

Progress in ^{14}C dating of ice at Utrecht

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For ^{14}C dating of ice, only a limited amount of CO_2 is available (20–100 $\mu\text{g C/kg ice}$). To avoid contamination, a special milling device has been constructed to chip the ice at -20°C . The background of 7.0 ± 2.0 percent modern carbon (pmC) for a sample of 50 $\mu\text{g C}$, including extraction and conversion, limits the ^{14}C dating of ice with accelerator mass spectrometry (AMS) to about 20 000 years B.P. Results are presented for an ice core from the Pakitsoq area, West Greenland, with a known age of 9000 ± 1000 yrs B.P., established by means of $\delta^{18}\text{O}$ variations and ice flow model calculations.

1. Introduction

It has been known for about twenty years that ice cores contain a tremendous amount of information on climate and atmospheric composition of the last 200 000 years. Interpretation of the records obtained by chemical analysis requires a reliable time scale. In many cases, counting layers caused by seasonally varying parameters makes it possible to date ice cores back to 10 000 B.P. This method is limited to cores from inland parts of an ice sheet, with a homogeneous sequence of annual layers and a sufficiently high snow accumulation. For ice cores from the margins of an ice sheet the method fails. Here surface melting leads to upward ice motion, so that the age of the surface is unknown. So there is a need for alternative techniques, like carbon-14 dating.

Accelerator mass spectrometry (AMS) enables dating of ice cores by measuring the $^{14}\text{C}/^{12}\text{C}$ ratio of the CO_2 , captured in the air bubbles in an ice core [1]. An ice core of 5–7 kg ice (gross weight) with a concentration of 100 ml air (300 ppm CO_2) per kg ice is sufficient for one dating. In this report the equipment built for dry extraction of CO_2 from ice and the conversion into graphite for AMS ^{14}C dating is described. The contribution to the background contamination due to the various steps in the method is investigated, and the influence on the result obtained for an ice core from the margin of West Greenland is discussed.

2. Method

For dry extraction of gas from air bubbles trapped in ice, the ice cores are chipped in the ice milling

machine (fig. 1). The construction of Moor and Stauffer [2] has been modified to make the vacuum conditions more stable during operation of the machine. To avoid leakage a special coupling has been designed using bellows between the bent driving shaft and the milling wheel with sharp blades. A magnetic coupling pushes the ice core towards the milling wheel. The wheel chips the core in millimeter-sized ice debris which is collected in the lower reservoir. The machine has been built inside a refrigerator so chipping can be done at -20°C . Desorption of contaminating gasses from the inner walls is furthermore minimized by reducing the pressure in the system to 10^{-3} Pa. In a gas collection device the CO_2 is simply separated from the other gasses by using liquid nitrogen and dry ice/acetone (-80°C).

The resulting CO_2 is reduced to C using H_2 , and Fe as a catalyst at 610°C [3]. The mini-unit used in this process is shown in fig. 2. Finally the $^{14}\text{C}/^{12}\text{C}$ ratio is determined with the tandem accelerator of the University of Utrecht [4].

3. Results

Since the amount of CO_2 extracted from ice is small (50–150 $\mu\text{g C}$) compared with the routine 1–2 mg C samples, special experiments are performed to test laboratory contamination. Major influences on the background due to desorption of gas from the walls of the milling machine and from the conversion process in the graphitization unit are examined.

Routine conversion of ^{14}C -free CO_2 gas (NAX) yields an average background of 0.25 ± 0.1 pmC (1–2 mg C). In fig. 3 the results are plotted for small (50–550 μg) samples. The figure suggests a slightly increasing back-

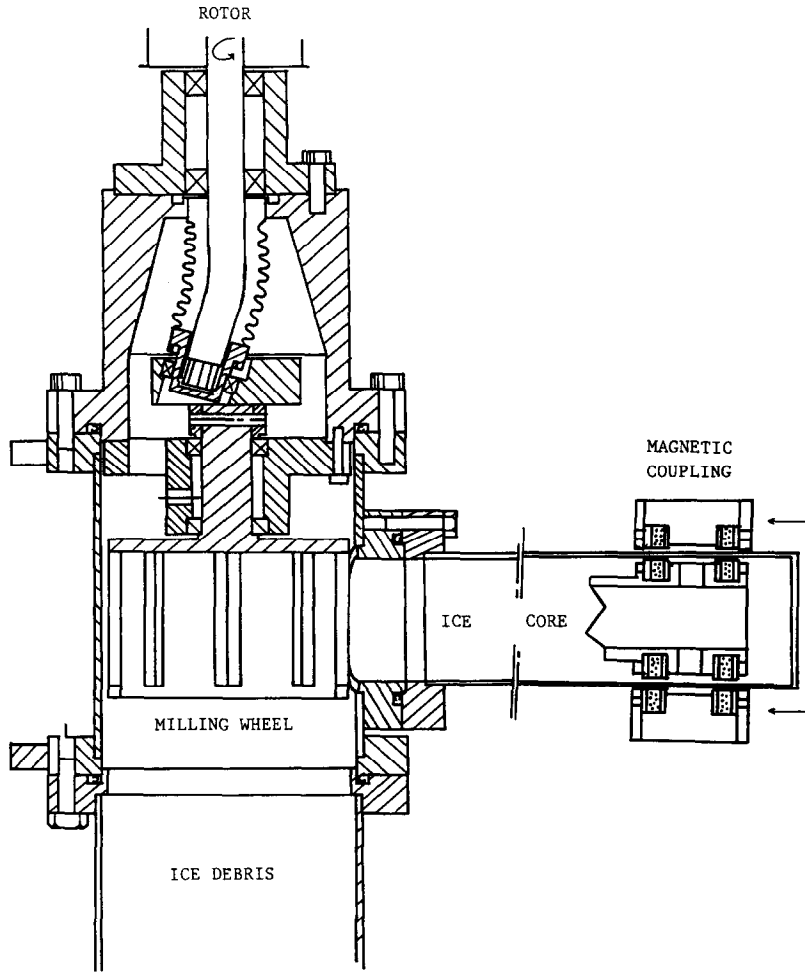


Fig. 1. The ice milling machine.

ground contamination for sample smaller than $150 \mu\text{g}$ C. The background, estimated to be $2.0 \pm 1.0 \text{ pmC}$, is low enough to enable dating of $50 \mu\text{g}$ samples back to

30 000 yr B.P. The measured background corresponds to an absolute contamination of $\pm 1.0 \mu\text{g}$ recent C.

To study the influence of absorption and desorption

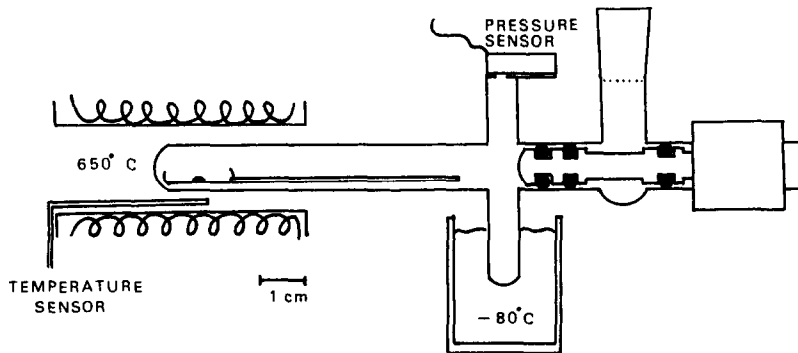


Fig. 2. The mini-graphitization unit.

from the walls of the whole system, the evacuated milling machine was filled with a small amount of NAX gas. After equilibrium for half an hour with the gasses absorbed on the walls the CO_2 was extracted. The experiment was continued by filling the machine with air, so an equilibrium with the surrounding air could be established. The air was evacuated again and the procedure was repeated. Finally the two samples were combined.

No significant increase of the background was revealed for these relatively large samples (corresponding to an absolute contamination smaller than $1 \mu\text{g}$ recent C). In fig. 3, these results are plotted together with the corresponding values for the small NAX gas samples. A realistic comparison with the dating of a real ice core is the assemblage of a $60 \mu\text{g}$ C sample after repeating the above mentioned procedure seven times. The results is a background of 7 pmC , corresponding to an absolute contamination of $\pm 3 \mu\text{g}$ recent C. This is the combined effect of desorption and absorption processes, and graphitisation.

To get an idea of the precision and accuracy of the measurements, a short series of ^{14}C measurements was performed. Standard NAX gas (0 pmC) and standard NOX gas (136.1 pmC) were mixed at different ratios and sizes. In table 1 it can be seen that the precision is more or less independent of the sample size. Dating material with a sample size of about $100 \mu\text{g}$ C and younger than 10000 yr B.P. ($> 30 \text{ pmC}$) can be performed with an estimated accuracy of 2–3%, which is the same order of magnitude as mentioned in ref. [5]. Routine samples give a precision of 1% for modern material.

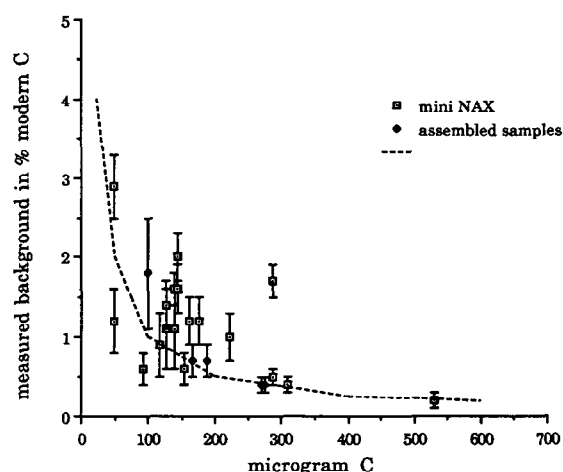


Fig. 3. Background after graphitization of variable amounts of NAX gas. The result of a constant contribution of $1 \mu\text{g}$ recent carbon is given by the dotted curve. Error bars indicate the standard deviation in the measurement. Black dots indicate samples which are assembled in the milling machine.

Table 1
 $^{14}\text{C}/^{12}\text{C}$ ratios for large and small samples

Sample size [μg]	NOX/(NOX+NAX) [%]	Expected [pmC]	Measured [pmC]
116	49.0	66.4	67.9 ± 1.3
1100	49.0	66.4	68.3 ± 1.1
149	74.7	101.6	101.4 ± 1.7
1205	74.7	101.6	101.5 ± 1.5
116	100.0	136.1	133 ± 4
165	100.0	136.1	134.9 ± 1.7
214	100.0	136.1	135 ± 3

In March 1990 an ice core was dated from the margins of West Greenland, Pakitsoq. The estimated age based on comparison with $\delta^{18}\text{O}$ variations in other ice cores, together with ice flow model calculations is about $9000 \pm 1000 \text{ yr B.P.}$ After removing the outer 5 mm of the core, the pieces were loaded and chipped. This procedure was repeated seven times to obtain $60 \mu\text{g}$ C ($20 \mu\text{g}$ C/kg ice and $\pm 100 \text{ ml}$ air/kg ice). The ^{14}C age of $3200 \pm 1000 \text{ yr B.P.}$ ($67 \pm 9 \text{ pmC}$) is obviously far too young. We are convinced that contamination due to the experimental procedure cannot explain this large discrepancy. The age difference corresponds to a ^{14}C activity of $\pm 30 \text{ pmC}$, where the order of magnitude for the contamination is estimated to be only a few pmC, even for $50 \mu\text{g}$ samples. An absolute contamination of $30 \mu\text{g}$ modern carbon is necessary to explain the measured difference in ^{14}C activity. The question remains how to explain the difference in age. The only unknown laboratory contamination might occur during sawing and cutting the ice core to the proper format. The heat caused by this mechanical handling melts the outer surface, so that refreezing of this water film might include recent CO_2 in the core. If we suppose a contamination of 1% of the volume (corresponding roughly to a water film of 1 mm on a core with $\varnothing = 5 \text{ cm}$ and length = 1.4 m), 2500 ppm CO_2 [6], and a solubility of 30 ml air per kg for freezing water, a contamination of $\pm 1 \mu\text{g}$ recent C will result. Adding all laboratory contamination together is equivalent to $\pm 4 \mu\text{g}$ modern carbon. This would have increased the expected value for a core of 9000 years old from $\pm 30 \text{ pmC}$ to $\pm 36 \text{ pmC}$ only. We therefore conclude that a contamination in situ is the most likely explanation. The processed part of the ice core has been taken from 1.7–2.9 m below the ice surface. So meltwater containing dissolved recent CO_2 may have penetrated into the core leading to a high contamination. Several thin blue bands observed in the core consisting of ice that, to judge from its $\delta^{18}\text{O}$ -value, has a different origin than the surrounding ice, support this explanation.

4. Conclusions

Summarizing all sources of contamination gives an estimated total contamination equivalent to $\pm 4\text{--}5\ \mu\text{g}$ modern C. In the future we plan to improve the preparation method on several points (like CO_2 -free gas flushing), and hope to get this value down to $\pm 2\text{--}3\ \mu\text{g}$ modern C.

A contamination of $\pm 4\ \mu\text{g}$ modern C gives an overestimation of the ^{14}C activity of a 9000 year old ice core ($60\ \mu\text{g C}$) by 6 pmC. It certainly cannot explain the age difference (30 pmC) between our result for the Pakitsoq ice core and the result obtained by the $\delta^{18}\text{O}$ variations and ice flow model calculations. Further tests with very old ice are needed to obtain definite evidence on the dating limit of this method.

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