

Review of: “Ideas and perspectives: Emerging contours of a dynamic exogenous kerogen cycle”

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Overall impression:

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.

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).

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 ¹⁴C content from the LGM to present, which is consistent with input of radiocarbon-dead CO₂ to the atmosphere. The authors should elaborate on how erosion and weathering intensity changes across glacial-interglacial periods (e.g., Schachtman et al., 2019).

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 CO₂ 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).

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 ~60% and ~29 PgC/kyr is oxidized.

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.

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.

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.

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.

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.

Line 24: need reference for 15 million PgC kerogen

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.

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).

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.

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.

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

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.

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

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?

References cited:

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