Response to Report #1 from Referee #4 « Ideas and perspectives: Emerging contours of a dynamic exogenous kerogen cycle » by Thomas Blattmann

I am happy to see that, finally, this new version of the manuscript attempts to discuss the question of the carbon isotopic budget as a fundamental constraint on the origin of the deglacial atmospheric carbon increase. But still, the author seems to cherry pick only some oceanic data as a way to stick to his original hypothesis and therefore does not provide a fair account of the litterature on this topic. As a result, I feel the author tries to blur the marine isotopic evidence in order to make his point that kerogens contributed significantly to the pCO2 glacial-interglacial increase. Overall, I believe this is damaging to the paper, since it does not provide a fair account of the available litterature on this topic and a fair account of the actual numbers.

Dear Reviewer,

Thank you for your review and keeping up the pressure to motivate me for another round of improvement. As a result, I feel the contribution has reached a very high level. Now included is an example of a carbon budget that illustrates that the hypothesis of kerogen oxidation is both plausible and compatible with the carbon isotope trajectories of both the atmosphere and marine DIC.

Along with improvements to the text, I am convinced that this contribution will promote constructive discussion between interdisciplinary communities and will motivate new research surrounding glacial-interglacial cycles as well as kerogen oxidation. We have much to learn about both.

Sincerely,

Thomas Blattmann

19.10.2021 Zurich

In the response :

« generalizing the positive Last Glacial Maximum to Holocene δ13C shift to the global oceans is imprecise… »

In the revised paper :

« the global deglacial increase in carbon isotopes shows a notable exception: For much of the North Atlantic, the Holocene stable carbon isotope values of DIC are lighter than those of the Last Glacial Maximum … This is notable because the northernmost Atlantic is the locus of major downwelling driving global thermohaline circulation … »

The question is not to « generalize » the isotopic shift to the world ocean, but simply to compute the net global budget. From the above Fig. (from Peterson et al 2020) the author does « cherry-pick » the North Atlantic intermediate waters (the top part of the red curves) as an example of oceanic 13C data that heavier during the last glacial.Without doing any complex computation, my conclusion from this Figure is that most of the Ocean (and in particular the heavy players like the Pacific) are lighter during LGM. Since the DIC in the ocean accounts for about 95% of the Earth surface carbon, since most curves on this figure are negative, since doing carbon (or any) budget implies accounting first for the largest reservoirs, I conclude that the global carbon signature was negative, therefore the contribution of light carbon (living organic matter, permafrosts or kerogens) is globally to stock more carbon during the Holocene than during the LGM. Again, this is well known for many decades in the carbon community and it stands indeed as a major contraint. It therefore « does not help » to solve the pCO2 increase, but on the contrary raises the burden for the oceanic contribution. Peterson et al (2020) conclude their paper with a revised estimate of this global budget, on the Figure below (the stars with error bars).

It is interesting to note that ALL estimations since the very first one (Shackleton 1977) agree that the MEAN ocean 13C signal was lighter during the LGM, and therefore that the (terrestrial) light carbon stocks (living organic matter, permafrosts or kerogens) were therefore smaller during LGM by several hundreds of GtC. This appears to me quite a strong and robust consensus on this question, and it seems to me not fair to avoid this piece of evidence by downplaying it. Of course, if the deglacial terrestrial vegetation regrowth is very large, this may allow for a significant release of permafrosts or kerogens : the isotopic constraint applies only to the overall budget.

The revised main text now includes a carbon budget. This carbon budget is pegged to multiple parameters including the size and carbon isotope composition of atmospheric CO_2, marine DIC, marine DOC, and terrestrial biosphere carbon pools in the Holocene, transition phase, and the Last Glacial Maximum. Additional constraints are set by assuming that marine DOC remained constant in size, the ratio of C_3 to C_4 biospheric mass is estimated at 4:1 during the Holocene according to areal distribution and productivity constraints provided by Still et al. (2003). Furthermore, stable carbon isotope constraints for marine DIC and atmospheric CO_2 are pegged to paleorecord values and marine DOC, C_4, and C_3 values were fixed according to literature values. Additionally, the kerogen oxidation component was set at 600 PgC which previous studies (e.g., Zeng, 2003) proposed based on models using radiocarbon and other constraints while the carbon isotope composition of kerogen-derived CO_2 was fixed at -25‰. For this latter value, observational or experimental values for the relationship between bulk kerogen and kerogen-derived CO_2 are lacking in the literature; however, given the many uncertainties this represents a reasonable assumption that still illustrates the main point of the proof-of-concept carbon budget. The budget strictly requires 1) carbon mass balance and 2) carbon isotope mass balance. With these geochemical and mathematical constraints, an array of solutions is possible, however, the budget presents a plausible set of numbers which suggests a growth in the terrestrial biosphere on the order of 1000 PgC – coincidentally in the ballpark of Shackleton's (1977) estimate. This estimate aligns with palaeoecological studies suggesting growths of this size – larger than most geochemical estimates based solely on the $DI^{13}C$ shift. An important degree of freedom is the ratio of C_4 to C_3 vegetation, which is needed to maintain carbon isotope mass balance. C_4-C_3 shifts are expected given the change in vegetation across glacial-interglacial transitions; the scenario suggested in Table 1 shows an increasing proportion of C_3 vegetation aligning with such expectations. While each parameter contains uncertainty (e.g., +0.34±0.19‰ 2-σ increase for global marine DIC, Peterson et al., 2014), many parameters are fair game for debate, and the parameter space/sensitivity is explorable in many directions, the key point immediately relevant for this contribution is plausibly illustrated: kerogen oxidation is compatible with the global carbon isotope mass budget – both with trends in atmospheric CO_2 and marine DIC and a regrowing biosphere.

In the paper :

« In contrast to DIC of the oceans, atmospheric carbon isotope composition of CO2 directly measured from ice core recovered CO2 reflects a well-mixed, global signal. »

Indeed, but it only accounts for 1 or 2% of the Earth surface carbon (about 600 GtC compared to 40000 GtC) : the isotopic signal is interesting for the dynamics of the deglaciation, in particular the timing of the different contibutions (vegetation, permafrost, ocean, …) since it stands « at the center » of these exchanges. But it is certainly not very relevant for the overall glacial-interglacial budget.

In the paper :

« Reconstructed stable carbon isotope composition of DIC stems primarily from foraminifera which may also include bias from vital effects (e.g., Erez, 1978; Spero et al., 1997; Lea et al., 1999; see also Schmittner et al., 2017). Unlike the global, nearly unison rhythm of the glacial-interglacial marine oxygen isotope record, the global deglacial increase in carbon isotopes shows a notable exception »

There are also many notable exceptions in the oxygen isotopes… as well as many unconstrained vital effects. Still, the carbon isotopes measured in modern foraminifera follows closely the carbon isotopes measured in modern seawater, and they have been calibrated and used for almost 50 years as THE main tracer of carbon in the ocean in paleoceanography. I therefore do not agree with the author's sentence, whose purpose seems only to avoid discussing seriously the isotopic budget problem.

« in summary, the modeling work by Ciais et al. (2012) and Crichton et al. (2016) suggest that the observed δ13C patterns in atmosphere and ocean are compatible with kerogen oxidation. »

Of course they are… WHEN accounting for the problem and accepting that (basically) MORE than 100% of the glacial-interglacial carbon came from the ocean, since the NET organic matter contribution is globally negative. The figures below (from Crichton et al. 2016), also cited by the author in his response, are very explicit on this point when discussing the role of permafrost.

The red curve corresponds to the « ocean-only » (including vegetation changes) contribution, which explains (more that) entirely the pCO2 rise as well as the (South Atlantic) oceanic 13C signal, due to a net increase in terrestrial organic carbon stocks linked to vegetation regrowth. This of course may leave some room for a permafrost (or a kerogen) contribution that may help explain the atmospheric 13C signal as shown in the Crichton paper, to the extent that it is smaller that the vegetation regrowth (since the net organic carbon contribution must remain negative).

To conclude, I want to stress that I have no objection against the author's hypothesis that kerogens may have some role in the deglaciation. But his paper would be much more interesting and valuable if it would present an unbiased view of the current knowledge on the glacial-interglacial carbon problem.

With the addition of a plausible carbon budget showing the compatibility of the presented hypothesis with marine $DI^{13}C$, a key Earth system parameter, and a refocusing of the text the above concerns are addressed. However, unlike a review, this contribution is an "Ideas and perspectives" article. A perspective is always biased and was welcomed by another reviewer who got a kick out of reading the article – the first time for me to get this kind of feedback. However, I agree with your critique. As a result, I have rewritten the section "2 Carbon isotopes and contradictions?" clearly separating the literature review component from the perspective component. I think through this improvement the reader will get a fair perspective and together with the “6 Synthesis and outlook” section will have a blend of literature references for further reading on the subject while at the same time maintaining a streamlined, fast-paced reading experience presenting perspectives and ideas on kerogen oxidation and its hypothesized connection with glacial-interglacial cycles.

Thanks to your review, I am convinced that the readers will receive a balanced perspective highlighting the caveats and that this contribution will stimulate new thinking towards testing this and other hypotheses surrounding biogeosciences, atmospheric chemistry, and glacial-interglacial cycles.