

Dear Reviewer,

Thank you for your feedback and input. Ideas and perspectives articles in Biogeosciences “report new ideas and novel aspects of scientific investigations within the journal scope. Manuscripts of this type should be short (a few pages only).” This contribution is not written as nor intended as review. Other publications (e.g. Petsch, 2014) already serve this purpose. This work presents a simple and bold hypothesis of broad significance for atmospheric chemistry and the organic carbon cycle that is supported by the synthesized literature referenced within.

Yes, previous work (e.g. Petch, 2014; Bolton et al., 2006) discusses the million-year timeframe over which the kerogen cycle is relevant. The refocusing on kyr-atmospheric CO₂ variability with emphasis on the Ice Ages and their possible connection with kerogen oxidation is a new idea which has thus far not been enunciated in the literature. This important aspect was not properly expressed in the manuscript and will be stated in the revised version for readers to understand the significance and novelty of the presented “Ideas and perspectives”.

Previous work does consider erosion, temperature, precipitation etc. (e.g. Bolton et al. (2006)), and yes, will be brought up in the revised manuscript as well. However, recent insights highlighting the dynamic role of glacial activity on kerogen oxidation (e.g. Horan et al., 2017) and kerogen reburial (see references in Blattmann et al., 2018) make this an exciting possibility for explaining atmospheric CO₂ increase in the wake of waning glacial episodes affecting vast areas of high latitude area as outlined in this contribution. Figure 2 will be edited to make the hypothesis illustration clear in its meaning with respect to “open” and “closed” exogenous kerogen cycle.

Discussion of weathering efficiency and intensity are evidently key aspects in kerogen oxidation. While it is somewhat difficult to follow your (the reviewer's) exact line of thinking (i.e. distinguishing between physical and chemical weathering), chemical weathering efficiency (i.e. oxidation) of kerogen is greatly increased in glacial forefields with high surface area substrate left behind by glacial grinding and further fining driven by frost shattering (Horan et al., 2017). Alternatively, kerogen can also be incorporated in biomass by way of microbial activity consuming this fossil carbon (Petsch, 2014). The apportionment between fossil carbon entering the atmosphere directly or by first transiting the biosphere is subject of ongoing debate and complicates this discussion. In this context, kerogen reburial efficiency is a simple conceptual metric to view the kerogen cycle and its relevance for atmospheric chemistry, as kerogen that is reburied has no communication with (relatively) rapidly exchanging surficial carbon pools and therefore no effect on atmospheric CO₂. Ultimately, seawater osmium isotope signatures (and other trace elements) may provide a key constraint in quantifying kerogen reburial on a global scale with the amount of exhumed carbon contained in kerogen expressed as the sum of carbon in reburied kerogen and degraded kerogen. If kerogen exhumation is approximated as constant, osmium isotopes (and other trace elements) can then be used to constrain global levels of kerogen decay on the Earth's surface through time, thereby giving us the key to kerogen reburial.

The question as to what extent weathering efficiency and weathering flux vary across inorganic and organic carbon cycles is a key question that needs to be addressed if we are to achieve a holistic understanding of the carbon cycle. To this end, Blattmann et al. (2019) and Horan et al. (2019) have presented regional studies from Taiwan and the Mackenzie River, respectively, that provide integrated carbon budgets based on chemical weathering of silicates, carbonates and quantitatively distinguish between sulfuric and carbonic acid weathering and combine these with estimates of kerogen oxidation. More such studies (to the knowledge of myself there are only two such regions in modern-day geologic space that are so rigorously characterized) are needed but is clearly beyond the scope of this “Ideas and perspectives” article (newly appeared Horan et al. 2019 will also be cited to the revised manuscript). However, yes, going back in time we need more constraints on these chemical weathering

pathways and their fluxes. In this context, I argue that kerogen oxidation is a particularly dynamic component that appears promising to lay strong future research focus.

In this context, I would also like to add reference to Zeng (2003) who proposed the “Glacial Burial Hypothesis”, which contains parallels to the hypothesis presented in this contribution. Zeng (2003) proposes the release of ice sheet-covered soil organic carbon in the wake of glacial episodes. One main problem that the idea faces is the bulldozing activity of glaciers leading to diminished presence of such soil organic carbon preserved under the ice (see Zeng (2007)). Overall, the modeling results of Zeng (2003, 2007), if soil organic carbon is reinterpreted as kerogen, lend further support to the plausibility to the idea of kerogen oxidation driving a substantial part of atmospheric CO₂ increase in the wake of glacial episodes. However, in the hypothesis presented here, the bulldozing effect of ice and erosion of bedrock would produce a large supply of glacially ground rock, with kerogen contained within subject to oxidation once transported to the glacial forefront or more quickly exposed and “defrosted” during glacial retreat, thereby enhancing the overall effect. Another “alternative” land-based hypothesis is discussed in the volcanic degassing hypothesis (e.g. Sternai et al., 2016), which although similar in some respects (e.g. dilution of atmosphere with ¹⁴C-dead CO₂), is unable to account for the precise response of atmospheric CO₂ to orbital forcing (see Roth and Joos, 2012). Ocean-based hypotheses suffer from complicated, contorted explanations that cannot fully account for variations in carbon isotopic composition (¹³C and ¹⁴C) of atmospheric CO₂ over glacial-interglacial cycles (Broecker and Clark, 2010; Schmitt et al., 2012). Overall, the simple and, in my opinion, elegant hypothesis presented here appears well-positioned to explain a significant part of the enigmatic CO₂ variability across glacial-interglacial cycles.

This work enunciates the possibility of kerogen oxidation as a major driver in atmospheric CO₂ increase in the wake of glacial episodes. This hypothesis of kyr-timescale-relevance for this chemical weathering pathway is substantiated by several lines of independent evidence synthesized in this contribution including CO₂ carbon isotopic composition (¹³C and ¹⁴C), timing of CO₂ increase, seawater osmium record, kerogen oxidation studies, observations of kerogen reburial, and modeling results presented in other studies. Furthermore, bringing together the currently very small body of pioneering literature that has begun to sprout on this subject, a perspective is given on the relevance of kerogen oxidation for atmospheric CO₂ variability in the deep geologic past. One common denominator appears to emerge: the contours of a dynamic exogenous kerogen cycle!

I thank the reviewer for his/her time and effort and look forward to future discussions and strengthening the manuscript based on this input.

Sincerely,
Thomas Blattmann
18.09.2019 Yokosuka

References

- Blattmann, T. M., Letsch, D., and Eglinton, T. I., 2018, On the geological and scientific legacy of petrogenic organic carbon: *American Journal of Science*, v. 318, no. 8, p. 861-881.
- Blattmann, T. M., Wang, S. L., Lupker, M., Märki, L., Haghypour, N., Wacker, L., Chung, L. H., Bernasconi, S. M., Plötze, M., and Eglinton, T. I., 2019, Sulphuric acid-mediated weathering on Taiwan buffers geological atmospheric carbon sinks: *Scientific Reports*, v. 9, no. 1, p. 2945.
- Bolton, E. W., Berner, R. A., and Petsch, S. T., 2006, The weathering of sedimentary organic matter as a control on atmospheric O₂: II. Theoretical modeling: *American Journal of Science*, v. 306, no. 8, p. 575-615.
- Broecker, W., and Clark, E., 2010, Search for a glacial-age ¹⁴C-depleted ocean reservoir: *Geophysical Research Letters*, v. 37, no. 13.
- Horan, K., Hilton, R. G., Selby, D., Ottley, C. J., Gröcke, D. R., Hicks, M., and Burton, K. W., 2017, Mountain glaciation drives rapid oxidation of rock-bound organic carbon: *Science Advances*, v. 3, no. 10.
- Horan, K., Hilton, R. G., Dellinger, M., Tipper, E., Galy, V., Calmels, D., Selby, D., Gaillardet, J., Ottley, C. J., Parsons, D. R., and Burton, K. W., 2019, Carbon dioxide emissions by rock organic carbon oxidation and the net geochemical carbon budget of the Mackenzie River Basin: *American Journal of Science*, v. 319, no. 6, p. 473-499.
- Petsch, S. T., 2014, Weathering of organic carbon, *in* Holland, H. D., and Turekian, K. K., eds., *Treatise on Geochemistry*: Oxford, Elsevier, p. 217-238.
- Roth, R., and Joos, F., 2012, Model limits on the role of volcanic carbon emissions in regulating glacial–interglacial CO₂ variations: *Earth and Planetary Science Letters*, v. 329-330, p. 141-149.
- Schmitt, J., Schneider, R., Elsig, J., Leuenberger, D., Lourdantou, A., Chappellaz, J., Köhler, P., Joos, F., Stocker, T. F., Leuenberger, M., and Fischer, H., 2012, Carbon isotope constraints on the deglacial CO₂ rise from ice cores: *Science*, v. 336, no. 6082, p. 711-714.
- Sternai, P., Caricchi, L., Castelltort, S., and Champagnac, J.-D., 2016, Deglaciation and glacial erosion: A joint control on magma productivity by continental unloading: *Geophysical Research Letters*, v. 43, no. 4, p. 1632-1641.
- Zeng, N., 2003, Glacial-interglacial atmospheric CO₂ change — The glacial burial hypothesis: *Advances in Atmospheric Sciences*, v. 20, no. 5, p. 677-693.
- Zeng, N., 2007, Quasi-100 ky glacial-interglacial cycles triggered by subglacial burial carbon release: *Climate of the Past*, v. 3, no. 1, p. 135-153.