

Queiroz Alves and colleagues present a record of organic biomarkers and carbon isotopes from a sediment core from the Bay of Biscay, which provides observational evidence of post-glacial release of terrestrial carbon. Using source-fingerprinting of different biomarker indices and a dual-carbon isotope-based carbon mixing model, the authors deduce carbon remobilization from ancient and frozen peat during deglacial climate warming. Because permafrost/peat thaw processes may have released a larger amount of organic carbon at the time, the authors suggest that in-situ remineralization of the liberated organic matter may have contributed to the onset of the rise of atmospheric CO₂ concentrations around 17.5 kyr ago as seen in Antarctic ice cores.

The paper is overall well-written and structured logically. The topic is timely and important as climate change scientists seek to better understand the functioning and potential climate impact permafrost thaw and carbon release may have. The methods used in this study are sound and I am convinced that the work was carried out in a careful and rigorous manner. However, I see some weaknesses in the writing of the paper and its data interpretation, which I believe can be addressed during major revisions.

We express our gratitude to the reviewer for their thorough review of our paper. We appreciate their valuable comments, which will certainly help to improve our study. Below, we provide answers to address the referee's comments.

Overarching comments

Methods: Some of the methods are insufficiently explained in the main manuscript, and I would like the authors to include more information about the functioning and limitations of the different proxies used in their work. For instance, a big part of their story rests on a ¹³C/¹⁴C mixing model, which involves quite large uncertainties and assumptions and thus needs to be explained in detail in the main manuscript. Also, it is not really clear from the methods which data were generated in the present work and which originate from earlier work.

We have provided more information about our methods based on the specific reviewer's requests below.

Age model: This is a central part of this study, and much of the results and interpretation rest on this. From my understanding, the age model of the GeoB23302-2 is not published elsewhere, so I would ask the authors to provide more detail about the ¹⁴C measurements of the planktic foraminifera, including a data table of conventional ¹⁴C ages and resulting calibrated ages. I also have concerns about the choice of the Marine20 calibration curve and the potential impact of an additional marine reservoir effect in planktonic foraminifera. Particularly during the last glacial, there may have been a large difference in terms of ventilation between the ocean surface and the interior. Hence, I wonder if the reservoir is not over-estimated when applied to planktonic ¹⁴C ages. I would like the authors to expand on this topic in more detail and include a concise statement in the methods section of the paper.

The age-depth model has not been published elsewhere. We have included more information about the model in the supplementary material, including a data table and the OxCal code necessary to reproduce the model.

Concerns about the use of Marine20 seem to be more significant in polar regions, as mentioned by Heaton et al. (2020):

In higher-latitude polar regions, MRAs and critically their possible fluctuations over time are expected to be larger due to significantly increased variability in ocean ventilation and air-sea gas exchange mostly arising from changes in sea ice extent and differences in wind strength (Butzin et al. 2005). This is particularly likely to be the case during glacial periods.

Between ca. 15 and 32 kcal BP, the larger global-average MRA observed in Marine20 compared to Marine13 is due to methodological improvements in the former. The MRA estimates incorporated in Marine20 are more realistic than those of previous curves. As stated in Heaton et al. (2023), the radiocarbon community does not recommend using Marine13 over Marine20 in any situation. We have added a short sentence about this in the supplementary material, where the methods for the construction of the age-depth model are described.

Carbon sources: There is much talk about petrogenic carbon throughout the paper, although the authors do not seem to find petrogenic carbon (but ancient peat) to be an important source to the sediment C. If petrogenic carbon is not important, I wonder why a petrogenic (^{14}C -free) carbon source is even quantified here (your dual isotope model suggests petrogenic carbon contributions up to 60%), which contradicts your discussion and conclusion. I also wonder about the use of D^{14}C values of *n*-alkanoic acids as a terr-OC end member, as they may follow different transport and aging dynamics than the bulk material. Furthermore, *n*-alkanoic acids are more degradation resistant than other organic compounds and may thus represent a pre-aged terrestrial carbon pool. Have you considered to distinguish between a contemporary (^{14}C -young) terrestrial OM source (e.g., soil OM) and strongly pre-aged (^{14}C -depleted, but not free of ^{14}C) terrestrial sources that represents LGM (or pre-LGM) peat OM?

We start the manuscript by stating the possible sources of C to our marine sediment record, including petrogenic C. To test this possible contribution of a ^{14}C -depleted petrogenic source, we defined an OC_petro end-member. However, in our mixing model, we used the isotopic values of ancient peat material (i.e., lignite, a type of coal) to represent this end-member. Our choices of end-members are clearly stated in the manuscript, but we acknowledge that having a "OC_petro" end-member may be the cause of confusion here. Therefore, we have renamed this end-member as "OC_fossil".

Dual-carbon isotope mixing models present the constraint of having only three end-members, despite the likelihood of multiple sources contributing to the deposit. The model is just an approximation and most likely does not adequately represent reality. It is important to note that all end-members have limitations. In addition, it would not be appropriate to use a contemporary terrestrial OM source as an end-member in our mixing model because the sources of C are not the same as in the period of interest, meaning that the isotopic composition is probably different too.

The reviewer is right in pointing out that *n*-alkanoic acids might not be representative of the whole continuum of organic materials present in natural soils and permafrost deposits. Indeed, these biomarkers may be older than more labile compounds such as organic acids, proteins, pigments or even lignin phenols. On the other hand, the advantage of using biomarker ages is that these materials can be unambiguously assigned to the terrestrial realm, which is of great importance when examining marine records receiving considerable amounts of young marine materials. We would like to stress, however, that long-chain fatty acids have been used as indicators for terrestrial organic matter in a large number of studies (see reviews by Eglinton et al., 2021 and Kusch et al., 2021), making the data comparable. We have revised the supplementary material to mention that the use of the fatty acids is an initial approximation.

Minor points

Abstract

Line 9: What kind of processes? Carbon release, degradation and CO₂ emissions?

The sentence reads "...result points to the possibility of permafrost carbon export to the ocean, caused by processes that likely furthered the observed changes in atmospheric carbon dioxide." Therefore, in this sentence we are referring to the processes that led to terrestrial carbon export to the ocean, preceding factors such as carbon release and CO₂ emissions from the affected carbon pools. We have revised the sentence to explicitly mention the relevant processes, i.e., deglacial warming and glacial erosion.

Line 12-13: It would be helpful to clarify add how thawing permafrost affects the global carbon cycle.

Thawing permafrost can affect the global carbon cycle in several ways. However, for the sake of conciseness, we have revised the sentence to mention the most immediate outcome of thawing permafrost, which is the release of greenhouse gases.

Line 17: Rising atmospheric levels?

We have revised the sentence, replacing "elevated" with "rising".

Line 43-45: This sentence reads a bit awkward. What is the "strong response from this system" specifically?

Tributaries of the Channel River responded to changes in precipitation patterns and the melting of ice sheets with enhanced amounts of water flow. We have revised the sentence to make this clearer.

Line 50: The continental shelf and what about the deeper ocean?

Since our core records the input of terrestrial OM to the continental shelf, at the mouth of the Channel River, we did not mention export to the deeper ocean here as it is not something we can assess in this study.

Methods

Line 57-60: Please explain briefly how these elemental ratios work; i.e. why Zr/Rb is thought to mirror grain size and Fe/Ca is a proxy for terrigenous sediments.

We have added a brief explanation about these proxies.

Line 68: Similar here; how does the CPI indicate OM degradation?

We have added a brief explanation about the use of this proxy to assess OM degradation.

Line 69: Also the BIT and $f\beta\beta$ indices need to be explained a bit more in the main manuscript.

We have added a short explanation for both proxies in the main manuscript.

Results

Line 80-81: Isn't the age model based on foraminiferal ^{14}C ages? What is the OxCal time series agreement index?

Yes, the chronology of the core is based on an age-depth model constructed with ^{14}C ages obtained from planktic foraminifera. The details of radiocarbon analyses and model construction are given in the supplementary material. We have added a sentence at the start of the methods section in the main manuscript to briefly mention how the chronology of the core was established. The OxCal overall agreement index of 99% is given in the results and it shows the good agreement between the ^{14}C data and the model.

Line 81-83: Please add more information about these reconstructions. Clarify that the NGRIP and CO_2 reconstructed are based on ice cores, and explain what the sea surface temperature record based on.

We have added this information to the text.

Line 95: What are "relatively high contributions"? A dominating fraction?

During the period of enhanced deposition, the contribution of terrestrial and fossil carbon to the samples is relatively high compared to other periods in the core. These carbon sources dominate the samples during this period, as shown in Figure 3. We have changed the sentence to:

The results of our Bayesian mixing model (Figure 3) corroborate the BIT index record, showing that terrestrial and fossil C dominantly contributed to samples during the period of enhanced terrigenous deposition, while OM in Holocene samples is mostly marine.

Discussion

Overall: Most of the data interpretation rests on concentrations and relative contributions of terrestrial compounds and OC fractions. Have the authors considered to estimate fluxes of the terrestrial OC fractions and compounds (e.g., of alkanes or the terrigenous OM fraction in g per sqm per year), which may provide an additional perspective to the paleo-variability of terrestrial carbon release. If not, I encourage the authors to do so.

We now present mass accumulation rates of terrigenous biomarkers in the supplementary material.

Line 104-106: Please explain how the Zr/Rb ratio or coarse-grained sediments are consistent or indicative of terrestrial material.

The Zr/Rb ratio is a proxy for grain size and the deposition of coarse-grained sediments is enhanced during periods of flood and intense fluvial activity. We have added this explanation to the text.

Line 107: How are these two periods different? Why not say 20.5-16.5 ka BP?

The sentence was written in this way to account for a BIT decrease at approximately 19 kcal BP. We have revised the sentence now to explicitly mention this.

Line 111: Heinrich events are not introduced or explained.

A brief definition has been added.

Line 127: Isn't the CPI by definition >1 or 1? It's not surprising the CPI values remain above 1 throughout the core in such a near-coastal environment.

Bray and Evans (1961) have measured values slightly below 1. In our study the values remain way above this value and values > 3 are interpreted as indicators for fresh biospheric material. If the OM peak observed in our record was caused by the deposition of petrogenic OM, the CPI values would reflect that and we would probably observe values closer to 1.

Line 144-146: A few lines above you provide a discussion about different processes (transport vs. petrogenic C) that may lead to high pre-depositional ages. Which of those processes/end members were included in the mixing model, and will the resulting C fractions not just be dependent on the end members chosen? Did you account for possible C aging during transport, which would probably affect the age of peat material?

It is unlikely that transport alone would account for the values we observe in our study, e.g., pre-depositional ages of several thousand ^{14}C yr. Phenomena related to OM remobilization in the ocean are mentioned as a possible explanation for the presence of pre-aged compounds at the core location during the Holocene but not as the most relevant cause of their aging.

Using data from a single location precludes estimates of transit time, as we do not know what the OM age was at the point of origin. Moreover, it is difficult to account for

OM transport in our analyses because the various ways in which C cycles during this transit time are not completely understood. The mixing model works as a first approximation to identify the most probable sources for the OM, but it can certainly be improved as more information on the several processes of OM transformation and degradation becomes available.

Line 169: Do the authors mean that peat from older periods (e.g. the last interglacial) was frozen during the glacial? Perhaps add something like “OM from older periods (e.g., frozen peat OM)” to clarify this.

We have accepted the suggestion and changed the sentence accordingly.

Line 195: Could post-glacial sea level rise and erosion of terrestrial deposits also contributed to thermo-erosion of frozen deposits?

The deglacial erosion of coastal deposits by sea-level rise is a relevant phenomenon that has been observed in other locations (e.g., Meyer et al. 2019). We acknowledge this possibility in the discussion:

Furthermore, the process of post-glacial sea-level rise may have played a role in the erosion of coastal permafrost deposits, potentially serving as an additional pathway for the transport of OM to the ocean (e.g., Meyer et al., 2019).

Line 225-229: It may have contributed to the post-glacial carbon cycle perturbations but it could be good to mention that the loss of terrestrial carbon reservoirs was likely compensated by expansion of soil carbon stocks and vegetation growth at the time or thereafter (e.g., see Lindgren et al., 2018, <https://www.nature.com/articles/s41586-018-0371-0>).

We agree that it is important to mention how carbon stocks developed after the deglacial perturbation analyzed in our study, and we have added the information to the manuscript.

Line 233-235: What kind of leads and lags do we expect during permafrost carbon feedback? I would think that permafrost thawing leads to CO₂ emissions rather instantaneously, while the lateral transport of permafrost organic matter to rivers and the ocean may cause a lag, such that the 'peak signal' is seen delayed in the offshore sediment archive. So this would actually point to the opposite; that the post-glacial release of old peat/permafrost organic matter in central Europe did not affect atmospheric CO₂. So again, how certain are the authors about the correctness of their age-depth model (see my main comment)?

In the early stages of permafrost thawing, vegetation regrowth may have partly offset carbon release (see e.g., Schuur et al. 2015). Moreover, the OM decomposition and resulting CO₂ emissions from permafrost can be influenced by various environmental parameters (see e.g., Grosse et al. 2011). In the case of our study area, it is possible that these rates were further enhanced as climate warmed. Particles travelling downstream spend the majority of their total transit time at rest in transient floodplain storage (see Bradley and Tucker, 2013). Clastic particles have been shown to spend 4-5 orders of magnitude more time in storage than in motion (e.g., Repasch et al.

2020). So the reviewer is correct in suggesting that particles mobilized after permafrost thaw might arrive in the recipient marine reservoir with a time delay relative to the event of thawing. However, rapid erosional processes like river braiding and sea-level rise induced coastal erosion will supply particles at a high rate, albeit their carbon age might be old. It is this concept that is underlying our research approach.

While we have taken great care to construct a robust age-depth model, any model is inherently an estimate. Following established best practices in the field, we used the most up-to-date marine calibration curve and have provided a detailed description of the model, along with the necessary data and code, to enable readers to assess and reproduce our results. The agreement of the age-depth model as well as the result of the outlier model indicate that the measured foraminifera radiocarbon ages are represented well.

Line 236: How do the authors explain the sudden drop of terrestrial C discharge (as shown by the BIT index, Paq and the age of *n*-alkanoic acids). Could the river re-routing be related to that? It is not very clear from reading this paragraph.

At around 18 kyr BP, the Elbe-Weser system underwent a re-routing, followed by a sea-level rise after 17 kyr BP. As a consequence, the GeoB23302-2 core location no longer received the strong terrigenous signal observed previously, which may account for the sudden drop in the indicators measured in our study. We have revised the sentence to clarify this point.

Line 254-255: Why is there so much weight on petrogenic C in the paper if it is not one of the main sources?

Given the great pre-depositional ages measured in our study, petrogenic C could be a dominant source of terrigenous C in our core. This has been shown to be the case in other regions (e.g., Meyer et al. 2019) and, therefore, the manuscript was written to explore and test this possibility, which was discarded based on the geochemical signature of the organic matter in the core. However, since the conclusions are meant to summarize the findings of the paper, we mention petrogenic C here to acknowledge its potential to explain some of the results we observe. To address the referee's comment, we have made changes in the introduction: i) the discussion of petrogenic sources has been reduced and ii) ancient peats are now also mentioned as a potential source of aged OM.

Line 261-263: This is a quite complicated way to say that terrestrial/permafrost carbon release likely continued also after 17 kyr, although this was not recorded in your core. I suggest to write this more clearly.

It is true that the sentence as originally written suggested that although the export of terrigenous C to the ocean was not recorded in our core, it continued. However, it also indicated its routing. We have split the original sentence into two to make it less complicated.

Line 263: In the light of the findings and the offset between the terrestrial carbon peak and the period of CO₂ rise I would not call this 'likely'. I think that 'it is possible' reflects this and the underlying certainty better.

The first terrestrial carbon peak precedes the period of CO₂ increase, while the second peak coincides with the start of rising atmospheric CO₂ levels. Previous studies have shown a causal relationship between rising atmospheric CO₂ levels and degrading permafrost (e.g., Winterfeld et al. 2018), which is why we initially used the word "likely". However, we acknowledge that many of the mechanisms of carbon cycling from source to sink need to be better understood in this region, and therefore we have revised the text to use the word "possible" instead.

Line 267: And what are these important consequences? Please be more precise with these implications.

We have revised the sentence to specify that increases in atmospheric greenhouse gas concentrations are the factors that would affect Earth's climate in this context.