

**Review of Technical Note: Silica stable isotopes and silicification in a carnivorous sponge
Asbestopluma sp.**

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General comments

This paper presents original $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ data obtained from a single specimen of carnivorous sponge spicules. The main results show that i) $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ variations within a single specimen are of the same order as variations shown in calibration or fossil datasets, ii) external parts appear depleted in heavy isotopes relatively to internal parts. Some tracks of interpretation are given although the lack of knowledge on the kinetic and mechanisms involved in silica formation of the specimen prevents to conclude.

These original data may help to discuss the genericity of $\Delta^{30}\text{Si}_{\text{spicule-water}}$ vs dissolved Si concentration calibrations. They contribute to the few available $\delta^{18}\text{O}_{\text{spicule}}$ datasets and may help to further assess the reliability of the use of $\delta^{18}\text{O}_{\text{spicule}}$ signature as a paleoenvironmental proxy. However, for that purpose, several points should be clarified (or reworked):

- The overall interest (question? hypothesis?) of the study is not presented in a straightforward way in the introductory section.
- $\delta^{30}\text{Si}$ 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 paragraphs where the lecturer does not know which isotopic system is referred to (cf specific comments).
- Variations of $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ within the specimen should be properly described before being interpreted. It looks like there is no clear trend with distance from the base of the sponge, as suggested, but two trends (first trend: A and B, sometimes C; second and opposite trend; C, D and E). In addition, one of the main figure (fig. 4) contains an error (cf specific comments). At least a question arises: what are the scatterings of $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ values for a given part of the sponge (A, B, C, D E, external or internal parts)? Are they smaller than $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ values scatterings from a part to another? Interpretation of the data depends on this appraisal.
- 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)?

- 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 $\delta^{18}\text{O}$).

Specific comments

- The use of the term “isotopic signature” is confusing. Is it used for silicon isotopes, for oxygen isotopes, or both depending on the paragraphs.
- 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.
- p 16577, L26: *The silicon isotope ($\delta^{30}\text{Si}$) and oxygen isotope ($\delta^{18}\text{O}$) composition of biogenic silica including that of sponges has been used to infer modern nutrient cycling, past nutrient supply and utilization, and hydrological cycling (De La Rocha, 2006; Leng et al., 2009).* This general sentence is not exact and does not refer to the relevant references: while $\delta^{30}\text{Si}$ signature of sponge spicule was widely investigated few and contradictory studies have dealt with the $\delta^{18}\text{O}$ signature of sponge spicules (e.g. Matheney and Knauth, 1989; Jochum et al. 2012; Matteuzzo et al., 2013; Snelling et al., 2014). The « state of the art » which follows (p16579, L7-20) is more accurate and should be moved forward.
- P16579, L12. *Ambient potential temperature, salinity, and $\text{Si}(\text{OH})_4$ concentrations are estimated as 2.5–3 °C, 34.5, and 60 μM , respectively (from on-board measurements and literature data, www.eWOCE.org).* What are potential temperature, salinity, $\text{Si}(\text{OH})_4$ concentrations ? How were they estimated? Are they representative of the sponge spicule growth period? Hypotheses for the sponge spicule growth dynamic?
- 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?

-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.

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

- *P 16583*, L11: *Consequently, these anaxial desmas must grow via a mechanism different from that taking place in other demosponge spicules, which may account for their distinctive silicon and oxygen isotopic composition.* Although some calibrations were made for $\delta^{30}\text{Si}$ signatures, there is no agreement on any calibration regarding $\delta^{18}\text{O}$ signatures. 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.

Technical corrections

Figure captions: letters referring to the figures should be in capital.

References

Matheney, R.K., and Knauth, L.P. (1989). Oxygen-isotope fractionation between marine biogenic silica and seawater. *Geochim. Cosmochim. Acta* 53, 3207–3214.

Matteuzzo, M.C., Alexandre, A., Varajão, A.F.D.C., Volkmer-Ribeiro, C., Almeida, A.C.S., Varajão, C.A.C., Vallet-Coulomb, C., Sonzogni, C., and Miche, H. (2013). Assessing the relationship between the $\delta^{18}\text{O}$ signatures of siliceous sponge spicules and water in a-tropical lacustrine environment (Minas Gerais, Brazil). *Biogeosciences Discuss* 10, 12887–12918.

Snelling, A.M., Swann, G.E.A., Pike, J., and Leng, M.J. (2014). Pliocene diatom and sponge spicule oxygen isotope ratios from the Bering Sea: isotopic offsets and future directions. *Clim Past* 10, 1837–1842.

Wille, M., Sutton, J., Ellwood, M.J., Sambridge, M., Maher, W., Eggins, S., and Kelly, M. (2010). Silicon isotopic fractionation in marine sponges: A new model for understanding silicon isotopic variations in sponges. *Earth Planet. Sci. Lett.* 292, 281–289.