

## Reply to Anonymous Referee#2

We thank Anonymous Reviewer#2 for his/her comments on our manuscript. It allows us to expand the discussion and to clarify our point of view in more detail.

*Zech et al. report precipitation and leaf wax n-alkane  $\delta^2H$  values along an altitudinal gradient at Mt. Kilimanjaro. They find that precipitation  $\delta^2H$  values decline with altitude while leaf wax n-alkane  $\delta^2H$  values increase with altitude. The authors assign this discrepancy to increasing evaporative leaf water  $\delta^2H$  enrichment with altitude. The data Zech et al. report here largely confirm the results of a previous study by Peterse et al. Yet, Zech et al. stress that this previous study needs “major re-interpretation”. Unfortunately, they fail to tell the reader why this is the case : : : .*

→ This statement is surprising because already in the abstract we explain that (i)“... [it is a] widely accepted assumption that n-alkanes in soils and sediments generally reflect  $\delta^2H$  of precipitation ( $\delta^2H_{prec}$ ).”, (ii) “... a major re-interpretation is required given that the  $\delta^2H_{n-alkane}$  results do not reflect the  $\delta^2H_{prec}$  results.” and (iii) “...our results demonstrate that n-alkanes in soils do not simply reflect  $\delta^2H_{prec}$  but rather  $\delta^2H_{leaf\ water}$  ...”. In order to clarify this better, we will include in the introduction explicitly that Peterse et al. (2009) interpret their  $\delta^2H_{n-alkane}$  results as reflecting  $\delta^2H_{prec}$ .

*In general the manuscript by Zech et al. reports interesting data. The findings are, however, not very novel and report water and organic hydrogen isotope data that can be expected in such environments. In fact, there are several previous studies that have shown that hydrogen and oxygen isotopes in plant organic material becomes enriched with altitude in tropical mountain ranges, while precipitation  $\delta^2H$  and  $\delta^{18}O$  declines with altitude.*

→ While we acknowledge that e.g. Kahmen et al. (2011) report on cellulose becoming enriched with altitude, also this statement is quite surprising because the studies we are aware of mostly report on decreasing  $\delta^2H_{n-alkane}$  values with altitude (Bai et al., 2011; Jia et al., 2008; Luo et al., 2011).

*There are no major flaws in this manuscript. I have, however, several comments related to the methodology used in this work, the inappropriate referencing of previous research and the style by which the work of Peterse et al. is criticized, that I feel should be addressed before this manuscript can be published.*

*1) The leaf water model that Zech et al. use is not the standard Craig-Gordon Pecllet –modified model that is conventionally used to simulate evaporative leaf water  $\delta^2H$  enrichment. While I have no objectives against this choice, the authors need to better explain why they used this model, how it works and cite papers that have shown this model can correctly predict leaf water  $\delta^2H$  values.*

→ We chose this model because our co-author K. Rozanski is very familiar with it. In Chapter “3.4. Model-data comparison: n-alkanes in soils reflect  $\delta^2H_{leaf\ water}$ “ we explain in detail from ll. 324 to 370 how our model works, which input parameters we use and we cite the according to our knowledge relevant literature.

*2) The analytical procedure and quality control using the GC-C-IRMS is not entirely clear. The authors state that all peaks <750 mV were omitted because they do not withstand the linearity criteria. It is, however, unclear how these linearity criteria were assessed. I think that it is important to report this. Otherwise it is difficult to trust the data reported in this manuscript. How can the authors be sure that their analyses were in a linear range above 750 mV?*

→ Compound-specific  $\delta^2H_{n-alkane}$  analyses at the Max Planck Institute of Jena are routine analyses and follow a standard procedure described in detail by Sachse et al. (2006). We therefore only briefly describe the procedure from l. 179 to l. 192. Like in most laboratories carrying out compound-specific  $\delta^2H$  analyses, linearity is checked by examining the

amplitude dependence of  $\delta^2\text{H}$  measurements. Normally, linearity criteria are assumed to be fulfilled within a certain range of amplitude and no respective corrections are then carried out. Actually, this might not be correct especially at the lower and upper limit of the proposed linear range. That's why we favour to exclude peaks/data points with amplitudes lower than 750 mV and encourage for future  $\delta^2\text{H}_{n\text{-alkane}}$  analyses a sample-size correction of the type proposed by Zech and Glaser (2008) for compound-specific  $\delta^{13}\text{C}$  analyses of *n*-alkanes (ll. 291 to 298). By the way, we introduced such a sample-size correction routinely also for compound-specific  $\delta^{18}\text{O}$  analyses (Zech and Glaser, 2009; Zech et al., 2013).

3) *The authors interpret small excursions in their data in Fig. 3b (below 2000 m) as meaningful environmental signals. Without any information of the natural variability of the data, such interpretations are somewhat difficult to follow and should be omitted.*

→ Please allow us to clarify that we do not interpret the small excursions of our  $\delta^2\text{H}_{\text{prec}}$  results below 2000 m, but the obvious absence of an altitude effect below 2000 m.

4) *There is a very strong tendency in this manuscript to ignore previous original work of other groups in favor of citing the author's own research. I feel that the extent by which this is done in this manuscript is quite unusual or even blunt. For example, on page 7835 line 1 – 5 the authors state “like 18O in hemi cellulose : : : the deuterium isotopic composition of plant biomarkers can be expected to depend on three main factors : : : .”. Instead of referring to the original work that has postulated this for n-alkanes 10 years ago (Sachse et al. 2004 and Smith et al. 2006) they cite their own very recent work that in parts does not even deal with d2h values in n-alkanes. Likewise, the authors argue that leaf water evaporative 2H enrichment is a key variable that determined the leaf wax n-alkane d2H values along Mt. Kilimanjaro. Yet, the recent and original work by several groups that have shown the effect of leaf water 2H enrichment on leaf wax n-alkane d2H values is largely ignored. Instead, the authors cite again their own work on 18O in hemi cellulose. There are many more examples throughout the manuscript with similar examples. I recommend the authors very carefully reevaluate their citations, and revisit the existing literature.*

→ Please note that my co-authors and I are working for over a decade on Mt. Kilimanjaro, with *n*-alkane biomarkers and their  $\delta^2\text{H}$  values, with isotope patterns of precipitation etc... We therefore assume that most colleagues will understand that we also cite our own work. Both Sachse et al. (2004) and Smith et al. (2006) are already listed in our reference list and following the recommendation of Reviewer#2 we will readily cite them additionally in l. 316. When discussing the effect of leaf water  $^2\text{H}$  enrichment on *n*-alkanes we so far cite Kahmen et al. (2013) in l. 322. We will add here further appropriate citations during revision. Concerning  $\delta^{18}\text{O}$ , we consider the comparison with compound-specific  $\delta^{18}\text{O}$  results of hemicellulose-derived sugar biomarkers to be illuminating given that this novel method is an appropriate analogue to compound-specific  $\delta^2\text{H}_{n\text{-alkane}}$  results and the respective results nicely complement the here presented  $\delta^2\text{H}_{n\text{-alkane}}$  results. We therefore prefer not to delete the respective citations.

5) *The authors make a very strong case throughout their manuscript that the work by Peterse et al. needs “major re-interpretation”. As mentioned above, it is not explicitly explained by the authors what this “major re-interpretation” should look like. In fact, I feel that in general Peterse et al. show the same patterns as reported in the present manuscript, although Zech et al. add some additional data (e.g. precipitation d2H values). In general, the manner by which the work of Peterse et al. is criticized in the present manuscript is quite blunt and for my taste a bit too aggressive. I almost have the impression that the authors try to make a stronger case of their own work by heavily criticizing these previously published data. I am not sure that this is the way we should communicate scientific results!*

→ As clarified in our first response to Reviewer#2 (see above), Peterse et al. (2009) interpret their  $\delta^2\text{H}_{n\text{-alkane}}$  results to reflect  $\delta^2\text{H}_{\text{prec}}$ . The same holds true for Bai et al. (2011), Jia et al. (2008) and Luo et al. (2011) working on mountain transects, too, and presumably it also still holds true for many if not most geochemists using  $\delta^2\text{H}_{n\text{-alkanes}}$  in order to reconstruct

paleoclimate/-hydrology. However, our data suggest that the *n*-alkanes of soils actually reflect  $\delta^2\text{H}$  of leaf water rather than  $\delta^2\text{H}$  of precipitation. That's why in our opinion a re-interpretation of  $\delta^2\text{H}_{n\text{-alkanes}}$  results is needed.

Note that there is neither any intention from our side to be offending against our appreciated colleague F. Peterse and co-authors nor are we aware of any aggressive formulation in our MS. We are in contact with F. Peterse and will do our best to ensure that possibly offending formulations are rephrased during revision.