

## ***Interactive comment on “The oxygen isotopic composition of phytoliths from tropical rainforest soils (Queensland, Australia): application of a new paleoenvironmental tool” by A. Alexandre et al.***

### **Anonymous Referee #2**

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The manuscript by Alexandre et al examines the  $\delta^{18}\text{O}$  composition of wood phytoliths collected from the Queensland (Australia) rainforests. Measurements are compared to estimates of mean annual temperature and precipitation as well as estimated values of precipitation  $\delta^{18}\text{O}$  to derive calibrations for wood phytolith  $\delta^{18}\text{O}$ . The paper concludes by suggesting that wood phytolith  $\delta^{18}\text{O}$  has potential for furthering scientific understanding of terrestrial climate changes.

The paper represents an important advance in this field in that it contains the first attempt to calibrate and develop wood phytolith  $\delta^{18}\text{O}$  as a paleo proxy. However, as summarised below, the findings are undermined by numerous assumptions and

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uncertainties over the accuracy of the analytical methods. Perhaps the authors are able to defend these. However, given the number and fundamental nature of these issues I would be surprised and I see no easy way in which this paper can be improved to the state where it can be published in *Climate of the Past*. A first step could be to analyse the samples at another laboratory to verify the accuracy of the raw  $\delta^{18}\text{O}$  data. However, the need to apply large corrections for sample contamination would remain and I see no way to resolve this issue.

1) “Tropical rainforests from Queensland are non-evaporative”. Justify this statement.

2) Pg 1696, line 2: “...amorphous silica that forms within a matter of hours to days...”. This raises the issue of what (temporal) signal the  $\delta^{18}\text{O}$  of wood phytoliths actual represents. What consequence does this have for this study where measurements are compared to mean annual records and what impact does this have for future paleo studies?

3) Pg. 1697, line 29: 80% of the phytoliths are “Globular granulate”, can more information be provided as to what the remaining 20% are?

4) MSG40 is used here as a phytolith standard. Crespin et al (2008) has previously provided a value of +38.4‰ for this standard, however the recent inter-lab calibration paper of Chaplignin (2011) now provides a value of +37.0‰. Please state which value has been used in this study.

5) I have significant concerns over the accuracy of the  $\delta^{18}\text{O}$  isotope data provided in this study. The recent biogenic silica inter-laboratory study of Chaplignin et al (2011) showed that values from the CEREGE lab were offset from other laboratories (this explains the discrepancy between the +38.4‰ value initially reported for MSG40 by CEREGE and the new inter-laboratory value of +37.0‰. This offset is not convincingly explained in the Chaplignin paper (or on page 1704 of this manuscript) but a linear correction is applied in an attempt to bring the CEREGE data in-line with results from other laboratories.

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When applied in the Chaplign paper this correction does bring the CEREGE data in-line with other laboratories for the MSG40 phytolith standard and the marine diatom standard PS1772-8. However, for other biogenic silica standards the “corrected” CEREGE data remains an outlier, e.g., for the BFC diatom standard and most worryingly the G95-25-CL phytolith standard which has values 2.9‰ higher than that reported by other laboratories. Since the G95-25-CL standard comprised of fresh phytoliths is likely to be the closest match to the samples analysed in this paper (MSG40 is comprised of fossil phytoliths) I fail to see how we can have any confidence in the accuracy of this data.

6) Having highlight above my concerns on the accuracy of the raw  $\delta^{18}\text{O}$  data, pg. 1705-1706 further modify the data to correct for oxygen extracted from non-wood phytoliths including quartz, grasses and palm phytoliths. These corrections end up altering the  $\delta^{18}\text{O}$  dataset from anywhere between 2‰ and 10‰ (Table 3). The propagation of errors associated with all these correction on top of the existing methodological uncertainties highlighted above and an analytical error of 0.5‰ means that by this stage I have lost all faith in being able to accept that the final data shows anything meaningful... except that the “wood-phytolith” samples are significantly contaminated.

7) When correcting for quartz contamination why is an arbitrary quartz  $\delta^{18}\text{O}$  value of 8‰ used?

8) The correction of palm phytolith is guessed as being the same as for grass phytoliths. I appreciate that we do not know how grass phytolith may fractionate, but this just further reinforces that we can not fully trust the data in this study.

9) Why was precipitation  $\delta^{18}\text{O}$  not directly measured in the field? Similarly why was soil water  $\delta^{18}\text{O}$  not measured? Having to estimate these values introduces yet more uncertainty to the manuscript.

10) It is well known that phytoliths can be rapidly dissolved/recycled in the soils (see Struyf et al 2009, Silicon 1: 207–213 for a review on this topic). Was any attempt made

to look at dissolution in this study? Can the authors comment on this issue as any dissolution would presumably lead to a fractionation of the phytolith oxygen.

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