Response to Reviewer Comment 3

This work hypothesizes that de-glaciation and weathering of kerogen-rich lithologies in western Canada made a major contribution to CO2 rise at glacial terminations by compiling and re-interpreting empirical evidence. I have several comments regarding the interpretation and methods of the manuscript, which I hope to help to improve the manuscript. I'd recommend revisions before acceptance for publication.

Dear Reviewer,

Thank you very much for your critical and constructive review. I disagree with a few of the raised points. In the interest of idea flow and concise messaging, I have opted to keep the manuscript short - and this is exactly what gives readers a kick, just like with reviewer 2. My detailed responses are given below.

For decades, modelers have twisted ocean circulation and ensuing ocean-atmosphere exchanges into all sorts of pretzels to explain glacial-interglacial cyclicity and its fascinating patterns of atmospheric chemistry. Various hypotheses invoking terrestrial mechanisms have been presented in the literature with little breakthrough in our greater scientific progress. The faithful rise in atmospheric CO_2 at glacial terminations has in many ways been a mystery that has evaded satisfactory explanation as highlighted multiple times by W. Broecker and others. This "*Ideas and perspectives*" article brings a radically new mechanism to the table supported by simple, first principal arguments. Clearly, quantitative constraints are rudimentary and are in need of refinement and many questions are far from being answered. To work towards this, the author hopes that this article will energize a new community effort to research the exogeneous kerogen cycle to inquire how dynamic it truly is.

Overall, clearly much more research needs to be undertaken to answer the many questions that rise from this "Ideas and Perspectives" article. Through the review process and thanks to your comments, this work has improved greatly. Thank you very much.

Sincerely,

Thomas Blattmann

Major comments:

Comment 1: 'kerogen' should be clearly defined: how does this term compare to the other terms used in the relevant studies, for example, rock-derived organic carbon, and petrogenic carbon. Do those concepts overlap/differ or are they the same? Would organic carbon in metamorphic rocks also be termed 'kerogen'?

Kerogen is indeed a term used quite differently by different authors. Durand (1980) probably provides the most "mainstream" definition with kerogen being a term reserved for insoluble rock-disseminated forms of organic matter. Geochemists who started using the term in the 2000s along with a slew of other terms: “In literature, petrogenic OC is also referred to as fossil carbon, geogenic carbon, rock(-derived) carbon, ancient carbon, relic carbon, detrital carbon, and kerogen” (Blattmann et al., 2018). In biogeosciences (the field of the journal this contribution is submitted to), they are mostly used interchangeably. In this contribution, the author opts for kerogen as it is a single word that requires no abbreviation and is instantly recognizable across a wide spectrum of Earth science disciplines. A definition has been added as a footnote in the beginning to clarify the author’s usage of the term: *In this work, kerogen is used as an umbrella term for all rock-derived forms of reduced carbon including soluble, insoluble, rock disseminated, rock forming, solid and liquid forms, as well as fossil palynomorphs, biogenic and abiogenic graphite.*

Durand, B.: Sedimentary organic matter and kerogen. Definition and quantitative importance of kerogen, in: Kerogen: Insoluble organic matter from sedimentary rocks, edited by: Durand, B., Éditions Technip, 13-34, 1980.

Comment 2: it needs to acknowledge existing understandings/studies about carbon fluxes during glacial-interglacial time periods. What did previous work find/conclude about glacial terminations and CO2 rise? How does the kerogen weathering hypothesis in this manuscript differ from the previous studies? What were the magnitudes of other carbon fluxes during deglaciation (e.g. the carbon exchange between the atmosphere and ocean reservoirs) and how do those compare to the kerogen weathering flux?

Fluxes of carbon between atmosphere-terrestrial biosphere and atmosphere-ocean are several orders of magnitude greater than any pathways of mineral weathering or kerogen oxidation fluxes. However, these are also compensated with nearly equal reverse fluxes across space and annual timescales (e.g., CO_2 uptake and CO_2 release from different parts of the ocean, e.g., Menviel et al., 2018; Takahashi et al., 1997). References to studies championing different hypotheses of CO_2 release pathways are concentrated in lines 260-286. The magnitudes of carbon fluxes during deglaciation have been subject of great many studies and it is clear that all of these studies leave basic observed parameters unexplained (see e.g., Broecker & Barker, 2007). This contribution introduces a new, simple, and plausible mechanism into this longstanding discussion, which is able to reconcile many of these parameters and also have a clear physical basis. I envision that this work will serve as foundation for new discussion and iterating improvement of our understanding of the global carbon cycle so that we can work towards a quantitative understanding, beyond the isolated processes, deconvolving the individual components acting in the integrated Earth system (e.g., Kohfeld and Ridgwell, 2009). With this, figure 2 in Kohfeld and Ridgwell (now referenced in the article) is the ideal goal of what would be desirable to achieve.

Takahashi, T., Feely, R. A., Weiss, R. F., Wanninkhof, R. H., Chipman, D. W., Sutherland, S. C., and Takahashi, T. T.: Global air-sea flux of CO_2: An estimate based on measurements of sea–air pCO_2 difference, Proceedings of the National Academy of Sciences, 94, 8292, 10.1073/pnas.94.16.8292, 1997.

Comment 3: there’s no detailed lithology/kerogen amount/kerogen weathering kinetics/kerogen 13C signal/topography information (e.g. maps or data compilation) about western Canada – all those variables are important and relevant to the total oxidation flux of kerogen, and need to be discussed.

Table 1 contains all the kerogen weathering kinetics available in the literature. This is the product of 30 years of research and it is compiled here for the first time representing the most thorough review of kerogen oxidation fluxes known to the author. Stock estimates of kerogen on Earth's surface are reported by Copard et al. (2007) and provide clear support for the hypothesis. However, the data by Copard et al. are too coarse spatially and need refinement to allow for quantitative application in models. A general reference is now added regarding the $\delta^{13}C$ isotope composition of organic matter in rocks (Lewan, 1986), and it is also clear that glacial till composition is also important for which there is a lack of data. Compiling these maps (with $\delta^{13}C$) is beyond the scope of the current work. For now, it is important to know that kerogen is isotopically light as has been documented extensively for major sedimentary units through geologic time (Lewan, 1986) and for different metamorphic grades (e.g., Hoefs and Frey, 1976). Calculating total and time resolved oxidation flux of kerogen requires more parameters than we have available. Concerted research efforts are needed to deconvolve glacial-interglacial effects on kerogen oxidation (systematically extending the 30 years of data presented in Table 1). This would be desirable for any mechanism (e.g., atmosphere-ocean exchange), but model estimates are the best we have for these (as elaborated in previous answer). However, the paper outlines a research pathway so that this can be achieved in the future as enunciated in the abstract and conclusions. The possibility of kerogen oxidation as a key driver of CO_2 increase at glacial-interglacial transitions is enunciated for the first time in this paper. Plausible arguments support this, and this paper seeks to energize research in this new direction.

Hoefs, J., and Frey, M.: The isotopic composition of carbonaceous matter in a metamorphic profile from the Swiss Alps, Geochimica et Cosmochimica Acta, 40, 945-951, 1976.

Comment 4: over glacial-interglacial timescales, would weathering of aged soil organic carbon (with residence time of thousands to tens of thousands of years) play an important role for CO2? Was aged soil organic carbon considered a part of kerogen in this work? How did the aged soil carbon flux/pool compare to those of kerogen organic carbon?

The soil hypothesis is championed by other works (e.g., Zeng, 2003). This work champions rock-derived carbon. I personally disagree with the soil hypothesis as a large subglacial storage of soil organic matter is required (c.f., Lindgren et al., 2018). While some soil is certainly overridden by glaciers, kerogen supply from bedrock is virtually limitless as long as it is exhumed, making supply easy to explain. The Earth system is underdetermined, so deconvolution is riddled with unsatisfactory uncertainties; even a single isolated Earth system component is challenging to model. Soil and kerogen oxidation signatures on atmospheric chemistry are equivalent in terms of atmospheric chemistry for $\delta^{13}C$ and direct conversion to CO_2, therefore, modeling work by Zeng (2003) and Simmons et al.'s (2016) is adapted and used here.

Comment 5: it sounds like the exhumed kerogen was all delivered to the oceans and got buried in marine sediments during the interested timescale of deglaciation (e.g. Figure 1) – was this true?

Sediment residence time in floodplains and sedimentary basins could reach tens of thousands of years – meaning some of the kerogen might not be delivered to the oceans during the deglaciation. Then, would the conditions in floodplains and sedimentary basins also influence kerogen carbon reburial efficiency? can add relevant discussions.

I totally agree. Intermediate traps of kerogen on land certainly add a layer of complexity that has gone largely unaddressed in studies to date. I have added a short discussion on this: *In tandem with this, quantification is needed for (temporary) kerogen reburial in subaerial and subaquatic terrestrial systems (e.g., moraines, lakes) on global and regional scales (e.g., Meybeck, 1993; Vonk et al., 2016; Blattmann et al., 2019b; Fox et al., 2020).*

Title: can be more focused and straightforward – sth like 'oxidation of kerogen contributed to CO2 rise at glacial terminations'

The author disagrees. Making a strong statement in the title like this would be too strong for a presentation of ideas and perspectives. A dynamic exogenous kerogen cycle was also suggested for other events in Earth's history by other studies, such as during the PETM and this literature is unified in this contribution.

L25: please clarify how the 150 PgC/kyr was determined? uncertainties?

This is from the review by Hedges and Oades (1997). While this estimate will likely be revised in the future with improved budgeting of the fluxes, changes to this number produce no changes to the thoughts presented here. Please see response to reviewer 1 for further discussion on this value and its negligible sensitivity to the end result of this work.

L30-35: should also introduce major thoughts of the causes of glacial terminations

Thank you for this suggestion. I have added a sentence at the beginning of section "2 Carbon isotopes and contradictions?" to get the reader on the same page.

L40-45: this carbon cycle framework is very incomplete – at least should put in silicate weathering, see more in Berner et al. (1983)

Thank you for this constructive suggestion. I have reorganized section "3 Kerogen and glaciers" by adding an introductory section that does carbonate and silicate weathering justice. I totally agree, this was treated in a very peripheral manner and now it is given proper context and helps guide the reader in a balanced way. Please see lines 66-78.

L100: Equation 2 is unclear…explain what Zeng (2003), Simmons et al. (2006), and Horan et al. (2017) have done? Where were those studies conducted? What did they find?

The equations have been revised so that variables are used. I believe these references are sufficiently described and flow of ideas is maintained by keeping this part of the work straight and to the point. Please see lines 105-120.

L125-130: how much did the 14C composition of the then atmosphere-ocean carbon reservoir change? Any comment on 13C?

All of this is reported graphically and referenced with Fig. 3.

L230-235: could expand a bit and discuss some existing mechanisms – their pros and cons?

Thank you. I have expanded briefly on this and refer to reviews that provide the space to discuss pros and cons in detail: *Various mechanisms have been proposed to explain CO2 increases at glacial interglacial transitions including for example the solubility pump hypothesis, iron fertilization hypothesis, ocean circulation hypotheses and many more (see hypotheses and reviews by Martin, 1990; Broecker and Peng, 1993; Kohfeld and Ridgwell, 2009; Rapp, 2019).*

L500 – Table 1: how did the laboratory experiment-based results translate to a flux of unit area? for example, bituminous coal and oil sands – how to convert the reaction kinetics results of several samples to fluxes over certain areas of landscapes?

Thank you. In response to this comment, I have made an online supplemental which details the conversion of the data from the references contained in table 1.

L525: Figure 4 can be improved by displaying topography and lithology maps

The author disagrees. Overlaying additional maps make the figure too busy. Refinement comes later as the subject of future work. The map already contains geographical information, major geological units, and two isochrons for the extent of the Laurentide Ice Sheet for the time bracket of interest. Adding more information will make the reader lose the core message. References are clearly given (with a new addition) and the interested reader can delve deeper into lithological maps, etc. to explore for themselves using dedicated maps. The focus needs to be on the temporal and megascale dimensions of the phenomenon: namely that CO_2 rises relentlessly throughout the ice sheet’s retreat across the sedimentary units of western Canada and reaches its inflection point shortly after the ice sheet recedes into the Canadian Shield. This is the important feature and the core of the hypothesis as manifested in the known history of the deglaciation of North America.