

Interactive comment on “Assessing the relationship between the $\delta^{18}\text{O}$ signatures of siliceous sponge spicules and water in a tropical lacustrine environment (Minas Gerais, Brazil)” by M. C. Matteuzzo et al.

M. C. Matteuzzo et al.

mmatteuzzo@gmail.com

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Authors’ response to Anonymous Referee #2.

We first would like to thank Referee #2 for his detailed review.

The main concern that was expressed relates to the correction that was made for the
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methodological bias encountered during the Controlled Isotopic Exchange (CIE) procedure at CEREGE. This indeed led to high uncertainties. In order to get over this problem, the CEREGE Stable Isotope Lab recently moved from the CIE to the inert Gas Flow Dehydration technique (iGFD) (Chapligin et al., 2010), using N₂ gas. Measured $\delta^{18}\text{O}$ values were corrected on a daily basis using a quartz lab standard previously calibrated to NBS28. The long term precision of the quartz lab standard is $\pm 0.2\%$ (1σ). Amorphous silica working standards previously used for the inter-laboratory comparison (Chapligin et al., 2011) were analysed. MSG60 (CEREGE), BFC (NERC), PS (AWI) and HT (FZJ) gave $\delta^{18}\text{O}$ values of $37.0 \pm 0.5\%$ ($n=4$), $29.3 \pm 0.4\%$ ($n=3$), $43.0 \pm 0.1\%$ ($n=4$), $23.1 \pm 0.1\%$ ($n=2$). These values are in the range of averaged values obtained during the inter-laboratory comparison (MSG60: 37.0 ± 0.8 ; BFC: 29.0 ± 0.3 ; PS1772-8; 42.8 ± 0.8 ; HT: 23.2 ± 0.9) (Chapligin et al., 2011). We re-analysed the set of sponge spicule samples. Replicate analyses of the sponge spicules yielded a reproducibility better than $\pm 0.5\%$ (1σ). When plotting $\delta^{18}\text{O}_{\text{silica}}$ data obtained after the iGFD against $\delta^{18}\text{O}_{\text{silica}}$ data obtained after the CIE a slope of 1.07 was obtained ($R^2=0.97$; Figure 1). iGHD $\delta^{18}\text{O}_{\text{silica}}$ values were used for re-assessing the relationships between $\delta^{18}\text{O}_{\text{silica}}$ of the sponge spicules, $\delta^{18}\text{O}_{\text{water}}$ and water temperature. The obtained relationships are very close to the relationships previously obtained using the CIE $\delta^{18}\text{O}_{\text{silica}}$ values: $\delta^{18}\text{O}_{\text{silica}} = 0.55 * \text{measured } \delta^{18}\text{O}_{\text{water}} + 29.2$ ($R^2 = 0.80$; $p < 0.01$) instead of $\delta^{18}\text{O}_{\text{silica}} = 0.6 * \text{measured } \delta^{18}\text{O}_{\text{water}} + 27.6$ ($R^2 = 0.80$; $p < 0.01$) (fig. 5a of the corrected draft). $\delta^{18}\text{O}_{\text{silica}} = -0.4 * \text{measured } t_{\text{water}} + 39.1$ ($R^2 = 0.75$; $p < 0.01$) instead of $\delta^{18}\text{O}_{\text{silica}} = -0.5 * \text{measured } t_{\text{water}} + 38.5$ ($R^2 = 0.77$; $p < 0.01$) (fig.5b of the corrected draft). $\Delta^{18}\text{O}_{\text{silica}} - \text{measured } t_{\text{water}} = 0.4 * \text{measured } t_{\text{water}} + 20.8$ ($R^2 = 0.72$; $p < 0.01$) instead of $\Delta^{18}\text{O}_{\text{silica}} - \text{measured } t_{\text{water}} = 0.3 * \text{measured } t_{\text{water}} + 20.2$ ($R^2 = 0.63$; $p < 0.01$) (fig. 6a of the corrected draft). $\Delta^{18}\text{O}_{\text{silica}} - \text{measured } t_{\text{water}} = -0.9 * \text{Si} + 34.3$ ($R^2 = 0.57$; $p < 0.01$) instead of $\Delta^{18}\text{O}_{\text{silica}} - \text{measured } t_{\text{water}} = -0.8 * \text{Si} + 32$ ($R^2 = 0.48$; $p < 0.01$) (fig. 7 of the corrected draft). A corrected draft (to be sent to the Editor) is now based on this new dataset. The method section was modified accordingly, with Fig. 1 showing the relationship between the two datasets

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included in supplementary material. It is especially noted that “Plot of iGFD $\delta^{18}\text{O}_{\text{silica}}$ vs corrected CIE $\delta^{18}\text{O}_{\text{silica}}$ values showed a slope of 1.07 ($r^2=0.97$) (fig. S1). These results support the conclusion that despite absolute $\delta^{18}\text{O}_{\text{silica}}$ values having an offset, trends in former $\delta^{18}\text{O}_{\text{silica}}$ datasets, obtained using the CEREGE CIE, were accurate (Crespin et al., 2008; Crespin et al., 2010; Alexandre et al., 2012).” As the obtained relationships did not significantly change, interpretations/conclusions are similar in the non-corrected and corrected drafts.

A second concern of referee #2 is related to the timing of spicule growth: “For a real calibration study to occur, there needs to be a more rigorous exploration of when spicule growth occurs and measurements of the water $\delta^{18}\text{O}$ values and temperature during spicule growth.” In order to take into account this remark, the following point was added to the conclusion section of the corrected draft: Choice of natural vs artificial environment for calibrating isotopic relationships between biogenic minerals, water and temperature is frequently debated. Using an artificial environment allows to set up or continuously measure some environmental parameters (eg. $\delta^{18}\text{O}_{\text{water}}$, water temperature). However other parameters of interest a posteriori may be dismissed or biased during the set-up of the experiment (e.g. in the present case amount and types of nutrients, changes in Si concentration). Using a natural environment does not allow to continuously measure the different parameters. However heterogeneity and complexity of the environment responsible for the biogenic mineral precipitation is taken into account as a whole. In the present study, we resolved to work on a natural small pond as 1) the ecosystem was well constrained. One species of sponge proliferated according to an annual cycle previously quantified (Melão and Rocha, 1999), under conditions of Si concentration, $\delta^{18}\text{O}_{\text{water}}$ and water temperature that could be measured or reconstructed; 2) it is a complex environment similar to other Minas Gerais ponds where thick layers of sponge spicules, paleo-environmentally interesting, were deposited over the Holocene period.

We also added to the discussion section of the corrected draft: “In order to further

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assess the parameters responsible of the $\delta^{18}\text{O}$ imprint in lacustrine sponge spicules, additional calibration experiment are needed, using a single species grown under laboratory controlled conditions of $\delta^{18}\text{O}$ water, water temperature, dissolved Si and nutrient concentration”.

Regarding the timing of spicule growth, and as now explained in section 2.4 of the corrected draft, we would like to emphasize that “although silica formation is rapid - Schroder et al. (2003) reported that spicules several hundreds of micrometers long grew in several tenths of hours- the collected sponge samples gather spicules grown over one year cycle” during the growth and the degeneration phases. As additionally explain in section 2.4 of the corrected draft “in Lagoa Verde, the proliferation cycles last nine months. A growth phase occurs from November to April and is followed by a degeneration phase from May to July. The sponge samples collected during a given year thus contain sponges growing since November of the previous year. To assess whether sponges precipitate their spicules in isotopic equilibrium with water over their growth period, the water temperature and $\delta^{18}\text{O}$ water values were, as a first step, reconstructed from November 2009 to May 2011 (latest sponge sampling).”

Referee #2 also raised some concern about large daily variations of water temperature that may characterize the small shallow pond. This was also underlined by Referee #1. Indeed large daily variations of the environmental parameters may be smoothed by reconstructed averages. This is a drawback which is now underlined at the beginning of the discussion section in the corrected draft. However, uncertainties on reconstructed values of water temperature and $\delta^{18}\text{O}$ water cannot inverse the positive relationships obtained between $\delta^{18}\text{O}$ silica-water and water temperature when data from the time of sample collection are considered. Such a positive relationship clearly indicates that no isotopic equilibrium has been reached between the silica in the sponge spicules and the pond water, which is the main conclusion of this paper.

Referee #2 asked about potential contribution of groundwater to the lake water and the possible heterogeneity of the pond water regarding temperature and $\delta^{18}\text{O}$. Here

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we would like to underline that the pond is shallow and small (section 2.1 and fig. 1 of the BGD draft). The pond water is thus expected to be well mixed, and to have a short response time to hydroclimatic forcing parameters. As noted in the result section, figure 4 rather suggests that seasonal trends in the water level, $\delta^{18}\text{O}_{\text{water}}$, temperature and Si concentration are the results of a balance between precipitation and evaporation. As noted in the result section of the corrected draft, “despite smoothing the actual variations, our $\delta^{18}\text{O}_{\text{water}}$ reconstructions reproduce the seasonal trends.”

“It is not clear why the authors have gone to such lengths to reconstruct the water temperature and water $\delta^{18}\text{O}$ values rather than use the measured values.” As noted by Referee #2 and written at the beginning of the corrected draft “The unique relationships between the $\delta^{18}\text{O}_{\text{silica}}$ -water value and water temperature when the data from the time of sample collection are considered suggests that successive precipitation/dissolution processes occur over the time of spicule formation, and the latest precipitation gives its $\delta^{18}\text{O}$ imprint to the entire spicule assemblage”. We believe that existence of such a late imprint could not have been demonstrated a priori without comparing relationships with temperature reconstructed over the whole period of sponge growth and relationships with temperature measured at the time of sample collection.

“If the spicules were growing throughout the month, why would it be most strongly correlated with the final $\delta^{18}\text{O}$ values? It seems unlikely that the spicules, which are much more dense than other biogenic silica like diatoms, would not record the $\delta^{18}\text{O}$ values throughout the entire period of growth”. We are not sure to understand this remark (cf answer to previous comment). As underlined in the introductory section of the manuscript, “in contrast to diatom frustules, in which silica is deposited from a saturated solution onto organic templates, siliceous spicules in sponges are formed in an enzymatic way . . .” and in the discussion section “the actions of the silicatein and silicase, which respectively polymerize and depolymerize silica, and the reorganization of the silica sheath in the forming spicule may contribute to give the spicule assemblage

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a late $\delta^{18}\text{O}$ imprint.”

Referee #2 finally disagree with the conclusion that our results prevent the use of $\delta^{18}\text{O}$ silica values from the spongillites of northwestern Minas Gerais as a direct proxy for past $\delta^{18}\text{O}$ water and/or temperature changes, but admit that our data support a potential kinetic fractionation. As noted in the BGD paper, several kinetic fractionations may occur during enzymatically controlled Si uptake, polymerization, depolymerization, and reorganization of the silica sheath inherent to spicule formation. In the present case, the summed amplitude of these fractionations increases with temperature during the latest month of growth at a rate of approximately $0.4\% \cdot ^\circ\text{C}^{-1}$ (corrected draft). However, other parameters co-varying with temperature, such as nutrient feeding or dissolved Si concentration, that were not considered in the present study, need to be assessed as potential controlling factors before using any kinetic fractionation coefficient for paleoenvironmental reconstruction purposes. In order to further assess the parameters responsible of the $\delta^{18}\text{O}$ imprint in lacustrine sponge spicules, additional calibrations are needed, e.g. using a single species grown under laboratory controlled conditions of $\delta^{18}\text{O}$ water, water temperature, dissolved Si and nutrient concentration. This is now written in the corrected draft at the end of the discussion section, in the conclusion section and in the abstract: “Thus, additional calibrations are necessary to assess the influence of other parameters co-varying with temperature, such as nutrient feeding or dissolved Si concentration, that were not considered in the present study. Unless such detailed studies are performed, $\delta^{18}\text{O}$ silica values from the spongillites of northwestern Minas Gerais cannot be used as a direct proxy for past $\delta^{18}\text{O}$ water and/or temperature values.”

Technical corrections were taken into account in the method section of the corrected draft. Corrected draft : to be sent to the Editor.

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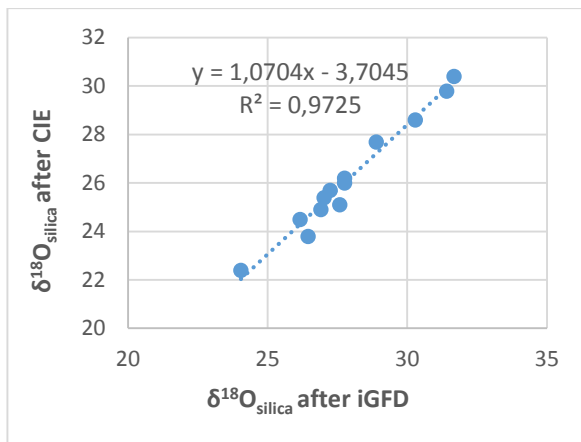


Figure 1. $\delta^{18}\text{O}_{\text{silica}}$ data obtained after the iGFD (corrected draft) vs $\delta^{18}\text{O}_{\text{silica}}$ data obtained after the CIE.

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