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Very little in situ produced radiocarbon retained in accumulating Antarctic ice

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Abstract

Ice samples from Dronning Maud Land, Antarctica, were analyzed for $^{14}CO_2$ and ^{14}CO by accelerator mass spectrometry. Only a small amount (~2%) of in situ produced radiocarbon was detected. The calibrated radiocarbon ages, corrected for in situ produced ^{14}C, are in fair agreement with age estimates obtained from stratigraphical methods added to a gas inclusion model. The ages of the entrapped air range from recent to ca. 1200 AD.

Keywords: In situ ^{14}C production; Radiocarbon dating; Ice; AMS; Antarctica

1. Introduction

Radiocarbon dating of atmospheric CO_2 entrapped in polar ice is complicated. First, the samples to be used for dating are very small (typically ~35 μg of carbon) and the effects of (laboratory) contamination are accordingly large. Then, one does not have a perfectly closed system: in situ production of ^{14}C by cosmic rays is by no means negligible at high latitude [1,2].

Fast neutrons, generated by cosmic rays, produce ^{14}C in spallation reactions on oxygen nuclei in ice (and in snow or firn). The hot ^{14}C atoms are oxidised to ^{14}CO or to $^{14}CO_2$, which will mix with the atmospheric $^{14}CO_2$ component; correction for this effect is obviously a pre-requisite for radiocarbon dating [3–6]. Such a correction can be derived from the measured amount of ^{14}CO (completely due to in situ production, as the atmospheric ^{14}CO component is negligible), provided that the $(^{14}CO_2/^{14}CO)_{\text{in situ}}$ ratio is known. In that case, the in situ process presents not only a complication but also a new possibility: in an ablation area, measured ^{14}CO and $^{14}CO_2$

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concentrations as a function of depth can be used to calculate ablation rates [1–4].

Previous work in our laboratory, on ice from an *ablation* area in Scharffenbergbotnen, Antarctica [3,4], has revealed an average $(^{14}CO_2/^{14}CO)_{\text{in situ}}$ ratio of 3.8 ± 0.8 [4]. In the present study, we analyze a number of ice samples from an *accumulation* area at an altitude of 2400 m, at Camp Victoria, Amundsenisen, 76°S, 8°W. Significant in situ production of radiocarbon by fast neutrons is restricted to the first ~15 m of firn, while the pore closure at this site occurs at 71 m depth [7]. So it is to be expected that most of the in situ produced $^{14}CO_2$ and ^{14}CO will diffuse out of the firn matrix and subsequently escape via the pores before these are closed, although a small fraction may stay behind. The purpose of this study is to check and quantify this idea. In addition, the validity of radiocarbon dating will be checked by comparison with stratigraphic methods.

2. Experimental set-up

The ice milling machine (IMM) [3,4] consists of a core holder with a magnetically driven piston to push the ice core, a rotating wheel with knives and a vessel for the ice debris. The IMM is mounted in a freezing box at −35°C and connected to a (Pyrex) gas collection system at room temperature. The (revised) gas collection system contains cold traps, to remove water vapor and CO_2, and a reaction vessel with a platinum wire for the oxidation of CO. A schematic drawing of the present-day experimental set-up is shown in Fig. 1.

3. Experimental procedure

Ice cores were sealed in polyethylene bags and transported and stored below −15°C. After weighing, a core (ca. 2.5 kg) was placed in the core holder of the IMM and the system pumped to water vapor pressure with an oil-free pump. Surface contaminants were removed by sublimating the outer layer of the core, for one day, under dynamic vacuum at temperatures below −15°C. An accurately known amount of ^{14}C-free CO-gas (ca. 70 μl STP) was injected into the IMM and the ice core was milled at −35°C in ca. 20 min. The amount of released air was deduced from pressure measurements with a capacitance manometer. Water vapor and CO_2 were collected in cold traps. A second CO_2 fraction was subsequently obtained from the remaining air/CO mixture, by leading it over platinum wire at 300°C; the CO combustion efficiency was better than 95%. The mass of the two carbon dioxide fractions was calculated from the pressure measured with the capacitance manometer. The CO_2 fractions were then converted into graphite samples for accelerator mass spectrometry (AMS) measurement of the ^{14}C activity.

A number of simulation tests both with 'dead' and with modern (CO_2 + CO), and with oxygen as carrier gas were performed, in order to determine a ^{14}C background for the CO_2 and CO extraction/graphitization procedures.

4. Radiocarbon results and discussion

The AMS-measured ^{14}C activities are corrected for sample mass-dependent fractionation and

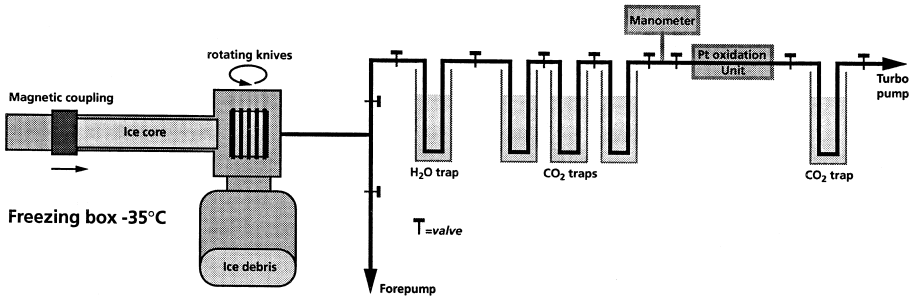

Fig. 1. Schematic drawing of the ice milling machine and the gas extraction system.

Table 1
Measured ^{14}C activities (corrected for line blanks) of CO_2 fractions extracted from the ice

Av. sample depth/m	Air content/ml STP/kg ice	^{14}C Activity/pmC		^{14}C Age range/yr cal AD
		$CO_{2,\ measured}$	$CO_{2,\ corrected}$[a]	
77.3	93.5	101 ± 1	97 ± 3	1433–1955
77.9	95.3	102 ± 3	98 ± 4	1436–1955
126.1	104.8	96 ± 1	92 ± 3	1162–1449

[a] Corrected for in situ production, using a ratio $(^{14}CO_2/^{14}CO)_{in\ situ}$ of 3.8 ± 0.8 [4] and an average ^{14}CO activity of 0.9 ± 0.6 pmC.

contamination as described by Alderliesten et al. [8], using blanks and standards treated in the same manner as during gas extraction of ice samples. The ^{14}C activities of the CO fractions are close to the background value for CO blanks. A mean concentration of 9 ± 6 molecules ^{14}CO/g ice was deduced for the three ice samples. The relatively large error is primarily caused by the observed fluctuations in the background level. When this result is combined with the in situ $^{14}CO_2/^{14}CO$ ratio of 3.8 [4], this leads to approximately 40 in situ produced ^{14}C atoms per gram of ice. For ice still containing all in situ produced ^{14}C atoms (no escape before pore closure), the ^{14}C concentration can be calculated using the model by Lal et al. [1]. For the altitude, latitude and meteorological data [7,9] of the present location we find approximately 2400 at./g. So we observe that ~98% of the in situ produced ^{14}C escaped from the firn before pore closure. This result compares well with the ~3% retained in situ ^{14}C, obtained by Wilson and Donahue [5] on two ice samples of the GISP ice core.

The measured air contents and ^{14}C activities of the ice samples are summarized in Table 1. From the total $^{14}CO_2$ activities (column 3) the in situ corrected values (column 4) are derived. For the present samples the correction is rather small, but its relatively large uncertainty, due to the error in the mean ^{14}CO concentration, clearly increases the uncertainty in the corrected values, see Table 1. The in situ corrected values are converted into historical ages (column 5) using the calibration program of Stuiver and Reimer [10].

To compare our radiocarbon ages with ages derived from volcanic horizon identification with di-electrical profiling (DEP)/electrical DC conductivity (ECM) measurements, the age difference between trapped air and the ice matrix must be known. The age of the ice matrix at pore closure, at this site, can be calculated from the accumulation rate (62 mm water equivalent/yr), the −10 m temperature (−38.5°C) and the initial density of the snow pack (325 kg/m^3) [7,9,11], which leads to 740 yr. According to Schwander and Stauffer [12], the average age difference between the air captured in the ice and the ice matrix is equal to the age of the ice matrix at a density of 815 kg/m^3. For this site, this leads to 670 yr (estimated error ± 100 yr), see Fig. 2. (At 815 kg/m^3 ca. 50% of the air which will be eventually in the ice has been trapped.) Details about the underlying gas enclosure modeling can be found in Schwander and Stauffer [12] and Barnola et al. [13]. A comparison between the radiocarbon ages of the air and the air ages obtained from stratigraphical methods, using the

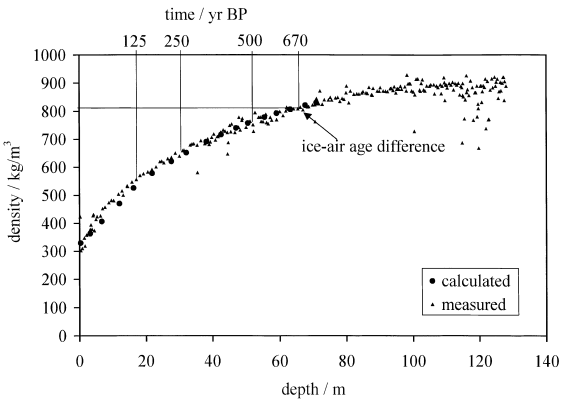

Fig. 2. Measured and calculated firn/ice densities as a function of depth. Calculations are based on the method by Herron and Langway [11] for an accumulation rate of 62 mm weq/yr, a mean annual −10 m temperature of −38.5°C, and an initial snow density of 325 kg/m^3 [7].

Table 2
Age of ice matrix and captured air, based on (i) well-dated volcanic eruptions identified with DEP/ECM [9], (ii) the theoretical Nye time scale, assuming a constant vertical strain rate [14], and (iii) radiocarbon. The (ice–air) age difference used is 670 yr (estimated error ± 100 yr). Estimated error DEP/ECM interpolations ± 25 yr

Depth/m	Age ice/yr cal AD		Age air/yr cal AD		
	Nye	DEP/ECM	Nye	DEP/ECM	^{14}C[a]
71.0[b]	1231	1254	1901	1924	–
77.3[c]	1144	1187	1814	1857	1433–1955
77.9[c]	1134	1178	1804	1848	1436–1955
126.1[c]	420	466	1090	1136	1162–1449

[a] From Table 1.
[b] Pore closure.
[c] Average depth of samples.

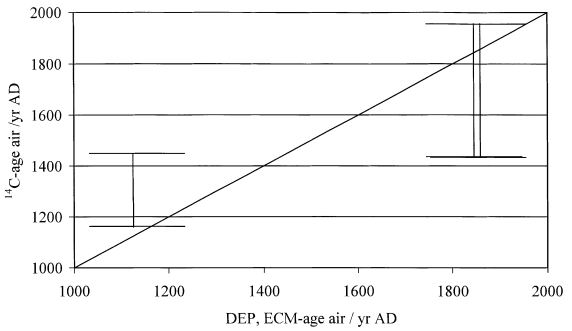

Fig. 3. Comparison of calibrated ^{14}C ages of captured air with results derived by interpolation between volcanic horizons identified with di-electrical profiling and electrical conductivity measurements [7,9], extrapolated to sample depth. An (ice–air) age difference of 670 ± 100 yr was used.

approximate age difference between air and ice of 670 yr, is shown in Table 2 and Fig. 3.

The line drawn in Fig. 3 represents the one-to-one relation between radiocarbon and DEP/ECM results. Note that disregarding in situ production of radiocarbon would make the correlation worse: the radiocarbon ages would become younger. The large uncertainty in radiocarbon AD age for the youngest samples is mainly caused by the radiocarbon calibration curve.

As could be expected a priori, the results obtained at this site by radiocarbon dating of ice at shallow depth cannot compete in accuracy with those obtained by the DEP/ECM methods. However, for drill sites with very low accumulation rates, sites where hiati exist, or at greater depth where stratigraphical methods become more uncertain due to layer thinning, ^{14}C measurements can provide absolute age estimates of the captured air from which ages of the ice matrix can be approximated.

Moreover, at sites where both methods can be applied succesfully, the ice–air age difference can be used to obtain climatic information i.e. temperature and accumulation rates, via inverse modeling with a firn compaction/ice flow model.

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