Review of
Radiocarbon dating of alpine ice cores with the dissolved organic carbon (DOC) fraction
by Ling Fang, Theo M. Jenk, Thomas Singer, Shugui Hou, Margit Schwikowski

The manuscript from Fang et al. investigates the possibility to use the dissolved organic carbon (DOC) fraction for 14C dating in high Alpine glacier ice. To do so the authors present an ice core sample set (17 ice core sections) taken from the deep parts of the high altitude Eurasian glaciers Colle Gnifetti, Belukha, Chongce, and Shule Nanshan, for which a direct 14C dating comparison between the water-insoluble organic carbon fraction (WIOC) and the DOC fraction was achieved for each sample.
It should be noted that "direct comparison" means that each of the 17 ice core sections samples was cut lengthwise and WIOC as well a DOC 14C was measured on each ice core section, i.e. on exact the same depth interval of the ice core.
Whereas the WIOC method is already well established, doubts were reported about suitability of the DOC fraction for 14C dating in an earlier study (May, 2009), what makes this study very challenging and important.
After a short description of the deployed WIOC and DOC sample preparation methods, WIOC and DOC concentration as well as the radiocarbon results are presented and discussed.
3 of the 4 sites show almost identically (not significantly different within the error) 14C ages for the corresponding samples, with a slight but systematic offset towards higher F14C values for DOC compared to WIOC. For one site (Chongce) this offset is enhanced. Since this latter site contains a high influence of dust in the ice the observed F14C DOC-WIOC offset is discussed by testing the hypothesis of an incomplete removal of carbonate during the WIOC sample preparation using the Ca2+ concentration in the samples as tracer for calcium carbonate

The paper is well structured and written in almost all parts and addresses an important scientific question, which is in the scope of TC. The study presents an up to this point unique data set which is suitable and convincing for the discussed topic and most of the conclusions made, and for which I would like to felicitate the authors.
The description of experiments and the presentation of the data as well as the discussion on the potential influence of incomplete removal of mineral dust on the WIOC sample preparation are except a few points (see my minor comments below) sufficiently complete and precise.
Therefore I think the manuscript should be published after a few minor and one major revision were made.

Apart from the minor points which are listed below, my major concern is that the paper lacks a more detailed discussion about the potential influence of in-situ produced 14C on the DOC radiocarbon content in high altitude glacier ice. Present state of the art in literature is that this effect makes the use of DOC unsuitable for 14C dating, at least at low accumulation, high altitude mountain site as the Colle Gnifetti (denoted CG in the following) (May 2009, Hoffmann 2016) from which samples are presented here.
At present state of the manuscript, the authors state:
"*The fact that none of the samples analyzed in this study (n=17) resulted in super modern F14C values (> 1) and the obtained significant correlation between the F14C of WIOC and*

DOC (Sect. 3.2) and the resulting calibrated 14C ages (Pearson r = 0.988, p < .01, n=14, Figure S1) represent strong evidence against the previously suggested 14C in-situ production in the DOC fraction (May, 2009)."

This argumentation could possibly be drawn referring to work from May (2009) only. Within this particular study 14C DOC measurements underlie relative high blank contributions and therefore a high uncertainty, and corresponding 14C POC data are likely influenced by altered soil and dust material incorporated in the ice due to high combustion temperatures. Thus the dataset of this study is very scattered and May (2009) could at that point only speculate on the existence of an in-situ 14C production on the DOC content in ice at CG.

However the work of Hoffmann (2016) proofed via neutron irradiation experiments that (i) the production of 14C in glacier ice and the incorporation into the DOC fraction is possible and (ii) gave a quantitative estimate of the DOC incorporated fraction of produced 14C in Alpine ice. Based on this, the study finally also details a way to calculate its influence on ice core samples from this site.

Since this work is not yet referenced in the present study, here a brief summary of what is outlined there:
In view that:

1) The production of 14C atoms within the ice matrix by spallation of oxygen within the water molecule, induced by cosmic radiation (cited references: Lal et al., 1987; van de Wal et al., 1994; Mazarik and Reedy, 1995) is a known process.
2) Potential 14C production in organic compounds as CO and CO2, but also in CH4 (cited: Kemp et al., 2002, Petrenko et al., 2009, 2013), as well as the possibility to hydrogenate the CO molecule to higher organic species (cited: Woon, 2002) are already reported in literature

Hoffmann (2016) performed the irradiation experiment mentioned above to confirm or not what is proposed in literature. The experiment showed that 14C in-situ production in DOC is a real process and suggests that between 11-25 % of the initially produced 14C atoms entered into the DOC fraction of Alpine Glacier ice.

On the base of that, as outlined by Hoffman (2016),
1) the theoretically produced number of 14C atoms for mid latitude glacier site at an altitude of 4500 m asl can be estimated as a function of accumulation rate and depth (based on literature data), and
2) the relative amount of 14C, which entered in the DOC fraction of Alpine Glacier ice can be estimated quantitatively from the neutron irradiation experiment.

Since this study exists, and the in-situ production in the DOC fraction would result in enhanced F14C fractions, I think it is really worth and necessary to take this effect into account. It should be discussed in this manuscript as partial or at least potential cause of the systematically observed DOC-WIOC difference, beside the hypothesis of the incomplete inorganic carbon removal within the WIOC sample preparation (which surely is also a good candidate for the observed offset in case mineral dust is present in the samples).

Having been curious myself on the order of magnitude this effect would have on the DOC 14C values measured in this study, I did a back-of-the-envelope calculation of the in-situ effect by applying the calculations of Hoffmann (2016) on the CG samples of this study.

Accumulation rate and depth in water equivalent of CG15 are not given in the manuscript. Since however similar ages were found at similar depths in the cores CG15 and CG03 (see table 3 and section 4.3) the respective data from the CG03 (drilled in 2003 almost directly at the saddle point of CG, Jenk et al., 2009) were used for the estimation. As the ice in the deeper part of the C15 core probably originates from upstream the drill site, i.e. from a position on the north flank of the CG, where the accumulation is lower (e.g. Licciulli et al., 2020), and since the accumulation rate is one of the driving factors of the magnitude of the in-situ production in the estimation, calculations for different accumulation rates were carried out. The mean of uppermost 30 years of CG3 (0.47 mwe/yr) was used, and additionally two values (0.25, and 0.12 mwe/yr), which are in the order of magnitude of what is found upstream in the north flank of the CG. Since all four samples were taken from about the same depth, and had the same sample and carbon masses, mean values of (220g, 24ugC, and 56.75 mweq) were used in the calculation. As relative fraction of 14C, which entered in the DOC fraction 15% were assumed.

The estimation resulted in potential F14C offsets of 0.025, 0.047, and 0.096 for the assumed accumulation rates of 0.47 mwe/yr, 0.25, and 0.12 mwe/yr, respectively, which fits quite well with the observed offset within this study (0.055±0.014).

Therefore, as stated above, a discussion of the in-situ production of 14C influencing the DOC 14C dating should not be neglected but done here. It would also significantly improve the scientific output of the manuscript. In addition, in view of the expected results, all existing studies on this topic would become conclusive and an important gap of knowledge in literature could be closed.

Minor comments:

Line 34-36: it would be good if you could give an idea of how much ice would be needed (inclusive the lost during decontamination) for an Antarctic sample (see also my comment on line 389).
In addition, be aware and mention that the potential in-situ effects will be much stronger in Polar Regions than in the high altitude sites in mid-latitudes, since the neutron flux and thus production rate is higher and accumulation rates are generally lower there.

Line 48-50: … Ice flow models, which are widely used to retrieve full depth age scales (e.g. Nye, 1963; Bolzan, 1985; Thompson et al., 2006), also fail in the deepest part of high-alpine glaciers due to the complex bedrock geometry. ….

Please clarify or revise this sentence. To my knowledge the high model uncertainty in the deepest part of the glacier (which includes for me the deepest 5-10m above bedrock) its not only due to the bedrock geometry, but rather to the uncertainties in the assumptions needed to be made to constrain the model and which include beside the bedrock geometry also mass balance upstream, equation of temperature depended shear stress, steady state conditions.

Line 59-62: Samples of >10 µg WIOC can be dated with reasonable uncertainty (10-20%), requiring less than 1 kg of ice from typical mid-latitude and low-latitude glaciers (Jenk et al., 2007; Jenk et al., 2009; Sigl et al., 2009; Uglietti et al., 2016).

Please include also the study of Hoffmann et al., 2018, in which 14C dating on the WIOC franction was achived with an other sample preparation setup. Be also please more precise on the sample and carbon mass needed to achieve such an uncertainties of 10-20%. It seems that Hofmann et al. 2018 achieves this uncertainty with an ice mass <500g and a carbon mass of <10 µgC. Also it would be good to mention whether the AMS or the sample preparation error dominates the uncertainty.

Line 79-81: In view of the analytical precision achievable with this method, the turn-over time from atmospheric CO2 to deposited aerosol is negligible (Fang et al., in prep.).

I am not sure if I got the meaning here.
Do you mean the analytical uncertainty, which results in an age error, which is much higher than the turn-over time?

Line 93- 95: … possible mechanisms of 14C in-situ formation in organic compounds seem far less likely and have not been investigated to date…

This sentence needs to be revised (see my major comment), since 14C in-situ formation in DOC of high Alpine glacier ice was investigated.

Line 103-104: ….allowing 14C analysis on samples with DOC concentrations as low as 25 µg/kg ….

I guess this assumption is made in view of the required carbon mass needed for 14C sample preparation and/or measurements. If true please mention that and change the sentence to something like:
The system can handle samples with volumes of up to ~350 mL. To achieve a minimal carbon mass required for 14C sample ……? A minimal DOC concentration of 25 µg/kg is needed.

Line 116 – 133: It might be worth to summarize the meta data on the ice cores and samples listed here in a table (including geographic coordinates of the drill site, ice core lengths, accumulation rate at the drill site, sampled depths in this study, … the mountain range and reference to study in which more meta data on the cores are given).
In any case at least the accumulation rate and the references to further meta data of the different cores should be added in the text.

Line 185-187: … and procedure blanks (1.26±0.59 µgC with F14C of 0.69±0.15 for WIOC samples and 1.9±1.6 µgC with a F14C value of 0.68±0.13 for DOC samples)…

The way the WIOC and DOC procedure blanks were made and the frequency or number of blanks achieved during the analysis of this study should be given.

Line 254 – 259: The fact that…. to … (May, 2009).
In view of my request to discuss the potential bias due to 14C in-situ production by calculating its effect, these lines should be deleted.

Line 266 – 269: For DOC concentrations observed in this study, an initial ice mass of about 250 g was required, with about 20-30 % of the ice being removed during the decontamination processes inside the DOC set-up, yielding ~200 g of ice available
269 for final analysis.

This sentence should be moved to Section 2 in the paragraph, which starts in line 156.

Line 271:
Please specify here that the reduction of the sample mass in DOC refers to the WIOC method used at the PSI.

Line 276: Please add a section (4.2 or 4.3) on the "Potential contribution of 14C in-situ production to 14C of DOC" (see major comment)

Line 281-182: please change to something similar to:
… upper parts of the Chongce Cores 2 and 4, less than 2 and ~6 km away from Core 1, (measured with the same analytic device as used here), …
…

Line 326-329: … For final calibration of 14C ages, most of those earlier studies took advantage of the assumption of sequential deposition in the archive, which seems very reasonable considering the deposition of annual snow layers on top of each other on the glacier surface…..

Please be more prudent here and revise this sentence since several studies emphasized that a sequential deposition in the archive of high Alpine glaciers is not evident (a least in the case for CG, see Jenk et al., 2009, Hoffmann et al., 2018, Bohleber, 2019).
E.g. Bohleber 2019 wrote:
"… as already noted by Jenk et al. (2009), the finding of a continuous age-depth relation in the deep core parts is not a priori to be expected (e.g., as strong shear could potentially decouple the deformation of the basal ice frozen to bed from its adjacent top layer, which would be reflected in a hiatus in the age-depth relation). In fact, the 14C profile obtained by Hoffmann et al. (2018) for a core located on CG's north-facing slope (with significant bedrock inclination, cf. the saddle location of the core investigated by Jenk et al., 2009) revealed a localized discontinuity in 14C ages…"

Therefore I propose to argument like that:
1) Despite the fact that a sequential deposition in the archive is not evident in the deepest layers … (references…)
2) but in view that in case of relatively large analytical uncertainties compared to the age difference of the samples, the sequential deposition model can moderately constrain the probability distribution of the calibrated age ….

=> The sequence model was used but results were compared using the conventional calibration approach. ...

Line 323: 4.3 DO14C ages in the context of published chronologies
In view of what is discussed in this paragraph I recommend to change the title to: DO14C ages in the context of published near bedrock ice ages

Line 351 – 356, Table 5 and Figure 4:
1) to be complete for the CG site, please add also near bedrock ice age data obtained by Hoffmann et al., 2018 on an CG ice core (KCC) located on the north facing slope of the glacier, to the compilation of near bedrock ice ages. In the latter study the age difference of near bedrock ice between CG03 and the KCC is discussed, and might worth to be mentioned that here.
2) As already mentioned, the comparison of absolute depths between CG03 and CG15 leads to assume that both ice cores were drilled at the same location of CG. If true add this information in line 116

Line 389 … This new dating method opens up new fields for radiocarbon dating of ice for example from remote or Polar Regions, where concentrations of organic impurities in the ice are particularly low ….
To illustrate this statement, please give an estimation of how much ice (in g or kg inclusive the ice mass which is needed for decontamination) would be necessary to achieve a 14C dating on an ice sample. Typical DOC concentrations from Antarctic ice with an for 14C dating accessible age (< 10 ppb) are given e.g. in Legrand et al., 2013.
In addition as already stated in my comment to line 34-36, you should mention the potential influence of the 14C in-situ production which is expected to be enhanced

compared to high altitude sites in mid latitudes, and will thus result in an enhanced age uncertainty.

Literature cited in review:

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