

Response to Reviewer Comment 1

This discussion manuscript presents a new hypothesis and a review of data that qualitatively support that hypothesis. The author argues that kerogen oxidation and burial efficiency are important mechanisms for modulating atmospheric CO₂ concentrations across glacial-interglacial periods (over 10²-10⁴ year timescales). This is contrary to the common hypothesis that rock organic carbon oxidation and terrestrial organic carbon burial are important only over 10⁵-10⁶ year timescales. Because we currently lack the data to sufficiently test this hypothesis, the author uses this manuscript to campaign for new studies to gather the datasets needed to improve our quantitative constraints on the feedback between kerogen oxidation and atmospheric CO₂ concentrations over glacial-interglacial cycles. This is an interesting hypothesis that should be given attention and the manuscript is well-written. However, there are several weak points that should be addressed.

I will also note that an earlier version of this manuscript was submitted in 2019, but was rejected for publication, largely due to lack of quantitative arguments and unconvincing discussion on the changes in weathering efficiency over time. This revised manuscript addresses most of the earlier reviewers' concerns, by adding some back-of-the-envelope calculations of potential atmospheric CO₂ changes due to kerogen oxidation, and a more thorough literature review and discussion. However, I think there are flaws in the quantitative argument, and I recommend substantial revisions before the manuscript can be accepted.

Dear Reviewer,

Thank you for your constructive review. We indeed lack the background knowledge to test this hypothesis, and yes, the goal is to call to attention the potentially major role kerogen cycling on atmospheric chemistry, particularly with respect to the mystery of glacial-interglacial cycles. Responses to your concerns and feedback are given below. As a result of your input, the manuscript has greatly improved. Thank you very much.

Sincerely,

Thomas Blattmann

Major points of concern:

The author fails to bring kerogen oxidation into context with the other key processes modulating atmospheric CO₂ over glacial-interglacial timescales (e.g., silicate weathering, OC burial, changing biosphere). These processes are briefly mentioned, but should be acknowledged with a quantitative comparison (e.g., Hilton and West, 2020).

I agree. Context is now provided as a new paragraph starting off the section "3 Kerogen and glaciers – Dynamic modulators of the global carbon cycle?". The introduction is by design qualitative to avoid miring the reader's attention in the numbers and keep the reader focused on the core message of this work. However, to this end, the reader is referred to Hilton and West (2020) multiple times throughout the article. The important point emphasized is that mineral weathering (carbonate and silicate decay via carbonic and sulfuric acids) and biogeochemical processes (organic matter burial and kerogen oxidation) stand in close balance to one another over longer geologic timescales.

The author argues, rightfully so, that in the wake of glaciations, glacial retreat exposes kerogen-rich rocks and grinds them down, stimulating rock weathering and kerogen oxidation. This

hypothesis is supported by decreasing atmospheric ^{14}C content from the LGM to present, which is consistent with input of radiocarbon-dead CO_2 to the atmosphere. The authors should elaborate on how erosion and weathering intensity changes across glacial-interglacial periods (e.g., Schachtman et al., 2019).

Schachtman et al. (2019) is referenced as a comparison together with a list of other studies discussing changes in weathering across glacial-interglacial periods. Their study is in contrast to the studies cited for glaciated catchments. This is contained in this same new paragraph as mentioned above.

Deglaciation would also enhance carbonate weathering by the same physical breakdown mechanisms and subsequent meltwater dissolution, but the author argues that kerogen oxidation is a more important CO_2 source to the atmosphere than carbonate weathering during deglaciation, due to its faster weathering kinetics. The author support this argument with quantitative data (see Hilton and West, 2020).

This is argued with the more primary references Horan et al., 2017 (and references therein) and Fischer et al., 2007.

Regarding the calculation made in Equation 1, the author overestimates the modern global average kerogen oxidation flux. They use a value of 150 PgC/kyr for kerogen exhumation, however, with a global fossil organic carbon stock of 1100 PgC (Copard et al., 2007) and a global average denudation rate of 5.4-6.5 cm/yr (Wittmann et al., 2020; Hedges and Oades, 1997), kerogen exhumation is at most 71.5 PgC/kyr. This agrees with the estimate of 40-100 PgC/kyr reported by Hilton and West (2020). Together, this would suggest that the modern kerogen reburial efficiency is $\sim 60\%$ and ~ 29 PgC/kyr is oxidized.

Firstly, Hilton and West (2020) report 40-100 PgC/kyr release from the oxidation of kerogen (please correct me if I am wrong). Also, Galy et al. (2015) suggest a detrital kerogen export of $43_{-25}^{+61} \frac{\text{PgC}}{\text{km}^2\text{yr}}$, with uncertainty higher than the total kerogen exhumation estimate cited above, which would lead to a mass balancing problem. Additionally, kerogen exhumation and export is highly disproportionate and unevenly distributed (e.g., orogenic settings). Furthermore, the fossil organic carbon stock reported by Copard et al. (2007) integrates only over the top one meter of the earth surface. We know that kerogen oxidation starts taking place much below one meter (e.g., Petsch, 2014). Therefore, the kerogen exhumation rate suggested by the reviewer is an underestimation from the author's perspective. However, ultimately, reburial efficiency comes to lie in the same bracket (10-70%). The numbers today are poorly constrained and as the article argues: detrital kerogen export and oxidation fluxes varied through time, where our constraints are much poorer. Regardless of what numbers we choose the arguments in this "Ideas and Perspectives" article remain the same:

F_{L-A} calculated with Eq. 1 will be a small number no matter what. This means that this has essentially no effect on the outcome of Eq. 2 and it makes no difference in terms of the overall picture of the magnitudes of the fluxes presented in Table 1.

In this first equation, the author also uses kerogen oxidation rate estimates from Horan et al (2017), which were measured in the southern Alps of New Zealand. This setting is tectonically active, which enhances physical erosion and chemical weathering. As a result, the kerogen oxidation fluxes are overestimated and not likely representative of ice sheet retreat. In the case of the Laurentide ice sheet, the underlying lithosphere was passive, and physical erosion was only

enhanced after glacial retreat induced isostatic uplift. While there are no other data for fully glaciated catchments, there are data for the Yukon and Mackenzie Rivers, which are likely more representative of large spatial scale kerogen oxidation fluxes in paraglacial conditions.

As the author argues, the author actually considers the oxidation rates by Horan et al. (2017) to represent an underestimate of the Laurentide Ice Sheet case for multiple reasons: one of which is the presence of “super carbon source terrains” in Western Canada with bituminous lithologies that show extremely high oxidation rates which are way beyond those of rock disseminated forms of kerogen (Table 1). This is a completely understudied aspect and definitely needs to be addressed in future research efforts.

The author also fails to cite Hilton and West (2020), which is a key review paper that discusses the balance of CO₂ production and sequestration using data from river catchments around the globe. This manuscript could be improved by making a balanced carbon budgets for glacial periods and comparing them with those estimated for modern/interglacial conditions.

After initially “failing”, the author now successfully cites Hilton and West (2020) and quantitative-qualitative arguments are made while maintaining focus and flow for the reader.

There are several physical and biological mechanisms that the author should address in this manuscript, to place kerogen oxidation into context with other mechanisms recognized to modulate atmospheric CO₂ over millennial-centennial timescales. See Schachtman et al. (2019) for physical and chemical erosion mechanisms over glacial-interglacial cycles, and perhaps Sigman and Boyle (2000) for quantitative insights to glacial-interglacial variability in biologic productivity.

A plethora of physical and biological mechanisms are discussed throughout the article (which presents a completely original and highly interdisciplinary blend of literature!); an exhaustive review has already been provided by Hilton and West (2020). In contrast to a conventional review article, the readers reading this article are seeking new ideas and perspectives (hence the chosen article type) and this is what the author delivers: in a concise way with imaginative reasoning that will get a lot of people out of their comfort zones to go beyond textbook lines of thinking.

The author does not consider the lag time between sediment production and export to the ocean. Presumably, upon glacial retreat, the pathway from glacier to ocean is short, and burial efficiency would overall be higher than today. However, sediment supply from glacial erosion is high, and much of the eroded material was deposited in moraines and glacial till, where it remains today. In the current manuscript, the author assumes that eroded material is largely delivered to the ocean and buried, but in reality this material can be stored for thousands of years during which it can be oxidized. If the author argues that atmospheric CO₂ changes occurred within 300 years following glacial retreat, then kerogen oxidation must be very rapid. The author should consider transient sediment storage and potential lag times therein.

The author agrees that terrestrial redeposition of detrital kerogen in terrestrial environments are important for the exogenous kerogen cycle. This intermediate storage is constrained only loosely in a few regional settings (e.g., Blattmann et al., 2019b) and poorly constrained on a global scale (e.g., Meybeck, 1993). Transient storage should definitely be considered and this is expressed a couple of times with making recommendations for future research, “*Chronosequence studies of kerogen oxidation rates in deglaciated terrains are needed to provide constraints on time-integrated CO₂ release to the atmosphere.*” In response to the reviewer’s comments, the following was added to emphasize the detrital kerogen reburial aspect of the problem: “*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)."

The 300-year number is derived from the observed megascale spatiotemporal evolution of the Laurentide Ice Sheet as it retreats into the Canadian Shield with the timing of the inflection point in CO₂ increase. The author hypothesizes that kerogen oxidation happens continuously and parallel to glaciers retreating, the pedosphere transgressing, so everything is fluid an integrated perspective is needed to understand this number; this is the author's perspective hence the "Ideas and Perspectives" category of the article.

Detailed comments:

Lines 15-16: The term "contributed majorly" doesn't really convey a clear message of how significant the increase in atmospheric CO₂ was as a result of deglaciation. It would be nice to give some estimate of the relative change in atmospheric CO₂ at the inflection point. If a more quantitative estimate is not feasible, then I suggest the author provide more context as to what other processes may have also contributed to the post-glacial increase in atmospheric CO₂.

I agree. However, as the sentence makes clear, this is hypothesis, and as the next sentence makes clear, quantitative constraints are needed. With the improvements made throughout the manuscript (e.g., adding in context with mineral weathering as elaborated previously above), the readers have more information to develop their own thoughts.

Line 24: need reference for 15 million PgC kerogen

Hedges and Oades (1997) and now the reference is moved to make it clear. Thank you.

Line 29-31: Here, the author discusses the timescales over which kerogen oxidation and sedimentary organic carbon burial, mentioning that kerogen oxidation is important for atmospheric chemistry over million-year timescales, while sedimentary organic carbon burial is relevant over geological timescales. These timescales are apparently the same, so I think the second part of this sentence ("with kerogen oxidation considered important for atmospheric chemistry over million-year timescales (e.g., Petsch, 2014; Bolton et al., 2006") should be moved to the end of the sentence on line 27. For example, "Upon oxidation of kerogen, O₂ is consumed and CO₂ is released to the atmosphere, *affecting atmospheric chemistry over million-year timescales.*" Additionally, I'm unsure how the author can tie kerogen oxidation to atmospheric CO₂ changes over glacial-interglacial timescales when the relevant timescale for kerogen-atmosphere feedbacks is millions of years.

This is what the presented hypothesis is about. If this hypothesis motivates new research, future testing of this hypothesis will shed light on these ideas and perspectives. As the author argues throughout, there are several lines of strong, independent evidence that fit with this hypothesis. This work seeks to energize research interest in this direction.

Lines 32-34: I would also re-word this sentence because kerogen decay can also be complete if organic-rich lithic fragments sit at earth's surface for a sufficient length of time such that the organic carbon is oxidized before being re-buried (e.g., Hemingway et al., 2018).

In this section of the article, the author would like to keep the context on a global perspective. More local considerations are delved into later in the manuscript. As the sentence starts with a "however", it implies that previous studies often considered this to be the case. More often than

not, kerogen oxidation is incomplete (e.g., Hemingway et al., 2018; Leythaeuser 1973, and many more).

Lines 35-37: The author raises several questions to be addressed in this manuscript: (i) what is the reburial efficiency of kerogen? (ii) what is the weathering efficiency of kerogen? (iii) what are their controlling factors? (iv) what are the implications of them changing for atmospheric chemistry over geologic timescales? In question (iv), the author should say “millennial/centennial timescales” rather than “geologic” because we generally know the implications over geologic timescales, as summarized by Petsch (2014). Their next sentence then presents the hypothesis that kerogen reburial and weathering efficiencies are important over centennial to millennial-scale atmospheric CO₂ changes.

Thank you for this constructively critical comment. The author has reformulated question (iv) in different direction: (i) what is the reburial efficiency of kerogen, (ii) what is the weathering efficiency of kerogen, (iii) what are their controlling factors, and (iv) how do reburial and weathering efficiency vary over geologic time and space?

The review by Petsch (2014) was given insufficient credit in this contribution and is now referenced in section 5 “Tackling geologic deep time” to highlight these contributions. Overall, the author is of the opinion that kerogen cycling (whether on geologically “short” or “long” timescales) is understudied, with very little primary data extending back in geologic time.

Line 37: Here, the author should highlight the overall knowledge gap, and emphasize how kerogen oxidation during glacial periods may be a key mechanism for changing atmospheric CO₂ concentrations across glacial-interglacial periods.

The knowledge gap and apparent contradictions in the existing body of literature gets addressed in the next section. However, I have added a transitional sentence to make the transition of ideas smoother. Thank you.

Line 42: clarify that export of organic matter and carbonate is from the surface ocean to the deep ocean or ocean floor

Thank you. This has been fixed.

Lines 85 and 102: For the equations, the author should use variables in place of the numbers, then define the variables in the text. For example, rather than writing 149,000,000 km² in the denominator of equation 1, use the variable A for area. After describing the equations, then state what values or ranges of values were used to parameterize the equations, and finally the solution to the equation. This will make it easier for the reader to read and interpret.

Thank you for pointing this out. I have formalized the equations with variables defined in the text.

Line 139: Is this supposed to read, “shales *and* oil sands”?

Yes. Thank you. Corrected.

Lines 233-236: The author writes that the dilution of radiocarbon-dead CO₂ in the atmosphere could have been complemented by other terrestrial sources such as subglacial paleosol oxidation, permafrost-bound organic carbon oxidation, and by volcanic emissions due to unloading of the lithosphere. Base on the cited literature therein, can the author make some estimates about the relative contributions of each of these processes to increasing atmospheric CO₂ in the wake of glaciation?

At the moment, our quantitative constraints are too rudimentary. Even the quantitative constraints for today’s carbon cycle are still “emerging” as explicitly mentioned by Hilton and West (2020). However, based on the cited modeling studies, the following is stated in the

manuscript: “With this, a plausible scenario for releasing kerogen-derived CO₂ to the atmosphere that could account for a 30-60 ppm rise during the glacial-interglacial transition encompassing an area equal to or less than the terrestrial extent of the Laurentide Ice Sheet is identified.” In the author’s opinion, this is the best we can say at the moment for how much kerogen oxidation may have impacted atmospheric CO₂ rise during deglaciation. Due to the limited uniqueness of the geochemical parameters (e.g., ¹³C and ¹⁴C for permafrost and kerogen) simple geochemical models will not suffice in deconvolving the source mechanisms (auxiliary lines of clues however do point towards kerogen, as elaborated in the manuscript). Therefore, the author suggests basic research directions as elaborated in the text on how to proceed. All in all, the megascale spatiotemporal trends in the deglaciation of North America across the geologic boundary between the Canadian Shield and the adjacent sedimentary basins suggest a connection – a compelling piece of evidence that has seemingly gone overlooked!