

Response to Reviewer Comment 2

I found this a novel, interesting, and generally well-written paper that argues that weathering of kerogen-containing lithologies exposed at the surface after continental deglaciation may prove to be a significant source of carbon dioxide to the atmosphere, and one which is of particular significance in terms of climate forcing. Whilst the argument is supported more by calculations and logical arguments than it is by direct measurements and observations, I still found it fairly compelling – to the point that I am convinced that the idea is worth pursuing via in situ measurements and carefully designed and executed experiments. It is certainly worth publishing if only to give exposure to the idea and to stimulate discussion and field monitoring of natural carbon emissions from kerogen sources as well as to provoke detailed modelling of likely CO₂ fluxes from kerogen sources on geologically and climatically relevant timescales (and detailed mapping (in time and space) of likely source regions for kerogen-derived greenhouse gas emissions). Some articulation of likely important source regions for such emissions would be a valuable contribution to the paper and the broader scientific discussion that it is likely to stimulate. It is certainly a paper that gave me a kick and made me challenge my prior assumptions and thinking about climate/greenhouse gas emission linkages. On that basis I think it is worthy of publication, although, at the detailed level, I think the text needs a thorough edit. Below I have provided a set of suggestions that I hope might help with this.

Dear Reviewer,

Thank you for your thorough and constructive review. It is surprising how poorly constrained CO₂ fluxes emanating from kerogen are. Monitoring of such would provide valuable baseline data for understanding our Earth system. And I agree, articulating the possible source region (western Canada) is useful for pinpointing our discussion and focusing future research efforts.

Finally, I am so happy that this article gave you a “kick”! This novel idea presented with a blend of interdisciplinary literature in this “Ideas and Perspectives” format provides a platform to challenge and progress our thinking!

Sincerely,

Thomas Blattmann

Line by Line Review (i.e. suggested changes to the text that I think would improve it's readability and clarity):

9: suggests that this largest pool

Corrected. Thank you.

10: interglacial cycles and beyond

Corrected. Thank you.

15: in western Canada contributed in a major way

Corrected. Thank you.

25: subjected 150 PgC/kyr.....

This is present tense as it is an ongoing process. This sentence has been simplified following the next comment.

26: of this geologically ancient carbon and other closely connected surficial carbon pools into the atmosphere (Hedges and Oakes, 1997)

This sentence has been simplified to make it more readable. Thank you.

30: compensatory roles

Thank you for your correction.

32: as physical erosion is followed by riverine transport

This is part of a subclause, so I think the grammar is correct.

37: This contribution hypothesizes.....atmospheric CO₂ increases during glacial terminations

Thank you for your suggestion and correction. Implemented.

42: and (4) the export of organic matter and carbonate from the surface waters of the oceans - Question – export to where?

This has now been specified. Thank you:

... from the surface to deep waters and sediments of the oceans ...

43: During deglaciation

Thank you for the suggestion. Implemented.

44-45: an increasingly voluminous terrestrial biosphere (but is it mass or volume that matters here?).....is inferred to have controlled an increase in the stable carbon isotope ratio of dissolved organic carbon in ocean waters.

Here, I did mean dissolved inorganic carbon. This should be correct as is.

In order to avoid misunderstanding, the reference to volume has been removed and improved to: "...an increasingly large terrestriospheric carbon pool ...". Thank you.

46: carbon pools changing in size at the same time as stable carbon isotope fractionation occurs, as carbon is exchanged between pools such as the terrestrial biosphere and pedosphere (see also Zeng, 2003,2007)

Thank you. Your suggestion has been fully implemented.

47: In addition, during times of most rapid CO₂ increase during transitions from glacial to interglacial periods, negative stable carbon isotope shifts in atmospheric CO₂ occurred (Fig.3; Smith et al., 1999; Schmitt et al., 2012).

Thank you for these corrections. Helps a lot to receive these.

49: This is a strong indicator that respired organic carbon was acting as a direct source to the atmosphere (Bauska et al., 2016).

Thank you. This was implemented with a small modification: This is a strong indicator that respired organic carbon acted as a direct source to the atmosphere (Bauska et al., 2016).

51: that was depleted in or devoid of radiocarbon.....thereby limiting the potential contributions from a modern biospheric organic carbon source. BUT does it actually limit the contributions, or just their detectability?

In my understanding, it does limit the contribution size, because biospheric carbon and kerogen-derived carbon represent extreme end members in natural abundance ¹⁴C. Detectability is another matter, but the trends in atmospheric chemistry (CO₂ ppm, δ¹³C, δ¹⁴C) are quite large.

53-54: deep ocean was the predominant source for carbon transferred to the atmosphere during glacial terminations

Thank you for these corrections. Implemented.

55-56: please explain what you mean by "requires a complex overlay of processes to reconcile"

To maintain flow in the text, I have simplified the statement to: However, this hypothesis appears inconsistent with the negative fluctuation observed in the ¹³C fingerprint of atmospheric CO₂ (see discussion in Broecker and McGee, 2013).

58-59: suggest that the release, via kerogen oxidation, of CO₂ to the atmosphere during deglaciation contradicts or complements the commonly held notions of a strictly increasing terrestrial organic carbon pool and major changes in CO₂ exchange between the ocean and the atmosphere.

This sentence has been completely rearranged.

58-60: needs some supporting references

References have been added. Thank you.

62: accumulated from....supports the idea that.....was more extensive

Thank you very much. Corrected.

63: cold interludes in Earth history during which glacial erosion and ice rafting dominated (BUT – what did they dominate?)

I replaced this with a better phrase: “was widespread”. Thank you.

64: reburial in high latitude glaciated regions...

Thank your for this improvement.

66: kerogen cycle by keeping.....

Thank you. Corrected.

69: frost shattering, together with the retreat of glaciers, exposes.....thereby accelerating oxidation and the release of kerogen-derived CO₂.....declines into an interglacial period.

Thank you. All of these points have been corrected.

73. Analogously, glaciers have also been invoked as agents for accelerating chemical weathering of carbonate and silicate minerals by increasing sediment yield and creating a reactive substrate with high surface area. Carbonate weathering can be a source of CO₂ to the atmosphere when sulphuric acid is the solvent involved. (I assume this is a by product of sulphide mineral (pyrite) oxidation? Please clarify this)

Thank you for these improvements, and yes, this is the byproduct of sulfide mineral oxidation.

77. direct conversion to CO₂ leads to considerable....

Thank you for this improvement.

78-79: This is a process by which CO₂ can be injected directly into the atmosphere and impact glacial-interglacial cycles (Figure 2)

Thank you for this improvement.

90: faster than those of the average Earth surface

Thank you. Implemented.

95: also proposes the oxidation of overridden soil organic carbon during and after glaciation and calculates a 600 PgC release....

Thank you for your careful reading. I have implemented a modified version of your suggestion. In my opinion, XX et al. refers to multiple authors, so is grammatically equivalent to “they”: Similarly, modeling by Simmons et al. (2016) also propose the oxidation of overridden soil organic carbon subsequent to deglaciation...

115: fluxes an order of magnitude greater than the global average

Thank you. Implemented.

120-127: Are the kerogen oxidation and oceanic release mechanisms for CO₂ increase mutually exclusive? You make it sound as though they are, but I’m not clear why that would be the case.

Thank you for pointing this out. I have fixed this area by removing a reference that was very poorly chosen by me which alluded to oceanic release in a confusing way. The text is now

straightforward and of course they (kerogen oxidation and oceanic CO₂ release) operate independently of one another.

115: oxidation fluxes an order of magnitude greater than the global average can be sustained for millennia after deglaciation.

Thank you. I have implemented this.

134: extending across much..

Thank you. Corrected.

137: within the Province of Alberta

Thank you. I have corrected this.

139: Cretaceous soils and the oil sands.....the latter enhanced by aerial exposure across palaeosurfaces

Thank you. I have corrected this.

140: over tens of thousands

Corrected. Thank you.

145: Laboratory incubations designed to simulate CO₂ respiration from bituminous materials reveal fluxes that are markedly higher than those associated with oxidation of rock disseminated forms of kerogen (Table 1)

Thank you for this improvement.

147-148: at rates 1-2 orders of magnitude higher than those reported for rock disseminated kerogen, and 3 orders of magnitude greater than the average for Earth's surface.

Thank you for these corrections. Implemented.

152: when temperatures of subaerially exposed outcrops of oil sands reach 60°C

Thank you for this improvement.

153: experiments on bitumen

Thank you. Corrected.

155-156: that investigated the oxidative decay of hydrocarbon fractions also suggest similarly high fluxes when scaled to natural systems, even though these studies were conducted over periods of only a few weeks

Thank you for this improvement.

158: fluxes reported by Chang and Berner (1998,1999)...an underestimate

Thank you for these corrections.

160: CO₂ can be released under anaerobic conditions

Thank you this has been corrected.

162-163: what is meant by a super-carbon source terrain? Maybe useful to identify some specific examples

I have added a hypothetical definition to the concept of: "super carbon source terrains": *areas laced or covered with coal, bituminous materials, etc.*

163: during glacial-interglacial transitions. This statement makes me wonder whether you have given any thought to what happens in interglacial-glacial transitions. Are you just assuming that overriding by ice shuts off exchanges between substrate and atmosphere – but would that necessarily preclude gas transfer through permeable substrates along the hydraulic potential gradient from thick ice in the interior to thin ice at the margins where gas could escape to the atmosphere?

I have improved the wording in this part. Previously, it read like there was a conflict, where there was none. Now the paragraph ends with: *Overall, it is conceivable that super carbon source terrains (hypothetically, areas laced or covered with coal, bituminous materials, etc.) across western Canada could supply an overproportionate quantity of radiocarbon dead CO₂ to the atmosphere during glacial-interglacial transitions.*

164-5: Sheet had retreated.....and was exposing

Thank you for this correction.

167: <= 300 years after....Sheet advanced onto the Canadian Shield, suggesting reduced decay of...

Thank you. I have adopted a change modified after your suggestion.

170: Fennoscandian Ice Sheet

Thank you for this correction.

173: is chemically recalcitrant

Thank you for this improvement.

175: was the most extensive element of the cryosphere that waxed and waned across the continents.....and, in conjunction with its lithological underpinning...2007),

Thank you for these improvements.

178: estimates of CO₂ fluxes.....and there is considerable uncertainty in our current state of knowledge

Thank you for these corrections.

179-180: weathering studies that provide estimates of CO₂ fluxes from bedrock-derived kerogen under relevant environmental conditions and over appropriate timescales are lacking

Thank you for these improvements. Implemented.

182: high resolution reconstructions of changes in land ice extent and the lithologies of bedrock and glacial till being exposed by glacial retreat can, in theory, quantitatively disentangle the contribution of kerogen-derived CO₂ to the atmosphere during glacialinterglacial transitions

A question here – can isotopic fingerprinting methods distinguish between the kerogenderived CO₂and CO₂ from other potential sources?

Thank you for this correction. Implemented.

Other organic sources can only distinguished if they contain radiocarbon. In the case of old permafrost, this may not be the case. However, detrital kerogen redeposition, osmium isotopes, rhenium, iodine isotopes, etc. offer complementary tools to disentangle the carbon isotope record.

189-90: Also important are the bedrock lithology and regolith composition

Thank you for this correction.

192: increasingly suggests that...

Thank you for this correction.

194: increased the flux.....Over Earth's history, on 10⁹ year timescales the reburial efficiency of kerogen presumably varied....

Thank you. These corrections have been implemented.

198-199: O₂ on 10⁶ year timescales

Thank you. Corrected.

200: to understand changes in atmospheric chemistry through geologic time...

Corrected. Thank you.

201: the changing efficiency of the reburial of kerogen needs to be evaluated

Thank you for your improvement.

204: geospatial variability in what ?

This has been improved to: "uneven spatial dispersal". This captures the meaning much better in referring to the sedimentation behavior.

205: for quantifying, and establishing the importance of the reburial of kerogen in recent times, it's utility diminishes quickly for strata that pre-date the Last Glacial Maximum owing to it's radioactive decay.

Thank you for these changes. I have implemented modified changes.

210: isotopic shifts at the beginning of interglacials that are attributable to kerogen oxidation.....

Thank you. I have made modified improvements.

211: consistent with the hypothesis presented here

Thank you for this improvement.

216: the hypothesis presented proposes

Thank you. Implemented.

218: the rate of decrease of ^{14}C CO₂ subsided.....mirrored by changes, during deglaciation, in the lithologies of the Canadian Shield that were exposed at the surface, which contain relatively minor amounts of reactive kerogen.

Thank you for these improvements. I have adopted modified changes.

220-...The coincidence in time of global trends in atmospheric chemistry with spatiotemporal patterns in the distribution of freshly deglaciated terrain.....suggests that a burst (or bursts) of respired CO₂ contributed to the characteristic deglacial increase in atmospheric CO₂.

Thank you. I have implemented these improvements.

224: soil and vegetation taking hold on the deglaciated landscape

Thank you.

228: patterns of glacial retreat that expose glacially ground, kerogen-rich or even bituminous parent material.

Thank you.

230: have been proposed to explain CO₂ increases

Thank you.

232: retreat, and the oxidation of finely ground kerogen, provide.....

Thank you.

234: such as the oxidation of subglacial paleosols and permafrost-bound organic carbon....and by volcanic emissions triggered by deglacial unloading of the lithosphere

Thank you.

243-4: accelerated oxidation of ancient terrestrial organic carbon at glacial terminations...

Thank you.

246-7: the hypothesis presented...

Thank you.

250: timescales, entirely....

Thank you.

252: exposed fresh weathering profiles....

Thank you.

255-6: and increased supplies of ground kerogen

Thank you.

268: provide a strong incentive

Thank you.

269: kerogen cycle in glacial-interglacial climate patterns

Thank you. I would however like to avoid the word climate right here in direct connection with kerogen cycle. As Hilton and West (2020) state: "CO₂ sources might also be sensitive to climate indirectly through facilitation of oxidative weathering by glacial processes." I agree with this and this is also expressed in Figure 2.

270-271: may provide an outlook for geological processes that is relevant today

Thank you.

271: (Steffen et al. 2018) is missing from the reference list

Thank you for checking.

Figure 1 caption: showing the fixation of atmospheric CO₂ by both terrestrial and marine primary productivity.....constitutes the total organic carbon burial into the endogenous kerogen pool.

Thank you for all these excellent improvements and careful corrections. The manuscript has greatly improved as a result of your hard work.