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In situ produced ^{14}C by cosmic ray muons in ablating Antarctic ice

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ABSTRACT

Samples of a core (52 m) of ablating Antarctic ice were analysed for ^{14}CO and $^{14}CO_2$ by accelerator mass spectrometry. The data were compared with a ^{14}C *in situ* production model that includes muon capture in addition to oxygen spallation by neutrons. The analysis reveals significant *in situ* ^{14}C at depths below 10 m, which we attribute to ^{14}C production by cosmic ray muons. The age of the ice was determined as 9.3 ± 0.4 ^{14}C ka BP.

1. Introduction

In situ production of ^{14}C in ice and quartz by fast cosmogenic neutrons is a well known process in which hot ^{14}C atoms are generated by spallation of oxygen nuclei. In quartz, the hot carbon atoms can only be oxidised to ^{14}CO and $^{14}CO_2$ and field studies of *in situ* ^{14}C production in ice have also focussed only on these two oxidation products. Depth profiles of ^{14}CO and $^{14}CO_2$ have been measured in ice cores, using dry and wet extraction techniques and accelerator mass spectrometry (AMS) (Lal et al., 1987, 1990; Wilson and Donahue, 1992; Van Roijen et al., 1994; Wilson, 1995; Levchenko et al., 1997; Van der Kemp et al., 2000). In ablation areas such profiles may contain information on ice ablation rates (Lal et al., 1987, 1990; Van Roijen et al., 1994).

In situ isotope production by muon capture however, although known in general, thus far has been neglected in ^{14}C studies of polar ice. Here we report the first experimental results on ^{14}C production by muon capture in oxygen nuclei in polar ice.

The *in situ* ^{14}C concentration in ice as a function of depth z can be written as the sum of the neutron and captured-muon contributions, analogous to the equation proposed by Lal et al. (1990). For vertically outcropping ice, originally from a depth with negligible *in situ* production by neutrons and captured muons, and ablating with a constant rate a (cm yr^{-1}) one finds under steady-state conditions

$$^{14}C_{is}(z) = \frac{P_{0n}\, e^{-z\rho/\Lambda_n}}{\lambda + a\rho/\Lambda_n} + \frac{P_{0\mu}\, e^{-z\rho/\Lambda_\mu}}{\lambda + a\rho/\Lambda_\mu}. \quad (1)$$

Here λ denotes the ^{14}C decay constant (1/8267 yr^{-1}), P_0 the ^{14}C production rate (atoms ^{14}C g^{-1} yr^{-1}) at the surface, Λ the absorption mean free path (g cm^{-2}) and ρ the density of the ice (0.9 g cm^{-3}); the subscripts n and μ stand for neutrons and captured muons, respectively. The contribution from knockout reactions by fast muons is small and can be neglected (Heisinger and Nolte, 2000). The 'true' decay constant is used in eqs. (1)–(4); in radiocarbon dating (leading

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to radiocarbon years BP) the Libby value $1/8033\ \mathrm{yr}^{-1}$ is used by convention.

Recently, Heisinger and Nolte (2000) measured $P_{0\mu}$ for quartz by irradiating quartz samples with muons in a laboratory set-up. They deduced $P_{0\mu}(\mathrm{quartz}) = 3.7 \pm 0.3$ atoms $^{14}\mathrm{C\ g}^{-1}\ \mathrm{yr}^{-1}$ for the ^{14}C production at polar latitudes and sea level. This result can be transferred to ice, using the O and Si muonic Coulomb capture probabilities reported by Von Egidy and Hartmann (1982); since the probability for H is not known, but presumably very low, the influence of the hydrogen in the ice was neglected. This leads to $P_{0\mu} = 5.3 \pm 0.4$ atoms $^{14}\mathrm{C\ g}^{-1}\ \mathrm{yr}^{-1}$ for muon capture in ice at sea level and polar latitudes. The best value for the absorption mean free path of muons, derived from a fit to experimental data compiled by Heisinger (1998), is $\Lambda_\mu = 1365\ \mathrm{g\ cm}^{-2}$.

The value for $P_{0\mathrm{n}}$ in ice can be derived from the total (neutron plus muon) surface production rate for quartz (20 ± 4 atoms $^{14}\mathrm{C\ g}^{-1}\ \mathrm{yr}^{-1}$, at polar latitudes and sea level) reported by Jull et al. (1994). Subtracting the muon component and correcting for the difference in oxygen composition leads for ice to $P_{0\mathrm{n}} = 27 \pm 7$ atoms $^{14}\mathrm{C\ g}^{-1}\ \mathrm{yr}^{-1}$. Note that this value is almost a factor of two higher than the value of 15 atoms $^{14}\mathrm{C\ g}^{-1}\ \mathrm{yr}^{-1}$ previously reported as an estimate by Lal et al. (1987; 1990). For Λ_n we adopt the value of $150\ \mathrm{g\ cm}^{-2}$ (Lal et al., 1987). Using the $P_{0\mathrm{n}}$ vs. altitude relation of Lal et al. (1987; 1990) and the above Λ_μ-value, the ^{14}C surface production rates at sea level can be converted into those at the altitude of the coring location (1173 m asl), which leads to $P_{0\mathrm{n}} = 81 \pm 20$ and $P_{0\mu} = 6.0 \pm 0.5$ atoms $^{14}\mathrm{C\ g}^{-1}\ \mathrm{yr}^{-1}$ in eq. (1). With the neutron and muon parameters thus fixed, the ablation rate a is the only unknown in eq. (1).

2. Experimental procedure

A 52 m ice core was drilled at Scharffenbergbotnen, Antarctica, (74°34′40″S, 11°02′58″W, 1173 m asl) during the 1997–1998 SWEDARP (Swedish Antarctic Research Program) field expedition. The coring location is situated in a region with vertical ice flow and a total ice depth of approximately 1000 m. The ice is from local origin and the estimated age based on glaciological data is approximately 10 ka (Van Roijen, 1996). Mean transport depth prior to ablation is estimated to be 500 m.

Gases were extracted from the ice samples (longitudinal section, average length 60 cm, and mass ~ 2 kg) using a dry-extraction technique. The apparatus and the experimental procedure have been described in detail elsewhere (Van Roijen et al., 1994; Van Roijen, 1996; Van der Kemp et al., 2000). Before gas extraction, a spike of an accurately known amount of ^{14}C-dead CO was added to the ice sample and after gas extraction the CO fraction was oxidised over a hot platinum wire to a second CO_2 fraction. The two CO_2 fractions from the ice sample were graphitised on iron powder, following our standard mini-sample procedures (Alderliesten et al., 1998). Radiocarbon measurements were performed on the small graphite samples (~ 35 μg) with the Utrecht AMS facility (Van der Borg et al., 1997). A number of line blank experiments have been performed to determine the background of the entire procedure. Each consisted of a complete gas extraction procedure (with ice, but without milling it), using dead CO and CO_2 and with oxygen as a carrier gas. This revealed a sample-mass dependent background of $58/m_\mathrm{c}$ and $92/m_\mathrm{c}$ pmC for samples originating from CO_2 and CO, respectively, with m_c (in μg) the carbon mass of the sample. In view of the variability of the blank values a worst case error of 50% has been adopted. Note that the samples originating from CO have the higher background, most likely due to a small contamination caused by the platinum catalyst. So CO_2 samples in the $m_\mathrm{c} = 25$–40 μg range have a background of 2.3–1.5 pmC and CO samples in this m_c range of 3.7–2.3 pmC. These backgrounds are taken into account in the data analysis. More details about AMS measurements on very small graphite samples and correction of the data using a fractionation/contamination model are given by Alderliesten et al. (1998).

3. Results and data interpretation

The gas extraction results of the ten samples of the core are listed in Table 1. The gas content ranges from 98 to 123 ml STP/kg ice and shows no evidence for a decrease of gas extraction efficiency with depth, which a possible decrease of bubble size with depth could have induced. (The

Table 1. *Gas extraction data of ice samples*

Depth (m)	Air content (ml STP/kg)	Mass of ice sample (g)	CO_2 concentration (ppmV)
0.9	98	2032	321
1.7	100	1738	328
2.7	99	2058	320
4.1	100	2376	301
8.4	119	1986	296
10.0	103	2256	310
16.5	123	2246	300
25.5	104	2068	300
38.0	100	2173	299
45.0	119	2292	303

The air content and carbon dioxide concentrations have estimated errors of 2%.

ice samples had been stored in our laboratory for two years prior to gas extraction). The CO_2 concentration ranges from 296 to 328 ppmV, which is at the upper end of the range for Holocene ice formed at a mean annual temperature of approximately $-20\,^{\circ}C$ (Stauffer et al., 1984).

The results of the radiocarbon analyses are summarised in Table 2. The errors in the reported ^{14}C activities include the uncertainty in the line blank correction (see Section 2). The measured concentrations of ^{14}CO and $^{14}CO_2$, expressed as molecules per gram of ice, are plotted as a function of depth in Figs. 1 and 2, respectively.

Before reaching the ablation area, natural ice usually contains ^{14}C already, e.g. as $^{14}CO_2$ in trapped air or produced *in situ*, either in the accumulation area or, by fast muons, during horizontal flow. Hence, an extension to eq. (1) is required before it can be fitted to the experimental data, as is outlined below.

We assume that a fixed fraction α of $^{14}C_{is}(z)$ is present as $^{14}CO_2$ and $(1-\alpha)$ in the ^{14}CO form, i.e.

$$^{14}CO_{is}(z) = (1-\alpha)\,^{14}C_{is}(z)$$

and

$$^{14}CO_{2,is}(z) = \alpha\,^{14}C_{is}(z). \tag{2}$$

The measured ^{14}CO profile is fitted with

$$^{14}CO^{fit}(z) = (1-\alpha)\,^{14}C_{is}(z) + {}^{14}CO^{p.a.}_{is}(45\text{ m})\,e^{-\lambda(45-z)/a}, \tag{3}$$

where $CO^{p.a.}_{is}(45\text{ m})$ is the reference value for the 'pre-ablation' *in situ* ^{14}CO component, chosen at the lowest measured depth of the profile (atmospheric ^{14}CO in the enclosed air bubbles is below our detection limit). The exponential in eq. (3) corrects for radioactive decay during the flow of the ice from the reference point to the surface. Similarly, the measured $^{14}CO_2$ profile is fitted with

$$^{14}CO_2^{fit}(z) = \alpha\,^{14}C_{is}(z) + \left[f(z)\,^{14}CO_2^{air}(45\text{ m}) + {}^{14}CO^{p.a.}_{is}(45\text{ m})\left(\frac{\alpha}{1-\alpha}\right)\right] \times e^{-\lambda(45-z)/a}, \tag{4}$$

where $CO_2^{air}(45\text{ m})$ is the reference value for the $^{14}CO_2$ concentration of the trapped-air component

Table 2. *Radiocarbon analyses*

$<z>$ (m)	$m_c(CO_2)$ (μg)	$m_c(CO)$ (μg)	A_{CO_2} (pmC)	$^{14}CO_2$ (molecules g^{-1})	A_{CO} (pmC)	^{14}CO (molecules g^{-1})
0.9	*	35	*	*	12.9 ± 1.4	134 ± 15
1.7	28	36	61.4 ± 3.2	587 ± 30	12.6 ± 1.4	156 ± 17
2.7	32	36	57.6 ± 2.9	530 ± 27	10.1 ± 1.5	105 ± 15
4.1	35	37	48.9 ± 2.1	427 ± 19	6.7 ± 1.3	62 ± 12
8.4	34	36	44.5 ± 2.2	453 ± 23	8.3 ± 1.3	89 ± 14
10.0	35	42	46.6 ± 2.0	429 ± 19	6.1 ± 1.1	67 ± 12
16.5	40	41	40.2 ± 1.7	429 ± 18	5.6 ± 1.2	58 ± 12
25.5	31	37	41.9 ± 2.2	379 ± 20	3.8 ± 1.2	40 ± 13
38.0	32	39	38.7 ± 2.0	337 ± 18	2.2 ± 1.1	24 ± 12
45.0	41	34	39.0 ± 1.7	408 ± 18	4.0 ± 1.3	36 ± 12

$<z>$ is average sample depth; $m_c(CO_2)$ and $m_c(CO)$ are total amount of carbon in the CO_2 fraction and the CO spike, respectively; A is the measured ^{14}C activity; pmC stands for percent modern carbon.
* Graphitisation of CO_2 sample failed.

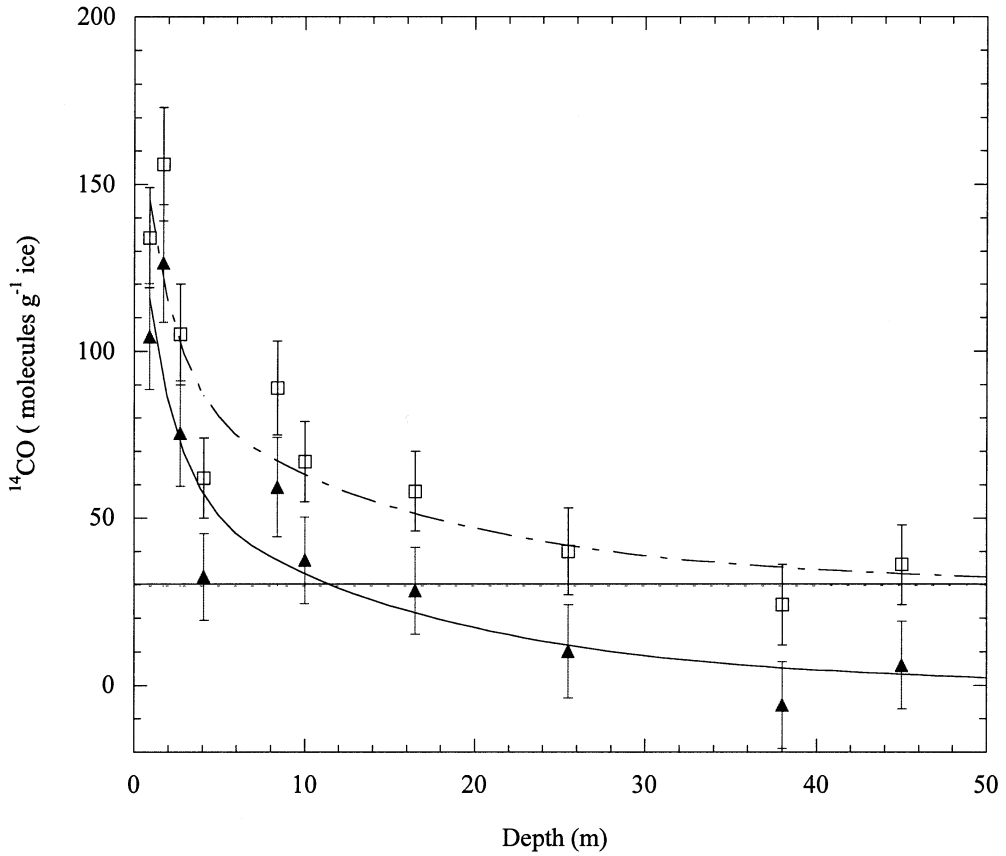

Fig. 1. Concentration of ^{14}CO in Antarctic ice as a function of depth. □, ^{14}CO(total); ▲, ^{14}CO(*in situ*, ablation). The latter is deduced from the measured ^{14}CO concentration by correction for a 'pre-ablation' *in situ* component, eq. (3), of 30 ± 5 molecules ^{14}CO per gram of ice at a depth of 45 m. The dashed line shows this offset in ^{14}CO, corrected for radioactive decay.

and $f(z)$ corrects for the (measured) variation of the CO_2 concentration in the ice at depth z, relative to its reference value. [$f(45\text{ m}) \equiv 1$, and $f(z)$ varies from 0.83 to 1.02.] The z-dependence in eqs. (3) and (4) results primarily from $^{14}C_{is}(z)$, i.e. from eq. (1). The unknowns a, α, $^{14}CO_2^{air}(45\text{ m})$ and $^{14}CO_{is}^{p.a.}(45\text{ m})$ in eqs. (3) and (4) are determined in a least-squares fitting procedure, by minimising Q^2 defined as

$$Q^2 = \sum_i \frac{(^{14}CO^{exp}(z_i) - {}^{14}CO^{fit}(z_i))^2}{\sigma^2_{CO}(z_i)} + \sum_i \frac{(^{14}CO_2^{exp}(z_i) - {}^{14}CO_2^{fit}(z_i))^2}{\sigma^2_{CO_2}(z_i)}, \quad (5)$$

where the σ denote the experimental errors from Table 2. The fitted profiles are shown in Figs. 1–3. The fit yields an ablation rate $a = 44 \pm 3$ cm yr^{-1} and a ^{14}CO fraction $\alpha = 0.69 \pm 0.03$ in the *in situ* component. The two reference values are determined as

$$^{14}CO_{is}^{p.a.}(45\text{ m}) = 30 \pm 5 \text{ molecules/g ice}$$

and

$$^{14}CO_2^{air}(45\text{ m}) = 327 \pm 16 \text{ molecules/g ice;}$$

the age of (the air in) the ablating ice at 45 m depth can be calculated from the latter value as 9.3 ± 0.4 ^{14}C ka BP.

Figure 3 clearly shows *in situ* production of ^{14}C by muon capture: after subtraction of the pre-ablation *in situ* component and the atmospheric

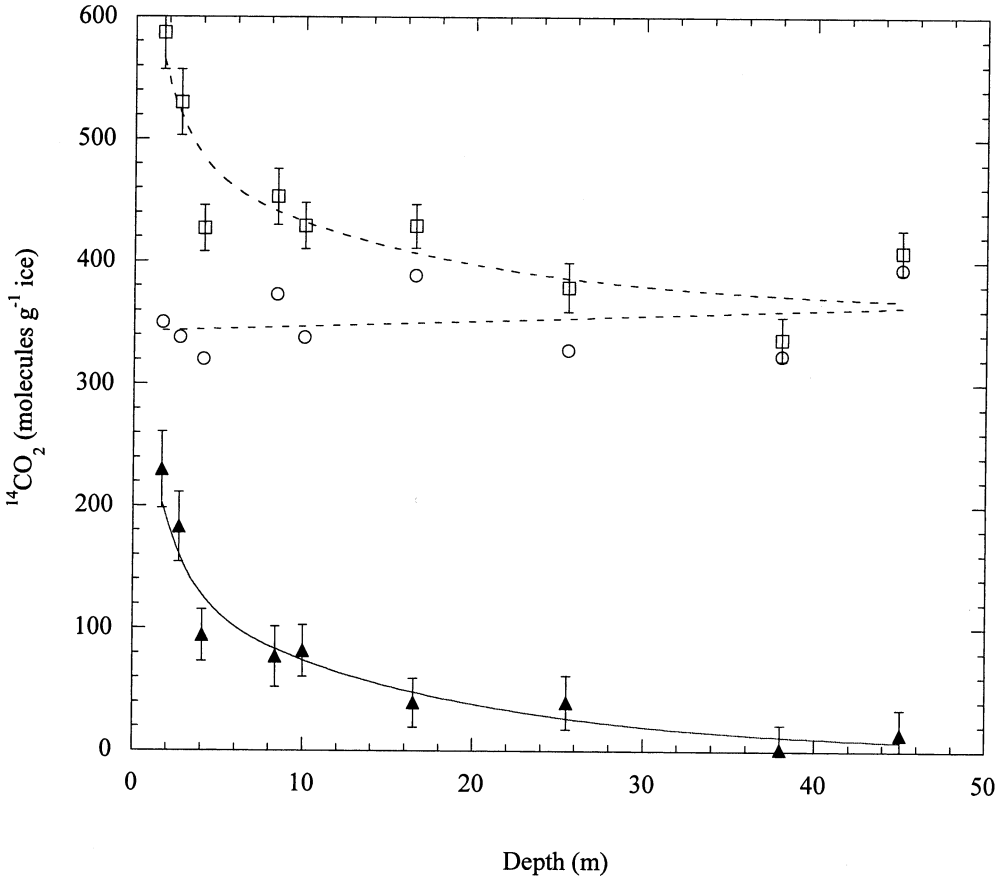

Fig. 2. Concentration of $^{14}CO_2$ in Antarctic ice as a function of depth. □, $^{14}CO_2$(total); ○, $^{14}CO_2$(decay-corrected offset); ▲, $^{14}CO_2$(*in situ*, ablation). The measured total $^{14}CO_2$ concentration is corrected for the variable trapped-air component and for a 'pre-ablation' *in situ* component, using eq. (3). The sum of the two offset contributions at 45 m is 394 ± 9 molecules $^{14}CO_2$ per gram of ice. The dashed lines are to guide the eye. Note that the correction for the variable trapped-air content reduces the scatter in the *in situ* $^{14}CO_2$ points compared to that of the total-$^{14}CO_2$ points.

component, a significant ^{14}C profile remains, reaching far beyond the ~ 5 m layer with measurable n-induced ^{14}C, with the right z-range and the right (order of) magnitude for muon capture, the only other option for *in situ* production.

Quantitatively, however, the amplitude of the ^{14}C *in situ* profile presents a problem: the resulting ablation rate of 44 ± 3 cm ice per year compares badly with a 4-yr average (1988–1992) $a = 16 \pm 4$ cm yr^{-1} from stake readings (S. Jonsson, personal communication), a value well within the empirical range of 9–24 cm yr^{-1} given by Bintanja (1999).

For the following discussion of this factor of 2.8 discrepancy, the small corrections for varying CO_2 concentrations and ^{14}C decay during outcropping are neglected [i.e., we set $\lambda = 0$ and $f(z) = 1$ in eqs. (1), (3) and (4)] and for $^{14}C_{is}(0)$, the amplitude of $^{14}C_{is}$, this gives:

$$^{14}C_{is}(0) = \frac{\varepsilon}{a\rho}(\Lambda_n P_{0n} + \Lambda_\mu P_{0\mu}) = \frac{\varepsilon \bar{P}_0}{a\rho} \qquad (6)$$

where ε is now introduced as the $^{14}C_{is}$ extraction efficiency. A fit to the measured $^{14}C_{is}$ profile (Fig. 3) basically yields $^{14}C_{is}(0)$, and therewith $\varepsilon \bar{P}_0/\rho a$. The discrepancy between results from ^{14}C

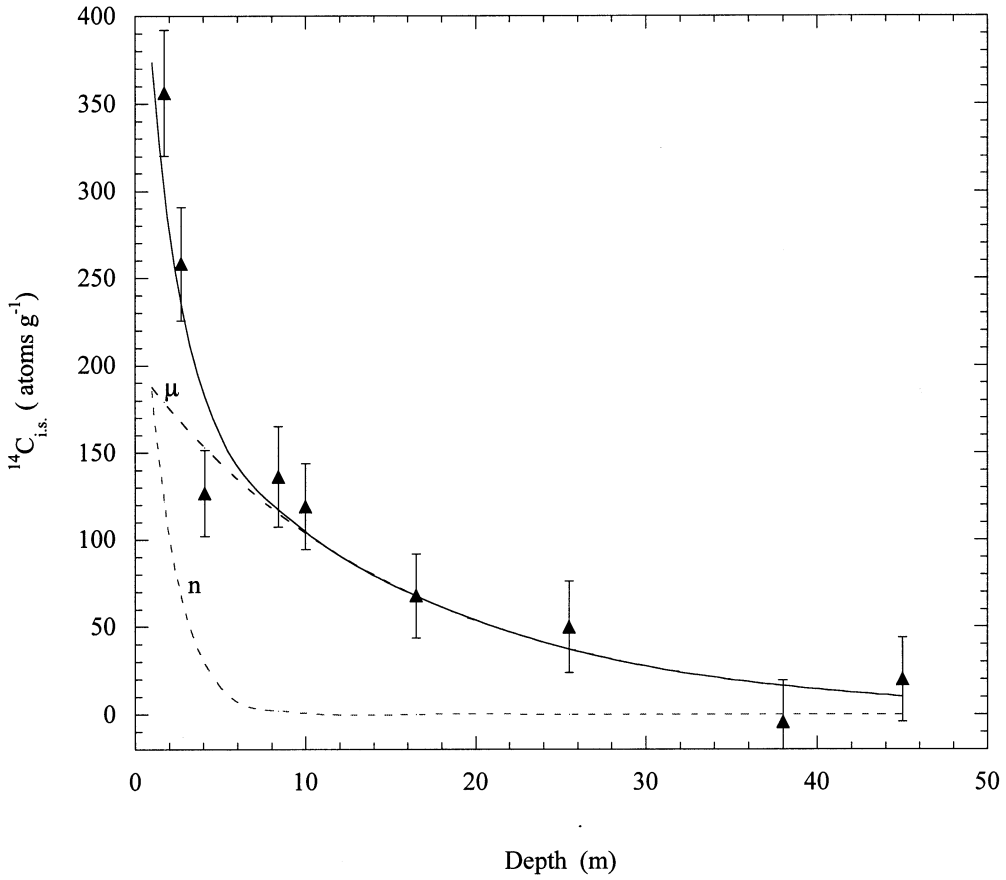

Fig. 3. In situ produced ^{14}C concentrations: ▲, $^{14}CO_{2,is} + {}^{14}CO_{is}$, in Antarctic ice, fitted with eq. (1). For comparison, the separate contributions of neutrons (n) and captured muons (μ) are also shown. Note that the data points between 8 and 25 m cannot be explained by neutron induced ^{14}C or uncertainties in background.

and from stake readings is probably too large to be explained by uncertainties in the ^{14}C surface production rates P_0 alone. As a check, the value of the ratio $P_{0n}/P_{0\mu}$ can be calculated from the measured ^{14}C profile (Fig. 3); the result depends on Λ_n and Λ_μ but hardly on a or α. We find $P_{0n}/P_{0\mu} = 17 \pm 3$, while the ratio (for 1173 m asl) that follows from the literature data is 14 ± 4. This agreement within error seems to support the P_0 values and consequently to indicate that it is primarily our extraction efficiency ε for *in situ* produced ^{14}C which is likely to be wrong, i.e. significantly smaller than one. Laboratory irradiation experiments (Nebeling et al., 1986) have shown that ^{14}CO and $^{14}CO_2$ are not the only possible reaction products of the hot ^{14}C atom in water or ice: methane, methanol, methanal and formic acid can also be formed. These reaction products might be more difficult to extract with our procedure and even when they are extracted, direct graphitisation (without oxidation to CO_2) is not likely to occur. This problem also affects earlier field studies on *in situ* ^{14}C in ice. Previous determinations of ice ablation rates by means of the ^{14}C method (Lal et al., 1990; Van Roijen, 1996) coincidentally showed good agreement with stake readings. Coincidentally, because the P_{0n} value used was based on an estimate (Lal et al., 1987), almost a factor of two below the more recent experimental value of Jull et al. (1994), while *in situ* ^{14}C production by muons was not taken into account.

We conclude that the present uncertainties in P_0 and also in ε require further investigation before more reliable ablation rates can be derived from measured ^{14}C profiles. On the other hand, the significance of muons for the *in situ* production of ^{14}C in polar ice is quite evident from Fig. 3 and fairly in line with the results of Heisinger and Nolte (2000) on quartz.

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