

# ***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.***

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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)’ Authors’ response to Anonymous Referee #1.

The authors want to thank anonymous referee #1 for his very detailed and constructive review. Comments were answered point by point in a supplementary file. The supplementary file also includes a corrected draft where most of referee #1 suggestions were

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taken into account. The main concerns raised by Referee #1 are answered below.

Methodological bias correction applied to the measured  $\delta^{18}\text{O}$ silica values. This correction was previously discussed in Chaplignin et al., 2011 and Alexandre et al., 2012. Although this methodological bias remained unexplained, it is reproducible and could thus be quantified. As pointed out by referee #1, this correction can lead to large uncertainties (Chaplignin et al., 2011), although its consistency was verified on independent datasets (Alexandre et al., 2012). In the present case, the simulated uncertainty (calculated by Monte Carlo simulation using R software) on final corrected  $\delta^{18}\text{O}$ silica values ranges from 0.5 and 0.8 ‰ (cf Table 1 of the corrected draft and L144). Corrected  $\delta^{18}\text{O}$ silica values are linearly correlated with measured  $\delta^{18}\text{O}$ silica values (corrected  $\delta^{18}\text{O}$ silica = 1.006 \* measured  $\delta^{18}\text{O}$ silica - 2.96;  $r^2=0.96$ ). Thus the methodological bias correction is not responsible for the occurrence or absence of relationship found between  $\delta^{18}\text{O}$ silica - water values and water temperature values. When using measured  $\delta^{18}\text{O}$ silica values instead of corrected  $\delta^{18}\text{O}$ silica values, as suggested by referee #1, there is no relationship between  $\delta^{18}\text{O}$ silica – weighted water and weighted temperature (  $r^2=0.03$  instead of 0.02 with the corrected  $\delta^{18}\text{O}$ silica values).

The use of an internal biogenic amorphous silica standard. We always use a phytolith lab standard (MSG40 or MSG60) to check that data obtained after the two controlled isotopic exchanges (CIE) ( $\delta^{18}\text{O}_{\text{measured 1}}$  and  $\delta^{18}\text{O}_{\text{measured 2}}$  in table 1) values are in the standard deviation of the mean value measured during a long term calibration (Crespin et al., 2008). This was not precised in the submitted draft as the entire procedure has been previously described in detail (Crespin et al., 2008; Alexandre et al., 2012). This was added in the corrected draft (L141).

The choice of a shallow pond, characterized by large daily variations of water temperature, for calibrating the relationship between  $\delta^{18}\text{O}$ silica,  $\delta^{18}\text{O}_{\text{water}}$  and temperature. Indeed large daily variations of the environmental parameters may be smoothed by reconstructed averages. This is a drawback which is underlined in the corrected draft (L242). However, as noted in the GBD paper, we checked that although modest, there

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is still a positive correlation between the reconstructed monthly mean water temperature and water temperature measured at midday ( $r^2=0.5$ ). Moreover, uncertainties on reconstructed values of water temperature and  $\delta^{18}\text{O}_{\text{water}}$  do not put into question the positive relationships obtained between  $\delta^{18}\text{O}_{\text{silica}}$  - water and water temperature when measured data are considered. This excludes that any isotopic equilibrium has been reached and prevents 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.

Referee #1 finally suggests that the positive correlation between the  $\delta^{18}\text{O}_{\text{silica}}$ -water value and water temperature, obtained when the data from the time of sample collection are considered, may be of interest for paleoenvironmental reconstructions. 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  $0.3\% \text{ } ^\circ\text{C}^{-1}$ . 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  $\delta^{18}\text{O}_{\text{water}}$ , water temperature, dissolved Si and nutrient concentration. This was added in the corrected draft (L297).

References Alexandre, A., Crespin, J., Sylvestre, F., Sonzogni, C., and Hilbert, D.W. (2012). The oxygen isotopic composition of phytolith assemblages from tropical rainforest soil tops (Queensland, Australia): validation of a new paleoenvironmental tool. *Clim.* 8, 307–324. Chaplignin, B., Leng, M.J., Webb, E., Alexandre, A., Dodd, J.P., Ijiri, A., Lucke, A., Shemesh, A., Abelmann, A., Herzs Schuh, U., et al. (2011).

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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/10/C6108/2013/bgd-10-C6108-2013-supplement.pdf>

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