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A NEW SAMPLE PREPARATION SYSTEM FOR MICRO-¹⁴C DATING OF GLACIER ICE WITH A FIRST APPLICATION TO A HIGH ALPINE ICE CORE FROM COLLE GNIFETTI (SWITZERLAND)

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ABSTRACT. Radiometric dating of glacier ice is an essential tool where stratigraphic dating methods cannot be applied. This study focuses on Alpine glacier ice and presents a new sample preparation system for dating of glacier ice samples via radiocarbon (¹⁴C) dating of the microscopic particulate organic carbon (POC) fraction incorporated in the ice matrix. An adaptable, low-cost inline filtration-oxidation-unit (REFILOX) has been developed, which for the first time unifies all sample preparation steps from ice filtration to CO₂ quantification in one closed setup. A systematic ¹⁴C investigation of modern European aerosol samples revealed that a POC combustion temperature of 340°C provides the best representation of the real sample age. A very low process blank of maximally 0.3 ± 0.1 µgC now enables ¹⁴C dating of high Alpine ice samples, where POC concentrations are generally low (typically 10–50 µgC/kg), in an ice sample mass range of 300–500 g. In a first successful application, the method was used to obtain age constraints for an ice core from the cold, high Alpine firn saddle Colle Gnifetti (Switzerland). Analysis of the bottom ice core sections revealed a basal age of 4171–3923 cal yr BP but also a so far enigmatic discontinuity in the age-depth relationship.

KEYWORDS: ice core, particulate organic carbon, radiocarbon AMS dating.

INTRODUCTION

For every climate archive, the construction of a reliable age-depth relationship is a crucial step to enable paleoclimatic interpretation of the extracted proxy records. Regarding ice cores drilled at polar ice sheets, conventional stratigraphic dating methods, i.e. annual layer counting in isotope and impurity profiles, have proven to be highly successful (e.g. Meese et al. 1994; Ram and Koenig 1997; Ruth et al. 2007; Svensson et al. 2015). However, in case of small scale mountain drilling sites, stratigraphic dating methods are often severely limited. For cold, high Alpine stratified glaciers, characterized by complex bedrock geometry and highly variable accumulation regimes, previous attempts at annual layer counting were found to be limited to the last few hundred years (Wagenbach and Geis 1989; Wagenbach et al. 2012; Bohleber et al. 2013). Ice bodies with a non-stratigraphic ice build-up, like small ice patches, cave ice or rock glaciers completely lack annual layering. However, also the basal age determining the onset of formation of the ice body contains important climatic information itself. In this context, an alternative dating method delivering absolute ages is required. For ice samples older than 1000 yr BP, radiocarbon (¹⁴C) dating of microscopic organic impurities incorporated into the ice is so far the only option. The main challenge of this method lies in the overall very small concentrations of organic material in high Alpine ice samples in the range of micrograms. Microscopic organic material in glacier ice can mainly by size be separated into dissolved organic carbon (DOC) and particulate organic carbon (POC). The concentrations of DOC

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have been determined to be in the range of ca. 50–100 $\mu\text{gC/kg}$ for high Alpine ice samples (May 2009; May et al. 2013), whereas the concentrations for POC are a factor of two to ten smaller, in the range of 10–50 $\mu\text{gC/kg}$ (Steier et al. 2006; Jenk et al. 2009). At the Institute for Environmental Physics (IUP) Heidelberg, it was therefore initially attempted to use the DOC fraction for ^{14}C dating of ice samples. For high altitude, low accumulation glaciers however this organic carbon fraction proved to be significantly biased by in situ produced ^{14}C (May 2009; Hoffmann 2016) and is thus not suitable for dating applications at this kind of sites.

For POC extraction from glacier ice, several systems have been developed over the last ten years in different laboratories including also the construction of a prototype at the Institute for Environmental Physics, Heidelberg (IUP) (Steier et al. 2006; May 2009; Jenk et al. 2007; Uglietti et al. 2016). At present, apart from the sample preparation and extraction system presented in this study, only one other system exists at the Paul-Scherrer-Institute in Switzerland (Uglietti et al. 2016). One of the major problems for all ^{14}C preparation systems is to guarantee a stable and very low procedural blank in carbon mass. This procedural blank mass should ideally stay below 1 μgC to enable an application of the method to high Alpine ice cores, where available sample masses do not exceed 1 kg of ice. This is due to the limited core diameter and the restrictions of a reasonable vertical extent of the sample in terms of age averaging. Apart from the process blank challenge, a major assumption for the dating of glacier ice via POC ^{14}C -analyses is that the age of the dated organic material represents the age of the encompassing ice. However, this assumption does not have to be a priori true. Especially the incorporation of material, which has been significantly aged before deposition onto the glacier surface, can lead to significant age biases. Studies on such effects and methods to circumvent them are sparse and mostly based on assumptions like for the influences of Saharan dust (Jenk et al. 2006).

In this study, we present the POC extraction system REFILOX (Reinigungs – Filtrations – Oxidationssystem) which is a simple and low cost alternative to the use of a commercial Sunset OC/EC (organic carbon/elemental carbon) analyzer, with the additional benefit of comprising all sample preparation steps of pre-cleaning, POC extraction from the ice and oxidation to CO_2 in one closed and unique system. To develop a strategy for prevention of age biasing effects caused by incorporation of aged material like Saharan dust, a selection of well characterized modern aerosol samples collected within the CARBOSOL project (Legrand and Puxbaum 2007) have been analyzed in the REFILOX. The successfully developed POC ^{14}C -dating method is then applied to obtain age constraints from the high Alpine firn saddle Colle Gnifetti (Switzerland).

METHODS

Setup of the POC Extraction System, Ice-Sample Handling Procedure, and AMS Measurements

Since the ice sample mass used for ^{14}C dating needs to be kept as small as possible, extracted POC sample sizes in the order of tens of micrograms of carbon have to be expected. Thus, the main objective of any sample preparation system must be the minimization of possible contamination sources, together with a simultaneous maximization of the POC extraction efficiency. To minimize contamination caused by contact of the sample material with surfaces of the system components, all critical parts of the melting and filtration unit in direct contact with sample material are made of either quartz glass, stainless steel or PFA (perfluoroalkoxy alkanes). Quartz glass can be efficiently cleaned from organic substances by preheating. The stainless steel components are cleaned in an ultrasonic bath. All valves in direct contact with sample material are rinsed thoroughly with ultra-pure (ELGA-Labwater, 18 $\text{M}\Omega$, 1–2 ppb TOC, PURELAB Ultra Analytic). PFA offers a very hydrophobic surface, which allows an

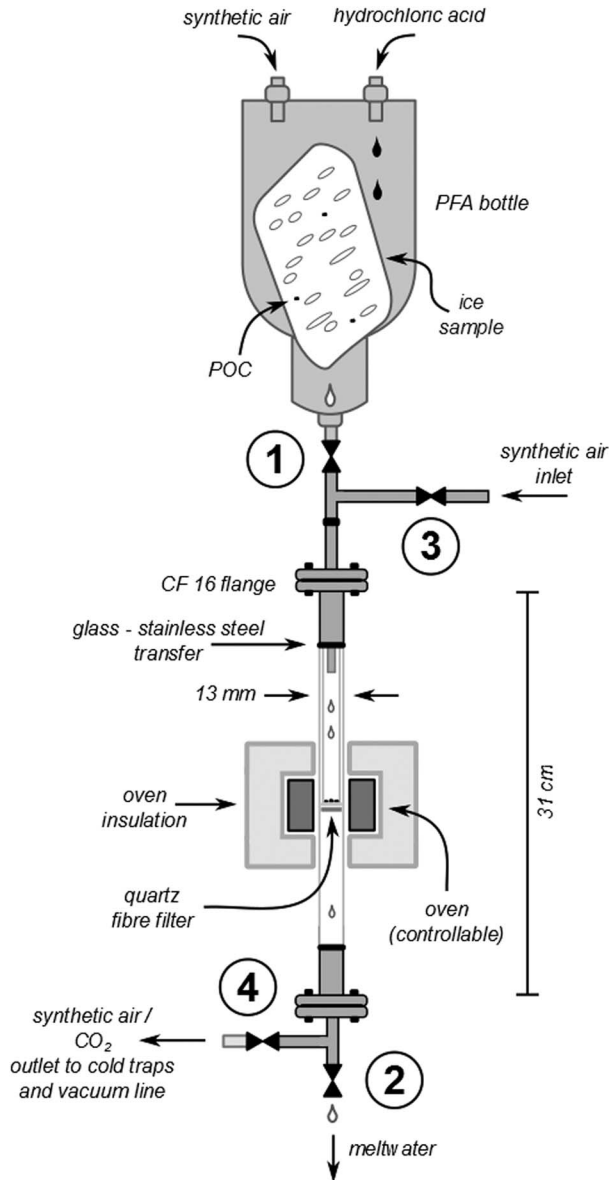


Figure 1 Technical setup of the filtration-combustion unit REFILOX. The system layout unifies all processing steps of filtration, acidification, combustion and CO₂ cleaning and quantification in one closed construction.

almost complete runoff of water without residuals. To avoid adsorption of dust from ambient air onto the sample surface, all processing steps involving open sample material are carried out in a laminar flow box.

The central part of the filtration-combustion unit REFILOX (Figure 1) consists of the melting vessel (a 2-L PFA bottle placed upside down), which is connected to a quartz glass tube. Sealed in the center of the tube is a quartz frit (porosity 2), on which a quartz fiber filter

(9 mm, Whatman QM-A) is placed. The filter can be heated from the outside to a maximum temperature of ca. $900^{\circ}\text{C} \pm 5^{\circ}\text{C}$ by a custom-built, attachable oven which can be clipped around the quartz tube. The whole filtration and combustion system is airtight. Prior to every sample, a new filter is inserted to the tube and the melting vessel together with the filtration unit is rinsed with HCl (0.2M), and an inorganic alkaline cleaner (Roth, RBS 50), followed by ca. 4 L of ultrapure water. Afterwards, the filtration system is closed (valve 1 and 2 in Figure 1), purged with particle filtered (15 μm) synthetic air (80% N_2 / 20% O_2 , hydrocarbons: <0.05 ppmv, CO_2 : <0.1 ppmv) to flush out remaining ambient air. This process is monitored by an infrared CO_2 detector (Teledyne, 360U). When a CO_2 concentration below 0.3 ppmv in the purging air is reached, the oven is set to 900°C and heated for 60 min, to combust residual organic substances that have been accumulated on the filter during the flushing of the system with cleaning liquids. This immediate cleaning of the filter material directly within the filtration system is a large advantage compared to the other system (Uglietti et al. 2016), where the preheated filter has to be handled once more outside the filtration system before use, entailing the risk of new surface contamination.

Pre-cleaning of the sample is carried out similar to well established procedures used for DOC, analyses which are even more prone to (surface) contamination (Preunkert et al. 2011; De Angelis et al. 2012). The ice sample is first cut by use of an electric band saw to remove the potentially contaminated outer surface. Then, the sample surface is scraped with a ceramic knife to remove remaining potentially contaminated sawing powder from the open cut bubbles. After scraping, the sample is stored in a closed PFA container and warmed at room temperature to 0°C for 30 min to minimize tensions and the risk of cracking. It is then quickly rinsed with ultrapure water and transferred by a stainless steel forceps into the pre-cleaned melting vessel. The vessel is attached to the filtration unit, valves 1 and 2 are opened and melting and filtration starts. During melting, the system is flushed with synthetic air, to press the accumulating meltwater through the filter matrix. When melting is finished, a few drops of HCl (0.2M) are applied onto the filter through the bottom of the PFA bottle to remove the inorganic carbon fraction, mainly carbonates. The oven is set to 75°C to speed up the reaction and dry the filter, meanwhile the filtration tube is closed (valve 1 and 2) and purged again with synthetic air (400 mL/min). When the CO_2 concentration drops below 0.2 ppmv, valves 3 and 4 are closed and combustion at the desired temperature is started. By closing the valves above and below the filter, the quartz tube functions as a closed combustion volume, comparable to a conventional sealed glass ampoule. When combustion is finished, the unit is again flushed with synthetic air to purge out the resulting CO_2 created by oxidation of the organic species during the combustion process. The air stream is guided through two cold traps immersed in liquid nitrogen traps for 15 min at a flow rate of 0.5 L/min into a vacuum line to freeze out the CO_2 . After this freezing out, the collected CO_2 is cleaned from water vapor and quantified manometrically. Details on the setup of the CO_2 cleaning and quantification line can be found in May et al. (2013) and Hoffmann (2016). The minimal detectable sample size determined by the precision of the manometric quantification is $0.6 \mu\text{gC}$. After quantification, the CO_2 samples are flame sealed into glass ampoules and ready for AMS measurement. The ^{14}C measurements are carried out at the Klaus-Tschira-Lab in Mannheim using a MICADAS AMS system (Kromer et al. 2013) equipped with a gas ion source (Ruff et al. 2007; Fahrni et al. 2013) built by Ionplus. The gas ion source system in Mannheim allows dating of sample masses in the range of 2–10 μgC with a relative error of 3–7% and dating of samples $>10 \mu\text{gC}$ with a relative error of 1–2% (Hoffmann 2016).

Blank Material ^{14}C Measurements

For characterization of the REFILOX filtration and combustion system performance and correction of the retrieved ^{14}C results it is essential to know the process blank, both in terms

of carbon mass and ¹⁴C signature. In general, ¹⁴C results are reported as F¹⁴C according to Stuiver and Polach (1977) and the blank corrected F¹⁴C value F_s of a sample is calculated according to

$$F_s = \frac{F_m \cdot m_m - F_b \cdot m_b}{m_m - m_b} \quad (1)$$

where F_m and m_m denote the measured F¹⁴C and carbon mass of the sample and F_b and m_b the blank values respectively. The blank mass, thus the organic carbon contamination introduced or insufficiently removed from the ice sample during handling, preparation and processing in the REFILOX system was determined by use of virtually POC free blank ice samples. Therefore, artificial blank ice samples were produced from ultra-pure water, which has been slowly frozen in polyethylene (PE) foil on a lab shaker under constant movement. This method has been used for growing single ice crystals for many years (Higashi 1974; Thibert and Dominé 1997) and leads to a virtually complete separation on solutes and particles in the liquid phase from the impurity-free solid ice crystal (Halde 1980; Shafique et al. 2012). Six blank ice samples have been processed in the REFILOX system and were combusted either at 800°C completely or stepwise at 340°C first and second at 800°C (see Table S1a in the supplementary information). For the 340°C fraction the carbon mass was for all samples apart from one technically not detectable by manometric quantification in the measuring volume. For all 340°C fractions it was below the formal detection limit determined by the precision and the variation of the pressure sensor, therefore <0.6 µg. This is a reduction by at least a factor of 10 compared to the previously used POC prototype extraction system at the IUP. For the total and 800°C only combustion an average value of (3.3 ± 2.3) µgC was found. These blank ice measurements were complemented by process blank samples of ca. 500 mL of liquid ultrapure water, processed between every two ice samples, to ensure that the REFILOX cleaning routine was applied successfully. For the 340°C combustion step, none of these liquid water samples ever yielded a carbon mass above detection limit and for the 800°C fraction, the average carbon mass was (1.7 ± 1.2) µgC.

Because the carbon masses for the blank ice measurements were below the detection limit of the pressure sensor in the measuring volume, another method of blank mass quantification for the 340°C fraction had to be developed. This mass determination was performed by using the linear correlation (R² = 0.995) of the CO₂ pressure in the cooling trap volume (before transfer of the sample into the measuring volume) and the retrieved carbon mass in the measuring volume for 100 samples (see Figure S1 in the supplementary information) in the range of 0.3–10 µgC. The pressure sensor in this part of the cleaning and quantification line (May et al. 2013; Hoffmann 2016) is a Compact full range gauge (Pfeiffer vacuum) with a pressure range of 10⁻⁸–100 mbar and thus able to measure much smaller pressures than the sensor in the measuring volume. The linear regression of this pressure – mass relation yielded a slope of (1.677·10⁻² ± 2·10⁻⁴ mbar/µgC). The y-intercept was fixed at a pressure of 5·10⁻⁵ mbar, which equals a typical value of the completely evacuated line. By extrapolation of this linear function towards zero it was possible to calculate the masses of the blank ice samples, which were too small to be detected in the measuring volume. As an average carbon mass of all blank ice samples, thus an average of m_b = (0.2 ± 0.1) µgC (uncorrected for combustion efficiency) was determined and this mass has been used for correction of all glacier ice samples (see discussion below). It is worth noting that even assuming a minimal combustion efficiency of only 50%, would result in an absolute blank carbon mass of only m_b = (0.4 ± 0.1) µgC, which is significantly smaller than usually determined for other systems being used for glacier ice analyses (Uglietti et al. 2016). However, because of the very small carbon masses, a direct determination of the blank F¹⁴C was not possible. Therefore, this value had to be estimated. Based on previous glacier ice POC studies

(May 2009; Sigl et al. 2009; Uglietti et al. 2016) which despite large differences in the extraction systems all found blank $F^{14}\text{C}$ values in a range of $F_b = 0.5\text{--}0.7$, an average ^{14}C value of $F_b = 0.6 \pm 0.2$ was assumed to cover a reasonably large range for F_b and this value was used for correction. The 800°C fraction was also blank corrected with the blank mass retrieved from the blank ice measurements not the liquid water samples. One blank ice sample, combusted completely at 800°C with a carbon mass of $(2.5 \pm 0.3) \mu\text{gC}$, could be measured directly for ^{14}C and resulting in $F_b(\text{complete}) = (0.574 \pm 0.030)$. This value was used for correction of all total combustion results with a 40% increased error to account for blank variations, which are not covered by only one blank $F^{14}\text{C}$ measurement result. Thus, the applied value is $F_b(\text{complete_corr}) = (0.574 \pm 0.031)$. For the 800°C only fraction an average $F^{14}\text{C}$ -value of $F_b(800^\circ\text{C}) = (0.130 \pm 0.022)$ was obtained and again with a 40% error addition used for correction. Therefore, assuming average POC concentrations in high Alpine ice samples of ca. $25 \mu\text{gC/kg}$ and a mass loss of ca. 20–40% during decontamination, the combustion at 340°C requires a minimal ice sample size of ca. 300 g ice to keep the influence of the blank mass in the retrieved POC sample below 10%. For total combustion or combustion at 800°C only, according to the retrieved blank values a minimal sample mass of 1 kg would therefore be required to keep the fraction of the blank mass below 10%. The gas ion source technique of the AMS is able to measure samples $>10 \mu\text{gC}$ with 1–2% precision and samples $<10 \mu\text{gC}$ with 3–7% precision. These uncertainties add to the total uncertainty of the ^{14}C date.

Standard Material ^{14}C Measurements

To further ensure the reliability and reproducibility of the sample preparation process and to determine the overall combustion efficiency of the system, standard materials of known ^{14}C content in a mass range of ca. 8–60 μgC have been combusted in the REFILOX system and were ^{14}C analyzed. These materials are cellulose (IAEA standard material C3 [Rozanski et al. 1992]) with $F^{14}\text{C}_{\text{cell}} = 1.294$, oxalic acid (OxII, SRM 4990 C [Mann 1983]) with $F^{14}\text{C}_{\text{oxa}} = 1.341$ and brown coal, which should according to (Lowe 1989) have a conventional ^{14}C age of 25,000–40,000 yr BP corresponding to $F^{14}\text{C}_{\text{coal}} = 0.006\text{--}0.044$. All samples have been inserted directly into the combustion tube on top of a pre-heated filter and have been combusted at 800°C total or at 340°C as indicated in Table S1b (see supplementary information). The error-weighted average of the cellulose samples is $F_{\text{cell}} = (1.281 \pm 0.029)$, for the oxalic acid samples $F_{\text{oxa}} = (1.334 \pm 0.008)$ and for the brown coal samples $F_{\text{coal}} = (0.036 \pm 0.010)$. All averaged results thus agree within 1σ error ranges with the expected consensus values stated above. Only the $F^{14}\text{C}$ value of the smallest cellulose sample is slightly lower than expected, which could hint to a small contamination, but no systematic mass dependent deviation could be found. Therefore, the combustion procedure in the REFILOX does not show indications of either a systematic $F^{14}\text{C}$ mass dependence or signs of fractionation and is highly effective even for small samples with carbon masses below $50 \mu\text{gC}$.

To quantify the combustion and CO_2 extraction efficiency of the REFILOX system in terms of retrieved carbon mass, the input and output masses of the standard material samples in Table S1b (see supplementary material) have been compared, weighed with the theoretical carbon content of the respective material. The extracted carbon masses range between ca. 65% and 90% of the expected masses, with the smaller samples showing poorer calculated yields than the larger samples. This is mainly due to a larger uncertainty of the inserted sample masses for small samples. Very small samples are very difficult to handle at insertion into the combustion tube, where potential losses to the tube walls can occur. Thus, on average, a combustion and CO_2 extraction efficiency of 70% for real samples was assumed, which should be considered as a lower limit and is also supported by the results of the aerosol filter analyses discussed below.

Modern Aerosol Filter Analysis

Combustion of the total POC at very high temperatures (800°C) can lead to age biasing effects due to influences of already aged material like e.g. insufficiently removed carbonates in the sample. This shortcoming has been addressed for example in (Jenk et al. 2006) and (Sigl et al. 2009) for a potential Saharan dust bias of the EC fraction (elemental carbon), however no decisive conclusion was drawn. It was therefore envisaged to further investigate these effects using well characterized aerosol filter samples collected within the European CARBOSOL project (Legrand and Puxbaum 2007). The aim of this investigation was to establish the optimal combustion procedure for ice POC samples in the REFILOX with respect to minimization of such reservoir effects via an optimal separation of the potentially age biased carbon fractions from the unbiased primary biogenic or coagulated and degenerated secondary fractions. The use of different combustion temperatures for separation of organic carbon fractions, especially organic carbon (OC) and elemental carbon (EC) has been applied for source apportionment analysis of modern aerosol samples for many years (see e.g. Pio et al. 1994, 2007; Szidat et al. 2004b). During the CARBOSOL project, a thermo-optical method (Pio et al. 1994) has been used, which allows a separation of the carbonaceous species into five sub-fractions denoted as OC1, OC2, OC3 (organic carbon sub-separated by volatility), PC (pyrolytic carbon) and EC. This detailed separation cannot be reproduced by the REFILOX system. Therefore, a simplified three-step heating procedure (340°C, 380°C, and 800°C) similar to Szidat et al. (2004b) has been applied, aiming to attribute the CARBOSOL carbon fractions stated above to these three combustion temperature steps.

To picture a wide range of aerosol characteristics, filter samples from four different CARBOSOL sites (Sonnblick observatory (SBO), Schauinsland (SIL), K-Pusztá (HU) and Aveiro (AVE)) have been selected, see Pio et al. (2007) for site descriptions. Following the protocol of May et al. (2009), the filter samples have been cut out (10 mm diameter), acidified in HCl acid vapor (0.2M) and were subsequently inserted into the REFILOX system. Two samples (SIL 3/28-W and HU-04-W, see Table S2a in supplementary material) have additionally been rinsed with ultrapure water after insertion to the REFILOX to reduce the sample to its insoluble part, which is more similar to a POC sample from ice, obtained as insoluble residue after filtration of the melted ice sample. The combustion then followed the procedure for ice POC samples described above, each temperature step (340°C, 380°C, and 800°C) has been applied for ca. 40 min, aiming for a similar carbon fraction separation as reported in Szidat et al. (2004b). The combustion times therein were shorter (10 min) but pure oxygen had been used for combustion. We used 40 min to compensate for the lower oxygen fraction in the synthetic air. According to Cachier et al. (1989) and our own tests this extended combustion time has no significant influence on the separation of the carbon sub-fractions. The retrieved carbon concentrations (supplementary Table S2a) are reported in concentrations [$\mu\text{gC}/\text{m}^3$] referred to the filtered air volume to make them comparable with the CARBOSOL results. Based on the results from the standard material measurements, a combustion efficiency of 70% for the REFILOX has been assumed and factored in the calculation.

It was found that despite the fundamental analytical differences of the OC/EC measurements made within CARBOSOL (Pio et al. 2007) and the carbon mass determination made via the REFILOX extraction system, the total carbon concentrations (TOC) retrieved with the REFILOX system correspond very well to the TOC concentrations extracted in CARBOSOL (Figure 2), with a linear regression slope of 1.1 ± 0.2 . This finding additionally supports that the assumption of a 70% combustion efficiency for the REFILOX system is reliable and realistic. A comparison by linear regression of the CARBOSOL fractions OC1 + OC2 (heated a few

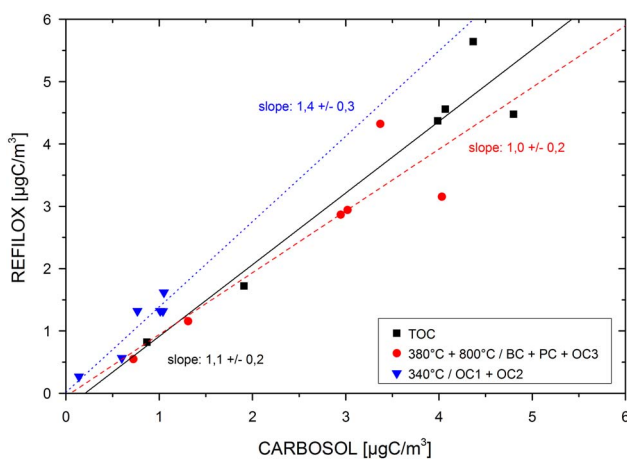


Figure 2 Comparison of carbon concentrations recovered with different combustion temperatures in REFILOX compared to concentrations recovered with the CARBOSOL system for different combustion temperature fractions.

minutes each to 150°C and 350°C under a N₂-atmosphere, respectively), with the 340°C REFILOX fraction yielded a slope of 1.4 ± 0.3 . This means that the 340°C fraction incorporated slightly more than the sum of OC1 and OC2. According to the thermo-optical method (Pio et al, 2007), this excess likely consists of a small amount of PC (heated a few minutes from 350°C to 600°C under N₂ with 4% O₂) combusting at low temperatures and possibly also a small fraction of OC3 (heated a few minutes at 600°C under N₂). Comparison of the sum of the 380°C and 800°C fractions of REFILOX to the corresponding OC3, PC and EC fractions of CARBOSOL leads in a linear regression to a slope of 1.0 ± 0.2 , thus representing these fractions very well. A direct comparison of the samples which have been pretreated with acid vapor only and the ones from the same aerosol filter that have additionally been rinsed with water prior to combustion shows a TOC-loss of 40–60% for the rinsed samples. A more detailed investigation (Figure 3 upper panel) reveals that the main mass loss (up to 60%) occurred on the 380°C and 800°C fractions and not on the 340°C fraction. The average mass loss on the low temperature fraction was only ca. 20%. This implies, that the material that combusted at high temperatures contained a higher fraction of water soluble substances that have been washed out and removed from the filter during the rinsing step than the 340°C fraction. Therefore, the higher temperature fractions seem to contain a larger amount of polar (water soluble) substances e.g. humic acids, which can represent very stable organic compounds, also prone to significant ageing. This finding indicates that the 340°C fraction has the largest probability to represent the real age of the sample.

To investigate the differences of ¹⁴C ages for each combustion temperature fraction, the CO₂ from each combustion step has been collected and ¹⁴C dated via the gas ion source of the MICADAS AMS in Mannheim. To compare the ¹⁴C content of the samples processed in the REFILOX system to the results obtained in the CARBOSOL project, from the single temperature results (Tab. S2b supplementary material), the average F¹⁴C value F_{ave} of all temperature fractions for each sample has been calculated according to

$$F_{\text{ave}} = \frac{F_{340} \cdot m_{340} + F_{380} \cdot m_{380} + F_{800} \cdot m_{800}}{m_{340} + m_{380} + m_{800}} \quad (2)$$

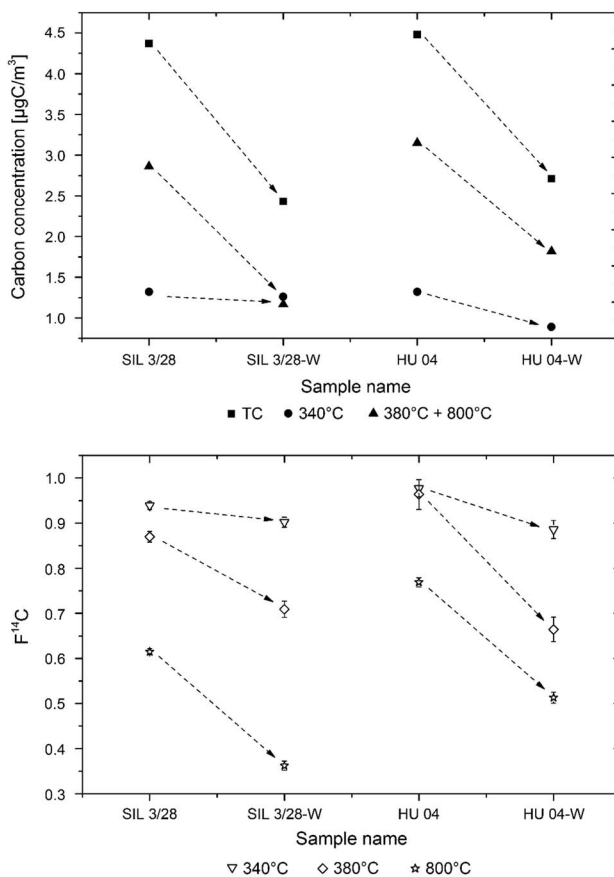


Figure 3 Comparison of carbon concentrations (upper panel) and ^{14}C -values (lower panel) for different combustion temperatures extracted with the REFILOX system for the filters treated in acid vapor only and additionally rinsed (ending -W) with ultrapure water.

with F_x and m_x representing the $F^{14}\text{C}$ values and sample masses of the denoted temperature fractions. Most averaged values of the unrinsed filters agree within the 2σ range with the seasonal averages, combusted completely at 900°C retrieved by May et al. (2009) for the respective sites (see Figure 4), only the results of SIL differ significantly. This overall very good agreement confirms the conclusion already drawn on the base of standards, i.e. means that the REFILOX system shows no significant fractionation processes during the separated combustion and CO_2 extraction steps. This is also backed up by the results of sample SIL 3/28-W, which has been processed twice, first by stepwise combustion and second by total combustion at 800°C (see Table S2b). Both $F^{14}\text{C}$ results, the total and the three-fraction average, agree perfectly within the 1σ error range. Overall, the ^{14}C content of the different combustion temperature fractions for each filter sample shows a strong depletion in $F^{14}\text{C}$ going to higher combustion temperatures. Earlier ^{14}C investigations of modern aerosol samples (Szidat et al. 2004a) showed similar results due to influences of fossil fuel burning products combusting mostly at high temperatures. In pre-industrial glacier ice samples, these fossil fuel influences should not be present. However, other potentially age biasing materials (e.g. insufficiently removed carbonates, Saharan dust) are also suspected to combust at higher temperatures and to potentially

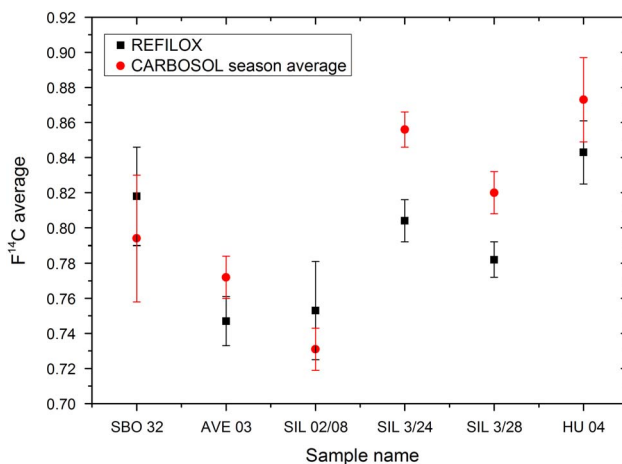


Figure 4 Comparison of the averaged $F^{14}C$ values retrieved with the REFILOX system compared to the CARBOSOL seasonal averages for the respective sampling sites. 2σ ranges are shown.

blend the EC fraction of some OC/EC measuring systems (Jenk et al. 2006; Sigl et al. 2009). This finding is supported in the present study by the direct comparison of the summer samples SIL 3/24 and SIL 3/28. The sampling period of these two samples was separated by three weeks and sample SIL 3/28 was influenced by a Saharan dust event. The REFILOX 800°C carbon concentration of the SIL 3/28 sample compared to the corresponding CARBOSOL EC fraction (see Table S2a supplementary material) shows an enhancement of a factor of seven, which is also 12% more than for the REFILOX 800°C fraction of sample SIL 3/24. Also the comparison of the respective $F^{14}C$ -values shows a stronger depletion in the higher temperature fractions for SIL 3/28 compared to SIL 3/24, whereas the 340°C fractions of both samples are equal within the error. Therefore, in the REFILOX system, the 340°C fraction, representing mainly the CARBOSOL OC1 and OC2 fractions predominantly made up of direct emission products from the living biosphere should give the best representation of the real sample age. As a consequence, this is the carbon fraction which will be used for glacier ice dating applications.

RESULTS

Colle Gnifetti Ice Core (KCC) POC ^{14}C Measurements

Colle Gnifetti is a high Alpine firn saddle in the summit region of the Monte Rosa Massif, Switzerland, located at 4500 m asl. The key properties of this glacier with respect to the potential to serve as a long-term climate archive are (1) Perennial firn and ice temperatures below 0°C (Haeberli and Funk 1991; Hoelzle et al. 2011) and (2) an overall very low accumulation regime rarely exceeding 1 m water equivalent (w.e.) (see e.g. Haeberli et al. 1983; Haeberli and Alean 1985; Lüthi 2000). Also total loss of the annual precipitation by wind erosion over the ice cliff confining the saddle to the east is possible. The low net accumulation rates comparable to polar sites in combination with the small glacier thickness in the order of 100 m (Wagenbach et al. 2012) lead to a rapid layer thinning with depth (Bohleber et al. 2013). This results in a strongly non-linear age-depth relationship with expected basal ice ages substantially exceeding 1000 yr BP. Over the last 40 years, the Colle Gnifetti has been the target of many glaciological studies including several deep ice coring projects of which five were led by the Institute for Environmental Physics, Heidelberg University. The latest ice core, KCC on which

this study is focused, was drilled to bedrock in 2013. It has a total length of 71.81 m, the main glaciological parameters of this core are summarized in Table 1.

For the POC ¹⁴C analysis a fraction of the ice core with a cross section of 17 cm² is available over the entire core length. To ensure a successful application of the decontamination routine, 19 different depth intervals below the firn ice transition have been measured until now (see Table 2). They have been selected to cover the complete lower half of the core with a special focus on the basal layers. The topmost sample was also selected to be presumably older than 400 yr BP, based on annual layer counting in multiple impurity species measured by continuous melting of a dedicated ice core fraction. This selection was done to exclude the industrial period

Table 1 Glaciological parameters of the new Colle Gnifetti ice core (KCC) drilled under lead of the IUP Heidelberg. Parameters of the CG 03 core drilled by the Paul-Scherrer-Institute (Switzerland) for comparison. Information taken from Jenk et al. (2009).

| Core parameter | KCC ice core | CG03 ice core |
|------------------------------|-------------------------------|---------------------------|
| Depth absolute (m) | 71.81 | 80.18 |
| Depth (m.w.e.) | 53.77 | 62.79 |
| Year of drilling | 2013 | 2003 |
| Accumulation (m.w.e./yr) | 0.22 | 0.46 |
| Firn-ice-transition (m.w.e.) | 21 | No data |
| GPS coordinates | 45°55'44.2''N 7°52'34.6''E | 45°55'50''N 7°52'33''E |

Table 2 Overview of the blank corrected sample masses (not combustion efficiency weighted) and ¹⁴C ages of the Colle Gnifetti ice core samples combusted at 340°C. All results have been blank corrected using a blank mass of $m_b = (0.2 \pm 0.1) \mu\text{gC}$ and a $14\text{C } F_b = 0.6 \pm 0.2$. The sample KCC 70/71 was neglected in the discussion because it was considered to be too small. 1σ error ranges are shown and the calibrated ages are rounded according to the convention stated in Stuiver and Polach (1977).

| Sample name | Core depth (m.w.e.) | Ice sample mass (g) | POC mass corrected (μgC) | ¹⁴ C corrected ($F^{14}\text{C}$) | Calibrated ¹⁴ C-age (yr BP) |
|-------------|---------------------|---------------------|---------------------------------------|--|--|
| KCC 63/64 | 36.16 ± 0.27 | 440 | 3.4 | 0.981 ± 0.053 | 490–modern |
| KCC 69 | 38.46 ± 0.16 | 304 | 3.0 | 0.935 ± 0.049 | 910–modern |
| KCC 70/71 | 39.21 ± 0.23 | 386 | 0.9 | 1.034 ± 0.139 | — |
| KCC 75a | 40.93 ± 0.18 | 342 | 4.6 | 0.946 ± 0.026 | 660–modern |
| KCC 75/76 | 41.33 ± 0.23 | 438 | 5.7 | 0.884 ± 0.021 | 1170–700 |
| KCC 78 | 42.58 ± 0.23 | 380 | 2.7 | 0.853 ± 0.036 | 1540–800 |
| KCC 79 | 43.07 ± 0.27 | 412 | 3.8 | 0.846 ± 0.031 | 1550–960 |
| KCC 82/83 | 44.58 ± 0.18 | 323 | 5.0 | 0.961 ± 0.034 | 540–modern |
| KCC 83/84 | 45.12 ± 0.27 | 460 | 1.7 | 0.983 ± 0.069 | 640–modern |
| KCC 86 | 46.33 ± 0.23 | 404 | 6.4 | 0.944 ± 0.022 | 650–310 |
| KCC 89/90 | 48.38 ± 0.23 | 400 | 5.1 | 0.917 ± 0.027 | 910–510 |
| KCC 94 | 50.50 ± 0.18 | 277 | 7.7 | 0.854 ± 0.018 | 1320–980 |
| KCC 97a | 51.90 ± 0.18 | 280 | 8.1 | 0.806 ± 0.017 | 1860–1420 |
| KCC 100 | 53.30 ± 0.16 | 250 | 10.4 | 0.689 ± 0.015 | 3370–2950 |
| KCC 101-1 | 53.60 ± 0.05 | 160 | 10.3 | 0.657 ± 0.014 | 3840–3410 |
| KCC 101-2 | 53.70 ± 0.05 | 118 | 7.1 | 0.625 ± 0.015 | 4220–3900 |

and also the age range where unambiguous ^{14}C age calibration is not possible (Reimer et al. 2013). Extraordinarily large peaks in dust content and conductivity have also been avoided to circumvent strong Saharan dust events.

With the available core cross-section of only 17 cm^2 , most samples cover a length of 40–60 cm core depth. All samples have been prepared in the REFILOX system using the routine described above. Because of the principal assumption that pre-industrial ice samples should not be biased by fossil fuel contributions, in a first attempt three samples from different depth intervals have been combusted completely at 800°C (see Table 1, bottom) and blank corrected accordingly. This attempt was ventured since the expected sample masses are already at the lower limit to be feasibly processed. Carbon fraction separation would reduce sample masses even further. As can be seen from the retrieved $F^{14}\text{C}$ -values (Table 1, bottom), no systematic age increase over more than 10 m depth is visible for these samples and the $F^{14}\text{C}$ values scatter very much. They are also overall very low compared to the rough age estimate based on the conventional annual layer counting in the impurity signal in the upper part of the core. The reason for these high and scattering ages could on one hand be incomplete removal of old carbonate material during the acidification step. This is, however, not reasonable considering the small amounts of sample material and the comparably large amounts of acid and the long reaction times ($>30\text{ min}$) On the other hand and much more probable, the samples are influenced by aged organic material e. g. from Saharan dust. Thus, it is concluded that also for the preindustrial period the total combustion of POC particles at high temperatures does not lead to reliable results and is therefore not an option for ^{14}C dating of ice samples. The 800°C combustion fraction was therefore not used for dating of the ice core.

Based on the results retrieved from the analysis of the CARBOSOL aerosol samples, all other KCC ice core POC samples have therefore been combusted at 340°C and only this carbon fraction was used for glacier ice dating. The POC masses and $F^{14}\text{C}$ values have been blank corrected according to the values determined from the blank ice measurements. For correction neither the sample masses nor the blank masses have been weighted with combustion efficiency, because it would only add a constant factor. In this context, it has to be emphasized that the $F^{14}\text{C}$ of the blank contribution only could be estimated at the present stage of investigation. The assumed F_b and its error covers a reasonable range of possible values. However, it has to be kept in mind that the actual ^{14}C value of the blank needs to be determined in future investigations. On average, a POC content of ca. $23\ \mu\text{gC}/\text{kg}$ was extracted on the 340°C fraction, which is in the range of concentrations for high Alpine ice samples measured by other setups (Steier et al. 2006; Legrand et al. 2007; Jenk et al. 2009). The total carbon masses for each sample did in most cases not exceed $10\ \mu\text{gC}$. All ^{14}C -measurements have been carried out at the MICADAS AMS at the Klaus-Tschira-Lab in Mannheim, Germany (Kromer et al. 2013) by use of the gas ion source. The ^{14}C -results could be measured with an average statistical precision of 4%. The retrieved $F^{14}\text{C}$ -values have been calibrated using OxCal v.2.4 (Bronk Ramsey 1995) and the 1σ range of the calibrated ages is reported (Table 1) according to Stuiver and Polach (1977).

DISCUSSION

Ice Core ^{14}C Results

The calibrated ages of all KCC ice core POC samples combusted at 340°C , the only fraction used for dating, in the REFILOX system are shown in Figure 5. Apart from the sample at ca. 39 m w.e. depth, which was with $0.9\ \mu\text{gC}$ the smallest of the whole set and has been omitted in the discussion due to its large uncertainty, all statistical measurement errors are below 5%

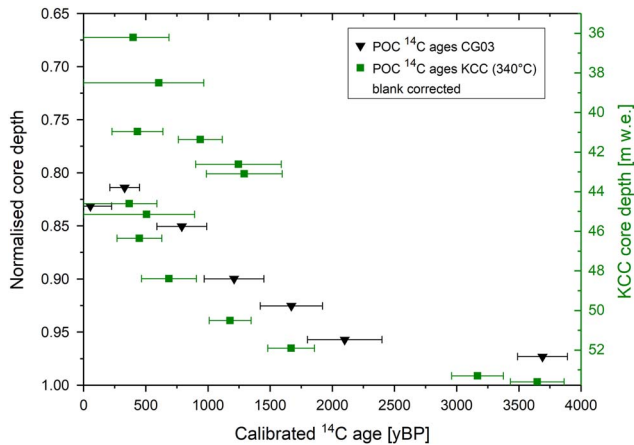


Figure 5 Mean blank corrected and calibrated ¹⁴C ages with 1 σ age ranges given in Table 2 as error bars. The 340°C combustion temperature fraction of samples from the lower half of the KCC ice core from the high Alpine firm saddle Colle Gnifetti is shown compared to POC ¹⁴C ages from the CG 03 core (Jenk et al. 2009).

resulting in age errors typically not exceeding 250 yr. Below 44 m w.e., the POC ages show a gradual non-linear increase in age with the deepest sample reaching a maximum age of ca. 4421–3907 cal yr BP. Especially within the last 75 cm of core length a very strong age increase of more than 1000 years can be observed. The systematically non-linear age depth relationship below 44 m w.e. follows a course which is very characteristic for high Alpine glacier bodies (Lüthi and Funk 2000) frozen to bedrock like Colle Gnifetti. This finding is also supported by a direct comparison of the age depth-relationship on a normalized depth scale (Figure 5) to another ice core (CG 03) from Colle Gnifetti (see Table 1) drilled under the lead of the Paul-Scherrer-Institute and dated by similar POC ¹⁴C analyses (Jenk et al. 2009). This core was drilled at a different location than the KCC core, almost directly at the saddle point of Colle Gnifetti, whereas the KCC is located on the north facing slope of the glacier. The CG 03 has a horizontal distance to KCC of ca. 200 m. It has a higher accumulation rate, almost double, and probably a different main snow source region. Therefore both cores are not comparable in a straightforward quantitative way, but should be expected to inherit similar features in general. The average extracted POC concentrations in the compared core sections were calculated to be ca. 33 $\mu\text{gC/kg}$ for the CG 03 core (Jenk et al. 2009) and ca. 30 $\mu\text{gC/kg}$ in this study. They thus agree very well. The POC concentrations in the KCC core increase to almost double of the average approaching bedrock, which has also been observed in the CG 03 core. These comparison to an independent system supports the capability of the REFILOX to produce reliable ¹⁴C results. The overall comparison of both age-depth relationships reveals a very good agreement in shape and curvature of the principal age increase for both cores with an almost constant age offset of ca. 500 yr between 90 and 95% of the relative core depths, where both chronologies start to diverge.

However, the basal ¹⁴C age of the CG 03 core was measured to be larger than 10,000 yr BP (Jenk et al. 2009), which is more than double the basal age of the KCC core retrieved in this study. If the glacier body would be entirely homogeneous, in a similar relative depth, similar ages could be expected. Possible reasons for this large discrepancy of the total basal ages despite the good correlation of the curvature of the age-depth relationship could therefore be basic

differences in the glaciological settings of both ice cores including another source region of the basal ice and the differences in accumulation regime. Also an overdeepening in bedrock creating stagnant ice at the CG 03 drilling site could contribute to this effect. Due to the strong non-linearity of the age-depth relationship in the very basal parts all these differences could lead to an age discrepancy, but need further glaciological investigations, which are out of the scope of this paper.

Another enigmatic glaciological feature emerges in the age structure above ca. 44 m w.e. The ^{14}C ages in the part above seem to follow a different course of age increase than below this depth. Between 43 and 45 m w.e., a sudden age shift back to almost modern values occurs. Methodological reasons for the appearance of this feature, like insufficient blank corrections, could be ruled out, especially by a repeated analysis of the depth interval around 43 m w.e. The glaciological reasons for this apparent age discontinuity and possible consequences for the deeper section including the basal maximum age have to remain unsolved so far, but are under current investigation including additional ^{14}C analyses. At this stage, however, the ^{14}C analyses revealed an outstanding structural feature of the ice core which could not have been detected based on the impurity profiles. The ^{14}C age constraints retrieved within this study are thus an invaluable contribution in the context of a multi method approach for the development of a reliable ice core chronology, which will be discussed elsewhere.

CONCLUSION

A new system (REFILOX) for extraction of POC from high Alpine ice samples has been developed and is now operational at the IUP Heidelberg. Together with the gas ion source technique at the MICADAS AMS in Mannheim it enables reliable dating of sample masses down to $3\ \mu\text{gC}$ or even less with a relative statistical error of $<10\%$. This results in a minimal required sample mass of ca. 300 g ice for average high Alpine POC concentrations of ca. $25\ \mu\text{gC/kg}$. The REFILOX system is also able to process and combust aerosol filters for ^{14}C dating and carbon mass fraction analyses in variable temperature steps. It can therefore serve as a simple and adaptable but yet powerful alternative to commercial OC/EC analyzers like the Sunset systems, with lower automatization and without the optical components, but sufficient for many basic applications. For the OC fraction (340°C combustion temperature) a blank mass of $m_b = (0.2 \pm 0.1)\ \mu\text{gC}$ was determined, which is highly sufficient for ^{14}C analyses of high Alpine samples with average POC concentrations. A detailed carbon fraction and ^{14}C analysis of modern European aerosol samples from the CARBOSOL project revealed that the ^{14}C age of organic material combusting at very low temperatures (340°C) gives the best representation of the true sample age. This combustion temperature should thus be chosen for POC as the best way to avoid reservoir effects caused by influences of already aged material incorporated into the sample. In a first successful application of the new system, the lower half of an ice core from the cold, high Alpine firn saddle Colle Gnifetti has been analyzed, with relative age errors below 10% for most samples. In the deepest part the retrieved ^{14}C ages show a gradual non-linear increase like expected from basic age depth models to a maximum age of more than 4000 yr BP. Above ca. 44 m w.e. a discontinuity in the measured ice ages is present, which cannot be explained by methodological reasons and needs further glaciological investigations. With this first application the new REFILOX system impressively demonstrated its capability to reliably extract and date even very small POC samples in the range of $10\ \mu\text{gC}$ or even less. For the future, many further applications for ^{14}C dating of Alpine glacier ice samples are planned including the dating of ice structures as small ice patches and ice caves.

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SUPPLEMENTARY MATERIAL

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