

DATING POLAR ICE BY ^{14}C ACCELERATOR MASS SPECTROMETRY

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ABSTRACT. Results of $^{14}\text{C}/^{12}\text{C}$ ratio measurements on CO_2 extracted from air bubbles in polar ice are presented. The samples investigated originate from the Dye 3, South Greenland, deep ice core and span approximately the last 10,000 years. The results are calibrated with tree-ring records. The ^{14}C ages are compared with information obtained from seasonal variations of ice-core parameters and rheologic model calculation.

INTRODUCTION

Samples of past precipitation are stored in an undisturbed sequence in polar ice sheets. In very cold regions, where the ice is formed by sintering of firn, the gas trapped in air bubbles in the ice represents the gas of the atmosphere at the time of ice formation. The history of many climatic parameters stored in the ice can be reconstructed if an appropriate time scale can be provided for the ice samples.

The time scale can be derived in several ways, as described by Hammer *et al* (1978), who also discuss the advantages and disadvantages of these methods. Attempts to date ice by the ^{14}C technique have been made since the 1950s, when about three tons of ice were molten to recover gas samples which were subsequently analyzed in proportional counters (Coachman, Enns & Scholander, 1958; Oeschger, Alder & Langway, 1967). AMS seems to be an appropriate method to tackle this problem, as it allows reduction of the sample size to ca 10kg due to its factor of 1000 higher ^{14}C detection efficiency (Suter *et al*, 1984). A newly developed dry extraction system (Moor & Stauffer, 1984) reduces contamination with CO_2 originating from the extraction procedure (Zumbrunn, Nefel & Oeschger, 1982) as well as contamination from dissolving carbonates in dust-loaded ice while melting (Schwander, 1980). This increases confidence in ^{14}C ice dating and enables us to extend the dating range and precision.

Possible contributions to the background were mentioned and partly investigated previously (Andrée *et al*, 1984b). We will discuss here only the improvements of reducing and stabilizing the background of sample CO_2 conversion into amorphous carbon as required by the AMS technique.

RESULTS

The ice samples were taken from the Dye 3 deep ice core (65° 11' N, 43° 50' W) South Greenland, drilled from 1979 to 1981 as part of the Greenland Ice Sheet Program (GISP), an American-Danish-Swiss project. Table 1 gives some information on the samples.

TABLE 1
Sample information, Dye 3 ice core

Sample no.	CK28	CK33	CK31	CK29
Depth range (m)	1660.00–1670.91	1703.87–1714.37	1747.53–1750.11 1751.22–1759.30	1770.44–1775.38 1776.46–1785.22
Amount of ice before cleaning (kg)	25.5	21.1	26.2	31.8
Amount of crushed ice after cleaning (kg)	10.3	8.8	9.7	12.1
Amount of CO ₂ after gas separation (cc STP)	0.19	0.20	0.22	0.26
Equivalent amount of carbon before conversion (μg)	99 ± 10	109 ± 10	119 ± 10	138 ± 10

One of the main problems in ¹⁴C dating ice is control of contamination introduced by the extraction and target preparation step. The contribution to the background of the measurement by the dry extraction method can be determined in two ways:

1) Excess CO₂ produced during the extraction process can be measured by milling a gas-free single ice crystal in pure nitrogen gas or in an air standard with well-defined CO₂ concentration. Results of such measurements were published earlier (Andrée *et al*, 1984b). With a correction function the amount of excess CO₂ produced by the milling process can be approximated. In our samples, the excess was $0.40 \pm 0.01\%$ of the CO₂ extracted during a normal sample run. We assume that this excess CO₂ is modern (1950) carbon, but this is not yet confirmed.

2) ¹⁴C concentration in ¹⁴C-free CO₂ after a simulated extraction run can be determined. For this test, ¹⁴C-free CO₂ as extracted from an ice sample was filled into the sample collection container of the dry extraction system. A gas-free single ice crystal and nitrogen gas that had been tested for negligible CO₂ content were put into the mill. Then the single ice crystal was milled and the N₂ gas frozen out. A target was prepared with the separated CO₂ and its ¹⁴C concentration measured, which was $5.96 \pm 0.94\%$ of the standard. This can be compared with the blank value of the target preparation alone as calculated with the calibration curve (see below and Fig 1). The calculated value is $5.56 \pm 0.63\%$ of the NBS standard. The difference between the combined blank of the mill plus the target preparation and the blank of the target preparation alone is $0.40 \pm 1.13\%$. This agrees well with the value measured by method 1, supporting the assumption that the excess CO₂ is modern carbon.

The blank of the small target preparation system can be stabilized and improved by a new cleaning procedure. It can be shown by measurements on blanks of different size that the relative amount of contamination depends on the size of the blank. The results of these measurements are

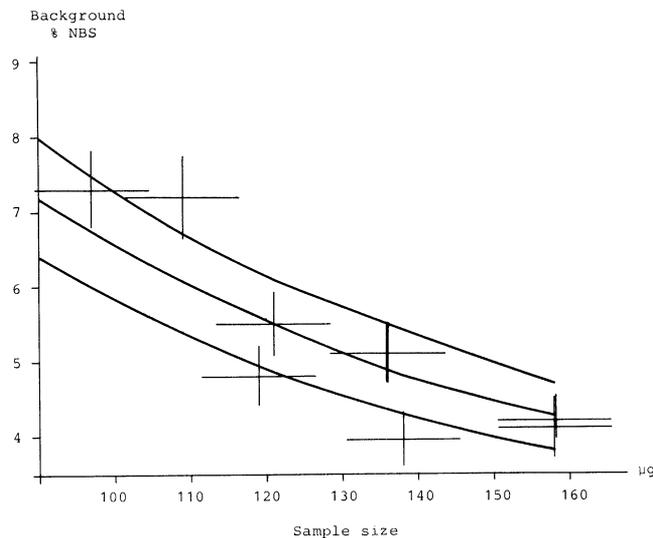


Fig 1. Dependence of background of target preparation on sample size. The middle curve represents the dependence of the background on sample size calculated assuming sample contamination with $7\mu\text{g}$ of modern (1950) carbon. The upper and lower curves mark the error band.

shown in Figure 1. They can be explained by contamination with a constant amount of modern carbon. For our small target preparation system, this amount is $7.0 \pm 0.8\mu\text{g}$.

For background correction of our measurements, the blank of the target preparation system was calculated according to the size of the sample and the blank of the extraction was included. This gave a blank of $5.2 \pm 0.6\%$ to $7.0 \pm 0.8\%$ of the oxalic acid standard for sample sizes from 138 to $99\mu\text{g}$. For the $^{14}\text{C}/^{12}\text{C}$ ratio correction the formula given by Andrée *et al* (1984a) was used with blank values matching the size of the sample and the NBS standard, respectively. The conventional ^{14}C ages are given in Table 2. For the $\delta^{13}\text{C}$ correction, the AMS measured value of $-8.3 \pm 2.0\%$ PDB was used, which is in the range of air $\delta^{13}\text{C}$ values as measured by Friedli *et al* (1984). The errors combine those of the counting statistics and those of the influence of the blank variation with the sample size. The calculation of the absolute ice ages is shown in Table 2. First, the conventional ^{14}C ages must be corrected for ^{14}C variations using the calibration curve of Kromer *et al* (1986) based on tree-ring measurements from Heidelberg and La Jolla (Linick, Suess & Becker, 1985). The correction increases the ^{14}C ages by 900 to 1100 yr and would remain about the same if the ^{14}C ages were some hundred years older or younger. A not yet fully wiggle-matched tree-ring series by Kromer (pers commun) had to be used for the oldest two dates. In order to cross-check and establish the upper error limit of these dates, a compilation of varve data by Stuiver *et al* (1986) was used. Some uncertainty in the absolute ages has to be expected for the older dates because of the still unconfirmed calibration curve.

TABLE 2
Age corrections needed to convert ^{14}C age of air CO_2 into absolute age of ice

Sample no.	Mean depth (m)	^{14}C age of air CO_2 (yr BP)	Absolute age of air CO_2 ($\Delta^{14}\text{C}$ corrected) (yr BP)	Absolute age of ice (yr BP)
CK28	1665.46	5860 \pm 250	6700 $\begin{smallmatrix} + 310 \\ - 330 \end{smallmatrix}$	6790 $\begin{smallmatrix} + 310 \\ - 330 \end{smallmatrix}$
CK33	1709.12	6640 \pm 220	7520 $\begin{smallmatrix} + 170 \\ - 190 \end{smallmatrix}$	7610 $\begin{smallmatrix} + 170 \\ - 190 \end{smallmatrix}$
CK31	1753.42	8380 \pm 510	9460 $\begin{smallmatrix} + 540^* \\ - 850 \end{smallmatrix}$	9550 $\begin{smallmatrix} + 540 \\ - 850 \end{smallmatrix}$
CK29	1777.83	8590 \pm 420	9580 $\begin{smallmatrix} + 420^* \\ - 580 \end{smallmatrix}$	9670 $\begin{smallmatrix} + 420 \\ - 580 \end{smallmatrix}$

* Errors obtained by varve data (Stuiver, 1986).

At this stage, the absolute age of the air in the ice bubbles was obtained. As the gas exchange with the atmosphere is not suppressed until the firn-ice transition is reached and the ice bubbles are closed off, there is a time lag between the age of the ice and the age of the occluded air. In Dye 3, the firn-ice transition is ca 50m deep. For current accumulation, Schwander and Stauffer (1984) measured the close-off depth and obtained a 90-yr time lag. Thus, the absolute age of the ice is 90 yr higher than that of the occluded air (last column, Table 2). It has to be kept in mind that this correction assumes constant accumulation rates. If the accumulation during the early Preboreal and the Younger Dryas (from which periods the samples originate according to the Danish $\delta^{18}\text{O}$ measurements) had been considerably smaller than in the Holocene, the time lag between occluded air and ice would be higher, at least for the oldest date, being close to the transition into Younger Dryas. With the two results published earlier (Andrée *et al*, 1984b) six points are available for comparison with rheologic model results and with ages obtained by counting seasonal variation of the $\delta^{18}\text{O}$ values (Table 3).

TABLE 3
Comparison of all AMS ice-dates with those obtained by ice flow model calculations and variations of the $\delta^{18}\text{O}$ signal (Hammer, Tauber & Clausen, 1986)

Sample no.	Mean depth (m)	Absolute age of ice (AMS) (yr BP)	Absolute age of ice (flow model) (yr BP)	Absolute age of ice ($\delta^{18}\text{O}$ variations) (yr BP)
CK28	1665.46	6790 $\begin{smallmatrix} + 310 \\ - 330 \end{smallmatrix}$	7971	7670 \pm 50
CK5*	1697.85	7660 $\begin{smallmatrix} + 500 \\ - 690 \end{smallmatrix}$	8624	8350 \pm 50
CK33	1709.12	7610 $\begin{smallmatrix} + 170 \\ - 190 \end{smallmatrix}$	8883	8610 \pm 50
CK8*	1732.25	9190 $\begin{smallmatrix} + 800 \\ - 790 \end{smallmatrix}$	9479	9220 \pm 50
CK31	1753.42	9550 $\begin{smallmatrix} + 540 \\ - 850 \end{smallmatrix}$	10118	9840 \pm 100
CK29	1777.83	9670 $\begin{smallmatrix} + 420 \\ - 580 \end{smallmatrix}$	10997	10510 \pm 150

* Andrée *et al* (1984b).

DISCUSSION

The main interest of the authors is to test the ^{14}C dating technique through comparison with other age determination methods. Rheologic model results and data obtained by counting seasonal variation of $\delta^{18}\text{O}$ values (Hammer, Tauber & Clausen, 1986) are presented in Table 3. Ages obtained by dating the CO_2 in the air bubbles are generally younger. First, absolute ages based on AMS ^{14}C measurements are compared with results of a model calculation using a rheologic model by Hammer *et al.* (1978). If the absolute age obtained with this method is expressed as percent of the NBS oxalic acid standard and the ratio of the model result to the AMS result is calculated, the ratio is astonishingly constant, namely 0.890 ± 0.046 . As the comparison of the $\delta^{18}\text{O}$ results with the model results shows, the model seems to yield ages that are too old. The ratio was recalculated with the $\delta^{18}\text{O}$ ages and yielded 0.926 ± 0.043 . The first ratio determination can be considered an upper limit for the offset of the ice data. The second is probably the better estimate, but more data points are needed to establish the true ratio.

How can this offset be explained? As the correlation between sample size and the ratio of the AMS determined age to $\delta^{18}\text{O}$ seasonal variation determined age is low (correlation coefficient 0.58), a constant, system-specific contribution of modern carbon can only be part of the explanation. The following are possibilities for error:

- 1) The sample becomes contaminated by the coring process, *ie*, by the fluid filled into the bore hole. However, this should lead to older ages as the fluid is from fossil fuel. Further, it seems unlikely that the carbon in the fluid could exchange with the CO_2 in the air bubbles. A third argument against this hypothesis is the thorough cleaning of the ice before milling.

- 2) Modern carbon gets into the sample during storage of the cleaned ice before milling, perhaps through adsorption of CO_2 in cracks or at the ice surface. The influence of this effect is hard to estimate. It seems astonishing that the adsorbed CO_2 should not desorb due to sublimation during the evacuation of the ice mill before the actual milling process. Further, obvious cracks were cut out during cleaning.

- 3) The milling process contaminates the sample. This should show up in the blank check of the ice mill. As the mill was only opened once during the blank test extraction and the ^{14}C -free CO_2 had not been expanded into the ice mill, this contribution may have been underestimated. To check this hypothesis the absolute amount of contaminating modern carbon (in μg) was calculated and divided by the number of fillings of the ice mill needed for each sample. On the average, $0.4 \pm 0.2\mu\text{g}$ modern carbon was added per filling, but the scatter is large and not systematic. Although it is difficult to simulate realistic extraction runs, further checks of the background of the milling process are necessary. It would be helpful to have very old ice ($>100\text{ky}$) available for such tests.

- 4) The sample is contaminated during gas separation. Such contamination should have shown up in the blank check of the ice mill. Again, we would expect it to be sample-size-dependent.

- 5) The background of the target preparation system has been underestimated. This can be checked by further studies of the background of the

target system. An argument against this hypothesis is that the offset remained the same although the blank of the target preparation had been improved and the cleaning procedure changed.

6) The measurement has an offset. It could be that air CO₂ adsorbed at the amorphous carbon deposits plays an important role with such small sample sizes and thin deposits. We would expect this to show up in the target preparation background checks.

As this discussion shows, the origin of the offset needs further investigation to eliminate the offset or, at least, to get a well-defined correction factor.

CONCLUSION

Our research shows that ¹⁴C dating of ice samples of reasonable size from cores of good quality is possible. The uncertainty in the age determination is still considerable. It is, as yet, not possible to check the synchronism of events in the northern and southern hemispheres with enough accuracy. Nevertheless, the method can be useful to establish an approximate time scale if no other dating method can be applied, *ie*, in deep cores of the Antarctic. The technique is also useful in setting limits to the minimum ages obtained by deep drilling. Presently, the maximum measurable age for 100 μg samples, assuming a blank value of 7% (ice mill + target preparation blank) and using the methods of Stuiver and Polach (1977), is ca 35,000 yr. ¹⁴C dating of ice is a complex problem. Some steps have been made towards its solution, but more research is necessary.

ACKNOWLEDGMENTS

This work was financially supported by the Swiss National Science Foundation. The deep drilling program to recover ice samples was supported by the American National Science Foundation, the Danish National Science Foundation Council, the Commission for Scientific Research in Greenland, and the Swiss National Science Foundation. We thank W Dansgaard and H Tauber, University of Copenhagen, for providing us with their δ¹⁸O results before publication. We also thank B Kromer, Heidelberg, for providing us with his latest tree-ring data.

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