

Response to Associate Editor

Associate Editor Decision: Reconsider after major revisions (18 May 2021) by Markus Kienast

Comments to the Author:

Dear Thomas,

Your idea continues to intrigue the referees. Despite favourable reviews by some colleagues, one of the main concerns/objections remain, the oceanic ^{13}C signal. Together with the critical referee, I perceive this to be a key data constraint that you need to reconcile with your hypothesis. Thus, unless you provide a thorough discussion and reconciliation of your idea with the overall ^{13}C constraints on the Earth's carbon budget, I am afraid I cannot accept your contribution for publication.

Sincerely,

Markus

Dear Markus, Editor,

Thank you very much for your review. The issue of reconciling atmospheric with marine $\delta^{13}\text{C}$ arose with the emergence of increasingly detailed atmospheric $\delta^{13}\text{C}$ records into the 2000s. These atmospheric $\delta^{13}\text{C}$ records prompted a wave of hypotheses invoking a terrestrial organic matter source of carbon to the atmosphere (e.g., Bauska et al., PNAS, 2016; Tesi et al., Nat. Commun., 2016; Crichton et al., Nat. Geosci., 2016; Martens et al., Sci. Adv., 2020; Winterfeld et al., Nat. Commun., 2018; Lindgren et al., Nature, 2018; Köhler et al., Nat. Commun., 2014; Ciais et al., Nat. Geosci., 2012) with however only few addressing the overall $\delta^{13}\text{C}$ constraints of Earth's carbon budget.

For the responses and revisions, I have assembled my thoughts on marine $\delta^{13}\text{C}$ and its compatibility with the kerogen oxidation hypothesis leading to an improved discussion in section 2 "*Carbon isotopes and contradictions?*". I rebut a few of the comments made by the reviewer which includes clarifying the findings of Ciais et al. (2012). Using $\delta^{13}\text{C}$ and additional constraints, Ciais et al. (2012) concluded that with a release of 700 PgC from an "inert" carbon terrestrial carbon pool, the growth of the terrestrial biosphere from glacial to interglacial was smaller than many studies previously surmised, i.e., only 300 PgC of increase rather than the 300-700 PgC increase reported by most other studies. As elaborated in the technical response to the reviewer, this is compatible with globally observed $\delta^{13}\text{C}$ trends for the atmosphere and oceans. In the case of the latter, generalizing the positive Last Glacial Maximum to Holocene $\delta^{13}\text{C}$ shift to the global oceans is imprecise: the North Atlantic, which is fed directly by deep water formation in the global ocean conveyor belt, exhibits a negative $\delta^{13}\text{C}$ shift from Last Glacial Maximum to Holocene (e.g., Peterson et al., 2020; Broecker and McGee, 2013). The opposing directions of $\delta^{13}\text{C}$ change in different parts of the ocean was modeled by Crichton et al. (2016) who demonstrate that these observations are compatible with the release of an isotopically light carbon source from land reflected in the $\delta^{13}\text{C}$ trajectory of the North Atlantic. In summary, the modeling work by Ciais et al. (2012) and Crichton et al. (2016) suggest that the observed $\delta^{13}\text{C}$ patterns in atmosphere and ocean are compatible with kerogen oxidation.

Glacial-interglacial cyclicity remains one of the great mysteries of our time. This *Ideas and Perspectives* article provides a concise overview of the state of knowledge on kerogen weathering that I hope will stimulate constructive discussion and research action in hitherto unexplored directions – in particular in its hypothesized connection with glacial-interglacial cyclicity. After two years of manuscript development driven by rigorous and constructive peer review as well as stimulating input by colleagues and readers online, the contribution has made another marked improvement with an outcome that I am eager to formally present to the readers of *Biogeosciences*.

Thank you very much for your editorial handling. I look forward to your response.

Sincerely,

Thomas

28.06.2021 Zurich

Response to Report #2, Referee #4

This manuscript deals with most comments from the reviewers. Still I am disappointed that it fails to address the question raised during its first submission concerning the overall ^{13}C constraints on the Earth's carbon budget (<https://bg.copernicus.org/preprints/bg-2019-273/bg-2019-273-RC2.pdf>).

Indeed, a strong point against the idea that kerogens and more generally organic matter could have a decisive contribution in the glacial-interglacial CO_2 problem is the well-established observation that the global ocean ^{13}C was about 0.3‰ lower during glacial times and increased accordingly during the deglaciation. Since the 1970s, this is taken as a proof that the total amount of organic matter (« living or dead», forests or buried) was smaller during glacial times. In contrast, releasing carbon from kerogens to Earth's atmosphere and ocean, as suggested by the author, would lower oceanic ^{13}C but not increase it. Looking at the atmospheric ^{13}C is not quite relevant since the main carbon reservoir is the ocean. Atmospheric shows very interesting ^{13}C variations (first a decrease then an increase) that are associated with the dynamics of carbon during the deglaciation, but it is certainly not constraining the overall glacial-interglacial carbon budget since it contains only about 600 GtC (the ocean about 38000 GtC): if the glacial-interglacial carbon change is due to low ^{13}C carbon released during the deglaciation, then the ocean ^{13}C should decrease. It does not.

The same is also true for carbon stored in permafrost areas, which were probably significantly larger during glacial times and thus released large amounts of carbon during deglaciation. The only way to account for such a release of « dead carbon » in the glacial-interglacial ^{13}C problem is to consider a significant reduction of the living biosphere on the continents, since forests represent the largest « living carbon » reservoir. This was discussed for instance in Ciais et al. (Nature Geosciences, 2011).

In other words, it is indeed quite possible that a significant release of kerogens and permafrost carbon occurred during the deglaciation, but this must be over-compensated in terms of forests reduction in order to have an overall negative contribution of organic matter to the carbon budget. Finding new sources of deglacial organic matter release does not help to solve the glacial-interglacial CO_2 problem since the overall effect of organic matter (forests, permafrost or kerogens) must be negative.

Ciais et al. (2011) Large inert carbon pool in the terrestrial biosphere during the Last Glacial Maximum
DOI: 10.1038/ngeo1324.

Dear Reviewer,

I agree, I inadequately addressed the ^{13}C constraints on Earth's carbon budget. The longstanding issue of the overall constraints on the Earth's carbon budget over glacial-interglacial cycles is key to understanding our Earth System. Thanks to your input, I have improved the discussion in section 2 "*Carbon isotopes and contradictions?*" to highlight the ^{13}C mystery – a mystery which, as I see it, begins with the primary datasets themselves, irrespective of the hypothesis one supports.

I begin with responding to and rebutting a few lines in the review: "*Looking at the atmospheric ^{13}C is not quite relevant since the main carbon reservoir is the ocean. Atmospheric shows very interesting ^{13}C variations (first a decrease then an increase) that are associated with the dynamics of carbon during the*

deglaciation, ..." (Referee #4). First of all, ^{13}C of the atmosphere is relevant because it is a direct marker for change in atmospheric CO_2 , which is directly relevant for global climate (unlike marine dissolved inorganic carbon, which has no immediate influence on climate in terms of a greenhouse gas effect). However, regarding your second point, I fully agree: **the atmosphere does show very interesting ^{13}C variations, which are associated with the dynamics of carbon during deglaciation** and this contribution hypothesizes kerogen oxidation to explain a part of these ^{13}C variations. Regarding a third point, in discussing the conclusions from Ciais et al. (2012): *"The only way to account for such a release of « dead carbon » in the glacial-interglacial ^{13}C problem is to consider a significantly reduction of the living biosphere on the continents"* (Referee #4). **No, what Ciais et al. (2012) concluded was different.** Ciais et al. (2012) concluded that with a release of 700 PgC from an inert carbon terrestrial carbon pool (which they ascribe to oxidation of organic carbon from permafrost), the growth of the terrestrial biosphere from glacial to interglacial was smaller than many studies previously surmised, i.e., only 300 PgC of increase rather than the 300-700 PgC increase reported by most other studies. This is possible as during the redistribution of carbon from inorganic to organic pools, isotope fractionation occurs with increased selectivity for lighter carbon at increasingly higher atmospheric CO_2 concentrations (Farquhar et al., 1989; see also Broecker and McGee, 2013). Therefore, as supported by the study of Ciais et al. (2012), the idea of oxidation of an "inert" terrestrial organic carbon pool alongside the growth of the terrestrial biosphere as highlighted in Fig. 3 of this manuscript is compatible with the atmosphere's and ocean's carbon isotope trajectory.

Starting from the primary datasets, oceanic and atmospheric $\delta^{13}\text{C}$ show different trends and signal characteristics. Atmospheric $\delta^{13}\text{C}$ of CO_2 directly measured from ice core recovered CO_2 reflects a globally well-mixed signal which varies through time in a steadier manner than marine dissolved inorganic carbon (e.g., compare Schmitt et al., 2012 and Galaasen et al., 2020). Glacial-interglacial marine $\delta^{13}\text{C}$ of dissolved inorganic carbon reconstructed from the foraminifera proxy, incorporating some bias and uncertainty (e.g., Spero et al., 1997; Lea et al., 1999; see also Fig. 7 in Schmittner et al., 2017), are spatially variable in their temporal patterns. In contrast to well-behaved global marine $\delta^{18}\text{O}$ pattern, the increase in $\delta^{13}\text{C}_{\text{DIC}}$ is not observed moving into interglacials in parts of the ocean (see Fig. 1 in this response showing global compilation). In fact, the opposite of the Shackleton generalization is observed for much of the North Atlantic, where the Holocene $\delta^{13}\text{C}$ values are lighter than those of the Last Glacial Maximum (see Fig. 2 in response; e.g., Peterson et al., 2020; Broecker and McGee, 2013). This is notable because the northernmost Atlantic is the locus of major downwelling feeding global thermohaline circulation (de Carvalho Ferreira and Kerr, 2017). This negative shift observed in the N. Atlantic was modeled by Crichton et al. (2016) (see Fig. 3 in response) who using Ocean-Land-Atmosphere models show this is explainable by the marine uptake and subduction of light carbon released to the atmosphere by terrestrial organic matter oxidation (hypothesized as permafrost in their case). Similarly, Broecker and McGee (2013) also conclude that the LGM-Holocene shift in atmospheric $\delta^{13}\text{C}$ towards heavier values is smaller than would otherwise be expected based on changes in 1) photosynthetic isotope fractionation, 2) air-sea exchange due to change in temperature, and 3) the upper ocean $\delta^{13}\text{C}$. One explanation towards closing this gap between expected and measured $\delta^{13}\text{C}$ in the atmosphere would be to include a source of light carbon as suggested in this contribution (see Fig. 2 in Broecker and McGee 2013). Going a step further, using the input of a light carbon sourced from land in their Ocean-Land-Atmosphere models, Crichton et al. (2016) model the positive $\delta^{13}\text{C}$ shift observed in the S. Atlantic demonstrating that contemporaneous positive and negative shifts, as observed in primary datasets from the southern and northern sectors of the Atlantic ocean, respectively, are compatible with the release of isotopically light carbon from land. In

summary, global atmospheric $\delta^{13}\text{C}$ records and region-specific marine $\delta^{13}\text{C}$ records are reconcilable with the release of CO_2 via kerogen oxidation operating alongside classically considered processes as suggested by the results by Ciais et al. (2012), Crichton et al. (2016), and others. However, in the author's opinion, much more needs to be done in future work to constrain the glacial-interglacial carbon budget: for example, marine dissolved organic matter (similar in carbon amount to the atmosphere) remains poorly constrained beyond the Holocene (e.g., Wagner et al., 2020) and a global, holistic carbon budget would require that all carbon pools are accounted for.

With the emergence of atmospheric $\delta^{13}\text{C}$ records into the 2000s, hypotheses invoking a terrestrial organic matter source of carbon to the atmosphere were proposed (e.g., Bauska et al., PNAS, 2016; Tesi et al., Nat. Commun., 2016; Crichton et al., Nat. Geosci., 2016; Martens et al., Sci. Adv., 2020; Winterfeld et al., Nat. Commun., 2018; Lindgren et al., Nature, 2018; Köhler et al., Nat. Commun., 2014; Ciais et al., Nat. Geosci., 2012). However, the spatiotemporal pattern of glacial retreat of the Laurentide Ice Sheet from kerogen-rich substrates and concurrent changes in atmospheric chemistry point to the intriguing possibility that kerogen oxidation played a significant role in the deglacial rise of CO_2 . The review component of this contribution lays out a roadmap for advancing our basic knowledge of kerogen cycling to work towards testing this hypothesis.

Sincerely,

Thomas Blattmann
28.06.2021 Zurich

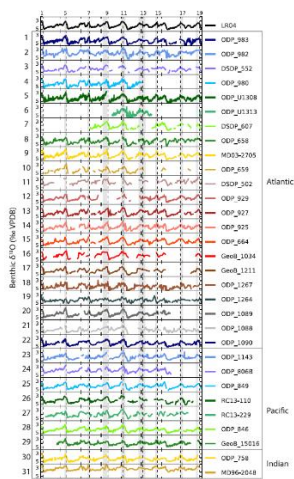


Figure 3. $\delta^{18}\text{O}$ (permil) evolution for each marine sediment core (Table 1) over the last 800,000 years. Gray shading indicate the $\delta^{18}\text{O}$ data intervals, the dotted lines indicate the dates for the orbital configurations and CO_2 used for the model simulations. The numbers to the left refer to the core numbers (Table 1, Figure 2).

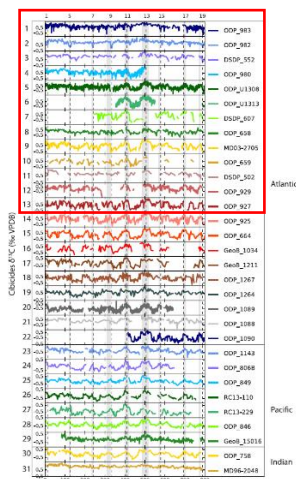


Figure 4. $\delta^{13}\text{C}$ (permil) evolution for each marine sediment core (Table 1) over the last 800,000 years. Gray shading indicate the $\delta^{13}\text{C}$ data intervals, the dotted lines indicate the dates for the orbital configurations and CO_2 used for the model simulations. The numbers to the left refer to the core numbers (Table 1, Figure 2).

Figure 1: Oxygen and carbon isotope variations over the past 800,000 years for different ocean sites globally (Bouttes et al., 2020). Oxygen isotope variations show a globally rhythmic pattern (left panel), while carbon isotope records show some arrhythmic sedimentary sequences (right panel). North Atlantic sites display regionally distinct behavior compared to other oceans (right panel).

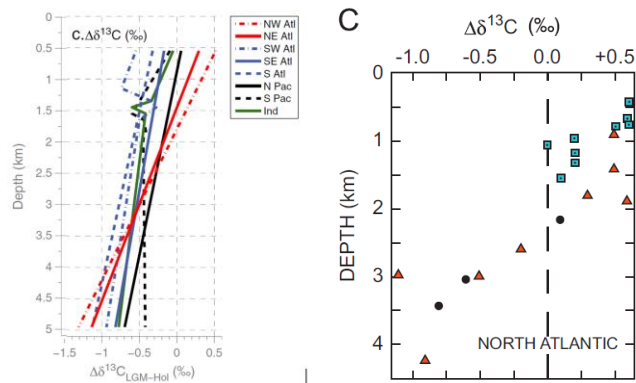


Figure 2: Left: Average Last Glacial Maximum-Holocene change in the carbon isotope composition of marine dissolved inorganic carbon averaged across different oceans and depths (Peterson et al., 2020); Right: Last Glacial Maximum-Holocene change in the carbon isotope composition of marine dissolved inorganic carbon for the North Atlantic with a negative shift observed at depths <2500 meters (Broecker and McGee 2013).

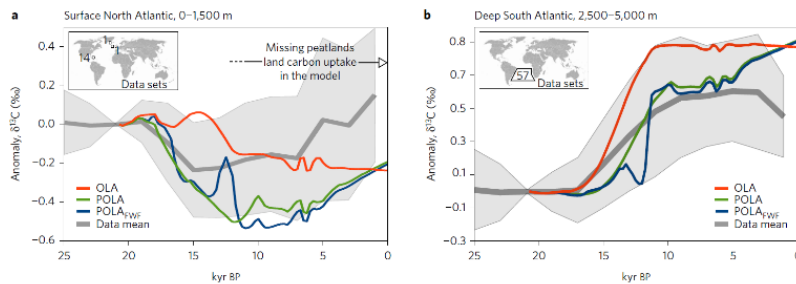


Figure 3 | Evolution of ocean $\delta^{13}C$ in model and data. **a, b.** Data¹⁹ are for benthic $\delta^{13}C$ with one standard deviation data range (grey shading). Model output is for matching depth and latitude bands as data. The number of data sets and their locations are indicated on the maps. Missing peatlands expansion period shown. **a.** Surface North Atlantic waters (data only for the western current). **b.** Deep South Atlantic waters.

Figure 3: Carbon isotope change across deglaciation modeled using Ocean-Land-Atmosphere models for North and South Atlantic which incorporates the addition of isotopically light carbon sourced from land (Crichton et al., 2016).

References not in manuscript:

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- Wagner, S., Schubotz, F., Kaiser, K., Hallmann, C., Waska, H., Rossel, P.E., Hansman, R., Elvert, M., Middelburg, J.J., Engel, A., Blattmann, T.M., Catalá, T.S., Lennartz, S.T., Gomez-Saez, G.V., Pantoja-Gutiérrez, S., Bao, R. and Galy, V. (2020) Soothsaying DOM: A Current Perspective on the Future of Oceanic Dissolved Organic Carbon. *Frontiers in Marine Science* 7.