

## Response to Referee #2

First we would like to thank the reviewer for the time invested to review our paper with a critical view and the suggestion and comments. Comments that will lead to substantial modification of the manuscript are discussed below. As for the more specific minor corrections, they will be addressed in the revised version of the paper.

### General comments

*"I fear the manuscript falls into a common trope of being too quick to overlook the possibility of clumped isotope resetting during burial ..."*

The possibility of clumped isotope resetting in our data was clearly stated in our MS, but we recognize that the sections dedicated to this aspect could be clarified and expanded in the revised version. The various available elements constraining sample burial and our current understanding of clumped isotope resetting are very limited. The Rock Eval results from a previous study (L 60-61) indicate the organic matter is immature, thus constraining the upper limit of burial to the oil window. We agree that this information is not sufficient to prove that there was no clumped isotope resetting as we measured samples (unpublished data) from slightly more mature Arctic sites that indisputably show resetting while below the oil window. This is why we also estimated the local burial based on available sedimentology data (L 61 to 65) and present the local geothermal gradient to constrain the heat the samples could have undergone. Surely the geothermal gradient evolved during the thermal history of the samples but we make the approximation that it remained relatively low, as the site lies on the Siberian craton. For these reasons we estimate that the samples are very unlikely to have been substantially reset (again based on our current knowledge of clumped isotope resetting). Yet later in the discussion, we cite the recent work of Nooitgedacht et al (2021) who propose that internal water can facilitate clumped isotopes reordering and explicitly declare that "We cannot exclude that this process altered the fossils studied here..." (Line 203).

*"... and too ready to extrapolate results across paleolatitudes and Phanerozoic timescales with grand paleoclimate ambition."*

This remark, together with comments from the other anonymous referee, indicate that the comparison between the data presented in this manuscript and those from the literature may have been confusing to the readers. We will therefore substantially rework this section by focusing on the comparison of Toarcian data with other very warm periods (Cenomanian-Turonian, Early Eocene ...) and made clearer that existing data indicate that the whole Mesozoic was not a uniform greenhouse period.

*In their revision I would encourage the authors take a more logical, considered, and even skeptical approach.*

We agree with this remark and will make our possible to better consider every hypothesis.

*What if the shells are not as pristinely aragonite as their SEM and Raman data imply? The chalky and fractured nature of some of their samples from the photographs in Fig. 2 calls into question the ubiquity of their SEM and Raman-based conclusions.*

*Similarly, is it possible that the burial temperatures are slightly warmer than the best estimates from the literature? Aragonite clumped isotope bond reordering is complex (relative to calcite and dolomite), poorly understood, and seemingly faster for a given thermal history than calcite (see Chen et al. 2019, GCA). The authors hardly dwell on this fact and its associated uncertainty.*

As mentioned above, the section dedicated to the possibility clumped isotope reordering of may have been too quickly expedited and we will expand it substantially in the revised version to address these various aspects, including specificities related to aragonite mineralogy. We note however that the calcite and aragonite bivalve shells from NE France provided statistically indistinguishable clumped isotope values, in line with recent published data from the Jurassic of the UK (Vickers et al., 2021).

*Also, might the Polovinnaya River samples be estuarine, and not marine? Terrestrial fossils from the same shale exposures indicate that it might be a possibility, or at least one that needs detailed recognition even if it is not the preferred interpretation. An estuarine or non-marine origin might not impact the importance of their clumped isotope paleotemperatures, but it complicates the calculated water oxygen isotope ratios in ways that are interesting and not exclusive of comparisons in Fig. 5a.*

This possibility is ruled out by the paleontological assemblages. Terrestrial fossils are entirely missing in the studied succession, except for fossil wood remains, which are common throughout shelf deposits and cannot be used as a proxy for marine / brackish / non-marine environments. All fossils recorded from the Polovinnaya section (bivalves, belemnites, forams) are fully marine. Mesohaline or brackish-water faunas are missing here. It should be noted that cephalopods are especially sensitive to salinity reduction, including belemnites (Hoffmann and Stevens, 2020). Although belemnites are sometimes considered as more tolerant to salinity decrease if compared with ammonites (Baraboshkin and Mutterlose, 2004), their occurrence is restricted to marine settings. The influx of fresh water and salinity decrease in early Toarcian of Siberia is possible, especially in those sites lacking ammonites. Saks and Nalnyaeva (1972) considered this issue during the discussion about overestimated isotope-based paleotemperatures derived from Toarcian belemnites of this area. An influence of freshwater influx during the early Toarcian was independently suggested by Kaplan (1976) in his studies of Mesozoic sedimentation of Siberia. Lastly, Protobranch bivalves (to which Dacryomya belongs) are not well adapted for salinities lower than 20‰ (Zardus, 2002). We will add some of these various and useful considerations to the revised version.

*Finally, in the text and in Figure 5 there is a casualness with comparing datasets over nearly 150 million years of the Mesozoic and Cenozoic, with dramatically different global paleoclimates and continental configurations, that makes the discussion hard to follow. For example, there is a large leap between the Early Jurassic and the Early Eocene on lines 254-259 that converts latitudinally ambiguous precipitation oxygen isotope ratios from Eocene proxy datasets to the calculation of paleosalinity during the Early Jurassic arctic. The leap is so large that it seems to obviate their point. In instances like this (see below for more line-specific commentary) I would encourage the authors to stick with datamodel comparisons*

*and well-reasoned hypotheticals. This reframing would still allow for the multi-period comparisons shown in Figure 5 with an edited discussion that better conforms to the study motivations outlined in the abstract and introduction.*

We recognize that there is a large leap between these two time-intervals. Yet we believe our hypothesis are quite reasonable and explicitly stated, as we consider this approach as a better alternative than simply using modern freshwater values, which would constitute an even larger leap of faith. Given the salinity tolerance of modern representative of the studied fossil (see above) an alternative fossil based approach would be to use a range of salinity to estimate freshwater isotope composition. Using 20-30 ‰ range for salinity and reconstructed  $\delta^{18}\text{O}_{\text{sw}}$  values would give freshwater  $\delta^{18}\text{O}$  of  $\sim -8\text{‰}$  VSMOW for the lowest salinity hypothesis and down to  $\sim -22\text{‰}$  VSMOW for the highest salinity hypothesis. We will add these complementary considerations to the revised version.

### **Specific comments**

**17-18** – *The connection with the previous sentence is not very clear; why the distinction in time interval?*

As explained in the introduction, there is no latitudinal gradient estimated for the Early Jurassic, as opposed to the Cretaceous-Early Paleogene periods.

**36-38** – *The authors could elaborate on this statement for better effect, I think. It may not be obvious to all readers how clumped isotopes are sensitive to burial.*

We will add here references to better support these statements and develop this issue in the discussion for the revised manuscript.

**43** – *Regarding "marine carbonate shells", there is some ambiguity on their marine origin in the discussion and I think the authors should specify that they are aragonitic fossils. This is important for two reasons: 1) aragonitic is exceptionally susceptible to geochemical alteration by conversion to calcite and 2) the bond reordering kinetics for aragonite are such that they are more prone to 'solid-state' clumped isotope change than calcite or dolomite.*

We will add that the fossils presented here are mostly aragonitic (one bivalve shell from NE France is in calcite). We agree and are aware that aragonite is more prone to solid-state reordering. This will also be specified.

**61-66** – *It would be useful for the authors to commit to a maximum burial temperature. Using models of bond reordering and a simple burial history curve, it would be possible to estimate the possible change in clumped isotopes due to burial heating alone.*

We will estimate possible changes in clumped isotopes using published models as suggested.

**Figure 2** – *Samples (a), (b), (d), (i), (j), (k), and (l) all look too weathered or fractured to demonstrate that they retain primary shell material. Later it is revealed that (i) is not aragonitic (Fig. 3h). How are the authors able to admit that (i) is not aragonite, but call (e), (f), or (j) "pristine"? Each of these samples have the same coloration in these images.*

It was not stated in the original manuscript and will be added in the revised version, but (e), (f) and (i) mostly show internal moulds after sampling of the shell with little aragonite material left. As for (j) most of the shell is lacking from mechanical alteration most probably while preparing and manipulating the specimen.

Indeed (i) is calcitic, but given the presence of mainly aragonite shells around it with no evidence for mineralogical conversion, it can be reasonably assumed the shell was originally in calcite.

**102-103** – *Regarding the white color, this chalky appearance can indicate shell alteration (mineralogical conversion or geochemically).*

We must first mention that all samples are creamy white and not white as suggested here; perhaps our photographs do not do justice to their real aspect. Besides, we did not find any evidence for mineralogical conversion in either the Raman spectra or the SEM observations. We note that the superficial (optical) aspect of the shell can be dramatically altered by the mechanical crushing of the shell, which is common in such fine-grained sediments and clearly visible in SEM images for some samples.

**158** – *Was the prismatic layer avoided when microsampling the shells?*

This thin part evidences in the SEM images could not be avoided for technical reasons and bulk analysis of the shells were performed. We will add this aspect in the revised version.

**Figure 3** – *Why are the Raman spectra truncated  $<200\text{ cm}^{-1}$  for (b) and (d) and not for (f) and (h)? Also, it is not clear here (or in the text) how the position of these images and spectra relate to the subsamples for isotope analysis.*

Different users took the spectra with slight different configuration. Yet this truncation does not hamper the identification of carbonate minerals. The main Raman shift rays used to differentiate calcite from aragonite are all above  $200\text{ cm}^{-1}$  ( $282$  and  $713\text{ cm}^{-1}$  for calcite, and  $209$ ,  $702$  and  $706\text{ cm}^{-1}$  for aragonite). The sampling strategy relative to the spectra (acquired on the sampled powders) and images will be clarified.

**194-196** – *The temperature ranges cited are canonical values for calcite, not aragonite.*

We are not aware of published reordering models specific to aragonite but will look into it.

**203-204** – *Regarding the possibility that small shell-water interaction has been shown to change clumped isotope ratios with only modest change in oxygen isotopes, what might be specific, independent evidence that this sort of thing had occurred (or not) in these shells?*

Perhaps precise La-ICPMS or NanoSIMS could evidence isotopic gradients around fluid inclusion related to fluid inclusion-mineral interactions.

**204-206** – *I think the implication here, subtly, is that 31 °C is something like a maximum burial temperature. Given that this is a fracture-fill carbonate without any other paragenetic sequencing context, it is equally possible that it's an exhumation temperature (i.e., a temperature experienced during fluid infiltration after maximum burial was reached).*

This is correct, we do not have any data constraining the timing of this fracture infilling calcite. We will make it clear in the revised version.

**219** – *I think it is notable that this range narrows considerably after removing the coolest temperature. The remaining 7 of 8 shells have an average of ~15 °C.*

We will add the mean of our data to avoid confusion and better point the distribution of the clumped isotope temperature values.

**230-231** – *Discussion of Jurassic food availability during the polar night, without any additional information, is entirely speculative and is too extrapolative from their isotope dataset.*

We agree this section is speculative and it will be reduced to its minimum using supporting references.

**243-237** – *As mentioned above, this is an apples-to-oranges comparison. The similarity in SST between two shell populations separated in time by over a 100 million years might be entirely coincidental.*

We found it reasonable to compare two datasets obtained using the same proxy on similar samples (bivalve shells) from high latitudes dated from periods both generally considered to register a warm climate, even though those periods are 140 million years apart.

**257-259** – *Also as mentioned above, I don't understand the relevance of Eocene high latitude precipitation values here. Who knows what they were in the early Jurassic?! As the authors show in Fig. 5, the modeled Jurassic poles were warmer than modeled Eocene poles, yielding lower latitudinal gradients in precipitation oxygen isotopes (see dashed lines for Eocene and Cretaceous data).*

See the response above about the rationale used here. The referee might be confused here, as the modelled polar temperatures shown in figure 5 are actually much warmer in the most Eocene polar simulations than in the FOAM Early Jurassic simulation. Only the older 6x HadCM3 model yield similar temperatures. The reconstructed temperatures using proxy data are, however, quite similar (which is the reason why we used Eocene d18Op values).

**266-268** – *The authors should reframe this statement to consider an alternative scenario in which this locality and these shells are not marine at all. What if -4.9 to -2.5 are estuarine or mostly freshwater oxygen isotope values?*

As stated above, the fossil data indicate marine conditions and rule out this possibility. In addition, assuming the analyzed interval was ice-free, such freshwater values would

correspond to modern river values of  $-3.9$  to  $-1.5$  permil. This range of values in river water bodies is nowadays encountered only in warm tropical areas where precipitations are source from marine areas with very high rates of evaporation (e.g., Africa, central E Australia) and would imply climate conditions that are also at odds with available geological data. We will hence consider adding a phrase to rule out this possibility in the revised MS to make this point clearer to the readers.

**Figure 5** – *Are the model results new or replotting of published results? If it's the latter than proper attribution needs to be clear in the figure or the figure caption.*

The modelled temperatures and oxygen isotope values are replotted from published Earth system results. The associated references will be added in the revised manuscript.

## References

- Baraboshkin, E.J., Mutterlose, J., 2004. Correlation of the Barremian belemnite successions of northwest Europe and the Ulyanovsk – Saratov area (Russian Platform) 14. <https://geojournals.pgi.gov.pl/agp/article/view/10295/8807>
- Hoffmann, R., Stevens, K., 2020. The palaeobiology of belemnites – foundation for the interpretation of rostrum geochemistry. *Biol Rev* 95, 94–123. <https://doi.org/10.1111/brv.12557>
- Saks, V., Nalnyaeva, T., 1972. Belemnites. The Jurassic–Cretaceous Boundary and the Berriasian Stage in the Boreal Realm 216–29.
- Zardus, J.D., 2002. Protobranch bivalves, in: *Advances in Marine Biology*. Elsevier, pp. 1–65. [https://doi.org/10.1016/S0065-2881\(02\)42012-3](https://doi.org/10.1016/S0065-2881(02)42012-3)