Radiocarbon determination of particulate organic carbon in glacier ice

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ABSTRACT

Dating drill cores of glacial ice with radiocarbon is still an unsolved problem. This work describes our developments towards extraction and AMS radiocarbon dating of the particulate organic carbon (POC) fraction in ice samples at VERA (Vienna Environmental Research Accelerator). Test measurements were performed with ice and snow samples from the glacier Grenzgletscher near Colle Gnifetti (4454 m) in the Monte Rosa Mountain Range, Switzerland. The sample masses used were between 300 g and 1000 g ice yielding between ~32 µg and ~182 µg of sample carbon. The main carbon background (9 µg to 32 µg) is introduced by the quartz filters and the rinsing liquids used, requiring preparation of a separate process blank for each sample. Minimum sample sizes for successful graphitization of carbon dioxide in our laboratory have been reduced to less than 10 µg carbon. The background in the graphitization process is approximately 0.5 µg carbon of 40 pMC.

Introduction

Glacial ice contains only small amounts of carbon. Measurements on CO_2 released from gas pores during melting revealed a substantial contribution of ^{14}C produced in-situ by the $^{17}O(n, a)^{14}C$ reaction (Lal et al. 2000), which renders CO_2 disadvantageous for dating applications. Other promising carbon fractions present in glacial ice are POC (particulate organic carbon) and DOC (dissolved organic carbon). The radiocarbon measurement of POC is the topic of this paper.

The main challenge was the small carbon mass of the samples, thus reducing the background was crucial. A number of systematic tests was performed to pinpoint the sources of possible contamination. Whereas only minor changes were required in the AMS measurement procedures, sample preparation required substantial developmental effort. Although another group has investigated vacuum sublimation to separate the POC from the ice (Biegalski et al. 1998) we have decided to develop a filtration procedure, since this allows processing of much larger amounts of ice in shorter time.

Our samples originate from the tongue of the Grenzgletscher near Colle Gnifetti, Monte Rosa Mountain Range in Switzerland. Two different sites along the flow line of the ice were chosen for ice sampling, both in the ablation zone of the glacier, where ice with an age of at least several hundred years is expected. Additionally, snow was collected from the accumulation zone. The samples were stored at -23 °C and cut to suitable pieces (~500 - 1000 g) in a clean-room at the University of Heidelberg and wrapped in aluminum foil and sealed plastic bags. After shipment to Vienna they were kept in a freezer at a temperature of about -15 °C.

In the following we characterize the ^{14}C content by pMC values (percent Modern Carbon), as defined by Stuiver and Pollach (1977).

Melting and filtration

Since ambient dust imposes a substantial problem for the POC measurement, the critical steps during handling of the ice and the sample filters are done in a laminar-flow box (class 100). Materials used in the setup are (almost exclusively) quartz, glass, stainless steel, and Teflon. Teflon tubing seems to prevent particles from sticking to the tube walls. All parts and tools are cleaned in an ultrasonic bath, and dust is blown off with clean N_2.

Where possible, the materials (filters, quartz vials, CuO etc.) are preheated shortly before use to 950 °C for 4h, and left in the closed oven to cool down to about 500 °C. Still hot, they are put into a container with saturated H_2O atmosphere. This helps reducing carbon adhesion from laboratory air during storage and is especially important for the sample filters.

The heart of the melting apparatus (see Fig. 1) is a double-walled glass vessel. Tempered water flowing through the double walls allows controlling of the melting rate. A water temperature of about 30 °C (measured at the exit) allowed melting of one sample in ~1 hour. All tubes leading into the melting pot are supplied with filters, so all liquids and gases entering the melting pot are

cleaned. During operation, the melting pot is partially submerged in a large ultrasonic bath, and the port used as melt water outlet is the deepest point. The purpose of the ultrasonic bath is to prevent particles from sticking to the glass walls of the melting pot. The sample filter holder is made of stainless steel and Teflon with a stainless steel frit supporting the quartz fiber filter (Sartorius QMF, 85 gm^{-3}, binder-free, 2.5 cm diameter).

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

The melting pot is temporarily taken into the laminar flow box to insert the sample. The tubing is long enough, so all connections can stay closed. Melting and filtration are done under over-pressure with clean N_2. This protects the melt water from contamination with laboratory air, allowing for additional measurements on the collected water. The filter holder is mounted after disposal of the first ~100 ml of sample water to get rid of surface contamination.

In the final filtration procedure, we kept the N_2 pressure constant (~400 mbar) and controlled the filtration speed with a hose clamp after the filter holder (~0.2 ml/sec). Filtration of accumulated melt water was done in intervals, with the ultrasonic bath switched off in-between. The melt water is not pushed out completely, since gas inside the filter holder requires a strong pressure increase to start the filtration process again. The filtrated melt water is collected in a glass bottle inside a glove bag filled with clean N_2, and it is treated with ~1 ml NaN_3 solution (0.2 g/ml) to prevent growth of microorganisms. Thus, further measurements on the melt water are possible.

After all ice has melted, the apparatus is rinsed. ~150 ml 0.1 M HCl are filled into the transfer flask and pushed with N_2 into the melting pot. A quartz filter (similar to the melt water filter) is mounted in this transfer line. The melting pot is shaken well and the ultrasonic is switched on for 5 minutes to mobilize particles sticking to the walls. The liquid is pushed out with N_2, also through the melt water filter. By using HCl in the first rinsing we expect to remove the carbonate part of the particles. Rinsing is repeated twice with ~100 ml H_2O.

The wet filter is placed in a quartz vial together with 500 mg CuO as oxidizing agent and a small piece of silver wire to remove sulfur and halogens. Systematic investigations revealed that the CuO contributes less than 1 μg to the carbon contamination (compare (Vandeputte et al. 1998)).

The vial is evacuated and heated for ~1 h to ~130 °C to remove moisture and volatile carbon before flame sealing. The samples are tested for leaks and then combusted for 4 hours at 950 °C. After cooling down inside the oven, the samples are ready for graphitization.

Before each use the melting pot is cleaned and a process blank is taken. Cleaning of the melting apparatus is done similar to the rinsing after ice melting, with ~200 ml 0.7 mol/l HNO_3 and two times with ~100 ml H_2O. No sample filter is attached. Then a process blank is prepared, separately for each sample, without any ice but with the same amount of rinsing liquids (~150 ml 0.1 M HCl and two times ~100 ml H_2O) yielding between 9 µg and 32 µg carbon. The amount of carbon collected on this blank filter correlates with the amount of liquids used (Fig. 2). From new, unused but wetted filters typically 3 µg carbon were extracted.

Graphitization and AMS measurement

Different from previous work described by Weissenbök et al. (2000) the graphitization of the sample CO_2 to graphite is now done in the VERA Laboratory, mainly according to the procedure described by Vogel et al. (1984). We have modified the small-sample graphitization unit developed at VERA for ^{14}CO measurements in atmospheric air (Rom et al. 2000) for our needs (Fig. 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. The reaction is monitored with pressure gauges that are independent of the kind of gas used. To keep the reactor volume small (~3 cm^3) we use very small pressure sensors (Type FX72-015AV by Omega). For the low CO_2 pressures encountered for our samples (1.3 µg C » 1 mbar CO_2) these sensors show significant drifts, and they are not completely temperature compensated. Therefore an air-cooled copper heat shield insulates the pressure sensors from the hot reaction volume. By calibrating the pressure sensor immediately before every important measurement and by averaging, the computer program can achieve a precision better than ±0.3 mbar. The pretreatment 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 outgassing. The Viton o-rings previously used for the reactors were replaced by Teflon gaskets, for which we observe less outgassing at high temperatures. A Pirani gauge connected to the central manifold allows to detect leaks quickly.

Systematic measurements were performed to test the graphitization unit. The standard material used was CO_2 from a bulk combustion (13 g) of IAEA C-3 cellulose reference material (129.4 pMC, Rozanski et al. (1992)). As blank material we used commercially available "dead" CO_2 (Linde, purity >99.9993 Vol%) from a Hungarian mineral spring (Rom et al. 2000). Graphitizations were performed for CO_2 amounts corresponding to 4.0, 6.5, 13, 39, 130, and 390 µg C. The respective radiocarbon measurement results (Figure 4) allow to split the carbon contamination into a "dead" (0 pMC) and a "modern" (100 pMC) contribution. The formulas fitted to the data are:

$$pMC_{dead,meas} = \frac{100}{1 + \dfrac{M_{dead,meas}}{M_{modern\,cont}}}, \quad pMC_{C-3,meas} = \frac{129.4}{1 + \dfrac{M_{dead\,cont}}{M_{C-3,meas}}}$$

with

$M_{modern\,cont}$, $M_{dead\,cont}$:   mass of "modern" and "dead" carbon contamination, respectively.

$M_{dead,meas}$, $M_{C-3,meas}$:   carbon mass of dead CO_2 and C-3 CO_2, calculated from the measured CO_2 pressure.

$pMC_{dead,meas}$, $pMC_{C-3,meas}$: measured pMC of the dead CO_2 and the C-3 CO_2.

129.4:   nominal pMC value of the C-3 material.

The fit yields an average total contamination of 0.5 µg carbon with a pMC value of 40 in the graphitization and AMS measurement.

We used between 0.6 and 3.0 mg iron as catalyst, leading to very low C:Fe ratios for our small samples. We observed no significant influence of the amount of iron on the reaction speed, 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 revealed that the amount of modern carbon contamination grows with the amount of iron used. This result is in agreement with Vadebutte et al. (1998). In future experiments we will minimize this background contribution by using as little iron as possible.

When the graphitization reaction is complete, the computer program pumps of the excess H_2 and switches off the heating. The water traps warm up and the vapor comes in contact with the fresh

graphite. By these means we intend to deactivate the reactive surface to reduce adhesion of ambient carbon. The mixture of iron powder and graphite is pressed into aluminum sample holders suited for our ion source.

The radiocarbon measurement by AMS was performed at the Vienna Environmental Research Accelerator (VERA) mainly following routine procedures (Steier et al. 2003). The main change for small samples is that the stable-isotope beams ($^{12}C^-$ and $^{13}C^-$) are injected for a longer time and that the sensitivities of the beam current amplifiers are adjusted for each sample automatically. Successful measurements were performed for samples down to ~10 µg carbon.

To investigate the dependency of the ionization yield on the sample size, we looked at the time development of the $^{12}C^{3+}$ currents during the AMS-measurement (see Fig. 5). We achieved a total detection efficiency of 2%, calculated from the number of $^{12}C^{3+}$ ions in the Faraday cup integrated over the measurement time, divided by the number of C atoms in the sample CO_2. The efficiency is independent of the sample size, and the same value can be assumed for ^{14}C. Included are the chemical yield, the negative ion yield in the source, the stripping yield to C^{3+} (0.50 ± 0.02), and the duty factor for ^{14}C counting (~0.8).

For some very small samples we observed currents which were exceptionally low. The reason is not yet understood and will be further investigated. The affected samples were excluded from further evaluation.

First measurements on true glacier ice and snow

A total of five measurements on true glacier ice or snow were performed (Table 1). Where an associated process blank existed, the measured pMC was corrected using a simple mixing formula for sample carbon and contamination:

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

$pMC_{sample,corr}$: pMC value for the sample, blank corrected.

$pMC_{sample,meas}$, $pMC_{blank,meas}$: pMC measured for sample and process blank, respectively.

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

More systematic investigations are required to quantify the uncertainty introduced by this blank correction. The ±5 pMC uncertainty quoted for the corrected sample values in Table 1 assumes an uncertainty of the blank of about ±15 pMC.

The snow sample HD60 was taken in August 2000 as surface snow at a sampling site in the accumulation zone of the glacier. The measured value is higher than modern, similar to the results of Weissenbök et al. (2000) and Biegalski et al. (1998). Samples HD-T13, HD44, HD59, and HD56 were taken from the ablation zone from two different sampling sites along the flow line of the glacier. It is expected that the ice from the lower sampling site is older than the ice from the upper sampling site (Paterson 1994).

HD-T13 and HD44 are aliquots of the same ice sample. The value obtained for HD44 (74 pMC) appears reasonable. HD-T13 was not prepared following the final procedure and no directly associated process blank exists. Considering this, the agreement of the pMC value with HD44 is encouraging. For sample HD56, the amount of CO_2 extracted is exceptionally high, and the sample is modern. In our opinion, contamination of HD56 is the most likely interpretation for this deviation. Therefore HD56 is rejected. The result for HD44 is the best value for the age of the ice in the lower sampling site.

For the upper sampling site, only one sample has been measured so far. The pMC value obtained for HD59 is 78 ± 5 pMC. At the present level of precision, we cannot resolve an age difference between HD59 and HD44.

Conclusions and outlook

We demonstrated that it is possible to graphitize and measure CO_2 samples as small as ~10 µg C reliably. Improvements should be made to reduce the carbon background during melt water filtration. This will be achieved by reducing the amount of processing liquids, improving their filtration, and perhaps by reducing the filter size.

Up to now only a few ice samples have been processed, with encouraging results. More investigations will be done to determine the reproducibility of the results and to allow for a realistic

uncertainty estimation. There are ten more samples available at the VERA Laboratory, which at this point in time should be sufficient. After that, we can investigate how well the pMC of the POC reflects the age of the ice. For this purpose, ice samples of known age are required, with the age determined by independent methods or by radiocarbon dating of enclosed larger objects.

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Tables

Table 1: Results of measurements on glacier snow and ice. For the measured values $pMC_{sample,meas}$ and $pMC_{blank,meas}$ the statistical uncertainty (1 s) is given. For the samples HD44, HD56, HD59, and HD60 a process blank was prepared. The uncertainty quoted for the blank corrected values $pMC_{sample,corr}$ is only a rough estimate.

Sample number	Material	Melt water (mL)	$M_{sample,meas}$ or $M_{blank,meas}$ (µg carbon)	$pMC_{sample,meas}$ or $pMC_{blank,meas}$	$pMC_{sample,corr}$
HD-T13	Ice from ablation zone, lower sampling site	200	32.7	68.3 ± 0.6	-
HD44	Ice from ablation zone, lower sampling site	~400	36.2	71.7 ± 0.8	74 ± 5
HD51	Process blank for HD44	0	8.8	65.8 ± 1.0	-
HD56	Ice from ablation zone, lower sampling site	700	211	100.8 ± 0.5	100 ± 5
HD54	Process blank for HD56	0	33.3	77.7 ± 0.8	-
HD59	Ice from ablation zone, upper sampling site	580	39.0	89.8 ± 0.7	78 ± 5
HD58	Process blank for HD59	0	10.9	120.0 ± 1.4	-
HD60	Colle Gnifetti snow	500	314	117.8 ± 0.6	118 ± 5
HD63	Process blank for HD60	0	11.3	103.9 ± 1.5	-

Figure Captions

Figure 1 The apparatus for ice melting and collection of POC on the sample filter. (1) N_2 bottle, (2) pressure gauge, (3) pressure exhaust, (4) pressure release valve for melting pot, (5) filter for gas, (6) N_2 pressure supply/release pipe, (7) melting pot, (8) ice sample, (9) ultrasonic bath, (10,11) tempered water in and out, (12) POC sample filter, (13) hose clamp (14) bottle for melt water sample, (15) N_2 supply for melt water bottle/glove bag, (16) glove bag, (17) transfer flask for rinsing liquids, (18) filter for rinsing liquids. The arrows indicate the flow direction. For operational procedures see text.

Figure 2 Carbon contamination in the rinsing liquids. After the filtration of the melt water sample, rinsing liquids also pass through the filter. The carbon extracted from various blanks is plotted vs. the total amount of rinsing liquid used. Process blanks (?) were produced either with artificial, clean ice or with rinsing liquids only. Filter blanks (?) have not been used for filtration at all (the amount of liquid used is 0 ml); The fit shows that the carbon background grows with the amount of liquids used. For two blanks (?) we found out later that the filter between the transfer flask and the melting pot had ripped, demonstrating that the filtration of all liquids entering the melting pot is essential.

Figure 3 The graphitization unit for small CO_2 samples. (1) Reaction vial with Fe-catalyst, (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) turbomolecular pump, (11) Pirani pressure gauge, (12) CO_2 sample vial, (13) tube cracker, (14) dust filter, (15) water trap, (16) H2 bottle, (17) "dead" CO_2, (18) C-3 CO_2, (19,20) buffer volumes - evacuated during sample CO_2 transfer.

Figure 4 Contamination in graphitization and AMS measurement. Measured pMC values for blank and standard samples are plotted vs. carbon mass of sample CO_2. (a) For small standards a contamination of unknown pMC results in measured pMC values which are too low. (b) For small blanks the measured pMC values are too high. Even though the data have large scatter, model fits allow to asses the carbon contamination.

Figure 5 Measurement sensitivity. The $^{12}C^{3+}$ current integrated over time is shown for all samples which were apparently sputtered completely in the AMS measurement. For most samples the integrated current is proportional to the carbon mass calculated from the CO_2 pressure before

graphitization. The slope of the fit corresponds to a total detection efficiency of 2.1%. The data points framed in the box where not included in the fit.
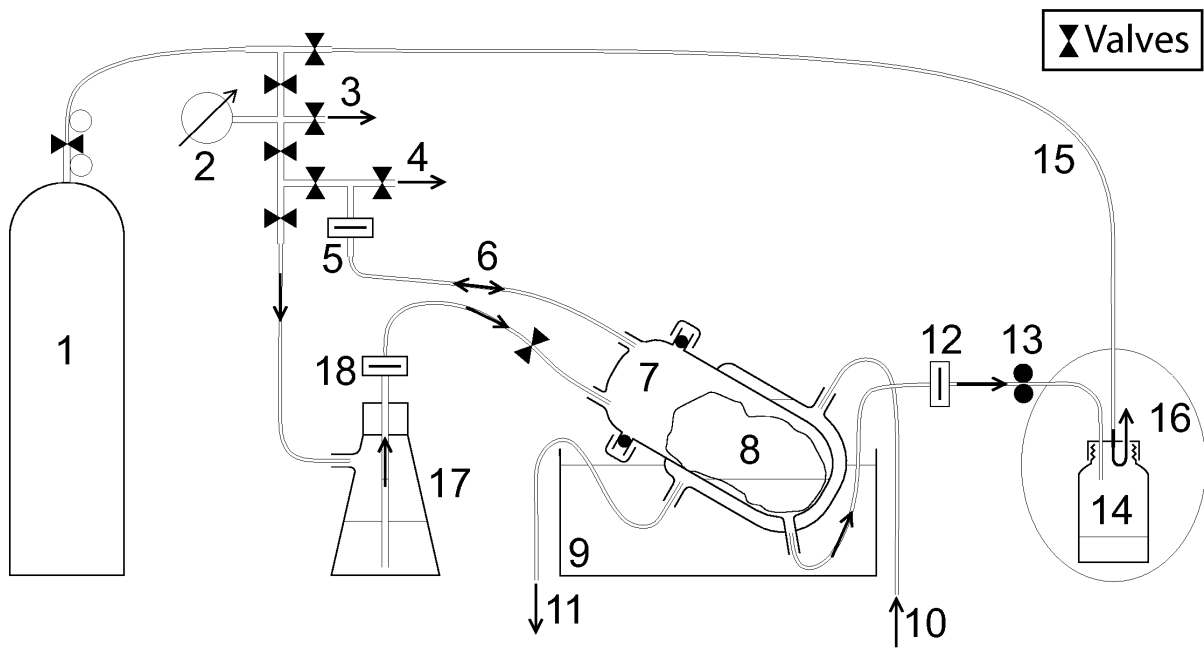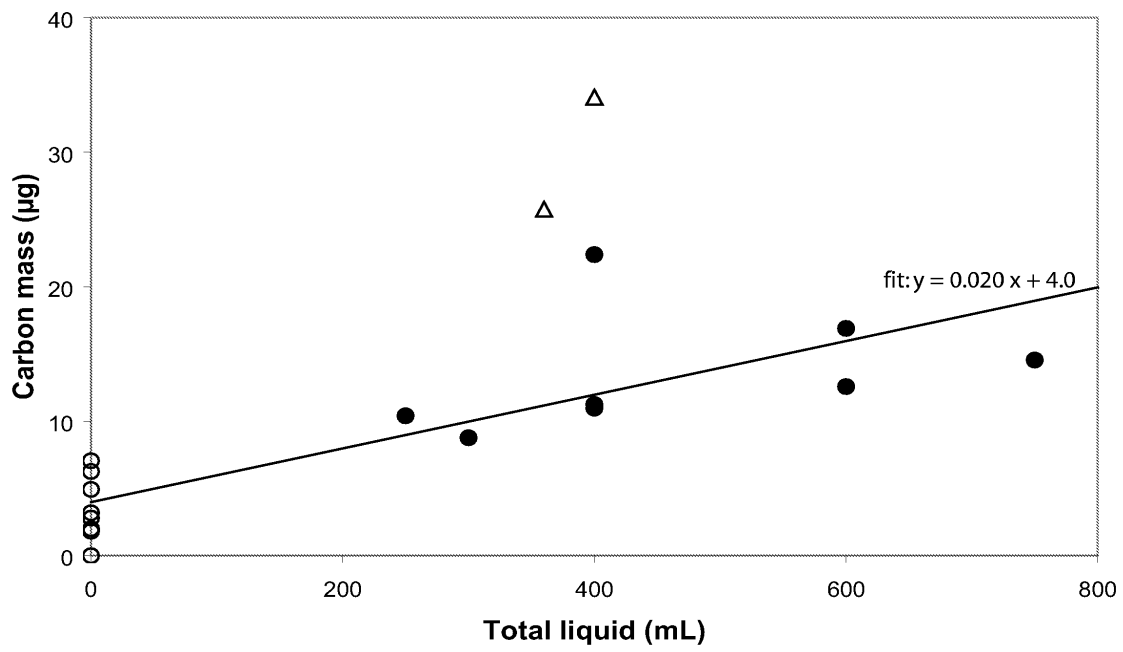
Figure 1

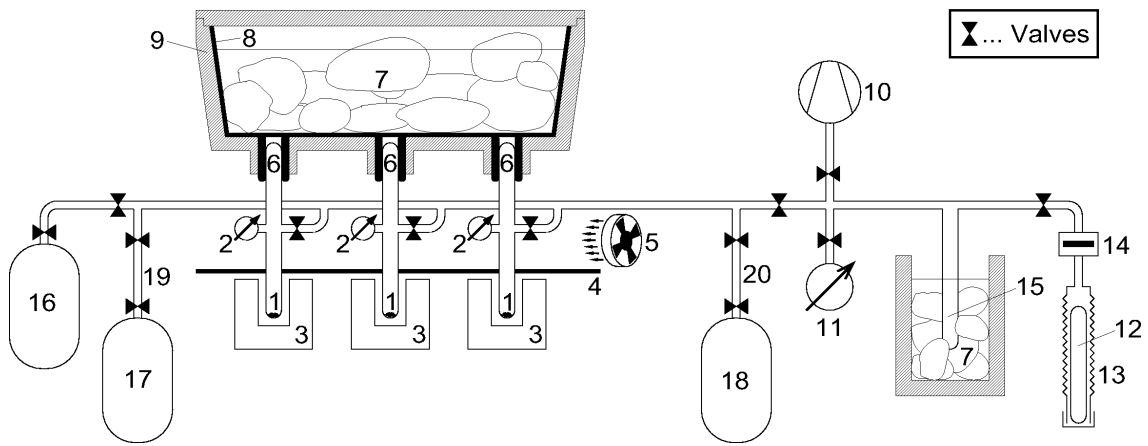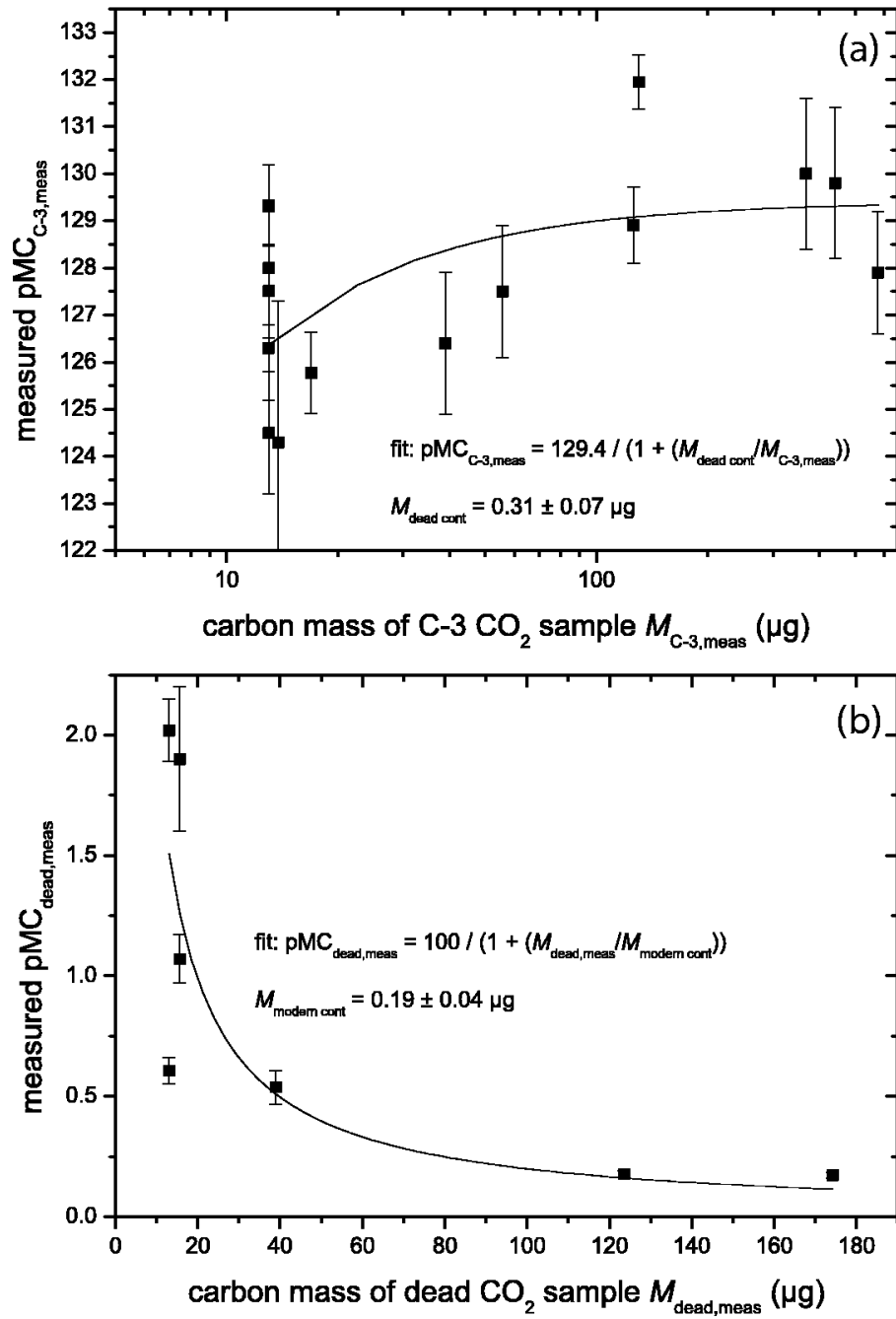**Figure 2**

Figure 3

(a)

measured $pMC_{C-3,meas}$ vs carbon mass of C-3 CO_2 sample $M_{C-3,meas}$ (µg)

fit: $pMC_{C-3,meas} = 129.4 / (1 + (M_{dead\,cont}/M_{C-3,meas}))$

$M_{dead\,cont} = 0.31 \pm 0.07$ µg

(b)

measured $pMC_{dead,meas}$ vs carbon mass of dead CO_2 sample $M_{dead,meas}$ (µg)

fit: $pMC_{dead,meas} = 100 / (1 + (M_{dead,meas}/M_{modern\,cont}))$

$M_{modern\,cont} = 0.19 \pm 0.04$ µg

Figure 4

Figure 5