Comments from Steve Killops

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

The authors greatly appreciate these comments from Dr Killops and respond to each point below.

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.

We made an error in referring to continental shelves, where the effects of a fall in sea level might be expected, but hydrates typically form in deeper water >1000 m, where these effects would be minimal. We will change "on continental shelves" to "at continental margins", which is in line with the model presented by Dickens (2003). No need for further changes as this a minor element in the paper.

Fig 3 – the positive correlation might be easier to see with a linear TOC axis. The fits aren't impressive from the R2 values. I wonder if linear correlations are really important, as it's likely that CO2 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 d13C are correlated, the relationship might not be linear.

The primary purpose of this figure is to emphasise a feature that is central to the definition of Waipawa organofacies: that TOC and bulk organic $\delta^{13}C$ are correlated. The various reasons for this correlation, including CO_2, are addressed subsequently. A log scale is chosen to make it easier to view trends within sections with varying ranges in TOC (e.g., Glendhu vs Black's Quarry).

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.

Fluorescence was used to differentiate algal material from phytoclasts. We agree that the correlations in Fig. 5 are not that strong, but the main point of this figure is to show how palynofacies fractions vary between organofacies. The bulk and light fractions exhibit a trend in which $\delta^{13}C$ increases as the proportion of degraded phytoclasts increases (Whangai/Wanstead to OM-poor to OM-rich Waipawa facies), whereas for the heavy fraction there is much less variation in $\delta^{13}C$, suggesting less mixing of sources and that the 5 per mil offset in $\delta^{13}C$ between the Whangai and the degraded phytoclasts-dominated Waipawa may be mainly due to the process of degradation.

We further note that, although the linear correlations in Fig. 5 are not strong, they are, nonetheless, statistically significant. Recognition of degraded phytoclasts vs other phytoclasts is to some degree subjective, based on visual identification and commonly requiring a judgement call on what may be slightly degraded versus non-degraded. The two parameters ($\delta^{13}C_{OM}$ and % degraded phytoclasts) are also based on different fractions of the entire OM assemblage. For palynofacies, material <6 micron in size is filtered out because it is generally too small for reliable visual identification of palynofacies classes. The fact that moderate correlations exist between $\delta^{13}C_{OM}$ and % degraded phytoclasts despite these limitations, gives confidence that the relationships are indeed intrinsic characteristics of the OM assemblages.

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 d34Sorg say anything about sulphate supply and likely S incorporation?

Good point. We will add an additional comment that phytoclast degradation also impacts the preservation of carbohydrates, supporting our conclusion that sulfurization cannot explain the ^{13}C enrichment. We discussed the relationship between bulk $\delta^{34}S$ and redox conditions in Naeher et al. (2019).

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).

Thanks for noting this error in labelling. We will remove all labels from this figure because, as the reviewer notes, the correlation is weak and there is no need to interrogate the data in further detail.

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.

We will add this statement to the caption of Fig. 7. "Naphthalene is used to normalise these compounds because it is a generic compound independent of source".

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 shakey. (a) is a more useful plot in terms of variation in d13C with TOC, so it could be worth considering omitting (b).

Fig. 8b was an effort to emphasise the terrestrial nature of the OM but we agree that is problematic applying a method designed for oils to sediment extracts. As the terrestrial nature of the OM has already been demonstrated, this figure is not required. As suggested, we will redraft Fig. 8a (now Fig. 8 – see below) to distinguish the organofacies (TOC groups).

Some discussion would be helpful of why d13C 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 d13C of the higher plant n-alkanes cf phytoplankton biomass is conserved?

We will clarify that there is a significant positive correlation between terrestrial OM derived from palynofacies and the abundance of aromatics relative the saturated fraction, and especially so with degraded phytoclasts ($r^2 = 0.54$, n = 20, Taylor White section). Although higher plant n-alkanes are abundant in Waipawa organofacies, the total saturated fraction represents a mixture of terrestrial and marine OM and the latter will not have been affected by transport-related degradation. Indeed, the difference between aromatic and saturated $\delta^{13}C$ may provide a further clue to the component of the $\delta^{13}C$ excursion that can be linked to degradation. Palynofacies study indicates that there is very little leaf cuticle present.

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.

We will completely revise and simplify this section so that it is restricted to considering the differences between aromatic and saturated fractions.

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

With simplification of this section, this reference is no longer needed.

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 d13C values?

We will revise concluding remarks for this section accordingly.

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).

C-number range is a reasonable proxy for terrestrial vs aquatic primary production and is used in many published studies. It appears to work OK in this study and is consistent with several other such proxies that we have used, i.e., we have not relied solely on C-number range.

We find no evidence of *Botryococcus* in Waipawa sediments. Botryococcane is common in NZ lacustrine sediments but has not been found in Waipawa samples. While it's true that the dominance of C30 steranes points to an abundance of unusual algae, there is no evidence that these algae had an unusual C-number range. Therefore, we make no change to the text.

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).

This is an interesting topic for future study. Preliminary data do, in fact, suggest that perylene is abundant in Waipawa organofacies; however, there is no correlation with $\delta^{13}C$. Therefore, the possible link between fungal degradation and ^{13}C enrichment cannot be demonstrated with this proxy. Pyrene is correlated with $\delta^{13}C$, suggesting a possible link with wildfires but further analyses would be needed to pursue this further.

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 magnitude of the increase in terrestrial OM in the Waipawa Formation indicates that it reflects a massive influx of terrestrial plant matter, not simply a relative increase due to decreased marine OM input. Many indicators suggest that marine primary production increased during Waipawa deposition (Hollis et al., 2014; Hines et al., 2019; Naeher et al., 2019).

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)?

Whilst it is true that the 24-n-propylcholestanes are of exceptionally high abundance within the Waipawa Fm, we attribute this to the particular water column chemistry conditions resulting from the massive influx of terrestrial OM, rather than to heavy reworking of the terrestrial OM

component. Our palynofacies analyses do not provide any clear evidence for such heavy reworking beyond simple transportation and deposition of the terrestrial OM. The terrestrial OM is dominated by brown phytoclasts, not opaque (black), highly oxidised OM, which would have been expected if the OM had been heavily reworked.

Kerogen d13C is likely to be more useful than total organic extract or fraction d13C 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 d13C was obtained, so some clarification in the methods and a comment in the text about what d13Com represents would be helpful.

We did not include any kerogen fraction $\delta^{13}C$ measurements within this study. Rather we used $\delta^{13}C$ analyses of decalcified bulk samples (method as described in Naeher et al. 2019) comprising both the kerogen and bitumen fractions. The use of decalcified rock samples for bulk carbon content and isotope analyses has now been made clearer in the revised text.

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 d13C trends. In Fig 12 the deviation between the two groups at nC27+ looks dependable, but it would be dangerous to go further than that.

The deviation between the two groups are all we are aiming to show for this figure.

As pointed out in the m/s, the big problem is what the background d13C 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 d13Ckero via multivariate stats to derive estimates of the terrestrial-aquatic balance in each sample, rather than using end-member d13C 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 d13C down but not affect TOC so much – the final ternary might help assess that.

As noted above, we did not analyse $\delta^{13}C$ specifically of the kerogen fraction, thus precluding comparison between $\delta^{13}C$ kero and pyrolysis-GC-derived compounds as suggested by Dr Killops. We would also note that the ternary plot templates suggested by Dr Killops to investigate the relative proportions of terrestrial and marine OM are very generic in nature and based on international data sets, whereas our study has quantified the proportions of terrestrial and marine organic matter more directly using palynofacies analyses. However, it is still not clear what analytical approach might best be used to ascertain the respective shifts in $\delta^{13}C$ of the separate terrestrial and marine organic matter assemblages from the underlying facies to the Waipawa. For now, we have estimated the $\delta^{13}C$ shift for the bulk OM assemblages by comparison between the Waipawa and underlying facies.

Dr Killops also speculates whether high inertinite contents within the Waipawa Fm might have affected the relationship between $\delta^{13}C$ and TOC. However, inertinite contents are not high within the Waipawa Formation.

Additional References

Dickens, G.R. (2003) Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor. Earth and Planetary Science Letters 213, 169-183.