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Climate of the Past Discussions

Interactive comment on "High resolution measurements of carbon monoxide along a late Holocene Greenland ice core: evidence for in-situ production" *by* X. Faïn et al.

Anonymous Referee #3

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Manuscript Summary:

This discussion paper by Fain et al presents a new method of continuous analysis of CO concentration in ice cores. Results for CO and supporting trace chemistry from a shallow ice core from the NEEM site in Greenland are also presented and discussed, providing insights into system performance as well as in-situ production of CO in the ice.

Overall assessment:

This is an exciting new technique, and presents the first continuous ice core CO measurements. The OF-CEAS instrument performance for dry air is very impressive, both

in its precision and in its minimal rate of sample consumption. As such, this instrument clearly has tremendous promise for ice core analysis. Unfortunately, the same cannot be said for the full system that includes the continuous ice melter and gas separation. The system CO blanks are too high, variable, and imperfectly characterized at this stage to be useful for investigating the relatively small natural atmospheric CO signals that may be contained in ice cores. The work performed on investigating in-situ CO production in NEEM ice is extensive and new, providing interesting insights on feasibility and possible approaches to reliable reconstructions of CO from ice cores. Reliable reconstructions of past CO is an important long-term goal of the ice core and atmospheric research communities, and the insights about in-situ CO presented here are a valuable step toward this goal. In my opinion this discussion paper needs substantial further revisions, but could ultimately be well-suited for this special issue of CP.

Major comments:

I recommend stating clearly, in the abstract or the conclusion (or both) that at this stage the full system is not suitable for meaningful past atmospheric CO reconstructions from ice cores (unless further system blank characterization is done; see below). Past atmospheric CO signals (such as those described in Wang et al, 2010, Science) are of the same order of magnitude (or even smaller) as the uncertainties currently characterizing the described analytical system. The system would, however, be suitable for identifying ice layers that are promising targets for more accurate discrete measurements of CO and possibly CO isotopes.

While the presented evidence is strong that the measured CO record (specifically, intensity of in-situ CO) is imprinted by the intensity of biomass burning (particularly at Northern high latitudes), the suggestion that this could be used as an integrative proxy for past biomass burning is, in my opinion, over-reaching and should be removed. Other trace chemistry in ice cores (such as BC and NH4 discussed in the manuscript) present much more direct indicators; with CO you have the additional poorly understood process of BB-derived organics serving as a substrate for in-situ CO.

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The procedural CO blanks for the overall system do not seem well characterized.

a) Dissolution should be a very minor effect for CO, whose solubility is very close to that of air. A quantitative estimate of the dissolution effect could be obtained, for example, by taking the well-characterized CH4 dissolution effect (as in Rhodes et al 2013) and considering the CO vs CH4 solubility in pure water.

b) From Table 1, it seems to me that the system blank depends on the CO concentration of the air being analyzed – higher blank for lower CO. This suggests not only CO production (or desorption), but also CO consumption (or adsorption) in the system. A more complete characterization would involve more CO standards, with concentrations ranging up to the high values found in most ice core samples; this should be done if possible.

c) As far as I could understand, neither the "internal loop" nor the "full loop" procedural tests are fully representative of the overall procedural blank, because they include some components that are not in the real sample flow path, and exclude others (such as the melt-plate). While it is difficult to re-create a truly representative procedural blank test with this type of continuous measurement, could a more realistic assessment of the blank be obtained by measuring replicate ice samples on a discrete-sample system that has better-characterized blanks (such as the old Haan et al system or the newer Wang et al system)? This would add confidence to the (now very questionable) ability of the system to capture even the larger past atmospheric trends from the "baseline" levels discussed in Section 3.1.1

d) While it does seem that there is evidence for drilling fluid affecting CO in at least some of the ice, the method of establishing this seems indirect and leaves much ambiguity in interpretation. Instead, could the authors try taking two replicate halves of a dry-drilled ice core section, dipping one of the halves in the drilling fluid, then cleaning and drying it (using regular protocol), and then proceed with cutting and analysis as usual? It seems that this kind of test would give a less ambiguous result. As it stands

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now, the drilling fluid question adds much uncertainty into the discussion of in-situ CO production.

Wording and minor comments:

The paper overall is well written and clear; but I would recommend that one of the native English speakers on the author list takes the time to edit the grammar.

Abstract, line 12. Poor grammar – re-word this sentence

p.2824, line 23. “applying a depression” – do you mean a pressure gradient?

p.2826, line 19. “more than ten” – it would be more precise to state exactly how many

p. 2831, line 7. Is “FWHM” already defined in the paper?

p. 2831, lines 12-13. I don’t understand how two different depth ranges can correspond to the same time interval Fig 3 caption. For clarity, it would be helpful to state here that all the data are corrected for the estimated (and large) procedural blank

Fig 4 and caption. Please add a description of which line represents which tracer. Why not plot more of the data (CO vs BC and NH4)?

p.2831, line 20 – 23. Not that air in closed porosity is older than air in open porosity at the same depth level, so should probably contain lower CO than firn air measurements

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Interactive comment on Clim. Past Discuss., 9, 2817, 2013.