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 $\delta^{13}C$ 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 $\delta^{13}C$ values are caused by a combination of lignin degradation and low CO_2 levels. Associated with this event is global cooling (and growth of ice sheets and fall in sea level) that likely resulted from lower atmospheric CO_2 (evidenced by the high $\delta^{13}C$ values), which may have been caused by reduced volcanism and increased carbon burial.

The authors make the connection between the high $\delta^{13}C$ values and low CO_2, but a quantitative estimate of CO_2 is lacking. Using the terrestrial $\delta^{13}C$ data to quantify CO_2 would allow for a more useful comparison of CO_2 and temperature, and greatly improve what is presently a very qualitative comparison (high $\delta^{13}C$ = low CO_2 and cooling = low CO_2). 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 CO_2 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 CO_2 is not going to be estimated quantitatively (even if only a back of the envelope calculation to show a possible range of CO_2 drawdowns, given possible marine influences, and autogenic processes)?

Alternatively, the authors could calculate CO_2 given their interpretation that (376-377), "the pristane CIE implies that the primary terrestrial substrate is enriched in ^{13}C by ~4‰." The authors could also calculate CO_2 for a range of CIE magnitudes, to show the magnitude of CO_2 change that would be required to get any size CIE. It would certainly help to better answer the question of whether a drawdown in CO_2 is a plausible explanation for the $\delta^{13}C$ trends and the observed cooling (the current assumption is there was cooling therefore CO_2 must have decreased). Is the purported 20-30% decrease in CO_2 required for a 1 °C decrease in deep sea temperature (455) consistent with CO_2 estimated assuming a +4‰ terrestrial CIE (based on the terrestrial CIE)? If so, that would greatly support the stated conclusions linking high $\delta^{13}C$ to low CO_2 (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 CO_2 based on the CIE?

(453-455) "We refrain from estimating a CO_2 change due to the complex mixing of OM sources. However, the deep-sea benthic $\delta^{18}O$ 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 CO_2, 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 CO_2 decline is even a plausible interpretation from the $\delta^{13}C$ data. Otherwise the entire premise of a CO_2 decline is based solely on data separate from this study (deep-sea benthic $\delta^{18}O$ 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 CO_2 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 CO_2 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 $\delta^{13}C$ 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 $\delta^{13}C$ excursion in both primary terrestrial and marine OM and use these values to infer broad changes in the concentration of atmospheric CO_2." Where is the calculation of CO_2 from the $\delta^{13}C$ 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 "^{13}C enrichment attributable to drawdown of atmospheric CO_2" lacks any description of how ^{13}C enrichment relates to drawdown of CO_2.

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 CO_2 from the $\delta^{13}C$ data would go a long way towards bolstering the linkages between CO_2, cooling, C burial, volcanism, and sea level, etc proposed in the conclusions.

Yes, agreed.

Technical Corrections:

Throughout, delta values ($\delta^{13}C$, $\delta^{18}O$) 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., ^{13}C), but cannot be enriched/depleted in $\delta^{13}C$ (or $\delta^{18}O$). Some examples of these various permutations are noted here:

17: enriched in $\delta^{13}C$ --> enriched in ^{13}C

19: heaviest $\delta^{13}C$ values --> greatest $\delta^{13}C$ values

70: $\delta^{13}C_{OM}$ value of -20‰, which is ~7‰ heavier --> ~7‰ greater

236/249: more depleted $\delta^{13}C_{OM}$ values --> lower $\delta^{13}C$ values

527: depleted $\delta^{18}O$ values --> lower $\delta^{18}O$ 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, 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 $\delta^{13}C$ in the first phase of diagenesis.

486: It difficult --> it is difficult

Got it.

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Calculating atmospheric CO_2

We have explored the relationship between atmospheric CO_2 and C_3 plant tissue $\delta^{13}C$ values (Cui and Schubert, 2016; Cui and Schubert, 2017; Cui and Schubert, 2018; Schubert and Jahren, 2012; Schubert and Jahren, 2018) to estimate atmospheric CO_2 concentrations prior to and during Waipawa deposition. The change in $\delta^{13}C$ ($\Delta^{13}C$) per ppm of CO_2 follows a hyperbolic relationship (Schubert and Jahren, 2012) and is based on the model of carbon isotope fractionation in plants originally described by Farquhar et al. (1989). This proxy yields an estimate for CO_2 that is based on the relative change in $\Delta^{13}C$ between the time of interest ($\Delta^{13}C_{(t)}$) and the $\Delta^{13}C$ value at a chosen initial time ($\Delta^{13}C_{(t=0)}$), which is designated as $\Delta(\Delta^{13}C)$ and expressed as Equation 1:

$$\Delta\left(\Delta^{13}\mathrm{C}\right)=\frac{[(\mathrm{A})(\mathrm{B})(\mathrm{CO}_{2(t)}+\mathrm{C})]}{[\mathrm{A}+(\mathrm{B})(\mathrm{CO}_{2(t)}+C)]}-\frac{[(\mathrm{A})(\mathrm{B})(\mathrm{CO}_{2(t=0)}+\mathrm{C})]}{[\mathrm{A}+(\mathrm{B})(\mathrm{CO}_{2(t=0)}+\mathrm{C})]} \qquad (1)$$

where A, B and C are curve fitting parameters, and solved for CO_2 at any time t ($CO_{2(t)}$) as Equation 2 (Cui and Schubert, 2016):

$$CO_{2(t)}=\frac{\Delta(\Delta^{13}C)\cdot A^2+\Delta(\Delta^{13}C)\cdot A\cdot B\cdot CO_{2(t=0)}+2\cdot\Delta(\Delta^{13}C)\cdot A\cdot B\cdot C+\Delta(\Delta^{13}C)\cdot B^2\cdot C\cdot CO_{2(t=0)}+\Delta(\Delta^{13}C)\cdot B^2\cdot C^2+A^2\cdot B\cdot CO_{2(t=0)}}{A^2\cdot B-\Delta(\Delta^{13}C)\cdot A\cdot B-\Delta(\Delta^{13}C)\cdot B^2\cdot CO_{2(t=0)}-\Delta(\Delta^{13}C)\cdot B^2\cdot C}$$

(2)

The combined uncertainty of parameters used to derived the estimate for atmospheric CO_2 is relatively large and increases with increasing CO_2 (Cui and Schubert, 2016, 2018).

As in Cui and Schubert (2018), we use the latest Paleocene (56.1–56.5 Ma, t=0) as the reference time and adopt the same parameters (Table 1) with some modifications. We exclude an unusually low estimate of 100 ppm for CO_2 derived from paleosols by Sinha and Stott (1994) and we base our estimates for the $\delta^{13}C$ of atmospheric CO_2 ($\delta^{13}C_{CO2}$) on the method described by Tipple et al. (2010) but recalculated using the smoothed LOESS benthic foraminiferal $\delta^{13}C$ and $\delta^{18}O$ curves of Westerhold et al. (2020). [Add equations 3, 4, 5 and 7 of Tipple et al. (2010) here]. For this calculation, we use the temperature equation of Kim and O'Neil (1997) rather than that of Erez and Luz (1983), which is not appropriate for benthic foraminiferal calcite (Hollis et al., 2019). We assume ice-free conditions for this calculation (i.e., $\delta^{18}Ow = -1‰$), while noting that the findings of this study imply the growth of ice sheets during Paleocene episodes. The three time slices used for our $\delta^{13}C_{CO2}$ reconstructions are: latest Paleocene (pre-PETM) reference time slice, 56–56.2 Ma; Waipawa organofacies (WOF), 59–59.2 Ma; underlying organofacies (pre-WOF), 59.6–59.8 Ma (Table 1, Figure 1).

We have derived three estimates for the change in CO_2 that can be linked to Waipawa deposition. These are based on estimated bulk terrestrial $\delta^{13}C$ values as well as $\delta^{13}C$ values for the higher plant biomarkers, odd-numbered HMW *n*-alkanes (C_{27}-C_{33}) and even-numbered HMW fatty acids (C_{26}–C_{32}). For these lipid biomarkers we add 4‰ to the raw $\delta^{13}C$ values to account for isotope effects during the biosynthesis of *n*-alkyl biomolecules (Diefendorf et al., 2015). Similarly, in the absence of equivalent *n*-alkane and fatty acid data for the latest Paleocene, we subtract 4‰ from the terrestrial reference value, which is derived from a latest PETM coal deposit in northeast China (Chen et al., 2014).

For HMW fatty acids in the mid-Waipara section, the carbon isotope excursion (CIE) from the mean value for underlying facies to the mean value for the main phase of Waipawa deposition is 2.6‰ (Table S6, mean raw values of -31.6 and -29‰). For HMW *n*-alkanes in the Taylor White section, we have argued that the HMW *n*-alkanes in the Waipawa facies have been affected by mixing. If we substitute values from the nearby Angora Road site, we derive a CIE of 3.3‰ based on the average of two OM-rich Waipawa samples from Angora Road (raw value of -27.9‰) and a single sample from underlying Whangai facies in the Taylor White section (raw value of -30.7; Table S4). Because we cannot be sure of the extent to which the bulk terrestrial δ^{13}C values are affected by lignin alteration, we have adopted an intermediate value of 3‰ for the bulk organic CIE. We use the δ^{13}C values from the density fractions from the Taylor White section (Section 5.2.1) to derive a value of -21‰ for terrestrial OM in underlying Whangai facies. A CIE of 3‰ implies a value of -18‰ for Waipawa organofacies. As the maximum value for Waipawa organofacies is -16.7‰, this suggests that lignin degradation may only account for ~1‰ of the total excursion.

The three approaches result in significant differences in CO_2 estimates, both for Waipawa facies and the underlying facies (Table 1). CO_2 estimates range from 208 to 368 ppm for Waipawa organofacies and from 333 to 609 ppm for the underlying facies. This represents a 37–44% decrease in CO_2 during Waipawa deposition. This variation in values is to be expected given the many sources of uncertainty related to estimating the magnitudes of the CIEs for each parameter, variability within biomarkers and uncertainties in the calibration itself. Nevertheless, the different approaches yield consistent estimates of a ~40% decrease in CO_2 that can be linked to Waipawa deposition. Temperature estimates derived from the benthic foraminiferal compilation indicates global temperature decreased by ~1°C from the pre-WOF to WOF time slices (Figure 1). An accompanying decrease of ~40% in CO_2 implies a climate sensitivity of ~2.5 (i.e., a 1°C decrease in temperature for a 40% decrease in CO_2 equates to a decrease of 2.5°C for a halving of CO_2). However, as noted above, our temperature calculations assume ice-free conditions. If cooling was associated with ice growth, a portion of the positive shift in δ^{18}O should be attributed to this increase in ice volume, which would lead to a smaller decrease in temperature and, therefore, lower climate sensitivity.

Our estimates for CO_2 in the underlying facies are consistent with published estimates for CO_2 in the Paleocene (Figure 1; LOESS curve from Foster et al., 2017, data from sources cited in Foster et al., 2017; Hollis et al., 2019), with best fit shown by terrestrial OM and *n*-alkanes. Whilst we acknowledge our CO_2 estimates rely on several assumptions and some potentially large sources of error, the implication is that CO_2 levels during Waipawa deposition were in the range of 200–300 ppm, i.e., below modern levels and low enough for polar ice sheet growth.

References

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Table 1. Parameters used to calculate atmospheric CO_2 and resulting CO_2 estimates for Waipawa and underlying organofacies

	Age (Ma)	A [1]	B [1]	C [2]	$\delta^{13}C$ [3]	$\delta^{13}C[CO_2]$ [4]	$\Delta(\Delta^{13}C)$ [1]	CO_2 [2]	% Decrease [5]	Sensitivity [6]
Terrestrial OM										
Latest Paleocene (t = 0	56.5-56.1	28.26	0.22	23.69	-22.00	-5.80		385		
OM-rich Waipawa	59-58.5	28.26	0.22	23.69	-18.00	-5.00	-3.33	208	0.37	2.7
Underlying facies	60-59.5	28.26	0.22	23.69	-21.00	-5.50	-0.73	333		
N-alkanes										
Latest Paleocene (t = 0	56.5-56.1	28.26	0.22	23.69	-26.00	-5.80		385		
OM-rich Waipawa	59-58.5	28.26	0.22	23.69	-23.45	-5.00	-1.85	270	0.44	2.3
Underlying facies	60-59.5	28.26	0.22	23.69	-26.72	-5.50	1.06	485		
Fatty acids										
Latest Paleocene (t = 0	56.5-56.1	28.26	0.22	23.69	-26.00	-5.80		385		
OM-rich Waipawa	59-58.5	28.26	0.22	23.69	-25.00	-5.00	-0.23	368	0.40	2.5
Underlying facies	60-59.5	28.26	0.22	23.69	-27.60	-5.50	1.99	609		

Notes

1. From Cui and Schubert (2016).
2. From Cui and Schubert (2018). Latest Palecene CO2 reconstruction based on data sources listed therein, but exluding Sinha and Stott (1994).
3. From Chen et al. (2014).
4. Calculated from Westerhold et al. (2020) using method of Tipple et al. (2010).
5. Percentage decrease in CO_2 in Waipawa organofacies
6. Decrease in temperature (°C) with one halving of CO_2.

Figure 1. Compilation of early Paleogene variation in deep-sea benthic foraminiferal (a) carbon and (b) oxygen isotopes (LOESS smoothed curves from Westerhold et al. 2020), (c) oxygen isotope-based temperatures, (d) carbon isotope values for atmospheric CO_2 and (e) estimates for atmospheric CO_2 volume (after Foster et al., 2017; Hollis et al., 2019; LOESS curve from Foster et al., 2017). Horizontal pink lines – hyperthermals; horizontal yellow lines – reference time slices for CO_2 determinations.