

## ***Interactive comment on “Technical Note: Silica stable isotopes and silicification in a carnivorous sponge *Asbestopluma* sp.” by K. R. Hendry et al.***

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## **Response to reviews**

**Many thanks to both reviewers for their thoughtful reviews, and the time and effort spent to help us improve our manuscript.**

**Response to reviewer 1 (responses in bold):**

**We would like to thank reviewer 1 for their constructive review, and would like to address the issues raised**

1. The overall interest (question? hypothesis?) of the study is not presented in a straightforward way in the introductory section.  
**We have rearranged the introduction to bring the isotope geochemistry aspects of the paper to the forefront. We believe that this has made the main crux of our paper clearer and more upfront.**
2.  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  signatures are not supposed to be controlled by the same parameters. While the  $\delta^{30}\text{Si}$  signature of sponge spicule was largely investigated, few and contradictory studies have dealt with the  $\delta^{18}\text{O}$  signature. State of the art, results and interpretations should be presented separately and successively for each of those isotopic systems. In its present state there are several confusing

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paragraphs where the lecturer does not know which isotopic system is referred to (cf specific comments).

**It should be pointed out that we are still far from understanding the precise controls over either silicon or oxygen isotope systematics in sponge biomineralisation. However, we take the reviewers point that the results section could be restructured: we have now separated the silicon and oxygen isotope results for clarification.**

3. Variations of  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  within the specimen should be properly described before being interpreted...

**We have taken this comment on board and have expanded our results section to fully describe the variations as requested. Many thanks for the additional references, and we agree that we should keep to the most recent "state of the art" cutting-edge papers for both silicon and oxygen isotope discussions.**

4. All the factors that may be responsible for the inner/outer  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  differences should be discussed. This should include potential fractionations due to dissolution/precipitation processes that may affect the external parts in natural context or during silica purification. Abundance of desmas (or desmas contamination) is presented as the most plausible factor of  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  variations. However, there is no estimate (or proxy) of desma abundances presented here to sustain this hypothesis. A Raleigh distillation is additionally suggested as a potential factor for explaining  $\delta^{30}\text{Si}$  variations. If occurring, it should also be relevant for explaining  $\delta^{18}\text{O}$  variations. Is this the case? Any tracks for explaining  $\delta^{18}\text{O}$  variations? Any alternative model (e.g. Wille et al., 2010)? **It should be noted that Wille et al., 2010, did not comment upon any fractionation models for oxygen isotopes in sponge silica. The model presented by Wille et al., 2010, is already discussed within the manuscript. However, we agree that the discussion could be expanded and separated for silicon and oxygen isotopes**

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**(which we have done). We have included an estimate of desma abundance.**

5. The "summary and conclusions" contains overstated claims regarding i) occurrence of kinetic fractionations, ii) differences in silicification modes from a part of the sponge to another, iii) differences in isotopic signature from a kind of spicule to another (e.g. desmas vs others) that could rather be presented as assumptions. Instead, the main results (e.g.  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  variations within a single specimen of the same order as variations shown in calibration or fossil datasets) could be emphasized and further discussed (eg. implications for paleoenvironmental reconstructions using  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$ ). **We have changed our summary and conclusions section to reflect the "palaeoclimate implications and outlook" of our findings, and have adapted our conclusions accordingly.**

**Reviewer 1 also had the following specific comments, which we would like to address:**

1. The use of the term "isotopic signature" is confusing. Is it used for silicon isotopes, for oxygen isotopes, or both depending on the paragraphs [sic]  
**We have removed the phrase "isotopic signature" and replaced with isotope signature, as requested.**
2. Description of the sponges anatomy in the introductory section is very interesting but overwhelmed the purpose of the study. References are missing. A diagram with a detailed caption would be clearer  
**As stated above, we have rearranged the introduction to bring the isotope geochemistry aspects of the paper to the forefront. We considered a diagram but believe that our full description of the relevant sponge biology is sufficient for the reader.**
3. ...The «state of the art»which follows (p16579, L7-20) is more accurate and should be moved forward.

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**We have restructured the introduction, and hopefully have taken all the other comments into consideration.**

4. What are potential temperature, salinity,  $\text{Si(OH)}_4$  concentrations ? How were they estimated? Are they representative of the sponge spicule growth period? Hypotheses for the sponge spicule growth dynamic?

**Potential temperature is used in physical oceanography to denote the temperature of seawater at depth that it would acquire if it was brought adiabatically to the surface. For ease of interpretation, we have used in-situ seawater temperature (from ship board measurements), rather than potential temperature (from eWOCE), to estimate the temperature at which the sponges grew (note these estimates are essentially the same). The salinity and nutrient concentrations were estimated from both ship-board measurements during the cruise from which the sponge specimen was collected, and from published records (eWOCE), as stated in the manuscript.**

5. Sample preparation: temperature of biogenic silica purification was shown to impact  $\delta^{18}\text{O}$  signature. What were the temperatures of hydrogen peroxide and nitric acid heating steps?

**This is a key point, and we agree that this should be discussed. The heating steps were carried out at 80C. Heating opal to over 70C during the organic matter removal process does not result in additional fractionation of silicon or oxygen isotopes (Tyler et al., 2007; Hendry et al., 2011), and heating to higher temperatures of 80-90C is routine in opal  $\delta^{18}\text{O}$  analyses (e.g. Swann and Snelling, 2015). This is now stated in the manuscript.**

6. Figure 4: There must be an error here. Green bars are supposed to show the difference between the internal (red) and external (black) spicules, which is not the case.

**There is no error here: the difference between the external and internal**

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**spicules had a secondary y axis on the right hand side. However, for clarification, we have now scaled this secondary axis to be the same as the left hand primary axis.**

7. Figure 5:  $\delta^{30}\text{Si}_{\text{seawater}}$ . Reference for this value?

**Both reviewers commented that they would like to see a reference for the seawater  $\delta^{30}\text{Si}$  values. Accordingly, a reference is now given for the seawater  $\delta^{30}\text{Si}$  values used to construct the lower panel of Figure 5 in the caption.**

8. The authors should separate  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  discussion; the two isotopic systems are not constrained by the same parameters... All the factors that may be responsible for the inner/outer  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  differences should be discussed, including fractionation due to potential dissolution/precipitation processes that may affect the spicules surfaces.

**See comment above.**

9. Figure captions: letters referring to the figures should be in capital. **This has been corrected.**

**Response to reviewer 2 (responses in bold):**

**We would like to thank reviewer 2 for their constructive review. We would like to address the minor comments raised.**

1. 16575, L. 7,8 biological or vital. I would not use both.

**In the abstract, we have removed the word biological, as requested.**

2. 16581, L12: I would prefer to use 2sd for both isotope systems. I know that traditionally the standard deviation for oxygen isotopes are given as 1sd, but if

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we are strict with the reproducibility for Si isotopes, why not also with oxygen isotopes.

**In the methods, and accordingly in Figure 4, we have used 2SD for the oxygen isotopes, as requested.**

3. 16582, L. 18-26: I think it is better to separate the discussion about  $\delta^{30}\text{Si}$  from  $\delta^{18}\text{O}$  in this paragraph.

**We have separated out the results section for  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$ , as requested. We have also formulated a separate discussions section for clarification.**

4. I agree with the authors that there is a significant variation in  $\delta^{30}\text{Si}$  between the internal and the external samples, but not for  $\delta^{30}\text{Si}$ , if a 2sd of 0.6 would be considered. Also the authors could discuss the  $\delta^{18}\text{O}$  signature more in detail, especially in comparison to existing data. We have clarified that, although the difference between the  $\delta^{18}\text{O}$  of the internal and external spicules is within analytical error, the offsets are systematic (i.e. the external are systematically lighter than the internal spicules).

**There is very little published data on  $\delta^{18}\text{O}$  in sponges - we have included everything to the best of our knowledge that is currently available.**

5. Interestingly there is a strong relation between  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  ( $r^2 = 0.9$ ), even though both isotope systems are not controlled by the same mechanism. Why? I think a more distinct discussion of the two isotope systems would be helpful.

**As stated above, we have expanded the discussion and separated the interpretation of silicon and oxygen isotopes. We have then included a section on the possible mechanistic links (or lack thereof) that could be responsible for the positive correlation between the two isotope systems.**

6. In terms of the variation in  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$  I defiantly agree with the authors that there is a clear variation between the Internal and the external samples, but there is no clear trend from the basal part of the sponge towards the periphery. Why is

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the difference between the external and the internal sample decreasing from the base of the sponge?

**We think that there is a systematic change along the axis for  $\delta^{30}\text{Si}$ , but agree that this is not so clear cut for  $\delta^{18}\text{O}$ , most likely as a result of the smaller variations with respect to the level of uncertainty. We have included this in the discussion.**

7. 16582, L.12: I wouldn't use phrases like "appears to be related". Is there a significant relation or not? The term "appears" is rather vague.

**The reviewer commented that they would not use phrases like "appears to be related". We have removed the vaguer phrases including the word "appears" and have attempted to be more specific in each case.**

8. 16582, L24-26: For the lower part of figure 5 (better separate in a and b) the  $\Delta\delta^{30}\text{Si}$  value is plotted against  $\text{Si}(\text{OH})_4$ . Which  $\delta^{30}\text{Si}$  for seawater was assumed here for the calculation? In general the  $\delta^{30}\text{Si}$  of ambient seawater is never mentioned in any part of the manuscript, even though it has an impact on the  $\delta^{30}\text{Si}$  of sponges.

**See above.**

9. The authors should also discuss other processes (precipitation/dissolution) that can have an influence on  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$ .

**Both reviewers comment that there should be additional discussion about other processes that could influence  $\delta^{30}\text{Si}$  and  $\delta^{18}\text{O}$ . We agree that these processes are important and have already included a discussion about precipitation. We have now also included a discussion about the impact of dissolution. Very little is known about the impact of any additional surface precipitation processes on any isotope system in spicule silica.**

10. 16584, L. 11: I think in general an important factor is the age and growth rate of the sponge already mentioned by the authors. Would it be possible to obtain data

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that give information for the age of the different parts??

**We agree that dating the spicules, and determining the age of the sponge, would add to our manuscript. Unfortunately, it is not possible to assess the age of the spicules in different regions of the sponges using existing analytical methods.**

11. Fig. 3: shows an empty square in the lower right part, which is not supposed to be there I guess.

**This rectangle is supposed to be in the figure (it is the analysis of cleaned hand-picked monaxial spicules, as opposed to bulk samples) and this is now clarified in the caption.**

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Interactive comment on Biogeosciences Discuss., 11, 16573, 2014.

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