Review of: “Characterization of in situ cosmogenic ^{14}CO production, retention and loss in firn and shallow ice at Summit, Greenland”

by Benjamin Hmiel et al., submitted to The Cryosphere.

This manuscript targets understanding and constraint of the production, movement and retention of in-situ cosmogenic ^{14}C in ice. This is done based on the analysis of ^{14}CO at different depths in the firn, both, in gas from the porous, open firn space (firn air) and the gas trapped in extracted firn/ice samples (firn matrix and bubbly ice below the firn zone, respectively). The authors achieved to perform the highly challenging analysis of ^{14}CO in firn and ice with convincingly high accuracy, which is a fantastic achievement. While the contribution to in-situ ^{14}CO (and total ^{14}C) from production by neutrons is relatively well studied and seems reasonably well understood, more recent findings indicated that the signal from production by deep-penetrating muons via the negative muon and fast muon capturing mechanisms is lower than one would expect based on the literature by around a factor of 5 (Dyonisius et al., 2023). This is a relevant difference and can have important implications on the interpretation of results in a variety of research areas where cosmogenic isotope production affecting the background is an issue. The manuscript therefore strongly focuses to further investigate this discrepancy. A modelling framework, essentially combing a previously established ^{14}C production model (Balco et al., 2008; adapted for a firn/ice matrix) with the firn gas transport model by Buizert et al. (2012) and a new box model to consider retention (or leakage, respectively) of the evolving ^{14}CO partition/fraction to the firn gas was accordingly developed. For the processes and conditions assumed in this model approach and compiled up-to-date atmospheric histories used for input, a close match between model results and the paleo-observational data was achieved but noteworthy, includes a variety of free (tunable) parameters (factors) associated with the various, archive specific (at least partly inter-related) physical and chemical processes and mechanisms involved. The authors show these parameters to be well constrained and thus reasonably close predictions of the expected cosmogenic ^{14}C in-situ contribution to ^{14}CO (and likely also $^{14}CO_2$) should be achievable, which is certainly valuable and beneficial for future studies in firn and ice.

The paper is very well written, the analytical methods are of highest standard (pushing the boundaries) as are the technical aspect of the modeling. However, while the study confirms the previous findings of lower-than-expected contribution from the negative muon and fast muon capturing mechanisms, it needs to be seen if a revision of the respective production rate estimates is required or if a lack of understanding in many of the complex (and directly related) processes in ice and firn currently remains the more likely explanation. My main concern is linked to this last point (see details below), and I suggest the manuscript to be published after minor reviews.

Main issues

General:

The topics covered by the manuscript, from the analytics to the postprocessing of measured data as well as interpretation, are manifold and rather complex. Therefore, and although the authors already did a great job in writing, the manuscript is challenging to read and comprehend. What I struggled most with, was to keep the overview what model parameters/input and mechanisms are well (or reasonably well) determined based on previous studies and which are introduced factors, required to allow matching of model results with the data (model tuning factors; to just name some examples e.g. R, f_{u-}, f_{uf} or factors introduced to account for (additional?) uncertainty like F_n). I thus suggest providing an overview table, where the relevant parameters and reconstructed input (e.g. $P_n(0)$, “baseline” atmospheric [^{14}CO]) is summarized including the relevant description and some associated information (e.g. uncertainty).

Such an overview would not only facilitate reading, but also be beneficial for the reader to understand if a tight match between model result and data or a well constrained factor is largely the result of an in-depth understanding of processes and mechanisms at play or at least partly the result of a sufficient high number of free parameters allowing for tight model tuning. With “processes and mechanisms at play” I hereby refer to the physical and chemical processes involved and happening in the ice. For the different species, both in the gaseous (e.g. CO, CO_2, CH_4) and liquid phase (e.g. DOC) the following come to mind: (i) the specific chemical reaction mechanisms and reaction kinetics on ice surfaces/in quasi-liquid-layers, maybe associated with fractionation and considering equilibria in the partitioning of in-situ ^{14}C into different species (e.g. CO, CO_2, CH_4, DOC) potentially also temperature dependent, (ii) the diffusion of gases in ice, which is certainly different from the diffusion of DOC (and also its releases into the porous open space of the firn), (iii) snow and firn metamosrphism (i.e. recristalisation), (iv) the potential effect of impurities in ice on ^{14}C production rates, (v) the gas transport in the firn and firn ventilation, etc.. Some of these points are more or less thoroughly addressed and discussed in the current manuscript while others are not mentioned. For this reason, I suggest that a revised version of the manuscript aims to better clarify and distinguish the level of process/mechanism understanding and the likelihood that a lack thereof might (or might not) explain the observed discrepancy, e.g. between the observed ^{14}CO in ice and the one expected based on previous determinations of ^{14}C production rates from studies in quartz.

The authors should note that for in-situ cosmogenic ^{14}C analysis in quartz the analytical procedures and techniques are very well established and a very large number of studies exist, the use of reference standard reference materials for inter-laboratory comparison is common practice (e.g. Lupker et al., 2019; Nichols et al., 2022). Generally, the analysis in quartz is likely a more direct measurement than in ice, because potential processes in the archive (i.e. quartz) are assumingly less and easier to understand compared to the many (not fully understood factors) in firn and ice discussed in the manuscript and supplemented in the paragraph above. Therefore, statements like in line 614 ff. “…our results also indirectly confirm … that muogenic ^{14}C production rates in ice are several times lower than what would be predicted from studies in quartz – a puzzle that currently lacks a good explanation.” should be put a bit more into context (also see line 42 in the abstract or L 647 ff in the conclusions). Obvious to me, the by far most likely explanation seems to be that the processes in firn and ice are still not fully understood yet.

Detailed:

L 54 ff. “The in situ produced ^{14}C mainly forms $^{14}CO_2$ and ^{14}CO, with a smaller fraction forming $^{14}CH_4$ and possibly other simple organics such as formaldehyde (Dyonisius et al., 2023; Hoffman, 2016; van der Kemp et al., 2002; Fang et al., 2021).” Of the total number of in-situ produced ^{14}C atoms per gram ice, Hoffmann (2016) found a fraction of 11-25 % incorporated into the DOC fraction when performing a neutron irradiation experiment on Alpine ice core samples. The incorporation of cosmogenic in-situ ^{14}C into DOC has later been supported by measurements in environmental samples (Fang et al., 2021). In Dyonisius et al., 2023 (and obviously all studies before 2022 or at least 2016) this partition has not been considered and is obviously also missing in the reviewed study here (see next point). Unlike $^{14}CH_4$ this does not seem to be a minor fraction and should be considered (maybe needed therefore: DOC concentrations, around 5 μg C / kg ice for polar ice; Preunkert et al. 2011). As you assume for CO, same partitioning for the n and muon mechanism needs to be similarly assumed here. Important might also be that the cosmogenic produced ^{14}C incorporated into DOC is likely to behave differently in the firn/ice than the gaseous species (CO etc) in terms of diffusion and release into the porous firn (and transport therein), basically being fixated after incorporation (removed ^{14}C partition in subsequent modeling of firn gas transport/retention/leakage).

L 319 ff. “We use a value of Ω^{CO}= 0.31 for the fraction of total in situ ^{14}C in ice that forms ^{14}CO (Dyonisius et al., 2023; van der Kemp et al., 2002).” In Dyonisius et al. (2023), the value for Ω^{CO} seems to be 33.7 % associated with an uncertainty of ±11.4 %. Has an uncertainty for Ω^{CO} been considered and propagated here? This seems relevant considering the narrow range of μ_- and μ_f and the difference compared to earlier values (see Table 2). If not, this should not be too difficult to be introduced for example in a similar way as done for the uncertainty of the n production rate (introduction of an additional, adjustable “uncertainty factor” like F_n in L 326). Also see above regarding the missing partition which is incorporated into DOC.

L 356,357 “…(we use α=0.75, consistent with Dyonisius et al., 2023 and Heisinger et al., 2002b),…”. Heisinger et al. (2002b) considered uncertainties in the muon energy and flux to be in the range of 10% each. It does not seem you similarly considered and propagated these uncertainties. Aiming for a comprehensive study, propagating all uncertainties will finally be more useful, resulting in the most realistic range estimates. Especially if there still persist a number of unknowns (i.e. a detailed understanding of all process and mechanisms involved). If not considered, the factors or uncertainties should at least be summarized in the discussion (reference to suggested additional table?), providing a possible tie-point for future studies.

L 378 ff. “We introduce these two reservoirs because a preliminary analysis showed that using a single ice grain reservoir does not provide a good fit to the observations.” Is there any hypothesis of a possible mechanism/process to justify this partitioning into two reservoirs? What is considered as a good fit (especially if considering all other uncertainties, including the ones mentioned above and some of the points mentioned below), i.e. how bad would the fit be?

Section 4.2, L 481 ff. Is ventilation not part of gas transport/movement in the firn? Since you are using a frin transport model, I do not see why your proposed mechanism would not also (to some extent at the least) include ventilation. Further, snow metamorphism (the most common type of recrystallization of snow and the uppermost firn) is a very fast process (days to weeks); e.g. Pinzer et al., 2012. With depth and higher density of the firn, the recrystallization process will become slower, probably in the order of a few years at the LIZ (e.g. Duval et al., 1995). Thus, would it not be more appropriate to, in the model, combine the processes of diffusion and metamorphism / recrystallization, essentially leading to an “enhanced diffusion” (strong enhancement in the upper firn and much less close/at the LIZ)? Maybe a partitioning of the model into two reservoirs could then be avoided?

Minor issues

L 187, equation 1. Definition of x_{CO} seems to be missing in the text.

L 188 "…pMC is the sample or blank ^{14}C activity in pMC units…". pMC denotes percent modern carbon, a pMC unit does not exist (as the name tells, it is a percentage).

L 191 (& equation 1) "1.1694×10^{-12} is the ^{14}C / (^{13}C + ^{12}C) ratio corresponding to the absolute international ^{14}C standard activity (Hippe and Lifton, 2014), …" pMC is defined based on a half life of 5730 (as you mention elsewhere, the half life you used), but Hippe and Lifton, in their reformulation, from which your value of 1.1694×10^{-12} results, considered a half-life of 5700. Note that their reformulation is performed for two main reasons: (i) to omit a necessary correction in activity for the decay from 1950 to the year of measurement of the international ^{14}C standard used for AMS calibration (yielding the number for the activity to be used with 1.1694×10^{-12}) and (ii) to account for the conventionally introduced ^{13}C normalization for AMS measurements (to -25 per mil; not to be confused with the additionally performed normalization of the standard to -19 per mil to account for the switch to a new material of the international AMS reference standard; see e.g. https://www.hic.ch.ntu.edu.tw/AMS/A%20guide%20to%20radiocarbon%20units%20and%20calculations.pdf). In any case, the reformulation eventually leads to their Eq 22, which in principle corresponds to your Eq 1 (without the terms accounting for CO molecules per volume). Your equation misses one important term (since this is one of the two main reasons to perform the reformulation in the first place), $Ab12_s$, which results from accounting/correcting for ^{13}C normalization. I suggest checking carefully (maybe using the activity of the reference standard and correcting to the year of measurement might be more appropriate for your data anyhow; not that all that matters much with regards to all other uncertainties, I think…).

L 297 "Figure 1 illustrates total ^{14}C production rates by each mechanism versus depth at Summit, …". The term "each mechanism" might not be ideal with regards to the previous sentence where also the mechanism of "loss of this ^{14}C from the ice grains via leakage into the open porosity (firn air) or closed porosity (air bubbles)." is mentioned. Maybe clearer would be, "Figure 1 illustrates total ^{14}C production rates by secondary cosmic ray neutrons and muons versus depth at Summit, …", even though not the most pretty due to repetition.

L 355 "…β(h) is a unitless depth dependence factor…". Shouldn't that be mass-depth dependence factor?

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Y. S. Yi, Y. Han, K. D. Kwon, S. K. Lee and S. D. Hur ACS Earth and Space Chemistry 2021 Vol. 5 Issue 11 Pages 3258-3267 DOI: 10.1021/acsearthspacechem.1c00308
https://doi.org/10.1021/acsearthspacechem.1c00308