General comment to the editor

We decided to include another author, Michael Sigl, who is part of our group at PSI and discovered the fly found in the Tsambagarav ice core which was used as one of the significant validation cases. Therefore we think it is important to include him as co-author. Moreover, we acknowledge the people who prepared the sample and took the photo of the fly.

In the following responses all Line numbering always refers to the revised version.

Anonymous Referee #1
Received and published: 23 August 2016

The authors present an overview of existing radiocarbon dating results from a suite of global ice cores, and new information on updated analysis techniques and validation exercises. On the whole, these approaches are invaluable for providing chronological information from deep portions of alpine cores, where other techniques fail yet there is still sufficient ^{14}C available to provide reliable dates. I have no comments or concerns regarding the updated techniques or validation procedures demonstrated in the paper - all show the care and precision typical of this group. My main comment for the authors to consider during revision is the overall presentation (and title) of the paper itself. As suggested by the title, and in the introduction (lines 90-106), on one hand the authors see this as an overview paper. But a second goal (lines 105-106) is to present recent optimizations in the analytical technique. These are not mutually exclusive; however it seems to me that the original portion of this paper is the validation exercise (section 5.2). Make no mistake, I find the optimization and validation to be novel, useful, and certainly worthy of publication here. I'm simply suggesting that the authors refine the title and introduction to reflect this. The overview portions can stay as is -
The summary in section 6 and Figure 6 are quite useful for projecting how the technique could be useful in other situations.

Response of the authors
Thank you very much for your review and your comments.

We agree that the title can be more explanatory of the content of the paper and modified it accordingly:
"Radiocarbon dating of glacier ice: overview, optimizations, validation and potential".

We also modified the last sentence of the introduction section to clarify the intention and content of the paper as following (line 109-111):
"Here we give an overview of the current status of the now routinely applied ^{14}C dating method for glacier ice including an update on recent optimizations and method validation. Uncertainties and potential of this novel approach are discussed and its successful application to a number of ice cores presented."

Anonymous Referee #2
Received and published: 7 September 2016

Response of the authors
Thank you very much for your review and your comments.

Radiocarbon dating of glacier ice is an important asset to ice core sciences in mid-latitudes when classical methods to derive age-depth models (layer counting, ice flow modelling, tephra-chronology) fail. However, suitable material for radiocarbon dating of macrofossils is sparse in the ice making it desirable to date other organic carbon compounds. Water-insoluble organic carbon (WIOC) has been shown to be a suitable candidate for radiocarbon dating of mid-latitude ice. Uglietti et al. review the efforts to develop the analytical methodology for radiocarbon dating of WIOC in ice, and test its accuracy. The group of Bern/PSI has been instrumental in developing the method so it seems only natural that they provide a review thereof and is certainly a valuable contribution to the literature of this topic. The paper is generally well written, thorough, suitable for the Cryosphere, and should be published. However, I have some comments that the authors might want to consider for the sake of clarity in the paper and some details the authors may want to check before publication.

1. My main comment is that in the context of analytical precision, I find it slightly misleading to discuss calibrated ages instead of ^{14}C ages or fraction modern. The calibration of radiocarbon dates is a second methodology, introducing additional uncertainty due to the uncertainty of the calibration curve itself. Hence, 2 significantly different radiocarbon ages may lead to statistically indistinguishable calibrated ages. However, if the radiocarbon dates and their uncertainties are reliable, then 2 different radiocarbon ages are indicative of different calendar ages. This applies for example to Table 2 and 3 and Figure 1. These experiments refer to analytical accuracy of radiocarbon preparation and measurement, independent of the calibrated age and it is hence worth discussing (and showing) the differences in ^{14}C years or F^{14}C instead of calibrated years. A comparison of the ^{14}C measurement results could for example be indicative whether the pure analytical precision does reflect the true uncertainty of the method. I would assume that the true uncertainty is somewhat larger, due to the inhomogeneous distribution of WIOC over an ice sample. This can for example be seen in Table 3 where the samples JUV 0_5/6 as well as JUV 0_7/8 yield significantly different radiocarbon ages, despite being from the same ice block. This questions whether these samples can be summarized to an error weighted mean and standard error as done in table 3. The final uncertainty of 9 ^{14}C yrs. for JUV 0_3-8 seems very small given the scatter of the individual measurements. A reduced Chi2 statistic of the sample pools in Table 3 could be used to assess and discuss whether the uncertainties of single measurements are realistic. In a second step, it can then be discussed whether these uncertainties matter in terms of the absolute chronology, given that the calibration adds additional uncertainty.
We understand that the final uncertainties of the calibrated ages are different than those of the ^{14}C ages and also include the additional (method unrelated) uncertainty of the calibration curve. Nevertheless the main purpose of ice core dating is to provide a final age range and therefore we consider it more important to discuss and compare the uncertainties on the calibrated ages. In any case, Tables 2 to 4 do contain ^{14}C ages and F^{14}C, so the information about the method related (analytical) precision is also available (also see cited literature).
We further agree that the uncertainty of a single measurement is indicative for the analytical uncertainty only and does not consider variation due to potential inhomogeneity in the ice sample (as indicated by different WIOC concentrations). Therefore, even if replicate results for the same sample do slightly differ from each other, considering the analytical 1σ uncertainty we think they can still be combined (in case the thinning does not suggest otherwise which of course has to be checked). In fact, replicate measurements or measurements in high spatial resolution are thus preferable to avoid dating bias due to these (small) variations caused by inhomogeneity (averaging out of variations). This is feasible and a strength of the method described. After thorough consideration we however concluded that the OxCal combine tool is not appropriate to average such samples because it is not intended to take such possibility of inhomogeneity into account. We therefore revised our results by using the averages of the ^{14}C ages (or equal F^{14}C values) with the uncertainties estimated using the standard error of the unbiased standard deviation (i.e. accounting for number of replicates) (Tables 2 and 3). Results of combined samples thus changed slightly but changes are negligible considering the uncertainties which now increased to likely more realistic estimates. We would like to emphasize, that for all the age-depth modeling performed in the past and summarized here, the model uncertainty estimates have always been selected very conservatively, one reason being exactly the consideration of potential inhomogeneity in the ice.
The unreasonably small uncertainty you mentioned (Table 3) was a typo. Thank you for spotting it. For JUV 0-B the standard deviation was 79 instead of the given value of 9 (it now increased to 168 years using the new approach). There was another typo: for JUV 0_7 the ^{14}C age uncertainty was indicated with 18 instead of 218 years (now 219, because we now consider 3 instead of 2 digits for F^{14}C). Using 3 digits now generally resulted in small changes of the results (usually in the order of 1 to 5 years).

2. Please check the data in the Tables. I was confused seeing that the samples Bel2_THEODORE and Bel2_Sunset yield significantly different F^{14}C values while their ^{14}C ages agree. Using an F^{14}C of 0.425 for Bel2_THEODORE I obtain a radiocarbon age of 6874 ^{14}C BP, as compared to 7329 ^{14}C BP given in Table 2. So unless I missed something either the F^{14}C or the ^{14}C age of this sample is erroneous which might also impact on the calibrated ages shown in Figure 1. Please check.

We apologize; this was indeed an error. Thank you for spotting this. The Bel2_THEODORE F^{14}C is 0.402, but was given as 0.425 which was picked from the wrong column in the data files and is the value before procedural blank subtraction. The correct value is given now (Table 2) and all other data in the manuscript have been cross-checked for correctness. In addition the Sunset values have slightly changed because of the blank correction. For the THEODORE – Sunset comparison the samples measured with the Sunset system were intended to be blank corrected with the corresponding blank values (1.21 ± 0.51 µg of carbon with an F^{14}C of 0.73± 0.13)) but in the excel file there was an automatic link to the new combined procedural blank value (1.34 ± 0.62 µg of carbon with an F^{14}C of 0.69± 0.13) which is used for all the other samples, but not intended for the comparison, as also already stated in the main text (Lines 223-225). Therefore in the new version the values appear slightly different because we used the correct blank values (1.21 ± 0.51 µg of carbon with an F^{14}C of 0.73± 0.13). Moreover, we changed the sample names in Table 2 and Figure 1, to be consistent with Table 3 for the Juvfonne samples. For the Belukha samples we also changed the names. For example Bel2_THEODORE is now 4_THEODORE (BEL 2).

3. Throughout the manuscript the term “conventional” ^{14}C dating is used to describe the dating of macrofossils. However, in the radiocarbon literature “conventional” ^{14}C dating refers to ^{14}C measurements using liquid scintillation and gas proportional counting techniques as opposed to AMS measurements. Please either use a different term than “conventional” or add a sentence defining how it is used in this paper.
Yes, good point. We included a sentence to define this term in the introduction at Lines 60-61:
“In the following we refer to dating of ice with macrofossils as conventional ^{14}C dating”.

L 45 *(now line 48)*: please replace “nuclear” with “radiometric”
We normally use the term “nuclear dating”, which is common in the radiochemistry community (see for example textbook Nuclear- and Radiochemistry Vol. 2 (https://www.degruyter.com/view/product/41711).

L 179-182: This is a very long sentence and a little unclear. Maybe divide it up into 2 sentences. Are the sample background corrected using OxII? I suppose the standard is used for normalization and not background correction? Please rephrase.
We agree that the sentence is quite complicated and long but we think it is better to give only a short and easy explanation. We tried to improve the phrasing though (Lines 189-191):
“With the current setup, the ^{14}C/^{12}C ratio of the samples is background subtracted, normalized and corrected for mass fractionation by using fossil sodium acetate (^{14}C free, NaOAc, p.a., Merck, Germany), the reference material NIST standard oxalic acid II (modern, SRM 4990C) and the δ^{13}C simultaneously measured in the AMS, respectively (Wacker et al 2010)”.

L 183: Please insert “relative” before deviation, as the samples are normalized to the standard.
We realized that the term “deviation” is not correct in this context and therefore confusing. We rephrase as the following (Lines 192-193):
“…which is the ^{14}C/^{12}C ratio of the sample divided by the same ratio of the modern standard”

L 183: “BP” is not explained at this point yet, but only in line 185. Please explain it here instead.
We corrected (Line 196):
“^{14}C ages (before present (BP), i.e. before 1950)) are calibrated using OxCal v4.2.4 (Bronk Ramsey and Lee, 2013) with the Northern (IntCal13) or Southern Hemisphere (ShCal13) calibration curves (Reimer et al. 2013, Hogg et al. 2013), depending on the sample site location. Calibrated dates are given in years before present (cal BP)”.

L 227-228: Are the uncertainties given in ^{14}C years here? If so, please write “^{14}C yrs” instead of years to be clear.
We here talk about an assumed age of the ice sample and thus refer here to the “true” age and not the ^{14}C age. Accordingly the uncertainties denote the final overall uncertainty of the dating method which as such also includes the calibration so they refer to the calibrated age. To clarify we changed the sentence to “As an example, for hypothetical samples with a WIOC mass of 5 or 10 µg, the resulting uncertainty of the finally calibrated ages for 1000 year old ice would be around ± 600 yrs or ± 250 yrs and for 8000 year old ice around ± 1600 yrs or ± 700 yrs, respectively (Line 249-253)

L 249 and following: See comment number 3. Please either define what you mean by conventional or use a different term throughout the manuscript instead.
See reply above (comment 3.) and see Lines 60-61 in revised version.

L 252: This may be nitpicking, but AD 1258 – AD 1050 = 208 years, not 200 years.
With an error of 70 years, rounding to down to 200 seems appropriate. However, we changed to ”around 200 years” then omitting the need for indication of the uncertainty which could be derived anyhow with the value of AD 1050±70 being provided (Line 274).

L 259-271: Several times it is stated that the WIOC dates “agree well” with the macrofossil dates, while the ^{14}C ages are indeed significantly different. I am not arguing against the general agreement but it would be great if you could add 1-2 sentences to make this more precise. Are the differences due to sampling differences (i.e., different ice layers have been sampled for macrofossils and WIOC)? If so, are the results in stratigraphic order?

Yes, the differences arise from the sampling procedure. The samples in the Juvfonne ice patch were obtained extracting clear ice just adjacent to the organic remains layers where the macrofossil ^{14}C ages are from. Thus a 1:1 agreement cannot be expected. Here, the samples from Ødegard et al. (2016) are simply given as a reference age range to compare our samples with. To allow for the most reasonable comparison we always considered the organic layers closest to our ice layers. In this version we thus changed for example the organic layer Poz-37879 with Poz-37877 which is closer to the ice sample JUV 2 and was not available for the original study by Zapf et al., 2013 which is why we did not consider it initially but now decided to. The same for JUV 1 and the corresponding closest organic layers Poz-36460 which we kept and Poz-37878 which was replaced with a closer layer Poz-56952 only sampled in 2012 and therefore also not available in the study by Zapf et al. 2013.
We now describe the issue more carefully by including the stratigraphic order in Table 3 and an explanation in the related caption text and also in the main text (Lines 292-294).

L 351: Please write “climate wiggle matching” instead of just “wiggle matching” which could also refer to the wiggle matching of radiocarbon dates.
Yes, done, thanks (Line 389).

L 357: Please add a reference to [Godwin, H. 1962. Nature, 195 (4845)] for the half-life of radiocarbon.
Yes added. Thank you (Line 396).

Anonymous Referee #3
Received and published: 30 September 2016

Response of the authors
Thank you very much for your review and your comments.

The manuscript "Radiocarbon dating of glacier ice“ by Uglietti et al. aims to give an overview of the actual 14C dating method applied by the authors group (i.e. at the Paul-Scherrer-Institute (PSI) for absolute dating of glacier ice via 14C analysis of the water insoluble organic carbon fraction WIOC. After the presentation of the dating problematic, an overview of the method development at PSI over the last 10 years is given in the introduction. This is followed by a description of the actual analytic procedure and comparison with the previous method is presented. Dating uncertainties are estimated, followed by an overview of different validation attempts for the 14C dating method performed by the authors group over the last years. Finally, a potential application of the method is provided by compilation of 14C dated non polar ice cores in which the discrete 14C ages are aligned with basic glaciological or empirical fits to retrieve continuous age depth relationships for the respective ice cores.
The application of the 14C method is an important topic within the challenge of ice core dating and it is suitable to be published in The Cryosphere. The scientific level of the manuscript is already good, however I would have some suggestions and comments, which the authors might consider to further improve the quality of the manuscript.

The manuscript seems to slightly hover between a historical review and very specific descriptions of recent methodological improvements and validation exercises done by the PSI group. Since the manuscript is strongly focused on the activities of the authors group, I think the title can be somewhat misleading and I would suggest to adjust it in an adequate way. If the manuscript should keep the general review character of the ^{14}C ice core dating topic, as the title implies until now, it could benefit from a slightly broader view and discussion of radiocarbon dating methods for glacier ice that have been developed by other groups in the past. This could for example include dating of the dissolved organic carbon fraction but also a more detailed discussion on potential dating difficulties e.g. due to reservoir effects introduced by dating of material which was already aged at deposition etc. A few references to the work of other groups would be very helpful in this case.
We revised the title as the following as also suggested by other reviewers: ***“Radiocarbon dating of glacier ice: overview, optimizations, validation and potential”.***
*We do give references to other groups regarding ^{14}C in DOC (see Introduction). These studies include method validation but no published DOC ice core dating results which is the topic of this overview. For studies of ^{14}C in POC, see comment further down. Concerning the potential dating difficulties (e.g. reservoir effect) we discuss it already in Lines 84 to 89 (**line numbering related to revised version**). We did include a sentence though (Lines 327-328), that samples of high dust load were avoided giving also a reference to Hoffmann, 2016 (also see comment further down).*

Specific comments:
The two-parameter model (Section 6) is only a fit to the data by adaption of the two variables, no independently derived age-depth-relationship and should possibly also be discussed like this. Nye’s flow model can only be reasonably applied in the vicinity of ice divides of the polar ice sheets, where no additional horizontal flow component e.g. by a tilted bedrock, occurs. For cold Alpine glaciers frozen to bedrock it will systematically underestimate the age in larger depths. Also the assumption of a net accumulation to be constant in space and time will not hold for most Alpine glaciers. Therefore the fitted results will only give a very rough estimate of the age depth-relationship. Could you comment on that in the manuscript?
We completely agree that Nye’s flow model cannot be applied for all the reasons stated by the reviewer. This is why absolute dating of the bottom ice is so important especially for Alpine glaciers. This was in fact one of the main drivers to develop this method since also much more complex flow models are not able to give reliable results for this part of the cores.
The two parameter model (Thompson et al 1990) is exactly used just as a fit through the reference horizons and the ^{14}C data points to derive a best estimate of a continuous age-depth relationship (see Line 339). Considering the size of the ^{14}C uncertainties it should of course only be “rough” but does allow an estimate at least. In any case, there is no intent of using the model to infer absolute dates or confirm the dating results as clearly the obtained age ranges are derived based on the ^{14}C analyses (and the other time horizons in the younger part).
However, being unable to fit the absolute time markers with the two parameters model (e.g. Ortles and Tsambagarav ice cores) can give some indication that: (i) the underlying assumptions of constant accumulation does not hold and net accumulation might have changed significantly over time which is of course a possibility and should then be investigated more carefully (e.g. Tsambagarav and likely also Illimani although there the uncertainties might be too large for a solid conclusion, find more details in the cited original references for both) or (ii) the degree of layer thinning might be different from what the rather simple model can assume with the given degree of freedom to the parameters (e.g. Ortles, see cited reference Gabrielli et al., 2016). In the revised version we modified the relevant paragraph in order to clarify (Lines 355-384).

Fig. 1: I think this figure is highly redundant with the data shown in Tab. 2 and provides no additional information. The probability distributions are shown in very small size and do not show any special wiggle features of the calibration curve, so in my opinion this figure could also be omitted.

We do not agree and we consider the figure self-explicative and significant to be shown, while the table is needed to document the data we used to produce the figure.

The probability distributions are compressed and therefore less clear only for the modern samples (which are not really relevant for the dating by ^{14}C anyhow). Anyway, they are shown here as another piece of evidence that the comparison between the two combustion systems is good.

Fig. 3 and Section 5: I think it is critical to infer general conclusions on the accuracy of the method for any application from only seven data points shown in this figure. It is not a priori given that this validation will work in the same way for ice bodies in all kinds of different environments and glaciological settings. I think it is good to state the successful applications discussed in this manuscript, but I would be careful to draw general conclusions for future applications of all kinds. I recommend to slightly weakening the paragraph in this respect.

We do not think one can reduce the presented results to "only seven data points". First of all there is also strong evidence for the validity of the method based on the larch leaf in the Ortles core which is not shown in this figure and second, these 8 (including Ortles) points do represent 4 different sites from very different regions, different environments and different glaciological settings and thus can be considered to be rather representative. Anyhow, we now added a sentence saying that all validation experiments were performed on low-dust samples, thus avoiding potential issues related to high dust content in the dating (Hoffman 2016). Lines 327-328.

Fig 6: This figure seems to be problematic to me. What is the goal to show all the ice core chronologies on one timescale? Is it just a methodological compilation of all dating applications so far?

Yes, indeed the figure is exactly a compilation of all dating applications to show that for these ice cores it was the only method to date ice older than 1000 years.

The figure also summarizes (better than words on our view) typical ages, depths and thinning rates for high-alpine ice cores which are very different to those from polar ice cores.

Then in my opinion it should also be discussed in a purely methodological sense. At the moment, the figure is a compilation of ice core chronologies from glaciers with very different glaciological and geographical settings. It could be highly misleading in a fact that all the very different ice bodies are assumed to show comparable age-depth-relationships, which is not the case as also mentioned in the text.

Yes, the text clearly states that we do not assume that all the ice cores have the same age-depth relationship. To clarify this more clearly, we changed the first sentence in the figure caption to: "Compilation of age-depth relationships for five different ice cores, highlighting the importance of the WIOC 14C dating to obtain continuous chronologies and to constrain the very specific glaciological conditions and settings of each site.."

Could it be a possibility to compare only the glaciers with common features in one plot? Like only the cold ones or the three that have been fitted with the two-parameter model? Or separated geographically? In this context I have another question: What is the reason for the different basal behavior of the Illimani and Tsambagarav ice cores compared to the others? The basal chronology sections of these two cores differ significantly from the others. Thus, I think presenting all chronologies in one figure with only a very short glaciological description is insufficient. Either the chronologies should be discussed in a more methodological sense or the glaciological description and evaluation of the 14C-Data (section 6) needs to be extended with respect to the specific dating problems (e.g. ambiguity of volcanic horizons for the Alpine cores) of each sampling site.

This is not intended to be a glaciological paper. The intention of this figure is to show the various applications of the method for the dating of ice cores previously presented in much greater detail elsewhere (see cited references). There, more specific glaciological descriptions, careful considerations regarding the time horizons selected (e.g. volcanic horizons) and the interpretation of the age scale and analyzed parameters in general can be found.

Regarding the specific questions about the basal ages of Illimani and Tsambagarav we also would like to refer to the original literature for more details although for Tsambagarav it is already discussed in the manuscript here (significant change in accumulation, see Herren et al. 2013).

To clarify this, the paragraph has been modified and slightly extended (lines 355-384 in the revised version). Please also see further up where related and additional explanation is provided (first paragraph of the specific comments related to the two parameter model).

Tab. 2: The radiocarbon ages derived by the Sunset method seem to be systematically higher than the ages derived by the THEODORE system. What is the reason for that, can you comment? Like Referee #2, I also noticed the discrepancy between the F^{14}C value of Bel2_THEODORE and the given radiocarbon age. I calculate an uncalibrated 14C age of 6847 yBP for that sample, thus younger than the comparable Sunset sample.
Please check.

Thank you for spotting the erroneous F^{14}C value of the Bel2_THEODORE sample (see answer to Referee #2). Three of the samples give ages equal considering 1sigma for both systems (1, 2, 4), whereas only for sample 3 the Sunset results in older ages. Taking into account that these samples are not aliquots and may show some inhomogeneity, we think there is not sufficient evidence for a systematic bias.

L 11: Please specify what you mean by upper part of ice cores. How is the upper part characterized, which features separate it from the lower part?

Upper is related to the first 200 years which can be dated with the Pb210 method. In term of depth, this varies for each ice core dependent on the accumulation rate.

L 16: Note that Steier et al. 2006 also published a method for micro POC 14C-dating of glacier ice. Could you give a reference here?
We do not like to add a reference in the abstract, but we do cite Steier et al. 2006 at line 87.

L 30: I think the statement about the potential of the method for dating every piece of ice is a little too general. Can you specify the prerequisites for application of the method, like concentrations of organic carbon and knowledge about the sources of the organic material?
We already specified the needed OC concentration and the approximate size (mass) of the ice piece needed (see lines 18 to 23 in the revised version). The purely biogenic source of WIOC prior to industrialization is discussed later in the introduction (Lines 85-93) with reference to the according study from Jenk et al., 2006.

L 41: Could you give references for the seasonal variations of the trace components e.g. Preunkert et al. 2000 for ammonium and mineral dust components?
Yes, it has been included (line 43 in revised version).

L 45: Change nuclear to radiometric.
We normally use the term "nuclear dating", which is common in the radiochemistry community (see for example textbook Nuclear- and Radiochemistry Vol. 2 (https://www.degruyter.com/view/product/41711).

L 50: Please also reference Wagenbach et al. 2012 for layer thinning and the non-linear age depth relationship of Alpine glaciers.
In Wagenbach et al. 2012 no age-depth relationship and corresponding layer thinning of the deeper part is presented. Instead the "basal layer enigma" is evoked. We therefore think it is not relevant to refer to that publication in this section of our manuscript. We refer to that paper in section 6.

L 75: Can you be a little more precise here? Not only enough carbon mass is needed, but its needs to be ensured that the dated material represents the age of the surrounding ice and was not already aged at the time of deposition. Please add a comment on that.
It was specified a few lines later in the introduction (Lines 84 to 93).

L 78: DOC can be extracted not only by wet oxidation but also UV-irradiation like it was done in May et al. 2013.
Also the oxidation by UV-irradiation takes place in the wet phase. We therefore consider "wet oxidation" sufficient.

L 85: Is it possible to give a reference for the fact that OC has a lower probability for built in reservoir ages than EC?
Thank you, yes, Sigl et al 2009 and Gavin et al 2001 (Line 91)

L 109: How was the stainless steel band saw pre-cleaned?
The Band Saw Blades are cleaned before use with acetone on paper towels until the towels come out white (usually 3 times). A MQ frozen blank is also cut prior to samples cutting. We include this information in the description of the method (Lines 116-117).

L 121: Why does the HCL has to be removed by additional rinsing with ultra-pure water?
It should be removed in order not to interfere with or even damage the IR detector in the Sunset instrument as it was already written in Lines 168-169.

L 128: Typo: Of
*Thanks, but the upper case O is intentional because of the acronym: **T**wo-step **H**eating system for the **E**C/**O**C **D**etermination **O**f **R**adiocarbon in the **E**nvironment (**THEODORE**, Szidat et al., 2004)*

L 142: I think the statement on graphite target measurements becoming "needless" is maybe a little too harsh. Gas measurements can only complement graphite measurements in cases where not enough material is available at the price of lower precision.
Please reformulate.
We do not agree with this comment of the reviewer. Given the context of this sentence, we do not state that graphitization is needless in general. We emphasize that graphitization became needless for us and we describe how we were able to overcome this additional step. Anyhow, for small samples sizes (<100 µgC), uncertainties of gas and graphite measurements are similar. For larger sizes, graphite formation is still favorable for better dating precisions. However, all samples discussed in this manuscript are far below 100 µgC so that we regard further comments as not necessary in this context.

L 157: Can you describe or give a reference for the protocol Swiss 4S?

The reference was already given at the end of the sentence; it is Zhang et al 2012 (Line 168).

L 159: Did you take into account potential loss of material by the additional rinsing step? Did you investigate the filtration efficiency of the system in general before and after introduction of this step? This could provide information about the characteristics (size, etc.) of the retained particles. What kind of standard materials did you use?
Have they been treated exactly like the ice samples?
The rinsing step involves only 5 ml of MQ water compared to the ca 500 ml of sample (melted ice containing particles) which is flowing through the glass funnel and the filter during the filtration process. There is a potential loss of small particles on the walls of the glass funnel and through the filter (we are limited to the quartz fiber filters), but neither the entity of the loss nor the size of the particles is known. Nevertheless we are quite confident that the extra rinsing step does not significantly influence the filtration efficiency, again because the rinsing is done with only few ml of water.
We decided to remove the sentence regarding the tests with blanks and standard materials as it does not really fit here considering the context of this paragraph (removed from line 164 in the reviewed version). The current set-up and all set-ups used in the past (THEODORE, uncoupled Sunset system) have been thoroughly tested for the blank of the instrumental part (i.e. system blank). In this context, the additional step of rinsing after acidification was tested and was found to not add additional contamination. The entire ice samples preparation procedure results in the overall procedural blank described elsewhere in the manuscript. It includes this additional step, therefore the information will still be contained even if the sentence is deleted. The tests using the standard materials have also been repeatedly performed for each of the setups (e.g. Jenk et al., 2007; e.g. Zhang et al., 2012; and Agrios et al., 2015 respectively). Details about the standard materials used (IAEA and NIST standards such as IAEA-C5, C6, C7 or NISTHOx2) can be found in these studies which are cited in the manuscript. In order not to lose focus on the main point of this review paper due to an overload with technical details we think they should not be listed here again.
No, the treatment of standards was not exactly like the ice samples but the ice blanks were (resulting in the procedural blank values). The standards can ensure precision and accuracy of the instrumental part only. It is highly challenging to produce ice containing standard materials (introduced inhomogeneity due to the freezing step, loss to container walls etc.) which is a general issue for most parameters analyzed in ice cores. For this study, this is one of the main reasons and strong motivation for the discussed method validation experiments with independently dated ice.

L 201: Could you move the description of the procedural blanks from line 215 to this section? Here the term "procedural blank" occurs for the first time.
Thank you for spotting it. We prefer not to change the structure of the manuscript because the current sequence makes the most sense to us, but we now included a reference to the next Section 4 (Line 194-195).

L 202: Do the given masses and F^{14}C values only refer to the OC fraction or the total blank contribution of the system on all carbon fractions? How have the results been corrected for these blank values? Please clarify.
Thanks for the comment. Later in the manuscript, in Section 4, we state that procedural blanks are treated similarly to the samples (Lines 236-237). This also includes the combustion step (Line 239) which in this case is for the OC (i.e. WIOC) fraction. So, yes they do refer only to the WIOC (information added in line 240 in revised version). All results from ice samples are corrected for the procedural blank, which mean the F^{14}C values are blank subtracted using an isotopic mass balance equation which can be found in the original paper where the method is presented for the first time (Jenk et al., 2007).

L 207: Not only the size but also the age has a large influence on the counting statistics and the uncertainty. Please amend.
We here made a first and very general statement for easy understanding of the main issue with counting statistics. In lines 248-249 we then did amend the influence of the age: "Low carbon mass samples of old age contain even a lower number of ^{14}C compared to younger samples due to radioactive decay and are affected the most".

L 210: You state that "solid grains" of the standard materials have been used. How have they been combusted? In the Sunset system or in the standard AMS preparation routine using an EA? Could you please clarify?
As for the samples, we combusted the standards in the Sunset. Although this seems to be clear to us, since we never mentioned the EA, we added this info to the text (Line 229).

L 220: Why do you merge both procedural blanks of the THEODORE and the Sunset system into one number? I think this is not reasonable, because each sample should be corrected with the blank values of the respective system. Could you explain?
Because the blank values over the 10 years of analyses with the THEODORE and the new Sunset values were not observed to be significantly different from each other. For both systems the pure system blank which does not include the ice sample preparation has been thoroughly investigated (needed for correction of standard material measurements etc.). We know, that by far the major contribution of the procedural blank is related to the ice sample preparation and filtration step. Both these steps are not dependent on the instrumentation (i.e. whether the THEODORE or Sunset system is used). For all these reasons and based on the data currently available a combination of all blank values in order to get the most reliable value and the best statistics (best uncertainty estimate) seems to be the most appropriate approach. We explain this in the manuscript now (Lines 241-245).

L 270: Can you give a glaciological scenario which could explain such a large age increase (ca.1000 years) in only a few cm of depth increase (below the plant fragment layer) in such a small scale, low altitude and probably temperate ice body? Do you have any information on ice temperature? Could the samples JUV0_3-JUV0_8 also be influenced by basal sediment and thus produce a significantly higher age? Please comment on that, I think only a slightly larger depth in this order of magnitude is not a sufficient explanation for the observed age increase.
This is an interesting question. For this ice patch, many more organic remains layers have been analyzed by the conventional ^{14}C method than the ones presented here (Ødegård, et al. 2016). Based on those, the large age increase is not unexpected. Possible explanations are discussed in detail in Ødegård, et al. 2016

L 288: How long in depth were the subsamples? Can you provide information on the estimated) annual layer thickness in the respective core depths and thus the expected time span covered by the subsamples? This could help to evaluate if the assumption of same 14C-age of the adjacent samples is realistic for the two upper sampling depths. In turn, can you asses if the large age increase in the basal section is realistic in terms of covered core depth of the samples? Also the grey symbols in Fig. 5 are very small and hard to distinguish from the background.
Regarding the samples of the two upper sampling depths and the combination of sub-samples to one age, please see comment made to point 1 of Referee #2. Also, when combining samples to a common age we do of course always consider first if this is reasonable in terms of the expected thinning (see e.g. Fig. 5 for Mt. Ortles). Related to that, please refer to Ødegård, et al. 2016 for the expected thinning in the JUV ice patch (also see previous comment).

L 325: Note that especially for sites in the European Alps volcanic eruptions can be masked significantly by frequent inputs of Saharan dust (see e.g. Preunkert & Legrand 2001) and thus the signal can be highly ambiguous. Could you please comment on that?
We are very well aware of the potential impact of dust on the detection of volcanic signals in ice cores. We used multiple records to identify Saharan dust layers (e.g. Fe, Ca^{2+}) which by themselves can be valuable isochrones (on a regional scale). We were very conservative with the attribution of volcanic events in the Alps and are confident that those glacio-chemical signals we attributed to the few large magnitude eruptions (Laki, Tambora, Novarupta) are correctly identified. Nevertheless the topic of this paper is radiocarbon dating of glacier ice and not dating of glacier ice in general. In order to keep the storyline of the manuscript straight, we omit to include this aspect here (in the cited literature more details can be found by the readers interested in this topic).

L 335: What do you mean by “purely empirical approach”? Please clarify. Can you quantify that approach?
We intended to make the point that the model is not based on physical flow laws.

L 341: See comment to L 325. Please differentiate the different types of absolute horizons and their respective uncertainty.
In order to keep the storyline of the manuscript straight, we omit to include this aspect in more detail. For the different types of the reference horizons used we would like to refer to each original paper which we cited. The uncertainties are already included for both ^{14}C and RH by the error bars in Figure 6 (the text in the according Figure caption has been changed to clarify). Note that they are masked by the symbol size in some cases.

L 349: Can you be more precise here? What are the exact prerequisites for ice bodies to be dated by the method? Is it also applicable for temperate ice, where meltwater is present?
We included the info on cold and polithermal ice bodies (added at line 388 of the revised version). Until now we did not date any temperate ice body with ^{14}C.

L 354: Please add a reference to Wagenbach et al. 2012 for the bedrock $d^{18}O$anomaly.
Thank you, we did add it.

L 357: Because of the low depth resolution, the fact of mixed ages contained in one 14C-sample holds for almost every core depth (depending on accumulation), not only for the basal layer. Please clarify.
We clarify it by rephrasing as the following (Lines 394-397): “Because of the strong thinning, the ^{14}C age of the deepest sample represents a strongly mixed age of ice with a large age distribution. In these cases, the age limit was thus not determined by the ^{14}C half-life of 5730 yrs (Godwin et al 1962) but by the achievable spatial depth resolution since some hundred grams of ice is required.”

L 379: In section 2 you stated that in total 600-800g of ice are needed for decontamination. I think this number should also be given here.
The corresponding number was added (Lines 419-420 in the revised version) although the value of 600-800g of ice we gave in Section 2 was unfortunately but obviously incorrect (we apologize for that and corrected in this version). The ice mass required for the analysis is around 200 - 500g which is the mass of the decontaminated sample. The mass loss due to decontamination is around 20 - 30 % as stated in Section 2. With this, one can easily calculate that the number for the initial ice mass should be around 300 - 800 g of ice (conservative estimate, i.e. rounded up).

Radiocarbon dating of glacier ice: overview, optimisations, validation and potential

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Abstract. High altitude glaciers and ice caps from mid-latitudes and tropical regions contain valuable signals of past climatic and environmental conditions as well as human activities, but for a meaningful interpretation this information needs to be placed in a precise chronological context. For dating the upper part of ice cores from such sites several relatively precise methods exist, but they fail in the older and deeper part, where plastic deformation of the ice results in strong annual layer thinning and a non-linear age-depth relationship. If sufficient organic matter such as plant, wood or insect fragments were found, radiocarbon (^{14}C) analysis had thus been the only option for a direct and absolute dating of deeper ice core sections. However such fragments are rarely found and even then very likely not at the depths and in the resolution desired. About 10 years ago, a new, complementary dating tool was therefore introduced by our group. It is based on extracting the μg-amounts of the water-insoluble organic carbon (WIOC) fraction of carbonaceous aerosols embedded in the ice matrix for subsequent ^{14}C dating. Meanwhile this new approach was improved considerably, thereby reducing the measurement time and improving the overall precision. Samples with ~10 μg WIOC mass can now be dated with reasonable uncertainty of around 10-20% (variable depending on sample age). This requires about ~~100~~ 300 to ~~500~~ 800 g of ice considering the WIOC concentrations typically found in mid- and low-latitude glacier ice. Dating polar ice with satisfactory age precision is still not possible since WIOC concentrations are around one order of magnitude lower. The accuracy of the WIOC ^{14}C method was validated by applying it to independently dated ice. With this method the deepest parts of the ice cores from Colle Gnifetti and Mt. Ortles glacier in the European Alps, Illimani glacier in the Bolivian Andes, Tsambagarav ice cap in the Mongolian Altai, and Belukha glacier in the Siberian Altai have been dated. In all cases a strong annual layer thinning towards bedrock was observed and the oldest ages obtained were in the range of 10000 yrs. WIOC ^{14}C dating was not only crucial for interpretation of the embedded environmental and climatic histories, but additionally gave a better insight into glacier flow dynamics close to bedrock and past glacier coverage. For this the availability of multiple dating points in the deepest parts was essential, which is the strength of the presented WIOC ^{14}C dating method, allowing determination of absolute ages from principally every piece of ice.

Keywords: ice cores, mid- and low latitude glaciers, water-insoluble organic carbon, radiocarbon, chronology

1 Introduction

High altitude glaciers and ice caps from mid-latitudes and tropical regions contain valuable signals of past climate and atmospheric variability at regional and local scale and are located in areas with large biological diversity and inhabited by the majority of the world's population. Particularly mid-latitudes glaciers, for instance in the European Alps or in the Himalaya, are influenced by the nearby anthropogenic pollution sources, thereby additionally preserving the signature of human activities. This information can generally be retrieved from glacier ice cores, but needs to be placed in a precise chronological context to allow meaningful interpretation with respect to environmental and climatic changes.

Ice core dating is a sophisticated task and the most common approach is annual layer counting, which relies on seasonally fluctuating signals. A number of ice core parameters such as the stable isotope ratio of hydrogen or oxygen in the water (δ^2H, δ^{18}O), the concentration of trace components (e.g. ammonium, mineral-dust-related trace elements, black carbon), and the presence of melt layers may vary with the seasons. To reduce uncertainty in layer counting the time scale is additionally anchored with reference horizons like the radioactivity peak resulting from nuclear weapon tests in the 1960s or tephra and aerosol layers caused by volcanic eruptions (Thompson et al., 1998; Preunkert et al., 2000; Schwikowski, 2004; Eichler et al., 2009; Moore et al., 2012; Thompson et al., 2013). An independent method is nuclear dating with the naturally occurring radioisotope ^{210}Pb. Determined by the ^{210}Pb half-life of 22.3 years and its atmospheric concentration, the time period accessible for dating is in the order of a century (Gäggeler et al., 1983; Eichler et al., 2000; Herren et al., 2013). All these dating techniques fail in the older and deeper part of glaciers, where plastic deformation of the ice, under the weight of the overlying mass, results in horizontal ice flow, stretching annual layers continuously with increasing depth. Correspondingly, the depth-age relationship of high-alpine glaciers is strongly non-linear (Jenk et al., 2009) and annual layers and also volcanic signals become undetectable below a certain depth with the current spatial resolution of most analytical methods. Glacier flow modelling can only give rough age estimates with large uncertainties close to the bedrock of high-alpine glaciers (Lüthi and Funk, 2001). Radiocarbon (^{14}C) analysis has been the only option allowing a direct and absolute dating of these deeper ice core sections in the rare cases when sufficient organic matter such as plant, wood or insect fragments were found (Thompson et al., 1998; Thompson et al., 2002). However, in glacier ice such findings do not only happen very seldomly but even if lucky, they do not allow for continuous or at least regular dating which limits not only the application of the ^{14}C technique but also its use to derive a complete chronology based on absolutely dated layers. In the following we refer to dating of ice with macrofossils as conventional ^{14}C dating.

A new, complementary dating tool was therefore introduced by our group about 10 years ago, which is based on extracting the µg-amounts of the water-insoluble organic carbon fraction of carbonaceous aerosols embedded in the ice matrix for ^{14}C dating (Jenk et al., 2006; Jenk et al., 2007). Carbonaceous compounds represent a large, but highly variable fraction of the atmospheric aerosol mass (Gelencsér, 2004; Hallquist et al., 2009). Total organic carbon (TOC, also referred to as total carbon, TC) is instrumentally divided into two sub-fractions according to their refractory and optical properties. Elemental carbon (EC) consists of highly polymerized substances which are extremely refractory and light absorbent and therefore this fraction is also called black carbon (BC) or soot (Gelencsér, 2004; Hallquist et al., 2009). EC derives merely from the incomplete combustion of fossil fuels and biomass. Organic carbon (OC) is formed by weakly refractory hydrocarbons of low to medium molecular weight. Whereas EC is generally insoluble in water, OC is further subdivided into water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WIOC) (Szidat et al., 2004a). In water samples the former is also known as dissolved organic carbon (DOC) (Legrand et al., 2013; May et al., 2013). OC is emitted directly as primary aerosol from a vast diversity of sources and emission processes, including mobilization of plant debris, pollen, vegetation waxes, microorganisms, spores, the organic fraction of soil as well as emissions from biomass burning (e.g. forest fires) and anthropogenic processes (biomass burning and fossil fuel combustion), but it is also formed in the atmosphere by oxidation of gaseous precursors as secondary organic aerosol (Gelencsér, 2004; Gelencsér et al., 2007; Hallquist et al., 2009).

Carbonaceous aerosols are transported in the atmosphere to high-alpine glaciers, where they may be deposited by both wet and dry deposition processes and finally embedded in glacier ice (Lavanchy et al., 1999; Jenk et al., 2006; Legrand and Puxbaum, 2007; McConnell et al., 2007; Kaspari et al., 2011). Consequently using carbonaceous aerosols allows dating any piece of ice, given that it contains sufficient carbon mass. The WSOC fraction (i.e. DOC) would be ideal for dating, since it has the highest concentrations in ice. However, its extraction is complicated. It involves the outgassing of aqueous atmospheric CO_2, removal of dissolved carbonates, wet oxidation of the organic compounds to CO_2 under inert gas, and finally quantitative trapping of the evolved CO_2 (May et al., 2013). Since major contributors of DOC, like light carboxylic acids, are ubiquitous in the air, all these steps are prone to contamination. Therefore from the different carbonaceous particle fractions we selected WIOC as target for ^{14}C dating for several reasons. First, WIOC is mainly of biogenic origin in pre-industrial times (Jenk et al., 2006) and therefore supposed to contain a contemporary ^{14}C signal representative of the age of the ice (Jenk et al., 2006; Steier et al., 2006). Second, the average WIOC concentration in ice is higher than the respective EC concentration, allowing for smaller ice samples and potentially higher time resolution, which consequently provides a better signal to noise ratio (mainly determined by the overall blank) and smaller uncertainty of the dating results. Third, OC has a lower probability compared to EC for in-built reservoir ages from e.g. burning of old trees or old organic matter (Gavin, 2001; Sigl et al., 2009). Moreover OC is insensitive to potentially insufficiently removed carbonates in mineral dust rich layers (e.g. Saharan dust), which may contribute to the EC fraction because of the higher combustion temperature applied to EC (Jenk et al., 2006). The extraction of WIOC from the ice is straightforward as it can be collected by filtration of the melted ice. Note that in previous publications (Sigl et al., 2009; Zapf et al., 2013) the term POC was used for particulate organic carbon (Drosg et al., 2007). Since POC can be mistaken with primary organic carbon (Gelencsér, 2004; Zhang et al., 2012) we adopted the term water-insoluble organic carbon (WIOC) instead in this overview.

Our research group has a long history in ^{14}C dating of ice cores using the aforementioned WIOC fraction of carbonaceous particles. Lavanchy et al. (1999) introduced initial methods to determine the concentrations of carbonaceous particles in ice from a European high-alpine glacier. Next, the methodology was developed for source apportionment of aerosols by ^{14}C measurements in different carbonaceous particle fractions (Szidat et al., 2004b). This was conducted in close collaboration with the Laboratory of Ion Beam Physics of the ETH Zurich, a well established ^{14}C dating facility and a world-leading group in Accelerator Mass Spectrometry (AMS) technology, where simultaneously and continuously the analytical aspect of instrumentation was improved (Synal et al., 2000; Ruff et al., 2007; Synal et al., 2007; Ruff et al., 2010). The methodology of ^{14}C analysis of the different carbonaceous particle fractions was adopted to study the suitability of WIOC for ^{14}C dating of old ice, finding that it is of purely biogenic origin prior to industrialization (Jenk et al., 2006; Jenk et al., 2007). Since then this novel ^{14}C approach has been applied for dating a number of ice cores from different high-altitude mountain glaciers (Table 1), (Jenk et al., 2009; Sigl et al., 2009; Kellerhals et al., 2010; Herren et al., 2013; Zapf et al., 2013; Aizen et al., 2016). Meanwhile the method has been further optimized and was additionally validated by determining the age of independently dated ice. Here we give an overview of the current status of the now routinely applied WIOC ^{14}C dating method for glacier ice, including an update on recent optimizations and method validation. Uncertainties and the potential of this novel approach are discussed and its succesfull application to a number of ice cores presented ~~Here we give an overview of the current status of the now routinely applied ^{14}C dating method for glacier ice by presenting an update on recent optimizations and discussing the potential of this novel approach~~.

2 Sample preparation, OC/EC separation and ^{14}C analysis

The preparation of ice samples follows the procedure according to Jenk et al. (2007). First, samples are decontaminated in a cold room (-20˚C) by removing the outer layer (3 mm) with a pre-cleaned stainless steel band saw (wiped three times with acetone, followed bycutting of a frozen block of ultra-pure water, 18 MΩ cm quality), followed by rinsing the samples with ultra-pure water ~~(18 MΩ cm quality)~~ in a class 100 clean bench. Around 20-30% of the ice samples' mass is lost during these first steps, resulting in a final mass of about ~~100~~ 200 to 500 g (initial mass of around ~~600~~300-800 g of ice). The samples are then transferred and stored frozen at -20˚C in pre-cleaned (soaked and rinsed for three days with daily exchanged ultra-pure water) 1-L-containers (Semadeni, PETG) until being melted at room temperature directly before filtration. To ensure that carbonates potentially present in the ice are completely dissolved, ~20 mL of 1M HCl (30% Suprapure, Merck) are added to the melted samples (Cao et al., 2013), resulting in a pH of < 2, before being sonicated for 5 min. Subsequently, the insoluble carbonaceous particles are filtered onto preheated (5h at 800˚C) quartz fibre filters (Pallflex Tissuquartz, 2500QAO-UP), using a dedicated glass filtration unit, also carefully pre-cleaned by rinsing with ultra-pure water and by baking the glass at 450˚C for 3h. As a second carbonate removal step, the filters are acidified three times with a total amount of 50 µL 0.2M HCl (Jenk et al., 2007). Afterwards the filters are left in a class 100 clean bench for 1h to allow potentially present carbonates to be transformed into CO_2 by reaction with the HCl, followed by rinsing with 5 ml ultra-pure water to entirely remove remaining HCl. The filters are left again for 1h to reach complete dryness, packed in aluminium foil and kept frozen until analysis, for which filters are taken out of the freezer to let them reach ambient temperature (at least half an hour). Details regarding OC and EC separation, AMS ^{14}C analysis and improvements achieved since the first applications will be discussed in Sections 3 and 4.

3 Recent optimization in OC/EC separation and AMS analysis

In previous ice core dating applications using ^{14}C of WIOC (Jenk et al., 2009; Sigl et al., 2009; Kellerhals et al., 2010; Herren et al., 2013; Zapf et al., 2013), the OC and EC combustion was performed with the Two-step Heating system for the EC/OC Determination Of Radiocarbon in the Environment apparatus (THEODORE), developed for aerosol applications (Szidat et al., 2004b). The combustion was conducted in a stream of oxygen for the controlled separation of OC and EC fractions. The temperature for OC separation was set at 340˚C, while for recovery of EC the temperature was then increased to 650˚C. The CO_2 produced by oxidation during the combustion was cryogenically trapped, manometrically quantified and sealed in glass ampoules (Szidat et al., 2004b). In the earliest application described by Jenk et al. (2006) the CO_2 subsequently had to be transformed to filamentous carbon (graphitisation) using manganese granules and cobalt powder for final AMS ^{14}C analysis. This was initially performed at the ETH AMS facility (TANDY, 500 kV pelletron compact AMS system) (Synal et al., 2000). Since 2006, the 200kV compact AMS (MIni radioCArbon DAting System, MICADAS) has been operational at the ETH (Synal et al., 2007). The MICADAS is equipped with a gas ion source and a Gas Introduction interface System (GIS) (Ruff et al., 2007; Synal et al., 2007), allowing measurements of ^{14}C directly in CO_2 with an uncertainty level as low as 1% (Ruff et al., 2010). The GIS includes a gas-tight syringe for the CO_2 injection into the ion source (Ruff et al., 2010), with a maximum capacity of 1.3 ml of CO_2 as ~5% mixing ratios in helium (equivalent to 100 µg of carbon). The position of the syringe plunger is automatically adjusted according to the sample size as well as the helium flow carrying the sample to the ion source. With this, the tranformation of gaseous CO_2 to solid graphite targets became needless (Sigl et al., 2009). Instead, the glass ampoules sealed after the combustion of the filters with the THEODORE system were opened in a designated cracker, an integral part of the GIS (Ruff et al., 2007), and the resulting CO_2-He mixture could directly be fed into the MICADAS ion source.

The main advantages of switching from solid to gaseous targets were: 1. a decrease in the number of necessary preparation steps and the associated risk of lost samples from incomplete graphitisation, 2. a higher sample throughput, 3. a reduction in the variability and overall blank contribution as well as 4. the elimination of the correction applied to account for fractionation during the graphitisation step, which contributed with around 10% to the overall uncertainty (Jenk et al., 2007). As will be discussed in Section 4, a precision increase is one of the main challenges for improving the method.

Since spring 2013, ^{14}C analysis is performed with a MICADAS installed at the Laboratory for the Analysis of Radiocarbon with AMS (LARA laboratory) of the University of Bern, also equipped with a GIS interface (Szidat et al., 2014). There, an improvement was recently achieved by replacing the THEODORE with a commercial combustion system, which is a thermo-optical OC/EC analyzer (Model4L, Sunset Laboratory Inc., USA), normally used for aerosol OC/EC separation and source apportionment studies (Zhang et al., 2012; Zhang et al., 2013; Zhang et al., 2014; Zotter et al., 2014). Similar as in the THEODORE system, the carbonaceous particles are combusted in a stream of pure oxygen. The Sunset instrument is specially equipped with a non-dispersive infrared (NDIR) cell to quantify the CO_2 produced during the combustion. The combustion process in the Sunset system follows a well-established protocol (Swiss 4S) for the thermal separation of OC and EC fractions under controlled conditions (Zhang et al., 2012). To avoid potential damage of the infrared cell detector by residual HCl, the final rinsing of the filters after adding HCl for carbonates removal was introduced (see Section 2).~~ Tests with blank filters and standard materials were performed to exclude any potential contamination from this additional step~~. Recently ~~T~~the Sunset instrument ~~is~~ was directly coupled to the zeolite trap of the GIS (Ruff et al., 2010), which allows online ^{14}C measurements of the carbonaceous fractions separated in the Sunset system (Agrios et al., 2015). When combusted, the gaseous carbonaceous species pass through a MnO_2 bed heated to 850˚C for completing the oxidation to CO_2, which is further transported by helium to the zeolite trap. This trap is then heated up to 500˚C to release the CO_2 to the gas-tight syringe for final injection into the AMS ion source (Ruff et al., 2007; Synal et al., 2007).

The newly coupled Sunset-GIS-AMS system has major advantages compared to the old setup. The OC/EC separation in the THEODORE was relatively time consuming and only four ice samples could be processed per day. Two more days were needed to produce all the standards and blanks required for AMS calibration and for quality control and graphitisation (Jenk et al., 2007). Besides the disantvantages of solid graphite targets described before, there is also a risk of losing samples during the delicate phase of flame-sealing the ampoules and later on when scratching them to allow a clean break in the automated GIS cracker. With the online coupling of the Sunset, this risk is completely removed. Further the preparation and measurement time is significantly reduced because there is no need for offline combustion resulting in a total measurement time of approximately 35 min per sample only. In addition, it not only allows for an automated protocol of standard injection for AMS calibration, but also offers the possibility for easy and regular (daily) survey of the ^{14}C background in the entire process line (Sunset-GIS-AMS) by analysis of variably sized standards and blanks if required ~~(~~(Agrios et al., 2015).~~see last paragraph of this Section~~). Finally, the Sunset system enables continuous monitoring of the combustion process, reducing a potential bias due to charring, and the standardized and automated combustion protocol (Swiss 4S) ensures high reproducibility increasing the overall precision.

With the current setup, the $^{14}C/^{12}C$ ratio of the samples is background subtracted, normalized and corrected for mass fractionation by using fossil sodium acetate (^{14}C free, NaOAc, p.a., Merck, Germany), the reference material NIST standard oxalic acid II (modern, SRM 4990C) and the $\delta^{13}C$ simultaneously measured in the AMS, respectively (Wacker et al., 2010). All results are expressed as Fraction Modern ($F^{14}C$), which is the $^{14}C/^{12}C$ ratio of the sample divided by the same ratio of the modern standard~~which is the deviation of the $^{14}C/^{12}C$ ratio of the sample from that of the modern standard~~. Further corrections are subsequently applied to the $F^{14}C$ values considering isotopic mass balance (e.g. Jenk et al., 2007) to account for constant contamination, cross contamination and for the procedural blank contribution introduced by the preparation of ice samples (for details see Section 4). ^{14}C ages (before present (BP), i.e. before 1950) are calibrated using OxCal v4.2.4 (Bronk Ramsey and Lee, 2013) with the Northern (IntCal13) or Southern Hemisphere (ShCal13) calibration curves (Hogg et al., 2013; Reimer et al., 2013), depending on the sample site location. Calibrated dates are given in years before present (cal BP~~, with BP = 1950~~) with 1 σ uncertainty range (Stuiver and Polach, 1977; Mook and van der Plicht, 1999). For simplicity the ages dicussed in the text are given as the mean of this range ±1 σ. See Section 4 for further details regarding the applied corrections, ^{14}C calibration and discussion of uncertainties.

To ensure comparability between previous data and the newly derived results, using the above described improved setup configuration, ^{14}C analysis was conducted on remaining pieces of samples, which were previously processed with the THEODORE setup. Two samples (~~Juv1~~ JUV 1 and ~~Juv2~~JUV 3) from the Juvfonne ice patch in Norway (Zapf et al., 2013) and two samples (~~Bel1~~ BEL 1 and ~~Bel2~~BEL 2) from an ice core drilled at Belukha glacier in the Siberian Altai (Aizen et al., 2016) were used, covering an age range from modern to more than 8000 cal BP. The OC masses were above 10 µg carbon, except for sample Juv2_Sunset with a carbon mass of 9 µg (Table 2), still resulting in more than 4500 ^{14}C counts with a corresponding uncertainty of the $F^{14}C$ of 2%, which we consider sufficiently low for this comparison. At first, the obtained

WIOC concentrations are discussed, which are assumed to agree as indicated by a carbon quantification test carried out on homogeneous aerosol filters using both combustion instruments (Zotter et al., 2014). As expected a good consistency was found for the WIOC concentrations in the Belukha ice core (Table 2), whereas a discrepancy was observed for the Juvfonne samples, probably related to the natural inhomogeneity of particles in this small-scale ice patch with a distinct ice accumulation behaviour (see below). Concerning the ^{14}C ages, a very good agreement is shown between all parallel samples (Figure 1). This is also true for the procedural blanks , both in term of carbon amount and F^{14}C. ~~The THEODORE resulted in a blank contribution of 1.41 ± 0.69 µg with F^{14}C of 0.64 ± 0.12, and the Sunset in 1.21 ± 0.51 µg with a F^{14}C of 0.73± 0.13. We therefore conclude that dating results obtained with the old THEODORE combustion setup~~ (Jenk et al., 2009; Sigl et al., 2009; Herren et al., 2013; Zapf et al., 2013) ~~and with the improved coupled Sunset-GIS-AMS system are in good agreement~~. The WIOC procedural blank measured and used for correction in this comparision experiment was 1.41 ± 0.69 µg of carbon with an F^{14}C of 0.64 ± 0.12, and 1.21 ± 0.51 µg of carbon with an F^{14}C of 0.73± 0.13 for the THEODORE and the coupled Sunset setup, respectively (additional details can be found in Section 4). In summary, we conclude that dating results obtained with the previously used THEODORE combustion setup (Jenk et al., 2009; Sigl et al., 2009; Herren et al., 2013; Zapf et al., 2013) and the improved coupled Sunset-GIS-AMS system are in good agreement.

4 Radiocarbon dating uncertainties

First of all, the signal-to-noise ratio of the AMS measurement is defined by counting statistics. Generally, the smaller the sample, the shorter the measurement time, the higher the uncertainty. For defining the contamination contribution of the overall instrument setup (constant contamination) and the memory effect between subsequent samples of very different ^{14}C content and carbon mass (cross contamination), a series with varying amounts of solid grains of fossil NaOAc and the modern reference material oxalic acid II was combusted with the Sunset and measured for its ^{14}C content. The constant contaminant mass was estimated as 0.4 ± 0.2 µg carbon with a F^{14}C of 0.8 ± 0.4 and for the cross contamination 0.5 ± 0.4% of the carbon of the previous sample was found to mix with the next injection (Agrios et al., 2015).

The total carbon amounts in ice cores are rather low, in the µg/kg-range. Because of that, each step of sample preparation implies a potential risk of contamination with either modern or fossil carbon. Thus a large contribution to the final overall uncertainty on the age is induced by the procedural blank correction, especially for small size samples. It is therefore crucial that cutting, melting and filtrating the ice results in the lowest possible procedural blank with a stable F^{14}C value to ensure a high and stable signal-to-blank ratio for obtaining reliable results with the smallest possible uncertainties. Procedural blanks were estimated using artificial ice blocks of frozen ultra-pure water, treated in the same way as real ice samples (Jenk et al., 2007). Blanks were usually prepared together with samples and their analysis was performed during every AMS measurement session (Sunset combustion and AMS analysis). The ~~average~~ mean of the overall procedural blank (WIOC) used to correct all samples is 1.34 ± 0.62 µg of carbon with a F^{14}C of 0.69 ± 0.13 (100 and 54 measurements, respectively, performed over a 10-year period). This includes all values obtained with both, the THEODORE and Sunset system. We decided to use this combined value, since the ice sample preparation step is the by far largest contribution to the blank and is system independend. This mean value~~s~~ ~~are~~ is consistent with previously reported results (Jenk et al., 2007; Sigl et al., 2009), indicating the long-term stability of the procedural blanks.

In summary, all the corrections have the strongest effect on low carbon mass samples, resulting in the largest dating uncertainties. Further, such small samples can only be measured for a short period of time, with reduced stability of the ^{12}C current, additionally worsening of the signal-to-noise ratio. Low carbon mass samples of old age contain even a lower number of ^{14}C compared to younger samples due to radioactive decay and are affected the most. Among all uncertainties described, the correction for the procedural blank contributes typically around 60%. As an example, for hypothetical samples with a WIOC mass of 5 or 10 µg, the resulting uncertainty of the finally calibrated ages for 1000 year old ice would be around ± 600 yrs or ± 250 yrs and for 8000 year old ice around ± 1600 yrs or ± 700 yrs, respectively. Hence by doubling the mass, the uncertainty is reduced by more than 50%. We therefore generally discuss dating results only for sample masses larger than ~10 µg WIOC, which have an acceptable age uncertainty in the range of 10-20%.

While calibrating the ages with the OxCal, a sequence constraint can be applied based on the assumption of a monotonous increase of age with depth (Bronk Ramsey, 2008). This approach often leads to a reduction of the final uncertainty, which however strongly depends on the sample resolution with depth, see example in Jenk et al. (2009).

5 Validation of the dating accuracy

5.1. First attempts

Validating the accuracy of the here described approach for ^{14}C dating of ice is a challenging task since it requires ice samples with known ages, preferentially covering a large age range.

First attempts for validation by dating ice from Greenland with an age determined by annual layer counting failed, because WIOC concentrations are an order of magnitude lower compared to ice from glaciers located closer to biogenic emission sources (Figure 2). Large ice samples were thus needed, nevertheless resulting in small amounts of carbon. Our preparation method is not optimised for such sample sizes, and the required pooling of several pieces of ice may have induced a higher procedural blank. As a result ^{14}C ages tended to be biased by the procedural blank value (Sigl et al., 2009). ^{14}C ages of the Fiescherhorn ice core (Jenk et al., 2006) ranged from modern values to 1000 years, thus reasonably matching the age of the ice older than AD 1800 obtained by annual layer counting. For the ice core from Mercedario (31.98° S, 70.13° W; 6100 m a.s.l.) the deepest core sections show ages of <550 and 320–1120 cal BP, respectively, well in line with a tentative chronology based on annual layer counting (Sigl et al., 2009). However, considering the relatively large uncertainty of our method if compared to conventional ^{14}C dating typically derived from samples with much larger carbon masses and the flatness of the ^{14}C calibration curve between around 500 and 0 cal BP such samples of rather young ages are not ideal for a precise validation. Two samples from the Illimani ice core, bracketing the AD 1258 volcanic eruption time marker resulted in a combined calibrated age of AD 1050±70 (1 σ) overestimating the expected age by ~~ca.~~around 200~~±70~~ years~~ (1 σ)~~. This would be an acceptable accuracy if applicable to several thousand years old ice (Sigl et al. 2009).

Overall these were first indications that the ^{14}C method gives reliable ages. Meanwhile we have had access to independently dated ice from the Juvfonne ice patch and the Quelccaya ice cap, dated a fly which we discovered in the Tsambagarav ice core, and dated ice cores from Mt. Ortles glacier, in which a larch leaf was found, altogether allowing a more robust validation as outlined in the following.

5.2. Recent validation

Juvfonne is a small perennial ice patch in the Jotunheimen Mountains in central southern Norway (61.68° N, 8.35° E). In May 2010, a 30-m-long ice tunnel was excavated, revealing several up to 5 cm thick dark organic-rich layers containing organic remains ~~residues~~, which were interpreted as previous ice-patch surfaces and conventionally ^{14}C dated (Nesje et al., 2012). We received two samples of clear ice adjacent to the organic-rich layers and a surface sample (JUV 1, JUV 2, JUV 3, Table 3). The results derived using WIOC agreed well with the corresponding, conventionally dated ^{14}C ages with an age range between modern and 2900 cal BP (Zapf et al., 2013). In summer 2015 we collected additional clear ice samples adjacent to a ~~6600 years~~conventionally ^{14}C dated plant fragment ~~layer~~ found in an organic-rich layer at the base of a new tunnel excavated in 2012 and extending deeper into the ice patch (Ødegård et al., 2016). Four ice blocks were collected and afterwards subdivided in two sub-samples each. Ice block 1 (JUV 0_1 and JUV 0_2) was taken adjacent to the plant fragment layer, ice block 2 (JUV 0_3 and JUV 0_4), ice block 3 (JUV 0_5 and JUV 0_6) and ice block 4 (JUV 0_7 and JUV 0_8) at the bottom of the wall, a few cm below the plant fragment layer. JUV 0_1 and JUV 0_2 yielded an average age of 7127 ± 134 cal BP, which is in good agreement with the age of the plant fragment layer of 6608 ± 53 cal BP,~~.~~ considering the observed increase in ages with increasing depth. Accordingly, t~~T~~he other six samples collected even further below this organic-rich layer resulted in ~~are~~ significantly older ages (7593 ± 74 cal BP, Table 3).~~, which is reasonable since they were collected below the plant fragment layer~~.

Three sections of the ice core from the Quelccaya Summit Dome drilled in 2003 (QSD, Peruvian Andes, 168.68 m, 13°56’S, 70°50’W, 5670 m a.s.l.) were kindly provided by Lonnie Thompson, Ohio State University. The entire ice core was dated by annual layer counting indicating an age of 1800 years at the bottom (Thompson et al., 2013). Intentionally we received the samples without knowing their ages or depths in order to have the opportunity to perform a “blind test”. The three sections were not decontaminated as usual, but only rinsed with ultra-pure water, because the amount was not large enough for removing the outer layer mechanically. As shown in Figure 3 (see also Table 4 for the results) the resulting calibrated ages agree very well with the ages based on annual layer counting (L. Thompson, personal communication 2015).

Recently a number of core segments of the previously dated Tsambagarav ice core (Herren et al., 2013) were resampled. In segment 102 a tiny insect (Figure 4) was found and immediately separated from the ice matrix. Since it was small, a conventional ^{14}C analysis was not suitable and instead the Sunset-AMS system was deployed. The ice section containing the fly was melted, possible contamination from carbonates and humic acids were removed by an acid-base-acid treatment at 40°C (Szidat et al., 2014), the fly was dried, placed onto a quartz fibre filter and combusted in the Sunset, resulting in 13 µg of carbon. The age of 3442 ± 191 cal BP (BE-5013.1.1) is in perfect agreement with the age of WIOC from this ice segment of 3495 ± 225 cal BP (Herren et al., 2013) (Figure 3).

Additionally, we dated three sections from a set of ice cores drilled in 2011 on Mt. Ortles (see Table 1 for location) for which a preliminary age of 2612 ± 101 cal BP was derived by conventional ^{14}C dating of a larch leaf found at 73.2 m depth (59.60 m weq, ~1.5 m above bedrock) (Gabrielli et al., 2016). Every section was horizontally divided in three sub-samples (top, middle, bottom). For the section at 68.61 m depth (55.08 m weq, core #1) and the section at 71.25 m depth (57.94 m weq, core #3), ~~T~~the ages obtained for the sub-samples were not significantly different from each other ~~for of the sections at 68.61 m (55.08 m weq) depth (core #1) and the section at 71.25 m (57.94 m weq) depth (core #3)~~ especially if ~~also considering~~accounting for the expected thinning of annual layer thickness at these depths (Figure 5). Accordingly the results of the ~~according~~respective sub-samples were combined to derive the most accurate ages for the mid-depths of these two sections (mean F^{14}C~~ mean~~ with the estimated 1σ uncertainty being the standard error of the unbiased standard deviation).~~were not significantly different from each other, respectively. Accordingly the derived ages were combined using the corresponding function in OxCal v4.2.4 (^{14}C date combination)~~. On the contrary the ages of the three sub-samples from the deepest section at 74.13 m ~~(60.54 m weq)~~ (60.54 m weq, core #3) significantly increased with depth, implying strong glacier thinning close to bedrock (see also Gabrielli et al., 2016~~, this issue~~). Our WIOC ^{14}C ages obtained for the Mt. Ortles ice core agree well with the age of the larch leaf assuming an exponential increase of age with depth (Figure 5).

The scatter plot in Figure 3 summarizes the different validation experiments described above. The results for the Mt. Ortles ice core were not included because larch leaf and WIOC samples were extracted from depths of significantly different ages. As shown, within the uncertainties, the ^{14}C ages fall onto the 1:1 line in the age range from ~700-3500 cal BP, convincingly demonstrating good accuracy of our method. All validation experiments were performed on low-dust samples, thus avoiding potential dating bias due to the presence of dust (Hoffmann, 2016).

6 Applications and current potential of the ^{14}C method for dating glacier ice

Over the last 10 years the deepest parts of several ice cores have been dated applying the presented WIOC ^{14}C method. To illustrate the current potential of the method with respect to the time period accessible we compiled five ice core chronologies in Figure 6. The sites differ in recent net annual snow accumulation and ice thickness (in brackets): Tsambagarav ice cap in the Mongolian Altai 0.33 m weq (72 m) (Herren et al., 2013), Belukha glacier in the Siberian Altai

0.34 m weq (172 m) (Aizen et al., 2016), Colle Gnifetti glacier in the European Alps 0.46 m weq (80 m) (Jenk et al., 2009), Illimani glacier in the Bolivian Andes 0.58 m weq (138.7 m) (Kellerhals et al., 2010), Mt. Ortles glacier 0.85 m weq (75 m) (Gabrielli et al., 2016~~, this issue~~). All of these are cold glaciers and frozen to the bedrock with the exception of Mt. Ortles glacier, which is polythermal and experienced a recent acceleration of glacier flow due to sustained atmospheric warming over the past decades ~~and basal sliding can not totally be excluded at least for certain periods of time~~ (Gabrielli et al., 2016~~, this issue~~). To derive a continuous age depth relationship, a two parameter flow model (Bolzan, 1985; Thompson et al., 1990) was applied for Colle Gniffetti (Jenk et al., 2009), Illimani (Kellerhals et at., 2010) and here also for the core from Belukka using the data presented in Aizen et al. (2016). A different approach as discussed below, was implemented for the ice cores from the Tsambagarav ice cap (Herren et al., 2013) and the glacier on Mt. Ortles (see also Gabrielli et al., 2016 , ~~this issue~~). The two parameter model is based on a simple analytical expression for the decrease of the annual layer thickness $L_{(z)}$ (m weq) with depth:

$$L_{(z)} = b\left(1-\frac{z}{H}\right)^{p+1}$$

where z is depth (m weq), H the glacier thickness (m weq), b the annual accumulation (m weq) and p a thinning parameter (dimensionless). The age T(z) as a function of depth can be calculated when the inverse layer thickness is integrated over depth:

$$T_{(z)} = \int \frac{dz}{L_{(z)}} = \frac{1}{b}\int \left(1-\frac{z}{H}\right)^{-p-1} dz$$

Solving the integral and setting the age at the surface to be T(0) = 0, the final age-depth relation is obtained:

$$T_{(z)} = \frac{H}{bp}\left[\left(1-\frac{z}{H}\right)^{-p}-1\right]$$

The thinning rate (vertical strain rate) is the first derivative of the layer thickness:

$$L'_{(z)} = \frac{dL_{(z)}}{dz} = -\frac{b(p+1)}{H}\left(1-\frac{z}{H}\right)^{p}$$

The model has two degrees of freedom, the net annual accumulation rate b and the thinning parameter p both assumed to be constant over time. This allows to fit the model by a least squares approach through ~~selected reference~~the available reference horizons if the glacier thickness H is known (if drilled to bedrock) or can be reasonably well estimated (e.g. from radar sounding). In order to not overweight the data from the deepest horizons, the model is fitted using the logarithms of the age values. For the ice cores from Colle Gnifetti (Jenk et al., 2009), Illimani (Kellerhals et al., 2010) and Belukha (Aizen et al., 2016) these ages were based on annual layer counting, identification of reference horizons (radioactive fallout and well-known volcanic eruptions) and ^{14}C dates. The data is summarized in Table 1. In Figure 6, only reference horizons and ^{14}C dates were included for simplification.

In summary, a reasonable fit was achieved for these three glaciers and the derived annual net accumulations (Colle Gnifetti 0.45±0.03 m weq, Belukha 0.36 ± 0.03 m weq, Illimani 0.57 ± 0.13 m weq) are comparable with the values previously published (see above), which were determined either by surface measurements or ~~with the~~ were estimated ~~accumulation~~ based on ALC or/and the uppermost age horizons only (e.g. nuclear fallout peak), thereby accounting for the (slight) layer thinning occuring in these uppermost few meters (Nye, 1963). Since the assumption of constant accumulation (b) and a constant thinning parameter (p) over time/with depth is likely only true in a first order approximation it is thus no surprise that~~, with~~ the two parameter model ~~no~~ may fail to result in a reasonable fit within the derived age uncertainties. In such a case ~~fit could be achieved~~ these two underlying assumptions should then be investigated more thoroughly as it was e.g. done for the ice cores from Tsambagarav and Mt. Ortles. Whereas Tsambagarav also is a cold glacier, Mt. Ortles is polythermal. For Tsambagarav, a good fit can be achieved ~~a fit is only possible~~ if additional degree of freedom is given to account for variations in the net accumulation rate while p is fixed to the initially derived value, suggesting significant changes in the accumulation rate over time. This is supported by the fact that the resulting strong variation in net accumulation is consistent with precipitation changes in the Altai derived from lake sediment studies (Herren et al., 2013). Opposite to that, a reasonable fit for the Mt. Ortles ice core can only be obtained if the thinning parameter p is allowed to increase with depth~~.~~, while the annual net accumulation is assumed to be constant over time (i.e. b fixed to the value defined by the stake measurements and surface layers). This points to an exceptionally strong thinning. Mt. Ortles glacier is polythermal with temperate conditions in the upper part and still relatively warm ice with -2.8°C near bedrock. We hypothesize that the faster horizontal velocity of the warm ice causes exceptional horizontal stress (internal horizontal deformation) on the ice frozen to the bedrock, resulting in stronger thinning. In both cases, a purely empirical approach of fitting the age horizons was chosen to ~~yield~~ establish the age-depth relationship. Note that ~~(d~~due to the lack of absolute time markers prior to 1958, ^{210}Pb dated horizons ~~with a larger uncertainty compared to the age of time markers~~ were used for Mt. Ortles ~~)~~. For Tsambagarav a combination of different polynomial functions was used (Herren et al., 2013), whereas a slightly more sophisticated approach by means of Monte Carlo simulation was applied for Mt. Ortles, allowing an objective uncertainty estimate for each depth defined by the density of dating horizons and their individual uncertainty (Gabrielli et al., 2016 ~~, this issue~~). ~~Such a~~These purely empirical approaches are ~~is~~ justified given the high confidence assigned to the determined ages for the dated horizons. ~~For Tsambagarav, the strong variation in net accumulation was consistent with precipitation changes derived from lake sediment studies in the Altai (Herren et al., 2013). Mt. Ortles glacier is polythermal with temperate conditions in the upper part and still relatively warm ice with -2.8°C near bedrock. We hypothesize that the faster horizontal velocity of the warm ice causes exceptional horizontal stress (internal horizontal deformation) on the ice frozen to the bedrock, resulting in stronger thinning.~~

As shown in Figure 6, the time period dated with ^{14}C ranges from 200 to more than 10000 yrs. Due to their uncertainty, ^{14}C ages derived by our method cannot compete with the conventional methods for dating ice that is only a few centuries old. The strength of ^{14}C dating using WIOC is that it allows obtaining absolute ages from ~~principally~~ basically every piece of ice ~~core~~ from cold and poly~~i~~thermal ice bodies. This is especially valuable for glaciers not containing the last glacial/interglacial transition, as Tsambagarav and Mt. Ortles, since in such cases not even climate wiggle matching of the transition signal with other dated archives is possible. Anyhow, an absolute dating method is ~~superior~~ preferable to wiggle matching, which is not necessarily reliable. For example, a depletion in δ^{18}O presumably indicating the LGM-Holocene transition might not always be a true atmospheric signal, but can be caused by unknown mechanisms potentially happening close to bedrock (Jenk et al., 2009; Wagenbach et al., 2012). All five examples show strong thinning towards bedrock with ~~and~~ the oldest ages obtained ~~were~~ being in the range of 10000 years. Because of the strong thinning, the ^{14}C age of the deepest sample represents a strongly mixed age of ice with a large age distribution. In these cases, the age limit was thus not determined by the ^{14}C half-life of 5730 yrs (Godwin, 1962), but by the achievable spatial depth resolution~~,~~ since some hundred grams of ice ~~are~~ is required. ~~and not by the half life of ^{14}C of 5730 yrs (Godwin, 1962)~~. ~~With this strong thinning the ^{14}C age of the deepest sample may represent a mixed age of ice having a large age distribution.~~

Since an absolute WIOC mass of ~10 µg is needed to achieve a ^{14}C dating with reasonably low uncertainty, the overall applicability of the method essentially depends on the WIOC concentration in the ice and the ice mass available. Figure 2 summarizes WIOC concentrations determined in ice from various locations around the globe. In general, mid-latitude and low-latitude glaciers contain sufficient WIOC from 21 to 295 µg/kg, allowing dating with less than 1 kg of ice. The highest concentration was found at Juvfonne ice patch which is small and located a low elevation and therefore by far closest to biogenic emission sources. WIOC concentrations might be further elevated due to meltwater and superimposed ice formation, enriching water-insoluble particles in the surface layer present at that time. Lowest concentrations of only 2 to 15 µg/kg WIOC were observed in polar snow and ice from Greenland and Antarctica. For this concentration range a reliable dating is impossible with the current method capability.

7 Conclusions

Since the introduction about 10 years ago of the ^{14}C dating technique for glacier ice, utilizing the WIOC fraction of carbonaceous aerosol particles embedded in the ice matrix, major improvements in separating the OC from the EC fraction and in AMS technology have been achieved. The new configuration with direct coupling of a commercial thermo-optical OC/EC analyser to the gas ion source of the MICADAS AMS via its gas introduction interface has two major advantages. First, the measurement time was significantly reduced to approximately 35 min per sample. Second, the implemented automated protocol allows for a controlled routine analysis with high reproducibility and a stable blank, thereby increasing the overall precision.

The presented WIOC ^{14}C dating method was validated by determining the age of independently dated ice samples. It principally allows absolute and accurate dating of any piece of ice ~~-~~containing sufficient WIOC. With the current set~~-~~up, the age of samples with a minimum of ~10 µg WIOC can be determined with satisfying precision of about 10 to 20%, depending on the age. This requires about ~~100~~ 300 to ~~500~~ 800 g of ice, considering both, the mass loss of 20-30% during surface decontamination and the WIOC concentrations typically found in mid- and low latitude glaciers. Dating polar ice with satisfactory age uncertainties is still not possible since WIOC concentrations are around one order of magnitude lower. This would require further reduction of the procedural blank for such samples requiring larger ice volumes which potentially could be achieved by an additional, specifically designed sample preparation setup for such kind of samples.

The ^{14}C method is suitable for dating ice with ages from 200 to more than 10000 yrs. Whereas for a few century old ice the conventional dating methods are typically higher in precision, the WIOC ^{14}C method presents the only option for obtaining reliable continuous time scales for the older and deeper ice core sections of mountain glaciers. This is not only crucial for interpreting the embedded environmental and climatic history, but gives additional insight into glacier flow dynamics close to bedrock as demonstrated by the depth-age scales derived from ^{14}C dating of ice cores from various mid- and low latitude glaciers. Also, it can reveal information about the time of glacier formation.

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Author contribution

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Table 1: Characteristics of the sites discussed and the respective dating approach. ALC stands for Annual Layer Counting, RH for Reference Horizons and ^{210}Pb, ^{3}H, and ^{14}C for nuclear dating. 2p model (two parameter model), MC (Monte Carlo simulation) and EF (exponential fit) denotes the applied approach to finally derive a continuous age-depth relationship (see Section 6 for details).

Site	Coordinates Elevation	Location	Dating approach	Time span (years)	References
Belukha	49.80°N, 86.55°E 4115 m a.s.l.	Altai Mountains, Russia	ALC, RH, ^{3}H, ^{14}C, 2p model	~9100	Aizen et al., 2016
Colle Gnifetti	45.93°N, 7.88°E 4450 m a.s.l.	Western Alps, Swiss-Italian border	ALC, RH, ^{3}H, ^{210}Pb, ^{14}C, 2p model	>15200	Jenk et al., 2009
Juvfonne	61.68˚N, 8.35E 1916 m a.s.l.	Jotunheimen Mountains, Norway	^{14}C of plant fragment and WIOC	~7600	Zapf et al 2013 Ødegård et al., 2016
Illimani	17.03°S, 68.28°W 6300 m a.s.l.	Andes, Bolivia	ALC, RH, ^{3}H, ^{210}Pb, ^{14}C, 2p model	~12700	Sigl et al., 2009 Kellerhals et al., 2010
Mt. Ortles	46.51°N, 10.54°E 3905 m a.s.l.	Eastern Alps, Italy	ALC, RH, ^{3}H, ^{210}Pb, ^{14}C, MC	~6900	Gabrielli et al., 2016
Quelccaya	13.93°S, 70.83°W 5670 m a.s.l.	Andes, Peru	ALC, ^{14}C	~1800	Thompson et al., 2013
Tsambagarav	48.66°N, 90.86°E 4130 m a.s.l.	Altai Mountains, Mongolia	ALC, RH, ^{3}H, ^{210}Pb, ^{14}C, EF	~6100	Herren et al., 2013

Table 2: Samples analysed for the compararability test for OC/EC separation using the THEODORE apparatus and the Sunset OC/EC analyzer directly coupled to the AMS, with WIOC masses and concentrations. Calibrated ages (cal BP) denotes the 1 σ range.

Sample ID	AMS Lab. No.	WIOC mass (µg)	WIOC concentration µg/kg ice	F^{14}C	^{14}C age (BP)	cal age (cal BP)
1_THEODORE (JUV 3)	ETH 42845.1.1 ETH 42847.1.1 ETH 42849.1.1 ETH 43446.1.1	44	176	1.134 ± 0.017	-1010 ± 120	-46 - -7
1_Sunset (JUV 3)	BE 3683.1.1 BE 3701.1.1	46	119	1.~~160~~ 157 ± 0.~~013~~014	-~~1192~~ 1171 ± ~~90~~97	-~~41~~ 42 - -8
2_THEODORE (JUV 1)	ETH 43555.1.1 ETH 43557.1.1	18	60	0.743 ± 0.029	2386 ± 314	2011 - 2783
2_Sunset (JUV 1)	BE 3679.1.1	9	33	0.~~751~~ 744 ± 0.021	~~2300~~ 2376 ± 225	~~2068~~ 2158 - ~~2703~~2737
3_THEODORE (~~Bel~~ BEL 1)	ETH 42841.1.1	18	63	0.771 ± 0.017	2089 ± 177	1886 - 2310
3_Sunset (~~Bel~~ BEL 1)	BE 4282.1.1	15	61	0.~~739~~ 725 ± 0.022	~~2430~~ 2587 ± ~~239~~233	~~2159~~ 2353 - ~~2761~~2924
4_THEODORE (~~Bel~~ BEL 2)	ETH 43448.1.1	15	47	0.402 ± 0.022	7320 ± 440	7686 - 8588
4_Sunset (~~Bel~~ BEL 2)	BE 4175.1.1	18	48	0.~~388~~ 387 ± 0.022	~~7605~~ 7626 ± ~~455~~457	~~7983~~ 7999 - ~~9000~~9011

Table 3: Juvfonne samples analysed for method validation. JUV 1, JUV 2 and JUV 3 were ice blocks collected from the 2010 tunnel (Zapf et al., 2013; Ødegård et al., 2016) and JUV 0 from the 2012 tunnel (Ødegård et al., 2016). To visualize the expected increase in age with increasing depth of the ice patch, ~~S~~samples are listed in stratigraphic order from top to bottom~~-~~. Sample JUV 1 was collected between two separated organic-rich layers (Poz-56952 and Poz-36460). For comparision, an age range between these two layers was calculated (*, range between the lower and upper 2σ boundary, respectively). The results from sub-samples of the individual ice blocks were averaged to derive the combined values shown. Uncertainties (1σ) were calculated by error propagation of all analytical uncertainties for the individual measurements and for the combined values denote the standard error of the unbiased standard deviation. For a graphic display of the comparision see Fig. 3.

Sample ID	AMS Lab. No.	WIOC (µg)	g of ice	$F^{14}C$	^{14}C age (BP)	cal age (cal BP)
JUV 3_1	ETH 42845.1.1	55~~54.8~~	292 ~~291.5~~	1.124 ± 0.013~~1.12 ± 0.01~~	-939 ± 93~~-940 ± 91~~	
JUV 3_2	ETH 42847.1.1	43~~43.1~~	268 ~~267.7~~	1.094 ± 0.015~~1.09 ± 0.01~~	-722 ± 110~~–720 ± 110~~	
JUV 3_3	ETH 42849.1.1	47~~46.8~~	325~~325.0~~	1.155 ± 0.015~~1.15 ± 0.01~~	-1158 ± 104~~–1160 ± 100~~	
JUV 3_4	ETH 43446.1.1	43~~43.4~~	208~~207.7~~	1.164 ± 0.017~~1.16 ± 0.02~~	-1220 ± 117~~–1220 ± 120~~	
	JUV 3 (surface 2010)			1.134 ± 0.017~~1.13 ± 0.01~~	-1010 ± 120~~–996 ± 52~~	modern
	Organic remains, Poz-37877			0.873 ± 0.003	1091 ± 28	963 - 1052
JUV 2_1	ETH 43443.1.1	27~~27.3~~	215~~215.1~~	0.881 ± 0.023~~0.88 ± 0.02~~	1018 ± 210~~1020 ± 210~~	
JUV 2_2	ETH 43445.1.1	9~~9.0~~	171~~170.8~~	0.792 ± 0.066~~0.79 ± 0.07~~	1873 ± 669~~1870 ± 670~~	
JUV 2_3	ETH 43559.1.1	17~~16.5~~	257~~257.4~~	0.870 ± 0.035~~0.87 ± 0.04~~	1119 ± 323~~1120 ± 320~~	
JUV 2_4	ETH 45109.1.1	19~~19.4~~	219~~219.0~~	0.869 ± 0.031~~0.87 ± 0.03~~	1128 ± 287~~1130 ± 280~~	
	JUV 2 (2010)			0.853 ± 0.022~~0.85 ± 0.02~~	1277 ± 207~~1116 ± 146~~	965 - 1368~~(918–1237)~~
	~~**Organic remains, Poz-37879**~~			~~**0.838 ± 0.003**~~	~~**1420 ± 30**~~	~~**(1300–1338)**~~
	Organic remains, Poz-56952*			0.777 ± 0.003	2027 ± 31	1929 - 2033
JUV 1_3	ETH 43555.1.1	20~~20.2~~	281~~280.6~~	0.766 ± 0.029~~0.77 ± 0.03~~	2141 ± 304~~2144 ± 300~~	
JUV 1_4	ETH 43557.1.1	9~~9.2~~	214~~214.0~~	0.719 ± 0.064~~0.72 ± 0.06~~	2650 ± 715~~2650 ± 710~~	
	Organic remains, Poz-36460*			0.692 ± 0.003	2958 ± 35	3065 - 3174
	JUV 1 (2010)			0.743 ± 0.029~~0.76 ± 0.03~~	2386 ± 314~~2227 ± 277~~	2011 - 2783~~(1904–2697)~~
	~~Poz-37878~~			~~0.826 ± 0.003~~	~~1535 ± 30~~	
	~~Poz-36460~~			~~0.692 ± 0.003~~	~~2960 ± 30~~	
Organic remains, age range between the two layers*~~mean~~				0.735 ± 0.037~~0.76 ± 0.04~~	2473 ± 404~~2215 ± 410~~	2005 - 3004~~(1810–2750)~~

Organic remains (plant fragment), Poz-56955				0.486 ± 0.002	5796 ± 33	6561 - 6656
JUV 0_1	BE 4184.1.1	393~~393.2~~	283~~283.1~~	0.479 ± 0.015~~0.48 ± 0.01~~	5913 ± 252~~5905 ± 248~~	
JUV 0_2	BE 4380.1.1	246~~245.9~~	298~~298.1~~	0.457 ± 0.008~~0.46 ± 0.01~~	6290 ± 141~~6293 ± 137~~	
JUV 0-A (2015)				0.468 ± 0.014~~0.47 ± 0.01~~	6099 ± 240~~6207 ± 120~~	6720 - 7256~~(6969 – 7255)~~
JUV 0_3	BE 4185.1.1	219~~219.4~~	208~~207.9~~	0.445 ± 0.012~~0.44 ± 0.01~~	6504 ± 217~~6512 ± 216~~	
JUV 0_4	BE 4381.1.1	182~~182.4~~	188~~188.3~~	0.442 ± 0.007~~0.44 ± 0.01~~	6559 ± 127~~6555 ± 133~~	
JUV 0_5	BE 4186.1.1	238~~238.3~~	227~~226.9~~	0.403 ± 0.012~~0.40 ± 0.01~~	7301 ± 239~~7296 ± 231~~	
JUV 0_6	BE 4382.1.1	36~~36.4~~	184~~184.2~~	0.438 ± 0.011~~0.44 ± 0.01~~	6632 ± 202~~6626 ± 196~~	
JUV 0_7	BE 4187.1.1	262~~262.2~~	200~~200.4~~	0.404 ± 0.011~~0.40 ± 0.01~~	7281 ± 219~~7285 ± 18~~	
JUV 0_8	BE 4383.1.1	203~~202.9~~	214~~214.2~~	0.451 ± 0.013~~0.45 ± 0.01~~	6397 ± 232~~6396 ± 229~~	
JUV 0-B (2015)				0.431 ± 0.009~~0.43 ± 0.01~~	6761 ± 168~~6741 ± 9~~	7476 - 7785~~(7519 – 7670)~~

Table 4: Quelccaya samples analysed for method validation. Calibrated ages (cal BP) denote the 1 σ range. ALC stands for Annual Layer Counting.

Sample	**Depth (m)**	**AMS Lab. No.**	**WIOC (μg)**	**$F^{14}C$**	**^{14}C age (BP)**	**cal age (cal BP)**	**ALC (yrs BP)**
139-140	144.69-146.79	BE 4336.1.1	15	0.888 ± 0.026	954 ± 237	675 - 1036	730 - 788
149-150	155.21-157.31	BE 4335.1.1	24	0.859 ± 0.018	1216 ± 171	1005 - 1300	1072 - 1157
157-158	163.88-166.09	BE 4337.1.1	14	0.803 ± 0.025	1761 ± 246	1414 - 1957	1439 - 1543

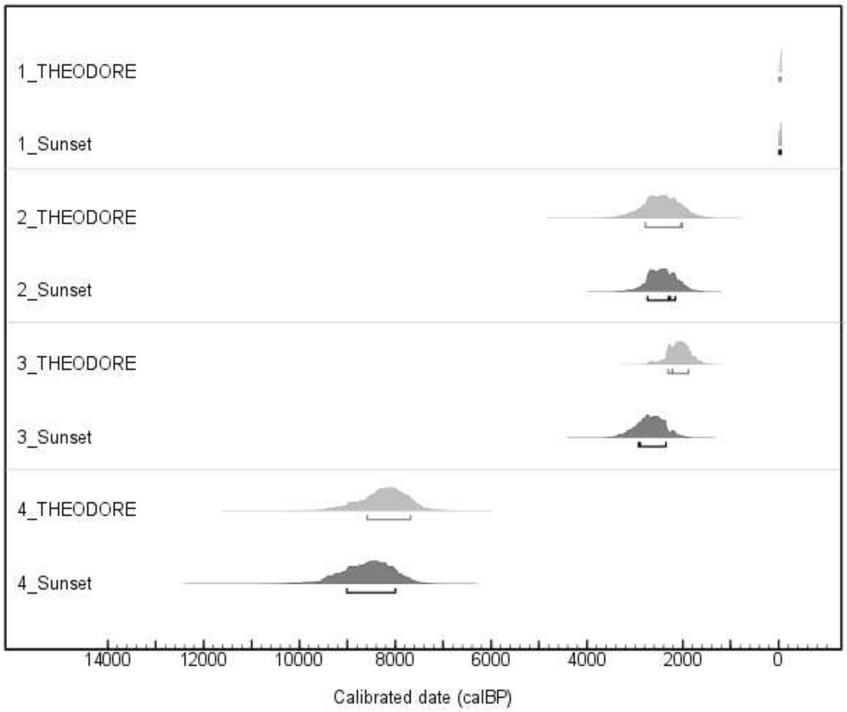

Figure 1: OxCal output for the compararability test for OC/EC separation using the THEODORE apparatus and the Sunset OC/EC analyzer directly coupled to the AMS. Bars below the age distributions indicate the 1 σ range. See Table 2 for the samples details.

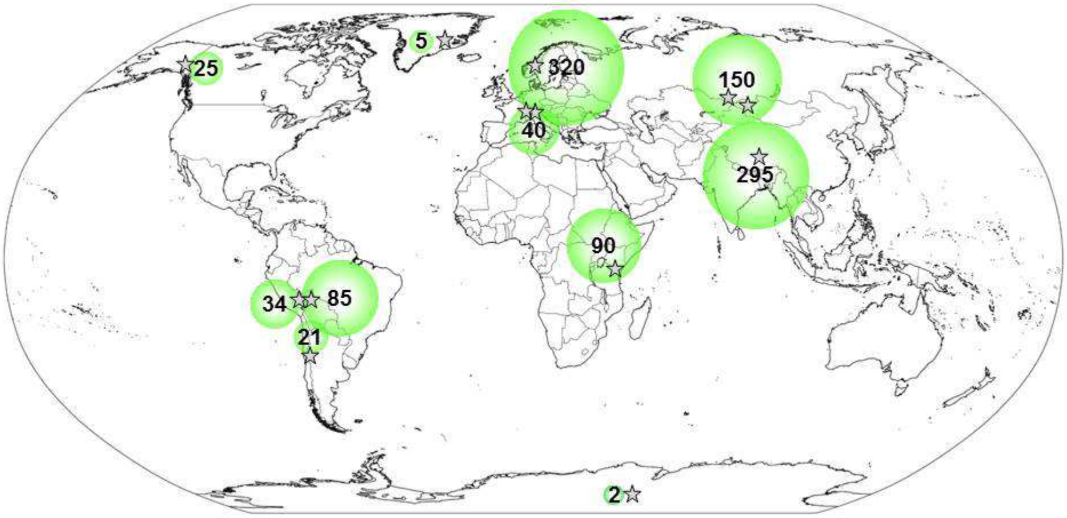

Figure 2: World map showing the sites from which ice samples were analysed with the ^{14}C method (gray stars): Edziza, Canada, 57.71° N 130.63° W; GRIP, Greenland, 72.59° N, 37.65° W, 3230 m a.s.l.; Juvfonne, Norway, 61.68 N, 8.35° E; Colle Gnifetti, Switzerland, 45.93° N, 7.87° E; Mt. Ortles, Italy, 46.51° N, 10.54° E; Belukha, Russia, 49.80° N, 86.55° E; Tsambagarav, Mongolia, 48.66° N, 90.86° E; Naimonanji, China 30.45° N, 81.54° E; Kilimanjaro, Tanzania, 3.06° S 37.34° E; Quelccaya, Peru, 13.93° S, 70.83° W; Nevado Illimani, Bolivia, 16.03° S, 67.28° W; Mercedario, Argentina, 31.97° S, 70.12° W; Scharffenbergbotnen, Antartica, 74.00° S, 11.00° W. The average WIOC concentration in µg/kg at each site is indicated with green bubbles.

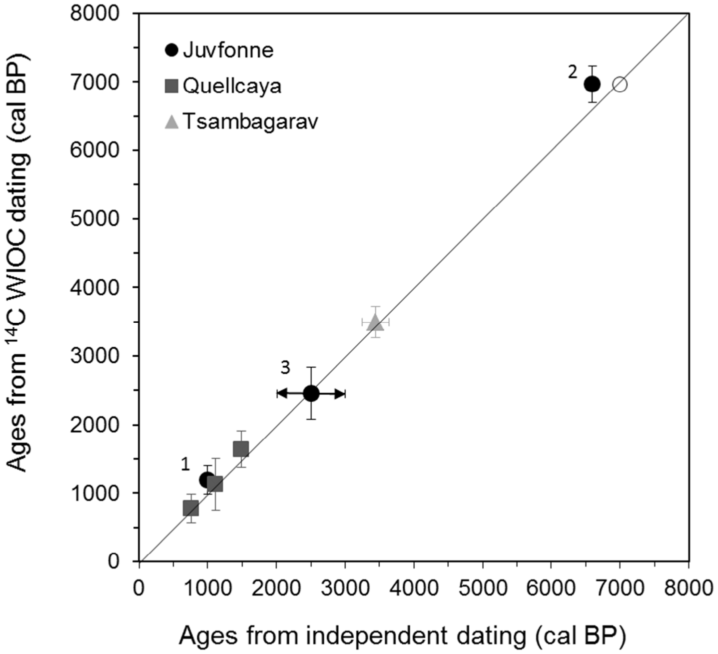

Figure 3: Scatter plot showing the ages obtained with the WIOC ^{14}C ~~WIOC~~ method for independently dated ice, including the conventionally ^{14}C dated Juvfonne organic-rich layers~~,~~ (Ødegård et al., 2016), the ^{14}C dated fly found in the Tsambagarav ice core, and the Quelccaya ice dated by annual layer counting~~,~~ (Thompson et al., 2013). Error bars denote the 1 σ uncertainty. Note that the Juvfonne WIOC samples and the organic-rich layers were not sampled from the exact same depth, but adjacent to each other. For the youngest (1) and oldest (2, containing the plant fragment) the ice for WIOC ^{14}C analysis was sampled below the layers whereas the third sample (3) was bracketed by two layers. For (3) the arrow thus indicates the age range between the lower and upper 2σ boundary of these two layers, respectively. For (2) the open circle indicates an estimated age for the according WIOC ice sampling depth based on a fit through all the conventionally dated organic-rich layers, presented in Ødegård et al., 2016).

Figure 4: Photo of the fly found in segment 102 of the Tsambagarav ice core. The age of the fly was 3442±191 cal BP, while the surrounding ice yielded an age of 3495±225 cal BP (photo by Sandra Brügger).

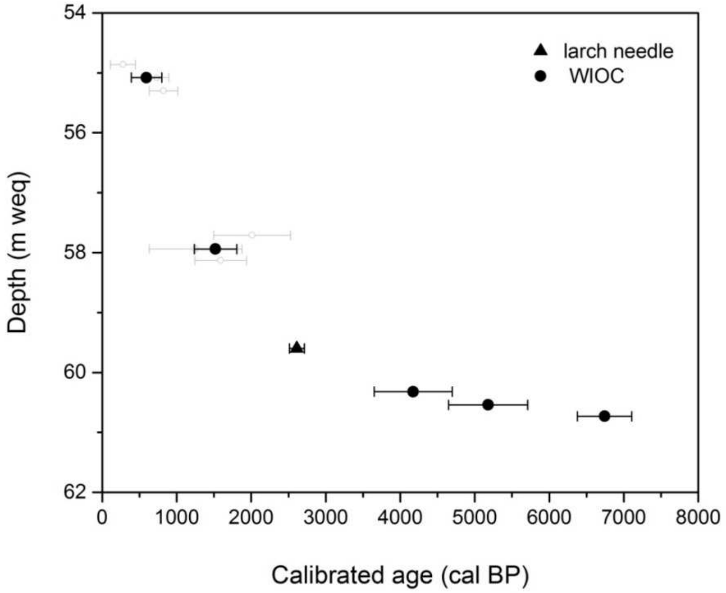

Figure 5: Dating of the bottom part of the Ortles ice core. Circles indicate the ages derived with the WIOC ^{14}C ~~WIOC~~ method and the triangle shows the age of the conventionally ^{14}C dated larch leaf found in the ice core (Gabrielli et al., 2016). Light grey circles show the ages obtained for the subsamples. Errors bars represent the 1 σ uncertainty.

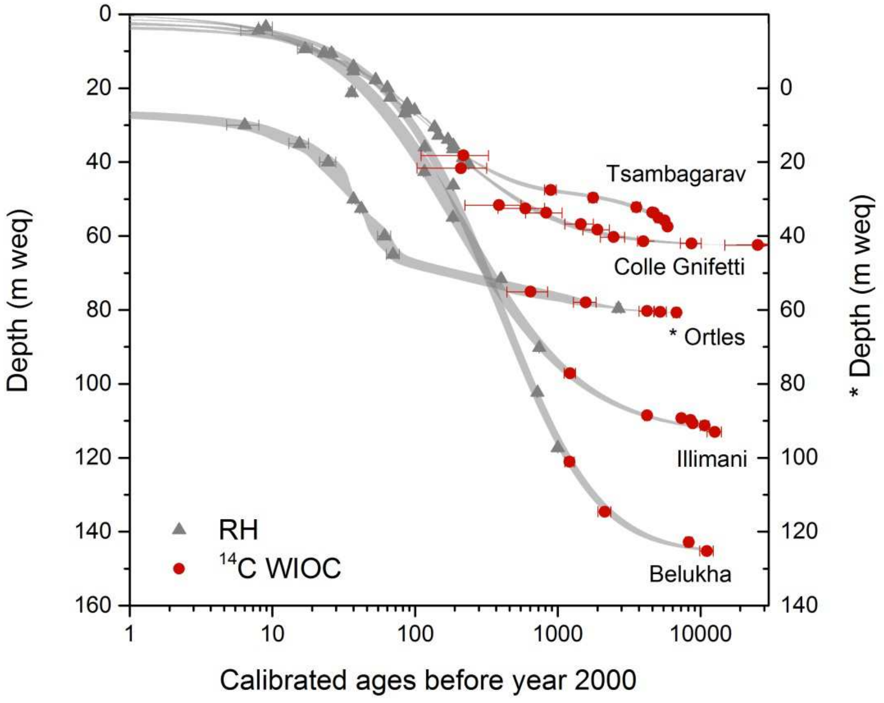

Figure 6: Compilation of age-depth relationships for five different ice cores, highlighting the importance of the WIOC ^{14}C dating to obtain continuous chronologies and to constrain the very specific glaciological conditions and settings of each site. For simplicity only reference horizons and ^{14}C dates were included. Gray triangles indicate reference horizons (RH) and red circles the ^{14}C-WIOC ages both plotted with 1σ uncertainties (smaller than the symbol size in some cases). For the Mt. Ortles core ^{210}Pb dated horizons with a larger uncertainty were used as RH due to the lack of absolute time markers prior to 1958; the gray triangle at 57.8 m weq depth is the conventional ^{14}C age of the larch leaf. Gray shaded areas represent the 1σ range of the respective fit for retrieving a continuous age depth relationship. For sample details and the fitting approaches applied, see main text and Table 1. References to the original data are summarized in Table 1. Note that for better visibility (avoiding overlap with Tsambagarav and Colle Gnifetti) the curve for the Mt. Ortles glacier was shifted down by 20 m and refers to the right-hand y-axis (*).

Radiocarbon dating of glacier ice: overview, optimisations, validation and potential

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Abstract. High altitude glaciers and ice caps from mid-latitudes and tropical regions contain valuable signals of past climatic and environmental conditions as well as human activities, but for a meaningful interpretation this information needs to be placed in a precise chronological context. For dating the upper part of ice cores from such sites several relatively precise methods exist, but they fail in the older and deeper part, where plastic deformation of the ice results in strong annual layer thinning and a non-linear age-depth relationship. If sufficient organic matter such as plant, wood or insect fragments were found, radiocarbon (^{14}C) analysis had thus been the only option for a direct and absolute dating of deeper ice core sections. However such fragments are rarely found and even then very likely not at the depths and in the resolution desired. About 10 years ago, a new, complementary dating tool was therefore introduced by our group. It is based on extracting the µg-amounts of the water-insoluble organic carbon (WIOC) fraction of carbonaceous aerosols embedded in the ice matrix for subsequent ^{14}C dating. Meanwhile this new approach was improved considerably, thereby reducing the measurement time and improving the overall precision. Samples with ~10 µg WIOC mass can now be dated with reasonable uncertainty of around 10-20% (variable depending on sample age). This requires about ~~100~~ 300 to ~~500~~ 800 g of ice considering the WIOC concentrations typically found in mid- and low-latitude glacier ice. Dating polar ice with satisfactory age precision is still not possible since WIOC concentrations are around one order of magnitude lower. The accuracy of the WIOC ^{14}C method was validated by applying it to independently dated ice. With this method the deepest parts of the ice cores from Colle Gnifetti and Mt. Ortles glacier in the European Alps, Illimani glacier in the Bolivian Andes, Tsambagarav ice cap in the Mongolian Altai, and Belukha glacier in the Siberian Altai have been dated. In all cases a strong annual layer thinning towards bedrock was observed and the oldest ages obtained were in the range of 10000 yrs. WIOC ^{14}C dating was not only crucial for interpretation of the embedded environmental and climatic histories, but additionally gave a better insight into glacier flow dynamics close to bedrock and past glacier coverage. For this the availability of multiple dating points in the deepest parts was essential, which is the strength of the presented WIOC ^{14}C dating method, allowing determination of absolute ages from principally every piece of ice.

Keywords: ice cores, mid- and low latitude glaciers, water-insoluble organic carbon, radiocarbon, chronology

1 Introduction

High altitude glaciers and ice caps from mid-latitudes and tropical regions contain valuable signals of past climate and atmospheric variability at regional and local scale and are located in areas with large biological diversity and inhabited by the majority of the world's population. Particularly mid-latitudes glaciers, for instance in the European Alps or in the Himalaya, are influenced by the nearby anthropogenic pollution sources, thereby additionally preserving the signature of human activities. This information can generally be retrieved from glacier ice cores, but needs to be placed in a precise chronological context to allow meaningful interpretation with respect to environmental and climatic changes.

Ice core dating is a sophisticated task and the most common approach is annual layer counting, which relies on seasonally fluctuating signals. A number of ice core parameters such as the stable isotope ratio of hydrogen or oxygen in the water (δ^2H, δ^{18}O), the concentration of trace components (e.g. ammonium, mineral-dust-related trace elements, black carbon), and the presence of melt layers may vary with the seasons. To reduce uncertainty in layer counting the time scale is additionally anchored with reference horizons like the radioactivity peak resulting from nuclear weapon tests in the 1960s or tephra and aerosol layers caused by volcanic eruptions (Eichler et al., 2009; Moore et al., 2012; Preunkert et al., 2000; Schwikowski, 2004; Thompson et al., 1998; Thompson et al., 2013). An independent method is nuclear dating with the naturally occurring radioisotope ^{210}Pb. Determined by the ^{210}Pb half-life of 22.3 years and its atmospheric concentration, the time period accessible for dating is in the order of a century (Eichler et al., 2000; Gäggeler et al., 1983; Herren et al., 2013). All these dating techniques fail in the older and deeper part of glaciers, where plastic deformation of the ice, under the weight of the overlying mass, results in horizontal ice flow, stretching annual layers continuously with increasing depth. Correspondingly, the depth-age relationship of high-alpine glaciers is strongly non-linear (Jenk et al., 2009) and annual layers and also volcanic signals become undetectable below a certain depth with the current spatial resolution of most analytical methods. Glacier flow modelling can only give rough age estimates with large uncertainties close to the bedrock of high-alpine glaciers (Lüthi and Funk, 2001). Radiocarbon (^{14}C) analysis has been the only option allowing a direct and absolute dating of these deeper ice core sections in the rare cases when sufficient organic matter such as plant, wood or insect fragments were found (Thompson et al., 1998; Thompson et al., 2002). However, in glacier ice such findings do not only happen very seldomly but even if lucky, they do not allow for continuous or at least regular dating which limits not only the application of the ^{14}C technique but also its use to derive a complete chronology based on absolutely dated layers. In the following we refer to dating of ice with macrofossils as conventional ^{14}C dating.

A new, complementary dating tool was therefore introduced by our group about 10 years ago, which is based on extracting the µg-amounts of the water-insoluble organic carbon fraction of carbonaceous aerosols embedded in the ice matrix for ^{14}C dating (Jenk et al., 2006; Jenk et al., 2007). Carbonaceous compounds represent a large, but highly variable fraction of the atmospheric aerosol mass (Gelencsér, 2004; Hallquist et al., 2009). Total organic carbon (TOC, also referred to as total carbon, TC) is instrumentally divided into two sub-fractions according to their refractory and optical properties. Elemental carbon (EC) consists of highly polymerized substances which are extremely refractory and light absorbent and therefore this fraction is also called black carbon (BC) or soot (Gelencsér, 2004; Hallquist et al., 2009). EC derives merely from the incomplete combustion of fossil fuels and biomass. Organic carbon (OC) is formed by weakly refractory hydrocarbons of low to medium molecular weight. Whereas EC is generally insoluble in water, OC is further subdivided into water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WIOC) (Szidat et al., 2004a). In water samples the former is also known as dissolved organic carbon (DOC) (Legrand et al., 2013; May et al., 2013). OC is emitted directly as primary aerosol from a vast diversity of sources and emission processes, including mobilization of plant debris, pollen, vegetation waxes, microorganisms, spores, the organic fraction of soil as well as emissions from biomass burning (e.g. forest fires) and anthropogenic processes (biomass burning and fossil fuel combustion), but it is also formed in the atmosphere by oxidation of gaseous precursors as secondary organic aerosol (Gelencsér, 2004; Gelencsér et al., 2007; Hallquist et al., 2009).

Carbonaceous aerosols are transported in the atmosphere to high-alpine glaciers, where they may be deposited by both wet and dry deposition processes and finally embedded in glacier ice (Jenk et al., 2006; Kaspari et al., 2011; Lavanchy et al., 1999; Legrand and Puxbaum, 2007; McConnell et al., 2007). Consequently using carbonaceous aerosols allows dating any piece of ice, given that it contains sufficient carbon mass. The WSOC fraction (i.e. DOC) would be ideal for dating, since it has the highest concentrations in ice. However, its extraction is complicated. It involves the outgassing of aqueous atmospheric CO_2, removal of dissolved carbonates, wet oxidation of the organic compounds to CO_2 under inert gas, and finally quantitative trapping of the evolved CO_2 (May et al., 2013). Since major contributors of DOC, like light carboxylic acids, are ubiquitous in the air, all these steps are prone to contamination. Therefore from the different carbonaceous particle fractions we selected WIOC as target for ^{14}C dating for several reasons. First, WIOC is mainly of biogenic origin in pre-industrial times (Jenk et al., 2006) and therefore supposed to contain a contemporary ^{14}C signal representative of the age of the ice (Jenk et al., 2006; Steier et al., 2006). Second, the average WIOC concentration in ice is higher than the respective EC concentration, allowing for smaller ice samples and potentially higher time resolution, which consequently provides a better signal to noise ratio (mainly determined by the overall blank) and smaller uncertainty of the dating results. Third, OC has a lower probability compared to EC for in-built reservoir ages from e.g. burning of old trees or old organic matter (Gavin, 2001; Sigl et al., 2009). Moreover OC is insensitive to potentially insufficiently removed carbonates in mineral dust rich layers (e.g. Saharan dust), which may contribute to the EC fraction because of the higher combustion temperature applied to EC (Jenk et al., 2006). The extraction of WIOC from the ice is straightforward as it can be collected by filtration of the melted ice. Note that in previous publications (Sigl et al., 2009; Zapf et al., 2013) the term POC was used for particulate organic carbon (Drosg et al., 2007). Since POC can be mistaken with primary organic carbon (Gelencsér, 2004; Zhang et al., 2012) we adopted the term water-insoluble organic carbon (WIOC) instead in this overview.

Our research group has a long history in ^{14}C dating of ice cores using the aforementioned WIOC fraction of carbonaceous particles. Lavanchy et al. (1999) introduced initial methods to determine the concentrations of carbonaceous particles in ice from a European high-alpine glacier. Next, the methodology was developed for source apportionment of aerosols by ^{14}C measurements in different carbonaceous particle fractions (Szidat et al., 2004b). This was conducted in close collaboration with the Laboratory of Ion Beam Physics of the ETH Zurich, a well established ^{14}C dating facility and a world-leading group in Accelerator Mass Spectrometry (AMS) technology, where simultaneously and continuously the analytical aspect of instrumentation was improved (Ruff et al., 2010; Ruff et al., 2007; Synal et al., 2000; Synal et al., 2007). The methodology of ^{14}C analysis of the different carbonaceous particle fractions was adopted to study the suitability of WIOC for ^{14}C dating of old ice, finding that it is of purely biogenic origin prior to industrialization (Jenk et al., 2006; Jenk et al., 2007). Since then this novel ^{14}C approach has been applied for dating a number of ice cores from different high-altitude mountain glaciers (Table 1), (Aizen et al., 2016; Herren et al., 2013; Jenk et al., 2009; Kellerhals et al., 2010; Sigl et al., 2009; Zapf et al., 2013). Meanwhile the method has been further optimized and was additionally validated by determining the age of independently dated ice. Here we give an overview of the current status of the now routinely applied WIOC ^{14}C dating method for glacier ice, including an update on recent optimizations and method validation. Uncertainties and the potential of this novel approach are discussed and its succesfull application to a number of ice cores presented ~~Here we give an overview of the current status of the now routinely applied ^{14}C dating method for glacier ice by presenting an update on recent optimizations and discussing the potential of this novel approach~~.

2 Sample preparation, OC/EC separation and ^{14}C analysis

The preparation of ice samples follows the procedure according to Jenk et al. (2007). First, samples are decontaminated in a cold room (-20˚C) by removing the outer layer (3 mm) with a pre-cleaned stainless steel band saw (wiped three times with acetone, followed bycutting of a frozen block of ultra-pure water, 18 MΩ cm quality), followed by rinsing the samples with ultra-pure water ~~(18 MΩ cm quality)~~ in a class 100 clean bench. Around 20-30% of the ice samples' mass is lost during these first steps, resulting in a final mass of about ~~100~~ 200 to 500 g (initial mass of around ~~600~~300-800 g of ice). The samples are then transferred and stored frozen at -20˚C in pre-cleaned (soaked and rinsed for three days with daily exchanged ultra-pure water) 1-L-containers (Semadeni, PETG) until being melted at room temperature directly before filtration. To ensure that carbonates potentially present in the ice are completely dissolved, ~20 mL of 1M HCl (30% Suprapure, Merck) are added to the melted samples (Cao et al., 2013), resulting in a pH of < 2, before being sonicated for 5 min. Subsequently, the insoluble carbonaceous particles are filtered onto preheated (5h at 800˚C) quartz fibre filters (Pallflex Tissuquartz, 2500QAO-UP), using a dedicated glass filtration unit, also carefully pre-cleaned by rinsing with ultra-pure water and by baking the glass at 450˚C for 3h. As a second carbonate removal step, the filters are acidified three times with a total amount of 50 µL 0.2M HCl (Jenk et al., 2007). Afterwards the filters are left in a class 100 clean bench for 1h to allow potentially present carbonates to be transformed into CO_2 by reaction with the HCl, followed by rinsing with 5 ml ultra-pure water to entirely remove remaining HCl. The filters are left again for 1h to reach complete dryness, packed in aluminium foil and kept frozen until analysis, for which filters are taken out of the freezer to let them reach ambient temperature (at least half an hour). Details regarding OC and EC separation, AMS ^{14}C analysis and improvements achieved since the first applications will be discussed in Sections 3 and 4.

3 Recent optimization in OC/EC separation and AMS analysis

In previous ice core dating applications using ^{14}C of WIOC (Herren et al., 2013; Jenk et al., 2009; Kellerhals et al., 2010; Sigl et al., 2009; Zapf et al., 2013), the OC and EC combustion was performed with the Two-step Heating system for the EC/OC Determination Of Radiocarbon in the Environment apparatus (THEODORE), developed for aerosol applications (Szidat et al., 2004b). The combustion was conducted in a stream of oxygen for the controlled separation of OC and EC fractions. The temperature for OC separation was set at 340˚C, while for recovery of EC the temperature was then increased to 650˚C. The CO_2 produced by oxidation during the combustion was cryogenically trapped, manometrically quantified and sealed in glass ampoules (Szidat et al., 2004b). In the earliest application described by Jenk et al. (2006) the CO_2 subsequently had to be transformed to filamentous carbon (graphitisation) using manganese granules and cobalt powder for final AMS ^{14}C analysis. This was initially performed at the ETH AMS facility (TANDY, 500 kV pelletron compact AMS system) (Synal et al., 2000). Since 2006, the 200kV compact AMS (MIni radioCArbon DAting System, MICADAS) has been operational at the ETH (Synal et al., 2007). The MICADAS is equipped with a gas ion source and a Gas Introduction interface System (GIS) (Ruff et al., 2007; Synal et al., 2007), allowing measurements of ^{14}C directly in CO_2 with an uncertainty level as low as 1% (Ruff et al., 2010). The GIS includes a gas-tight syringe for the CO_2 injection into the ion source (Ruff et al., 2010), with a maximum capacity of 1.3 ml of CO_2 as ~5% mixing ratios in helium (equivalent to 100 µg of carbon). The position of the syringe plunger is automatically adjusted according to the sample size as well as the helium flow carrying the sample to the ion source. With this, the tranformation of gaseous CO_2 to solid graphite targets became needless (Sigl et al., 2009). Instead, the glass ampoules sealed after the combustion of the filters with the THEODORE system were opened in a designated cracker, an integral part of the GIS (Ruff et al., 2007), and the resulting CO_2-He mixture could directly be fed into the MICADAS ion source.

The main advantages of switching from solid to gaseous targets were: 1. a decrease in the number of necessary preparation steps and the associated risk of lost samples from incomplete graphitisation, 2. a higher sample throughput, 3. a reduction in the variability and overall blank contribution as well as 4. the elimination of the correction applied to account for fractionation during the graphitisation step, which contributed with around 10% to the overall uncertainty (Jenk et al., 2007). As will be discussed in Section 4, a precision increase is one of the main challenges for improving the method.

Since spring 2013, ^{14}C analysis is performed with a MICADAS installed at the Laboratory for the Analysis of Radiocarbon with AMS (LARA laboratory) of the University of Bern, also equipped with a GIS interface (Szidat et al., 2014). There, an improvement was recently achieved by replacing the THEODORE with a commercial combustion system, which is a thermo-optical OC/EC analyzer (Model4L, Sunset Laboratory Inc., USA), normally used for aerosol OC/EC separation and source apportionment studies (Zhang et al., 2014; Zhang et al., 2012; Zhang et al., 2013; Zotter et al., 2014). Similar as in the THEODORE system, the carbonaceous particles are combusted in a stream of pure oxygen. The Sunset instrument is specially equipped with a non-dispersive infrared (NDIR) cell to quantify the CO_2 produced during the combustion. The combustion process in the Sunset system follows a well-established protocol (Swiss 4S) for the thermal separation of OC and EC fractions under controlled conditions (Zhang et al., 2012). To avoid potential damage of the infrared cell detector by residual HCl, the final rinsing of the filters after adding HCl for carbonates removal was introduced (see Section 2).~~ Tests with blank filters and standard materials were performed to exclude any potential contamination from this additional step~~. Recently ~~T~~the Sunset instrument ~~is~~ was directly coupled to the zeolite trap of the GIS (Ruff et al., 2010), which allows online ^{14}C measurements of the carbonaceous fractions separated in the Sunset system (Agrios et al., 2015). When combusted, the gaseous carbonaceous species pass through a MnO_2 bed heated to 850˚C for completing the oxidation to CO_2, which is further transported by helium to the zeolite trap. This trap is then heated up to 500˚C to release the CO_2 to the gas-tight syringe for final injection into the AMS ion source (Ruff et al., 2007; Synal et al., 2007).

The newly coupled Sunset-GIS-AMS system has major advantages compared to the old setup. The OC/EC separation in the THEODORE was relatively time consuming and only four ice samples could be processed per day. Two more days were needed to produce all the standards and blanks required for AMS calibration and for quality control and graphitisation (Jenk et al., 2007). Besides the disantvantages of solid graphite targets described before, there is also a risk of losing samples during the delicate phase of flame-sealing the ampoules and later on when scratching them to allow a clean break in the automated GIS cracker. With the online coupling of the Sunset, this risk is completely removed. Further the preparation and measurement time is significantly reduced because there is no need for offline combustion resulting in a total measurement time of approximately 35 min per sample only. In addition, it not only allows for an automated protocol of standard injection for AMS calibration, but also offers the possibility for easy and regular (daily) survey of the ^{14}C background in the entire process line (Sunset-GIS-AMS) by analysis of variably sized standards and blanks if required ~~(~~(Agrios et al., 2015).~~see last paragraph of this Section~~). Finally, the Sunset system enables continuous monitoring of the combustion process, reducing a potential bias due to charring, and the standardized and automated combustion protocol (Swiss 4S) ensures high reproducibility increasing the overall precision.

With the current setup, the ^{14}C/^{12}C ratio of the samples is background subtracted, normalized and corrected for mass fractionation by using fossil sodium acetate (^{14}C free, NaOAc, p.a., Merck, Germany), the reference material NIST standard oxalic acid II (modern, SRM 4990C) and the δ^{13}C simultaneously measured in the AMS, respectively (Wacker et al., 2010). All results are expressed as Fraction Modern (F^{14}C), which is the ^{14}C/^{12}C ratio of the sample divided by the same ratio of the modern standard~~which is the deviation of the ^{14}C/^{12}C ratio of the sample from that of the modern standard~~. Further corrections are subsequently applied to the F^{14}C values considering isotopic mass balance (e.g. Jenk et al., 2007) to account for constant contamination, cross contamination and for the procedural blank contribution introduced by the preparation of ice samples (for details see Section 4). ^{14}C ages (before present (BP), i.e. before 1950) are calibrated using OxCal v4.2.4 (Bronk Ramsey and Lee, 2013) with the Northern (IntCal13) or Southern Hemisphere (ShCal13) calibration curves (Hogg et al., 2013; Reimer et al., 2013), depending on the sample site location. Calibrated dates are given in years before present (cal BP~~, with BP = 1950~~) with 1 σ uncertainty range (Mook and van der Plicht, 1999; Stuiver and Polach, 1977). For simplicity the ages dicussed in the text are given as the mean of this range ±1 σ. See Section 4 for further details regarding the applied corrections, ^{14}C calibration and discussion of uncertainties.

To ensure comparability between previous data and the newly derived results, using the above described improved setup configuration, ^{14}C analysis was conducted on remaining pieces of samples, which were previously processed with the THEODORE setup. Two samples (~~Juv1~~ JUV 1 and ~~Juv2~~JUV 3) from the Juvfonne ice patch in Norway (Zapf et al., 2013) and two samples (~~Bel1~~ BEL 1 and ~~Bel2~~BEL 2) from an ice core drilled at Belukha glacier in the Siberian Altai (Aizen et al., 2016) were used, covering an age range from modern to more than 8000 cal BP. The OC masses were above 10 µg carbon, except for sample Juv2_Sunset with a carbon mass of 9 µg (Table 2), still resulting in more than 4500 ^{14}C counts with a corresponding uncertainty of the F^{14}C of 2%, which we consider sufficiently low for this comparison. At first, the obtained

WIOC concentrations are discussed, which are assumed to agree as indicated by a carbon quantification test carried out on homogeneous aerosol filters using both combustion instruments (Zotter et al., 2014). As expected a good consistency was found for the WIOC concentrations in the Belukha ice core (Table 2), whereas a discrepancy was observed for the Juvfonne samples, probably related to the natural inhomogeneity of particles in this small-scale ice patch with a distinct ice accumulation behaviour (see below). Concerning the ^{14}C ages, a very good agreement is shown between all parallel samples (Figure 1). This is also true for the procedural blanks , both in term of carbon amount and F^{14}C.~~ The THEODORE resulted in a blank contribution of 1.41 ± 0.69 µg with F^{14}C of 0.64 ± 0.12, and the Sunset in 1.21 ± 0.51 µg with a F^{14}C of 0.73± 0.13. We therefore conclude that dating results obtained with the old THEODORE combustion setup ~~(Herren et al., 2013; Jenk et al., 2009; Sigl et al., 2009; Zapf et al., 2013)~~ and with the improved coupled Sunset-GIS-AMS system are in good agreement~~. The WIOC procedural blank measured and used for correction in this comparision experiment was 1.41 ± 0.69 µg of carbon with an F^{14}C of 0.64 ± 0.12, and 1.21 ± 0.51 µg of carbon with an F^{14}C of 0.73± 0.13 for the THEODORE and the coupled Sunset setup, respectively (additional details can be found in Section 4). In summary, we conclude that dating results obtained with the previously used THEODORE combustion setup (Herren et al., 2013; Jenk et al., 2009; Sigl et al., 2009; Zapf et al., 2013) and the improved coupled Sunset-GIS-AMS system are in good agreement.

4 Radiocarbon dating uncertainties

First of all, the signal-to-noise ratio of the AMS measurement is defined by counting statistics. Generally, the smaller the sample, the shorter the measurement time, the higher the uncertainty. For defining the contamination contribution of the overall instrument setup (constant contamination) and the memory effect between subsequent samples of very different ^{14}C content and carbon mass (cross contamination), a series with varying amounts of solid grains of fossil NaOAc and the modern reference material oxalic acid II was combusted with the Sunset and measured for its ^{14}C content. The constant contaminant mass was estimated as 0.4 ± 0.2 µg carbon with a F^{14}C of 0.8 ± 0.4 and for the cross contamination 0.5 ± 0.4% of the carbon of the previous sample was found to mix with the next injection (Agrios et al., 2015).

The total carbon amounts in ice cores are rather low, in the µg/kg-range. Because of that, each step of sample preparation implies a potential risk of contamination with either modern or fossil carbon. Thus a large contribution to the final overall uncertainty on the age is induced by the procedural blank correction, especially for small size samples. It is therefore crucial that cutting, melting and filtrating the ice results in the lowest possible procedural blank with a stable F^{14}C value to ensure a high and stable signal-to-blank ratio for obtaining reliable results with the smallest possible uncertainties. Procedural blanks were estimated using artificial ice blocks of frozen ultra-pure water, treated in the same way as real ice samples (Jenk et al., 2007). Blanks were usually prepared together with samples and their analysis was performed during every AMS measurement session (Sunset combustion and AMS analysis). The ~~average~~ mean of the overall procedural blank (WIOC) used to correct all samples is 1.34 ± 0.62 µg of carbon with a F^{14}C of 0.69 ± 0.13 (100 and 54 measurements, respectively, performed over a 10-year period). This includes all values obtained with both, the THEODORE and Sunset system. We decided to use this combined value, since the ice sample preparation step is the by far largest contribution to the blank and is system independend. This mean value~~s~~ ~~are~~ is consistent with previously reported results (Jenk et al., 2007; Sigl et al., 2009), indicating the long-term stability of the procedural blanks.

In summary, all the corrections have the strongest effect on low carbon mass samples, resulting in the largest dating uncertainties. Further, such small samples can only be measured for a short period of time, with reduced stability of the ^{12}C current, additionally worsening of the signal-to-noise ratio. Low carbon mass samples of old age contain even a lower number of ^{14}C compared to younger samples due to radioactive decay and are affected the most. Among all uncertainties described, the correction for the procedural blank contributes typically around 60%. As an example, for hypothetical samples with a WIOC mass of 5 or 10 µg, the resulting uncertainty of the finally calibrated ages for 1000 year old ice would be around ± 600 yrs or ± 250 yrs and for 8000 year old ice around ± 1600 yrs or ± 700 yrs, respectively. Hence by doubling the mass, the uncertainty is reduced by more than 50%. We therefore generally discuss dating results only for sample masses larger than ~10 µg WIOC, which have an acceptable age uncertainty in the range of 10-20%.

While calibrating the ages with the OxCal, a sequence constraint can be applied based on the assumption of a monotonous increase of age with depth (Bronk Ramsey, 2008). This approach often leads to a reduction of the final uncertainty, which however strongly depends on the sample resolution with depth, see example in Jenk et al. (2009).

5 Validation of the dating accuracy

5.1. First attempts

Validating the accuracy of the here described approach for ^{14}C dating of ice is a challenging task since it requires ice samples with known ages, preferentially covering a large age range.

First attempts for validation by dating ice from Greenland with an age determined by annual layer counting failed, because WIOC concentrations are an order of magnitude lower compared to ice from glaciers located closer to biogenic emission sources (Figure 2). Large ice samples were thus needed, nevertheless resulting in small amounts of carbon. Our preparation method is not optimised for such sample sizes, and the required pooling of several pieces of ice may have induced a higher procedural blank. As a result ^{14}C ages tended to be biased by the procedural blank value (Sigl et al., 2009). ^{14}C ages of the Fiescherhorn ice core (Jenk et al., 2006) ranged from modern values to 1000 years, thus reasonably matching the age of the ice older than AD 1800 obtained by annual layer counting. For the ice core from Mercedario (31.98° S, 70.13° W; 6100 m a.s.l.) the deepest core sections show ages of <550 and 320–1120 cal BP, respectively, well in line with a tentative chronology based on annual layer counting (Sigl et al., 2009). However, considering the relatively large uncertainty of our method if compared to conventional ^{14}C dating typically derived from samples with much larger carbon masses and the flatness of the ^{14}C calibration curve between around 500 and 0 cal BP such samples of rather young ages are not ideal for a precise validation. Two samples from the Illimani ice core, bracketing the AD 1258 volcanic eruption time marker resulted in a combined calibrated age of AD 1050±70 (1 σ) overestimating the expected age by ~~ca.~~around 200~~±70~~ years~~ (1 σ)~~. This would be an acceptable accuracy if applicable to several thousand years old ice (Sigl et al. 2009).

Overall these were first indications that the ^{14}C method gives reliable ages. Meanwhile we have had access to independently dated ice from the Juvfonne ice patch and the Quelccaya ice cap, dated a fly which we discovered in the Tsambagarav ice core, and dated ice cores from Mt. Ortles glacier, in which a larch leaf was found, altogether allowing a more robust validation as outlined in the following.

5.2. Recent validation

Juvfonne is a small perennial ice patch in the Jotunheimen Mountains in central southern Norway (61.68° N, 8.35° E). In May 2010, a 30-m-long ice tunnel was excavated, revealing several up to 5 cm thick dark organic-rich layers containing organic remains ~~residues~~, which were interpreted as previous ice-patch surfaces and conventionally ^{14}C dated (Nesje et al., 2012). We received two samples of clear ice adjacent to the organic-rich layers and a surface sample (JUV 1, JUV 2, JUV 3, Table 3). The results derived using WIOC agreed well with the corresponding, conventionally dated ^{14}C ages with an age range between modern and 2900 cal BP (Zapf et al., 2013). In summer 2015 we collected additional clear ice samples adjacent to a ~~6600 years~~conventionally ^{14}C dated plant fragment ~~layer~~ found in an organic-rich layer at the base of a new tunnel excavated in 2012 and extending deeper into the ice patch (Ødegård et al., 2016). Four ice blocks were collected and afterwards subdivided in two sub-samples each. Ice block 1 (JUV 0_1 and JUV 0_2) was taken adjacent to the plant fragment layer, ice block 2 (JUV 0_3 and JUV 0_4), ice block 3 (JUV 0_5 and JUV 0_6) and ice block 4 (JUV 0_7 and JUV 0_8) at the bottom of the wall, a few cm below the plant fragment layer. JUV 0_1 and JUV 0_2 yielded an average age of 7127 ± 134 cal BP, which is in good agreement with the age of the plant fragment layer of 6608 ± 53 cal BP,~~.~~ considering the observed increase in ages with increasing depth. Accordingly, t~~T~~he other six samples collected even further below this organic-rich layer resulted in ~~are~~ significantly older ages (7593 ± 74 cal BP, Table 3).~~, which is reasonable since they were collected below the plant fragment layer~~.

Three sections of the ice core from the Quelccaya Summit Dome drilled in 2003 (QSD, Peruvian Andes, 168.68 m, 13°56'S, 70°50'W, 5670 m a.s.l.) were kindly provided by Lonnie Thompson, Ohio State University. The entire ice core was dated by annual layer counting indicating an age of 1800 years at the bottom (Thompson et al., 2013). Intentionally we received the samples without knowing their ages or depths in order to have the opportunity to perform a "blind test". The three sections were not decontaminated as usual, but only rinsed with ultra-pure water, because the amount was not large enough for removing the outer layer mechanically. As shown in Figure 3 (see also Table 4 for the results) the resulting calibrated ages agree very well with the ages based on annual layer counting (L. Thompson, personal communication 2015).

Recently a number of core segments of the previously dated Tsambagarav ice core (Herren et al., 2013) were resampled. In segment 102 a tiny insect (Figure 4) was found and immediately separated from the ice matrix. Since it was small, a conventional ^{14}C analysis was not suitable and instead the Sunset-AMS system was deployed. The ice section containing the fly was melted, possible contamination from carbonates and humic acids were removed by an acid-base-acid treatment at 40°C (Szidat et al., 2014), the fly was dried, placed onto a quartz fibre filter and combusted in the Sunset, resulting in 13 µg of carbon. The age of 3442 ± 191 cal BP (BE-5013.1.1) is in perfect agreement with the age of WIOC from this ice segment of 3495 ± 225 cal BP (Herren et al., 2013) (Figure 3).

Additionally, we dated three sections from a set of ice cores drilled in 2011 on Mt. Ortles (see Table 1 for location) for which a preliminary age of 2612 ± 101 cal BP was derived by conventional ^{14}C dating of a larch leaf found at 73.2 m depth (59.60 m weq, ~1.5 m above bedrock) (Gabrielli et al., 2016). Every section was horizontally divided in three sub-samples (top, middle, bottom). For the section at 68.61 m depth (55.08 m weq, core #1) and the section at 71.25 m depth (57.94 m weq, core #3), ~~T~~the ages obtained for the sub-samples were not significantly different from each other ~~for of the sections at 68.61 m (55.08 m weq) depth (core #1) and~~ the section ~~at 71.25 m (57.94 m weq) depth (core #3)~~ especially if also ~~considering~~accounting for the expected thinning of annual layer thickness at these depths (Figure 5). Accordingly the results of the ~~according~~respective sub-samples were combined to derive the most accurate ages for the mid-depths of these two sections (mean F^{14}C~~ mean~~ with the estimated 1σ uncertainty being the standard error of the unbiased standard deviation).~~were not significantly different from each other, respectively. Accordingly the derived ages were combined using the corresponding function in OxCal v4.2.4 (^{14}C date combination)~~. On the contrary the ages of the three sub-samples from the deepest section at 74.13 m ~~(60.54 m weq)~~ (60.54 m weq, core #3) significantly increased with depth, implying strong glacier thinning close to bedrock (see also Gabrielli et al., 2016~~, this issue~~). Our WIOC ^{14}C ages obtained for the Mt. Ortles ice core agree well with the age of the larch leaf assuming an exponential increase of age with depth (Figure 5).

The scatter plot in Figure 3 summarizes the different validation experiments described above. The results for the Mt. Ortles ice core were not included because larch leaf and WIOC samples were extracted from depths of significantly different ages. As shown, within the uncertainties, the ^{14}C ages fall onto the 1:1 line in the age range from ~700-3500 cal BP, convincingly demonstrating good accuracy of our method. All validation experiments were performed on low-dust samples, thus avoiding potential dating bias due to the presence of dust (Hoffmann, 2016).

6 Applications and current potential of the ^{14}C method for dating glacier ice

Over the last 10 years the deepest parts of several ice cores have been dated applying the presented WIOC ^{14}C method. To illustrate the current potential of the method with respect to the time period accessible we compiled five ice core chronologies in Figure 6. The sites differ in recent net annual snow accumulation and ice thickness (in brackets): Tsambagarav ice cap in the Mongolian Altai 0.33 m weq (72 m) (Herren et al., 2013), Belukha glacier in the Siberian Altai

0.34 m weq (172 m) (Aizen et al., 2016), Colle Gnifetti glacier in the European Alps 0.46 m weq (80 m) (Jenk et al., 2009), Illimani glacier in the Bolivian Andes 0.58 m weq (138.7 m) (Kellerhals et al., 2010), Mt. Ortles glacier 0.85 m weq (75 m) (Gabrielli et al., 2016~~, this issue~~). All of these are cold glaciers and frozen to the bedrock with the exception of Mt. Ortles glacier, which is polythermal and experienced a recent acceleration of glacier flow due to sustained atmospheric warming over the past decades ~~and basal sliding can not totally be excluded at least for certain periods of time~~ (Gabrielli et al., 2016~~, this issue~~). To derive a continuous age depth relationship, a two parameter flow model (Bolzan, 1985; Thompson et al., 1990) was applied for Colle Gniffetti (Jenk et al., 2009), Illimani (Kellerhals et at., 2010) and here also for the core from Belukka using the data presented in Aizen et al. (2016). A different approach as discussed below, was implemented for the ice cores from the Tsambagarav ice cap (Herren et al., 2013) and the glacier on Mt. Ortles (see also Gabrielli et al., 2016 , ~~this issue~~). The two parameter model is based on a simple analytical expression for the decrease of the annual layer thickness $L_{(z)}$ (m weq) with depth:

$$L_{(z)} = b(1-\frac{z}{H})^{p+1}$$

where z is depth (m weq), H the glacier thickness (m weq), b the annual accumulation (m weq) and p a thinning parameter (dimensionless). The age T(z) as a function of depth can be calculated when the inverse layer thickness is integrated over depth:

$$T_{(z)} = \int \frac{dz}{L_{(z)}} = \frac{1}{b}\int (1-\frac{z}{H})^{-p-1}dz$$

Solving the integral and setting the age at the surface to be T(0) = 0, the final age-depth relation is obtained:

$$T_{(z)} = \frac{H}{bp}[(1-\frac{z}{H})^{-p}-1]$$

The thinning rate (vertical strain rate) is the first derivative of the layer thickness:

$$L'_{(z)} = \frac{dL_{(z)}}{dz} = -\frac{b(p+1)}{H}\ (1-\frac{z}{H})^{p}$$

The model has two degrees of freedom, the net annual accumulation rate b and the thinning parameter p both assumed to be constant over time. This allows to fit the model by a least squares approach through ~~selected reference~~the available reference horizons if the glacier thickness H is known (if drilled to bedrock) or can be reasonably well estimated (e.g. from radar sounding). In order to not overweight the data from the deepest horizons, the model is fitted using the logarithms of the age values. For the ice cores from Colle Gnifetti (Jenk et al., 2009), Illimani (Kellerhals et al., 2010) and Belukha (Aizen et al., 2016) these ages were based on annual layer counting, identification of reference horizons (radioactive fallout and well-known volcanic eruptions) and ^{14}C dates. The data is summarized in Table 1. In Figure 6, only reference horizons and ^{14}C dates were included for simplification.

In summary, a reasonable fit was achieved for these three glaciers and the derived annual net accumulations (Colle Gnifetti 0.45±0.03 m weq, Belukha 0.36 ± 0.03 m weq, Illimani 0.57 ± 0.13 m weq) are comparable with the values previously published (see above), which were determined either by surface measurements or ~~with the~~ were estimated ~~accumulation~~ based on ALC or/and the uppermost age horizons only (e.g. nuclear fallout peak), thereby accounting for the (slight) layer thinning occuring in these uppermost few meters (Nye, 1963). Since the assumption of constant accumulation (b) and a constant thinning parameter (p) over time/with depth is likely only true in a first order approximation it is thus no surprise that~~, with~~ the two parameter model ~~no~~ may~~-~~fail to result in a reasonable fit within the derived age uncertainties. In such a case ~~fit could be achieved~~ these two underlying assumptions should then be investigated more thoroughly as it was e.g. done for the ice cores from Tsambagarav and Mt. Ortles. Whereas Tsambagarav also is a cold glacier, Mt. Ortles is polythermal. For Tsambagarav, a good fit can be achieved ~~a fit is only possible~~ if additional degree of freedom is given to account for variations in the net accumulation rate while p is fixed to the initially derived value, suggesting significant changes in the accumulation rate over time. This is supported by the fact that the resulting strong variation in net accumulation is consistent with precipitation changes in the Altai derived from lake sediment studies (Herren et al., 2013). Opposite to that, a reasonable fit for the Mt. Ortles ice core can only be obtained if the thinning parameter p is allowed to increase with depth~~.~~, while the annual net accumulation is assumed to be constant over time (i.e. b fixed to the value defined by the stake measurements and surface layers). This points to an exceptionally strong thinning. Mt. Ortles glacier is polythermal with temperate conditions in the upper part and still relatively warm ice with -2.8°C near bedrock. We hypothesize that the faster horizontal velocity of the warm ice causes exceptional horizontal stress (internal horizontal deformation) on the ice frozen to the bedrock, resulting in stronger thinning. In both cases, a purely empirical approach of fitting the age horizons was chosen to ~~yield~~ establish the age-depth relationship. Note that ~~(d~~due to the lack of absolute time markers prior to 1958, ^{210}Pb dated horizons ~~with a larger uncertainty compared to the age of time markers~~ were used for Mt. Ortles ~~)~~. For Tsambagarav a combination of different polynomial functions was used (Herren et al., 2013), whereas a slightly more sophisticated approach by means of Monte Carlo simulation was applied for Mt. Ortles, allowing an objective uncertainty estimate for each depth defined by the density of dating horizons and their individual uncertainty (Gabrielli et al., 2016 ,~~ this issue~~). ~~Such a~~These purely empirical approaches are ~~is~~ justified given the high confidence assigned to the determined ages for the dated horizons. ~~For Tsambagarav, the strong variation in net accumulation was consistent with precipitation changes derived from lake sediment studies in the Altai (Herren et al., 2013). Mt. Ortles glacier is polythermal with temperate conditions in the upper part and still relatively warm ice with -2.8°C near bedrock. We hypothesize that the faster horizontal velocity of the warm ice causes exceptional horizontal stress (internal horizontal deformation) on the ice frozen to the bedrock, resulting in stronger thinning.~~

As shown in Figure 6, the time period dated with ^{14}C ranges from 200 to more than 10000 yrs. Due to their uncertainty, ^{14}C ages derived by our method cannot compete with the conventional methods for dating ice that is only a few centuries old. The strength of ^{14}C dating using WIOC is that it allows obtaining absolute ages from ~~principally~~ basically every piece of ice ~~core~~ from cold and poly~~i~~thermal ice bodies. This is especially valuable for glaciers not containing the last glacial/interglacial transition, as Tsambagarav and Mt. Ortles, since in such cases not even climate wiggle matching of the transition signal with other dated archives is possible. Anyhow, an absolute dating method is ~~superior~~ preferable to wiggle matching, which is not necessarily reliable. For example, a depletion in δ^{18}O presumably indicating the LGM-Holocene transition might not always be a true atmospheric signal, but can be caused by unknown mechanisms potentially happening close to bedrock (Jenk et al., 2009; Wagenbach et al., 2012). All five examples show strong thinning towards bedrock with ~~and~~ the oldest ages obtained ~~were~~ being in the range of 10000 years. Because of the strong thinning, the ^{14}C age of the deepest sample represents a strongly mixed age of ice with a large age distribution. In these cases, the age limit was thus not determined by the ^{14}C half-life of 5730 yrs (Godwin, 1962), but by the achievable spatial depth resolution~~,~~ since some hundred grams of ice ~~are~~ is required. ~~and not by the half life of ^{14}C of 5730 yrs (Godwin, 1962)~~. ~~With this strong thinning the ^{14}C age of the deepest sample may represent a mixed age of ice having a large age distribution.~~

Since an absolute WIOC mass of ~10 µg is needed to achieve a ^{14}C dating with reasonably low uncertainty, the overall applicability of the method essentially depends on the WIOC concentration in the ice and the ice mass available. Figure 2 summarizes WIOC concentrations determined in ice from various locations around the globe. In general, mid-latitude and low-latitude glaciers contain sufficient WIOC from 21 to 295 µg/kg, allowing dating with less than 1 kg of ice. The highest concentration was found at Juvfonne ice patch which is small and located a low elevation and therefore by far closest to biogenic emission sources. WIOC concentrations might be further elevated due to meltwater and superimposed ice formation, enriching water-insoluble particles in the surface layer present at that time. Lowest concentrations of only 2 to 15 µg/kg WIOC were observed in polar snow and ice from Greenland and Antarctica. For this concentration range a reliable dating is impossible with the current method capability.

7 Conclusions

Since the introduction about 10 years ago of the ^{14}C dating technique for glacier ice, utilizing the WIOC fraction of carbonaceous aerosol particles embedded in the ice matrix, major improvements in separating the OC from the EC fraction and in AMS technology have been achieved. The new configuration with direct coupling of a commercial thermo-optical OC/EC analyser to the gas ion source of the MICADAS AMS via its gas introduction interface has two major advantages. First, the measurement time was significantly reduced to approximately 35 min per sample. Second, the implemented automated protocol allows for a controlled routine analysis with high reproducibility and a stable blank, thereby increasing the overall precision.

The presented WIOC ^{14}C dating method was validated by determining the age of independently dated ice samples. It principally allows absolute and accurate dating of any piece of ice ~~-~~containing sufficient WIOC. With the current set-up, the age of samples with a minimum of ~10 µg WIOC can be determined with satisfying precision of about 10 to 20%, depending on the age. This requires about ~~100~~ 300 to ~~500~~ 800 g of ice~~,~~ considering both, the mass loss of 20-30% during surface decontamination and the WIOC concentrations typically found in mid- and low latitude glaciers. Dating polar ice with satisfactory age uncertainties is still not possible since WIOC concentrations are around one order of magnitude lower. This would require further reduction of the procedural blank for such samples requiring larger ice volumes which potentially could be achieved by an additional, specifically designed sample preparation setup for such kind of samples.

The ^{14}C method is suitable for dating ice with ages from 200 to more than 10000 yrs. Whereas for a few century old ice the conventional dating methods are typically higher in precision, the WIOC ^{14}C method presents the only option for obtaining reliable continuous time scales for the older and deeper ice core sections of mountain glaciers. This is not only crucial for interpreting the embedded environmental and climatic history, but gives additional insight into glacier flow dynamics close to bedrock as demonstrated by the depth-age scales derived from ^{14}C dating of ice cores from various mid- and low latitude glaciers. Also, it can reveal information about the time of glacier formation.

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Author contribution

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Table 1: Characteristics of the sites discussed and the respective dating approach. ALC stands for Annual Layer Counting, RH for Reference Horizons and ^{210}Pb, ^{3}H, and ^{14}C for nuclear dating. 2p model (two parameter model), MC (Monte Carlo simulation) and EF (exponential fit) denotes the applied approach to finally derive a continuous age-depth relationship (see Section 6 for details).

Site	Coordinates Elevation	Location	Dating approach	Time span (years)	References
Belukha	49.80°N, 86.55°E 4115 m a.s.l.	Altai Mountains, Russia	ALC, RH, ^{3}H, ^{14}C, 2p model	~9100	Aizen et al., 2016
Colle Gnifetti	45.93°N, 7.88°E 4450 m a.s.l.	Western Alps, Swiss-Italian border	ALC, RH, ^{3}H, ^{210}Pb, ^{14}C, 2p model	>15200	Jenk et al., 2009
Juvfonne	61.68˚N, 8.35E 1916 m a.s.l.	Jotunheimen Mountains, Norway	^{14}C of plant fragment and WIOC	~7600	Zapf et al 2013 Ødegård et al., 2016
Illimani	17.03°S, 68.28°W 6300 m a.s.l.	Andes, Bolivia	ALC, RH, ^{3}H, ^{210}Pb, ^{14}C, 2p model	~12700	Sigl et al., 2009 Kellerhals et al., 2010
Mt. Ortles	46.51°N, 10.54°E 3905 m a.s.l.	Eastern Alps, Italy	ALC, RH, ^{3}H, ^{210}Pb, ^{14}C, MC	~6900	Gabrielli et al., 2016
Quelccaya	13.93°S, 70.83°W 5670 m a.s.l.	Andes, Peru	ALC, ^{14}C	~1800	Thompson et al., 2013
Tsambagarav	48.66°N, 90.86°E 4130 m a.s.l.	Altai Mountains, Mongolia	ALC, RH, ^{3}H, ^{210}Pb, ^{14}C, EF	~6100	Herren et al., 2013

Table 2: Samples analysed for the compararability test for OC/EC separation using the THEODORE apparatus and the Sunset OC/EC analyzer directly coupled to the AMS, with WIOC masses and concentrations. Calibrated ages (cal BP) denotes the 1 σ range.

Sample ID	AMS Lab. No.	WIOC mass (µg)	WIOC concentration µg/kg ice	F^{14}C	^{14}C age (BP)	cal age (cal BP)
1_THEODORE (JUV 3)	ETH 42845.1.1 ETH 42847.1.1 ETH 42849.1.1 ETH 43446.1.1	44	176	1.134 ± 0.017	-1010 ± 120	-46 - -7
1_Sunset (JUV 3)	BE 3683.1.1 BE 3701.1.1	46	119	1.~~160~~ 157 ± 0.~~013~~014	-~~1192~~ 1171 ± ~~90~~97	-~~41~~ 42 - -8
2_THEODORE (JUV 1)	ETH 43555.1.1 ETH 43557.1.1	18	60	0.743 ± 0.029	2386 ± 314	2011 - 2783
2_Sunset (JUV 1)	BE 3679.1.1	9	33	0.~~751~~ 744 ± 0.021	~~2300~~ 2376 ± 225	~~2068~~ 2158 - ~~2703~~2737
3_THEODORE (~~Bel~~ BEL 1)	ETH 42841.1.1	18	63	0.771 ± 0.017	2089 ± 177	1886 - 2310
3_Sunset (~~Bel~~ BEL 1)	BE 4282.1.1	15	61	0.~~739~~ 725 ± 0.022	~~2430~~ 2587 ± ~~239~~233	~~2159~~ 2353 - ~~2761~~2924
4_THEODORE (~~Bel~~ BEL 2)	ETH 43448.1.1	15	47	0.402 ± 0.022	7320 ± 440	7686 - 8588
4_Sunset (~~Bel~~ BEL 2)	BE 4175.1.1	18	48	0.~~388~~ 387 ± 0.022	~~7605~~ 7626 ± ~~455~~457	~~7983~~ 7999 - ~~9000~~9011

Table 3: Juvfonne samples analysed for method validation. JUV 1, JUV 2 and JUV 3 were ice blocks collected from the 2010 tunnel (Ødegård et al., 2016; Zapf et al., 2013) and JUV 0 from the 2012 tunnel (Ødegård et al., 2016). To visualize the expected increase in age with increasing depth of the ice patch, ~~S~~samples are listed in stratigraphic order from top to bottom~~-~~. Sample JUV 1 was collected between two separated organic-rich layers (Poz-56952 and Poz-36460). For comparision, an age range between these two layers was calculated (*, range between the lower and upper 2σ boundary, respectively). The results from sub-samples of the individual ice blocks were averaged to derive the combined values shown. Uncertainties (1σ) were calculated by error propagation of all analytical uncertainties for the individual measurements and for the combined values denote the standard error of the unbiased standard deviation. For a graphic display of the comparision see Fig. 3.

Sample ID	**AMS Lab. No.**	**WIOC (µg)**	**g of ice**	**F^{14}C**	**^{14}C age (BP)**	**cal age (cal BP)**
JUV 3_1	ETH 42845.1.1	55~~54.8~~	292 ~~291.5~~	1.124 ± 0.013~~1.12 ± 0.01~~	-939 ± 93~~-940 ± 91~~	
JUV 3_2	ETH 42847.1.1	43~~43.1~~	268 ~~267.7~~	1.094 ± 0.015~~1.09 ± 0.01~~	-722 ± 110~~–720 ± 110~~	
JUV 3_3	ETH 42849.1.1	47~~46.8~~	325~~325.0~~	1.155 ± 0.015~~1.15 ± 0.01~~	-1158 ± 104~~–1160 ± 100~~	
JUV 3_4	ETH 43446.1.1	43~~43.4~~	208~~207.7~~	1.164 ± 0.017~~1.16 ± 0.02~~	-1220 ± 117~~–1220 ± 120~~	
	JUV 3 (surface 2010)			1.134 ± 0.017~~1.13 ± 0.01~~	-1010 ± 120~~–996 ± 52~~	modern
	Organic remains, Poz-37877			0.873 ± 0.003	1091 ± 28	963 - 1052
JUV 2_1	ETH 43443.1.1	27~~27.3~~	215~~215.1~~	0.881 ± 0.023~~0.88 ± 0.02~~	1018 ± 210~~1020 ± 210~~	
JUV 2_2	ETH 43445.1.1	9~~9.0~~	171~~170.8~~	0.792 ± 0.066~~0.79 ± 0.07~~	1873 ± 669~~1870 ± 670~~	
JUV 2_3	ETH 43559.1.1	17~~16.5~~	257~~257.4~~	0.870 ± 0.035~~0.87 ± 0.04~~	1119 ± 323~~1120 ± 320~~	
JUV 2_4	ETH 45109.1.1	19~~19.4~~	219~~219.0~~	0.869 ± 0.031~~0.87 ± 0.03~~	1128 ± 287~~1130 ± 280~~	
	JUV 2 (2010)			0.853 ± 0.022~~0.85 ± 0.02~~	1277 ± 207~~1116 ± 146~~	965 - 1368~~(918–1237)~~
	~~**Organic remains, Poz-37879**~~			~~**0.838 ± 0.003**~~	~~**1420 ± 30**~~	~~**(1300–1338)**~~
	Organic remains, Poz-56952*			0.777 ± 0.003	2027 ± 31	1929 - 2033
JUV 1_3	ETH 43555.1.1	20~~20.2~~	281~~280.6~~	0.766 ± 0.029~~0.77 ± 0.03~~	2141 ± 304~~2144 ± 300~~	
JUV 1_4	ETH 43557.1.1	9~~9.2~~	214~~214.0~~	0.719 ± 0.064~~0.72 ± 0.06~~	2650 ± 715~~2650 ± 710~~	
	Organic remains, Poz-36460*			0.692 ± 0.003	2958 ± 35	3065 - 3174
	JUV 1 (2010)			0.743 ± 0.029~~0.76 ± 0.03~~	2386 ± 314~~2227 ± 277~~	2011 - 2783~~(1904–2697)~~
	~~Poz-37878~~			~~0.826 ± 0.003~~	~~1535 ± 30~~	
	~~Poz-36460~~			~~0.692 ± 0.003~~	~~2960 ± 30~~	
	Organic remains , age range between the two layers*~~mean~~			0.735 ± 0.037~~ 0.76 ± 0.04~~	2473 ± 404~~2215 ± 410~~	2005 - 3004~~(1810–2750)~~

Organic remains (plant fragment), Poz-56955				0.486 ± 0.002	5796 ± 33	6561 - 6656
JUV 0_1	BE 4184.1.1	393~~393.2~~	283~~283.1~~	0.479 ± 0.015~~0.48 ± 0.01~~	5913 ± 252~~5905 ± 248~~	
JUV 0_2	BE 4380.1.1	246~~245.9~~	298~~298.1~~	0.457 ± 0.008~~0.46 ± 0.01~~	6290 ± 141~~6293 ± 137~~	
JUV 0-A (2015)				0.468 ± 0.014~~0.47 ± 0.01~~	6099 ± 240~~6207 ± 120~~	6720 - 7256~~(6969 - 7255)~~
JUV 0_3	BE 4185.1.1	219~~219.4~~	208~~207.9~~	0.445 ± 0.012~~0.44 ± 0.01~~	6504 ± 217~~6512 ± 216~~	
JUV 0_4	BE 4381.1.1	182~~182.4~~	188~~188.3~~	0.442 ± 0.007~~0.44 ± 0.01~~	6559 ± 127~~6555 ± 133~~	
JUV 0_5	BE 4186.1.1	238~~238.3~~	227~~226.9~~	0.403 ± 0.012~~0.40 ± 0.01~~	7301 ± 239~~7296 ± 231~~	
JUV 0_6	BE 4382.1.1	36~~36.4~~	184~~184.2~~	0.438 ± 0.011~~0.44 ± 0.01~~	6632 ± 202~~6626 ± 196~~	
JUV 0_7	BE 4187.1.1	262~~262.2~~	200~~200.4~~	0.404 ± 0.011~~0.40 ± 0.01~~	7281 ± 219~~7285 ± 18~~	
JUV 0_8	BE 4383.1.1	203~~202.9~~	214~~214.2~~	0.451 ± 0.013~~0.45 ± 0.01~~	6397 ± 232~~6396 ± 229~~	
JUV 0-B (2015)				0.431 ± 0.009~~0.43 ± 0.01~~	6761 ± 168~~6741 ± 9~~	7476 - 7785~~(7519 - 7670)~~

Table 4: Quelccaya samples analysed for method validation. Calibrated ages (cal BP) denote the 1 σ range. ALC stands for Annual Layer Counting.

Sample	**Depth (m)**	**AMS Lab. No.**	**WIOC (µg)**	**F^{14}C**	**^{14}C age (BP)**	**cal age (cal BP)**	**ALC (yrs BP)**
139-140	144.69-146.79	BE 4336.1.1	15	0.888 ± 0.026	954 ± 237	675 - 1036	730 - 788
149-150	155.21-157.31	BE 4335.1.1	24	0.859 ± 0.018	1216 ± 171	1005 - 1300	1072 - 1157
157-158	163.88-166.09	BE 4337.1.1	14	0.803 ± 0.025	1761 ± 246	1414 - 1957	1439 - 1543

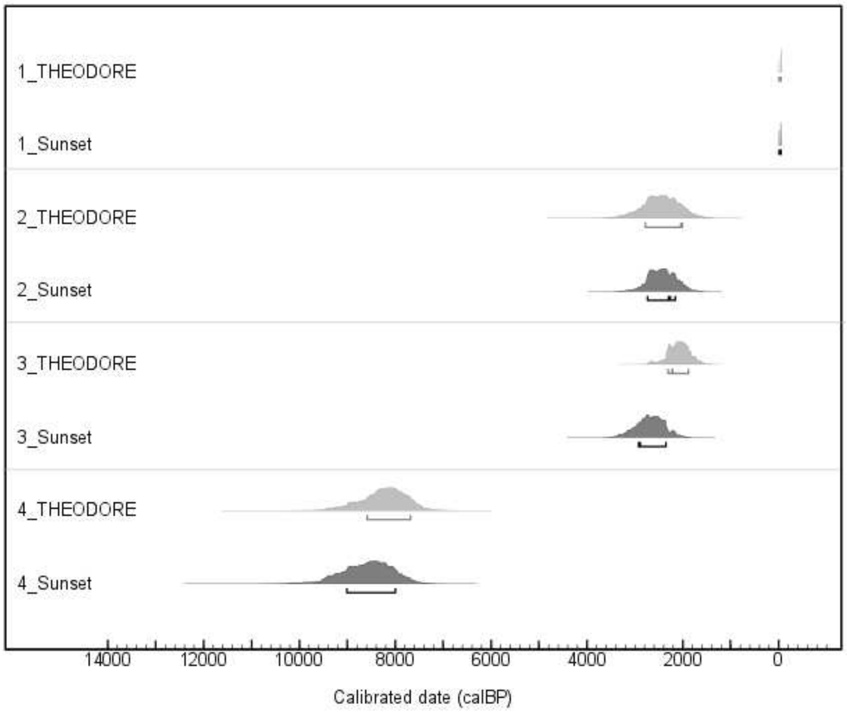

Figure 1: OxCal output for the compararability test for OC/EC separation using the THEODORE apparatus and the Sunset OC/EC analyzer directly coupled to the AMS. Bars below the age distributions indicate the 1 σ range. See Table 2 for the samples details.

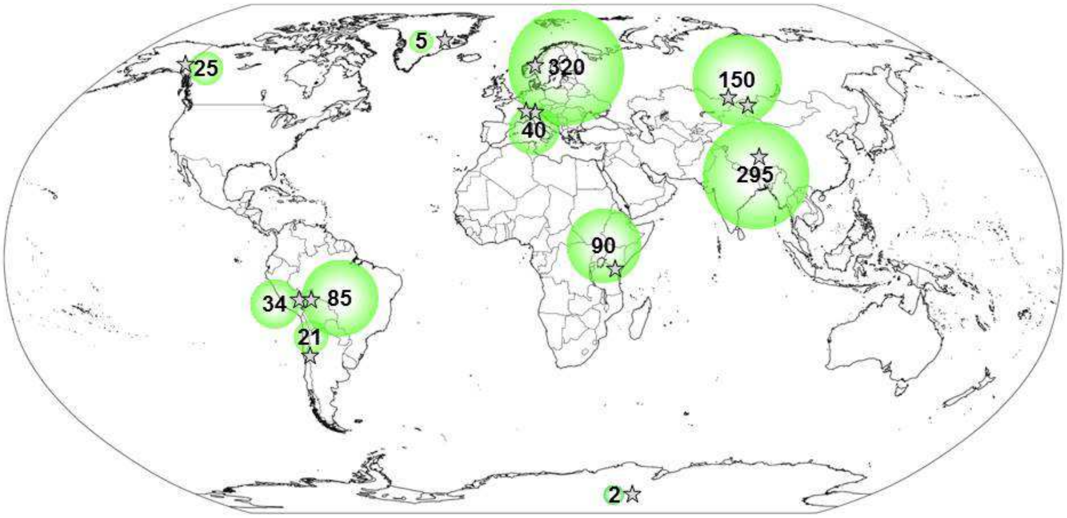

Figure 2: World map showing the sites from which ice samples were analysed with the ^{14}C method (gray stars): Edziza, Canada, 57.71° N 130.63° W; GRIP, Greenland, 72.59° N, 37.65° W, 3230 m a.s.l.; Juvfonne, Norway, 61.68 N, 8.35° E; Colle Gnifetti, Switzerland, 45.93° N, 7.87° E; Mt. Ortles, Italy, 46.51° N, 10.54° E; Belukha, Russia, 49.80° N, 86.55° E; Tsambagarav, Mongolia, 48.66° N, 90.86° E; Naimonanji, China 30.45° N, 81.54° E; Kilimanjaro, Tanzania, 3.06° S 37.34° E; Quelccaya, Peru, 13.93° S, 70.83° W; Nevado Illimani, Bolivia, 16.03° S, 67.28° W; Mercedario, Argentina, 31.97° S, 70.12° W; Scharffenbergbotnen, Antartica, 74.00° S, 11.00° W. The average WIOC concentration in µg/kg at each site is indicated with green bubbles.

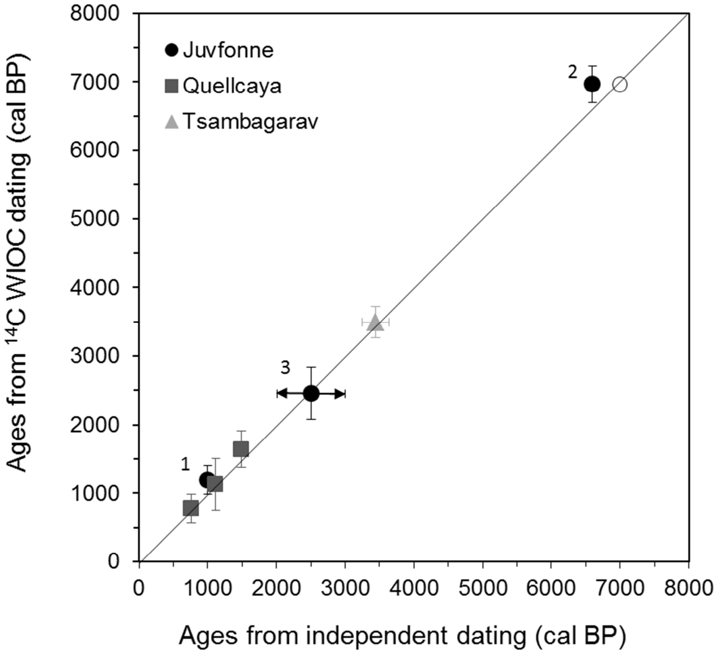

Figure 3: Scatter plot showing the ages obtained with the WIOC ^{14}C ~~WIOC~~ method for independently dated ice, including the conventionally ^{14}C dated Juvfonne organic-rich layers~~,~~ (Ødegård et al., 2016), the ^{14}C dated fly found in the Tsambagarav ice core, and the Quelccaya ice dated by annual layer counting~~,~~ (Thompson et al., 2013). Error bars denote the 1 σ uncertainty. Note that the Juvfonne WIOC samples and the organic-rich layers were not sampled from the exact same depth, but adjacent to each other. For the youngest (1) and oldest (2, containing the plant fragment) the ice for WIOC ^{14}C analysis was sampled below the layers whereas the third sample (3) was bracketed by two layers. For (3) the arrow thus indicates the age range between the lower and upper 2σ boundary of these two layers, respectively. For (2) the open circle indicates an estimated age for the according WIOC ice sampling depth based on a fit through all the conventionally dated organic-rich layers, presented in Ødegård et al., 2016).

Figure 4: Photo of the fly found in segment 102 of the Tsambagarav ice core. The age of the fly was 3442±191 cal BP, while the surrounding ice yielded an age of 3495±225 cal BP (photo by Sandra Brügger).

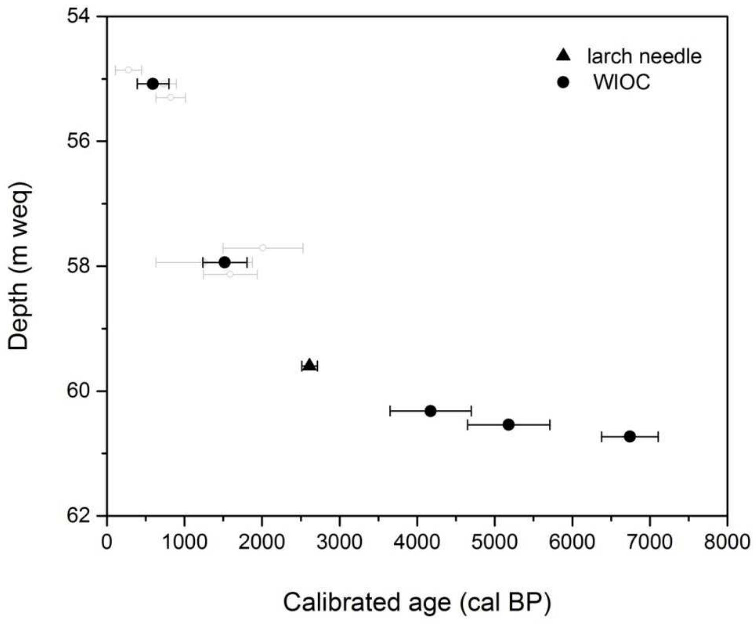

Figure 5: Dating of the bottom part of the Ortles ice core. Circles indicate the ages derived with the WIOC ^{14}C ~~WIOC~~ method and the triangle shows the age of the conventionally ^{14}C dated larch leaf found in the ice core (Gabrielli et al., 2016). Light grey circles show the ages obtained for the subsamples. Errors bars represent the 1 σ uncertainty.

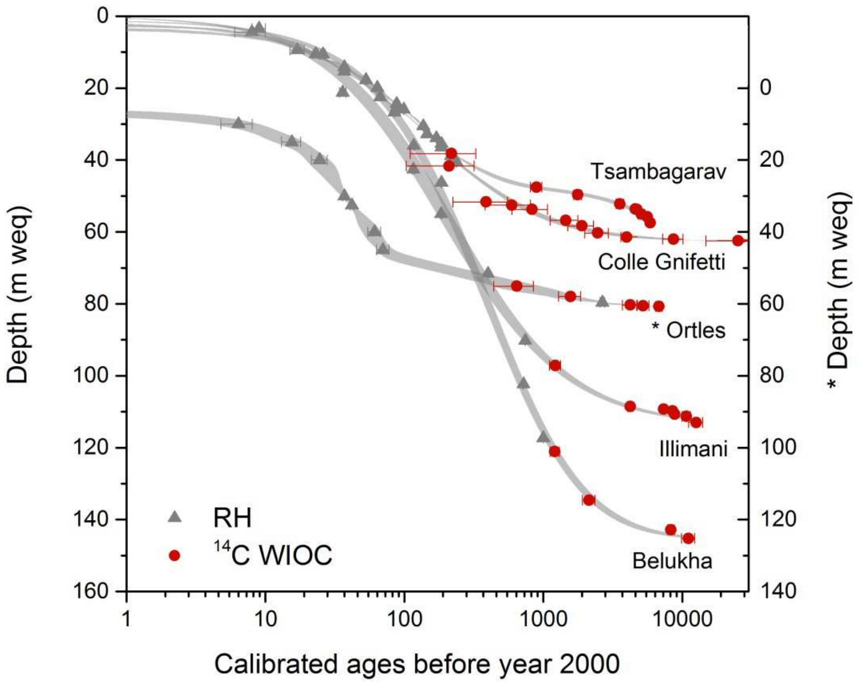

Figure 6: Compilation of age-depth relationships for five different ice cores, highlighting the importance of the WIOC ^{14}C dating to obtain continuous chronologies and to constrain the very specific glaciological conditions and settings of each site. For simplicity only reference horizons and ^{14}C dates were included. Gray triangles indicate reference horizons (RH) and red circles the -^{14}C--WIOC ages both plotted with 1σ uncertainties (smaller than the symbol size in some cases). For the Mt. Ortles core ^{210}Pb dated horizons with a larger uncertainty were used as RH due to the lack of absolute time markers prior to 1958; the gray triangle at 57.8 m weq depth is the conventional ^{14}C age of the larch leaf. Gray shaded areas represent the 1σ range of the respective fit for retrieving a continuous age depth relationship. For sample details and the fitting approaches applied, see main text and Table 1. -References to the original data are summarized in Table 1. Note that for better visibility (avoiding overlap with Tsambagarav and Colle Gnifetti) the curve for the Mt. Ortles glacier was shifted down by 20 m and refers to the right-hand y-axis (*). .