Radiocarbon Determination of Particulate Organic Carbon in Glacier Ice

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Introduction

Dating of drill cores of glacial ice with radiocarbon is still an unsolved problem. With the goal of exploring the possibility of dating ice via the particulate organic carbon (POC) fraction, ice and snow samples from Colle Gnifetti, Switzerland, were processed at the VERA Laboratory. The main challenge was the small size of the carbon samples. Whereas the AMS measurement was possible with standard procedures, sample preparation required developmental effort.

The samples originate from the glacier at Colle Gnifetti, Monte Rosa Mountains in Switzerland. Two different sampling sites along the flow line of the ice were chosen, both in the ablation zone of the glacier, where ice with an age of at least several hundred years is expected. The samples were stored and cut to suitable pieces (~500 - ~1000 g) at Institute for Environmental Physics of the University of Heidelberg and shipped to Vienna, wrapped in aluminum foil and sealed plastic bags. In Vienna they are kept in a freezer at a temperature of about -15°C.

Ambient dust imposes the main challenge for the POC measurement. Therefore critical steps of the melting procedure are done in a laminar flow box (class 100). Materials used are (almost only) glass, stainless steel, and teflon. With teflon tubing, no particles seem to stick to the tube walls.

Where possible, the materials (filter, quartz vials, *etc*.) were preheated shortly before use at 950°C for 4h, and left in the closed oven to cool down to about 500°C. The hot materials are then put into an exsiccator, filled with a little water. Storage in a saturated H_2O atmosphere reduces carbon adhesion from laboratory air. This is especially important for the sample filters (Sartorius FT-3-1109-025 quartz microfibre filters, grade QMF, grammage: 85 g m^{-3}, binder-free, 2.5 cm in diameter).

Melting and filtration are done under over-pressure with clean N_2. This protects the melting water from contamination with laboratory air, allowing for additional measurements on the collected water. The setup is shown in Figure 1.

Procedure

The melting pot is then temporarily taken into the laminar flow box to insert the sample (the tubing is long enough, so all connections can stay closed) and a new, clean filter is mounted. Temperated water flowing through the double walls allows to control the melting rate. A water temperature of about 30°C (measured at the exit) allowed to melt one sample in about 1 hour. The first 100-300 ml of sample water are thrown away to get rid of surface contamination.

In the final filtration procedure, we keep the N_2 pressure constant (~400 mbar) and control the filtration speed with a hose clamp downstream of the filter holder (~0.19 ml/sec). Filtration of accumulated melt water is done in intervals, with the ultrasonic bath switched off in between. The melting water is not pushed out completely, since gas in the filter holder requires a strong pressure increase to start the filtration process again.

After all ice has melted, the apparatus is rinsed. ~100 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 melting water filter, see below) is mounted in this transfer line. The melting pot is shaken well, the ultrasonics are switched on for 5 minutes. The liquid is pushed out with N_2, also through the melt water filter. This step is intended to remove the carbonate part of the particles. Rinsing is repeated twice with ~100ml H_2O bidest.

Before each use the melting pot is cleaned and a process blank is taken. Cleaning 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 bidest. No sample filter is attached. The process blank is taken with a sample filter in place. The liquids used (~100 ml 0.1 M HCl and two times ~100ml H_2O bidest) are the same as in the rinsing of the apparatus after ice melting. The amount of carbon collected on this blank filter seems to correlate with the amount of liquids used (see Figure 2).

With the help of tweezers and micro-spoons the wet filter is folded - keeping the sample side inside - and placed in the small quartz vial and put into a larger vial together with a small piece of Ag wire and 500 mg CuO. Systematic investigations revealed that the CuO does not contributes significantly to the carbon contamination (see Figure 3).

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.

Different from previous work decribed in [Weissenbök et al. 2000] the graphitization of the sample CO_2 to graphite is now done in the small graphitization unit used for environmental samples at VERA [Rom et al. 1998]. The procedure is mainly according to [Vogel et al. 1984] with iron as catalyst. The radiocarbon measurement by AMS was performed at the Vienna Environmental Research Accelerator (VERA) mainly following routine procedures. Successful measurements were performed for samples down to ~10 µg carbon. For some samples below ~10 mbar CO_2 pressure the measurement failed (see Figure 4) yielding almost no C^- currents from the ion source. The sensitivity achieved is 2%. This value includes chemical yield, negative ion yield, stripping yield to C^{3+} (0.50±0.02), and the duty factor for ^{14}C counting (~0.8).

The contamination during graphitization and AMS measurement was studied by systematic measurements on dead and modern CO_2 (see Figure 5).

First Measurements on True Glacier Ice and Snow

A total of five measurements on true glacier ice or snow were already performed, but only for two ice and one snow sample the origin is well documented. Additionally, sample "HD-T13" was not prepared following the final procedure and no process blank exists. The results are shown in Figure 6.

Ten more samples are available at the VERA Laboratory. Their measurement will show whether POC is suitable for dating glacial ice.

References

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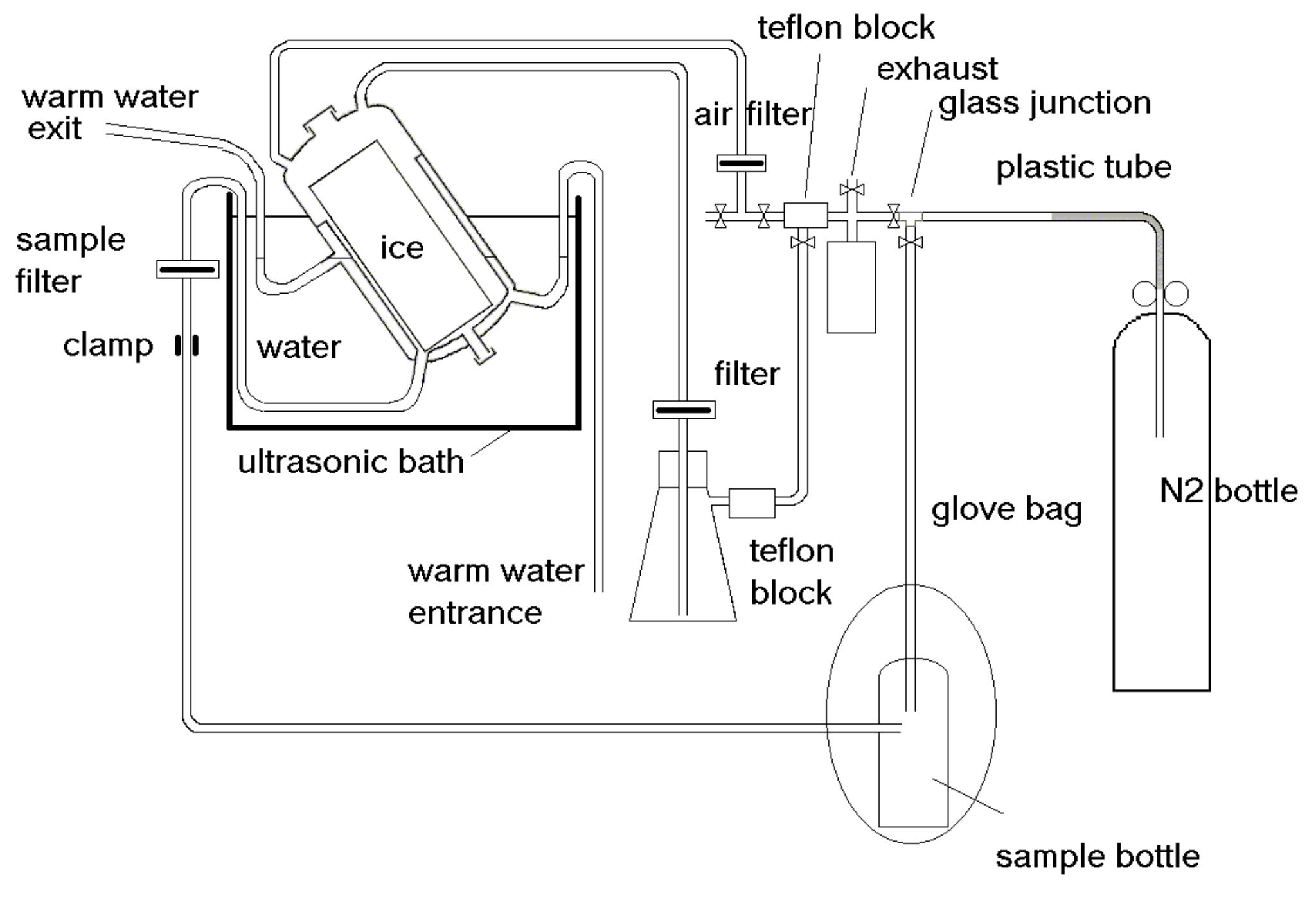

Figure 1: The Melting Apparatus

The heart of the melting apparatus is a double-walled glass vessel. All tubes leading into this melting pot are supplied with filters, so all liquids and gases entering the melting pot are filtered. Filtration and transfer is accomplished with pressurized N_2. During operation, the melting pot is partially submerged in a large ultrasonic bath and slanted by ~45° so that the port used as melt water outlet is the deepest point. The idea is to prevent particles from sticking to the glass walls of the melting pot.

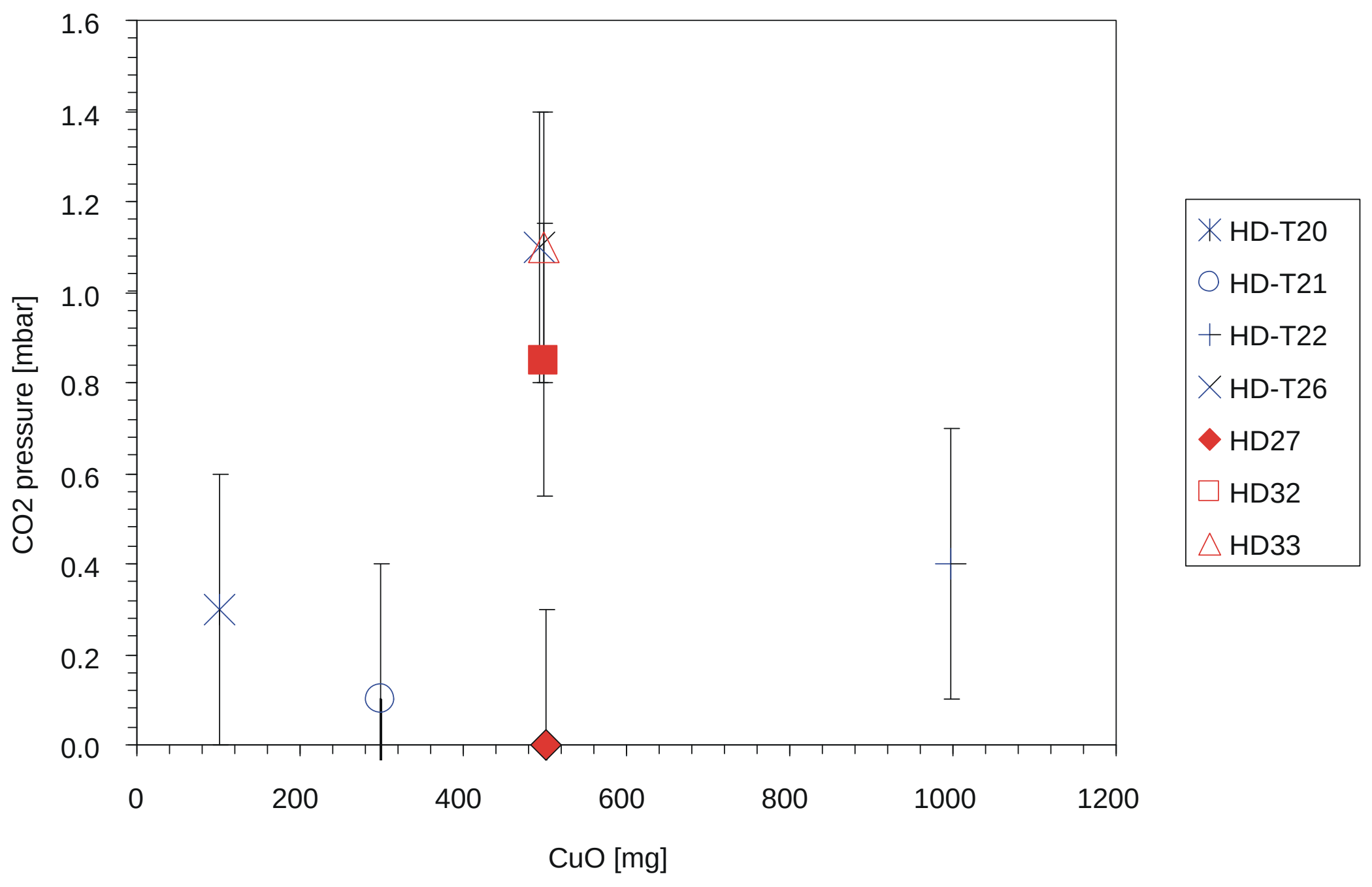

Figure 3: CuO Amount vs. Carbon Contamination

For combustion of different amounts of (pretreated) CuO the resulting CO_2 pressure was low and showed no clear trend. Obviously, the CuO does not contribute to the carbon contamination.

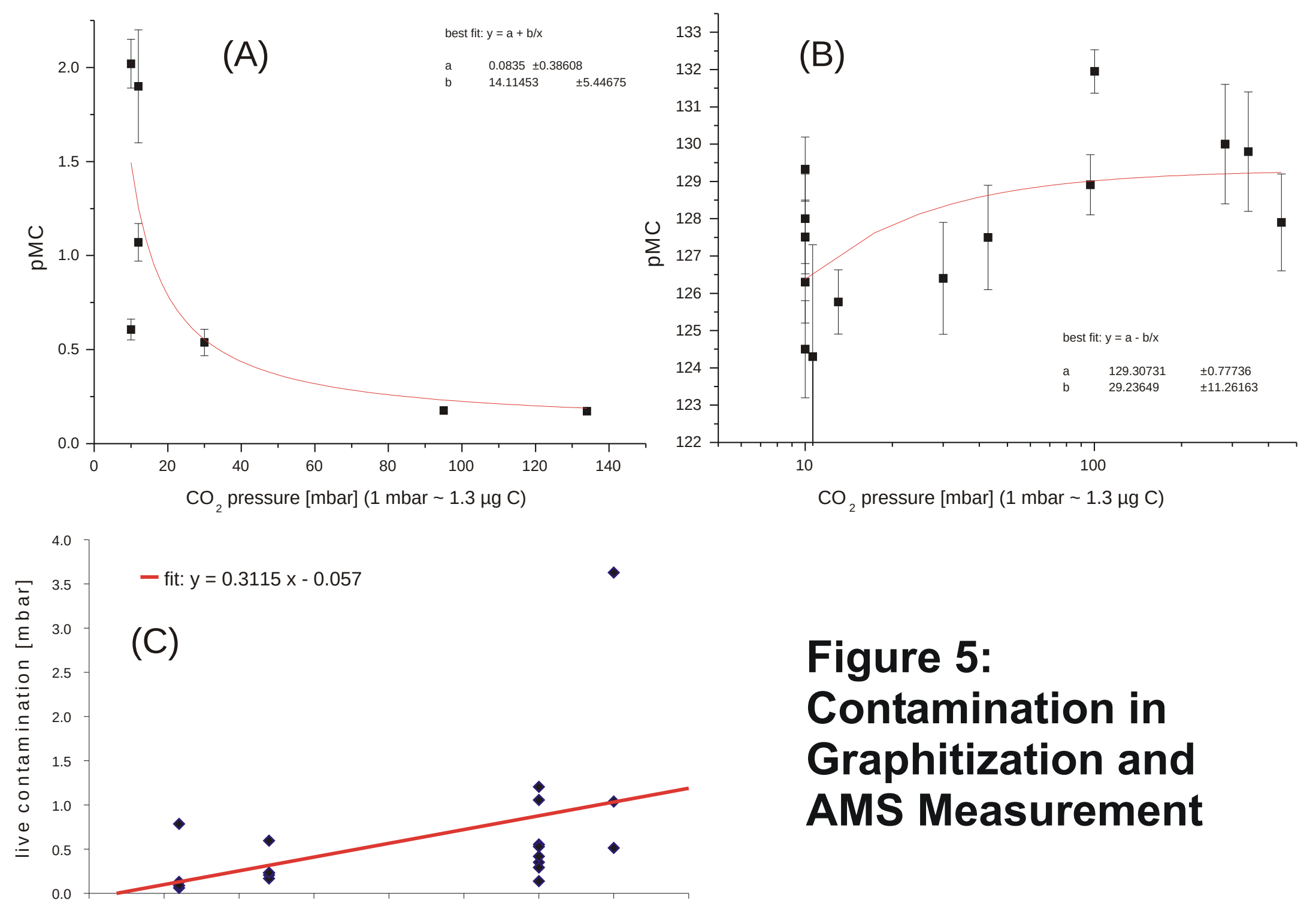

Figure 5: Contamination in Graphitization and AMS Measurement

For the systematic investigations commercially available dead CO_2 (Linde, purity >99.9993 Vol%; from a Hungarian mineral spring) and CO_2 from a bulk combustion of IAEA C-3 cellulose reference material (13 g, 129.4 pMC) were used.

The sample sizes were varied down to 13 µg carbon, corresponding to ~10 mbar CO_2 pressure in the reactor volume (~3 cm^3). The pMC values obtained for smaller CO_2 amounts are increased for the blanks (A) and reduced for the C-3 standards (B), respectively. This can be explained by a constant contaminating carbon mass. Assuming that the contamination is modern (100 pMC) we can calculate its mass for every blank.

In (C) the corresponding CO_2 pressure of this contamination is plotted, showing a correlation with the mass of iron catalyst used. The fit suggests a carbon content of ~0.4 µg/mg pretreated iron.

Foto taken from www.geo.unizh.ch/~stgruber/pics/colle/09070015.jpg. The saddle visible in the picture is the origin of the glacier studied in this work.

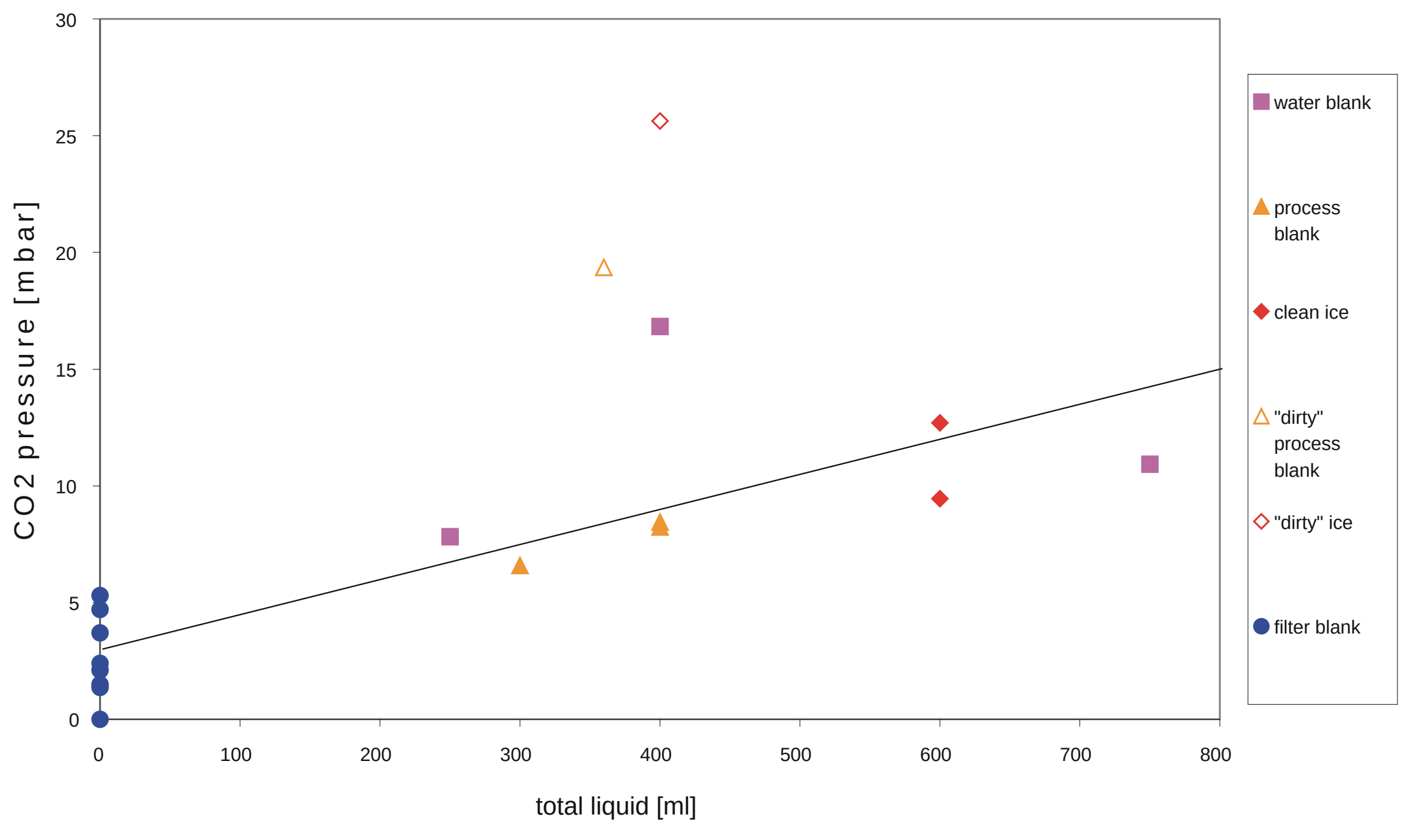

Figure 2: Liquid Amount vs. CO_2 Contamination

The contamination found in process blanks grows with the amount of liquids used in sample processing (HCl, H_2O). The straight line is an eye guide for this correlation.
Different types of blanks were included in the diagram: filter blanks have not been used for filtration at all (amount of liquid is 0 ml in the diagram); process blanks are blanks that have been done directly before an ice sample and which use the same amount of liquids as these; water blanks were done in the same way, except that no ice sample was filtered afterwards; clean ice samples are chunks of ice made by us from different types of "clean" water (freshly distilled water, VE water prepared at the IUP Heidelberg). For the samples marked "dirty" we found out later that the filter between the transfer flask and the melting pot had ripped. These "dirty" samples contain a sufficiently greater amount of CO_2 – this shows that the filter for liquids entering the melting pot really helps reduce the carbon background.

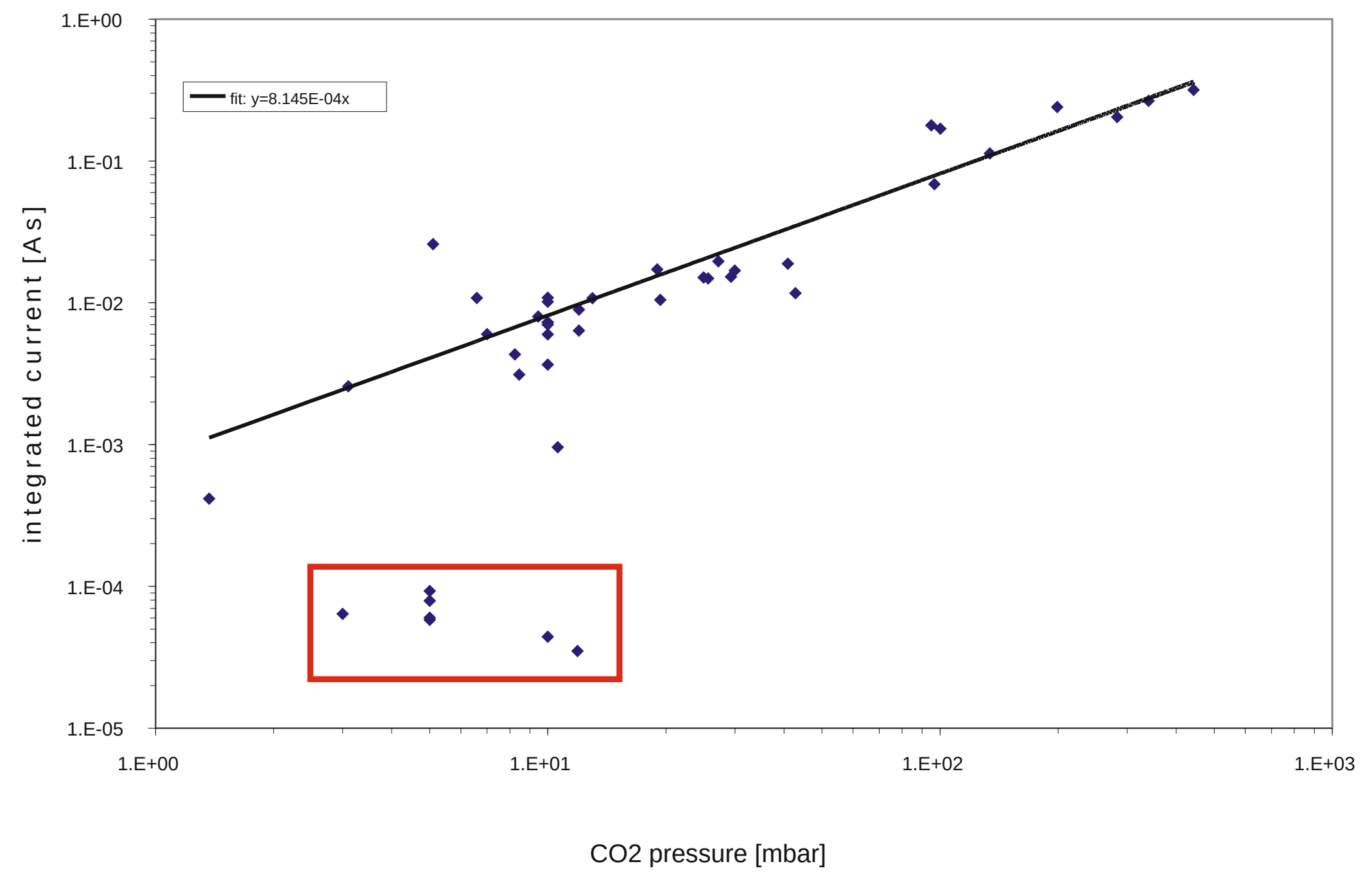

Figure 4: Determination of Measurement Sensitivity

Shown is the $^{12}C^{3+}$ current integrated over time for all samples graphitized for this work which were sputtered completely in the AMS measurement. For most samples the integrated current is correlated to the CO2 pressure (see fit). For some points below ~10 mbar CO_2 (red frame) the observed currents were significantly too low. One possible explanation is that the chemical graphitization reaction did not run properly. However, the pressure curves acquired during the reactions partly show regular behavior. In these cases, the carbon distribution in the sputter target may have been inhomogeneous and the carbon may not really have been used up. We observed such inhomogeneities in later measurements, and therefore now homogenize the material more carefully. The affected samples were excluded from further evaluation.

The total measurement efficiency determined from the slope of the fit is 2.1 %. This number is defined as the number of $^{12}C^{3+}$ ions integrated over the ^{14}C measurement time per C atom in the CO_2. The same efficiency can be assumed for ^{14}C.

Label	material	melt water [ml]	CO_2 pressure [mbar]	pMC	calibrated age
HD-T13	Ice from ablation zone	200	24.60	68.3 ± 0.6	1410 – 200 BC
HD44	Ice from ablation zone, same ice sample as HD-T13	~400	27.21	73.6 ± 2.0*	850 – 200 BC
HD51	process blank for HD44	-	6.59	65.8 ± 1.0	
HD56	Ice from ablation zone, lower sampling site	700	159.15	99.9 ± 2.0*	1680 – 1955 AD
HD54	process blank for HD56	-	24.96	77.7 ± 0.8	
HD59	Ice from ablation zone, upper sampling site	580	29.30	78.4 ± 2.0*	250 BC – 350 AD
HD58	process blank for HD59	-	8.24	120.0 ± 1.4	
HD60	Colle Gnifetti Snow	500	236.00	118.4 ± 2.0*	1985 – 1989 AD
HD63	process blank for HD60	-	8.45	103.9 ± 1.5	

Figure 6: First Results on Glacier Ice and Snow

Five actual ice and snow samples were measured. Sample HD60 was taken from 30 - 60 cm below the surface at the accumulation zone of the glacier. HD-T13 and HD44 are aliquots of the same ice, but the exact origin is not documented.

For the samples HD44, HD56, HD59, and HD60 a process blank was prepared. The pMC values marked with an asterisk are corrected with these process blanks, the uncertainty given is only a rough estimate. For HD-T13, where no process blank exists, the uncorrected value is used.