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Climate of the Past Discussions

Interactive comment on "An assessment of latest Cretaceous *Pycnodonte vesicularis* (Lamarck, 1806) shells as records for palaeoseasonality: A multi-proxy investigation" *by* Niels J. de Winter et al.

Anonymous Referee #1

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In the manuscript "An assessment of latest Cretaceous Pycnodonte vesicularis (Lamarck, 1806) shells as records for palaeoseasonality: A multi-proxy investigation", de Winter and co-authors report observations of shell preservation and geochemistry of Pycnodonte vesicularis and potential implications for palaeoclimate and palaeoenvironmental research that can be drawn from these results.

The authors advocate that, based on conventional oxygen isotope data, Mg/Ca ratios and clumped oxygen isotopes, P. vesicularis of the late Maastrichtian of the Neuquén Basin experienced limited annual seasonality with temperatures fluctuating around

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11°C or slightly more. These temperature estimates are markedly lower than existing TEX86 estimates. Additionally, general suitability of P. vesicularis for palaeoclimate research, water mass stratification and fresh water input into the Neuquén Basin are discussed.

The authors present a rigorously constrained, extensive dataset of high quality and remain generally cautious about interpretation of the data. The text, figures and tables are clear and easy to follow, even though the text is relatively long. The questions addressed are in the scope of CP and this study contains a wealth of novel data using partly very recently developed analytical techniques. Scientific methods are clearly outlined and valid, even though I partly disagree with interpretations in detail (see below). Description of the methodology is mostly sufficient to understand the workflows (see specific comments below). It is great to see that most raw data generated to write this manuscript is included in the supplements, but giving the reader some guidance to the significance of the data and more intuitive headers in the excel file would be useful. Could stable isotope ratio and clumped isotope data also be included in the supplements? In my opinion, after moderate revision, this contribution would be very suitable for Climate of the Past:

The one point I am struggling with is the inference that the oyster-based temperature estimate of 11°C can be reconciled with the 27°C TEX86 SST estimate. The authors acknowledge that the discrepancy is surprisingly large, putting forward that 1) TEX86 may be biased towards summer SST, 2) oysters are benthic creatures and bottom water temperatures at 50-75m depth would have been somewhat lower, 3) oyster growth may have been biased towards preferential shell formation in the cold season, 4) there may be an unconstrained bias on the oxygen isotope temperature estimate and Mg-based temperature estimates might be more accurate. I do fully agree with 1) and 2) even though the inferred SST-bottom water temperature gradient would be very large. In particular – if TEX86 may be biased towards high summer temperatures and oyster calcite towards winter lows, why is the seasonality recorded in the oysters so limited?

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After all the authors put forward an interpretation of continuous oyster growth over the entire year with somewhat reduced δ18O values only in the austral spring (October-December; Fig. 9) 3) It appears odd to me that oysters should have preferentially grown in the cold season. Modern oysters shut down growth in the cold season and show increased growth and fitness in warm temperatures (e.g., Pauley, 1988 for a review of the older literature). Average oxygen isotope values for oyster transects of modern specimens therefore show a bias towards warm temperatures (more than 5°C in a specimen from N Germany, Ullmann et al., 2010) and characteristic saw-tooth patterns with flat summer minima and sharp winter maxima of δ18O (Ullmann et al., 2010, 2013). 4) It is my understanding that clumped isotope measurements are thought to represent palaeotemperatures and ambient water isotopic composition unaffected by vital effects or any other potential bias. It is not clear to me how these temperatures (if the clumped signal is indeed preserved perfectly) could be underestimated. It is unfortunate that no clumped isotope measurements for the M0 specimen are available as the authors argue this fossil shell is overall best preserved and should yield the most trustworthy data. Connected to the clumped isotopes, is there an estimate of maximum burial depth of the late Maastrichtian strata (maximum burial temperatures) in the Neuquén Basin? Can re-equilibration at the atomic scale be excluded with confidence? As the authors rightly point out there are problems with identifying a suitable transfer function for Mg/Ca temperature reconstruction for Cretaceous oysters because of secular change of seawater Mg/Ca and a multitude of available oyster (and related species) calibrations. Any argument relating to such a tentative reconstruction based on the calibration that "appears to fit best" must therefore carry some element of circularity. Could the authors revisit their chain of arguments and address these points?

Abstract and Conclusion seem quite long-winded and could be shortened with non-essential information being transferred into other sections or deleted. The referencing and reference list require a thorough check for consistency and missing information.

Specific points: Line 20: "the late Maastrichtian of the Neuquén Basin". At the moment

it reads as if only Maastrichtian sediments are present in Neuquén Basin. Line 43: “allowed for a tentative” Line 57: References in wrong sequence. Line 68: Another point here is the rapid secretion of such shells allowing for the high time-resolution required. Line 78: What is meant here by “long timescale reconstruction”? Line 79: Could this sentence be rephrased? I am not sure “caveat” can be used in the way it is put here. Line 86: References in wrong sequence Line 106: “Fischer von Waldheim, 1835” Line 106: “shell” instead of “shelf”? Line 113: Oysters in general grow very rapidly as compared to other calcite secreting marine animals and the Maastrichtian Pycnodonte does not seem to be an exception. Line 116: “tridacnid bivalves”? Line 119: “Al-Aasm” Line 131: Here and in the following, please be consistent in the use of “paleo” or “palaeo” Line 164: Missing space after 2° Line 196: “5m below the Cretaceous-Paleogene”. Regardless of style, the spelling of “Paleogene” is fixed by the International Commission on Stratigraphy (e.g., Cohen et al., 2013). Line 226: “half shell”? Line 255: “Elderfield and Ganssen, 2000”. This reference is missing in the reference list Line 263: This statement is somewhat vague. Is this meant to be with reference to the composition of the ambient seawater or the mantle fluid? Line 271: It should be kept in mind that the Sr distribution coefficient is negatively correlated with temperature (Rimstidt et al., 1998). Studies inferring a temperature control on Sr in bivalve calcite are rare and conversely point towards higher Sr/Ca in shell secreted at higher temperature (Wanamaker et al., 2008). The article cited in line 271 does not promote a Sr calibration but one for Mg. Line 307: What is the 1sd uncertainty of the Marbella marble related to? Does this mean that its composition is only known within 0.2 permil for carbon and 0.4 permil for oxygen or that this is its heterogeneity? In the former case this would impose quite a large potential bias on analyses corrected against this standard. In the latter case I wonder how the analytical reproducibility can be so much better (Line 308) than the above stated uncertainty ranges. Line 331: What is the meaning of “error” for the $\Delta 47$ measurements? Is that to be read as potential bias against other labs or is this purely a measurement uncertainty? Line 333: Is there a reference to these Santrock/Gonfiantini or Brand (Line 336) parameters that could be

cited here? Line 371: What is the evidence for diagenesis of the calcite comprising the vesicular material at this stage? Line 380: “consists” Line 391: “correspond to” Line 401: I am not entirely sure how interferences could cause noise in the XRF spectrum. An interference should cause a bias in the measurement which cannot be corrected for by applying a running mean smoothing routine. Noise should be bias-free and related only to the problems in quantifying low-amplitude signals precisely. Line 403: Please check for grammar. Line 454: The finding of seawater δ18O values around -2 ‰be quite important. Previously some late Maastrichtian freshening of the Basin has been mentioned. Is a rough estimate of salinity possible from the reconstructed bottom water oxygen isotope ratio? Line 462: Recrystallization is a different process than cementation. This statement seems to be in contrast to what has been said in Line 371. Line 477: “laminae” Line 505: Consider adding that this is a threshold for both Mn and Fe for clarity. Line 522: “LMC” is never used again in the text so I do not think there is a need to introduce this abbreviation. Line 536: “exceedingly” seems a slightly extreme term to use. Compared to heavily altered calcite samples the ones reported here are moderately depleted in 18O. Line 540: This concept of “remote biomineralisation” has been commented on by a few studies but I am not sure how much acceptance it currently has. Line 558: The partially to fully (?) altered samples subjected to clumped isotope measurements may yield some interesting information about the type of diagenesis the samples underwent. Is there any meaningful information about burial conditions during recrystallization that can be extracted from these data? Line 595: Here and Line 596 – “Quaternary” Line 611: “altered vesicular calcite in the shell” Line 651: References in wrong sequence. Line 664: “alternating” Line 667: “correlate with” Line 677: “extrapallial fluid” Line 693: Is this meant to be a reference to Wisshak et al. (2009)? See also lines 704, 705. Line 704: Wisshak et al. (2009) report a minor (0.5 ‰ enrichment of 18O in N. zibrowii on the basis of the Anderson and Arthur (1983) oxygen isotope thermometer. I would not count this as a strong vital effect because their assessment would have been the opposite (enrichment of 16O of similar magnitude) if they had employed the Coplen (2007) oxygen isotope thermometer. At the sub-permil level it

is very hard to make strong inferences about kinetic isotope effects. Line 705: References in wrong sequence. Line 731: “evaporitic setting”? Or “setting characterized by common evaporites”? Line 780: If Sr/Ca was indeed controlled by growth rate and P. vesicularis would have grown more slowly in spring (why would this be the case?), this effect should be seen as an ontogenetic drift of Sr/Ca towards lower ratios as the shell extends more slowly as the animal ages. The only shell that may show this effect is potentially M11, however (Fig. 5). Line 823: The way it is expressed here is potentially misleading. The Mouchi et al. (2013) calibration is not only a calibration based on juvenile specimens, it is also reported as a calibration that can only be employed for juvenile specimens. Line 847: I am not entirely sure how the estimate of 20 psu was derived. Could this be elaborated on? If this model is based on water δ18O it must depend on the isotopic composition of the fresh water source which I suppose is poorly constrained? Line 901: Secondary carbonates may be enriched in Mn and Fe and depleted in 13C and 18O, but this is not necessarily always the case. Line 916: This seems to be a repetition of lines 886 and following. Line 937: “Maastrichtian of the Neuquén Basin” Line 956: I agree that the clumped isotope numbers appear to make some sense, but is there any independent evidence that they truly reflect environmental conditions at the time of shell formation? I have the feeling that clumped isotope values are accepted once they give values reasonably close to where one would expect them and reconstructed ambient water composition is not too far off the expected marine value. Line 970: Please critically revise the reference list for typographic errors, wrong reference sequence, missing information, italics of biological species, dash length for page numbers, and superscripts of isotopic masses. A list of errors encountered during a broad check is given below. Line 974: page numbers missing Line 979: Check for upper and lower case Line 992: Brand and Veizer (1981) is not cited in the text. Line 994: page numbers missing Line 1006: Only give initials for author given names Line 1012: doi or article/page numbers missing Line 1016: doi or article/page numbers missing Line 1024: volume and page numbers missing Line 1027: volume and page numbers missing Line 1030: volume and page numbers missing Line 1053: Elderfield

and Ganssen (2000) is not referenced here bust cited in the text. Line 1060: delete “PINNA NOBILIS RATIO PROFILES” Line 1061: replace “n/a” page numbers by article number. Line 1065: This discussion paper has been followed by a revise paper in Biogeosciences, which I think should be cited here. Line 1068: author names should not be all capitals Line 1078: Gillikin articles are in wrong sequence. Line 1079: doi missing Line 1106: Is there a final article in Climate of the Past which could be cited here instead? Line 1114: Is “Rasnnussen” indeed correct? It appears to be an error that could have been introduced by scanning and interpreting text from a paper hardcopy. Line 1155: Check reference style. Line 1159: Lorrain papers in wrong sequence. Line 1166: Information on the publication incomplete. Line 1185: “vesicularis” Line 1186: What kind of publication is “Geologie L4”? I cannot find it online. Line 1193: “Cosmochimica” Line 1212: “Acta Palaeontologica Polonica”; page numbers missing. Line 1242: Steuber papers in wrong sequence Line 1250: Surge papers in wrong sequence Line 1262: “Rickaby, R.E.M.” Line 1268: The papers cited as “a” and “b” seem to be exactly the same. Line 1280: Information on the publication details of this short course are missing. Line 1284: Please check punctuation of this reference. Line 1290: page numbers missing Line 1304: volume number missing

Figure 1: Line 1313 “A) Photograph”; “D) Lithology”. Could a legend explaining the lithological signatures be included in panel D? The caption of the y-axis in panel D should read “boundary” Figure 3: Why are the sum of Mn and Fe shown in panel be? Fe is a quenching element and Mn an activator of cathodoluminescence, so I would expect that an image of Mn only would more closely resemble the CL pattern. As it stands there seems very little communality between the CL and the XRF trace which is a bit surprising. Could the small panels (C-I) be enlarged? I find it very hard to see the blocky calcite crystals in C and the thin layer of vesicular calcite in G in print. Also I do not find panel I) very convincing as evidence for a Fe and Mn corona around a boring. This boring rather seems to be Mn and Fe depleted. Figure 4E): How was the porograph constructed? Does it present porosity strictly on the pixels covered by the red arrow or does it integrate pixels in the depth domain or even pixels in depth

and with? Figure 6): Please rephrase “Cross plots showing cross plots”. A): What this plot shows is a weak covariation of Mn with Fe, not that there is a link to diagenesis. This is an – admittedly well-founded – inference independent of this graph. C): This graph shows that there is no significant correlation of oxygen isotope ratios with Mn concentrations ($p > 0.05$). This contradicts the caption for this panel. In particular, most δ18O values < -3 ‰ actually seem to be related to relatively low Mn (and Fe) concentrations. Figure 7: Axis title for y-axis of panel A should be “Δ47”. Consider cutting the repetition of the symbol explanation in the caption for B) and state “Symbols as in A)”. Figure 8): Line 1389: “Stack of proxy records for shell M0”. Line 1402: A lot of the samples for which the Kim and O’Neil thermometer is employed yield results outside the calibration range (10-40°C). Consider opting for a different thermometer. Table 1: I do not understand how the average Δ47 value of 0.643 was calculated. The values given above should equate to $\sim$0.701.

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Anderson, T. F., and Arthur, M. A., 1983, Stable isotopes of oxygen and carbon and their application to sedimentologic and paleoenvironmental problems, in Arthur, M. A., Anderson, T. F., Kaplan, I.R., Veizer, J., and Land, L. S., eds., Stable isotopes in sedimentary geology: Society of Economic Paleontologists and Mineralogists Short Course 10, p. 1.1–1.151. Cohen, K.M., Finney, S.C., Gibbard, P.L., Fan, J.-X., 2013, The ICS International Chronostratigraphic Chart. Episodes 36 (3), 199-204. Coplen, T.B., 2007, Calibration of the calcite-water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory. Geochimica et Cosmochimica Acta 71, 3948-3957. Mouchi, V., de Rafélis, M., Lartaud, F., Fialin, M., Verrecchia, E., 2013, Chemical labelling of oyster shells used for time-calibrated high-resolution Mg/Ca ratios: A tool for estimation of past seasonal temperature variations. Palaeogeography, Palaeoclimatology, Palaeoecology 373, 66-74. Pauley, G. B., Van Der Raay, B., Troutt, D., 1988, Species profiles: Life histories and environmental requirements of coastal fishes and invertebrates (Pacific Northwest)âĂŤPacific oyster, U.S. FishWildl. Serv. Biol. Rep.

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