Review of Zhang et al.

In this paper, Zhang et al. applies a proxy- and model-based approach to reconstruct changes in the local hydrology of central California, from pre-PETM to the PETM. This work builds on data published from a previous study ($\delta^{13}C_{org}$; John et al., 2008) as well as contributing new proxy records (e.g. grain size analyses; clay assemblage analyses; $\delta^{13}C_{n\text{-alkane}}$; and $\delta^{2}H_{n\text{-alkane}}$). Climate model simulations further support the proxy-based findings and were additionally utilised to constrain the effects of seasonal precipitation on $\delta^{2}H_{n\text{-alkane}}$ values. They conclude that both the models and proxies indicate an overall drier central California, although the summer saw a slight increase in precipitation. Results from extreme events analyses suggests that intense rainfall events were more frequent during both the winter and the summer.

This paper is well written, containing very little spelling and/or grammatical mistakes. The introduction nicely outlines the significance and the key question that was being investigated. Multiple proxies are utilised in conjunction with a novel method employing models to improve proxy-based reconstructions. The findings address the relevant gaps in our knowledge regarding how the hydrological cycle in central California may respond to future warming. It is exciting to see another study that applies *n*-alkanes as a hydrology proxy, especially as there are only currently seven records for the PETM (Carmichael et al., 2017).

I believe the author can improve on the manuscript by refining the structure of the text. Specifically in regards to the discussion, in addition to creating more continuity between the main text and supplementary information (i.e., removing repetition) (See Section 3). Furthermore, there are a few major questions pertaining to how some of the $\delta^{2}H_{n\text{-alkane}}$ record has been interpreted (See Section 1).

1) Interpreting the $\delta^{2}H_{n\text{-alkane}}$ record

1.1 Orbitally driven shift in pre-PETM $\delta^{2}H_{n\text{-alkane}}$?

The author states that the 25‰ negative excursion in $\delta^{2}H_{n\text{-alkane}}$ record, just prior to the onset, is likely representative of orbitally forced variability (Line 303-304). Although this is just a brief sentence and not the focal point of the discussion, I am curious as to what the author based this on. Was there any spectral analyses done to see if the fluctuations in the $\delta^{2}H_{n\text{-alkane}}$ could correspond to any astronomical forcings? Could the author cite any papers that have looked into potential cyclicity in the hydrological cycle during the Paleogene (e.g., Campbell et al., 2023)? What does this interpretation mean for other sites? The author noted that several subtropical/mid-latitude sites have shown a similar magnitude (~20‰) negative shift at the onset of the PETM (e.g., Handley et al., 2008; Jaramillo et al., 2010). How can we go about deconvolving whether such trends are driven by the abrupt perturbations in temperature at the onset of the PETM vs. changes in orbital parameters?

1.2 Stable $\delta^{2}H_{n\text{-alkane}}$ through the PETM?

The results section states that the $\delta^{2}H_{n\text{-alkane}}$ are relatively invariable throughout the PETM (Line 178-179). Although the PETM is not defined in the figures, if assuming that the PETM includes the CIE up to 20 (unsure depth unit as not defined in figures), Figure 3 presents relative stability at the beginning of the CIE, yet the upper CIE shows larger variability. There is one very negative value at the onset, however, this is one data point and seems to be only with the C_{29} *n*-alkane. On the other hand, the variability in later in the section shows correlation between all the chain lengths and more than one data point. The discussion section largely focuses on explaining the reasons why the record is stable. I was wondering if the author could also touch on why the upper record is more variable. Several other

sites show such variability, for example, TDP Site 14 exhibits oscillations throughout the PETM although the frequency is higher and the magnitude of change lower (Handley et al., 2008).

1.3 Evidence for a stable hydrological cycle during the beginning of the PETM?

Although the author describes all the potential factors that may have muted any changes in $\delta^2H_{n\text{-alkane}}$ (i.e., changes in temperature on fractionation vs. the source of water), I was curious as to how they ruled out the simplest explanation that the hydrological cycle may have been stable during the main body of the PETM? Is it because the models and published proxy records suggest the opposite, i.e., higher frequency of extreme rainfall events (Carmichael et al., 2016, 2017). If so, could the author add a sentence to rule out that the lack of change in the $\delta^2H_{n\text{-alkane}}$ record is reflecting the climate, then go on to discuss the other potential explanations.

2) Utilising *n*-alkane distributions to help interpret the $\delta^2H_{n\text{-alkane}}$ record

The discussion section mentions that the lack of knowledge on vegetation changes through time hinders the ability to calculate the δ^2H of precipitation (Line 308-310). I think the lack of change in the average chain length (ACL) is very much worth mentioning here and fits well with the Korasidis et al. (2022) paper, which also shows little change in the Koppen-Geiger climate type within the central California region. There are limitations to using ACL as an indicator for vegetation type (Bush and McInerney, 2013), but it provides some evidence that suggests that the effects of varying fractionation (caused by changing plant types) may have been minimal. With the ACL indicating a mostly terrestrial higher-plant source for the *n*-alkanes, the comment on plant types recording hydrological conditions at a specific season (Line 324-326) can also be of a lesser concern. Even with a strong seasonal signal, if this remained constant throughout the record then the relative changes would be unaffected.

Line 310-312 highlights that the $\delta^2H_{n\text{-alkane}}$ values may be influenced by re-worked *n*-alkanes. I suggest that the author look into the carbon preference index (CPI; Bray and Evans, 1961). This would not require too much work as the author already has *n*-alkane abundance data. The CPI may help indicate any input of thermally mature older sediments/*n*-alkane. CPI values >3–30 would suggest that most of the organic matter is unaltered (Diefendorf and Freimuth, 2017). Furthermore, several studies have suggested input of thermally mature material based on an antiphase between the $\delta^{13}C$ of bulk organic vs. bulk carbonate (e.g., Lyons et al., 2019). If neither of these indicates re-worked *n*-alkanes, this may be highlighted as less of a concern.

3) Improving the structure

3.1 Structure of the methods section and supplementary information

There is repetition between the methods section in the main manuscript and supplementary information. In addition, there are information that is found in the main manuscript but not the supplementary information and vice versa. For example, it would be useful to have information on how many samples were analysed in Section 2.2.2, instead of noting the instrument used for analyses in both. Similarly, Section 2.2.4 contains a lot of detail that is in the supplementary information, but urea adduction is only in the main manuscript and the column chromatography method is only in the supplementary information. This means that unless the reader looks through both the manuscript and the supplementary information, they are not getting the full picture.

Furthermore, there are no references to the supplementary information in the methods or the results/discussion for the additional figures. This is a minor comment but if the subheadings were labelled in the supplementary information and ordered in a similar way to the main manuscript (i.e.,

leaf wax n-alkane extraction and separation – grain size analyses – extreme value analyses - leaf wax proxy model), then it may be easier to refer to for additional information.

3.2 Structure of the discussion section

The first paragraph of the discussion states how sedimentation rates may provide information on the hydrological cycle. Since this study does not present new constraints on the age model or sedimentation rates, I wonder if this could be incorporated into a couple of sentences within the 4.1 section. The crucial point is that higher sedimentation rates suggest more runoff and therefore more rainfall. It would also be interesting to compare the timing of the shift to higher sedimentation rates with the changes in the clay assemblages. The caveats surrounding the lack of tie-points can be raised, but is already discussed in John et al. (2008) and not so much linked to the main proxies within this study.

The discussion paragraphs begin with an introduction to the other studies that have used the same proxy, then highlight the caveats and main assumptions that have to be made. By starting with the issues, the subsequent discussion on the authors results is somewhat downplayed. I personally think that starting with the key findings of this study, then seeing how that compares to other published findings, and then discussing the caveats may flow better. This applies for the paragraph on sedimentation rates but also the paragraph beginning on Line 288 vs. the paragraph beginning on Line 332. Much of the suggestions for why the $\delta^2H_{n\text{-alkane}}$ values might be muted feel speculative in the first paragraph, however from Line 332 there are really nice evidential based explanations that could be discussed first then the other potential ideas after. In addition, since there is one sentence in the first paragraph (Line 231-232) pertaining to the modelling results, would it make sense to first discuss the modelling results then how the proxies compare to them? However, most of the suggestions on structural changes are based on a subjective preference, so please consider these comments as so.

Minor comments:

Line 28: the sentence beginning with “indeed” sounds like it should be related to the previous point, however I would argue that they are two separate and important points. In addition, I think there should be a “the” for “just over the last few decades”…

Line 35: this may be my misunderstanding of what defines a “drought”, but is it repetition to say “extreme droughts” and “longer precipitation deficits”?

Line 47-52: for ease of the reader finding the relevant literature, could the citations on Line 48-49 be put next to the relevant locality?

Line 55-57: Cramwinckel et al. (2023) also looks into this. Might be a citation to add here

Line 74: missing a comma after “Here”

Line 76 (plus many other locations): Most often “***n***-alkane” is found italicised

Line 99: how many samples of the originally collected were analysed?

Line 100: how many new samples were collected and also how many of these were analysed

Line 100: good place to note the acronym of bulk sediment organic carbon isotope ($\delta^{13}C_{org}$), and change “analyses” to with an “e” to make it plural

Line 103: spell out iRMS

Line 107: “analyses”

Line 108: how many samples were analysed for grain size analyses?

Line 112: “analyses”

Line 113: should “Kemp et al., 2016” be in brackets?

Line 118: what temperature were the samples dried in?

Line 120: “analyses”

Line 122: could the clay species be specified here?

Line 126: how many samples were analysed for biomarker work? And how many for the CSIA?

Line 127: *v/v* should be italicised

Line 129-130: “Normal-alkanes” can be “*n*-alkanes”

Line 136: numbers by C should be a subscript, e.g., C_{29}

Line 143: “analyses”

Line 147 and 141: missing “i" in front of iCESM 1.2?

Line 163: CIE can be abbreviated here rather than on Line 165. How big is the CIE (value ‰). Overall, the results could do with more values replacing descriptive words such as “slight” increase etc.

Line 165: The sentence beginning here and beginning on Line 166 can probably be merged into one sentence, but please cite the other records that are being referred to on Line 166

Line 169: is there a reason why the $\delta^{13}C_{org}$ was plotted in a separate figure to $\delta^{13}C_{n\text{-alkanes}}$? A figure with the bulk and biomarker based isotope records and a figure with the clay assemblage results may work better with the flow of the text

Line 188: how much does the illite/smectite (extra l in illite) and chlorite/smectite ratio increase by?

Line 198-199: how much does the monthly precipitation decrease by and how much is the increase in the summer?

Line 228: different labelling with ($^{2}H/^{1}H$ and $^{18}O/^{16}O$) may confuse some readers

Line 232-235: the two sentences here could be merged

Line 253-255: when was the increase in kaolinite/smectite (can be specified in terms of relative to PETM or depth)

Line 257-259: again when was this?

Line 265: similar to comment 1.1 (above) what is the suggestion of orbitally forced variations in the clay assemblage pre-PETM based on?

Line 272: is there a citation for this?

Line 287: $^{2}H/^{1}H$ can be used, however, it is nice to remain consistent with naming, i.e., $^{2}H/^{1}H$ or $\delta^{2}H$

Line 312-315: quite a long sentence which makes it hard to follow

Line 318-320: is there a citation for this?

Line 321: I think "affect" should be "effect"?

Line 328: Add "is" to "If most soil water is from…"

Line 333: could the word "significant" be replaced?

Line 335: This is the first time $\delta^{2}H_{precip}$ is being used. Could this be defined earlier and used throughout both the main text and supplementary information? (assuming the plant is always sourced by precipitation). Also, the "i" is missing in "precip"

Line 351-352: starting the sentence with "higher plants leaf wax" and then saying "long-chain n-alkane" is repetitive. This sentence could remove one and it would still make sense.

<u>Figures:</u>

Figure 1: Is it possible to make the site location more eye-catching by making the red spot larger?

Figure 2: Unit is missing on depth scale (meters?) and some of the clay ratios. Furthermore, could the PETM be highlighted, in addition to using a different symbol to show the already published $\delta^{13}C_{org}$ data (this should also be cited in the caption).

Figure 3: Unit is missing on depth scale. Could the PETM be highlighted? In addition, the caption says "Marine $\delta^{13}C$" (Line 182) which suggests $\delta^{13}C_{carbonate}$ but this is not plotted here. The "n-" can be removed from Line 184.

Figure 5: different labelling to figure 4 (PETM vs. 6x and LP vs. 3x). Is this because they are differently defined? If not, could the same labelling be used for continuity?

<u>Supplementary materials:</u>

Subheadings with analysis should be analyses with an "e" to make it plural.

Most often "***n***-alkane" is found italicised (3 places in supplementary materials).

Second paragraph on "Grain size analysis" section – missing a comma after "and thus hydroclimate during the PETM".

First sentence of “Leaf wax proxy model” – “affect” should be “effect”. This sentence currently reads to me like seasonal precipitation effects the fractionation process in plants. Unless this is what is intended, could the sentence be reworded to make clearer what is being discussed, e.g., “To investigate how seasonal variations in the δ^2H of precipitation effects $\delta^2H_{n\text{-alkanes}}$ values…” or something of that nature.

Fourth paragraph of “Leaf wax proxy model” – could the author cite the paper for which the average chain length equation was taken from or note the equation used in the supplementary information?

First paragraph of “Leaf wax n-alkane extraction and separation” – methanol can be shortened to MeOH as done for DCM. Further in the paragraph, when describing the amount of solvent used during column chromatography, these acronyms can be utilised again. Also “Normal-alkane” x2 can just be labelled as “*n*-alkane”

Third paragraph of “Leaf wax proxy model” – could specify that it is for compound specific analyses.

Fig. S1. Could the boxes be labelled a,b,c etc. to make the caption easier to follow? Also highlight the PETM in the lower most plot.

References

Campbell, J., Poulsen, C.J., Zhu, J., Tierney, J.E. and Keeler, J., 2023. CO 2-and orbitally-driven oxygen isotope variability in the Early Eocene. *Climate of the Past Discussions*, *2023*, pp.1-32.

Diefendorf, A.F. and Freimuth, E.J., 2017. Extracting the most from terrestrial plant-derived n-alkyl lipids and their carbon isotopes from the sedimentary record: A review. *Organic Geochemistry*, *103*, pp.1-21.

Lyons, S.L., Baczynski, A.A., Babila, T.L., Bralower, T.J., Hajek, E.A., Kump, L.R., Polites, E.G., Self-Trail, J.M., Trampush, S.M., Vornlocher, J.R. and Zachos, J.C., 2019. Palaeocene–Eocene thermal maximum prolonged by fossil carbon oxidation. *Nature Geoscience*, *12*(1), pp.54-60.

Signed Emily H Hollingsworth