Authors response to Anonymous Referee #1 report #1

Dear Prof. Tina Treude, dear referee, dear EGU sphere,

Here is our response to the comments of Anonymous Referee #1 in the last report and to the Associate Editor decision.

First, we answered the Referee suggestion and Associate Editor decision of adding a comparison of our data with the equation of Meinicke et al., (2021). However, for reasons stated in detail bellow, we extended this comparison also to the equations of Peral et al. (2022) and Huyghe et al. (2022) which also use low temperature (<30°C) datasets anchored to the I-CDES reference frame. This comparison highlight that a number of modern brachiopod calcite Δ_{47} values not only deviate from the equation of Anderson et al. (2021) but also form published equations based only on biogenic marine carbonates (foraminifera, bivalves). The detailed results of this comparison are made available in an updated version of Supplement S3.

We additionally corrected the values of Δ_{47} temperature offsets for Terebratellidina and Terebratulidina (Section 4.1.2). Values in previous versions of the manuscript resulted from a calculation with one sample attributed to the incorrect taxonomic group. This change has no impact on our conclusions. All these changes relate to Section 4.1.2, pages 18-19 in the revised manuscript.

We also take the opportunity that this document will be public to further answer in details the arguments advanced by the referee in the last report, regarding the potential cold bias of the Anderson et al. (2021) clumped isotope temperature equation.

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Author's response

That said, I believe the scientific disagreement between the authors and myself regarding a potential cold bias of the Anderson D47 equation in the lower temperature range has not been fully resolved. I appreciate the detailed reply to this issue the authors gave in the online discussion. I also fully agree that the way "true" temperatures are assigned to the foraminifera datapoints in the Meinicke, Piasecki and Peral datasets is not ideal. This is, in my opinion, not a fault of the authors, but a general issue with calibration datasets based on microfossils (unless grown in lab cultures).

We fully agree on that last point.

However, I remain of the opinion that the fact that data from lab-grown bivalve shells (with highly precise known temperatures) does align significantly better with the Meinicke dataset than the Anderson dataset should be a good reason for the authors to at least consider the reprocessed Meinicke equation in their analysis. The fact that data from mollusk shells, which are known to be precipitated close to equilibrium (as acknowledged by the author and demonstrated in Huyghe et al. 2022) is significantly offset from the Anderson line in the same direction as the brachiopod data in this study should also be mentioned in my view.

We acknowledge that some of the clumped isotope data from de Winter et al. (2022) are offset from the Anderson et al. (2021) equation in the same direction as our brachiopod data. The fact that these results align better with the equation of Meinicke et al. (2021) is however, only relevant to the *Arctica islandica* samples grown at 15 and 18°C, according to table 1 in de Winter et al. (2022). The better agreement with the Meinicke et al. (2021) equation rather than the Anderson et al. (2021) equation is not significantly relevant to the rest of the low temperature aragonite dataset according to de Winter et al. (2022) themselves: "*When including clumped isotope values of other low-temperature (<30°C) aragonites in the compilation, the regression remains indistinguishable from the calibration of Anderson et al. (2021) and similar to the foraminifera-based calibration by Peral et al. (2018) and Meinicke et al. (2020) combined with reference to I-CDES in Meinicke et al. (2021) and the Guo et al. (2009) theoretical temperature relationships (Figure 2b)*" (Section 3.2 in de Winter et al., 2022). This statement is supported by their supplementary data S8, where low temperature (<30°C) aragonite Δ_{47} values from their compilation show no statistically significant offset with the equation of Meinicke et al. (2020), neither with that of Anderson et al. (2021). In consequence there is no strong argument to support that either of these equations is significantly different or better than the other to characterize the low temperature aragonite dataset.

While we acknowledge the precise control over temperature in lab grown bivalves, this does not rule out any other control over shell geochemistry, especially biological controls that may create deviation from equilibrium. Indeed, while *Arctica islandica* precipitate its shell close to oxygen isotope equilibrium with seawater, it is not the case for carbon isotopes or trace elements (see the review of Schöne, 2013 on *Arctica islandica* and ref therein). In addition, while the dataset of Huyghe et al. (2022) highlight Δ_{47} values from bivalve calcite close to the expected equilibrium, to generalize this observation to all mollusc shells could be faulty, especially at light of the disequilibrium reported in juvenile oysters also by Huyghe et al. (2022).

With these considerations, the offset observed in *Arctica islandica* Δ_{47} values relative to the Anderson et al. (2021) equation could well be explained by other processes including biologic processes, rather than a bias in the equation. Indeed, Figure 1 and Table 1 of de Winter et al. (2022) shows that *Arctica islandica* Δ_{47} values of specimens grown at temperatures of 3.2 and 1.1°C are in agreement with the equation of Anderson et al., (2021) while specimens grown at temperatures of 15 and 18°C show significant deviations from this equation. Again from the review of Schöne (2013) several aspects of *Arctica islandica* physiology may explain such deviation.

_ "*This species tolerates temperature and salinity ranges of 1° to 16 °C (Golikov and Scarlato, 1973; Mann, 1989; Witbaard et al., 1997a; tolerance under experimental conditions for limited amounts of time up to 20 °C: Winter, 1969) and 22 to 35 PSU (Winter, 1969; Oeschger and Storey, 1993), respectively*" (Schöne, 2013)

_ "*Shell growth occurs at temperatures as low as 1 °C, increases strongly between 1° and 6 °C and shows a tenfold increase between 1° and 12 °C (Witbaard et al., 1997b).*" (Schöne, 2013)

We argue that a significant increase in shell growth rate between the specimens grown at 1 and 3°C and those grown at 15 and 18°C may result in kinetic effects similar to the ones suggested for brachiopod shells (Bajnai et al., 2018; this study). This hypothesis could be easily tested with constrains on shell growth which was monitored during the experiment according to Supplementary S1 from de Winter et al. (2022), but we were not able to find that information.

Finally, though admittedly slightly off-topic, I am not convinced that the author's argument (made in reply to my comment in the online discussion) that several D47 datasets agree within uncertainty with the Anderson dataset is very strong in this context, because the potential cold bias is only argued for by de Winter and colleagues in the cold end of the temperature range, and many of these datasets (e.g. Anderson and Jautzy) contain many hot datapoints that can strongly influence the slope of a linear regression (especially if the actual temperature relationship may not be linear).

The Anderson et al. (2021) equation is very well constrained by data points in the low temperature range stated by de Winter et al. (2022) (<30°C) by the reprocessed foraminifera datasets of Breitenbach et al. (2018), Peral et al. (2018) and Meinicke et al. (2020), by the very slow growing mammillary calcite of Laghetto Basso (8°C) (Anderson et al., 2021; Fiebig et al., 2021), by calcite from perennial ice-covered lakes (Anderson et al. 2021). Plus, the bivalve calcite dataset of Huyghe et al. (2022) further support the Anderson et al. (2021) equation in this low temperature range. That is what we illustrated in the figure in our previous response and is illustrated by Figure 3B in Anderson et al., (2021). Thus multiple datasets, some of them with very strong temperature control, argue against a cold bias of Anderson et al. (2021) in the low temperature range (<30°C). The bivalve aragonite data reported by de Winter et al. (2022) and some of brachiopod calcite data of Bajnai et al. (2018) and our study are for now only a few deviations from Anderson et al. (2021) equation relative the quantity of data that support that equation in the low temperature range.

Alternatively, we also raise the following question. In the hypothesis that the Anderson et al. (2021) has a cold bias related to the use of high temperature points in the regression, is there any reason to prefer the Meinicke et al. (2021) equation over other equations derived in marine temperature range and set in the I-CDES reference frame such as the equation of Peral et al. (2022) or that of Huyghe et al. (2022) ?

This is why in the revised version we compare our results not only to the equation of Meinicke et al. (2021) but also to that of Peral et al. (2022) and that of Huyghe et al. (2022) which do not include high temperature data points. The application of those two last equations to the brachiopod dataset result in similar cold bias as using the equation on Anderson et al. (2021), while applying the equation of Meinicke et al. (2021) only slightly reduces the cold bias in our dataset. Not only does this comparison discard the argument that the observed cold bias result from the regression of Anderson et al. (2021) equation with high temperature datapoints, it highlights that none of the published equation can fully resolve the cold bias observed in brachiopod shells.

In addition, the Anderson dataset includes common data points with most of the other datasets mentioned in the author's reply.

Indeed, as the Anderson et al. (2021) equation is a composite equation based on multiple previously published datasets. It also includes the Meinicke et al. (2020) foraminifera dataset albeit with different calcification temperature assignment as already discussed.

To sum up over the case of the Meinicke et al. (2021) vs Anderson et al. (2021) equations:

1) There is in our opinion no significant reason in the study of de Winter et al. (2022) to prefer either of the Meinicke et al. (2021) or Anderson et al. (2021) equation to describe aragonite Δ_{47} values.

2) There is no influence of the non-linearity of the T-D47 that result in a cold bias of the Anderson et al. (2021) equation in the low temperature range (<30°C). Indeed, the Anderson et al. (2021) composite equation is very well constrained by data points with temperature <30°C, plus, similar cold biases on the brachiopod dataset are observed applying equations constrained by marine samples (Peral et al., 2022; Huyghe et al. 2022).

3) We propose a hypothesis to explain the deviation of *Arctica islandica* Δ_{47} values from the Anderson et al. (2021) equation reported by de Winter et al. (2022), and call for a test of this hypothesis if possible.

Finally, with all these elements, as the Anderson et al. (2021) equation is a composite of datasets from various labs and various carbonate origins, it appears, to date, to be the best constrained equation to describe Δ_{47}-Temperature relationship in calcium carbonate materials (calcite and aragonite). Thus, it should be preferred to other equations with less data constrains such as those of Meinicke et al. (2021), Huyghe et al. (2022) and Peral et al. (2022). Nevertheless, this conclusion may be revised in a near future with increasing number of data reporting significant deviations from this equation (Bajnai et al., 2020; Fiebig et al., 2021; de Winter et al., 2022; this study)

References

Anderson, N. T., Kelson, J. R., Kele, S., Daëron, M., Bonifacie, M., Horita, J., Mackey, T. J., John, C. M., Kluge, T., Petschnig, P., Jost, A. B., Huntington, K. W., Bernasconi, S. M., and Bergmann, K. D.: A Unified Clumped Isotope Thermometer Calibration (0.5–1,100°C) Using Carbonate-Based Standardization, Geophys. Res. Lett., 48, https://doi.org/10.1029/2020GL092069, 2021.

Bajnai, D., Fiebig, J., Tomašových, A., Milner Garcia, S., Rollion-Bard, C., Raddatz, J., Löffler, N., Primo-Ramos, C., and Brand, U.: Assessing kinetic fractionation in brachiopod calcite using clumped isotopes, Sci. Rep., 8, 533, https://doi.org/10.1038/s41598-017-17353-7, 2018.

Bajnai, D., Guo, W., Spötl, C., Coplen, T. B., Methner, K., Löffler, N., Krsnik, E., Gischler, E., Hansen, M., Henkel, D., Price, G. D., Raddatz, J., Scholz, D., and Fiebig, J.: Dual clumped isotope thermometry resolves kinetic biases in carbonate formation temperatures, Nat. Commun., 11, 4005, https://doi.org/10.1038/s41467-020-17501-0, 2020.

Breitenbach, S. F. M., Mleneck-Vautravers, M. J., Grauel, A.-L., Lo, L., Bernasconi, S. M., Müller, I. A., Rolfe, J., Gázquez, F., Greaves, M., and Hodell, D. A.: Coupled Mg/Ca and clumped isotope analyses of foraminifera provide consistent water temperatures, Geochim. Cosmochim. Acta, 14, 2018.

Fiebig, J., Daëron, M., Bernecker, M., Guo, W., Schneider, G., Boch, R., Bernasconi, S. M., Jautzy, J., and Dietzel, M.: Calibration of the dual clumped isotope thermometer for carbonates, Geochim. Cosmochim. Acta, 312, 235–256, https://doi.org/10.1016/j.gca.2021.07.012, 2021.

Huyghe, D., Daëron, M., de Rafelis, M., Blamart, D., Sébilo, M., Paulet, Y.-M., and Lartaud, F.: Clumped isotopes in modern marine bivalves, Geochim. Cosmochim. Acta, 316, 41–58, https://doi.org/10.1016/j.gca.2021.09.019, 2022.

Meinicke, N., Ho, S. L., Hannisdal, B., Nürnberg, D., Tripati, A., Schiebel, R., and Meckler, A. N.: A robust calibration of the clumped isotopes to temperature relationship for foraminifers, Geochim. Cosmochim. 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, Paleoceanogr. Paleoclimatology, 36, https://doi.org/10.1029/2020PA004115, 2021.

Peral, M., Daëron, M., Blamart, D., Bassinot, F., Dewilde, F., Smialkowski, N., Isguder, G., Bonnin, J., Jorissen, F., Kissel, C., Michel, E., Vázquez Riveiros, N., and Waelbroeck, C.: Updated calibration of the clumped isotope thermometer in planktonic and benthic foraminifera, Geochim. Cosmochim. Acta, 239, 1–16, https://doi.org/10.1016/j.gca.2018.07.016, 2018.

Peral, M., Bassinot, F., Daëron, M., Blamart, D., Bonnin, J., Jorissen, F., Kissel, C., Michel, E., Waelbroeck, C., Rebaubier, H., and Gray, W. R.: On the combination of the planktonic foraminiferal Mg/Ca, clumped (Δ47) and conventional (δ18O) stable isotope paleothermometers in palaeoceanographic studies, Geochim. Cosmochim. Acta, 339, 22–34, https://doi.org/10.1016/j.gca.2022.10.030, 2022.

Schöne, B. R.: Arctica islandica (Bivalvia): A unique paleoenvironmental archive of the northern North Atlantic Ocean, Glob. Planet. Change, 111, 199–225, https://doi.org/10.1016/j.gloplacha.2013.09.013, 2013.

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, Geophys. Res. Lett., 49, https://doi.org/10.1029/2022GL099479, 2022.