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## Comment on cp-2021-122

Steve Killops

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Community comment on "Late Paleocene CO<sub>2</sub> drawdown, climatic cooling, and terrestrial denudation in the southwest Pacific" by Christopher J. Hollis et al., Clim. Past Discuss., <https://doi.org/10.5194/cp-2021-122-CC1>, 2021

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At the request of Chris, here are some thoughts I hope will be helpful

Intro – it seems difficult to tie methane hydrate formation to the interval if it's associated with a sea-level fall, given the interplay of temperature and pressure. The effects of global cooling are counteracted by eustatic sea-level fall, so estimating whether methane hydrate can account for the C isotopic changes is tricky.

Fig 3 – the positive correlation might be easier to see with a linear TOC axis. The fits aren't impressive from the R<sup>2</sup> values. I wonder if linear correlations are really important, as it's likely that CO<sub>2</sub> levels would have to fall quite low (due to significant local, if not global, draw-down) before fractionation is affected, which could mean that although TOC and d<sup>13</sup>C are correlated, the relationship might not be linear.

Lines 245+ – Could the fluorescence characteristics of the amorphous OM help distinguish algal from higher plant contributions, if available? The moderate linear regression correlations are not convincing – particularly when the Whangai and Wanstead samples are removed from Fig 5. Fig 6 is more convincing.

5.3.1 – This paragraph seems a little problematical. If phytoclasts are significantly degraded, carbohydrate residues will be almost non-existent (as noted in 5.3.2). Such a low linear regression coefficient might be considered to rule out correlation. Does d<sup>34</sup>Sorg say anything about sulphate supply and likely S incorporation?

Samples labelled TW-15 and TW-17 do not appear to correspond in Fig 7 – assuming these outliers in (b) are correctly labelled, the problem is with (a).

There's an assumption about the origin and abundance of naphthalene in interpreting Fig 7a that would be worth stating so the reader knows why the ratio works in the way proposed.

5.3.2 – Fitting a linear trend to the data in Fig.8b seems a bit optimistic. The figure legend is a bit confusing as it suggests the difference between low and high TOC samples is being emphasised, but that requires examining the TOC values by each data point. How about a different symbol shape for each TOC group to make it stand out better? The Sofer

distinction between terrestrial and marine is contentious and was based on oil data, rather than immature sediment extracts, so the CV value interpretation is a bit shaky. (a) is a more useful plot in terms of variation in  $\delta^{13}\text{C}$  with TOC, so it could be worth considering omitting (b).

Some discussion would be helpful of why  $\delta^{13}\text{C}$  sat is not affected by degradation when the dominantly lignin derived aromatic value is. Is the inference that epicuticular waxes are preferentially preserved, so the lighter  $\delta^{13}\text{C}$  of the higher plant n-alkanes of phytoplankton biomass is conserved?

line 337 – it might be better to say that one explanation for the position of TW-19 in Fig 8a is that it contains more marine OM than suggested by palynofacies results. The present wording looks a little like adjusting the results to fit the model.

line 340-1 – a ref to reducing conditions in NZ peats would be good.

Final paragraph notes the varying marine OM contribution, but is it worth discussing whether differing terrestrial contributions, reworking and transport to the depositional environment could be a major cause of the observed variation in bulk  $\delta^{13}\text{C}$  values?

5.4 lines 380-4 – As noted, the C-number range is usually a reasonable proxy for terrestrial vs aquatic primary production. However, the dominance of *Sarcinochrysidales* suggests that we may not be dealing with the usual marine primary producers. It's worth bearing in mind that algae such as *Botryococcus* produces long-chain n-alkanes (and C29 steroids).

6.2 lines 446-7 – Evidence of fungal degradation of lignin might be sought from perylene. Monitoring m/z 252 in aromatics fractions gives both perylene and benzopyrenes (pyrolytic PAHs), so you can combine looking at lignin degradation with the influence of wildfires (which might show some negative correlation with cooling).

lines 479-84. As relative abundances are being assessed, could suppression of marine primary production help overcome the problem of deepening but relatively more terrestrial contribution? The prominence of 24-n-propylcholesteroid producing alga seems unique to the Waipawa Fm and suggests there is something funny going on. If these C30s often dominate steranes in Waipawa samples, could it suggest that the large terrestrial OM input is pretty heavily reworked (with steroid removal)?

Kerogen  $\delta^{13}\text{C}$  is likely to be more useful than total organic extract or fraction  $\delta^{13}\text{C}$  when assessing sources of the bulk of OM, but the method suggests only extract measurement or CSIA was undertaken. From Fig 1 and related text it looks like kerogen  $\delta^{13}\text{C}$  was obtained, so some clarification in the methods and a comment in the text about what  $\delta^{13}\text{C}_{\text{com}}$  represents would be helpful.

The CSIA data in Fig 12 are very spikey, which often happens if isolation of n-alkanes has not worked too well. It's useful to check recovery by GC. APT has been unable to reproduce the Grice et al (2008) method, which tends to give poor recovery and very spikey data. APT has developed a reliable urea adduction method now which gives good n-alkane recovery and smooth  $\delta^{13}\text{C}$  trends. In Fig 12 the deviation between the two groups at nC27+ looks dependable, but it would be dangerous to go further than that.

As pointed out in the m/s, the big problem is what the background  $\delta^{13}\text{C}$  signatures may be during Waipawa deposition for the end-member terrestrial and aquatic OM contributions – in order then to estimate relative amounts of each contribution. One

method that might be useful to examine terrestrial vs aquatic are plots from the pyrolysis-GC data that APT produced for GNS on many of the study samples (assuming no ownership issues). There are three ternary plots in the attached pdf that may be helpful. It might be possible to look at combinations of parameters from this data along with  $\delta^{13}\text{C}_{\text{kero}}$  via multivariate stats to derive estimates of the terrestrial-aquatic balance in each sample, rather than using end-member  $\delta^{13}\text{C}$  values for the Whangai and Wanstead, which may not be representative. Possibly a long shot, but who knows? If there is a lot of inertinite in the mix, that could really drag the  $\delta^{13}\text{C}$  down but not affect TOC so much – the final ternary might help assess that.

Please also note the supplement to this comment:

<https://cp.copernicus.org/preprints/cp-2021-122/cp-2021-122-CC1-supplement.pdf>