

Clim. Past Discuss., author comment AC3
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Reply on RC2

Christopher J. Hollis et al.

Author comment on "Late Paleocene CO₂ 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-AC3>, 2022

Review by Referee 2

Hollis et al report new stable carbon isotope measurements of organic matter from sediments deposited on the continental shelf and slope of New Zealand and eastern Australia during the late Paleocene (termed the Waipawa organofacies). The authors identify unusually high $\delta^{13}\text{C}$ values measured within the Waipawa organofacies, consistent with measurements made by others on contemporaneous sections in China and Argentina. The authors use a detailed suite of geochemical analyses (including bulk and compound specific stable isotope analysis) to claim the unusually high $\delta^{13}\text{C}$ values are caused by a combination of lignin degradation and low CO₂ levels. Associated with this event is global cooling (and growth of ice sheets and fall in sea level) that likely resulted from lower atmospheric CO₂ (evidenced by the high $\delta^{13}\text{C}$ values), which may have been caused by reduced volcanism and increased carbon burial.

The authors make the connection between the high $\delta^{13}\text{C}$ values and low CO₂, but a quantitative estimate of CO₂ is lacking. Using the terrestrial $\delta^{13}\text{C}$ data to quantify CO₂ would allow for a more useful comparison of CO₂ and temperature, and greatly improve what is presently a very qualitative comparison (high $\delta^{13}\text{C}$ = low CO₂ and cooling = low CO₂). This is particularly important given that "The relationship between temperature and atmospheric greenhouse gas levels through the Paleocene is very poorly resolved..." (40) and the authors state (75), "we explore the possibility that this ¹³C enrichment of bulk OM reflects a short-lived drawdown in atmospheric CO₂, reflecting the relationship in carbon isotope discrimination between atmospheric CO₂ and C3 plant biomass (Cui and Schubert, 2016, 2017, 2018; Schubert and Jahren, 2012, 2018)." Yet, any determination of CO₂ using this relationship is conspicuously absent.

Furthermore, the authors later state (290), "Only by accounting for potential processes of ¹³C-enrichment during OM transportation, deposition and early diagenesis it is possible to identify any residual enrichment that may be related to a drawdown in atmospheric CO₂ levels." Why do all this if CO₂ is not going to be estimated quantitatively (even if only a back of the envelope calculation to show a possible range of CO₂ drawdowns, given possible marine influences, and autogenic processes)?

Alternatively, the authors could calculate CO₂ given their interpretation that (376-377), "the pristane CIE implies that the primary terrestrial substrate is enriched in ¹³C by ~4‰." The authors could also calculate CO₂ for a range of CIE magnitudes, to show the magnitude of CO₂ change that would be required to get any size CIE. It would certainly

help to better answer the question of whether a drawdown in CO₂ is a plausible explanation for the δ¹³C trends and the observed cooling (the current assumption is there was cooling therefore CO₂ must have decreased). Is the purported 20-30% decrease in CO₂ required for a 1 °C decrease in deep sea temperature (455) consistent with CO₂ estimated assuming a +4‰ terrestrial CIE (based on the terrestrial CIE)? If so, that would greatly support the stated conclusions linking high δ¹³C to low CO₂ (and the various processes indicated within). If not, it may suggest climate sensitivity differed from the 3 °C assumed here, which would also be an interesting result. Much of the work to assess climate sensitivity in the Paleogene has focused on the warmest periods.

Besides, the aquatic sources show a similar 2-4‰ shift to the terrestrial sources (380-382). If so, why does the relative terrestrial vs aquatic influences matter? Both show similar magnitude CIE, so why would the % terrestrial affect determination of CO₂ based on the CIE?

(453-455) "We refrain from estimating a CO₂ change due to the complex mixing of OM sources. However, the deep-sea benthic δ¹⁸O record indicates that deep sea temperatures decreased by 1°C in the POIM (Barnet et al., 2019), which is consistent with a modest (20–30%) decline in CO₂, assuming a climate sensitivity of 3°C." Given all the work that was done to quantify the various OM sources and degradation, this statement is a bit disappointing (besides, the authors do assign values, e.g., 550-553, where they identify a residual excursion of ~2.5‰, exclusive of degradation processes, or the purported 4‰ CIE measured in phytane, 376). As noted above, even a back-of-the-envelope calculation given a few assumptions (or a range of CIE sizes) would be useful to see if a CO₂ decline is even a plausible interpretation from the δ¹³C data. Otherwise the entire premise of a CO₂ decline is based solely on data separate from this study (deep-sea benthic δ¹⁸O data and climate sensitivity estimates).

Thanks very much for these comments. To be honest this is an issue that was intensely debated by the co-authors. Some of us were very much in favour in making specific CO₂ determinations, whereas others argued that the uncertainties were too great to provide an estimate. As reviewer 1 notes, we were concerned that any specific estimate would likely be widely cited because data for this interval are so sparse and for this reason, we resiled from including an estimate. However, the reviewer has convinced us that this is a major shortcoming in the paper. Therefore, we have prepared a new section for the revised paper (see Calculating CO₂ in the attached file). Note that the requirement to differentiate between terrestrial and marine OM is simply because the method we employ is based on the δ¹³C of terrestrial OM.

We welcome further comments from the reviewer on this addition to the paper.

Specific Comments:

82: "From these analyses, we estimate the magnitudes of the δ¹³C excursion in both primary terrestrial and marine OM and use these values to infer broad changes in the concentration of atmospheric CO₂." Where is the calculation of CO₂ from the δ¹³C data?

This is now added as noted above.

Many of the geochemical methods are repeatedly simply cited back to Naeher et al. (2019), rather than being reported here. At least, a brief summary of the methods used here would be useful to the reader. For example, some important details on the standards used for IRMS and the analytical precision of these measurements, which may differ from the previous work? This was done for the compound specific work, but would make

reading this paper easier as a stand-alone product, without needing to read back to Naeher et al. (2019) for the methods.

Agreed. We will add summary methods to this paper.

The summary paragraph of Section 5.4 "¹³C enrichment attributable to drawdown of atmospheric CO₂" lacks any description of how ¹³C enrichment relates to drawdown of CO₂.

Yes. Text was transferred to section 6.2 but we realise that it leaves the question hanging, so will amalgamate these two sections.

Conclusions. I think a calculation of CO₂ from the δ¹³C data would go a long way towards bolstering the linkages between CO₂, cooling, C burial, volcanism, and sea level, etc proposed in the conclusions.

Yes, agreed.

Technical Corrections:

Throughout, delta values (δ¹³C, δ¹⁸O) are commonly described as heavy/enriched (or depleted), rather than as being higher/lower. It is my understanding that a sample is enriched (or depleted) in one isotope (e.g., ¹³C), but cannot be enriched/depleted in δ¹³C (or δ¹⁸O). Some examples of these various permutations are noted here:

17: enriched in δ¹³C --> enriched in ¹³C

19: heaviest δ¹³C values --> greatest δ¹³C values

70: δ¹³C_{OM} value of -20‰, which is ~7‰ heavier --> ~7‰ greater

236/249: more depleted δ¹³C_{OM} values --> lower δ¹³C values

527: depleted δ¹⁸O values --> lower δ¹⁸O values

Yes, OK, will correct these and other instances.

263-264: citation?

Sure. We will add reference to Rontani and Volkman, 2003 (Rontani, J.-F. and Volkman, J. K.: Phytol degradation products as biogeochemical tracers in aquatic environments, Organic Geochemistry, 34, 1-35, [https://doi.org/10.1016/S0146-6380\(02\)00185-7](https://doi.org/10.1016/S0146-6380(02)00185-7), 2003.)

308-310: See also Lukens et al. (2019): The effect of diagenesis on carbon isotope values of fossil wood: Geology, v. 47, p. 987-991, <https://doi.org/10.1130/G46412.1>.

Important reference but only discusses the negative shift in δ¹³C in the first phase of diagenesis.

486: It difficult --> it is difficult

Got it.

Please also note the supplement to this comment:

<https://cp.copernicus.org/preprints/cp-2021-122/cp-2021-122-AC3-supplement.pdf>