiple datasets is worth mentioning.

Line 624-625: As mentioned above, I tend towards disagreeing with this call for a brachiopod-specific clumped isotope calibration, since most of the offset in clumped isotope values may be explained by the Anderson et al. equation underestimating temperatures in general (not just for brachiopods). The authors should consider this

explanation before suggesting a taxon-specific calibration is needed.