

## A CORRECTION FOR *IN-SITU* $^{14}\text{C}$ IN ANTARCTIC ICE WITH $^{14}\text{CO}$

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**ABSTRACT.** We use a dry extraction method to obtain trapped  $\text{CO}_2$  of shallow ice cores from a blue ice area of East Antarctica. *In-situ*-produced  $^{14}\text{C}$  extracted in  $^{14}\text{CO}_2$  and  $^{14}\text{CO}$  concentrations show a mean ratio of  $3.4 \pm 0.4$ . Correction for *in-situ*  $^{14}\text{CO}_2$  resulted in ice ages within 7–13 ka. The accumulation and ablation rates determined from the *in-situ* production of 7–20  $\text{cm yr}^{-1}$  and 10–13  $\text{cm yr}^{-1}$ , respectively, agree with field measurements, and thus indicate close to total efficiency of extraction.

### INTRODUCTION

In contrast to observing annual layers to date ice,  $^{14}\text{C}$  dating may provide an absolute date and may also be suited for dating ice from ablation zones. Trapped atmospheric  $\text{CO}_2$  is used as the source for  $^{14}\text{C}$  because it remains unaffected after pore closure (Stauffer and Oeschger 1985). However, Lal *et al.* (1990) ascribed increased  $^{14}\text{CO}_2$  concentrations measured in Antarctic ice to *in-situ* production of  $^{14}\text{C}$  by nuclear reactions caused by cosmic rays. The same authors showed the presence of both *in-situ*  $^{14}\text{CO}$  and  $^{14}\text{CO}_2$  in Antarctic ice. In contrast to  $^{14}\text{CO}_2$ ,  $^{14}\text{CO}$  results exclusively from *in-situ* production. If the ratio of these components were constant, as indicated from laboratory experiments (Roessler 1988), we could use the  $^{14}\text{CO}$  component to correct for the *in-situ*  $^{14}\text{CO}_2$  component.

$^{14}\text{C}$  depth profiles in surface ice offer an excellent opportunity to deduce the ratio of *in-situ*  $^{14}\text{CO}_2$  and  $^{14}\text{CO}$ . We present measurements on shallow cores drilled in Antarctic surface blue ice, and use the results to deduce the ages of the cores. In addition, we use the *in-situ*  $^{14}\text{C}$  to deduce the erosion of the blue ice (ablation) and the burial of snow (accumulation) during ice formation.

### METHODS

We obtained samples from a blue ice zone located at Scharffenbergbotnen ( $74^\circ 34'\text{S}$ ,  $11^\circ 03'\text{W}$ ), a cirque-like basin downstream from the Heimefrontfjella nunataks, Western Queen Maud Land, East Antarctica. Several surface ice cores of 3 and 10 m were drilled during the 1993 field season. No drilling fluids were used, and immediately after drilling, the ice samples were sealed in polyethylene bags. The ice cores were kept below  $-12^\circ\text{C}$  during transport by sledge, boat and truck.

We used samples of Cores 5, 6, 15 and 16 in this investigation. Cores 5 (3 m) and 16 (10 m) are in the center of the blue ice area and Cores 15 (10 m) and 6 (3 m) are *ca.* 1 km downstream, close to the headwall. We used a dry extraction method to mill the samples of 1–3 kg. We kept the stainless steel walls at  $-30^\circ\text{C}$  during operation to minimize outgassing. The samples were chipped into small needle-sized particles of *ca.* 2 mm long and *ca.* 0.3 mm in diameter for 20 min. Desorption of  $\text{CO}_2$  was checked at  $< 0.5 \mu\text{l h}^{-1}$  STP.

We added in advance *ca.* 80  $\mu\text{l}$  STP of  $^{14}\text{C}$ -free  $\text{CO}$ , containing *ca.* 40  $\mu\text{g}$  C as a carrier for extraction of  $^{14}\text{CO}$  from the ice. After milling the ice, the  $\text{CO}_2$  of the released air was removed in traps cooled

with liquid nitrogen, and the air containing the CO carrier was adsorbed on a molecular sieve for 45 min. The CO was oxidized by flushing the mixture over CuO at 600°C and the CO<sub>2</sub> obtained was trapped. We made accurate volumetric measurements of CO<sub>2</sub> with a capacitance manometer. The CO<sub>2</sub> samples were converted into *ca.* 20–50 µg graphite samples and analyzed at the Utrecht AMS facility (van der Borg *et al.* 1987). We estimated the background in a study that simulated the entire extraction procedure and obtained a mean value of  $1.4 \pm 0.5\%$  modern carbon (pMC) for 70–140 µl CO and CO<sub>2</sub> samples (van Roijen *et al.* 1994).

## RESULTS AND DISCUSSION

### <sup>14</sup>C Depth Profiles

The CO<sub>2</sub> yields of the ice samples were within 14–18 µg kg<sup>-1</sup>. Further details of the samples were reported elsewhere (van Roijen *et al.* 1995). Table 1 shows the results of the <sup>14</sup>C analysis. Figures 1 and 2 show the <sup>14</sup>CO and the <sup>14</sup>CO<sub>2</sub> concentrations (in atoms g<sup>-1</sup>) vs. depth for Cores 5, 6, 15 and 16, respectively. The presence of <sup>14</sup>CO, even at 10-m depth, indicates that *in-situ* production is important. The exponential decrease of the concentrations vs. depth reflects an attenuation length of 170 cm as expected for cosmic rays in ice (Lal *et al.* 1990). The low <sup>14</sup>CO value in the surface sample of Core 5 cannot be attributed to an experimental uncertainty, but may be due to an enhanced air-loss *via* cracks in the ice. The scatter in the <sup>14</sup>CO<sub>2</sub> concentrations from Core 16 may be due to similar air-loss effects.

TABLE 1. <sup>14</sup>CO and <sup>14</sup>CO<sub>2</sub> Concentrations in Antarctic Ice from Scharffenbergbotnen

Sample	Depth (cm)	Lab no. (UtC-)	<sup>14</sup> CO conc. (at g <sup>-1</sup> )*	Lab no. (UtC-)	<sup>14</sup> CO <sub>2</sub> conc. (at g <sup>-1</sup> )
c-05/01	3–27	3220	92 ± 15	3219	1200 ± 30
c-05/02	30–95	2868	192 ± 11	2867	1000 ± 40
c-05/04	95–155	2990	154 ± 12	2989	790 ± 40
c-05/06	155–224	2998	129 ± 8	2997	740 ± 20
c-05/08	228–294	2992	112 ± 11	2991	710 ± 30
c-06/02	26–70	3017	171 ± 16	3016	780 ± 40
c-06/04	74–135	3231	109 ± 9	3230	626 ± 14
c-06/09	236–303	3011	64 ± 8	3010	456 ± 15
c-15/02	18–83	3020	153 ± 11	3018/3019	820 ± 30
c-15/04	88–152	3222	117 ± 9	3221	724 ± 17
c-15/08	238–300	3224	92 ± 6	3223	580 ± 15
c-15/14	442–499	3227	62 ± 7	3226	584 ± 14
c-15/24/a	721–793	2939	65 ± 13	2938	420 ± 20
c-15/24/b	721–793	2941	51 ± 9	2940	420 ± 16
c-15/32	944–1010	3229	54 ± 6	3228	413 ± 13
c-16/01	4–60	3026	180 ± 20	3024/3025	1280 ± 40
c-16/03	60–113	3241	180 ± 10	3240	1120 ± 20
c-16/08	244–313	3498	110 ± 9	3497	1070 ± 20
c-16/24	755–807	3015	92 ± 13	3013/3014	810 ± 20

\*<sup>14</sup>CO or <sup>14</sup>CO<sub>2</sub> concentrations in ice in atoms g<sup>-1</sup>

**In-situ and Trapped  $^{14}\text{C}$** 

To separate the *in-situ*  $^{14}\text{CO}_2$  signal from the natural component, we follow the procedure described by van Roijen *et al.* (1994). Thus, we fit the equation for *in-situ* production in ablating ice to the  $^{14}\text{CO}$  data

$$C(x) = C_1 \exp(-x/\Lambda) + C_0 \quad (1)$$

where  $C(x)$  is the concentration (at  $\text{g}^{-1}$ ) as a function of depth  $x$  (cm),  $\Lambda$  the attenuation length of cosmic rays in ice (170 cm),  $C_1$  the production coefficient (at  $\text{g}^{-1}$ ), and  $C_0$  a constant (asymptotic) level (at  $\text{g}^{-1}$ ). A similar fit is made to the  $^{14}\text{CO}_2$  data to derive the coefficients  $C_1'$  and  $C_0'$ . The ratio of the *in-situ* production of  $^{14}\text{CO}_2$  and  $^{14}\text{CO}$  is determined by the ratio  $C_1'/C_1$ . Applying this ratio to the  $^{14}\text{CO}$  constant level ( $C_0$ ), we determine the corresponding *in-situ*  $\text{CO}_2$  and use this to extract the natural component. Both *in-situ* contributions at great depth may originate from the accumulation zone when the ice formed. From the natural  $\text{CO}_2$  component deduced, we calculate the age (Table 2) using the zero-age concentration (estimated from the  $^{14}\text{C}$  content of a 100 pMC  $\text{CO}_2$  sample).

Lal *et al.* (1990) showed that the surface *in situ* concentration in ice for a constant ablation rate is

$$C_{\text{tot}} = P_0 / (\lambda + a/\Lambda) \quad (2)$$

where  $C_{\text{tot}}$  is  $C_1 + C_1'$ ,  $P_0$  is the production rate (at  $\text{g}^{-1} \text{yr}^{-1}$ ),  $a$  is the ablation rate ( $\text{cm yr}^{-1}$ ), and  $\lambda$  is the decay constant of  $^{14}\text{C}$  ( $\lambda = 1.25 \times 10^{-4} \text{yr}^{-1}$ ). Using this relation, we calculate the ablation rate with the  $^{14}\text{C}$  production rate  $P_0 = 45$  at  $\text{g}^{-1} \text{yr}^{-1}$  at 1200 m asl for Scharffenbergbotnen (Table 2). We calculate the accumulation rate  $s$  ( $\text{cm yr}^{-1}$  water equivalent (weq)) using the relation,  $R = 0.176 P_0 / s$  (Lal and Jull 1990), where  $R$  is the ratio of the *in-situ* and the natural component, and  $P_0$  is the production rate (at  $\text{g}^{-1} \text{yr}^{-1}$ ). We use  $P_0 = 45$  at  $\text{g}^{-1} \text{yr}^{-1}$  for the production rate at the proximal accumulation zone (van Roijen *et al.* 1995) and  $R$ , as determined from the asymptotic values of the  $^{14}\text{C}$  profiles. The results of the calculations are listed in Table 2, and are within the 0–20  $\text{cm yr}^{-1}$  weq from field observations (Jonsson 1990).

Table 2. Parameters  $C_0$ ,  $C_1$ ,  $C_0'$  and  $C_1'$  (atoms  $\text{g}^{-1}$ ) from fits with  $C(x) = C_1 \exp(-x/\Lambda) + C_0$  (see text) for *in-situ*  $^{14}\text{CO}$  and  $^{14}\text{CO}_2$ , respectively, and deduced  $^{14}\text{C}$  ages, ablation rates and accumulation rates

	Core 5	Core 6	Core 15	Core 16
CO: $C_1$ [at $\text{g}^{-1}$ ]	170 ± 30	170 ± 30	135 ± 14	140 ± 20
CO: $C_0$ [at $\text{g}^{-1}$ ]	74 ± 13	27 ± 12	55 ± 4	88 ± 10
$\text{CO}_2$ : $C_1'$ [at $\text{g}^{-1}$ ]	590 ± 100	530 ± 50	550 ± 130	470 ± 180
$\text{CO}_2$ : $C_0'$ [at $\text{g}^{-1}$ ]	550 ± 40	340 ± 20	450 ± 30	880 ± 80
Production ratio $C_1'/C_1$ *	3.5 ± 0.9	3.1 ± 0.6	4.1 ± 1.1	3.4 ± 1.4
Natural $^{14}\text{CO}_2$ concentration [at $\text{g}^{-1}$ ]	290 ± 120	260 ± 60	220 ± 80	580 ± 200
Zero-age $^{14}\text{CO}_2$ concentration [at $\text{g}^{-1}$ ]†	880	910	1050	1300
$^{14}\text{C}$ age [kyr]	9 ± 3	10 ± 2	13 ± 3	7 ± 3
Ablation rate [ $\text{cm yr}^{-1}$ ]	10.1 ± 1.4	10.9 ± 0.9	11 ± 2	13 ± 4
Ablation rate [ $\text{cm yr}^{-1}$ ] (literature)‡	10	13–16	13–16	10
Ratio $^{14}\text{C}$ ( <i>in situ</i> )/ $^{14}\text{C}$ (natural)	1.1 ± 0.5	0.4 ± 0.2	1.2 ± 0.7	0.7 ± 0.4
Accumulation rate [ $\text{cm yr}^{-1}$ weq]§	7 ± 3	20 ± 10	7 ± 4	11 ± 6

\*Ratio of *in-situ*  $^{14}\text{CO}_2$  and  $^{14}\text{CO}$  used to determine the natural  $^{14}\text{CO}_2$

†Estimated from the  $^{14}\text{C}$  content of a 100 pMC sample (deepest sample)

‡Stake readings (Näslund 1992)

§Elevation of 1240 m asl assumed for accumulation area

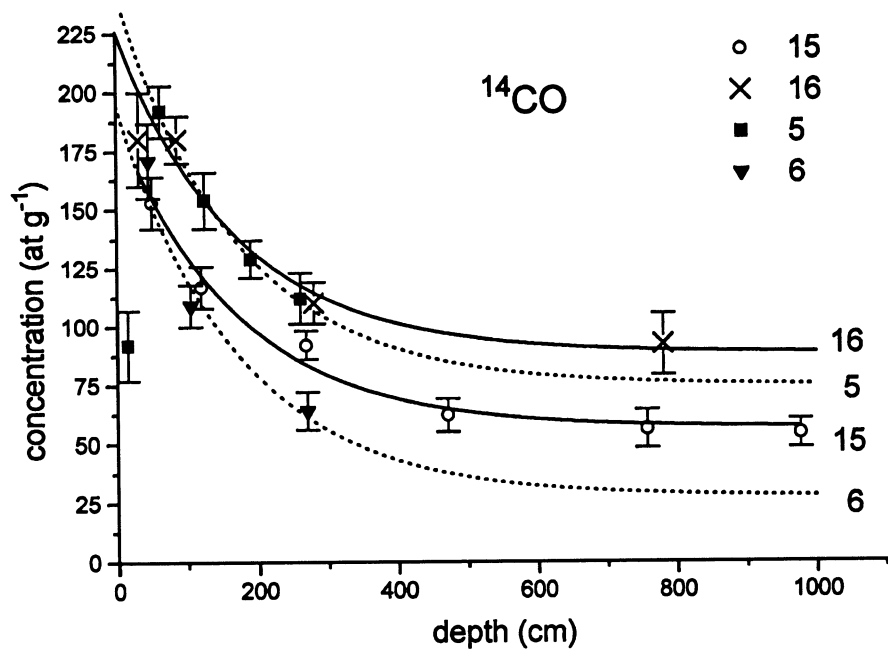


Fig. 1.  $^{14}\text{CO}$  concentration (atoms  $\text{g}^{-1}$ ) vs. depth for Cores 5, 6, 15 and 16. The lines represent fits to the data with  $C(x) = C_1 \exp(-x/170) + C_0$ . The surface sample of Core 5 is not included in the fit.

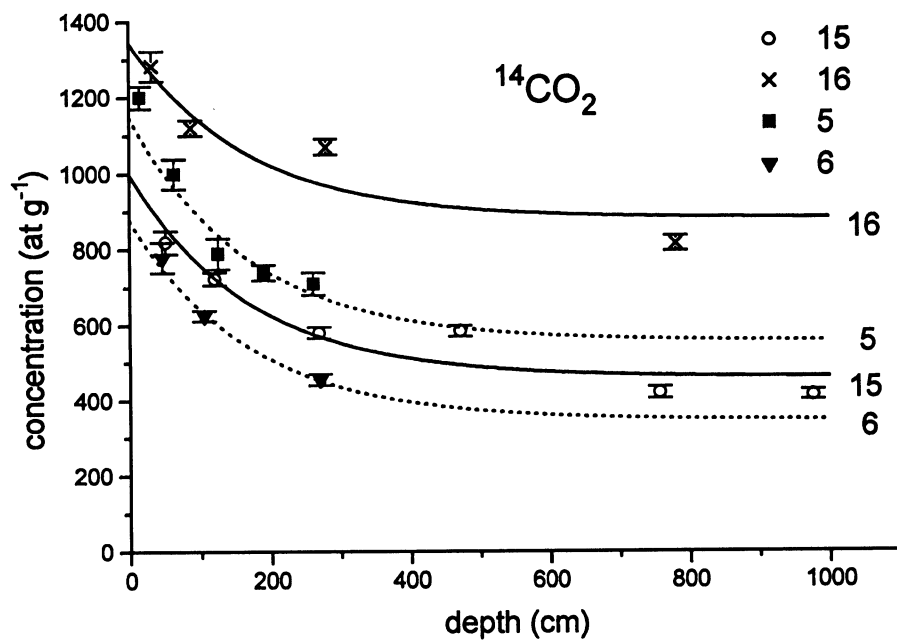


Fig. 2.  $^{14}\text{CO}_2$  concentration (atoms  $\text{g}^{-1}$ ) vs. depth for Cores 5, 6, 15 and 16. The lines represent fits to the data with  $C(x) = C_1' \exp(-x/170) + C_0'$ . The surface sample of Core 5 is not included in the fit.

### Ratio of *In-Situ* $^{14}\text{CO}_2$ and $^{14}\text{CO}$

The ratios  $^{14}\text{CO}_2/^{14}\text{CO}$  obtained for the *in-situ* production agree within uncertainty limits. The mean value is  $3.4 \pm 0.4$ , which is within the reported value of  $6 \pm 3$  from laboratory tests (Roessler 1988). The applicability of these ratios to accumulation areas is a prerequisite for the correction method that is described here. Assuming this, the extracted natural component and, hence, the calculation of the ages will not depend on the efficiency of the extraction method, as the correction method takes this into account. The calculated ablation and accumulation rates agree well with field observations, which would mean nearly total extraction of *in-situ*  $^{14}\text{CO}_2$  and  $^{14}\text{CO}$ . Although we calculated the accumulation rates indirectly from measurements in ablating ice, the values are realistic. This may imply that the total *in-situ*-produced  $^{14}\text{C}$  in the firm of the accumulation area is retained, as has been assumed. Jull *et al.* (1994) also report a high retention of *in-situ*  $^{14}\text{C}$ .

### CONCLUSION

Measurements of  $^{14}\text{C}$  surface profiles show decreasing values with depth. The decrease in depth corresponds to *in-situ* production. The measured production-rate ratios of  $^{14}\text{CO}_2$  and  $^{14}\text{CO}$  are within 3.1–4.1, correlating to a reported value from laboratory tests. Deduced ages are within 7–13 ka. The deduced ablation and accumulation rates agree with field observations, which indicate nearly total extraction efficiency of the method.

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