Radiocarbon determination of particulate organic carbon in non-
temperated, Alpine glacier ice

Peter Steier1,*, Roswitha Drosg1, Mariaelena Fedi3, Walter Kutschera1, Martin Schock2, Dietmar Wagenbach2, Eva Maria Wild1

1 Vienna Environmental Research Accelerator (VERA), Institut für Isotopenforschung und Kernphysik, Universität Wien, Währinger Straße 17, A-1090 Wien, Austria
2 Institut für Umweltphysik, Universität Heidelberg, Im Neuheimer Feld 229, 69120 Heidelberg, Germany
3 Dipartimento di Fisica dell'Università di Firenze and INFN Sezione di Firenze, via Sansone 1, 50019 Sesto Fiorentino (Fi), Italy

Abstract

Dating ice samples from cold glaciers via radiocarbon is still a challenge, still calling for systematic investigations. This work describes an approach towards extraction and AMS radiocarbon analysis of the particulate organic carbon (POC) fraction in ice samples. First measurements were performed at VERA (Vienna Environmental Research Accelerator) on ice samples mainly obtained from the non-temperated ablation zone of the Grenzgletscher system (Monte Rosa massif, Swiss Alps). The samples were obtained from two sampling sites situated roughly on a common flow line. The sample masses used were between 0.3 and 1.4 kg ice, yielding between 18 and 307 µg carbon as POC. The carbon contamination introduced during sample processing varied between 5.4 and 33 µg C, and is shown to originate mainly from the quartz filters and the rinsing liquids used. Minimum sample sizes for successful graphitization of carbon dioxide in our laboratory could be reduced to less than 10 µg carbon with a background in the graphitization process of approximately 0.5 µg carbon of 40 pMC. Evaluation of the whole procedure via 11 Grenzgletscher samples revealed a surprisingly large scatter of the pMC values. We obtain a mean calibrated age of 2100
BC to 900 AD (95.4% confidence level), which is not significantly different for the two sampling sites. Discussions of these results suggest that single radiocarbon dates of glacial POC are presently of limited significance only. Future improvements with respect to analytical precision and sample characterization are proposed as to fully explore the POC dating potential.

* Corresponding author:

Peter Steier
Institut für Isotopenforschung und Kernphysik,
Universität Wien, Währinger Straße 17, A-1090 Wien, Austria
Tel. +(43)-1-4277-51729
Fax. +(43)-1-4277-9517
e-mail: peter.steier@univie.ac.at
Introduction

Glaciers and ice sheets constitute an important archive of earth’s climate and environmental history. Compared to other paleo-archives, they are unique in providing proxy records related to climate parameters (e.g. stable water isotopes) as well as direct access to past atmospheric composition changes (e.g. greenhouse gases and atmospheric dust). Most investigations were performed on ice cores drilled in Greenland (e.g. GRIP and GISP2, Hammer et al. 1997) and Antarctica (e.g. Vostok, Petit et al. 1999; Dome C, EPICA Community Members 2004). In these high latitude ice sheets englacial temperatures are low enough to keep the isotopic and chemical ice composition “frozen” in time, whereas their large scale geometry commonly ensures a smooth and approximately linear depth-age relationship over a substantial fraction of the total ice thickness. Thus an appropriate chronology - which is the prime pre-requisite for exploiting the climatological information - can be derived basically from stratigraphical investigations over several ten thousand years (Meese et al. 1997). Annual layer counting and oxygen isotopic stage correlation are the most important stratigraphical methods, which became standard tools for dating polar ice cores.

However, stratigraphical dating is not applicable to all interesting ice archives, which includes also non-temperated mountain glaciers, rock glaciers, cave ice, cold ablation zones, and ice wedges. For example non-temperated mountain glaciers, as necessarily situated on the highest summit ranges, show relatively small glacier geometries. This leads to complex ice flow patterns, extensive ice thinning rates, and to irregular snow deposition. These shortcomings commonly restrict useful stratigraphical dating to some 100 years at best (e.g. Thomson et al. 2002, Wagenbach 1989, Eisen et al. 2003). Thus, to extend the domain of long term ice records to non-polar regions and to explore other promising ice archives, an alternative dating tool is urgently needed.
$^{14}$C analysis is the most precise tool for dating organic matter remains throughout the Holocene. Among others it is deployed in stratified archives like lake sediments or peat bogs (e.g. Goslar et al. 2005). Provided that the organic carbon entrapped in glacier bodies is representative for the deposition age, radiocarbon dating is expected to be useful for these kinds of archives as well. Organic micro-fossils like moss (Haeberli et al. 1999) or insect remains (Thompson et al. 1998) found by chance in ice cores have already been used. However, only small amounts of organic carbon are commonly contained in glacier ice, either entrapped as trace gases in air bubbles or preserved as aerosol related species in the ice matrix. The organic carbon fractions may be divided into POC (particulate organic carbon) and DOC (dissolved organic carbon), which are technically distinguished using a pore filter of typically 0.4 µm pore size.

Inorganic CO$_2$ eventually trapped in air bubbles below the firn–ice transition is a less suitable $^{14}$C-dating target since it may contain a substantial contribution of in-situ produced $^{14}$C (mainly via spallation of oxygen in the ice by energetic cosmic ray neutrons, Lal et al. 1990, Lal et al. 2000, Lal et al. 2001, Van Roijen et al. 1995). This is especially true for mountain drill sites, where the in-situ contribution is enhanced due to high altitudes and low accumulation rates.

In this work we explore the potential of radiocarbon dating the POC fraction of cold glacier ice. Intending to develop an appropriate procedure, we focused on ice block samples collected in the non-temperated ablation zone a poly-thermal valley glacier in the Alps. This approach offers samples of large volume at reasonable effort for testing and evaluation of the method. Still, various cold ice bodies from lower altitude as well as ice sheet margins may also present an important future application (see e.g. Reeh et al. 1991) of this dating tool.
Methods

Figure 1 shows the Monte Rosa massif, Switzerland. The samples were taken from the part of Gornergletscher which originates from the Grenzgletscher, flowing down the north-westerly flank of the Monte Rosa massif (Renaud 1952). The uppermost catchment area of the poly-thermal Grenzgletscher is non-temperated, which is also the case for a substantial part of its lower ablation zone. Here the cold ice re-emerges at the surface still at englacial temperatures significantly below the melting point (Haeberli 1975), which mostly ensures integrity of the ice since deposition in the accumulation zone. Surface sampling of ice blocks was performed at two position on the tongue of Gornergletscher, which are situated roughly on a common flow line of the emerging Grenzgletscher material. The sites are about 1500 m apart and situated at an altitude of about 2550 m and 2510 m asl, respectively. The typical ice flow and the glacier geometry suggest that the ice at these sampling sites should be some hundred years old at least. Indeed, $^{210}$Pb analyses at the Institut für Umweltphysik, Heidelberg, on ice blocks from both sites were close to the analytical background, showing that the ice is older than approximately 150 years. This age constraint was corroborated by analyses of the (partly anthropogenic) sulfate, ammonium, and nitrate ions, clearly indicating pre-industrial levels. It is basically expected that ice from the lower site should be systematically older compared to the upper one. However, assuming a depth averaged downslope ice velocity of about 10 m/year at the sampling sites, the expected age difference would be only on the order of 100 years, which can hardly be resolved by the applied radiocarbon method. In addition to the Gornergletscher ice samples, surface snow was collected from the highest accumulation zone of Grenzgletscher (Colle Gnifetti, 4450 m asl), serving as modern (bomb-$^{14}$C influenced) counterpart.

All samples were shipped in frozen state and stored at -23 °C at the University of Heidelberg. Here the ice blocks were cut into suitable pieces of ~500 g to 1000 g in a dust free cold room, wrapped in aluminum foil and sealed in polyethylene bags. After shipment to the University of Vienna they were kept in a freezer at a temperature of about -15 °C.
Pre-industrial atmospheric POC is mainly composed of biogenic particles (such as pollen, bacteria, spores, etc.), leave fragments, the organic fraction of soil dust, and of bio-mass burning products like elemental carbon (EC). Secondary organic aerosol as derived from gas-to-particle reactions (Seinfeld 1998) of volatile biogenic precursors are thought to be mainly water soluble and may thus not substantially contribute to the filterable POC contained in melt water samples. There is no need to separate the major POC fractions as e.g. organic carbon (OC) and elemental carbon (EC) as done for modern atmospheric aerosol e.g. by Szidat et al. (2004). In pre-industrial ice, we expect that all POC fractions yield radiocarbon ages correlated to the time of ice formation. Deviations from this assumption are a principal limitation of the method and are discussed below.

Two methods have been used by other groups to extract POC from ice samples: filtering of melt water (Chýlek et al., 1987) and sublimating the ice sample in vacuum whilst depositing the particles onto a surface substrate (Biegalski et al. 1998). Sublimation may provide a better particle recovery yield and would collect a part of the DOC fraction as well, but the melt water is unavoidably lost. We have chosen to develop a filtration method. If one considers rare and small ice samples from remote drill sites, this may allow to extract the POC of the complete sample without interfering with further measurements on the melt water (including separate DOC analyses). Additionally, it allows us to handle large samples in a relatively short time. The VERA Laboratory was already involved in radiocarbon measurements of snow (Weissenbök et al. 2000), but not in preparing the respective samples. Thus, we had to develop an appropriate filtration procedure from scratch, whereas only minor experimental changes were required in the AMS target preparation and measurement procedures.

The overall carbon content is as low as a few ten µg per kg of ice, thus care has to be taken to control the contamination introduced during sample preparation. Since ambient dust imposes a substantial problem, the critical steps during handling of the ice and the POC filters were performed in a laminar-flow box (nominally class 100). Materials used in the setup are (almost exclusively)
made of quartz, glass, stainless steel, and PTFE or PFA. Teflon tubing are expected to prevent that particles stick to the tube walls. Parts and tools are cleaned in an ultrasonic bath, residual surface dust was blown off with clean N$_2$. Materials that withstand high temperatures (quartz filters, quartz vials, and copper oxide for the combustion, see below) were heated shortly before use at 950 °C for 4h. Still hot (~500°C), they were put into a container with saturated H$_2$O atmosphere. This procedure should reduce re-adsorption of carbon containing trace gases from laboratory air.

The central part of the melting apparatus (see Figure 2) consists of a double-walled glass vessel, where warm water flowing through the double walls allows to control the melting rate. At a water temperature of about 30 °C (measured at the exit) one sample melts in ~1 hour. All tubes leading into the melting unit are equipped with protective dust filters, ensuring that all liquids and gases entering the melting unit are dust free. During operation, the melting unit is partially submerged in an ultrasonic bath, including the port used as melt water outlet at the lowest point. The purpose of the ultrasonic bath is to prevent insoluble particles from sticking to the glass walls of the melting container.

Before melting, the ice sample is put into a Styrofoam box where it warms up slowly to 0 °C. Large temperature gradients at the sample surface could cause stress induced micro-cracks, allowing melt water from the potentially contaminated surface to migrate into the inner, clean part of the ice body.

The melting unit is taken into the laminar flow box for sample loading with tubings closed. Melting and filtration are done under over-pressure with clean N$_2$. This procedure protects the melt water from contamination with laboratory air, which will be essential for future measurements of the DOC fraction.

The sample filter holder is made of stainless steel and Teflon with a stainless steel frit supporting the quartz fiber filter (Sartorius QMF, 85 g/m$^2$, binder-free, 25 mm diameter, later cut down to 12 mm). It was mounted only after disposal of the first ~100 mL of sample water to get rid of surface
contamination. A filtration rate of typically ~0.2 mL/sec was maintained and controlled by the N₂ overpressure (400 – 1000 mbar) and by a hose clamp at the sample filter outlet. Filtration of accumulated melt water was done at intervals, with the ultrasonic bath switched off in-between. The melt water was not pushed out completely, since gas bubbles inside the filter holder require a strong pressure increase to start the filtration process again. For possible subsequent analyses the filtrate can be collected in a glass bottle inside a glove bag filled with clean N₂.

After complete melting of the ice sample, the apparatus is rinsed with ~50 mL 1 M HCl, which is transferred from a flask by N₂ overpressure through a combination of several filters into the melting unit. In the final procedure, we use a combination of a glass frit, a quartz filter (similar to the POC sample filter), and a polycarbonate membrane filter (pore size 0.22 µm, Poretics). The melting unit filled with the rinsing liquid is thoroughly shaken. The ultrasonic is switched on for five minutes to mobilize particles sticking to the walls, and the rinsing liquid is drained also through the POC filter. By using HCl in the first rinsing we expect complete removal of carbonate particles. Rinsing is repeated twice using ~50 mL H₂O bidest.

Before each use the melting unit is cleaned and a process blank is taken. Cleaning of the melting apparatus is done similar to the rinsing after ice melting (except that no sample filter is attached), with ~200 mL 0.7 M HNO₃ and two rinses with ~100 mL H₂O bidest. A process blank is prepared for each sample, using the same amount of rinsing liquids as used afterwards for the corresponding ice sample. Table 1 shows the results for the process blanks actually used for blank correction. Here, as in the following, we characterize the ¹⁴C content by pMC values (percent Modern Carbon), as defined by Stuiver and Pollach (1977).

The filtration procedure was slightly different for the first two Gornergletscher samples from each site. For these, 100 mL HCl (0.1 M) and 2×100 mL H₂O bidest were used for rinsing, and the quartz filters for the POC samples had 25 mm diameter. The amount of carbon collected on the process blanks is variable in both amount and ¹⁴C content. The investigations performed so far do
not yet proof a clear correlation between the contamination and the amount of filtrated liquids. To assess and possibly improve the quality of the rinsing liquids remains one methodical focus for the future. For the present experiments we reduced the total amount of rinsing liquids down to the smallest amount which can be reliably handled by the present setup (150 mL). Another possible source of contamination is represented by the quartz filter itself. From unused, wetted filters typically 3 µg carbon were extracted. Thus, we decided to reduce the filter diameter to 12 mm. Additionally, we cut off the “unused” margin of the filter after the filtration, which yields an effective diameter of 8 mm.

By these means, the typical background fell to ~7 µg C. The disadvantage is, however, the reduction of the active filtration surface: for some very “dirty” ice samples, the 12-mm filters were completely blocked after a small amount of melt water (175 mL in one case) was passed through, so the remaining sample had to be discarded without filtration (the filtration was stopped when its rate had decreased down to 0.5 mL/min at a nitrogen pressure of 1000 mbar). Samples from the lower site show generally higher POC values. Thus, we decided to process the last sample of this batch (M26) again with a larger filter of 25 mm diameter. With the larger filter we introduced a higher carbon background. However, since the amount of collected POC was also higher in this case, the larger filter background imposes no significant problem.

The still wet filter is placed in a quartz vial together with 500 mg pretreated copper oxide (Merck, p.a., wire 0.65 mm × 3 mm) to provide oxygen during sample combustion, and with a small piece of silver wire to bind sulfur and halogens. The filled vial is evacuated and heated for ~1 h to ~130 °C to remove moisture and volatile carbon compounds in advance to flame sealing. Subsequently the POC sample is combusted to CO₂ for 4 hours at 950 °C. After cooling down inside the oven, the samples are ready for graphitization. Systematic investigations revealed that the copper oxide contributes less than 1 µg to the carbon contamination (compare Vandeputte et al., 1998).
Different from previous work by Weissenbök et al. (2000), the graphitization of the sample CO₂ to graphite is now done in the VERA Laboratory. The method used follows mainly Vogel et al. (1984). We have modified the small-sample graphitization unit (reactor volume 2.6 ± 0.2 cm³) previously used at VERA for ^14CO measurements in atmospheric air (Rom et al. 2000) for our needs (Figure 3).

The graphitization unit now works semi-automatically, with most valves controlled by a computer program. This makes operation easier, and we think that the inherent reproducibility of computer control improves the measurement precision. Very small pressure sensors (Type PX72-015AV by Omega) are used to monitor the pressure in the reactors. For the low CO₂ pressures encountered for our samples (1.3 µg C ≈ 1 mbar CO₂) these sensors show significant drifts, since they are not perfectly temperature compensated. Therefore an air-cooled copper heat shield was mounted to insulate the pressure sensors from the hot reaction volume. By calibrating the pressure sensor immediately before graphitization, a precision of the pressure readings better than ±0.3 mbar is achieved. The pre-treatment of the iron catalyst by heating in vacuum now takes place at 610 °C (same as the graphitization temperature). In this step, the copper heat shield is removed, and the complete reactor assembly heats up to ~50 - 60 °C. This improves the cleaning by out-gassing. The Viton O-rings previously used for the reactor chambers were replaced by Teflon gaskets, for which we observe less out-gassing at high temperatures. A Pirani gauge connected to the central manifold allows to detect leaks easily.

Systematic investigations were performed to test the graphitization unit. The standard material used was CO₂ from a bulk combustion of 13 g IAEA C-3 cellulose reference material of 129.41±0.06 pMC (Rozanski et al. 1992). As blank material we used commercially available "dead" CO₂ (Linde, purity >99.9993 Vol%) from a Hungarian mineral spring (Rom et al. 2000). Graphitizations were performed for CO₂ amounts corresponding to 4.0, 6.5, 13, 39, 130, and 390 µg C. The respective radiocarbon measurement results (Figure 4) allow to estimate the amount of carbon contamination
and its pMC by non-linear regression analysis. The simple mixing model fitted simultaneously to all 21 measurements on dead and C-3 carbon is:

\[
\begin{align*}
\text{pMC}_{\text{dead,meas}} & = \frac{\text{pMC}_{\text{cont}} M_{\text{cont}}}{M_{\text{dead,meas}}} , \\
\text{pMC}_{\text{C-3,meas}} & = \frac{129.41(M_{\text{C-3,meas}} - M_{\text{cont}}) + \text{pMC}_{\text{cont}} M_{\text{cont}}}{M_{\text{C-3,meas}}}
\end{align*}
\]

with

- \( M_{\text{cont}} \): mass of the carbon contamination.
- \( \text{pMC}_{\text{cont}} \): pMC of the carbon contamination.
- \( M_{\text{dead,meas}}, M_{\text{C-3,meas}} \): carbon mass of dead CO\(_2\) and C-3 CO\(_2\), calculated from the measured CO\(_2\) pressure.
- \( \text{pMC}_{\text{dead,meas}}, \text{pMC}_{\text{C-3,meas}} \): measured pMC of the dead CO\(_2\) and the C-3 CO\(_2\).
- 129.41: nominal pMC value of the C-3 material.

The fit yields an average total contamination of \( M_{\text{cont}} = (0.5 \pm 0.1) \mu \text{g carbon} \) with a pMC value of 43 ± 16 in the graphitization and AMS measurement.

We use between 0.6 and 3.0 mg iron (Merck, p.a., grain size 10 µm, produced by reduction) as catalyst, leading to very low C:Fe ratios for our small samples. We observe no significant influence of the amount of iron on the reaction rate, which mainly depends on the amount of sample CO\(_2\). Larger grain size of the iron results in slower graphitization, with 10 µm grain size the duration of the reactions was between 1 and 4 hours. These systematic measurements also reveal that the amount of modern carbon contamination increases with the amount of iron used. This result is in agreement with Vandeputte et al. (1998). In future experiments we will minimize this background contribution by using the smallest iron quantity possible.
When the graphitization reaction is complete, the computer program initiates pumping off excess H₂ and the heater switches off. The cold traps warm up and the water vapor comes in contact with the fresh graphite. By these means we intend to deactivate the reactive surface to reduce adhesion of ambient carbon, but we have not yet investigated this systematically. The mixture of iron powder and graphite is pressed into aluminum sample holders suited for our ion source.

The radiocarbon measurements were performed at the VERA AMS facility, mainly following routine procedures (Steier et al. 2004). Changes required for small samples are as follows: (i) the stable-isotope beams (¹²C⁻ and ¹³C⁻) are injected for a longer time, and (ii) the sensitivities of the beam current amplifiers are adjusted for each sample automatically. Successful measurements were performed for carbon sample masses down to ~10 µg.

To investigate the dependency of the ionization yield on the sample size, we looked at the temporal development of the ¹²C³⁺ currents during the AMS-measurement (see Figure 5). We achieved a total detection efficiency of 2%, calculated from the number of ¹²C³⁺ ions in the Faraday cup integrated over the measurement time, divided by the number of C atoms in the sample CO₂. The efficiency is independent of the sample size, and the same value can be assumed for ¹⁴C. Included in the observed efficiency value are the yield of the graphitization, the negative ion yield in the source, the stripping yield from C⁻ to C³⁺ (0.50 ± 0.02), and the duty factor for ¹⁴C counting (~0.8). For some very small test samples we observed currents which were exceptionally low (boxed data points in Figure 5). The reason is not yet understood and will be further investigated. None of the true ice samples and their corresponding process blanks were affected.

Results

Up to now, a total of twelve ¹⁴C measurements on POC in glacier ice or snow were performed. Table 2 lists the results.
Despite a separate process blank had been prepared for each sample, we decided to use average values for the blank correction. As $pMC_{\text{blank,meas}}$ we used the average of all process blanks, whereas $M_{\text{blank,meas}}$ was the average of all process blanks prepared with the same filter size. For the 7 corresponding blank filters of 12 mm diameter processed so far, we observed a mean carbon contamination of 6.8 µg C with a standard deviation of 1.2 µg C (Table 1). The 5 blanks with 25 mm filters, which were partly performed with preliminary versions of the preparation procedure, vary between 8 and 32 µg C (average 16.0 µg C with 9.7 µg C standard deviation). The average of all 12 blanks is 85 pMC with a standard deviation of 16 pMC. A simple mixing model for sample carbon and contamination is applied:

$$pMC_{\text{sample,corr}} = \frac{pMC_{\text{sample,meas}} M_{\text{sample,meas}} - pMC_{\text{blank,meas}} M_{\text{blank,meas}}}{M_{\text{sample,meas}} - M_{\text{blank,meas}}}$$

$pMC_{\text{sample,corr}}$ : blank corrected pMC value of the sample.

$pMC_{\text{sample,meas}}, pMC_{\text{blank,meas}}$ : measured pMC of sample and process blank, respectively.

$M_{\text{sample,meas}}, M_{\text{blank,meas}}$ : measured carbon mass of sample and process blank, respectively.

Error propagation yields uncertainties of typically ±1 pMC for the blank-corrected sample values.

The surface snow sample HD60 taken in August 2000 at Colle Gnifetti shows a pMC value significantly higher than the respective pMC level in atmospheric CO$_2$ (Levin and Hesshaimer 2000). Similar results have been reported by Weissenbök et al. (2000) and Biegalski et al. (1998), for POC of recent snow samples. Our measured value of 119.6 pMC corresponds to atmospheric $^{14}$CO$_2$ levels from ~1985. However, a straightforward transformation into a sample age is not possible for modern POC, since an unknown amount of particles from fossil fuel combustion will have diluted the $^{14}$C content.
As illustrated in Figure 6, a considerable scatter in the final pMC results of the ablation zone samples is evident, which appears to be partly introduced by some outliers. Among others, this may be due the following reasons: 1) laboratory contamination by both fossil and modern carbon. Note that the processing blank variability does not formally explain the observed outliers. 2) incomplete removal of carbonate particles, leading to too low pMC values for some samples. 3) substantial contribution of already “old” organic carbon e.g. by soil dust deposition and 4) intrusion of modern or younger carbon through snow deposited into crevasses upstream to the sampling sites. The first two effects may be minimized in future measurements by more refined procedures. Point 3) and 4) impose a principal limitation of the method. Additional measurements on the ice or melt water may allow in the future to sort out such unreliable samples. Extraordinary high soil dust levels could indicate “old” organic carbon, whereas samples which experienced a contribution of modern snow or melt water may be sorted out by tritium and $^{210}$Pb analyses, or by traces of blue (bubble free) ice. We have measured tritium and $^{210}$Pb on ice from our sampling sites, with negative results concerning any contamination by modern material. However, these measurements were not repeated on the ice samples processed for POC.

The statistical method used to further evaluate the present results should not be sensitive to these outliers, but should yield the “typical” pMC value which is representative for the true sample age. Additionally, the measurement uncertainties as given in Table 2 are to small too explain the scatter in the data, even for the samples which are not apparent outliers. Thus, the raw measurement uncertainties can not be used to calculate weighted averages. Two simple methods are popular for handling data where outliers are expected: First, apparent outliers are rejected and mean values of the remaining data are used. The results for HD56 (modern) and M13 (44 pMC) appear to be outliers. Second, the median of the data can be used instead of the arithmetic average. Table 3 presents the results obtained with the two statistical methods. The uncertainty of the median was calculated using the method of Müller (2000). In our case, the results of the two statistical methods
agree. The two sampling sites appear indistinguishable at the present measurement precision. Thus, we decided to combine the data from both sampling sites into one data set. We think that the most reliable method to evaluate this data is to take the median value of $(73.9 \pm 5.6)$ pMC.

However, the combined data set is now sufficiently large ($n=11$) for more sophisticated uncertainty analysis. The yet unexplained uncertainty component in the data can be determined by adjusting its assumed value until a reduced $\chi^2$ equal 1 is achieved. If all 11 samples are used, this additional uncertainty is $\pm 15.0$ pMC, leading to a weighted average of $(73.9 \pm 4.7)$ pMC. Both HD56 and M13 deviate from the weighted average by $1.9 \sigma$, whereas all other samples agree within $1 \sigma$. This supports our intuitive judgment that these two samples are outliers. Without these two samples, the additional uncertainty component is $\pm 8.3$ pMC, resulting in a weighted average of $(73.8 \pm 3.0)$ pMC.

In our opinion, the most accurate pMC value of the Grenzgletscher ice emerging in the area of the two ice pits is $73.9 \pm 5.6$. This corresponds to a calibrated age of 2100 BC to 900 AD at 95.4% confidence level, which is in broad agreement with the glaciological picture. At the present measurement precision, the wiggles of the calibration curve give only a minor contribution to the uncertainty.

**Discussion**

We developed and tested a system dedicated to AMS radiocarbon analyses of POC amounts in the range of some 10 to 100 $\mu$g C/kg ice as contained in high alpine snow and non-temperated glacier ice. Combustion yields CO$_2$ amounts down to $\sim 20$ $\mu$g C for the filtrated POC, and down to $\sim 5$ $\mu$g C for the filtration blanks, which can be analyzed for $^{14}$C at a typical precision of 1 to 3 %. A much larger contribution to the total uncertainty is introduced by the reproducibility of the filter blanks, leading to an uncertainty of up to 23% for the blank corrected result of the smallest samples.
Improvements of the sample preparation technique should concentrate on further minimizing the amount and the variability of the carbon background introduced during melt water processing. In this context attempts will be made to detach the collected particles from a suitable filter medium. This would allow for processing a larger amount of melt water though using a smaller filter area which should greatly reduce the contamination level.

Test samples from the non-temperated ablation zone of Grenzgletscher showed a surprisingly large scatter in the pMC values, which makes evident that presently, a single radiocarbon date of glacial POC seems to have limited significance. This observation calls for a set of several measurements on the same ice body to achieve a reliable evaluation in terms of age. This strategy will be taken into account in future measurements by dividing the melt water of one ice sample into aliquots of the smallest size still suitable for reliable radiocarbon determination. Especially in the case of ice samples from non-temperated ablation zones, also a full chemical and radiochemical characterization of the ice samples appears to be mandatory, in order to identify unreliable results.

Finally, selected ice samples of known age (e.g. by stratigraphical dating) will be analyzed, to tackle the question how well the radiocarbon age of POC represents the true age of the ice.

Acknowledgement

We thank Edwin Pak (14C Radiometric Laboratory, Institut für Isotopenforschung und Kernphysik, Universität Wien) for the bulk combustion of IAEA C-3 cellulose. The work was partly funded by the EC projects ALP-IMP (EVK2-CT-2002-00148) and CARBOSOL (EVK2-2001-00067).
References


### Table 1: Summary of $^{14}$C measurements on process blanks

<table>
<thead>
<tr>
<th>Label of process blank</th>
<th>Corresponding ice sample</th>
<th>Eff. filter diameter (mm)</th>
<th>Rinsing liquids (mL)</th>
<th>$M_{\text{blank,meas}}$ (µg carbon)</th>
<th>pMC$\text{blank,meas}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD51 HD44</td>
<td>25</td>
<td>300</td>
<td>8.6</td>
<td>65.8 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>HD54 HD56</td>
<td>25</td>
<td>340</td>
<td>32.4</td>
<td>77.7 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>HD58 HD59</td>
<td>25</td>
<td>400</td>
<td>10.7</td>
<td>119.2 ± 1.4</td>
<td></td>
</tr>
<tr>
<td>HD63 HD60</td>
<td>25</td>
<td>400</td>
<td>11.0</td>
<td>103.1 ± 1.4</td>
<td></td>
</tr>
<tr>
<td>M25 M26</td>
<td>25</td>
<td>150</td>
<td>17.3</td>
<td>78.1 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>Average of 25 mm filters</td>
<td></td>
<td></td>
<td></td>
<td>16.0 ± 9.71</td>
<td></td>
</tr>
<tr>
<td>M8 M9</td>
<td>8</td>
<td>150</td>
<td>6.0</td>
<td>85.5 ± 2.2</td>
<td></td>
</tr>
<tr>
<td>M10 M11</td>
<td>8</td>
<td>150</td>
<td>5.4</td>
<td>72.4 ± 2.6</td>
<td></td>
</tr>
<tr>
<td>M12 M13</td>
<td>8</td>
<td>150</td>
<td>6.2</td>
<td>102.1 ± 3.0</td>
<td></td>
</tr>
<tr>
<td>M14 M15</td>
<td>8</td>
<td>150</td>
<td>7.5</td>
<td>80.3 ± 2.2</td>
<td></td>
</tr>
<tr>
<td>M23 M24</td>
<td>8</td>
<td>150</td>
<td>8.7</td>
<td>71.0 ± 1.7</td>
<td></td>
</tr>
<tr>
<td>M21 M22</td>
<td>8</td>
<td>150</td>
<td>6.2</td>
<td>77.8 ± 3.7</td>
<td></td>
</tr>
<tr>
<td>M18 M19</td>
<td>8</td>
<td>150</td>
<td>7.8</td>
<td>89.7 ± 3.2</td>
<td></td>
</tr>
<tr>
<td>Average of 8 mm filters</td>
<td></td>
<td></td>
<td></td>
<td>6.8 ± 1.21</td>
<td></td>
</tr>
<tr>
<td>Overall average</td>
<td></td>
<td></td>
<td></td>
<td>85.2 ± 15.71</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ Standard deviation
Table 2: Results of radiocarbon measurements of POC in glacier ice obtained from the ablation zone of Grenzgletscher and from snow at the highest point of the glacier (Colle Gnifetti). All uncertainties are given at 1 $\sigma$.

<table>
<thead>
<tr>
<th>Ice from ablation zone, lower sampling site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample number</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>HD44</td>
</tr>
<tr>
<td>HD56</td>
</tr>
<tr>
<td>M19</td>
</tr>
<tr>
<td>M22</td>
</tr>
<tr>
<td>M24</td>
</tr>
<tr>
<td>M26</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ice from ablation zone, upper sampling site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample number</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>HD59</td>
</tr>
<tr>
<td>M9</td>
</tr>
<tr>
<td>M11</td>
</tr>
<tr>
<td>M13</td>
</tr>
<tr>
<td>M15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Snow from Colle Gnifetti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample number</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>HD60</td>
</tr>
</tbody>
</table>
Table 3: Evaluation of mean and median pMC values for POC from Gornergletscher ice samples.

<table>
<thead>
<tr>
<th></th>
<th>Upper site (pMC)</th>
<th>Lower site (pMC)</th>
<th>Site mean (pMC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arithmetic average with outlier(s) rejected</td>
<td>77.0 ± 4.8</td>
<td>70.5 ± 4.5</td>
<td>73.4 ± 3.3</td>
</tr>
<tr>
<td>Median, including outliers</td>
<td>71.7 ± 6.5</td>
<td>74.6 ± 9.7</td>
<td>73.9 ± 5.6</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1 Map of the sampling area in the Monte Rosa massif including Colle Gnifetti, the Grenzgletscher, and the Gornergletscher. Contour lines are shown every 20 m for the Grenzgletscher system and every 100 m elsewhere (figure based on Landeskarte der Schweiz 1:25000: Zermatt, 1995).

Figure 2 Schematic lay-out of the apparatus for ice melting and subsequent collection of POC on a particle filter. (1) N₂ bottle, (2) pressure gauge, (3) pressure exhaust, (4) pressure release valve for melting container, (5) filter for gas, (6) N₂ pressure supply/release pipe, (7) melting container, (8) ice sample, (9) ultrasonic bath, (10,11) warm water in and out, (12) POC sample filter, (13) hose clamp (14) bottle for melt water sample, (15) N₂ supply for melt water bottle/glove bag, (16) glove bag, (17) transfer flask for rinsing liquids, (18) manifold valve, (19) filter for rinsing liquids. The arrows indicate the flow direction. See text for operational procedure.

Figure 3 Schematic lay-out of the graphitization unit for small CO₂ samples. (1) Reaction vial with Fe-catalyst (volume: 2.6 ± 0.2 cm³), (2) pressure sensor, (3) removable furnace, (4) copper heat shield, (5) blower, (6) water trap, (7) isopropanol-dry-ice mixture, (8) copper tray with cold fingers, (9) Styrofoam insulation, (10) turbo molecular pump, (11) Pirani pressure gauge, (12) CO₂ sample vial, (13) tube cracker, (14) particle filter, (15) water trap, (16) H₂ bottle, (17) "dead" CO₂, (18) IAEA C-3 CO₂, (19,20) buffer volumes - evacuated during sample CO₂ transfer.

Figure 4 Contamination during CO₂ graphitization and AMS measurements. Measured pMC values for (a) IAEA C-3 CO₂ and (b) dead CO₂ are plotted versus carbon mass of processed CO₂. Note that contamination with unknown pMC leads for small standard amounts to too low pMC values (a). For small blanks the measured pMC values are too high (b). The curves shown are model fits which allow to assess the carbon contamination.
Figure 5 Indication of the analytical sensitivity of graphitization and AMS measurement. The integrated $^{12}\text{C}^3+$ current is shown for all completely sputtered samples versus the carbon mass calculated from the CO$_2$ pressure before graphitization. The slope of the linear fit corresponds to a total detection efficiency of 2.1%. The deviating data points in the box are discussed in the text.

Figure 6 Overview on the variability of pMC values of POC in glacier ice measured for two sampling sites at the ablation zone of Grenzgletscher (Gornergletscher). The dashed crosses indicate the median pMC levels for the individual sites.
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6