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CO_2 isotopes as tracers of firn air diffusion and age in an Arctic ice cap with summer melting, Devon Island, Canada

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[1] Firn air and ice have been sampled and analyzed for trace gases (CO_2, N_2O, CH_4, and CO) and isotopes (^{14}C, ^{13}C, and ^{18}O of CO_2; ^3H of ice) at 3 m intervals from the surface to the depth of closure at 60 m on the Devon Island Ice Cap, a low-elevation permanent glacier in the Canadian Arctic Islands, to investigate firn diffusion and the effects of summer melting. The $^{14}CO_2$ profile from the permeable firn includes the 1963 thermonuclear peak at a depth of 53.9 ± 1.5 m. The twofold increase and rapid decay that characterize the recent atmospheric history for $^{14}CO_2$ provide a robust atmospheric scenario that is used with a firn air diffusion model to inversely construct the firn diffusivity profile. The results show a permeable but essentially nondiffusive zone from 50 to 60 m depth. A firn-ice age profile was produced from density measurements, and accumulation rates were calibrated with the depth of the 1963 thermonuclear ^3H peak. The average ages for CO_2 in the sampled firn air profile were determined by a new method based on the rate of ^{18}O exchange between CO_2 and the ice matrix. Calibrated with the 1963 peak for thermonuclear $^{14}CO_2$, a 21.2-year reaction halftime is calculated for exchange taking place at the firn temperature of −22.8°C on Devon. This gives an average age of 54.9 (+6.0/−12.0) years for firn air at 60 m depth in 140-year-old ice. Thus CO_2 has a mean age 85 years younger than associated ice at the point of occlusion. The measured $\delta^{18}O_{CO_2}$ in firn air provides no indication of alteration by summer melting, which is attributed to a high degree of convective and diffusive flushing of the upper firn as shown by diffusion modeling. This suggests that ice sheets with summer melt layers can reliably preserve atmospheric trace gas signals.

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1. Introduction

[2] The trace gas record in air bubbles of ice cores from high-latitude glaciers provides a baseline for calibrating twentieth century increases in anthropogenic gases, although rates of firn accumulation and densification rarely generate an average age of trapped air younger than about 40 years [*Schwander and Stauffer*, 1984]. The atmospheric record found in the firn air column of selected ice sheets can be used to bridge ice core records with direct measurements begun in 1958 [*Keeling and Whorf*, 1998]. Trace gases in the firn air column also provide insights into the densification and air trapping process. Firn air diffusion partly controls the mean age of the firn gases being trapped. However, the rates of firn accumulation and temperature of the glacier greatly affect firn air diffusion, the depth of entrapment and hence the time period preserved by the firn air profile. The effective firn diffusivity profile is then the principal feature controlling firn air diffusion and so is important for reconstructions of the age profile within polar firn [*Fabre et al.*, 2000].

[3] Firn diffusion in dry accumulation ice sheets is well documented [*Schwander and Stauffer*, 1984; *Stauffer et al.*, 1985; *Schwander et al.*, 1988, 1993; *Schwander*, 1989, 1996; *Fabre et al.*, 2000]. Typically, three zones within the firn column are identified: (1) the convective zone, (2) the diffusive zone, and (3) the nondiffusive zone of occlusion [*Schwander*, 1996]. The shallowest is the convective zone, which occurs in the upper ∼10–15 m of firn. In this uppermost zone, wind pumping, barometric and temperature variations in the open atmosphere act to exchange firn

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air with the overlying atmosphere on short timescales and to attenuate any annual variations. In the underlying diffusive zone, mixing of trace gases is due to molecular diffusion with overprints of gravitational settling. Only when abrupt surface temperature change occurs does the diffusive zone experience temperature-driven fractionation of gas composition (thermal diffusion [*Severinghaus et al.*, 1998, 2001]). Between the diffusive zone and the depth of bubble close off (where open porosity is occluded) exists a narrow nondiffusive zone where open porosity exists, but highly restricted permeability precludes vertical diffusion. Typically, this 10–20 m zone starts around 50 to 100 m depth.

[4] Firn air diffusion and occlusion has been mostly studied for cold glaciers with dry firn to preclude the complications that seasonal melting might have on CO_2 mixing ratios and isotopes in preserved firn air. Summer melting is a common phenomenon for low-altitude or low-latitude glaciers. Surface temperatures over a several week period can rise above 0°C, causing snow from the previous season to melt and infiltrate the snow pack. Infiltrating melt water then percolates through the snow pack and refreezes near the base of the winter's accumulation as horizontal lenses and irregularly shaped infiltration channels [*Koerner*, 1977] according to the stratigraphy of the ice (Figure 1). The result is an increase in the anisotropy of firn air permeability, and a reduction in vertical diffusivity [*Fabre et al.*, 2000]. Such firn may preserve a longer firn air CO_2 record with a better time resolution than firn without summer melting. By contrast, the melting that occurs threatens to contaminate the CO_2 record, as well as the ^{13}C and ^{18}O record of the CO_2, through dissolution and chemical reactions during the melt-refreeze cycle [e.g., *Neftel et al.*, 1985]. A study conducted on a high-altitude French glacier did encounter seasonal melting, but the very high wind speed at this location generated unusually high effective diffusivities with depth [*Sturges et al.*, 1996], and erased any effect of melt layers on trace gases. *Trudinger et al.* [1997] noted a significant effect on firn air mixing by a melt layer on Law Dome, Antarctic. *Sturrock et al.* [2002] found that refrozen ice layers complicated firn air diffusion model tuning.

[5] Unlike most Antarctic sites, the low-altitude ice caps of the Canadian Arctic Islands are affected to varying degrees by summer melting, and provide the opportunity to study such effects on firn air diffusion. Accordingly, a firn-air sampling program on the Devon Ice Cap was undertaken in April 1998, in collaboration with the Geological Survey of Canada and the FIRETRACC/100 European research consortium (Firn record of trace gases relevant to atmospheric chemical change over 100 years [*Sturges et al.*, 2001]). In this work, we examine CO_2 and CH_4 in firn air from Devon to determine whether ice caps with summer melting can provide a useful record of atmospheric trace gases. In particular, the distribution of $^{14}CO_2$ is examined as a discrete trace gas with similar diffusive behavior to CO_2 but with a very different atmospheric input history. The 1963 $^{14}CO_2$ bomb peak provides a robust time horizon that can be observed in firn air [*Smith et al.*, 2000] and ice [*Levchenko et al.*, 1996, 1997]. Decoupling of these two trace gases in firn diffusion modeling provides a constraint on the age of firn air CO_2. The exercise also resolves the vertical diffusivity profile and depth of occlusion in firn on a glacier with seasonal melting.

1.1. Devon Island Ice Cap

[6] Firn air samples and core were collected from the summit of Devon Island Ice Cap, Nunavut, Canada (75°20′N, 82°08′W, 1929 m asl). The Devon Island Ice Cap is a subpolar cap within the Canadian Arctic Islands spanning 15,570 km^2 and occupies the eastern portion of Devon Island (31% of the island's area). Snow accumulation on the ice sheet varies from greater than 40 g cm^{-2} y^{-1} on the eastern slopes to less than 25 g cm^{-2} y^{-1} on the northwestern side of the ice cap [*Koerner*, 1979]. *Koerner and Taniguchi* [1976] calculated the accumulation rate to be approximately 22 g $cm^{-2}y^{-1}$ at a nearby site to the present one, on the basis of the depth at which the 1963 tritium peak from thermonuclear bomb-testing is preserved in the firn.

[7] The present atmospheric circulation of the Canadian Arctic Islands is dominated by a westerly circumpolar vortex in the middle to upper troposphere located over the Arctic Ocean [*Maxwell*, 1980]. Regionally, this results in a cold southwesterly air flow in winter. Upon retreat of the Arctic air mass in summer, a more zonal westerly flow predominates, with significant heat and moisture exchange from Baffin Bay to the east. An automatic weather station, located approximately 1 km east of the summit, has been recording weather data since the spring of 1997 and indicates the measured mean annual air temperature to be −23°C (Figure 2). Over the majority of the year, the temperature is well below freezing, reaching lows of −40°C in the winter months. However, up to two weeks in June and early July can experience temperatures above freezing, causing melting of the annual surface layer.

1.2. Field and Laboratory Methods

[8] Firn air was sampled in April of 1998 from 18 intervals between the surface and the firn-ice transition below 60 m depth, on the basis of the extraction method of *Schwander* [1989]. Firn air sampling took place during the initial stage of a drilling program to extract an ice core from the surface to the base of the ice cap. An electromechanical drill developed by the Geological Survey of Canada was used. Firn was cored to the desired firn air sampling depth, upon which the core and the drill were removed from the borehole. A 3 m long inflatable rubber packer with a 5 cm sampling port at the base was then lowered to the bottom of the borehole. The packer was tethered with a braided steel wire cable and an inert, three-tube Dekabon 1/4 inch sampling hose connected to a manifold on the surface that interfaced a metal bellows firn air pump, pressure gauges, and LiCOR infrared CO_2 analyzer. The packer was inflated through one of the three tubes with firn air from the packed-off zone pumped to surface through a sampling tube linked to the bottom sampling zone and back to the packer. Air was also continuously pumped to waste through the third tube connected to the zone immediately below the rubber packer, at a flow rate higher than the air sampled from the lower zone. The purpose of this so-called "Bender baffle" was to remove any possible contamination of firn air from rubber degassing. The CO_2 content of the air pumped through the sampling tube was monitored in order to assess when firn air uncontaminated

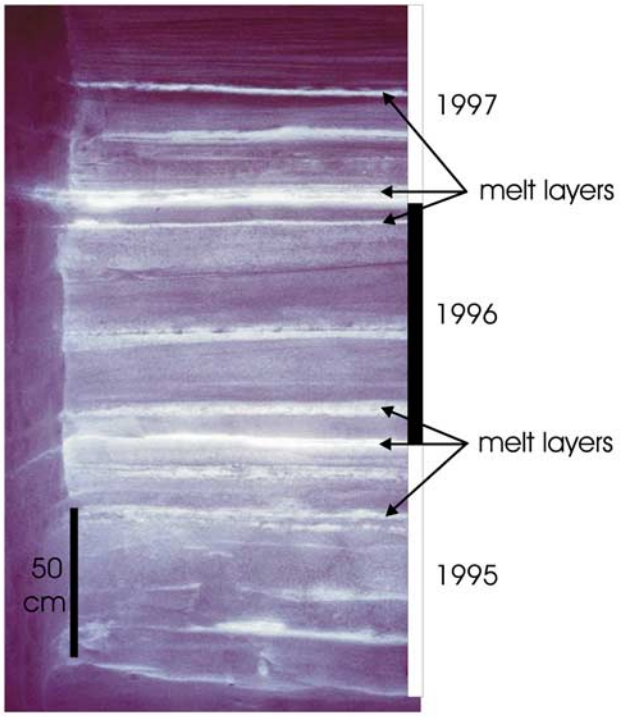


Figure 1. Backlit section of firn stratigraphy showing annual accumulation with melt layers (shown as clear laminations), Devon Island Ice Cap.

from ambient air in the borehole could be sampled. Once the LiCOR stabilized at a minimum CO_2 value (with variations typically in the range of 0.1 to 0.5 ppm), three pre-evacuated 2 L glass flasks were filled to two bars above ambient pressure from each sampling depth for our measurements. All air samples were dried by pumping in-line through an anhydrous magnesium perchlorate column. A surface air sample was also taken according to the same protocol by placing the bladder at the surface, approximately 100 m upwind (southwest) of the drilling site.

[9] Trace gas mixing ratios for CO_2, N_2O, CH_4, and CO were analyzed by gas chromatography at the Meteorological Service of Canada (MSC) laboratory in Downsview, Ontario, Canada (Figure 3). The CO_2, N_2O and CO measurements are directly traceable to the international CO_2, N_2O and CO mole fraction scales maintained by the WMO Central Calibration Laboratories (CCL) at the NOAA/CMDL facilities in Boulder, Colorado. The MSC maintains a set of National Standards that are regularly calibrated by NOAA/CMDL approximately every 2 years. The CH_4 reference scale is propagated from a Standard Reference Material cylinder purchased from the National Institute for Standards and Technology (NBS SRM-1658a, 913 ± 10 ppb). The CH_4 scale employed for this analysis is a factor of 1.0151 higher (approximately 25 ppb at ambient level) than those determined at NOAA/CMDL. The $^{13}C/^{12}C$ and $^{18}O/^{16}O$ composition of CO_2 were also measured at the MSC laboratory by isotope ratio mass spectrometry (MAT 252 dual-inlet mode), and have been corrected for the presence of N_2O (Table 1, Figure 5). The $\delta^{13}C$ and $\delta^{18}O$ values of the reference gas are −11.91 and −10.38, respectively, on the primary scale of VPDB-CO_2. Details of the traceability for isotope measurements at MSC can be found in the work of *Huang et al.* [2003]. Measurement precision was ±0.05‰ for $\delta^{13}C$ but was much larger (±1‰) for $\delta^{18}O$

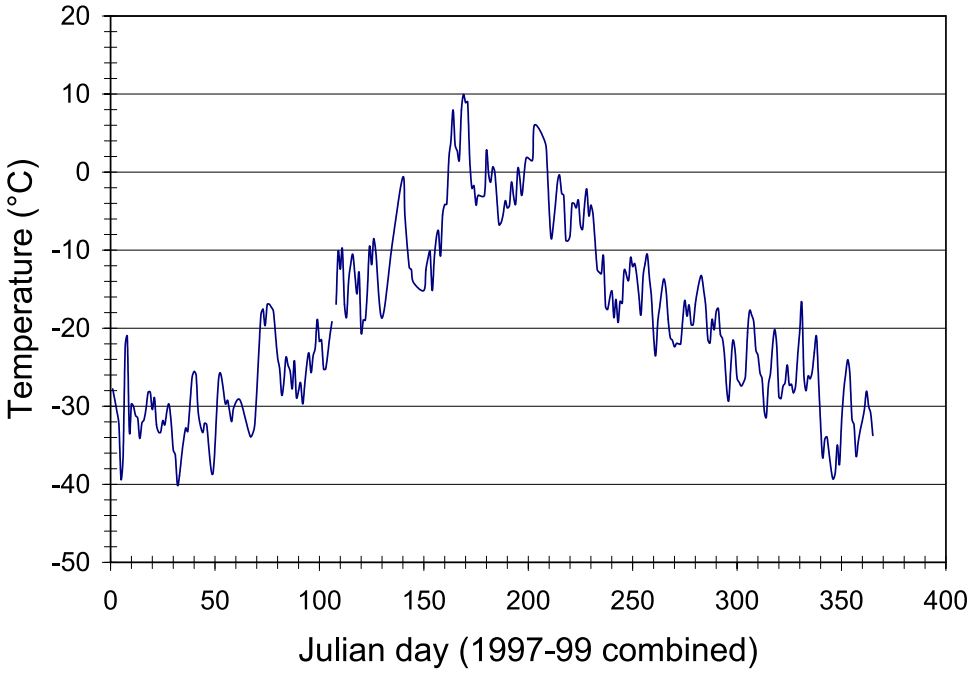


Figure 2. Seasonal temperature variation for the summit of the Devon Island Ice Cap.

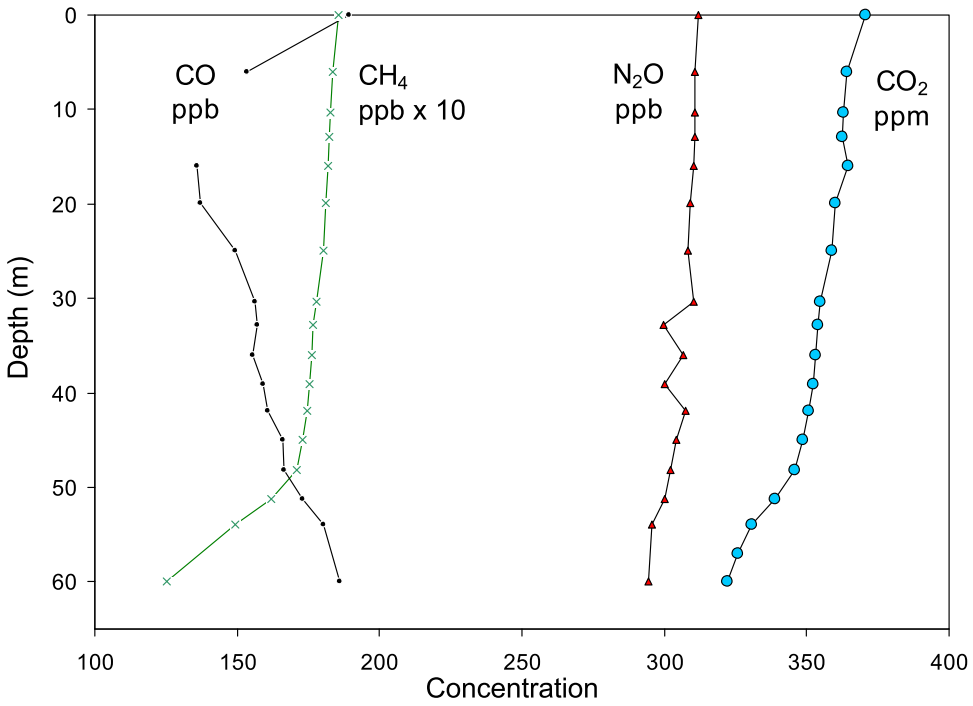


Figure 3. Trace gas concentrations in firn air sampled in the Devon 98-1 drill hole on the Devon Island Ice Cap.

in some samples owing to isobaric interference by trace amounts of ethanol believed to have originated from the vacuum line during sample flask preparation. Sample gas in the MAT 252 bellows was analyzed repeatedly (2x or more) to ensure reproducibility. Samples containing ethanol contamination (15.95, 30.33 and 32.85 m depth; Table 1) exhibited $\delta^{18}O$ values that were shifted significantly after approximately 10 minutes. The measured $\delta^{13}C$ values were unaffected. Previous tests of gas mixtures containing CO_2 of known isotope composition and containing trace amounts of ethanol suggest the initial $\delta^{18}O$ measurements were closest to the true value for CO_2, so initial rather than average $\delta^{18}O$ values for repeated runs are reported here.

[10] As can be seen in Figure 3, CO_2, N_2O, and CH_4 firn air profiles show a decreasing trend with depth, with a more pronounced slope below ~48 m. These features are similar to those observed from previous firn air sampling operations in polar glaciers and result from the increased atmospheric mixing ratios with time. On the contrary, CO decreases by about 50 ppb between the surface and 15 m, followed by a strong increase to 185 ppb at the close-off region. The first feature results from the strong seasonality of CO mixing ratios, which for Alert varied from 68.5 ppm in August 1997 to 182.8 ppm in February 1998 [*Steele et al.*, 2003], and was on its decreasing trend at the time of atmospheric sampling at Devon Island. The increase with depth (age), however, is not consistent with CO temporal trends over the last decades, which suggest an increase during industrial time until the late 1980s [*Zander et al.*, 1989] and a decrease of over 20 ppb since then [*Steele et al.*, 2003]. Ice core measurements performed on Greenland ice [*Haan et al.*, 1996] revealed a large decrease of atmospheric CO in the Arctic going back to pre-industrial levels of less than 100 ppb. In situ production by cosmic radiation of organic matter [*Colussi and Hoffmann*, 2003] can be excluded given the high rate of diffusive exchange with the open atmosphere. On the other hand, measurements of some halocarbons in Devon firn air sampled in our program also indicated larger mixing ratios in the close-off area compared with the surface. This suggests a common mechanism or atmospheric scenario in this region is responsible for artifacts in both CO and some organo-halogens [*Sturges et al.*, 2001].

[11] The CO_2 in 18 firn air samples was extracted from the flask samples at the University of Ottawa and submitted in glass break-seal tubes for ^{14}C AMS analysis at Isotrace Laboratories, Toronto, Ontario. Sample volumes for CO_2 averaged ~80 μmol at STP. Calculations of in situ ^{14}C produced in firn ice, as described by *Lal et al.* [1997], show this to be 60 atoms per gram of ice. For firn with density of 0.5, this amounts to 0.45% of the minimum concentration for ^{14}C in the firn air (30 atoms in situ ^{14}C per 6720 atoms atmospheric ^{14}C). Further, in situ ^{14}C, which occurs as both ^{14}CO and $^{14}CO_2$, is trapped within the firn ice matrix and is not necessarily sampled by firn-air pumping. Much of that which may diffuse to open firn air will be lost through exchange with the open atmosphere. This is consistent with the work of *Smith et al.* [2000], who found no evidence for additional contributions to $^{14}CO_2$ in the bomb peak measured in firn air from Law Dome.

[12] The age structure and rate of accumulation of the firn was established from tritium measurements. Forty-one firn samples, at approximately 50 cm intervals from the surface to 23 m ice depth, were analyzed for specific activity of tritium using a Wallac Quantulus 1220 liquid scintillation counter in the Low-Background Building counting facilities at AECL-Chalk River Laboratories. Sample aliquots of 10 mL were mixed with 10 mL of Packard Picofluor LLT

Table 1. CO_2 Concentration and Isotope Data From Flask Samples of Firn Air From the Devon 98-1 Drill Hole, Devon Island Ice Cap[a]

Depth, m	CO_2, ppm	$a^{14}C_{CO_2}$, pMC	$^{14}CO_2$, ppm	$\delta^{13}C_{CO_2}$, ‰ VPDB	$\delta^{18}O_{CO_2}$, ‰ VPDB
Surface	370.65	109.80 ± 0.87	5.57E-10	—	—
6.00	364.05	—	—	−8.12	−1.15
10.24	362.85	110.06 ± 0.73	5.47E-10	—	—
12.95	362.41	110.54 ± 1.10	5.49E-10	−8.02	−1.72
15.95	364.41	112.54 ± 1.04	5.62E-10	−8.07	−5.61
19.95	360.19	111.02 ± 2.64	5.48E-10	−7.98	−2.77
24.97	359.02	111.84 ± 2.23	5.50E-10	−8.01	−3.55
30.33	354.93	114.44 ± 1.09	5.56E-10	−7.95	−7.04
32.85	354.05	114.44 ± 0.75	5.55E-10	−7.88	−8.54
35.94	352.94	113.88 ± 0.94	5.51E-10	−7.87	−6.70
39.04	352.42	118.93 ± 0.80	5.74E-10	−7.90	−6.87
41.92	350.62	118.38 ± 0.80	5.69E-10	−7.84	−7.71
44.94	348.65	120.92 ± 0.80	5.77E-10	−7.86	−8.60
48.14	345.91	124.33 ± 0.77	5.89E-10	−7.79	−8.63
51.19	338.71	127.50 ± 0.84	5.92E-10	−7.51	−11.57
53.94	330.66	132.63 ± 0.82	6.01E-10	−7.45	−14.22
56.94	325.75	120.18 ± 0.79	5.36E-10	—	—
59.94	322.12	112.17 ± 0.73	4.95E-10	−6.79	−17.25

[a]pMC, percent modern carbon; VPDP, Vienna Peedee belemnite.

scintillator and beta-counted for 24 hours resulting in an overall precision of ±7 TU (Figure 4).

2. Results and Discussion

2.1. Age Structure of Firn Ice

[13] The distinct 1963 peak in the tritium profile appears at 16.6 m in firn ice whereas the $^{14}CO_2$ peak in firn air has a much wider distribution centered at 53.9 m (Figure 4). The depth of the tritium peak is used to calculate the average rate of accumulation over the last 35 years to be 30 g cm^{-2} yr^{-1} of ice, which is within the range found for sites on the northwestern and eastern ice cap [*Koerner*, 1979]. This rate of accumulation, corrected with firn density measurements (presented in Figure 9), is extrapolated to the lowest sampling point at 60 m, yielding an age for firn ice at this depth of 140 years before 1998, and 1858 as the year of accumulation (Figure 7). *Fisher et al.* [1996] show that the rates of accumulation on Devon and other Canadian Arctic Island ice caps have had little variability over the past few hundred years.

2.2. Age Structure of the Firn Air Column

[14] The age of firn air CO_2 has been reconstructed using a new method based on the exchange of ^{18}O between CO_2 and the ice matrix, calibrated with the firn air sample that

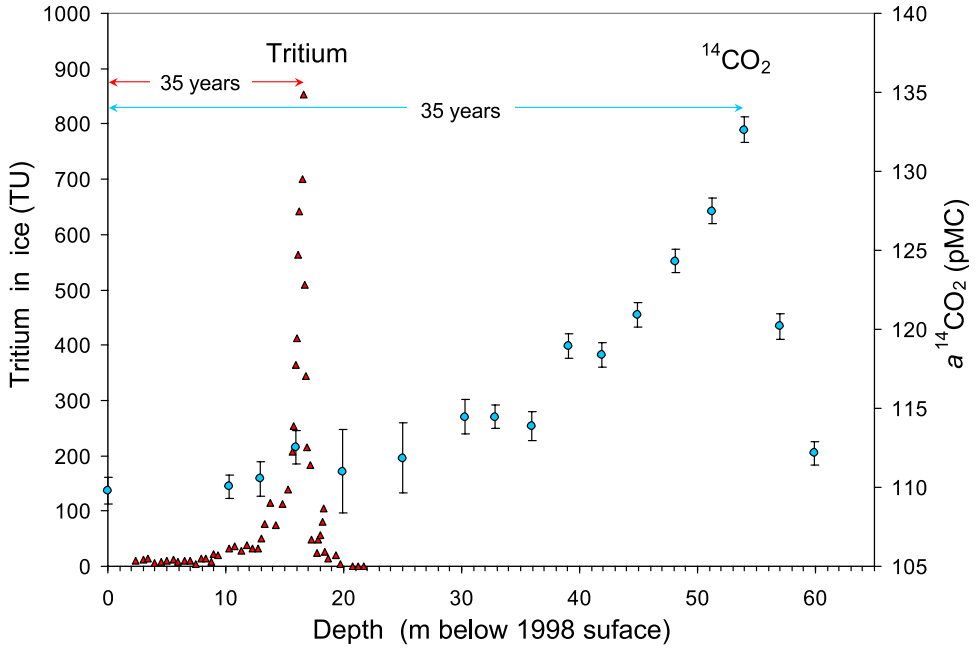


Figure 4. Tritium profile in the Devon 98-1 firn ice, together with atmospheric $^{14}CO_2$ in firn air, normalized to CO_2. Peaks in both profiles represent the 1963 thermonuclear bomb-test peak (35 years old in 1998).

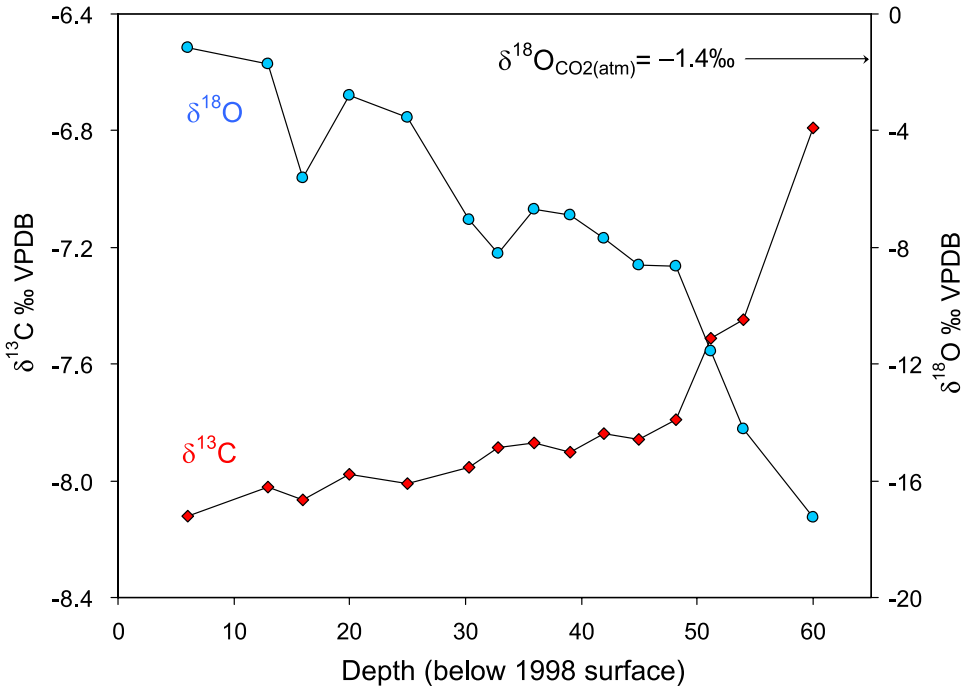


Figure 5. Depth profiles for the stable isotopic content of CO_2 (uncorrected for gravitational settling and diffusion) in Devon 98-1 firn air. Anomalous values for $\delta^{18}O$ at 15.95, 30.33, and 32.85 m are due to ethanol contamination during analysis.

includes the 1963 $^{14}C_{CO_2}$ thermonuclear bomb peak. Figure 5 shows the variation of the stable isotope contents (^{13}C and ^{18}O) of CO_2 in the firn air column. The ^{13}C profile shows a steady enrichment with depth from a modern value of −8.12‰, to a value of −6.79‰ at the transition zone. Corrected for gravitational settling under conditions of diffusive equilibrium [*Trudinger et al.*, 1997; *Francey et al.*, 1999], the deepest value would be −7.06. The inverse correlation of this trend with CO_2 concentration is consistent with atmospheric trends for the later twentieth century [e.g., *Friedli et al.*, 1986]. However, this record may be affected by in situ CO_2 contributions in the firn profile, discussed below.

[15] The record for $\delta^{18}O$ in CO_2 is characterized by a gradual shift with depth to lower values, with a net difference between surface and the firn-ice transition depth of over 16‰. The direct measurement record of atmospheric CO_2 shows that $\delta^{18}O_{CO_2}$, normally controlled by exchange with seawater and leaf water, has a value of −1.4‰ and varied by less than 0.6‰ over the past several decades [*Hopper et al.*, 1998]. With the exception of the anomalous samples at 15.95, 30.33, and 32.85 m, discussed above, the observed depletion trend with depth can be attributed to exchange with the ice matrix (−27.0 ± 1.7‰ VSMOW). This progressive exchange has been observed by *Assonov et al.* [2005] in firn air from three Antarctic sites, and shown to be a first-order reaction.

[16] The absence of a rapid negative shift in $\delta^{18}O_{CO_2}$ in the upper firn air column is evidence against contamination by summer melt layers. CO_2 affected by summer melting and refreezing has likely been lost to the open atmosphere by exchange through the upper convective firn air zone. An effect on the overall gradient of this trend by downward diffusion of CO_2 affected by melt layers can also be considered. If nonnegligible, this effect would act to reduce the calculated rate constant (discussed below) from that expected for the in situ temperature of Devon firn. However, good comparison with rate constants for three sites with different temperatures in Antarctica [*Assonov et al.*, 2005] suggests that such an effect is negligible for Devon Island (Figure 6).

[17] The halftime of the CO_2-firn exchange reaction provides a tool to establish a chronology for firn air CO_2 throughout the column. Isotope exchange between CO_2 and the firn ice matrix occurs in conjunction with CO_2 exchange with the open atmosphere by diffusion through the firn air column. This diffusive mixing of firn air CO_2 broadens the distribution of ages and so the measured $\delta^{18}O$ of CO_2 at a given depth represents the average for a range of exchange times (ages). Average CO_2 ages can then be calculated from the measured $\delta^{18}O_{CO_2}$ values, providing a calibration point of known age can be identified. The sample containing the 1963 $^{14}CO_2$ peak meets this requirement, for which the average age can be fixed at 35 years (53.9 m depth, $\delta^{18}O_{CO_2}$ = −14.22‰ VPDB). The exchange halftime can then be calculated from the difference between $\delta^{18}O_{CO_2}$ at this depth and the value for $\delta^{18}O_{CO_2}$ in equilibrium with the ice matrix, using an exponential decay equation:

$$A = A_o e^{-\lambda t}, \quad (1)$$

where $A = \delta^{18}O_{CO_2(t)} - \delta^{18}O_{CO_2(equil)}$, $A_o = \delta^{18}O_{CO_2(atm)} - \delta^{18}O_{CO_2(equil)}$, λ = rate constant = $\ln 2/T_{1/2}$, $T_{1/2}$ = halftime of the exchange reaction, and t = period of exchange, in years.

[18] The $\delta^{18}O_{CO_2(t)}$ value is derived from the $^{18}O/^{16}O$ ratio in firn air CO_2 and $\delta^{18}O_{CO_2(atm)}$ is the initial value at time t = 0. The value for $\delta^{18}O_{CO_2}$ in equilibrium with the ice

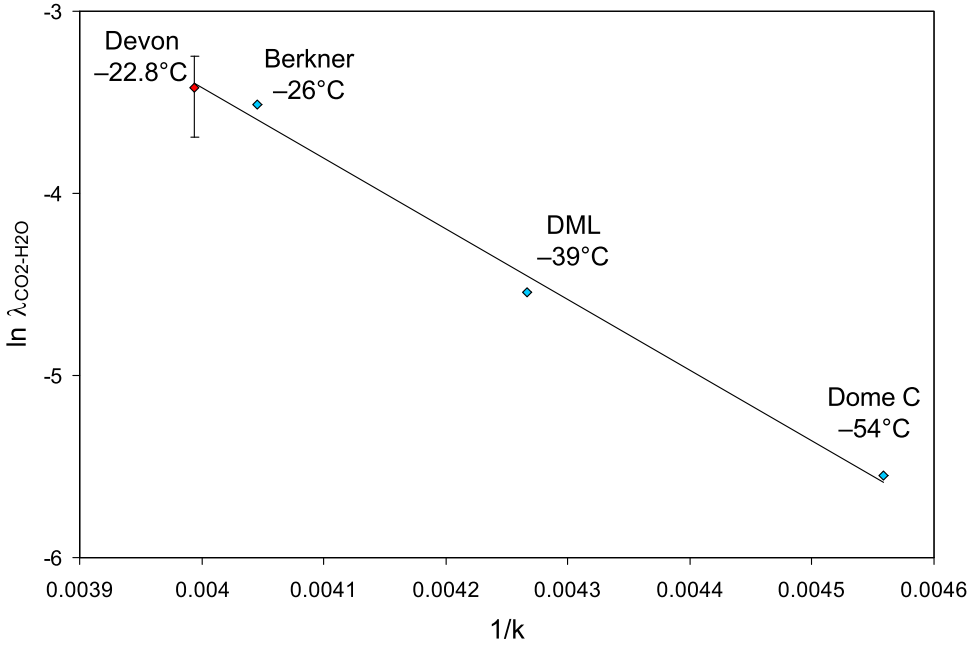


Figure 6. Correlation of firn temperature with rate of exchange of ^{18}O in CO_2 with firn ice for Devon in comparison with three Antarctic sites [*Assonov et al.*, 2005]. For Devon, error bars are for $\lambda_{CO_2\text{-}H_2O}$ = 0.03276 (+0.0062/−0.0078) on the basis of the uncertainty of the depth of the 1963 thermonuclear peak used to calibrate the exchange rate.

matrix ($\delta^{18}O_{CO_2(equil)}$) is calculated from the combined fractionation factors for ^{18}O exchange between CO_2 and water, between water and vapor, and between vapor and ice. This approach was used by *Siegenthaler et al.* [1988] to calculate the degree of ^{18}O equilibrium between entrapped CO_2 and the ice matrix for Antarctic ice cores (South Pole, Siple, and Byrd Station):

$$CO_2 - H_2O_{water} : 10^3 \ln \alpha^{18}O_{CO_2-wat} = -0.0206\left(10^6 T^{-2}\right) + 17.9942\left(10^3 T^{-1}\right) - 19.97 \quad (2)$$

[*Bottinga*, 1968],

$$H_2O_{water} - H_2O_{vapor} : 10^3 \ln \alpha^{18}O_{wat-vap} = 1.137\left(10^6 T^{-2}\right) - 0.4156\left(10^3 T^{-1}\right) - 2.0667 \quad (3)$$

[*Majoube*, 1971],

$$H_2O_{vapor} - H_2O_{ice} : 10^3 \ln \alpha^{18}O_{vap-ice} = -11.839\left(10^3 T^{-1}\right) + 28.782 \quad (4)$$

[*Siegenthaler et al.*, 1988].

Conversion for $\delta^{18}O$ of CO_2 measured against VPDB to the VSMOW scale is made with the conversion factor between VPDB-CO_2 and VSMOW- equilibrated CO_2 of 1.04142 established by *Friedman and O'Neil* [1977].

[19] Using the mean temperature for the firn profile in the Devon Island Ice Cap of −22.8 ± 0.1°C, and the average $\delta^{18}O$ value for the firn ice of −27.0‰, the calculated $\delta^{18}O$ value for CO_2 in equilibrium with the ice becomes $\delta^{18}O_{CO_2(equil)}$ = −20.18‰. The $\delta^{18}O_{CO_2}$ of ambient air measured at Alert over the past several years is −1.4‰ VPDB [*Hopper et al.*, 1998]. The isotope exchange reaction halftime can be determined by solving for $T_{1/2}$ in the exponential decay equation (1), using the 53.9 m sample containing the 1963 $^{14}CO_2$ peak. Here the average time t of exchange is 35 years, and the amount of exchange, A, is 5.97‰. Accordingly, for the firn temperature at Devon, the overall exchange reaction halftime is determined to be 21.2 years, and the rate constant, $\lambda = 0.0328\ yr^{-1}$.

[20] Considering the 3 m sampling interval used, and the asymmetry of the thermonuclear peak, the depth of the 1963 horizon cannot be constrained to better than ±1.5 m. This uncertainty on the rate constant was calculated using interpolated $\delta^{18}O_{CO_2}$ values at 53.9 ± 1.5 m depth which were then assigned the 35-year age in equation (1), giving λ = 0.0328 (+0.0062/−0.0078) yr^{-1} and a reaction halftime in the range, $18.9 < T_{1/2} < 25.6$ years. Varying the values used for $\delta^{18}O_{CO_2}$(atm) or $\delta^{18}O_{CO_2}$(equil) by ±1‰ changes $T_{1/2}$ by only ±2 years, well within the error on the depth of the 1963 peak.

[21] This rate constant was then used to generate the age profile for the firn air CO_2 and is presented in Figure 7. Error bars represent the uncertainty in the reaction halftime. Accordingly, firn air sampled at 59.94 m, just above the depth of occlusion, has an apparent CO_2 age of 56.7 (+6.0/−12.0) years. The offset in mean age between firn air CO_2 and the firn ice matrix increases from 22 years at 13 m depth to 84 years at the base of the firn air profile.

2.3. Firn Air Diffusion and Firn Diffusivity Using $^{14}CO_2$

[22] Atmospheric $^{14}CO_2$ provides an excellent analogue for the behavior of atmospheric CO_2 in firn air studies [*Smith et al.*, 2000]. $^{14}CO_2$ has diffusive properties that differ only marginally from those of CO_2 owing to its greater mass, and otherwise behaves the same as CO_2 in firn air. However, thermonuclear bomb tests from 1952 to

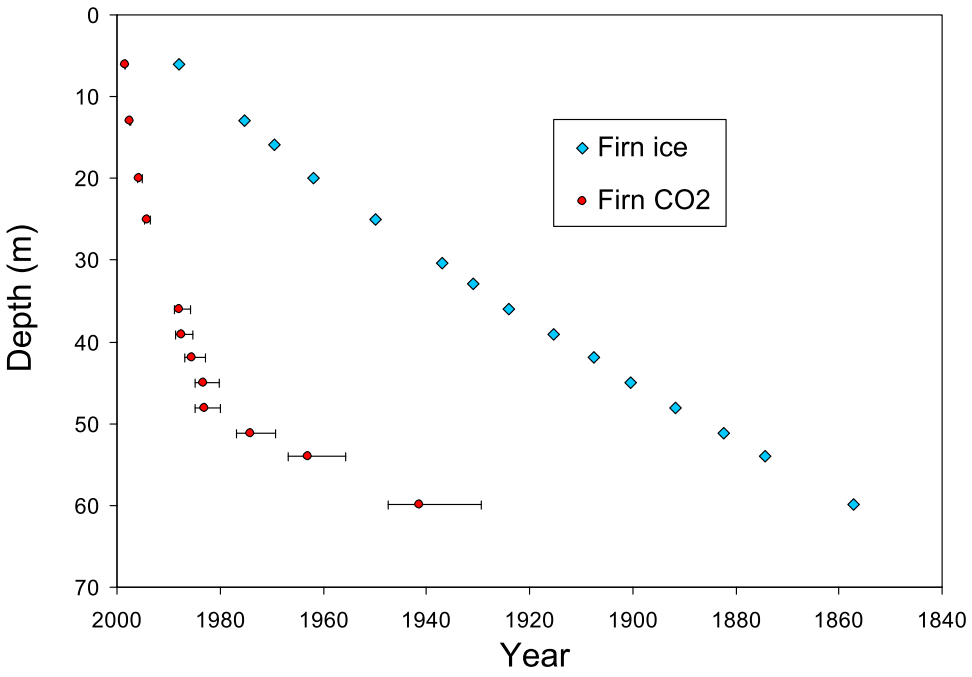


Figure 7. Reconstructions of the age structure of firn ice based on the rate of burial of the 1963 atmospheric tritium peak, and mean age of firn air based on ^{18}O exchange between CO_2 and firn ice in the Devon 98-1 drill hole. Error bars based on the range in $T1/2$ from uncertainties in the depth of the 1963 peak (±1.5 m).

1962 and the subsequent American-Soviet atmospheric test ban treaty have created an atmospheric history of $^{14}CO_2$ that is greatly different from that of CO_2 concentration. The depth and shape of the pronounced 1963 $^{14}CO_2$ peak provides a valuable tool to assess firn air age. Further, the twofold increase in $^{14}CO_2$ in 1963 and subsequent attenuation to near background levels provides a robust atmospheric scenario from which to inversely model firn diffusivity.

[23] In this study, $^{14}CO_2$ is decoupled from CO_2 concentration, by normalizing its activity to concentration in firn air and thus expressing it as a mixing ratio. In this way, $^{14}CO_2$ can be modeled as an independent tracer. The routine extraction and analysis of $^{14}CO_2$ in air provides ^{14}C activities normalized to mass carbon, and expressed as a percent of the activity of Modern Carbon (pMC). The ratio of ^{14}C to total carbon in ''Modern Carbon'' has been determined to be 1.176E−12 by *Karlen et al.* [1968].

[24] Using this value, the mixing ratio of $^{14}CO_2$ (ppm) in the firn air samples can be calculated from the measured $[CO_2]$ concentration (ppm) and the ^{14}C activity of firn air CO_2 ($a^{14}C_{CO_2}$). This is according to

$$^{14}CO_2 = 1.176E-12 \cdot \frac{a\,^{14}C_{CO_2}}{100} \cdot [CO_2]. \qquad (5)$$

The $^{14}CO_2$ profile in firn air from Devon was modeled using a 50-year atmospheric input scenario derived from the 1962 to 1993 record from Trondheim, Norway [*Nydal and Lovseth*, 1996], and extended to a full 1949–1998 record using a 50-year tree ring record from Kingston, Ontario [*Kotzer and Watson*, 2000] (Figure 8). Comparison with a tree ring record from Inuvik, Northwest Territories, Canada (latitude 68°N [*Battye*, 2000]) and Vermunt, Austria (latitude 47°N [*Levin et al.*, 1994]) shows less than 1 pMC variation with latitude.

[25] The atmospheric records and our firn air $^{14}CO_2$ measurements were first normalized to our measured atmospheric ^{13}C values rather than the radiocarbon standard of −25‰, to provide true $^{14}CO_2$ concentrations. The extended atmospheric $a^{14}CO_2$ (pMC) record was then normalized to an air-mixing ratio (ppm), according to equation (5), using the atmospheric CO_2 concentration record from the Mauna Loa observatory, Hawaii [*Keeling and Whorf*, 1998] (combined curve in Figure 8). The measurements of $a^{14}C$ (pMC) in firn air CO_2 from Devon were normalized to $^{14}CO_2$ (ppm) using our measured CO_2 concentrations (Table 1). The contributing effects of gravitational settling (+0.06 pMC at 60 m) and radioactive decay (−0.6 pMC at 35 years) were calculated to be less than the analytical uncertainty of $^{14}CO_2$.

[26] Expressed as a mixing ratio in the atmosphere, $^{14}CO_2$ (ppm) is uncoupled from the variable increase in CO_2 observed over the past 50 years. This allows modeling of $^{14}CO_2$ diffusion using its distinctive atmospheric scenario characterized by the sharp thermonuclear bomb peak of 1963 (Figure 8). This is a suitable scenario for modeling CO_2 diffusion in firn air, given the 30- to 50-year period for which firn air diffusion is active.

[27] A firn air diffusion model [*Rommelaere et al.*, 1997] was used in an inverse modeling exercise to calibrate the firn diffusivity profile with the measured $^{14}CO_2$ profile (ppm normalized) in the firn air. Reduced diffusion of $^{14}CO_2$ with respect to $^{12}CO_2$ due to the mass difference (as described by *Trudinger et al.* [1997]), is accounted for by the model. A firn diffusivity profile (Figure 9) was

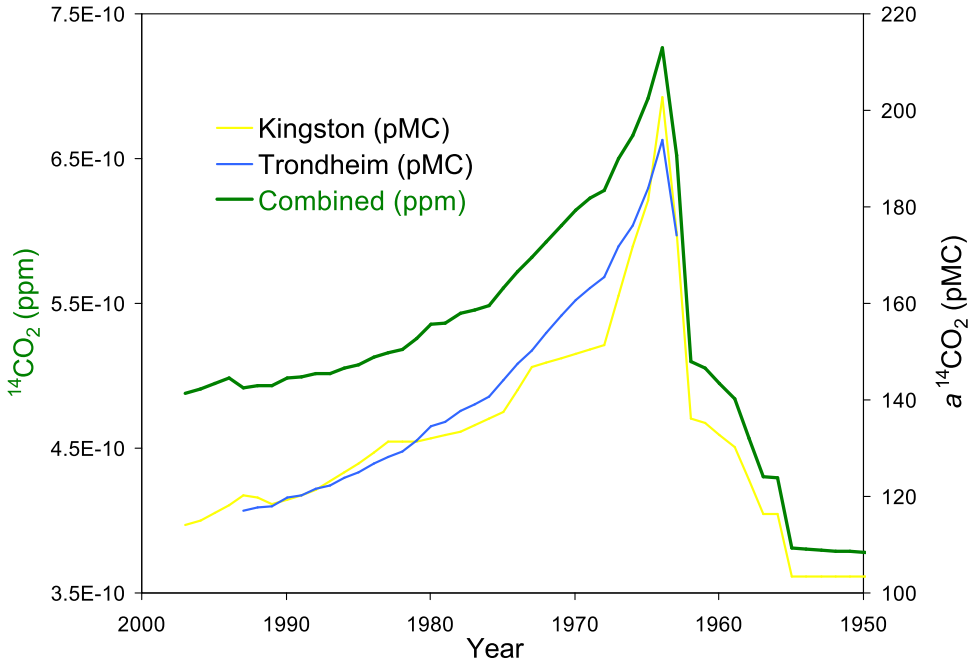


Figure 8. Combined atmospheric scenario for $^{14}CO_2$ (ppm) derived from the Trondheim atmospheric $^{14}CO_2$ record [*Nydal and Lovseth*, 1996] and the Kingston, Ontario, tree ring ^{14}C record [*Kotzer and Watson*, 2000]. Combined scenario is normalized to the $^{14}CO_2$ mixing ratio in air (ppm) using the Mauna Loa CO_2 record [*Keeling and Whorf*, 1998] and corrected to atmospheric ^{13}C [*Hopper et al.*, 1998].

produced with the model by iteratively modifying the diffusivity profile until a visual match between the modeled and measured 1998 $^{14}CO_2$ profile was achieved (Figure 10).

[28] The resulting diffusivity profile exhibits the three zones identified by *Schwander* [1996]. Values in the uppermost zone of convection decrease from 16.3 to about 14.6 mm^2s^{-1} in the first 10 m. The intermediate diffusive zone extends to about 45 m depth, where diffusivity values decrease to less than 0.15 mm^2s^{-1}. The nondiffusive zone, with diffusivities from 0.016 to 0.0003 mm^2s^{-1}, extends from 50 m to 60 m. Below this depth the horizontal permeability was too low to permit flow of firn air to the sample zone below the packer.

[29] This diffusivity profile is substantially lower than for diffusivities published for dry firn sites, consistent with *Fabre et al.* [2000], who compare laboratory measurements

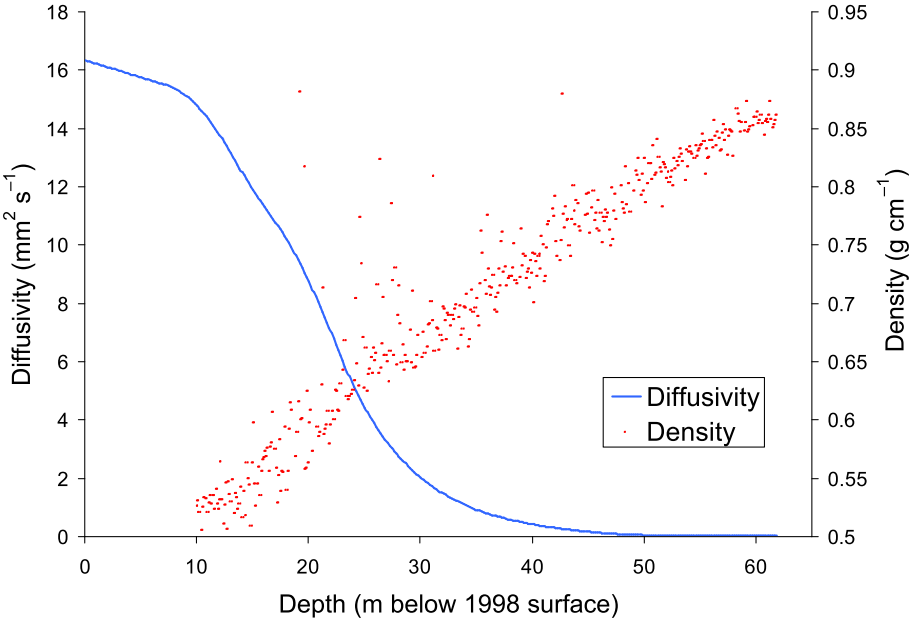


Figure 9. Diffusivity profile for Devon Ice Cap firn, produced by inverse modeling with $^{14}CO_2$, shown with density data measured on the Devon 98-1 core.

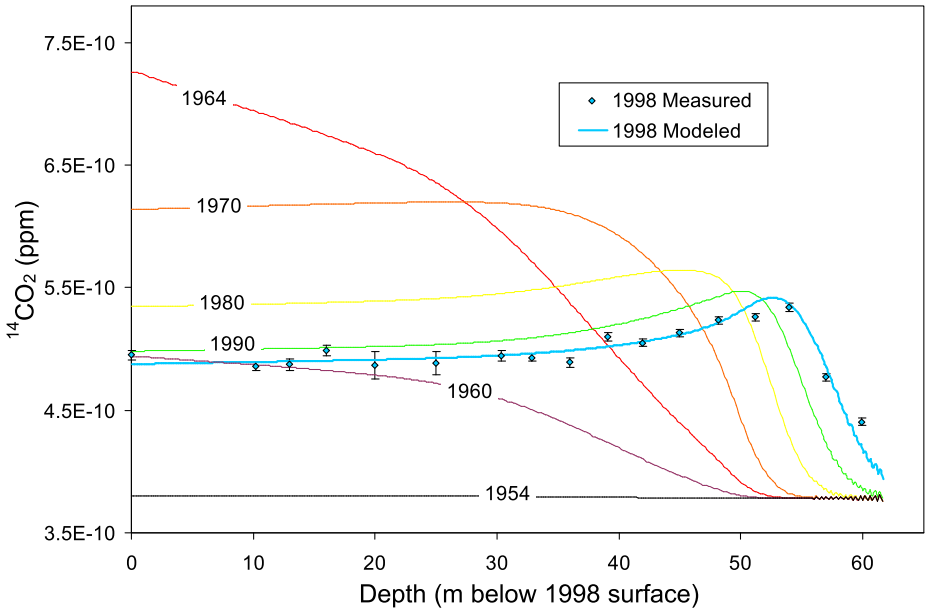


Figure 10. Modeled 1998 $^{14}CO_2$ profile compared with measured values from firn air in the Devon 98-1 core hole, together with modeled profiles for earlier decades showing the evolution of the $^{14}CO_2$ profile since the period of atmospheric tests.

of effective diffusivity with inverse modeling results obtained from gas mixing ratios. They show that the Devon site has effective diffusivities on the order of 20 to 30% of those for mild (Dronning Maud Land and Law Dome) and cold sites (Dome C and Vostok). This low diffusivity characterizing Devon Island firn can be attributed to the presence of ice layers which significantly reduces vertical diffusion.

[30] Following calibration of the diffusivity profile, diffusion was then modeled using a sequence of atmospheric scenarios for $^{14}CO_2$ evolving at 10-year intervals between 1950 and 1990. This allows visualization of the downward diffusion and burial of the 1963 thermonuclear peak (Figure 10). The mixing ratio of $^{14}CO_2$ prior to 1950 was assumed to be constant and equal to a pre-industrial value of 3.76E−10 ppm. The 1964 scenario shows the rapid downward diffusion of $^{14}CO_2$ following the dramatic atmospheric increase in 1963. By 1970, however, the $^{14}CO_2$ gradient in firn air has reversed, and net upward diffusion occurs owing to the attenuation of the $^{14}CO_2$ peak in the open atmosphere by exchange with terrestrial carbon and marine CO_2. High concentrations of $^{14}CO_2$ remnant from the 1963 peak are preserved in firn air only in the nondiffusive zone, where systematic burial of the peak begins to take place. The very low values for firn diffusivity required to preserve the 1963 thermonuclear peak clearly preclude significant vertical diffusion in firn below a depth of 50 m.

[31] The diffusivity profile generated from the ^{14}C atmospheric scenario then tested using reconstructed atmospheric scenarios for CH_4 and CO_2. These were produced from measured concentrations at Alert, Nunavut (for CH_4 from 1986 to 1993 from *Dlugokencky et al.* [1994], and for 1991 to 1998 from *Steele et al.* [2002]; for CO_2 from 1976 from *Keeling and Whorf* [2005]), extrapolated to 1950 using the global atmospheric records [*Ehhalt and Prather*, 2001; *Prentice*, 2001] and amplified by the difference between Alert and global concentrations during the 1986 to 1998 overlap period (Figures 11a and 11c).

[32] Diffusion modeling provides a reasonable fit to the measured CH_4 profile (Figure 11b). The deviation to higher measured CH_4 concentrations in the shallowest firn zone is likely due to diffusion of the strongly seasonal CH_4 signal (±∼70 ppbv with a maximum in late autumn) to depths of 15 m or more. By contrast, the modeled CO_2 profile poorly represents the measured concentrations. This suggests that the atmospheric scenario generated from measurements at Alert may under represent CO_2 levels at Devon over this period. In addition, contributions from dust and organics [*Delmas*, 1993; *Monnin et al.*, 2001; *Kramer Campen et al.*, 2003] is know to contaminate Northern Hemisphere ice sheets and may have contributed to an excess in CO_2.

[33] Despite the greater diffusivity for CH_4, the firn air profile provides a good match with atmospheric concentrations for years corresponding to the firn air CO_2 ages. A plot of the measured CH_4 concentrations in firn air samples against the atmospheric scenario CH_4 concentration (Figure 11) for the year corresponding with the $\delta^{18}O_{CO_2}$ age of the sample (Figure 7), produces close to a 1:1 correlation (Figure 12). Slight enrichments for the measured CH_4 concentrations likely reflect the greater diffusivity of CH_4 over CO_2.

3. Conclusions

[34] Melt layers in ice sheets have been considered problematic for firn air and entrapped gas studies owing to the potential for contamination of the atmospheric signal by dissolution and exsolution during melt-refreeze cycles. On the other hand, firn profiles with horizontal melt layers could potentially enhance the preservation of atmospheric gas records by reducing vertical diffusivity.

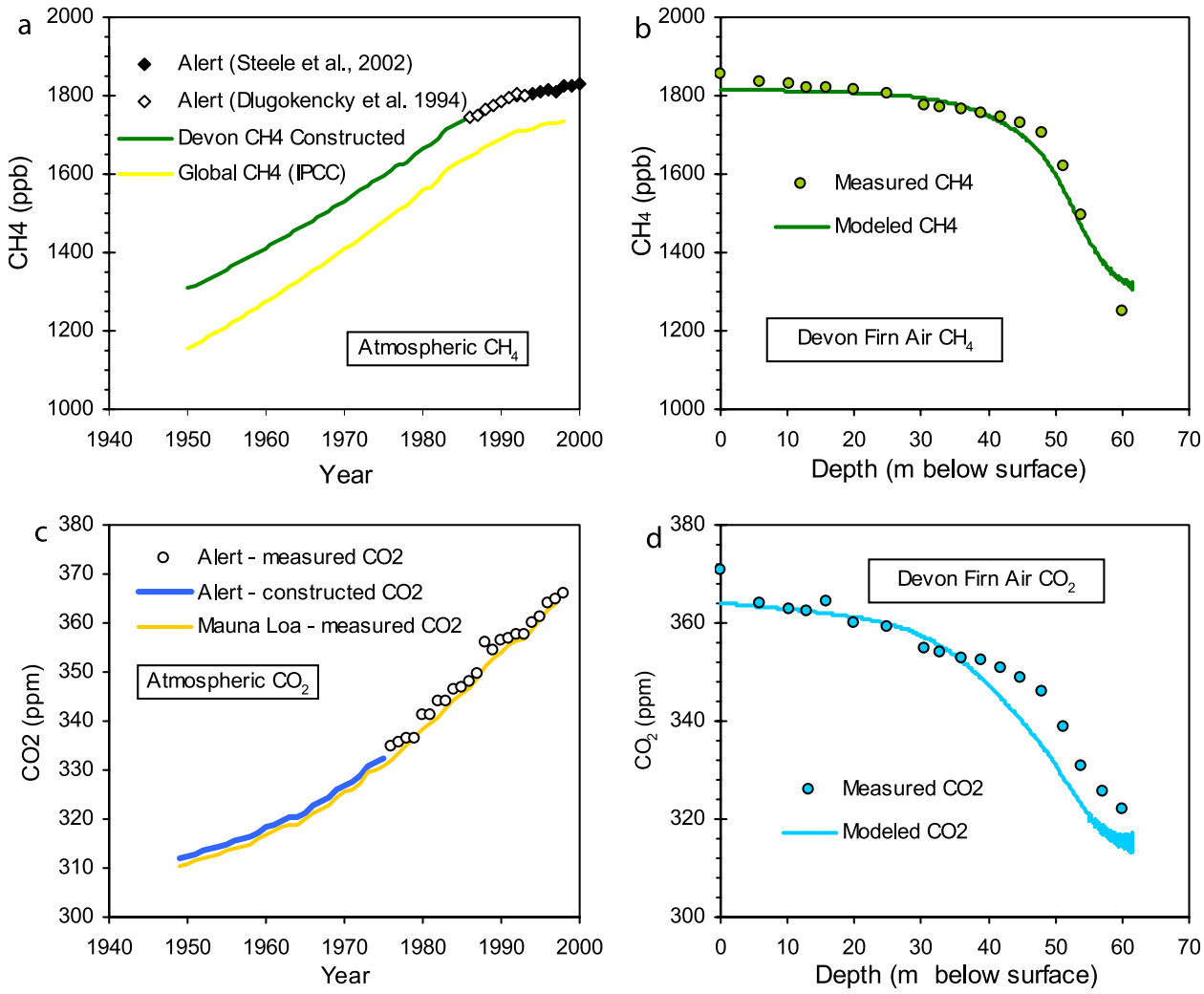


Figure 11. (a, c) Atmospheric scenarios derived from measured values from Alert, Nunavut (1986–1993 [*Dlugokencky et al.*, 1994]; 1991–1998 [*Steele et al.*, 2002; *Keeling and Whorf*, 2005]), for CH_4 and CO_2, respectively. The records constructed for the period prior to measurements at Alert are derived from the global atmospheric record (*Ehhalt and Prather* [2001] for global CH_4 and *Keeling and Whorf* [1998] for CO_2 at Mauna Loa extrapolated to 1950) with an amplification for high-latitude values derived from the difference between measured Alert and global concentrations. (b, d) Modeled depth profiles compared with measured values from firn air in the Devon 98-1 core hole, for CH_4 and CO_2, respectively.

[35] The $\delta^{18}O_{CO_2}$ values measured for the uppermost firn air CO_2 retain an open atmospheric signal with no evidence for alteration by exchange with water from summer melting. The rapid exchange of gas between the shallow firn air and the open atmosphere that occurs on a multiannual basis has diluted to negligible amounts any CO_2 affected by summer melting and refreezing. This suggests that firn profiles with summer melt layers can reliably preserve atmospheric trace gas signals. However, the melt layers themselves may include occluded gases that could potentially affect the older atmospheric record derived from gas bubbles in ice cores sampled by dry extraction methods.

[36] The 1963 thermonuclear bomb peak for $^{14}CO_2$ has been recovered in air samples from the permeable firn of the Devon Island Ice Cap, and provides a useful trace gas with a strong atmospheric anomaly to model firn diffusivity for an ice sheet with summer melting. The diffusivity profile produced by inverse modeling of the $^{14}CO_2$ mixing-ratio profile clearly shows the three zones identified by *Schwander* [1996]. Firn diffusivity values are high in the uppermost zone of convection. The intermediate zone extends to about 45 m depth, with diffusivity values less than 0.15 mm^2s^{-1}. The nondiffusive zone extends from below 50 m to 60 m with diffusivities from 0.016 to 0.0003 mm^2s^{-1}.

[37] *Fabre et al.* [2000] also find much lower diffusivity values for Devon firn. However, inverse modeling of the $^{14}CO_2$ peak indicates that the zone below 50 m depth has considerably lower diffusivity than those determined by modeling the atmospheric CO_2 mixing ratio. This may be an artifact of the much stronger $^{14}CO_2$ signal over that for the CO_2 mixing ratio which provides a better constraint for modeling the deeper diffusivity profile.

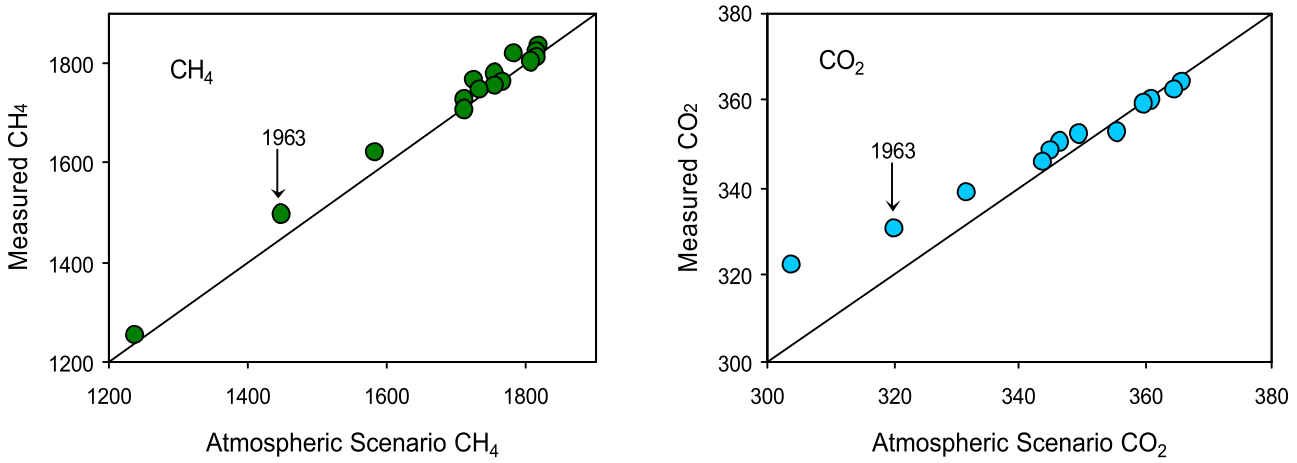


Figure 12. Measured CH_4 and CO_2 for samples versus CH_4 and CO_2 concentrations corresponding to $\delta^{18}O_{CO_2}$ ages. Samples with age inversions (15.95 m, 30.33 m, and 3.85 m; Figure 6) are not included. Enrichments in measured CH_4 likely reflect its enhanced diffusion over CO_2. Enrichments in measured CO_2, as discussed in text, may reflect uncertainties in the atmospheric scenario reconstructed for Devon and possible in situ CO_2 production.

[38] Modeled CH_4 and CO_2 firn air profiles were produced with this diffusivity profile using atmospheric scenarios reconstructed from measurements at Alert, Nunavut, and global trends. For CH_4 a reasonable fit to measured concentrations is produced. A poor fit is found for CO_2 where the modeled diffusion profile under predicts concentrations in the intermediate and nondiffusive zones, possibly reflecting in situ contributions from impurities and/or a poorly constrained atmospheric scenario at Devon.

[39] A profile of average CO_2 age has been produced using the extent of ^{18}O exchange between firn air CO_2 and firn ice on Devon. This chronology is based on the reaction halftime of 21.2 years (rate constant of 0.0328 yr^{-1}), calibrated using the firn air sample at 53.94 m, which preserves the 35-year-old (in 1998) thermonuclear $^{14}CO_2$ peak from 1963. This gives firn air CO_2 sampled at 59.94 m, just above the depth of occlusion an age of 56.7 (+6.0/−12.0) years. Firn ice at this depth has an age of 140 years derived from the accumulation rate based on the depth of the 1963 tritium peak, corresponding to accumulation in 1858. This gives an age offset for firn ice and firn air CO_2 at the point of occlusion of 85 years. Despite the difference in diffusivity, a good fit between measured CH_4 concentrations in firn air samples and atmospheric CH_4 concentrations for the years corresponding to equivalent $\delta^{18}O_{CO_2}$ ages. Given the ease of access to such low-altitude ice sheets as Devon and others in the Canadian Arctic, firn profiles with summer melting can provide a useful archive of trace gas records.

[40] **Acknowledgments.** The Meteorological Service of Canada (formerly the Atmospheric Environment Service) of Environment Canada is thanked for their support of this work through funding to the Canadian Institute for Climate Studies at the University of Victoria. The Canadian Continental Polar Shelf Project of Natural Resources Canada provided air support for fieldwork, and the French Polar Institute (IFRTP) provided additional funding and logistical support to J. C. Wayne Workman (AECL, Chalk River Laboratories) is thanked for providing technical assistance for tritium analyses, and Pingqing Zhang helped with preparation of CO_2 sampling equipment. This work is a contribution to the European Commission project FIRETRACC/100 (ENV4-CT97-0406) funded under the Environment and Climate Programme, 1994–1998, and to CRYOSTAT (EVK2-CT2001-00116) funded under the Energy, Environment, and Sustainable Development Programme, 1998–2002.

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