

From $^{14}\text{C}/^{12}\text{C}$ measurements towards radiocarbon dating of ice

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ABSTRACT

A dry extraction method of CO_2 included in glacier ice adds a contamination equivalent to $1.8 \mu\text{g}$ modern carbon for a $35 \mu\text{g}$ C sample. This enables radiocarbon dating by accelerator mass spectrometry of $35 \mu\text{g}$ C samples to about 25 000 BP. Measured $^{14}\text{C}/^{12}\text{C}$ ratios are presented for a part of the Vostok ice core, and for some surface samples; high $^{14}\text{C}/^{12}\text{C}$ values ranging between 65 and 105 pm C indicate in-situ ^{14}C production during the ablation. The reproducibility of radiocarbon dating of ice is demonstrated by results for some parts of the Caroline core, yielding an age versus depth profile, in which the age does not simply increase with depth. The results indicate that the accuracy of radiocarbon dating of ice is not limited by the statistical error arising in the accelerator measurements, but by the uncertainty in the contamination background of the samples and by the in-situ production of ^{14}C .

1. Introduction

The interpretation of ice-core analyses requires an absolute time scale. In some cases it is possible to date ice cores by counting layers caused by seasonally varying parameters. This method is limited by the magnitude of the snow accumulation, the diffusion rate, and the thinning of the layers. In addition ice flow restricts counting layers to inland areas of ice sheets since there are no homogeneous sequences of layers in an ablation zone.

Radiocarbon dating of ice is assumed to be independent of the accumulation rate and can be applied for cores from ablation zones as well. The principal idea is to extract the air included in ice

and to separate the CO_2 from the air. Once the CO_2 has been separated, it can be converted to graphite. Measurement of the $^{14}\text{C}/^{12}\text{C}$ -ratio with an accelerator and the routine procedures of radiocarbon dating will then finally yield the age of the ice sample.

Contamination is a major problem due to the small amount of CO_2 in an ice core. One kilogram of ice containing 100 ml air with 300 ppm CO_2 gives only $16 \mu\text{g}$ C. Large amounts of ice (tons) were needed in the past to obtain sufficient CO_2 for conventional β -decay dating (Oeschger et al., 1966). Nowadays, Accelerator Mass Spectrometry (AMS) enables $^{14}\text{C}/^{12}\text{C}$ measurements on the carbon from only 1–10 kg of cleaned glacier ice. The first successful radiocarbon ages of ice, from an accumulation zone, were presented by Andrée et al. (1984), for samples of 100–140 μg carbon. Variation in background contamination level is

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generally the limiting factor for radiocarbon dating, the more the sample is smaller and older. The small sample size applied for ice dating limits dating of small graphite samples from a ^{14}C -free CO_2 gas to 30 000 yr BP (Van de Wal et al., 1990).

Beside the small sample size, radiocarbon dating of ice is not only hindered by the small sample size but also by additional ^{14}C atoms, produced in-situ by spallation of oxygen by cosmogenic radiation (Lal et al., 1990). The importance of the in-situ production will be demonstrated in $^{14}\text{C}/^{12}\text{C}$ measurements on CO_2 from surface blocks from a blue ice zone in the Sør Rondane Mountains, East Antarctica, and in measurements on a part of the Vostok ice core. The emphasis of the paper will however be focused on the reproducibility of radiocarbon dating of ice, using ice from the Caroline core as a case study.

2. Method

We use an ice milling machine for dry extraction of air bubbles included in ice. This machine is a modified version of the construction used by

Moor and Stauffer (1984). To avoid leakage into the vacuum system a special coupling has been designed using bellows between the bent driving shaft and the milling wheel (Van de Wal et al., 1990). The milling machine is built inside a refrigerator, so chipping can be done at -20°C . A magnetic coupling pushes the ice core towards a milling wheel. The resulting ice debris is collected in a lower reservoir while the extracted air is immediately removed to a gas collection device. In the gas collection device the CO_2 is separated from the air by using liquid nitrogen and dry ice/alcohol (-80°C). The set up is presented schematically in Fig. 1.

The system is cleaned by heating at approximately 50°C for 1 h, maintaining the vacuum conditions by pumping. Before loading the machine with ice, the refrigerator is filled with purified Argon to suppress contamination of the inner walls of the system with modern CO_2 from the air. Finally the vacuum vessel is flushed twice with purified Argon, after the ice has been loaded, but before the milling is started. The operating pressure is determined by the water vapour pressure of the ice, and is in general around 1 mb.

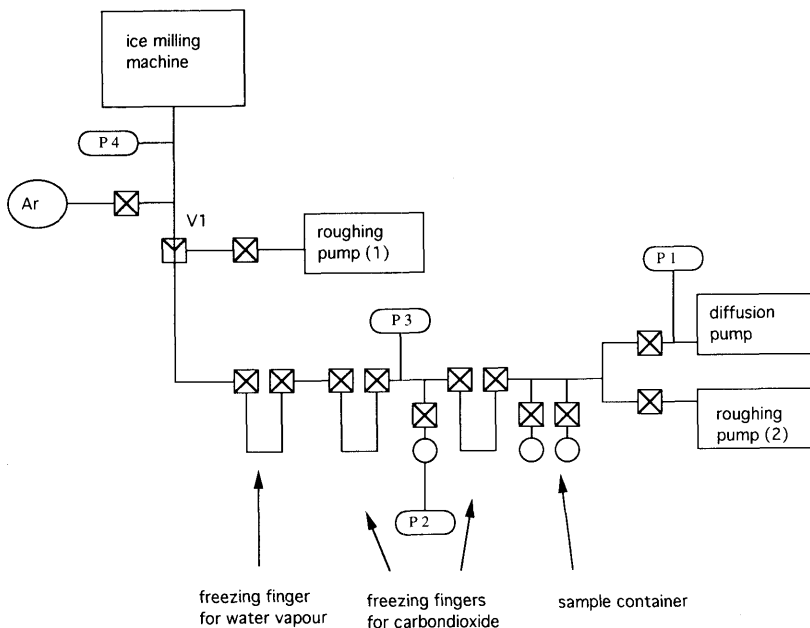


Fig. 1. A schematic view of the experimental set up. $P_{1,4}$ are pressure heads. The squares with crosses are valves. The circles are sample containers and V_1 is a three way valve preventing roughing pump 1 to evacuate the glass device.

To obtain sufficient CO₂ for an AMS measurement the system has to be loaded five to ten times, depending on the amount of CO₂ extracted from the ice. The milling itself takes approximately 20 min depending on the hardness of the ice. To test whether the system has been cleaned properly, desorbing gasses and volatiles are extracted during twenty minutes from a vacuum pumped system. With this experiment residual CO₂ from desorption of the inner walls and small leakages can be measured. The results indicate that the cleaning procedure reduces laboratory contamination during the milling process to less than the equivalence of 0.2 µg modern C for one milling operation.

The resulting CO₂ extracted from ice is reduced to graphite using H₂ and Fe as a catalyst at 610°C (Vogel et al., 1989). Finally the ¹⁴C/¹²C ratio is determined with the tandem accelerator of the University of Utrecht (Van der Borg et al., 1987).

The measured ¹⁴C/¹²C ratio has to be corrected before a radiocarbon age can be calculated. For small samples, as used in this study, this correction procedure is slightly different from the standard routine. Generally all measured ¹⁴C/¹²C values are calibrated using the ¹⁴C/¹²C value of the NOX-standard, to correct for fractionation in the accelerator. Because the ¹⁴C/¹²C value might be dependent on parameters related to the sample size, a NOX-standard matching the sample size, approximately 35 µg C, is measured and used for calibration. It appears that the ¹⁴C/¹²C value measured for these so-called mini NOX samples, are typically about 4% less than the ¹⁴C/¹²C ratio in normal NOX-standard samples of about 1 mg.

Background correction is carried out according to the following equation:

$$A_{\text{corrected}} = A_{\text{measured}} + \frac{M_c}{M_x} \times (A_{\text{measured}} - A_{\text{contaminant}}), \quad (1)$$

in which A is the ¹⁴C/¹²C ratio in pm C (pm C is a dimensionless unit often used in ¹⁴C dating, 100 pm C equals a ¹⁴C/¹²C ratio of 1.19×10^{-12} , being the 1950 value, 50 pm C means one half live time old). M_c and M_x are respectively the mass of the contaminant and the mass of the sample. M_c can be calculated with eq. (1) from background experiments as presented later on. Measurements indicate that all the contamination ($A_{\text{contaminant}}$) is

approximately modern (1991) or equivalent to 100 ± 20 pm C. This equation takes into account that M_c is a significant fraction of the sample size. Simply subtracting the measured ¹⁴C/¹²C of the background from the measured ¹⁴C/¹²C of the sample, yields therefore an overestimation of the background correction.

A third and minor correction is the δ¹³C correction. All ¹⁴C/¹²C measurements are presented by convention for a δ¹³C value of -25‰ . Friedli et al. (1984) measured a δ¹³C value of $-8.3 \pm 2\text{‰}$ PDB for air in Antarctic ice. We applied this value to normalise our measurements on ice samples to the international standard of -25‰ . This results in a correction of -3.3% for $A_{\text{corrected}}$.

The resulting corrected ¹⁴C/¹²C ratio is finally, according to the standard routine converted to a radiocarbon age.

3. Results and discussion

A series of experiments was developed to test the different steps that are taken to obtain a radiocarbon age from ice. In this section, these experiments will be described starting with two types of background experiments and two experiments on surface ice to show the importance of in-situ production for radiocarbon dating of ice. Finally results will be presented from an ice core. Ice from six depths in one core has been measured showing the reproducibility of the ¹⁴C/¹²C measurements and the implications of these measurements.

3.1. Background experiments

To show the possibility of dating very small samples, routine conversion of ¹⁴C-free CO₂ gas (NAX or Carare marble) has been carried out. In Fig. 2a the results are plotted as a function of the sample size. This figure suggests a slightly increasing background with decreasing sample size. A background of 2 ± 1 pm C as observed for 35 µg samples, in Fig. 2a, resulting from *graphitisation and target preparation* enables dating if samples are younger than approximately 30 000 yr BP. Desorption and absorption of modern CO₂ on the inner walls of the ice milling machine, might considerably increase the background for *ice samples*. The expected contamination is enlarged by the necessity to open the machine several times (5–10), before enough CO₂ is extracted for a measure-

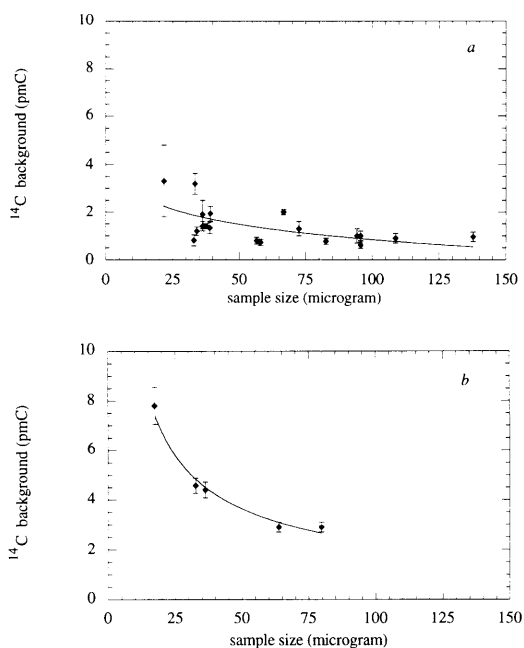


Fig. 2. The background for small CO_2 samples as a function of the sample size (a). The background for the Argon flush tests as a function of the sample size (b). The lines indicate a best fits.

ment. To simulate laboratory contamination more realistic the following simulation experiment has been developed.

After routine cleaning of the milling machine the evacuated machine was filled with a mixture of purified Argon and ^{14}C -free CO_2 (300 ppm). In

this experiment the amount of CO_2 was equal to the amount extracted during milling of a real ice core. The experiment was conducted with ice in the milling machine, to simulate the vacuum conditions as present during milling of a real ice core. The refreezing of the CO_2 took place in about twenty minutes while the milling machine operated, but without chipping ice. This procedure was repeated seven times to obtain an amount of CO_2 equivalent to approximately $35 \mu\text{g C}$. It should be stressed that between the cycles the milling device was opened as if a new ice core had to be loaded. It should also be noted that the vapour pressure during this background experiment equals the vapour pressure during milling of an ice core implicating a similar desorption rate from the milling machine. The results are also independent from the duration of the experiment implicating no leakages during the background experiment. Although this experiment seems complicated, we expect it to provide a good estimate of the background of graphitisation, target preparation, and desorption from the milling machine. The results are presented in Fig. 2b. The figure suggests, as expected, a higher background as compared to only the routine conversion of ^{14}C -free CO_2 shown in Fig. 2a. Based on these measurements we apply a background correction of $5 \pm 1 \text{ pm C}$ for a $35 \mu\text{g}$ sample, yielding a value of $1.84 \pm 0.51 \mu\text{g}$ for the mass of the contaminant (M_c in eq. (1)).

3.2. $^{14}\text{C}/^{12}\text{C}$ measurements and in-situ production

Obviously the best background experiment would be measuring a real ice core that is known

Table 1. Results of the $^{14}\text{C}/^{12}\text{C}$ measurements on ice

Name	Sample size $\mu\text{g C}$	Ice mass kg	$\mu\text{g C/kg ice}$	No. times of charging	$^{14}\text{C}/^{12}\text{C}$ ratio (pm C)	^{14}C age (years BP)	Type of sample
Caroline - 32.5 m	43 ± 1	2.65	16.2 ± 0.5	7	66 ± 2	3500 ± 300	deep core
Caroline - 34.5 m	38 ± 1	2.34	16.1 ± 0.5	8	56.1 ± 1.4	4900 ± 300	deep core
Caroline - 50.5 m	40 ± 1	4.46	8.9 ± 0.2	10	18.0 ± 0.7	15600 ± 900	deep core
Caroline - 58.5 m	33 ± 1	2.35	13.9 ± 0.5	5	34.5 ± 1.5	9400 ± 500	deep core
Caroline - 59.5 m	26 ± 1	2.27	11.6 ± 0.5	5	30.8 ± 1.3	10800 ± 700	deep core
Caroline - 63.5 m	38 ± 1	3.47	10.9 ± 0.3	8	33.2 ± 1.3	9600 ± 500	deep core
Philippe 500	36 ± 1	2.49	14.4 ± 0.5	6	65 ± 2	3600 ± 300	surface ice
Philippe 1500	32 ± 1	1.90	16.9 ± 0.7	5	105 ± 3	-400 ± 300	surface ice
Vostok - 2068 m	16 ± 1	2.13	7.4 ± 0.5	7	97 ± 3	700 ± 400	deep core/ surface ice

A background correction according to eq. (1) has been applied to calculate the radiocarbon age from the measured $^{14}\text{C}/^{12}\text{C}$ ratio. The accuracy of the mass of the samples in column 3 is 0.05 kg for all samples.

to be ^{14}C -free. For this purpose we got the opportunity to use a part of the Vostok ice core from 2061–2075 m below the surface which is 150 000 years old (Barnola et al., 1987), and therefore far below our ^{14}C dating limit. At a depth of 2050 m and 2077 m Barnola (et al., 1987) measured respectively 8.4 and 10.0 $\mu\text{g C/kg ice}$ (191 ppm CO_2 and 85 cm^3 air/kg ice and 196 ppm CO_2 and 95 cm^3 air/kg ice). The extracted amount of CO_2 from the core in our experiment, 7.3 $\mu\text{g C/kg ice}$, agrees with these measurements. It is known that dry extraction underestimates the air content of ice cores (Andr e et al., 1984). The measured $^{14}\text{C}/^{12}\text{C}$ ratio of 97 pm C indicates completely modern ice, see Table 1. It is appropriate here to mention that the extracted amount of CO_2 from the core is independent of the duration of the milling operation. This means that there is no leakage of the milling device during milling. Contamination can therefore be excluded to explain the measured $^{14}\text{C}/^{12}\text{C}$ ratio. In situ production of ^{14}C can therefore be the only possibility to explain the measured $^{14}\text{C}/^{12}\text{C}$ ratio of 97 pm C.

Cosmogenic production of ^{14}C should be considered for this core because the residence time (t) of this part of the core at Vostok, 3500 m.a.s.l., was 4 years (and shielding can be neglected). The in-situ production of ^{14}C is a function of the primary production rate (P_0), the fraction of in-situ produced ^{14}C atoms in the CO_2 (f) and the residence time of the ice at the surface (Lal et al., 1990). This results in 344 ^{14}C atoms/g ice for the Vostok ice core ($P_0 = 215$ atoms/g ice yr at 3500 m.a.s.l., $f = 40\%$, and $t = 4$ years). We measured 97 pm C and 7.3 $\mu\text{g C/kg ice}$ which equals 481 ^{14}C atoms/g ice. The difference between the measured and calculated value is probably due to an underestimation of the calculated in-situ production and can be explained by the uncer-

tainty in the calculations. Laboratory contamination can be excluded to explain the difference.

A second experiment with ice exposed to cosmogenic radiation, are the measurements from a blue ice zone in the S or Rondane Mountains Queens Maud Land, East Antarctica (71 49'S and 24 32'E). Two samples were analysed which have been taken at an altitude of 1051 and 1085 m.a.s.l. and 15 cm below the surface at 25 January 1990. These samples named "1500" and "500" were expected to be 3000 years and 10 000 year-old (based on $\delta^{18}\text{O}$ variations). We extracted 16.7 ± 0.7 and 14.2 ± 0.5 $\mu\text{g C/kg ice}$, respectively, for both samples, indicating a Holocene age. The measured $^{14}\text{C}/^{12}\text{C}$ ratio of these samples is far too high compared to the estimate based on the $\delta^{18}\text{O}$ variations, even more than modern in one case, see Table 1.

The results from the surface samples "500" and "1500" show that in-situ produced ^{14}C is added during the ablation. If we consider the in-situ production being described by the following equation (Lal et al., 1990), we can try to estimate the in-situ production.

$$C_i(x) = \frac{fP_0e^{-\rho x/\Lambda}}{\lambda + \rho a/\Lambda} \quad (2)$$

In this equation $C_i(x)$ is the in-situ production at a depth x below the surface (atoms/g ice), ρ the density of ice, 0.9 g cm^{-3} , a the ablation rate (cm/year), Λ is the absorption mean free path (g cm^{-2}) of cosmic rays causing oxygen spallation in ice, 150 g cm^{-2} , and λ the decay constant, 1/8270 year^{-1} . The ablation rate for the samples "500" and "1500" has been measured in the field for several years and is estimated to be 20 ± 10 cm/year. P_0 is 40 atoms/g year for a height of 1075 m.a.s.l. in polar regions. In Fig. 3a, the

Table 2. A comparison of theoretical expected ^{14}C atoms/gram ice and measured ^{14}C atoms/gram ice for surface ice samples

Name	Natural ^{14}C for modern ice (atoms/g ice)	Estimated natural ^{14}C (atoms/g ice)	Estimated in-situ ^{14}C (atoms/g ice)	Estimated total ^{14}C (atoms/g ice)	Measured ^{14}C (atoms/g ice)
Philippe 500	848	244	122 (81–244)	366 (325–488)	531
Philippe 1500	998	687	122 (81–244)	824 (768–931)	1038
Vostok – 2068 m	436	0	344	344	481

The values between brackets give the range of the calculation due to the uncertainty in the ablation rate.

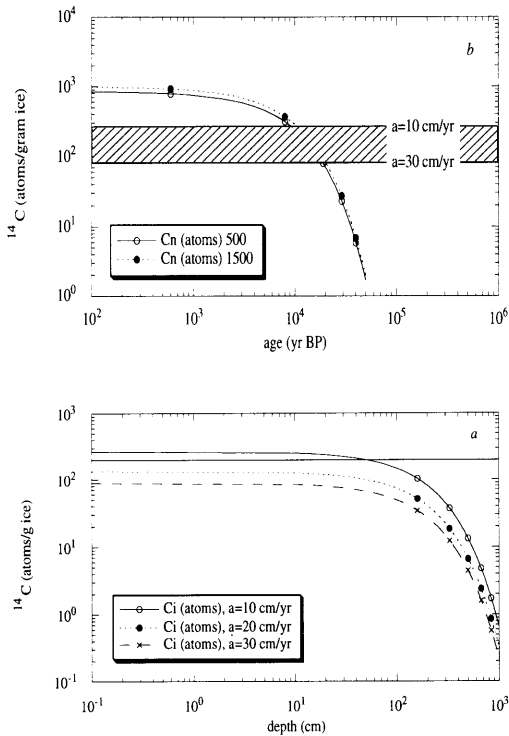


Fig. 3. The in-situ production as a function of the depth below the surface for different ablation rates (a), 10–30 cm/year, at an altitude of 1075 m.a.s.l. The thick horizontal line indicates the natural amount of ^{14}C atoms/g ice, for ice containing $10 \mu\text{g C/kg}$ ice and a ^{14}C age of 10 000 BP. $P_0 = 40$ atoms/g ice year, $a = 20$ cm/year, $\Lambda = 150$ g/cm 2 , $f = 40\%$ (a). The natural ^{14}C content as a function of the age for the "1500" and "500" samples (15 cm below the surface) and the shaded horizontal range indicates the in-situ production at 15 cm depth and 1075 m.a.s.l. for ablation rates of 10 and 30 cm/year (b).

in-situ produced ^{14}C is plotted as a function of the depth below the surface (in cm), for various ablation rates. A mean depth of 15 cm below the surface will result in approximately 122 atoms $^{14}\text{C/g}$ ice due to in-situ production, as presented in Table 2. The uncertainty in the in-situ production is for the moment assumed to be entirely due to the uncertainty in the ablation rate (10 cm/year), resulting in a range of 81–244 atoms, as can be seen in Table 2 and Fig. 3a.

The "natural" amount of ^{14}C atoms is determined by the amount of $\mu\text{g C/kg}$ ice and the age.

The estimated natural ^{14}C atoms/g ice is presented in Table 2. In Fig. 3b, the "natural" produced ^{14}C is plotted as a function of the age (in year BP) for the 2 measured samples "500" and "1500", using the extracted $\mu\text{g C/kg}$ ice as mentioned in Table 1. Additional to the natural ^{14}C atoms, we plotted in Fig. 3b the range for the in-situ produced ^{14}C atoms for a depth of 15 cm below the surface. The Figs. 3a, b show that in this particular case natural and in-situ produced ^{14}C have the same order of magnitude. In Table 2 one can see that the measured ^{14}C is higher than the estimated total amount of ^{14}C . Although the uncertainty mentioned in Table 2, is considerable it suggests an underestimation of the in-situ produced ^{14}C . Beside the uncertainty resulting from the variation in the ablation rate, variations in the in-situ produced ^{14}C atoms in the CO_2 (f) should be considered (Lal and Jull, personal communication), yielding an even larger uncertainty than the one already presented in Table 2. It is however obvious that recalculating measured $^{14}\text{C}/^{12}\text{C}$ ratios to radiocarbon ages is impossible for these surface samples since natural and in-situ produced ^{14}C have the same order of magnitude and the uncertainties in the calculations are very large.

It can be concluded from the surface ice measurements and calculations that in-situ production of ^{14}C should be considered for shallow cores in an ablation zone although this complication can be circumvented by measuring a depth profile or sampling lower than ± 10 m below the surface. Correction for in-situ production during the accumulation is more difficult since it is unknown to what extent ^{14}C atoms exchange with the free atmosphere before pore closure.

Summarising the discussion on the in-situ production one can say that knowledge about the in-situ production during accumulation is necessary before $^{14}\text{C}/^{12}\text{C}$ measurements from ice can be converted to radiocarbon ages.

3.3. Dating the Caroline core

To show the reliability of the $^{14}\text{C}/^{12}\text{C}$ measurements of ice 6 parts from one core have been analysed. For this purpose ice from the "Caroline" core has been used. The "Caroline" core has been drilled in the vicinity of Dumont d'Urville station, $66^\circ 40' \text{S}$, $140^\circ 01' \text{E}$, Terre Adélie East Antarctica in January 1987. It reached bedrock and had a length of 82 m. On the core ice crystal measure-

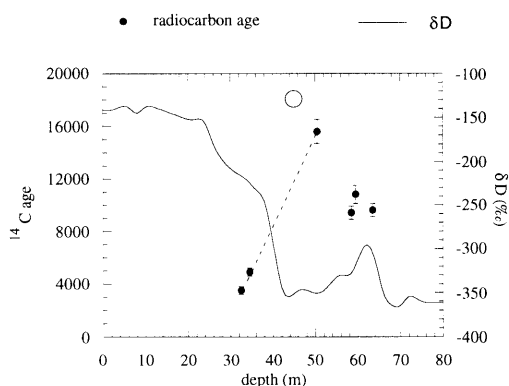


Fig. 4. The radiocarbon age (points) and the deuterium concentration (lines) of the Caroline core as a function of the depth below the surface. The dotted line indicates a logarithmic time scale according to eq. (2) with $C_1 = 26771$ years and $C_2 = 56.4$ m. The large open circle indicates the estimated age by Yao et al. (1990).

ments, bubble concentrations, micro particle and deuterium measurements were made (Yao et al., 1990).

Radiocarbon ages are determined for the parts at 32.5 m and 34.5 m below the surface of resp. 3500 and 4900 year BP (see Table 1). The extracted amount of C/kg ice is an indication for a proper milling procedure since both samples revealed a similar amount of C/kg ice. Moreover the relatively large amount of 15.5 ± 0.5 and $15.8 \pm 0.5 \mu\text{g C/kg}$ ice, respectively, indicates a Holocene Age as measured. These two values as well as the other measurements on the "Caroline" core are plotted in Fig. 4. At a depth of approximately 50 m, the radiocarbon age is 15 600 years BP. The amount of $\mu\text{g C}$ for the 50 m sample (Table 1) is also significantly lower than from both samples around 33.5 m, 8.7 ± 0.2 versus $15.8 \pm 0.5 \mu\text{g C/kg}$ ice, as expected for a sample from the last glacial period. A surprising result is obtained for the three samples around 60 m. Compared to the measurements at 50 m depth higher $^{14}\text{C}/^{12}\text{C}$ ratios have been determined for all three samples resulting in ages around 10 000 years BP. Considerable variation in the extracted amount of CO_2 has been observed for these samples.

Interpretation of the results of the Caroline core is quite interesting. To estimate the natural age difference due to the depth difference of two meters

for the samples of 32.5 and 34.5 m, a logarithmic time scale has been applied (Morgan, 1985).

$$^{14}\text{C}\text{-age} = -C_1 \times \ln\left(\frac{h}{C_2}\right). \quad (3)$$

In eq. (2), C_1 and C_2 are constants and h is the height above the bedrock (m). C_1 and C_2 are calculated from the age and depth corresponding to the measurements at 32.5 ($h = 49.5$) and 50.5 m ($h = 31.5$) depth. (Note that h in eq. (2) equals the length of the core minus the depth below the surface). Although the application of a time scale along an ice core in an ablation zone is a difficult problem we believe this approach gives a good estimate of the age difference, because we consider only a very small depth interval (2 m). The so calculated age difference is 1100 years ($h_1 = 49.5$ m, $h_2 = 31.5$ m, $C_1 = 26771$ years, $C_2 = 56.4$ m). The measured age difference between 32.5 and 34.5 m of 1400 ± 400 years (Table 1) can therefore entirely be explained by the expected natural time difference. This also illustrates that the accuracy of the $^{14}\text{C}/^{12}\text{C}$ measurements of approximately 300 years is not important since the time span covered in a 2-m core section is far larger.

The time lag due to pore close off is estimated to be 6000 years at most for the Caroline core. This means that the result for the 50 m part of $15\ 600 + (6000)$ years is, considering the uncertainty in the estimate of the time lag and the depth difference of 5 m, in quite good agreement with the estimate of 18 000 years BP for a depth of 45 m given by Yao et al. (1990) for the late glacial maximum, based on deuterium measurements, see Fig. 3.

A more complicated picture arises if we consider the radiocarbon age obtained from 63.5 m depth, see Fig. 3. Initially it was expected that the age increased with depth. This idea was based on deuterium content (Fig. 3) and bubble concentration measurements along the "Caroline" core, but dynamic inversion could not be excluded (Yao et al., 1990). Since three samples 58.5, 59.5 and 63.5 m all resulted in an age around 10 000 years BP, it seems to be justified to conclude that at least the $^{14}\text{C}/^{12}\text{C}$ ratio not simply decreases with depth in the core. Although dynamic inversion in this core can be an explanation for the younger age at 63.5 m depth, one other possibility can not be excluded. Assume that the in-situ produced $^{14}\text{CO}_2$ is present in the firn it would mean that the initial

^{14}C activity is dependent on the accumulation rate, a lower accumulation leads then to a higher amount of in-situ produced ^{14}C (Lal et al., 1987). So an apparent inversion of the ^{14}C -time scale might occur, when accumulation changes. In other words variations in accumulation rate resulting in variations of the in-situ production might complicate the interpretation of the measurements.

In favour of the dynamic inversion is the fact that there is a trough in the bedrock of about 1 km depth 250 km upstream from the Caroline core. This might result in a complicated ice flow regime downstream of this trough as indicated by the $^{14}\text{C}/^{12}\text{C}$ measurements. Folding of the ice might result in an inversion in the layering. This would mean that the bulge in the deuterium measurements (Fig. 3) around 60 m depth of -300‰ is not a result of a climate signal, but simply reflects the deuterium value corresponding to the transition of the late glacial maximum, -350‰ , to the Holocene values around -150‰ . $^{14}\text{C}/^{12}\text{C}$ measurements upstream from the trough along a core could clarify this point. Measurements of CO_2 concentration along the Caroline core will also contribute to a better understanding of these results. Another possibility is calculating the in-situ production in an ice core in connection with the flow regime. Presently, there is not enough evidence to be sure that dynamic inversion occurs, but it seems to be the most logical explanation for the observed $^{14}\text{C}/^{12}\text{C}$ measurements.

4. Conclusions

Radiocarbon dating of ice is a method still in progress. Measuring $^{14}\text{C}/^{12}\text{C}$ ratios of ice samples, yielding graphite samples of 35 μg is possible with an accuracy of approximately 1.5 pm C. The statistical error mentioned in Table 1, arising from

the $^{14}\text{C}/^{12}\text{C}$ measurement with the accelerator is typical only a few hundred years. It is also possible to reproduce $^{14}\text{C}/^{12}\text{C}$ ratios for ice in a core from approximately the same depth. The background caused by laboratory contamination seems to be low enough to date ice samples back to at least 15 600 years but probably to around 25 000 years. However the most convincing experiment measuring ^{14}C -free glacier ice never succeeded so far. So the limiting factor for radiocarbon dating of ice is neither the statistical error, arising in the accelerator measurement, nor the background for the small samples used. Uncertainty in the background does certainly not explain the observed inversion along the Caroline core, or the results concerning the in-situ production. The accuracy of converting a $^{14}\text{C}/^{12}\text{C}$ measurement to a radiocarbon age is determined by the in-situ production and the uncertainty due to pore close off from the bubbles. To calculate a radiocarbon age from a $^{14}\text{C}/^{12}\text{C}$ measurement requires beside final evidence on the background therefore more insight in the in-situ contamination. Measurements of modern ice in an accumulation zone and a depth profile in the ablation zone are necessary to provide this insight. The results presented here confirm the conclusions of Lal et al. (1990) concerning in-situ production during the ablation.

Although converting $^{14}\text{C}/^{12}\text{C}$ measurements to radiocarbon ages is a bit preliminary one can state that these measurements already contribute to the climatological interpretation of ice cores.

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