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Interactive comment on "The influence of temperature and seawater carbonate saturation state on ¹³C-¹⁸O bond ordering in bivalve mollusks" by R. A. Eagle et al.

Anonymous Referee #1

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In this study, the authors present an empirical calibration between the growth temperature and the measured Δ_{47} of extant bivalve mollusks, cultured in several laboratories and collected from natural environments. In so doing, the authors add to the growing dataset of Δ_{47} values as a function of carbonate formation temperature, which is required for the use of "clumped" isotope analysis for reconstruction of environmental temperature and fluid isotopic composition. The data presented in this study significantly expand the dataset derived from modern mollusks and are presented clearly and completely in a set of tables and figures. The methods are presented in detail, where necessary, and the study explores several possible correlations of sample type, synthesis conditions and analytical treatment with the measured values of Δ_{47} (e.g.,

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calcitic versus aragonitic tests, oxidative cleaning of organic matter, carbonate mineral saturation state during synthesis, etc.).

In addition to presenting these new data, the paper addresses an important issue in the use of "clumped" isotope thermometry—the apparent disagreement between early empirical calibrations of Ghosh et al. (2006) and biogenic carbonate compilations, and more recent calibrations based on the synthetic carbonates of Dennis and Schrag (2010) and several other unpublished datasets from a number of research groups. The latter group of calibrations, as well as a theoretical study of the temperature dependence of C and O isotope "clumping" in carbonates (Guo et al., 2009), all find a weaker dependence of Δ_{47} on temperature (i.e., a shallower slope on a plot of Δ_{47} versus $1/T^2$). The present study adds to the occurrence of datasets that display a shallower slope. The explanations offered by the authors include differences in the analytical procedures between the early and later measurements, an acid digestion fractionation of Δ_{47} that is not constant, but depends on the actual value of Δ_{47} , or vital effects particular to mollusks. In my opinion, the present study highlights the need for standardization of analytical techniques between different labs, so that real effects on Δ_{47} associated with the precipitation of different types of carbonates (aragonitic/calcitic, biogenic/abiogenic, with/without organic scaffolding, etc.) can be observed.

I have one major (?) concern and a handful of minor and technical comments. My concern has to do with the robustness of the derived slope, given the size and scatter of the new dataset. The authors mention that this dataset substantially expands existing data from modern mollusks (which it does), and they also explore the effect of removing from the regression several samples grown/collected at low temperatures. However, both with and without the low-temperature data, there is appreciable scatter in the mollusk data. In my opinion, this decreases confidence that the authors are, in fact, observing a slope significantly different from that of Ghosh *et al.* (2006) and the biogenic carbonate compilations.

Minor comments:

- 1. p 160, line 5: Comma missing after 'for example'.
- 2. p 161, lines12-13: The issue is not that the taxa deviate from the fluid δ^{18} O this is, of course, expected. The issue is that they deviate from the δ^{18} O they are expected to have, given the δ^{18} O of the fluid and their growth temperature.
- 3. p 161, line 25: The word 'material' should be plural.
- 4. p 161, line 27: Comma missing before i.e.
- p 162, lines 6-7: The 'e.g.' should be placed inside the parentheses, followed by a comma. This error appears several other times in the manuscript (see below and possibly other occurrences).
- 6. p 162, lines 17-21: The first sentence in this paragraph is long and awkward. Please consider rewriting it in short, clear sentences.
- 7. p 166, line 5: The phrase 'will vary' should probably be 'varies'.
- 8. p 166, lines 10-13: The sentence starting with 'Water temperatures' is grammatically incorrect.
- 9. p 168, line 10: There are some extra words in the sentence ('as was the'?).
- 10. p 168, line 13: Comma missing before, 'which'.
- 11. p 170, lines 4-9: This sentence is grammatically incorrect.
- 12. p 170, line 21: Missing 'by' between the words 'confirmed' and 'analysis'.
- 13. p 170, line 22: The word 'call' should be 'calls'.
- 14. p 170, line 24: A new sentence should be started with the word 'therefore' (end of the line).

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- 15. p 170, line 25: The words 'a summer months' should be 'the summer months'.
- 16. p 170, line 26: The word 'seam' should be 'seem'.
- 17. p 171, lines 13-15: The phrase 'the difference between these two slopes ... is not significantly different...' should probably be 'the difference between these two slopes ... is not significant...' or 'these two slopes are not significantly different...'.
- 18. p 172, line 4: Missing 'do' between the words 'and' and 'not'.
- 19. p 172, line 14: The word 'effected' should be 'affected'.
- 20. p 172, line 18: 'carbonate as for example the rate' should be 'carbonate, as, for example, the rate'.
- 21. p 172, line 25: The word 'to' is missing between the words 'order' and 'assess'.
- 22. p 172, lines 27-end: Awkward wording. Please consider ending the sentence with the reported slope and intercept and starting a new sentence along the lines of 'This slope is slightly steeper, but within the 95% confidence interval...'.
- 23. In several places in the manuscript, verbs related to the noun 'data' are singular. They should be plural.
- 24. p 174, line 24: The word 'less' should be 'fewer'.
- 25. p 175, lines 5-7: Two 'between' in the same sentence.
- 26. p 175, line 28: See comment 5.
- 27. p 176, line 3: The word 'effect' should be 'affect'.
- 28. p 176, line 9: The word 'revolve' should be plural.

- 29. p 176, lines 14-18: This sentence is awkward and difficult to understand.
- 30. p 176, line 24: Please consider adding 'This is' before the words 'In contrast'.
- 31. p 176, line 25: See comment 5.
- 32. Figure 1 caption: In the second to last sentence, the word 'thank' should be 'that'. A pox on autocorrect!

Interactive comment on Biogeosciences Discuss., 10, 157, 2013.