Authors response to referee comment 1

Dear editor, dear referee, dear EGU sphere,

First we would like to thank the referee for the time invested reviewing our paper, and the constructive comments and suggestions that were made.
We take this opportunity to answer the most important questioning and suggestions in detail. We took notes of other minor comments to correct and improve the manuscript in its revised form.

We start answering the main concern raised by referee 1, concerning the taxon-specific clumped isotope temperature equation which was the object of several comments.

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.

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.

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.

Reviewer #1 argues against our conclusion that our modern brachiopods observations are inconsistent with "general" calcite calibrations, proposing that we should compare them to a recently reprocessed foraminifer calibration (Meinicke et al., 2021), which predicts slightly greater calcite Δ47 values for temperatures below ~10 °C.

For reasons outlined below, we would argue that (1) Anderson et al. (2021) is in fact fully consistent with most other I-CDES data sets, and (2) the difference between Meinicke et al. (2021) and other calibrations is due to problematic choices in the assignment of calcification temperatures.

(1) We'd first like to point out that our use of the Anderson et al. (2021), despite being a rather consensual choice, is but one of many that would lead to an identical conclusion. For instance, Fig 3B from Anderson et al. illustrates the quasi-perfect agreement between their regression line and the low-temperature observations of Peral et al. (2018, foraminifera), Meinicke et al. (2020, foraminifera), Jautzy et al. (2020, synthetics), and slow-growing calcites from Laghetto Basso and Devils Hole. Based on this, we find it extremely difficult to claim that these five independent calibration datasets are inconsistent in any statistically significant way. A sixth data set on modern bivalves (Huyghe et al., 2022), as well as new measurements of slow-growing calcites (Fiebig et al., 2021) further strengthen the case that all of these calibration data, when (re)processed to the I-CDES, are fully consistent (Figure 1).

(2) At face value, this would seem to contradict the assertion that the I-CDES regression equation from Meinicke et al. (2021) yields substantially greater Δ47 values for cold temperatures. Yet, as noted in the original study by Meinicke et al. (2020) themselves, there is no disagreement between the foraminifer datasets from LSCE (Peral et al., 2018) and from Bergen (Meinicke et al., 2020 and other papers cited therein). The difference between the corresponding (reprocessed) I-CDES calibrations (Peral et al., 2022; Meinicke et al., 2021) is thus due to different approaches of assigning Δ47-independent calcification temperatures to planktic foraminifera (as discussed in detail by Meinicke et al., 2020). This in itself is not a problem: each of the two approaches appear reasonable a priori. However, we now have many precise Δ47 measurements for samples precipitated between -2 and +8 °C, including benthic foraminifera (Peral et al., 2018), Antarctic scallops (Huyghe et al., 2022), lacustrine carbonates from perenially ice-covered lakes (Anderson et al., 2021), and very slow-growing calcite from Laghetto Basso (Anderson et al., 2021; Fiebig et al., 2021), all of which have very narrow temperature constraints, and which agree extremely well with the original temperature assignments of Peral et al. (2018). Based on all of this evidence, it is very likely that the apparent discrepancy between Meinicke et al. (2021) and the other calibrations primarily reflects problematic choices in the assignment of calcification temperatures.

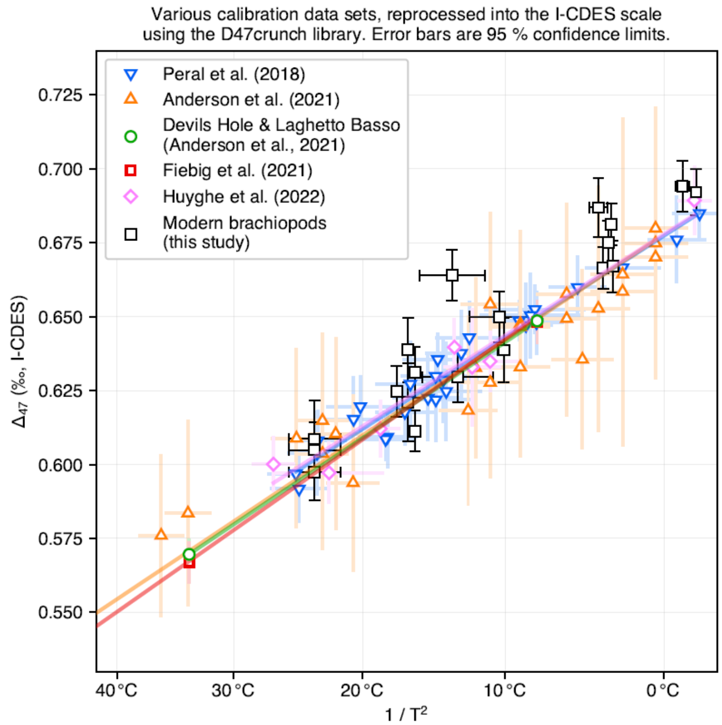

Figure 1: Plot comparison of the new brachiopod clumped isotope data with published datasets from foraminifera, calcite bivalves, slow growing calcite and synthetic carbonates, in the I-CDES reference frame and their associated regression lines. This illustrate the good agreement between brachiopods and previous datasets in the temperature range 10 to 25°C, at one exception. In the low temperature range (−2 - 7°C) however the brachiopod dataset shows significant differences.

Reviewer #1 also argues against the need for a taxon-specific equation. In this regard, while we have independently confirmed the conclusions of Bajnai et al. (2018) regarding the deviation from previous calibration, we agree that establishing a taxon-specific equation may not be the adequate way to correct for this deviation. Indeed, as discussed and illustrated in Figure 4 C of the manuscript, while we observe more deviation from the equation of Anderson et al., 2021 in the low temperature range (<10°C), this could also well be explained by biologic parameters, such as different growth rates between different taxa, as suggested by Bajnai et al. (2018). And as further discussed, temperature is not the only parameters controlling brachiopod shell growth rates. In line with the suggestion of reviewer#1, we will thus retract on suggesting the use a taxon-specific equation, but rather focus on the potential explanations for this discrepancy, and better tie this result the rest of the discussion (section 4.2).

To give a brief answer to this major comment by reviewer #1. For various reasons stated above we further assure our conclusion that the empirical Δ47-temperature relationship observed in brachiopod shells shows significant differences to previous relationships established on carbonates from different origins (foraminifera, calcite bivalves, synthetic) and best illustrated by the equation of Anderson et al. (2021). However, this conclusion is not sufficient to propose a taxon-specific equation to be applied to brachiopods shell, but rather highlight other controls on Δ47 values of carbonates than temperatures, that should be further investigated.

In the Introduction (lines 49-89), several potential temperature proxies in brachiopod calcite are introduced one by one. While these introductions are important and wellwritten, 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.*

We will rework the introduction to better tie the paragraph into the rest of the MS.

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.

The literature appears divided on the subject (Schöne et al., 2017; Key et al., 2020; for the most recent litterature). We have chosen to perform an oxidizing pre-treatment as most of the samples still had the animal within their shell. Most of the organic matter was removed manually but an oxidizing pre-treatment was deemed necessary to remove organic matter still attached to the shell before sampling for shell geochemistry. Although, we acknowledge that this could have been avoided for samples without clear evidence for organic material. Among the different pre-treatment method used in previous studies, we adopted a protocol close to the one used by Bajnai et al., (2018) as we preferred NaClO over H_2O_2 for logistical reasons. We note that bleaching is associated with little to no carbonate dissolution as opposed to H2O2 (Pingitore et al., 1993; Gaffey and Bronnimann, 1993).

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.

The uncertainties displayed in Figure 1 corresponds to the seasonal variation for temperature (highest and lowest monthly averages), and for $\delta^{18}O_w$ the uncertainty combines uncertainty of the salinity- $\delta^{18}O_w$ relationship (LeGrande and Schmidt, 2006) and propagated seasonal variation in salinity, although it is very low for most samples. The regression presented in Figure 1 and Table 3 are simple linear regressions which are primarily used to explore the dataset. While the linear model was proposed in the submitted manuscript for the fractionation equation, we take note of the point made here, and will rather display the results of the York regression (York et al., 2004), which account for uncertainties on the dataset, although in this particular case, it is not significantly different than the linear model. Note that this model is introduced and discussed later on in the submitted manuscript. We will also add some details as to how uncertainties were considered.

Minor comments

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.

Another referee also stated that this part was unclear. We will address this issue in the revised manuscript and provide further and clearer discussion regarding the difference in "slope" of different equations.

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.

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).

This trend may be related to growth rates. Unfortunately, our new dataset comprises only 5 species for which we have constraints on their growth rate, limiting quantitative comparisons.. This hypothesis could be mentioned into the discussion. A figure will be added to illustrate this dichotomy. We must also note that this difference is confined to the inner shell layers. The trends described here between Terebratellidina and Terebratulidina disappear while looking at the outer shell layers.

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 (δ13C and δ18O) 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.

We agree that the addition of literature regarding seasonal variability registered in brachiopod shells would be pertinent here. Although very interesting and convincing, the work of Garbelli et al. (2022) may not be the most pertinent reference here, when other papers studying modern brachiopods in monitored environment unambiguously highlight seasonal variability (Yamamoto et al., 2011; Takayanagi et al., 2015).

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

Here we intend to provide a critical look at our dataset as the differences in both trace elements and clumped isotopes may be explained by two kinds of groupings in our dataset: 1)High latitudes vs low latitudes with difference in seasonality of the ecosystem that may induce different growth rate dynamics and 2) taxonomic grouping which may involve differences in shell formation processes including growth rate. However, as the Terebratulidina are mostly associated with low latitudes and Terebratellidina with mid-high latitudes in the dataset, we lack strong arguments to prefer a hypothesis over the other. We will rephrase this part to make it easier to understand.

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.

Another referee has done a similar comment. This section will be removed from the revised version.

References

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