Interactive comment on “Revisiting Mt. Kilimanjaro: Do n-alkane biomarkers in soils reflect the δ²H isotopic composition of precipitation?” by M. Zech et al.

Anonymous Referee #1

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The manuscript “Revisiting Mt. Kilimanjaro: Do n-alkane biomarkers in soils reflect the δ²H isotopic composition of precipitation?” will be of interest to earth scientists who rely on sedimentary OM based proxies in paleoaltitude studies. The material covered here will also attract attention from organic geochemists that use organic compounds from terrestrial plants in palaeoclimatology. Because of the great current interest in the subject matter, the research questions explored here are certainly very timely. The authors of this manuscript, however, will need to address several major and a number of smaller issues before this manuscript can be accepted for publication in Biogeosciences.

MAJOR ISSUES
ISSUE 1. The authors make the following statements:

on lines 36-37 “the measured 2H leaf water enrichment as assessed by using the δ²δUprec and δ²Hn-alkane results and biosynthetic fractionation during n-alkane biosynthesis in leaves” and then

on lines 321-324 “Given that n-alkane biomarkers are synthesised in leaves, they reflect the isotopic composition of leaf water (Kahmen et al., 2013), albeit with a systematic offsets of approximately -160‰ (Sachse et al., 2006; Sessions et al., 1999) referred to as biosynthetic fractionation.”

First, the d2H values of n-alkanes do not always reflect the isotopic composition of leaf water. They are certainly dependent on leaf water, but it is hardly the only control on their values. Differences in H isotope biosynthetic fractionation during water uptake can result in vastly different n-alkane d2H values among the plants that are very similar in their leaf water d2H values (see Eley et al., 2014, GCA v. 128, 13-28, but also the review by Sachse et al., 2012, Annu. Rev. Earth Pl. Sc., v. 40, 221-249). Second, on line 126 the authors state that “Climatic factors and topography cause a pronounced vegetational zonation” in the study area.

In order for the assumptions used by the authors to assess 2H-enrichment along the altitude gradient to be valid the authors need explain why they think that the changes in plant communities along the altitudinal gradient had no effect on the extent of biosynthetic fractionation between leaf water and n-alkanes among different plants species?

Can the authors exclude a possibility that the trend (labeled as “measured”) they show in Figure 6 is caused by changes in plant communities (i.e. changes in the apparent fractionation factor between leaf water and n-alkanes) rather than changes in relative humidity as they claim?

ISSUE 2. Because “a major re-interpretation of Peterse et al. (2009) data is required, taking into account previously neglected changes of climatically controlled 2H-
enrichment of leaf water in plants with altitude” (lines 103-105) is considered to be key, it would be useful to see a more detailed explanation in the introduction as to what was wrong with the previous interpretation and what the significance of the re-interpretation offered here is.

MINOR ISSUES:

Lines 20-21, “generally reflect d2H of precipitation”: This statement should be expanded to add the phrase “and/or changes in relative humidity”.

Lines 41-42, “Both in paleoaltimetry and in paleoclimate ... values can completely mask ...”: I suggest restricting this statement only to paleoaltimetry. Even though it is likely that the mechanisms investigated in this study are applicable to paleoclimate studies, the authors do not explain why it would be the case.

Line 53, “and some others”: Either say what these “others” are or eliminate this phrase altogether.

Line 91, “seasonality of d2H of leaf wax n-alkanes was detected”: The authors need to provide more detail here as to what they mean by seasonality and what aspects of it were explored in the studies they site.

Line 94, “degradation effects on d2H of leaf litter”: Using the phrase “alteration effects” instead would be preferable.

Line 185, “‘Each sample was analyzed in triplicate’: What was the uncertainties associated with these measurements? It would be useful to mention it here and to refer the reader to SI where this is given.

Line 191, “H3+ factor was determined”: Over what range (in mV) was H3+ determined? Does it cover peak intensities for nC27 and nC29 alkanes reported in SI?

Lines 241-242, “It is well-known that the isotopic composition of transpired moisture is similar to that of the source water (see Section 3.4)”: It would be useful to site here...
previous research that demonstrates that.

Lines 258-259, “Decreasing condensation temperature (if occurs) can also contribute to the observe effect”: The role of decreasing condensation temperature needs to be clarified here. Wouldn’t be the case that a decrease in condensation temperate results in more negative d2H values, i.e. something opposite to what is stated in the preceding statement on lines 256-258?

Line 302, “thus corroborating the results of Peterse et al. (2009)”: This is a bit vague. Could the authors be more specific about what Peterse et al. (2009) have to say about the trend in this interval?

Lines 364-365, “The leaf temperatures were assumed to be equal ground-level air temperatures.”: Is this a valid assumption? Aren’t leaf temperatures generally several degrees C cooler than ambient air temperatures because of transpiration? If the authors maintain that their assumption is valid, they need to provide a reference to support it.

Lines 374-375, “corrected for biosynthetic fractionation equal to -160 per mil”: Is this use of this number justified? See the discussion in MAJOR ISSUES.

FIGURE 1 Line of longitude on the image, change 37 O to 37 E. Also, in the caption to the figure, mention what the numbers next to the markers mean.

FIGURE 4 (A) It would be useful to show uncertainty associated with each data point. FIGURE 5 I suggest removing the data points that are not reliable. They do not really contribute to the discussion. Also, add uncertainty associated with each data point like it is shown in the data from Peterse et al. (2009).

FIGURE 6 The label “measured”, when taking about 2H enrichment of leaf water, is misleading. The data are estimated using an approach with several assumption that need to be clarified. Also, given the importance of comparing the “measured” data and model results it would be useful a) to show the errors associated with “measured” d2H data and b) display modelled results as “line+symbol” rather than continuous lines.
TABLE S1 The authors give numbers for peak amplitudes in mV for the samples that were run in triplicate. What do these numbers represent? Is it a mean or all of the 3 runs resulted in exactly the same mV value for each sample (Which I find high improbable.)?

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