

Clim. Past Discuss., referee comment RC1
<https://doi.org/10.5194/cp-2021-28-RC1>, 2021
© Author(s) 2021. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on cp-2021-28

Murat Aydin (Referee)

Referee comment on "Northern Hemisphere atmospheric history of carbon monoxide since preindustrial times reconstructed from multiple Greenland ice cores" by Xavier Faïn et al., Clim. Past Discuss., <https://doi.org/10.5194/cp-2021-28-RC1>, 2021

This paper presents new CFA CO data from five different ice cores. The authors put in a substantial amount of work into the measurements and analysis over several years. The effort put into methods development and calibration is especially impressive. The final product (composite baseline CO record) will provide useful constraints for different disciplines of science. However, I do have reservations about certain aspects that requires revisions to the paper. I do not think the revisions will impede a timely publication. Immediately below is a very brief summary of my reservations, followed by more detailed general comments under two headings, then more specific line by line comments.

I still have suspicions about the spikes being entirely due to in situ production. I'm not convinced by the arguments for omitting the Tunu record from the final composite product. I think it is possible all records including the firn may be somewhat elevated above true atmospheric CO levels. The manuscript provides some discussions on possible mechanistic explanations for in situ production of CO, but does not make tangible progress. From an organizational perspective, it would help if the references to the supplement from the main text specifies exactly which section in the supplement is being referred to.

Murat Aydin

CO spikes in the CFA records

The spikes are reproducible with repeat measurements from the same ice core in the

same system. They are not photochemically produced in the ice after collection. It also doesn't seem likely that spikes of these magnitude can be produced during the melting. Following this process of elimination, in situ production is offered as the only plausible explanation for the spikes. To me, the term in situ production implies the type of observations from the deeper sections of NEEM and NGRIP ice cores: the amplitudes of the peaks and the mean levels grow with depth due to slow but continual CO production over long periods. However, the CO spikes seem to be present in the shallowest sections of all ice cores, presumably all the way up against the close-off depths. The authors state the variance (MAD) does not increase with time during the last 200-300 years. I'm struggling to envision where this production happens and over what kind of time frame? Can this happen without a firm component?

Figs. 7, S7, S16, S17 are central to the in situ production argument. It is important to show duplicate CFA measurements of the same core display the same spikes and the discrete measurements agree with the mean of the CFA data and not the baseline. Some suggestions/questions about these figures:

Fig. 7: It would be useful to see the mean of the PLACE CFA record in this figure.

Fig. S7: How were the CFA-based CO concentration corresponding to the discrete measurements calculated? This can be stated in the text or the caption.

Figs. S16, S17: The comparison of IGE vs. DRI CFA data suggests the spikes may not entirely be related to in situ production. There is higher variance in the IGE record compared with the DRI one. This is especially evident above 110-120 m, resulting in the picture we see in Fig. S17, which shows baselines in much better agreement than mean levels above 115 m. Clearly this is not just a smoothing issue. So, there appears to be some contribution to the spikes from either the analytical method at IGE or something happening during the sample prep stage at the IGE, or what else? Post-coring entrapment is mentioned as a possible mechanism. Is there a way this can happen in one lab vs. the other, or more in one lab vs. the other? What are the respective ambient temperatures in the freezers where the melts conducted? Are there corresponding spikes, or even mild elevations, in the CFA methane data that may suggest entrapment of lab/modern air?

Interpretation of baseline CO as an atmospheric record

The main point of section 3.3 and its subsections is that, aside from the Tunu record, the baselines of the other CFA records more or less represent true atmospheric variability of CO. I think section 3.3 is perhaps more complicated than it should be and the paper needs more nuance in discussion of the final composite record. Specifically, the possibility that

the entire ice core record and the bottom of the firn being impacted by some level of production should be mentioned.

One thing I struggled with is the decision to not include the Tunu record in the final compilation. The first argument for rejecting the Tunu record has to do with analytical smoothing due to a combination of lower accumulation rate at the site and the lower resolution CFA system at DRI relative to the IGE system. The argument makes sense qualitatively, but how large can this effect realistically be? Fig. S17 shows the difference between mean and baseline for the PLACE records is about 20 ppb. I would expect the impact of analytical smoothing on the baseline at Tunu would be much smaller. Peak attenuation percentage does not translate into same percentage elevation in baseline. More importantly, the Tunu record doesn't really look biased high from the other records in Fig. 1 (hard to evaluate the full record in Fig. S15), except for a brief period around 1810-1820 and again around 1710 (is the accumulation rate lower during these periods?). Since I do not see the Tunu record as an obvious outlier in Fig. 1, I consider the arguments about why in situ production could impact Tunu baseline but not the other four records to be of secondary importance. If these were first order processes, I would expect the Tunu record to be clearly offset from the others. Finally, I don't understand why the Tunu baseline in Fig. 1 bottom panel is not extended all the way through 1960. The large peak around 1930 can be treated as another missing section if that is the reason. Is that large peak related to an analytical issue?

The paper suggests CO might be produced from TOC, mostly relying on an earlier paper by Fain et al. (2014), although the language is tentative and qualitative regarding CO spikes being produced in situ from TOC spikes (see specific comments). On the other hand, there is a strong relationship between smoothed CO, TOC, accumulation rate data from Tunu (Fig. 5), followed by a seemingly conflicting statement about baselines not being correlated (Fig. 6) (see specific comments). It is also stated that PLACE does not display a similar relationship despite higher TOC levels. However, the accumulation rate is high and constant there and since the measured TOC levels might change after deposition, it is not clear how to interpret PLACE and Tunu data together. If one is convinced CO production happens in the ice from TOC, then it gets really difficult to argue Tunu with lower TOC incorporates more CO production than PLACE. Collectively, these partially contradictory lines of evidence make me think CO production might have a firn component, which may be impacting all ice core and firn records from Greenland. This does not necessarily imply any major change to the discussion of the composite ice core record since they already acknowledge this is an upper limit. The firn record on the other hand currently serves as a validation of the composite record as representative of true atmospheric CO, which I find myself questioning based on the ice core evidence presented here.

The last paragraph of section 3.3.2 and related figures about the relationship between TOC and ammonium does not contribute much to the paper in its current form. A clear explanation of how this all relates to in situ CO production is necessary, or it can be significantly reduced or mostly omitted.

Section 3.3.4 is also problematic. The main point of this subsection is that the long term record from Tunu can yield an atmospheric record. This directly contradicts with many of

the previous arguments used to disqualify the Tunu record from the interpretation of the last 300 years. I already stated above that I do not agree with the logic to reject the Tunu data from the short term interpretation, so I actually don't have any major issues with what is being said here, although it would be nice to see the actual plots of MAD for NEEM and Tunu. The last sentence about peroxide and the associated supplemental figures, while interesting, are tangential and can be omitted. TOC, ammonium, peroxide, and how this all relates to CO production in the ice sheet could perhaps be addressed in a separate paper that focuses on possible chemical mechanisms.

I am puzzled by the discrepancy with the previously published discrete Eurocore data. The only thing I can think about is the system blank applied to the Haan and Raynaud measurements. Is it known if the blank correction was higher for shallower sections? Another thing that comes to mind is to check if there is any long term increasing trends in terrestrial dust or sea salt-related proxies over the depth ranges corresponding to 1825 onward from PLACE. The running hypothesis has been that any in situ effects on CO should be associated with TOC. However, if TOC is not conservative, meaning if the measured TOC levels have been heavily altered by post-depositional processes, it might be more useful to think in terms more conservative proxies of ice impurities.

Specific comments:

These are listed in the order that they appear.

Line 14: Where does the 20 cm/y comes from?

L44: Would be helpful to state the mean background CO.

L71: CH4 typo.

L85-90: The last three sentences may be better suited for the end of the paper, in section 3.5.3 or conclusions.

L201-204: How is the relationship between CH4 solubility and CO solubility quantified?

L219-220: Incomplete sentence.

L239-240: Are these tests a good analogue for melting in the CFA system?

L285-290: The comment about not comparing the amplitude of variability between D4 and Tunu due to concerns about smoothing is undermined by the later sentence that states all cores exhibit similar MAD values for the 1700-1950 period. I'm not sure why the sentence about not comparing D4 to Tunu is needed.

L310-313: The validity of the Haan and Raynaud data from shallower depths is questioned later in the manuscript. Haan and Raynaud also use larger samples. The reference to Haan and Raynaud work here can be omitted.

Fig. 3: Perhaps change the x-axis label to "Time after melt starts".

L355: Was this a significant covariation or not? Often but not always is uninformative. It is never the case that all peaks match anyway.

L368: The argument here is based on a comparison of Fig. 2 to Fig. 4. These figures show ~2 m sections. Is there a way to support this argument with a method that utilizes to the entire cores?

L373: Shouldn't it be >1 yr?

L387-389: We can all understand something different from "often." Is it not possible to quantify this? I can suggest subtracting the mean or baseline then looking at r^2 in a linear regression analysis, for example.

L397-398: This sentence indicates there is a correlation between accumulation rate and TOC baseline at PLACE. This contradicts the sentence on L395, which states there is no correlation between accumulation rate and TOC at PLACE.

L402: Clarify what you mean by "at play"? What is the driving question here? This is where I start lose track of what you are after, hence my general comment above about possibly omitting the ammonium related text and figures.

L414: Reemphasizing the co-location of CO spikes and TOC... It's just hard to really buy into it without an analysis of at least one of the data sets in its entirety.

L423-425: The first sentence says baseline CO does not significantly correlate with mean or baseline TOC. The second sentence says there are similarities in trends and patterns of the same two quantities. The sentences are conveying conflicting messages.

L427-429: This is pretty speculative. If I could see the Tunu record being clearly biased high from the other data sets in Fig. 1, I would be fine with it.

L432-433: I don't see a MAD figure in section 3.1.

L439-440: I'm convinced that analytical smoothing is not a factor for the PLACE baseline. For any other production process, I am not convinced PLACE baseline would not be impacted.

L457: I do not see an extremely sharp increase in the Eurocore data.

L490: How are the composite record and the uncertainty range computed? Not all the cores cover the entire period.

L495-500: I agree with that these baseline CFA records probably provide a reliable upper bound, but where the lower end might lie is debatable. The uncertainty range does not capture the true uncertainty in the lower direction. There should be more cautionary language regarding how low atmospheric CO levels actually could have been in the preindustrial northern hemisphere atmosphere.