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Matteuzzo et al. manuscript ‘Assessing the relationship between the  $\delta^{18}\text{O}$  signatures of siliceous sponge spicules and water in a tropical lacustrine environment (Minas Gerais, Brazil)’

The paper presents new  $\delta^{18}\text{O}_{\text{silica}}$  data from recent freshwater sponge spicules (*Metania spinata*) from Lagoa Verde, Brazil. Despite larger uncertainties (which should be mentioned), due to the performed reconstruction of many parameters by meteorological data, the authors clearly show that there are correlations between  $\delta^{18}\text{O}_{\text{silica}}$  and  $t_{\text{water}}$  respectively  $\delta^{18}\text{O}_{\text{water}}$  no matter if measured/reconstructed or reconstructed and weighted (with spicule growth) conditions are applied. The measured difference between  $\delta^{18}\text{O}_{\text{silica}}$  and  $\delta^{18}\text{O}_{\text{water}}$  ( $\Delta^{18}\text{O}_{\text{silica-water}}$ ) is positively correlated with the pond water temperature. Hence, the authors conclude that *Metania spinata* does not form its spicules in oxygen isotopic equilibrium with the pond water. Additionally, they conclude that  $\delta^{18}\text{O}_{\text{silica}}$  from sponges of this region should not be used as a direct proxy for reconstructing past  $\delta^{18}\text{O}_{\text{water}}$  and/or water temperature changes.

The article is carefully written and based on an extensive, detailed investigation and short (1-1.5yrs) but well planned sampling campaign. Much effort has been put in a thoughtful reconstruction of required parameters such as water levels, water temperatures and  $\delta^{18}\text{O}_{\text{water}}$  values. The article has the right length and structure and content (aim and scope, objectives) for BGS and the data should definitely be published.

However, it has to be stated, that the pond is not ideal for the investigation of temperature-isotope relation and that due to this the conclusions should be drawn more carefully. For example the authors admit “significant variations in the pond water temperature [during the day] can be expected” with such a shallow water level and “atmospheric temp variations during the day  $>10^{\circ}\text{C}$ ”. More data from different, stable ponds would help here to underline the results. At least further discussion about the hydrology and the applicability of  $\delta^{18}\text{O}_{\text{silica}}$  from sponges is required (I disagree here with the drawn conclusion; see comments for the sections “Discussion” and “Conclusion”).

Additionally, it seems that the applied correction functions for  $\delta^{18}\text{O}_{\text{silica}}$  are partly reliable for the shown trends (cf. Table 1, column  $\delta^{18}\text{O}_{\text{silica}}$  vs. corrected  $\delta^{18}\text{O}_{\text{silica}}$  measured). As most of the result and the discussion section is based on the values from corrected  $\delta^{18}\text{O}_{\text{silica}}$  measured and as this method of corrections has large uncertainties the results are questionable (see comments for the sections “Methods” and “Results”). At least the uncertainties should be mentioned and the theoretic results for the uncorrected data should be discussed and if they provide a similar picture (which seems to be the case). The Editor should decide independently whether this is a major issue.

When accepting the performed empirical corrections for  $\delta^{18}\text{O}_{\text{silica}}$ , I suggest minor revision according to the comments. General and section specific recommendations are given below and within the annotated manuscript .pdf attached. I hope this will help in any case.

## 1) General comments

(overview of most important issues and general notes, detailed comments to be answered are given in (2))

- Corrected  $\delta^{18}\text{O}_{\text{silica}}$  values: This is my first concern for this study. It seems that the applied correction functions are partly reliable for the shown trends (cf. Table 1, column  $\delta^{18}\text{O}_{\text{silica}}$  vs. corrected  $\delta^{18}\text{O}_{\text{silica measured}}$ ). As most of the result and the discussion section is based on the values from corrected  $\delta^{18}\text{O}_{\text{silica measured}}$  and as this method of corrections has large uncertainties the results are questionable (see comments for the sections “Methods” and “Results”). At least the uncertainties should be mentioned and the theoretic results for the uncorrected data should be discussed and if they provide a similar picture.

- The second concern is that the pond is just not ideal for the investigation of temperature-isotope relation. For example the authors admit that “significant variations in the pond water temperature [during the day] can be expected” with such a shallow water level and “atmospheric temp variations during the day  $>10^{\circ}\text{C}$ ”. More data from different, more stable ponds would help here to underline the results.

- The pond issue leads to the third bigger concern: The authors conclude that due to spicule forming in non-equilibrium conditions this “prevents the use of  $\delta^{18}\text{O}_{\text{silica}}$  for reconstructing past  $\delta^{18}\text{O}_{\text{water}}$  and temperature changes”. This conclusion (mentioned in Conclusion and in a reduced form with a restriction on the locality in the Abstract) is a major aspect of the paper and has to be discussed, and I think partly withdrawn/limited. If there is a clear correlation between  $\delta^{18}\text{O}_{\text{silica}}$  ( $\Delta^{18}\text{O}_{\text{silica-water}}$ ) and  $t_{\text{water}}$  and the latest  $\delta^{18}\text{O}_{\text{precipitation}}$  “imprint” which can be seen in the spicules why should fossil sponge spicules in the sediment not be used as a proxy (not on a monthly base, of course)? I would not use it for this pond, but due to the extremely variable hydrology of this pond I would not recommend to perform a paleoclimate reconstruction on the sediments from this pond from many other proxies anyways. So, in my opinion mainly the hydrology here is responsible for this formulated prevention and the prevention should be formulated as in the abstract or even better with a focus on the limited suitability of this pond.

- All  $\delta^{18}\text{O}_{\text{silica}}$  values and  $\Delta^{18}\text{O}_{\text{silica-water}}$  values should be shortened to one digit, for all  $\delta^{18}\text{O}_{\text{water}}$  values it is enough to show two digits.

- The article is generally short and precise in text but voluminous in tables (4) and figures (8) showing partly redundant data (e.g. Table 3 vs. Fig. 3). I recommend shifting Table 2 and 3 to supplementary data and reduce Fig. 5/6/8 to one Figure with measured data only to further sharpen the focus.

## 2) Detailed comments for each section/subsection

### *Title*

- Title: The title matches the content of the article. However, I recommend a slight adaptation as using the delta signature in the title always causes problems when citing etc. I recommend using "oxygen isotope signature/composition" instead.

### *Abstract*

- The abstract is too long and provides more than just essential information. I suggested potential parts which could be shortened or deleted in the annotated notes in the attached .pdf.
- Apart from this, the abstract gives a good overview and summarises all sections shortly and correctly.

### *1. Introduction*

- The length of the introduction is appropriate, the topic is well introduced, the most important references for this topic are provided. The last paragraph is too long and can be shortened.
- More detailed thoughts should be given to the different fractionation factors and temperature relations as this is the major topic of the article. Be precise: Most articles agree to the temperature relation of  $-0.2\text{‰}/^{\circ}\text{C}$  for lacustrine environments. For marine there is still a discussion between  $-0.2\text{‰}/^{\circ}\text{C}$  and  $-0.5\text{‰}/^{\circ}\text{C}$ . Differ between the studies on recent and fossil material if mentioning the quartz fractionation as well. Add the recent article by Dodd et al. (2012).
- Delete or shift the last sentence up as it blurs the well formulated aims of the last paragraph.

*For detailed comments and smaller corrections see annotated notes in the attached .pdf.*

## *2. Materials and Methods*

### *2.1 Study Area*

- Some information can be deleted which is not essential to sharpen the focus of this article, e.g. the introductory sentence about spongillites (leave out the references, too) as well as the footprints of animals around the lake.
- I strongly recommend using a lake close-up in Figure 1 rather than the second image. This should include the different sampling points/campaigns and the (changing) bathymetry to get a visual quick shot.

### *2.2 Sampling and field measurements*

- Same point, see above: a lake close-up with all sampling points/transects would help.
- For a better overview in the text: mention all taken samples according to the numbers.
- From which depth were the water samples collected? Were these the samples for isotope analysis?
- Why did you chose to measure water temperature in 20cm depth? The sponges were placed on the floor of the pond which is 1.6 to 3m according to section 2.1. and 0.65 to 2.05m acc. to Table 1. As we look at a big evaporative "pan" the temperatures as well as the isotope values

might be quite different on the bottom of the pond (if taken at that depth, too). Add the bathymetry (isolines) of the lake to Fig. 1 for clarification.

### 2.3 Analytical methods

- Sponge spicule extraction/purification: okay.

- Water samples: okay

-  $\delta^{18}\text{O}_{\text{silica}}$ : In my opinion it is not enough to measure two quartz standards (NBS28 and one lab-internal working standard (Boulangé 50–100 $\mu\text{m}$ ) as biogenic silica is measured. These standards offer no control of dealing with exchangeable oxygen and if the essential step - CIE - works and provides reliable information. This is especially important as CEREGE had to empirically correct their values  $\delta^{18}\text{O}_{\text{silica}}$  in the inter-laboratory comparison by Chaplignin et al. (2011). Even after the correction the  $\delta^{18}\text{O}_{\text{silica}}$  values showed differences to the lab's mean average (pooled)  $\delta^{18}\text{O}_{\text{silica}}$  values for the six investigated working standards between  $-0.1\text{‰}$  (MSG60) to  $+2.9\text{‰}$  (G95), see Alexandre et al. 2012. Additionally, the chosen internal quartz standard's average  $\delta^{18}\text{O}_{\text{silica}}$  value ( $16.284\pm 0.1\text{‰}$ ) and the NBS28 ( $9.78\pm 0.14\text{‰}$ ) are far away from the measured range (app. 25-34 $\text{‰}$ , Table 1).

I strongly recommend using one of the amorphous biogenic silica secondary/working standards from Chaplignin et al. (2011), the BFC working standard seems to be ideal as it is in the required range with a low inter-lab standard deviation ( $29.0\pm 0.3\text{‰}$ ). However, CEREGE analysed a 3.8 $\text{‰}$  offset here (after correction still 1.8 $\text{‰}$ ).

### 2.4 Reconstruction of temperature and $\delta^{18}\text{O}$ water conditions over annual cycles of sponge proliferation

-  $t_{\text{water}}$  vs.  $t_{\text{atm}}$ : okay. Temperatures were not measured at the depth of the sponge growth but at 20cm depth. More comments here in the comments on the results.

- water levels: The reconstruction of water levels seems to work well. The estimated water levels match the measured ones. Apart from Eq. 3, the water balance equation responsible for this correlation should be mentioned.

- water levels vs  $\delta^{18}\text{O}$ : Regarding the evaporative character, I still recommend to add dD values to get a real picture of the evaporative effect on the water isotope composition as it is an isotope paper. More comments here in the comments on the results.

- sponge growth coefficient: I am not a sponge growth expert, and I might have missed this if any calculation has been performed here, but it might help not to just adapt the numbers/Eq.4 from the Melao and Rocha (1999) for Lagoa Dourada but to add a calculation with own data from the counts (Table 2, Fig. 2, Fig. 3) in Fig. 4 (top cart) and see if it roughly matches the data from Melao and Rocha (1999).

However, all formulated equations have been done with much thought and “as good as possible” with the known input parameters. The results from the reconstruction still should be relatively reliable, but it has to be mentioned that due to the reconstruction and all empirically assumed relations a higher uncertainty exists. Some sentences should be added in the results section.

*For detailed comments and smaller corrections in this section see annotated notes in the attached .pdf.*

### 3. Results

- Microscopic observations: Well done. The results are short and clear, the images telling.
- Water level/water temperature/ $\delta^{18}\text{O}_{\text{water}}$ :
  - these results are mixed up and should be presented in the order above as suggested by the authors in their introductory sentence.
  - Fig.4 shows that there are quite a difference between  $t_{\text{water}}$  reconstructed by  $t_{\text{atm}}$  and the measured  $t_{\text{water}}$  (variation in 4 out of 7 measurements 2-4°C with a complete amplitude of c. 6°C). This increases the uncertainty in the final results of temperature relations. Additionally, temperatures were not measured at the depth of the sponge growth but at 20cm depth.
  - The authors admit that “significant variations in the pond water temperature [during the day] can be expected”. With such a shallow water level and “atmospheric temp variations during the day >10°C” it has to be stated, that the pond is not ideal for the investigation of temperature-isotope relation and increases uncertainty. More data from different, stable ponds would help here to underline the results and decrease the uncertainty.
  - If optimising the reconstructions on seasonal trends, it would be important to state that sponge spicules grow consistently at night and day and incorporate a mean signal if this is the case.
  - Water levels vs  $\delta^{18}\text{O}_{\text{water}}$ : It has to be taken into account that there are quite large differences in  $\delta^{18}\text{O}_{\text{water}}$  values reconstructed vs. measured of up to 2.5‰ (-2.5 to +1.9‰, SD from absolute values 1.2‰). Even if the 2.5‰ offset is explained well by high rainfalls, there remain average offsets larger than 1‰. This has to be mentioned and added to the uncertainty of the results.
- $\delta^{18}\text{O}_{\text{silica}}$  values:
  - The results are thoroughly displayed in several figures showing that correlations between  $\delta^{18}\text{O}_{\text{silica}}$  values and (1)  $\delta^{18}\text{O}_{\text{water}}$  values/Fig. 5 (2) water temperature/Fig. 6 (3) dissolved Si concentration/Fig. 8 exist. These correlations exist no matter if measured, reconstructed or reconstructed and weighted conditions are applied. Additionally Fig. 7 shows  $\Delta^{18}\text{O}_{\text{silica-water}}$  values vs. water temperature.
  - As Fig. 5/6/8 have one main goal (correlation exists between respective parameters) they could be reduced to one figure a/b/c with the measured data (this has already been done in Fig. 8) for the three different relations. The reconstructed and rec/weighted correlation charts can be moved to the supplementary data. The text clearly states all  $r^2$  which is good and enough.
  - Fig. 7 is the Figure where the main conclusions are based on and which shows contradictory data for the correlations depending on which data is used (measures/rec/rec&weighted). Hence, this should remain one individual Figure.

-  $\delta^{18}\text{O}_{\text{silica}}$  values vs. dissolved Si concentration: This correlation is mentioned twice, before and after the  $\Delta^{18}\text{O}_{\text{silica-water}}$  results and refers to Fig. 8. Delete the first. I wonder why there is a difference in  $r^2$  (0.56 vs. 0.48, see text below)?

→ Corrected  $\delta^{18}\text{O}_{\text{silica}}$  values: It seems that the applied correction functions are partly reliable for the shown trends (cf. Table 1, column  $\delta^{18}\text{O}_{\text{silica}}$  vs. corrected  $\delta^{18}\text{O}_{\text{silica measured}}$ ). Before the correction the results were very close together, especially when looking at the Mar/Apr data showing roughly the same values when compared to Aug/May before the correction and the big difference by using the correction method. As most of the result and the discussion section is based on the values from corrected  $\delta^{18}\text{O}_{\text{silica measured}}$  and as this method of corrections has large uncertainties the results are questionable.

One comparably easy way out would be to further discuss this thoroughly and increase the reliability of the results by using just the measured data without the correction and add one column in Table 1 for the most important conclusion ( $\Delta^{18}\text{O}_{\text{uncorr silica-measured water}}$ ), if there is any difference the type of correction should definitely be discussed within the magnitude of uncertainty of the correction.

For example when calculating  $\Delta^{18}\text{O}_{\text{silica-weighted water}}$  with the uncorrected  $\delta^{18}\text{O}_{\text{silica}}$  values in contrast to the non-existing correlation of the corrected results (Fig. 7c) there would be a positive correlation (3.2‰/°C) of this parameter with the monthly mean temperature (weighted) and an  $r^2=0.89$  (which would question the performed reconstructions). Using measured uncorrected data against measured water temperature (taken from Table 1) the correlation would even be higher ( $r^2=0.92$ ) with a coefficient of 1.1‰/°C. At least these theoretic thoughts should be exercised and properly discussed.

- Equilibrium thoughts: This paragraph might better fit into the discussion section. The gained results are already presented at this point. I would not say "conversely" as the other studies dealt with minerals, quartz and mainly fossil phytoliths and diatoms.

*For detailed comments and smaller corrections in this section see annotated notes in the attached .pdf.*

#### 4. Discussion

- The discussion is rather short and focuses mainly on explaining the silica formation and dissolved Si as a potential trigger for sponge growth.

- Biologically controlled mineralisation of spicules (second paragraph): The general process of spicule silica formation should be shortened and partly moved to the introduction as the authors only conclude from this that several aspects in this chain could be responsible

- First paragraph (this should be discussed in more detail): The authors state that the latest precipitation gives its  $\delta^{18}\text{O}_{\text{precipitation}}$  "imprint" to the entire spicule assemblage. I think this is mainly because of the hydrology and a rapidly reacting (on a daily, even hourly base, see pond temperature variations) system. By completely and quickly changing the  $\delta^{18}\text{O}_{\text{water}}$  one

basically has a  $\delta^{18}\text{O}_{\text{water}}$  “imprint”, the time window of reconstruction is the issue. One should probably go with average values longer than the living period of the sponge to clearly separate the different “imprints” in the sedimentary assemblage for paleoclimate reconstruction. For longer records with resolutions way beyond “monthly” this is the case.

- Due to spicule forming in non-equilibrium conditions this “prevents the use of  $\delta^{18}\text{O}_{\text{silica}}$  for reconstructing past  $\delta^{18}\text{O}_{\text{water}}$  and temperature changes”. This conclusion (mentioned in Conclusion and Abstract) is a major aspect of the paper and has to be discussed here (belongs to the upper point), and I think partly withdrawn/limited. If there is a clear correlation between  $\delta^{18}\text{O}_{\text{silica}}$  ( $\Delta^{18}\text{O}_{\text{silica-water}}$ ) and  $t_{\text{water}}$  and the latest  $\delta^{18}\text{O}_{\text{precipitation}}$  “imprint” which can be seen in the spicules why should fossil sponge spicules in the sediment not be used as a proxy (not on a monthly base, of course)? So, the time interval of reconstruction should be discussed, too. I would not use  $\delta^{18}\text{O}_{\text{silica}}$  from sponges reconstruct any paleoenvironmental data for this pond, but due to the extremely variable hydrology of this pond I would not recommend to perform a paleoclimate reconstruction on the sediments from this pond using many other proxies anyways. So, in my opinion this mainly the hydrology here is responsible for this formulated prevention.

*For detailed comments and smaller corrections in this section see annotated notes in the attached .pdf.*

### 5. Conclusions

- The conclusion is generally short, well and careful enough written.  
- The point that the results prevent the use of  $\delta^{18}\text{O}_{\text{silica}}$  from sponge spicules as a direct proxy requires (a) further discussion and (b) a narrowing of this very courageously drawn conclusion on the locality (see comments in the discussion section). This has been already done in the abstract (non-applicability of the proxy for the region of northwestern Minas Gerais, Brazil).

*For detailed comments and smaller corrections in this section see annotated notes in the attached .pdf.*

### References

- I recommend taking not ten but only the most important publications from Volkmer-Ribeiro, C. et al.  
- Check references for consistency: leave doi, use official abbreviations for journal names (Geochim. Cosmochim. Acta; Earth Planet Sci. Lett., etc.)

*Tables (Further comments in each Table of the annotated .pdf)*

### Table 1

- Good table! Specify for n if the two measurements were gained from two different CIEs or from one but with two analyses? Mention how the number was gained as \*

#### Table 2

- Optional: Move to supplementary data.
- The parameters' indices are partly wrong. Check which equation has been used for each parameter.

#### Table 3

- The table is fine, but should be moved to supplementary data. It is redundant - Fig. 3 provides a quicker picture.

#### Table 4

- There is no reference in the text to this table.
- The information given here is redundant and shown in Figure 7c, apart from weighted  $\delta^{18}\text{O}_{\text{water}}$  which is only used for calculating the shown associated  $\Delta^{18}\text{O}_{\text{silica-weighted water}}$  values. Hence, move this table to the supplementary data.
- Reduce the number of digits for  $\Delta^{18}\text{O}_{\text{silica-weighted water}}$  values to one.

#### *Figures (Further comments in each Figure of the annotated .pdf)*

#### Figure 1

- Increase size of brasil (left). Leave out middle magnification. Show lake/pond close-up with (changing) bathymetry and sampling points / transects differing between natural and artificial samples.

#### Figure 2

- good figure, clear captions.
- From which samples are these four images from? Same sample, different samples, why different resolution?

#### Figure 3

- good figure, clear captions, no further comments.

#### Figure 4

- for clarification in the chart description use a) to f) as in other figures, to be used in the text and in the caption.
- y-axis labels: delete "reconstructed" for the water levels and water temperature as reconstructed as well as measured values are shown.
- x-axis label: delete the first three months as there is no data displayed.
- legend: shift some descriptions to the right (tab) for better reading
- caption: introduce charts from top to bottom

#### Figure 5



- I recommend using only Fig. a) in the main article together with 6a) and 8a) in one figure and shift b) and c) to supplementary data.
- Align y-axes of charts, apply same point size for data points, use same scale for x-axes.
- Caption: Be careful with the expression “measured values”. Differ between "measured" and "measured and corrected" here, if showing measured data in the revised version, too.

#### Figure 6

- I recommend using only Fig. a) in the main article together with 5a) and 8a) in one figure and shift b) and c) to supplementary data.
- Align y-axes of charts, apply same point size for data points, use same scale for x-axes.

#### Figure 7

- Align y-axes of charts, apply same point size for data points, use same scale for x-axes.

#### Figure 8

- Combine this figure to one together with 5a) and 6a).

This discussion paper is/has been under review for the journal Biogeosciences (BG).  
Please refer to the corresponding final paper in BG if available.

# Assessing the relationship between the $\delta^{18}\text{O}$ signatures of siliceous sponge spicules and water in a tropical lacustrine environment (Minas Gerais, Brazil)

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of sponge spicules  
and tropical  
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## Abstract

Siliceous sponge spicules constitute an important siliceous component of lacustrine sediments, together with widespread diatom frustules. In contrast to diatom frustules, siliceous spicules are formed in sponges in an enzymatic way. Previous attempts to use their oxygen isotopic signature ( $\delta^{18}\text{O}_{\text{silica}}$ ) as a paleoenvironmental proxy have led to contradictory conclusions. These attempts demonstrated the need to further assess whether sponges form their silica in oxygen isotopic equilibrium with water. For this reason, we measured the  $\delta^{18}\text{O}$  signature of sponge spicules from a single freshwater species (*Metania spinata*) grown on natural and artificial supports over nine months in a small Brazilian pond (Lagoa Verde, northwestern Minas Gerais). The  $\delta^{18}\text{O}_{\text{silica}}$  values were obtained using the infrared (IR) laser-heating fluorination technique following a controlled isotopic exchange (CIE). The  $\delta^{18}\text{O}$  values ( $\delta^{18}\text{O}_{\text{water}}$ ) and temperature of the pond water were periodically measured and reconstructed over the course of the sponge growth. Assuming that silica may form continuously in the spicules, temperature and  $\delta^{18}\text{O}_{\text{water}}$  values over the months of growth were weighted using a sponge growth coefficient previously established for *Metania spinata*. The  $\delta^{18}\text{O}_{\text{silica}}$  values of sponges grown simultaneously and on similar substrates were scattered. No relationships were observed between the  $\Delta^{18}\text{O}_{\text{silica-water}}$  and water temperature when the reconstructed values were considered. Conversely, a positive correlation was obtained, with a coefficient of  $0.3\text{‰}\text{C}^{-1}$  ( $R^2 = 0.63$ ), when  $\delta^{18}\text{O}_{\text{water}}$  values and water temperature at the time of sample collection were considered. Such a positive temperature coefficient clearly indicates that the freshwater sponge *Metania spinata* does not form its siliceous spicules in oxygen isotopic equilibrium with the pond water. Instead, one or several biologically controlled kinetic fractionation mechanisms may be in play during the various steps of silica formation. Our results suggest that the latest precipitation gives its  $\delta^{18}\text{O}$  imprint to the entire spicules assemblage. The amplitude of the apparent fractionations increases with temperature, but other controlling parameters, such as dissolved Si concentration and nutrient availability, co-varying with temperature may

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~~intervene.~~ These results prevent the use of  $\delta^{18}\text{O}_{\text{silica}}$  values from the spongillites of northwestern Minas Gerais as a direct proxy for past  $\delta^{18}\text{O}_{\text{water}}$  and/or temperature changes.

## 1 Introduction

Siliceous sponges are filter-feeding animals structured on three-dimensional arrangements of siliceous spicules with lengths of hundreds of micrometres (Hexactinellida and Demospongiae classes) to several metres (Hexactinellida class). These animals have proliferated since the Neoproterozoic at various latitudes in marine and fresh waters (Volkmer-Ribeiro and De Rosa-Barbosa, 1979; Volkmer-Ribeiro and Pauls, 2000; Müller et al., 2007; Love et al., 2009). In freshwater environments, the spicule assemblages are often used as indicators of changes in water chemistry and budget (Hall and Herrmann, 1980; Turcq et al., 1998; Sifeddine et al., 2001; Volkmer-Ribeiro et al., 2004, 2010; Volkmer-Ribeiro and Machado, 2007; Parolin et al., 2008; Machado et al., 2012; Silva et al., 2012). 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 (Schroder et al., 2007; Muller et al., 2009; Wang et al., 2012a).

Numerous studies recently indicated the paleoenvironmental usefulness of the oxygen isotope composition ( $\delta^{18}\text{O}$ ) of biogenic siliceous particles, such as diatom frustules and plant phytoliths. These studies demonstrated that the isotope signature of silica ( $\delta^{18}\text{O}_{\text{silica}}$ ) was dependent on the  $\delta^{18}\text{O}$  signature of the forming water ( $\delta^{18}\text{O}_{\text{water}}$ ) and temperature (Juillet-Leclerc and Labeyrie, 1987; Shemesh et al., 1992; Shahack-Gross et al., 1996; Brandriss et al., 1998; Moschen et al., 2005; Dodd and Sharp, 2010; Crespin et al., 2010; Webb and Longstaffe, 2000; Alexandre et al., 2012). Although the obtained fractionation factors differed significantly from one study to another, the associated temperature coefficients ranged from  $-0.2$  to  $-0.5\text{‰}\text{°C}^{-1}$ , close to the quartz fractionation coefficients measured previously (Clayton et al., 1972; Matsuhisa et al., 1979; Sharp and Kirschner, 1994). Regarding sponge spicules, few investigations led

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to contradictory interpretations. Matheney and Knauth (1989) found a scatter of the fractionation between water and silica ( $\Delta^{18}\text{O}_{\text{silica-water}}$ ) as high as 5‰ for a given sea-water temperature in marine assemblages collected from Caribbean and Pacific sites. These authors concluded that the sponges precipitate their spicules in isotopic disequilibrium with seawater oxygen, implying a kinetic fractionation mechanism. However, their data trend ( $-0.2\text{‰}\text{°C}^{-1}$ ) was in the range of equilibrium fractionation coefficients measured later for various silica-water couples (synthesis in Alexandre et al., 2012). More recently, five modern  $\Delta^{18}\text{O}_{\text{silica-water}}$  values obtained from an analysis of sea-water sponge spicules and one value obtained from the analysis of freshwater sponge spicules were plotted against water temperature (Jochum et al., 2012). The values were scattered and displayed no significant correlation with temperature. However, this result was interpreted as reflecting differences in the species characteristics and/or changes in the isotopic composition of the waters where the organisms lived. The  $\delta^{18}\text{O}_{\text{silica}}$  values obtained from a unique giant deep-sea sponge specimen were finally interpreted as changes in seawater temperature during the growth of the organism. The technique used for exchangeable oxygen removal (melting under an infrared (IR) laser beam with no fluorinating agent and in a vacuum) prior to  $\delta^{18}\text{O}_{\text{silica}}$  analyses was not evaluated by the recent inter-laboratory comparison of oxygen isotope compositions from biogenic silica (Chapligin et al., 2011). This scarcity of  $\delta^{18}\text{O}_{\text{silica}}$  data indicated the need to further investigate whether siliceous sponge spicules form in oxygen isotopic equilibrium with water and can be used as a proxy of past  $\delta^{18}\text{O}_{\text{water}}$  composition.

In this study, we measured the  $\delta^{18}\text{O}$  signature of *Metania spinata* (Carter, 1881) spicules formed over two annual cycles, on natural and artificial supports, in a small pond in northwestern Minas Gerais (Brazil). The correlations obtained between  $\delta^{18}\text{O}_{\text{silica}}$ ,  $\delta^{18}\text{O}_{\text{water}}$ , and water temperature values were assessed. **To our knowledge, the  $\delta^{18}\text{O}$  signatures of freshwater sponge spicules have never been investigated except for the unique sample from Lake Baikal analysed by Jochum et al. (2012).**

## 2 Materials and methods

### 2.1 Study area

When sponge spicules dominate a sedimentary deposit with secondary amounts of clay, sand, organic matter, and diatom residues, the sediment is classified as a spongillite (Traxler, 1895; Volkmer-Ribeiro, 1992; Volkmer-Ribeiro and Motta, 1995).

Large spongillite formations of Pleistocene and Holocene age have been reported in southeastern Brazil (Volkmer-Ribeiro et al., 1998). In northwestern Minas Gerais, more than 80 lens-shaped spongillites that are hundreds of metres in diameters and several metres thick lie beneath ponds where sponges proliferate (Almeida et al., 2009, 2010).

One of those ponds, Lagoa Verde (17°42'16" S; 46°23'32" W; 572 m.a.s.l.), was investigated for the present calibration.

The pond is located on an 85 km<sup>2</sup> karstic planation surface covered by Cenozoic siliciclastic sediments, including the spongillites (Almeida et al. 2010) (Fig. 1). The climate is tropical humid with a five-month dry season during the winter (from May to September). The mean annual temperature is 23.2 °C, and the mean annual precipitation is 1562 mm (INMET, 1961–1990 climate normals, platform Goiânia). The summer rains are convective and related to the southern shift of the Intertropical Convergence Zone (ITCZ) and the influence of the maritime tropical air mass (mT) (Tubelis and Nascimento, 1992). However, in January and February, strengthening of the South Atlantic Subtropical Anticyclone (SASA) typically leads to an Indian summer on the continent (*Veranico*). This weather is characterised by a strong reduction or absence of precipitation, low atmospheric humidity, and high temperature. The regional vegetation is a wooded savanna known as *cerrado* (Veloso et al., 1991), locally subjected to human disturbances (*eucalyptus* plantation, livestock, and mining). ~~Footprints of wild animals, such as antas (*Tapirus terrestris*), porcos-do-mato (*Tayassu pecari*), onças-parda (*Puma concolor*), and tatus (*Euphractus sexcinctus*), were also recognised near the pond.~~

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Lagoa Verde has a radius of 265 m, a perimeter of 1810 m, and a surface area of  $22.06 \cdot 10^5 \text{ m}^2$ . The volume of the pond reached  $6.72 \cdot 10^5 \text{ m}^3$  in March 2011, at the end of the rainy season. In 2011, the water depth in the deepest part of the pond was approximately 3 m but was drastically reduced by at least 1.6 m by the end of the dry season (September). The local vegetation is dominated by the aquatic macrophyte *Eleocharis interstincta* and shoreline grasses, onto which specimens of the *Metania spinata* sponges can attach. Although *Metania spinata* is the unique species observed in Lagoa Verde, it belongs to a group of six sponge species that dominates spongillites and current pond waters in southeastern Brazil and are common to the South American inter-tropical area (Volkmer-Ribeiro et al., 1998; Volkmer-Ribeiro and Costa, 1992; Volkmer-Ribeiro and Motta, 1995; Almeida et al., 2009).

### 2.2 Sampling and field measurements

In September 2010, at the end of the dry season, reproductive structures (called gemmules) of *Metania spinata* sponges were placed in black tulle bags (40 cm × 40 cm) and deposited on the floor of the pond along two transects that were approximately 25 m long from the margin to the centre. The bags from each transect were collected at the end of the following wet season. These bags were given designations based on their latest month of growth (March 2011: LV 04, 05, 06; April 2011: LV 09; Table 1). An empty bag was placed on the floor of the pond in May and collected at the beginning of June 2011 (designated Control May 2011: LV13; Table 1). In addition, natural sponge samples were collected on emergent aquatic macrophyte *Eleocharis interstincta* (April and May 2011: LV 07, 10, 11 and 12; Table 1), on submerged sediment (April 2011: LV08; Table 1), and on grasses at the margin of the pond (August 2010: LV01, 02, 03; Table 1).

Five water samples were collected at 12.00 p.m. (UTC/GMT −3 h) on the days of sponge sampling. Three additional water samples were collected during the period of sponge growth, in September and November 2010 and January 2011 (Table 2). The

water level and water temperature at a depth of 20 cm were measured during water sample collection (Table 2).

Monthly and daily values of atmospheric temperature, precipitation, and evapotranspiration were obtained from the INMET Platform Data Collection #83481 (João Pinheiro), located 21 km east of the site.

### 2.3 Analytical methods

The spicules were extracted using a three-step chemical protocol commonly used for phytoliths and diatoms (Crespin et al., 2010) that was adapted for sponges as follows: (1) oxidation of organic matter using  $\text{H}_2\text{O}_2$  (30%),  $\text{HNO}_3$ , and  $\text{HNO}_3 + \text{HClO}_4$  (2 : 1); (2) clay removal by sedimentation and centrifugation; (3) densimetric separation of the spicules using a 2.3 heavy liquid ( $\text{ZnBr}_2$ ). Step 1 was carried out at  $50^\circ\text{C}$  (Crespin et al., 2008) and repeated until the organic matter was completely oxidised. The purified spicules were mounted on microscope slides using Entelan<sup>®</sup> and analysed at  $100\times$  magnification. Approximately 300 spicules from each sample were counted and classified as alpha megascleres, beta megascleres, microscleres, and gemmoscleres.

The water samples were stored in amber bottles sealed with paraffin for isotopic analyses. These samples were filtered at  $0.45\ \mu\text{m}$  and acidified for dissolved Si analyses. The dissolved Si concentration was measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) at UFOP. The pond water temperature and pH values had been measured at midday at depths of 20–30 cm during the sampling campaigns.

The  $\delta^{18}\text{O}$  analyses of the sponge spicules and water samples were processed at CEREGE. The  $\delta^{18}\text{O}$  values were expressed in the standard  $\delta$ -notation relative to V-SMOW. Because sponge spicules are made of hydrous amorphous silica, the ground samples were subject to a controlled isotopic exchange (CIE) to set the  $\delta^{18}\text{O}$  value of exchangeable oxygen (Chapligin et al., 2011). Oxygen extractions were then performed using the IR laser-heating fluorination technique. ~~No ejection occurred.~~ The oxygen gas samples were directly sent to and analysed using a dual-

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inlet mass spectrometer ThermoQuest Finnigan Delta Plus<sup>®</sup>. The measured  $\delta^{18}\text{O}$  values of each sample were corrected on a daily basis using a quartz lab standard ( $\delta^{18}\text{O}_{\text{Boulangé } 50-100\mu\text{m}} = 16.284 \pm 0.1\text{‰}$ ,  $n = 18$ ). The calculated  $\delta^{18}\text{O}_{\text{silica}}$  value was corrected for a **reproducible methodological bias**. The entire procedure commonly applied to diatoms and phytoliths has been previously described in detail (Alexandre et al., 2006; Crespin et al., 2010; Alexandre et al., 2012). During the analysis period, measurement of the international quartz standard (NBS 28) yielded an average of  $9.78 \pm 0.14\text{‰}$  ( $n = 8$ ). Replicate analyses of the sponge spicules samples yielded a reproducibility better than  $\pm 0.39\text{‰}$  ( $1\sigma$ ). The  $\delta^{18}\text{O}$  values of the water samples were measured using an automated Thermo–Finnigan equilibrating unit connected to a dual inlet Delta Plus mass spectrometer. The reproducibility of the  $\delta^{18}\text{O}$  analyses was  $\pm 0.05\text{‰}$  ( $1\sigma$ ).

### 2.4 Reconstruction of temperature and $\delta^{18}\text{O}$ water conditions over annual cycles of sponge proliferation

Sponges ~~proliferate and~~ form their spicules over annual cycles. Spicules categorised as alpha megascleres and microscleres are produced during the growing phase of a cycle (Volkmer-Ribeiro, 1981). These spicules sustain the sponge's siliceous reticulate structure and strengthen its pinacoderm. A degenerative phase follows, particularly marked in shallow water environments, when conditions of hydrous stress occur. This phase is characterised by the production of beta megascleres and gemmoscleres (Volkmer-Ribeiro, 1981).

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

$\delta^{18}\text{O}_{\text{water}}$  values were, as a first step, reconstructed from November 2009 to May 2011 (latest sponge sampling).

– The water temperatures ( $t_{\text{water}}$ ) in Lagoa Verde measured at 12.00 p.m. were strongly correlated with the atmospheric temperature ( $t_{\text{atm}}$ ) measured the same day and time at the INMET station ( $t_{\text{water}} = 1.1098 \times t_{\text{atm}} + 1.0354$ ;  $R^2 = 0.7$ ;  $p < 0.01$ ; Eq. 1). Assuming that this relationship is constant over the course of the day, it was used to reconstruct monthly mean water temperatures from the monthly mean atmospheric temperatures from the database of INMET daily values.

– The measured values of  $\delta^{18}\text{O}_{\text{water}}$  were strongly correlated with the water levels ( $\delta^{18}\text{O}_{\text{water}} = -0.0536 \times \text{water level} + 5.9056$ ;  $R^2 = 0.8$ ;  $p < 0.01$ ; Eq. 2). This correlation corresponds to the classical behaviour of lake water isotopic composition (Vallet-Coulomb et al., 2006), in which an evaporative isotopic enrichment occurs during the dry season, whereas the rainy season leads to dilution by isotopically depleted precipitation. We used this relationship to reconstruct the  $\delta^{18}\text{O}_{\text{water}}$  values over the entire period of spicule formation. The water levels in the months without water sampling were calculated based on (1) a water balance equation based on monthly data of precipitation ( $P$ ) and evaporation (ETP) (Table 2) and (2) the relationship between calculated lake volumes and measured lake levels obtained for our measurements (water level =  $0.152 \times \text{water volume} - 101\,919$ ;  $R^2 = 0.95$ ;  $p < 0.01$ ; Eq. 3).

The changes in the water volume were estimated using the equation  $V_{i+1} = V_i + (P - \text{ETP})_{i+1}$ , using the water volume measured in March 2011 as an initial  $V_i$  value (Table 2). The  $\delta^{18}\text{O}_{\text{water}}$  values in the months without water sampling were thus reconstructed using a combination of water level estimates and Eq. (2).

In a second step, the water temperature and  $\delta^{18}\text{O}_{\text{water}}$  estimates were weighted using a sponge growth coefficient. The nine-month annual cycle of *Metania spinata* was

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previously monitored in an artificial reservoir, Lagoa Dourada, located 500 km south of Lagoa Verde, in the state of São Paulo (Melão and Rocha, 1999). The annual precipitation patterns at both sites are similar. The sponge dry biomass, expressed as ash-free dry weight (AFDW), exhibited an exponential trend over time at Lagoa Dourada (AFDW =  $8.1497^{0.2748 \times \text{number of growing months}}$ ;  $R^2 = 0.85$ ; Eq. 4); a similar trend was expected at Lagoa Verde. The AFDW is equal to the dry weight (DW) minus ash, which is essentially composed of silica, and varied proportionally to the DW (Melão and Rocha, 1999). We thus inferred that the sponge growth coefficient, obtained from Eq. (4) (Table 2), could be used as a proxy for silica formation at Lagoa Verde to weight the estimates of temperature and  $\delta^{18}\text{O}_{\text{water}}$ .

### 3 Results

Microscopic observation and counting of the chemically treated spicule assemblages indicated no trace of organic remains. The morphological features and abundance of alpha megascleres, microscleres, beta megascleres, and gemmoscleres are presented in Figs. 2 and 3 and Table 3, respectively. All of the spicules are devoid of dissolution features (Fig. 2). The percentage of spicule categories per samples exhibit the expected pattern (Fig. 3): alpha megascleres were dominant during the rainy months of March and April (2011); microscleres appeared at the end of the rainy season, in April (2011); and beta megascleres and gemmoscleres were produced during the degeneration phase in the dry season.

The measured and reconstructed values of the water level, water temperature, and  $\delta^{18}\text{O}_{\text{water}}$  are presented with the meteorological data in Table 2 and Fig. 4. The water level estimates are very close to the measured values. The levels were lower in 2010 than 2011. This finding is consistent with meteorological conditions: 2010 was drier, warmer, and thus more evaporative than 2011. As they are based on water level variations, the  $\delta^{18}\text{O}_{\text{water}}$  estimates are higher in 2010 than in 2011. Although both the reconstructed and measured  $\delta^{18}\text{O}_{\text{water}}$  values display the same trends, the water sam-

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ple collected on 8 January 2011, appears particularly  $^{18}\text{O}$  depleted ( $\Delta = 2.4\text{‰}$ ). This discrepancy may be explained by the high rainfalls that occurred just before the sampling. In fact, 70% of the January precipitation occurred during the first eight days of January, thus leading to a heavy dilution of lake water by isotopically depleted precipitation, whereas the monthly water balance does not account for heterogeneity in the rainfall distribution. In addition, the evaporative isotopic enrichment that occurred during the dry period in February is underestimated by our reconstructions. However, despite smoothing the actual variations, our  $\delta^{18}\text{O}_{\text{water}}$  reconstructions reproduce the seasonal trends. There is a modest fit between the reconstructed monthly mean water temperature and water temperature measured at midday. Given the important variability in daily and intra-daily atmospheric temperature (e.g.,  $T$  varies more than  $10^\circ\text{C}$  during the day, INMET database 2010–2011, João Pinheiro), significant variations in the pond water temperature can be expected, which explains the difference between the averaged temperatures and those measured at 12.00 p.m. The dissolved Si concentration ranges from approximately  $2.8$  to  $10.6\text{ mgL}^{-1}$  and decreases as the pond level rises as a result of dilution (Table 2).

For a given month, the  $\delta^{18}\text{O}_{\text{silica}}$  values are significantly scattered (standard deviation ranged from  $0.5$  to  $1.8\text{‰}$ ) (Table 1). This scatter is not related to the type of substrate to which the sponges were attached (e.g., natural vs. artificial or submerged sediment vs. *E. interstincta* macrophyte). The average values of  $\delta^{18}\text{O}_{\text{silica}}$  range from  $29.6\text{‰}$  when the sponges were collected during the dry season (August 2010) to  $24.0\text{‰}$  when collected during the rainy season (March 2011). The  $\delta^{18}\text{O}_{\text{silica}}$  values increase with the latest  $\delta^{18}\text{O}_{\text{water}}$  values, either measured ( $R^2 = 0.80$ ; Fig. 5a), reconstructed ( $R^2 = 0.75$ ; Fig. 5b), or reconstructed and weighted ( $R^2 = 0.65$ ; Fig. 5c). The  $\delta^{18}\text{O}_{\text{silica}}$  values decrease with the latest water temperature values, either measured ( $R^2 = 0.77$ ; Fig. 6a), reconstructed ( $R^2 = 0.57$ ; Fig. 6b), or reconstructed and weighted ( $R^2 = 0.79$ ; Fig. 6c). The  $\delta^{18}\text{O}_{\text{silica}}$  values also increase with dissolved Si concentration, although the correlation is moderate ( $R^2 = 0.56$ ). When measured data are considered, the  $\Delta^{18}\text{O}_{\text{silica-water}}$  values display a positive correlation with water temperature ( $R^2 = 0.63$ ).

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The associated coefficient is  $0.3\text{‰}\cdot\text{C}^{-1}$  (Fig. 7a). No correlation is observed when reconstructed or reconstructed and weighted values are considered (Fig. 7b and c). When measured  $\delta^{18}\text{O}_{\text{water}}$  values are considered, the  $\Delta^{18}\text{O}_{\text{silica-water}}$  values display a moderate negative correlation with the dissolved Si concentration ( $R^2 = 0.48$ ; Fig. 8).  
 5 Again, no correlation is observed when reconstructed or reconstructed and weighted  $\delta^{18}\text{O}_{\text{water}}$  values are considered ( $R^2 < 0.1$ ).

At equilibrium, mass-dependent oxygen fractionation of a mineral relative to water decreases with increasing temperature (e.g., Faure, 1998). This relationship has been illustrated by negative temperature fractionation coefficients measured for quartz, phyloliths, and diatoms (Clayton et al., 1972; Matsuhisa et al., 1979; Juillet-Leclerc and Labeyrie, 1987; Shemesh et al., 1992; Sharp and Kirschner, 1994; Shahack-Gross et al., 1996; Brandriss et al., 1998; Moschen et al., 2005; Crespin et al., 2010; Dodd and Sharp, 2010; Alexandre et al., 2012).  
 10 Conversely, our results clearly indicate the absence of an oxygen isotopic equilibrium between the silica in the sponge spicules and the pond water.  
 15

## 4 Discussion

There is a single correlation between the  $\Delta^{18}\text{O}_{\text{silica-water}}$  value and water temperature when the data from the time of sample collection are considered. This result 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.  
 20 The  $\delta^{18}\text{O}_{\text{water}}$  value and temperature averaged over the latest month or the entire period of spicule formation may influence the  $\delta^{18}\text{O}_{\text{silica}}$  signature (Figs. 5b, c, and 6b, c) but in opposite ways that cancel each other out (Fig. 7b and c).

The biologically controlled mineralisation of spicules has been described in detail (Schröder et al., 2003, 2007; Muller et al., 2007; Wang et al., 2012a). Silica formation is rapid. Schroder et al. (2003) reported that spicules several hundreds of micrometres  
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long grew in several tenths of hours. Dissolved Si is actively taken up by the sponge cells via a  $\text{Na}^+/\text{HCO}_3^-$  [ $\text{Si}(\text{OH})_4$ ] co-transporter (Schröder et al., 2004; Maldonado et al., 2011; Wang et al., 2012b) and stored in specialised cells called sclerocytes. Within the sclerocytes, axial enzymatic filaments termed silicatein are formed, around which silica is deposited. After formation of a first biosilica layer driven by the silicatein enzyme, immature spicules are released into the extracellular space. There, centrifugal and axial growth (respectively “thickening” and “elongation” processes) are driven by extraspicular silicatein. During this step, nanofibrillar bundles condense. A second enzyme, called silicase, localised on similar intra- and extracellular sites as silicatein, is able to dissolve amorphous silica and interact with silicatein during spicule formation (Schroder et al., 2003). The actions of the silicatein and silicase, which respectively polymerise and depolymerise silica, and the reorganisation of the silica sheath in the forming spicule may contribute to give the spicule assemblage a late  $\delta^{18}\text{O}$  imprint.

However, the positive correlations obtained between  $\Delta^{18}\text{O}_{\text{silica-water}}$  values and temperature excludes the possibility that any oxygen isotopic equilibrium between spicules and pond water has been reached, even during this late stage of silica precipitation. Instead, these correlations suggest that one or several biologically controlled kinetic fractionation mechanisms are in play. These mechanisms may occur during the various steps of silica formation, during water and dissolved Si uptake and up to the latest phase of silica polymerisation. Removal of water from the area of silica synthesis to the surrounding extraspicular environment (Wang et al., 2012a) may also lead to kinetic fractionation. However, a simple Rayleigh distillation would have increased the  $\Delta^{18}\text{O}_{\text{silica-water}}$  between May, when the spicules were still underwater, and August, when the spicules suffered hydrous stress, which is the opposite of the observed trend.

Other parameters, such as the dissolved Si concentration and nutrient availability, co-varying with temperature may also intervene. Laboratory studies considering marine demosponges previously demonstrated that sponges react to the availability of ambient dissolved Si (Reincke and Barthel, 1997; Maldonado et al., 2011). Although significant variability occurs between individuals, the rate of Si uptake increases rapidly at low Si

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concentrations and becomes lower at higher concentrations (from 2.3 to 5.6 mgL<sup>-1</sup> Si in the study by Reincke and Barthel, 1997). This pattern is in accordance with Michaelis–Menten enzyme kinetics (Reincke and Barthel, 1997). In the present case, *Metania spinata* forms its spicules under a range of high Si concentrations (from 2.8 to 6.2 mgL<sup>-1</sup>, Table 1). The AFDM coefficient calculated by Melão and Rocha (1999) and used as a silica formation coefficient at Lagoa Verde (Table 2) increases with dissolved Si concentration from the rainy to dry season. However, the measurements of dissolved Si are too few to allow for a determination of whether the rate of Si formation decreases at high Si concentrations, as expected in Michaelis–Menten enzyme kinetics. Nevertheless, the dataset obtained in the present study suggests that regardless of the controlling parameters and biological processes leading to kinetic oxygen isotope fractionation, they are less intense during the dry season, when dissolved Si (and possibly nutrients) are more concentrated.

## 5 Conclusions

This study provides clear evidence that the freshwater sponge *Metania spinata* does not form its siliceous spicules in oxygen isotopic equilibrium with the pond water. This fact prevents the use of  $\delta^{18}\text{O}_{\text{silica}}$  values in sponges as a direct proxy for past  $\delta^{18}\text{O}_{\text{water}}$  and temperature changes. However, a clear decreasing trend in  $\Delta^{18}\text{O}_{\text{silica-water}}$  values from the rainy summer season to the dry winter season is observed. Several kinetic fractionations may occur during enzymatically controlled Si uptake, polymerisation, depolymerisation, and reorganisation 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 0.3‰°C<sup>-1</sup>. However, for a given sponge species, other parameters co-varying with temperature, such as nutrient feeding or dissolved Si concentration, must be considered as potential controlling factors before using any kinetic fractionation coefficient for paleoenvironmental reconstruction purposes.

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**Table 1.** Characterisation of the samples of pond water and sponge spicules collected at Lagoa Verde: field and geochemical measurements.  $\Delta^{18}\text{O}_{\text{Silica-reconstructed water}}$  values calculated for the latest month of sponge growth.

Sponge sampling date	Pond water			Sponge samples		Isotopic measurements													
	Measured level	Measured $f_{\text{water}}$	Measured $\delta^{18}\text{O}_{\text{water}}$	Sample	Substrate	$\delta^{18}\text{O}_{\text{measured1}}$	$\delta^{18}\text{O}_{\text{measured2}}$	X	$\delta^{18}\text{O}_{\text{Silica}}$	Corrected* $\delta^{18}\text{O}_{\text{measured2}}$	$\Delta^{18}\text{O}_{\text{Silica-measured water}}$	$\Delta^{18}\text{O}_{\text{Silica-reconstructed water}}$							
	(cm)	(°C)	(‰ vs. VSMOW)	Artificial vs. natural	Description	Average (‰ vs. VSMOW)	Average (‰ vs. VSMOW)		(‰ vs. VSMOW)	(‰ vs. VSMOW)	(‰ vs. VSMOW)	(‰ vs. VSMOW)							
						Average	SD	n	Average	SD	n	Average	SD						
Aug 2010	65	19.1	3.3	LV01	Natural	dried grasses	30.4	0.0	2	33.5	0.2	2	0.074	27.6	30.4	29.6	0.9	27.1	27.6
				LV02	Natural	dried grasses	28.9	0.1	2	31.9	0.2	2	0.071	25.8	28.6			25.3	25.8
				LV03	Natural	dried grasses	30.0	0.1	2	32.6	0.2	2	0.063	27.0	29.8			26.6	27.0
Mar 2011	205	30.5	-6.0	LV04	Artificial	bag C8	23.3	0.3	2	25.4	0.4	2	0.059	27.5	22.4	24.0	1.8	28.4	27.5
				LV05	Artificial	bag A8	25.0	0.2	2	28.6	0.2	2	0.085	28.9	23.8			29.9	28.9
				LV06	Artificial	bag C13	26.6	0.0	2	29.0	0.1	2	0.057	31.1	26.0			32.0	31.1
Apr 2011	195	26.8	-4.0	LV07	Natural	<i>E. interstincta</i>	26.0	0.1	2	28.3	0.1	2	0.053	29.9	25.4	25.1	0.5	29.4	29.9
				LV08	Natural	Submerged sediment	26.4	0.1	2	29.2	0.0	1	0.066	30.2	25.7			29.6	30.2
				LV09	Artificial	bags A7 + A13 + A16	25.3	0.1	2	27.8	0.0	1	0.06	29.0	24.5			28.4	29.0
May 2011	172	24.0	-2.0	LV10	Natural	<i>E. interstincta</i>	26.8	0.1	2	29.4	0.2	2	0.061	30.1	26.2	27.0	1.0	28.2	30.1
				LV11	Natural	<i>E. interstincta</i>	28.1	0.0	2	30.8	0.0	1	0.064	31.6	27.7			29.7	31.6
				Control May 2011	Artificial	1 month control bag	25.8	0.0	2	28.8	0.2	2	0.072	28.8	24.9			-	-

\* Corrected for methodological bias (Alexandre et al., 2012).

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**Table 2.** Regional meteorological data, pond water parameters, and sponge growth coefficient calculated after Melão and Rocha (1999) for the months of sponge growth.  $\Delta^{18}\text{O}_{\text{silica-reconstructed water}}$  averages calculated for the latest month of sponge growth. Measured values are in bold. Reconstructed values are detailed in the text. Monthly mean values of precipitation ( $P$ ), evapotranspiration (ETP), and atmospheric temperature ( $T$ ) are from INMET (Station #83481; João Pinheiro).

Sampling date	Samples	Meteorological data						Pond characterisation									
		Precipitation (mm)	ETP (mm)	$P$ -ETP (mm)	Monthly mean $t_{\text{air}}$ (°C)	$t_{\text{air}}$ at the time of collection 12h (°C)	Volume (m <sup>3</sup> )	Measured level (cm)	Reconstructed level <sup>a</sup> (cm)	Measured $t_{\text{water}}$ (°C)	Reconstructed monthly mean $t_{\text{water}}$ (°C)	Dissolved Si (mg L <sup>-1</sup> )	Measured $\delta^{18}\text{O}_{\text{water}}$ (‰ vs. VSMOW)	Reconstructed $\delta^{18}\text{O}_{\text{water}}$ (‰ vs. VSMOW)	Sponge growth coefficient <sup>d</sup> $\Delta^{18}\text{O}_{\text{silica-reconstructed water}}$ (‰ vs. VSMOW)		
	1	Nov 2009	<b>85</b>	<b>133</b>	<b>-48</b>	<b>26.2</b>		670 837	48	30.1			3.324	2			
	2	Dec 2009	<b>413</b>	<b>113</b>	<b>301</b>	<b>24.3</b>		671 137	94	28.0			0.876	3			
	3	Jan 2010	<b>125</b>	<b>116</b>	<b>9</b>	<b>26.2</b>		671 146	95	30.1			0.801	6			
	4	Feb 2010	<b>83</b>	<b>129</b>	<b>-46</b>	<b>26.8</b>		671 101	88	30.8			1.174	10			
	5	Mar 2010	<b>180</b>	<b>119</b>	<b>61</b>	<b>25.4</b>		671 162	98	29.2			0.677	18			
	6	Apr 2010	<b>77</b>	<b>99</b>	<b>-22</b>	<b>24.2</b>		671 140	94	27.9			0.855	32			
	7	May 2010	<b>61</b>	<b>90</b>	<b>-29</b>	<b>23.9</b>		671 111	90	27.6			1.092	57			
	8	Jun 2010	<b>5</b>	<b>63</b>	<b>-58</b>	<b>21.2</b>		671 053	81	24.6			1.565	101			
	9	Jul 2010	<b>0</b>	<b>73</b>	<b>-73</b>	<b>22.1</b>		670 980	70	25.6			2.157	179			
16 Aug 2010		<b>Aug 2010</b>	<b>0</b>	<b>84</b>	<b>-84</b>	<b>22.9</b>	<b>17.6</b>	670 896	<b>65</b>	<b>57</b>	<b>19.1</b>	<b>26.5</b>	<b>6.2</b>	<b>3.250</b>	2.838	179	26.8
29 Sep 2010		<b>Sep 2010</b>	<b>5</b>	<b>64</b>	<b>-60</b>	<b>25.0</b>	<b>21.8</b>	670 837	<b>45</b>	<b>48</b>	<b>23.7</b>	<b>28.8</b>	<b>5.9</b>	<b>4.380</b>	3.325		
		Oct 2010	<b>202</b>	<b>134</b>	<b>68</b>	<b>26.4</b>		670 905	59	30.3			2.768				
23 Nov 2010	1	<b>Nov 2010</b>	<b>312</b>	<b>106</b>	<b>206</b>	<b>24.3</b>	<b>22.4</b>	671 111	<b>70</b>	<b>90</b>	<b>26.5</b>	<b>28.0</b>	<b>10.6</b>	<b>0.390</b>	1.088	2	
	2	Dec 2010	<b>355</b>	<b>131</b>	<b>224</b>	<b>24.9</b>		671 335	124	28.7			-0.738	3			
8 Jan 2011	3	<b>Jan 2011</b>	<b>346</b>	<b>121</b>	<b>226</b>	<b>25.0</b>	<b>24.8</b>	671 561	<b>150</b>	<b>158</b>	<b>29.3</b>	<b>28.8</b>	<b>3.9</b>	<b>-5.060</b>	-2.575	6	
15 Feb 2011	4	<b>Feb 2011</b>	<b>107</b>	<b>126</b>	<b>-19</b>	<b>26.5</b>	<b>27.2</b>	671 541	<b>160</b>	<b>155</b>	<b>29.7</b>	<b>30.4</b>	<b>5.8</b>	<b>-0.660</b>	-2.418	10	
3 Apr 2011	5	<b>Mar 2011</b>	<b>410</b>	<b>85</b>	<b>325</b>	<b>24.4</b>	<b>22.4</b>	<b>671 866</b>	<b>205</b>	<b>205</b>	<b>30.5</b>	<b>28.1</b>	<b>2.8</b>	<b>-6.030</b>	-5.063	18	29.1
1 May 2011	6	<b>Apr 2011</b>	<b>29</b>	<b>100</b>	<b>-71</b>	<b>24.6</b>	<b>24.4</b>	671 795	<b>195</b>	<b>194</b>	<b>26.8</b>	<b>28.3</b>	<b>3.4</b>	<b>-3.980</b>	-4.484	32	29.7
5 Jun 2011	7	<b>May 2011</b>	<b>11</b>	<b>87</b>	<b>-76</b>	<b>23.2</b>	<b>20.8</b>	671 719	<b>172</b>	<b>182</b>	<b>24.0</b>	<b>26.8</b>	<b>6.1</b>	<b>-2.020</b>	-3.866	57	30.8

<sup>a</sup> According to Eq. (1).

<sup>b</sup> According to Eq. (2).

<sup>c</sup> According to Eq. (3).

<sup>d</sup> According to Eq. (4) (see text for further details).

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**Table 3.** Abundance of spicules of various categories: alpha megasclere ( $\alpha\text{M}$ ); beta megasclere ( $\beta\text{M}$ ); microsclere (Mi); gemmosclere (Gm).  $n$ : sum of counted particles.

Last month of growth	Sample	$n$	$\alpha\text{M}$ (%)	$\beta\text{M}$ (%)	Mi (%)	Gm (%)
Aug 2010	LV01	300	11	15	17	57
	LV02	300	55	22	12	11
	LV03	300	55	22	12	11
Mar 2011	LV04	300	100	0	0	0
	LV05	300	100	0	0	0
	LV06	300	100	0	0	0
Apr 2011	LV07	300	24	0	75	1
	LV08	300	62	0	38	0
	LV12	300	62	0	38	0
	LV09	300	55	0	44	1
May 2011	LV10	300	48	3	42	7
	LV11	300	17	8	61	14
Control May 2011	LV13	300	25	18	43	14



**Table 4.** Weighted averages of  $\delta^{18}\text{O}_{\text{water}}$  and water temperature since the start of sponge growth and associated  $\Delta^{18}\text{O}_{\text{silica-weighted water}}$  values.

Last month of growth	Spicule growth weighted values		
	$\delta^{18}\text{O}_{\text{water}}$ (‰ vs. V-SMOW)	Monthly mean $t_{\text{water}}$ (°C)	$\Delta^{18}\text{O}_{\text{silica-weighted water}}$ (‰ vs. V-SMOW)
Aug 2010	2.012	26.2	28.388 26.588 27.788
Mar 2011	-3.368	28.9	25.768 27.168 29.368
Apr 2011	-3.873	28.6	29.273 29.573 28.373 28.973
May 2011	-3.870	27.8	30.070 31.570

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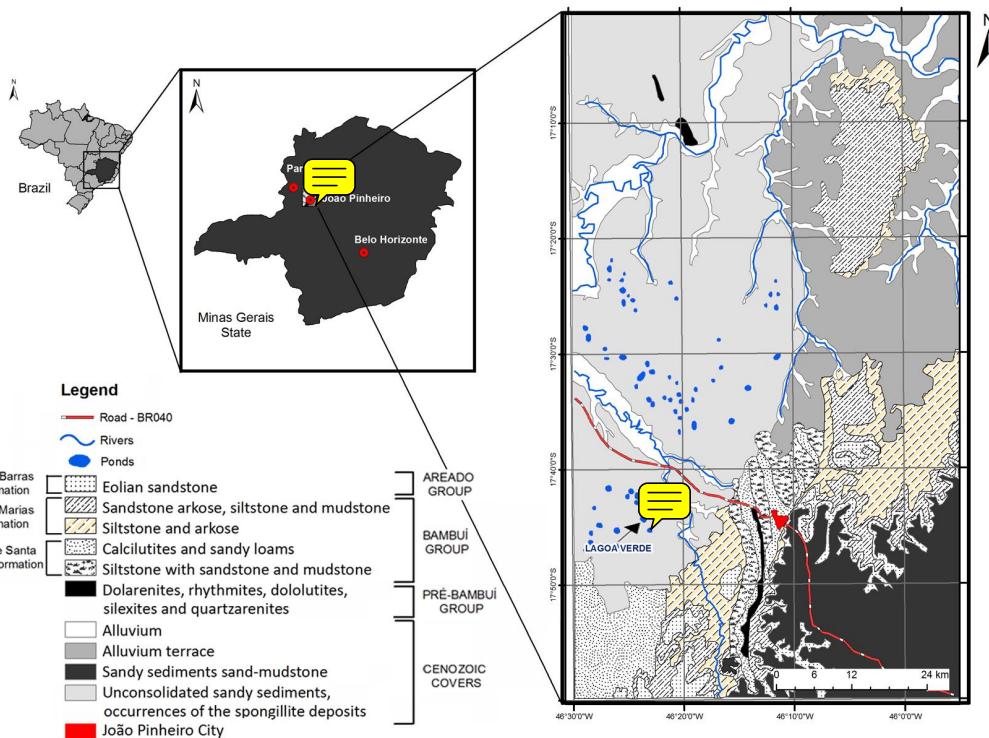
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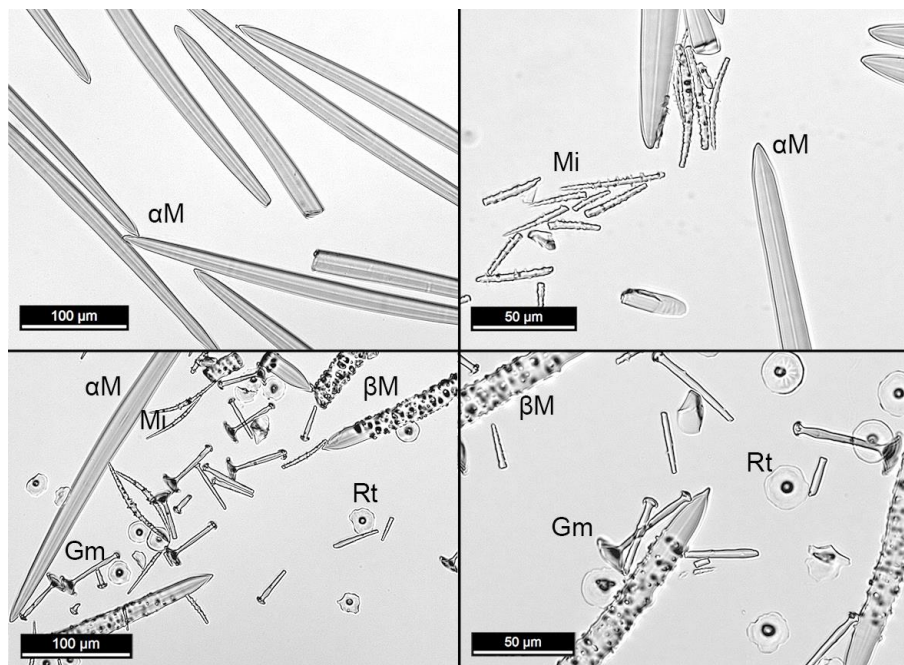
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**Fig. 1.** Geological description of the area and location of the 80 ponds and spongillite deposits reported by Oliveira et al. (2002) in northwestern Minas Gerais, Brazil. Lagoa Verde is indicated by the small arrow. Figure adapted from Oliveira et al. (2002).

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**Fig. 2.** Optical microscopy images of spicules of *Metania spinata* extracted from Lagoa Verde sponge samples.  $\alpha\text{M}$ : alpha megasclere;  $\beta\text{M}$ : beta megasclere. Mi: microsclere; Gm: gemmosclere; Rt: broken rotule of the gemmosclere.

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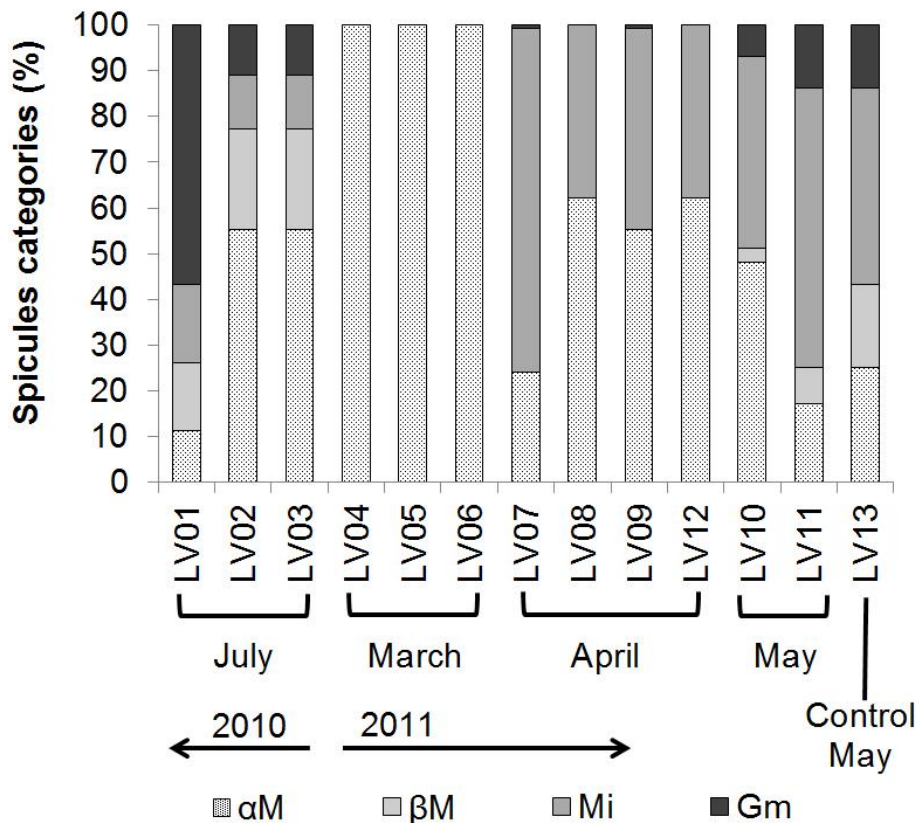
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**Fig. 3.** Percentages of spicule categories per sample.  $\alpha$ M: alpha megasclere;  $\beta$ M: beta megasclere. Mi: microsclere; Gm: gemmosclere.

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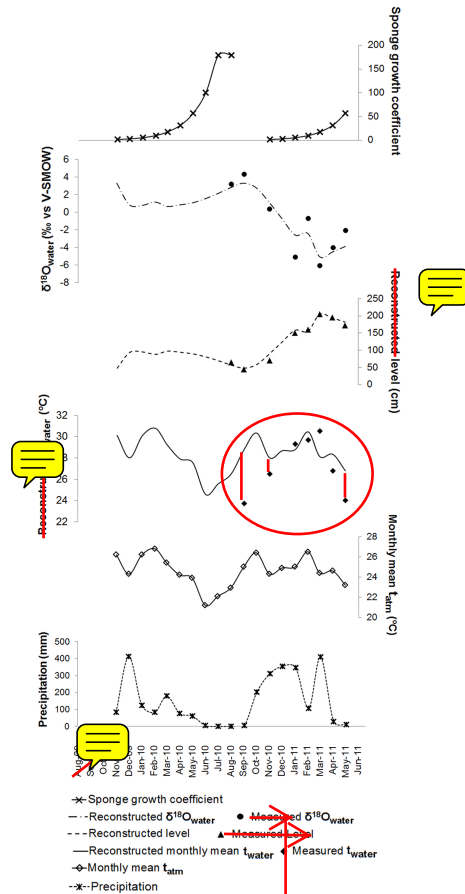
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**Fig. 4.** Reconstructed and/or measured values of monthly precipitation, monthly mean atmospheric temperature ( $t_{\text{atm}}$ ), water temperature ( $t_{\text{water}}$ ), pond level,  $\delta^{18}\text{O}_{\text{water}}$ , and sponge growth coefficient over the investigated sponge growth period.

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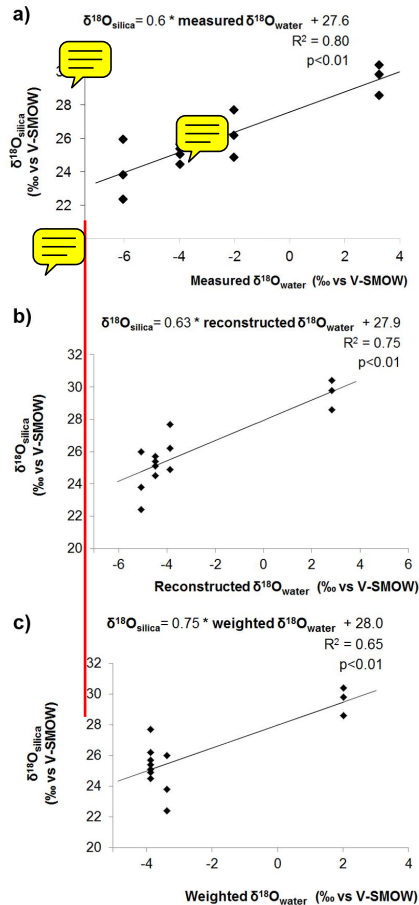
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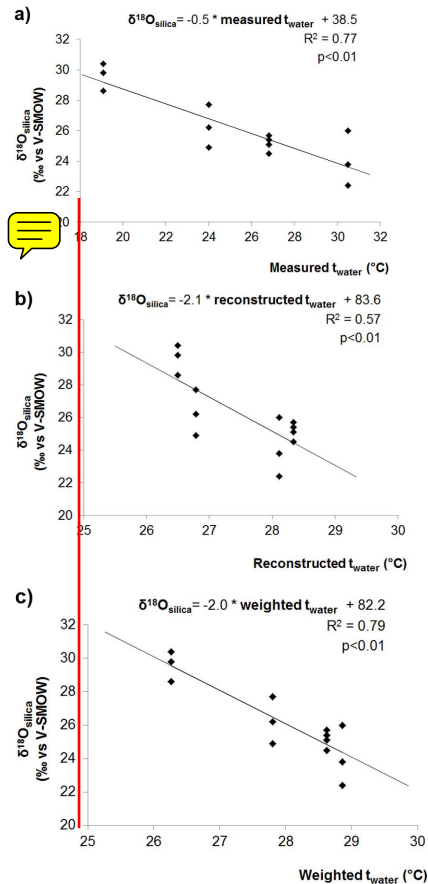


**Fig. 5.**  $\delta^{18}\text{O}_{\text{silica}}$  values plotted vs. **(a)** measured  $\delta^{18}\text{O}_{\text{water}}$  values at the time of collection, **(b)** reconstructed  $\delta^{18}\text{O}_{\text{water}}$  values, and **(c)** average of weighted  $\delta^{18}\text{O}_{\text{water}}$  estimates since the start of sponge growth.

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**Fig. 6.**  $\delta^{18}\text{O}_{\text{silica}}$  values vs. **(a)** measured temperature at the time of collection, **(b)** reconstructed monthly mean water temperature during the latest month of growth, and **(c)** average of weighted monthly mean water temperature estimates since the start of sponge growth.

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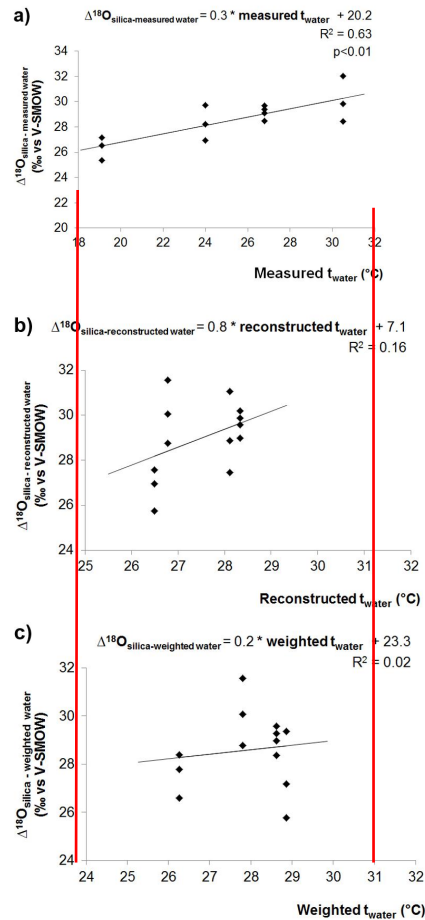
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**Fig. 7.**  $\Delta^{18}\text{O}_{\text{silica-water}}$  values vs. water temperature determined as the **(a)** measured water temperature, **(b)** reconstructed monthly mean water temperature, and **(c)** average of weighted monthly mean water temperature.

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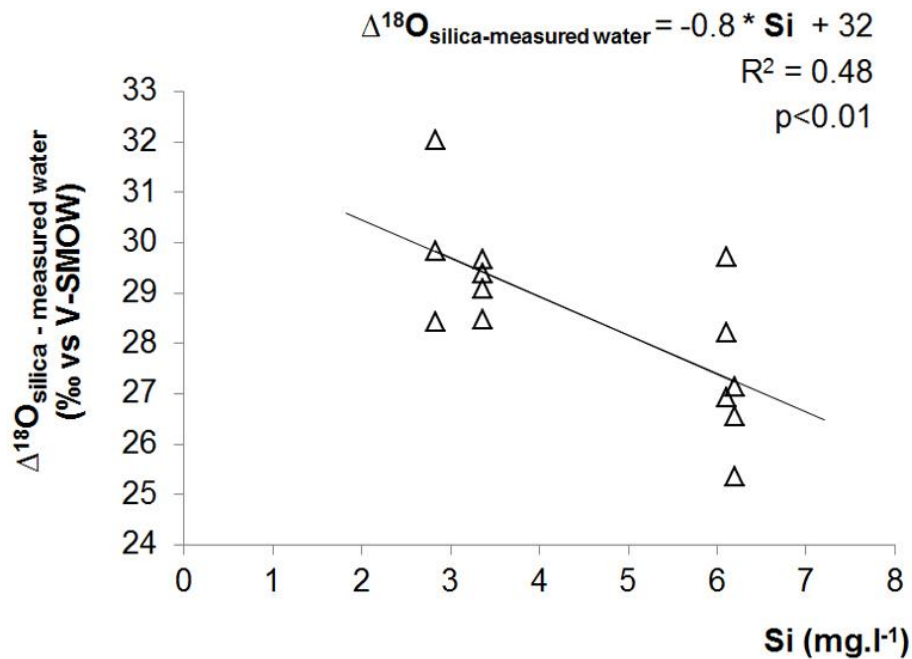


Fig. 8.  $\Delta^{18}\text{O}_{\text{silica-measured water}}$  values vs. dissolved Si concentration.

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