

Model calculations of the age of firn air across the Antarctic continent

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Abstract

The age of firn air in Antarctica at pore close-off depth is only known for a few specific sites where firn air has been sampled for analyses. We present a model that calculates the age of firn air at pore close-off depth for the entire Antarctic continent. The model
5 basically uses four meteorological parameters as input (surface temperature, pressure, accumulation rate and wind speed). Using parameterisations for surface snow density, pore close-off density and tortuosity, in combination with a density-depth model and data of a regional atmospheric climate model, distribution of pore close-off depth for the entire Antarctic continent is determined. The deepest pore close-off depth was
10 found for the East Antarctic Plateau near 72° E, 82° S, at 150±15 m (2 σ). A firn air diffusion model was applied to calculate the age of CO₂ at pore close-off depth. The results predict that the oldest firn gas (CO₂ age) is located between Dome Fuji, Dome Argos and Vostok at 43° E, 78° S being 148±23 (1 σ or 38 for 2 σ) years old. At this location an atmospheric trace gas record should be obtained. In this study we show
15 that methyl chloride could be recorded with a predicted length of 125 years as an example for trace gas records at this location. The longest record currently available from firn air is derived at South Pole, being 80 years.

Sensitivity tests reveal that the locations with old firn air (East Antarctic Plateau) have an estimated uncertainty (2 σ) for the modelled CO₂ age at pore close-off depth of
20 30% and of about 40% for locations with younger firn air (CO₂ age typically 40 years). Comparing the modelled age of CO₂ at pore close-off depth with directly determined ages at seven sites yielded a correlation coefficient of 0.90 and a slope close to 1, suggesting a high level of confidence for the modelled results in spite of considerable remaining uncertainties.

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1 Introduction

Air trapped in the open pores of a firn layer is ideal to acquire temporal records of atmospheric composition over the past 20–150 years. The Antarctic firn layer is known as a porous, permeable layer of snow on top of the ice sheet, which is compressed by the overlying snow pack. In Antarctica this firn layer is typically 50–150 m thick. Because of the porous structure of the firn layer, large firn air volumes can be sampled and a wide range of trace gas analyses become possible. The possibility to study a wide range of trace gases is the biggest advantage of firn air analyses over the analyses of air trapped in bubbles and therefore explains why we want to find the oldest firn air.

With a firn diffusion model (Schwander et al., 1993; Rommelaere et al., 1997; Trudinger et al., 1997) vertical concentration profiles measured in a firn layer can be translated to historical time series of a particular gas in the atmosphere. Using this method, Butler et al. (1999) obtained records for CFCs and chlorocarbons at South Pole station, Siple Dome and Tunu (Greenland). Brominated methanes were recorded by Sturges et al. (2001) in air sampled at Dronning Maud Land, Dome C and Berkner Island. Concentrations of CO₂ and CFCs at Law Dome were measured by Trudinger et al. (1997, 2002); non-methane hydrocarbons (ethane, propane and acetylene) were measured by Kaspers et al. (2004) for Dronning Maud Land. All the locations of previous firn air analyses are shown in Fig. 1. In this paper, we combine the information available from these experiments to model the age of CO₂ at pore close-off depth (PCOD) in Antarctica. This enables us to predict where the greatest PCOD can be found, and what the corresponding age of CO₂ at PCOD is and the modelled uncertainty of the age.

The following section explains how we use meteorological data to obtain the parameterisations for tortuosity, surface density and density at PCOD. We also briefly describe the diffusion model we have used. In Sect. 3, we present surface density and PCOD as well as the age of CO₂ at PCOD for the entire Antarctic continent. This section also

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covers sensitivity experiments carried out to quantify the influence of uncertainties in the density and tortuosity profiles on the modelled firn CO₂ age. We summarise our conclusions in Sect. 4.

2 Methods

To derive the age of firn air at PCOD one needs:

- The vertical velocity of air in the firn layer, derived from a firn air model (Sect. 2.1);
- The snow density profile $\rho_{(z)}$, including the surface density (ρ_0) (Sect. 2.2);
- The density at PCOD (ρ_{CO}) as marker, where PCOD is located (Sect. 2.2);
- The tortuosity profile, which is a measure of the 3D pore structure (Sect. 2.2);

2.1 Firn air model

We applied the firn air diffusion model based on the concepts proposed by Schwander et al. (1988, 1993) to calculate the age of CO₂ at PCOD. The model is described briefly here; a more detailed description is given in Kaspers et al. (2004). The model calculates the flux $j_{(z,t)}$ of air into the firn column, which depends on the flux of molecular diffusion $j_{\text{Diffusion}}$ and the flux due to gravity j_{gravity} (Eq. 1).

$$j_{z,t} = j_{\text{Diffusion}} + j_{\text{Gravity}} = -D_z \left(\frac{\partial C_{z,t}}{\partial z} + \frac{Mgz}{RT} \right). \quad (1)$$

Here, D_z is the diffusion coefficient ($\text{m}^2 \text{a}^{-1}$), $\partial C_{z,t}/\partial z$ is the variation of the time-dependent concentration ($C_{z,t}$) with depth (z), Mgz/RT describes the settling due to gravity with M the molecular mass (for CO₂, 44 g/mol), g the gravitational constant, R the gas constant and T the annual mean surface temperature (K). The diffusion

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coefficient D_z is described in more detail in Eqs. (2) and (3) (Schwander et al., 1993; Spahni et al., 2003).

$$D_{(z)} = \frac{D_{12}D_{m(z)}}{1 + 0.5\gamma_{(z)}(1 - \pi_{\text{open}(z)})} \quad (2)$$

$$D_{m(z)} = D_{T_0, P_0} \frac{P_0}{P_{(z)}} \left(\frac{T}{T_0} \right)^{1.85} \quad (3)$$

5 The diffusion coefficient $D_{(z)}$ is a function of the gas specific diffusion coefficient D_{12} , a correction term for atmospheric temperature and pressure $D_{m(z)}$, the open porosity $\pi_{\text{open}(z)}$ and the tortuosity structure $\gamma_{(z)}$. Equation (3) describes the correction term for temperature and pressure. In this equation, T_0 and P_0 are 253 K and 1013 hPa, respectively.

10 The open porosity can be determined from a semi-empirical relationship presented by Schwander (1989). In this relation, the open porosity is expressed inversely proportional to the density profile, which makes the density profile an important parameter in the diffusion model. Most of the firn air diffusion studies for specific sites apply a curve fit through a measured density profile (Schwander et al., 1993; Trudinger et al.,
15 1997). To extrapolate results over all of Antarctica, we applied a firn density model. The choice of the density-depth model is described in detail in Sect. 2.2.

Another important site-specific parameter in the diffusion model is the tortuosity profile $\gamma_{(z)}$ (Spahni et al., 2003; Schwander et al., 1993). This profile is the main tuning parameter in the diffusion model and represents a correction term for the three-
20 dimensional structure of the open porous firn. The tortuosity profile is described as

$$\gamma_z = \gamma_a + (1 - \gamma_a)(\pi_{\text{open}(z)})^{-\gamma_b} \quad (4)$$

Here, γ_a and γ_b are constants derived by tuning the diffusion model with a measured CO_2 profile. If the CO_2 profile is not available for a location, we need a parameterisation for the tortuosity constants (γ_a and γ_b). This parameterisation is described in Sect. 2.2.

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The age at PCOD can be derived from a modelled CO_2 profile. We used the concentration history of atmospheric CO_2 as upper boundary condition in the diffusion model: for 1750 to 1976 derived by Neftel et al. (1985) from the Siple Dome ice core and for 1976 to present from directly measured NOAA-CMDL South Pole data. We constructed
5 a CO_2 concentration profile in the firn layer for 150 layers in the vertical. Each vertical grid cell contains the same amount of air; therefore, the grid cell size increases near pore close-off, which is approximately 1 m for a site where the PCOD is 100 m. The CO_2 concentration at PCOD corresponds to the mean age of CO_2 at PCOD.

After we parameterised the site-specific density and tortuosity profiles with annual
10 meteorological variables, we used the diffusion model in combination with the Regional Atmospheric Climate Model (RACMO/ANT) and the measured accumulation field of Vaughan et al. (1999) for modelling the age of CO_2 at PCOD for entire Antarctica. The RACMO model covers the Antarctic continent with a horizontal grid spacing of 55 km, which is the resolution for the present work as well. RACMO is validated and described
15 in more detail in Van Lipzig et al. (1999 and 2002). Figure 2 shows the meteorological input fields.

2.2 Parameterisation of the density and tortuosity profiles

In order to apply the diffusion model over Antarctica, we have to parameterise a number of site-specific parameters and choose a convenient density-depth model to calculate
20 $\rho_{(z)}$. The latter is chosen after comparing 5 density-depth models with the measured density depth profiles of the 9 firn air sites (indicated in Table 1). This comparison is described in more detail in this section with caption "Comparison study of several density-depth models".

To obtain the site-specific parameters ρ_{CO} and $\gamma_{(z)}$, we applied the firn air diffusion model for eight sites in Antarctica and one in Greenland. Table 1 lists the locations and meteorological conditions of these sites. The measured density profiles were used as input for the diffusion model and the site-specific parameters ρ_{CO} and $\gamma_{(z)}$ were derived
25 after optimising the model for the measured CO_2 profile. The site-specific variables are

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parameterised as a linear function of the annual temperature, accumulation, surface pressure and wind speed as derived from RACMO and Vaughan et al. (1999) (the small data set of only 9 measurements does not justify a more sophisticated approach) and different variables were tested, using a standard statistical F test (95% confidence limits). We have chosen this statistical approach, as the physical meaning of the pore close-off density and tortuosity is not completely understood and the data set is too small to justify a detailed physical interpretation. We discuss each site-specific parameter (ρ_0 , ρ_{CO_2} and γ_z) separately and conclude this section with a comparison of the modelled ages of CO_2 at PCOD and firn air age data given in site-specific studies.

2.2.1 Comparison study of several density-depth models

In literature a number of density models are described in the past. Most of these density models are based on semi-empirical relations, like Herron and Langway (1980), Barnola et al. (1991), Kameda et al. (1994), Craven and Allison (1998) and Spencer et al. (2001), whereas the density model of Arnaud et al. (1998) relies on the physical processes of grain-boundary sliding and power-law creep. Because all these density-models use meteorological parameters (temperature, accumulation, surface pressure and wind speed) as input parameters, they can all be used in this study. For this reason we have compared the models of Arnaud, Craven and Allison, Herron and Langway, Kameda and Spencer with 9 measured density profiles (8 for Antarctica and one for Greenland, Table 1). We determined the root mean square error over the entire density profile (every 0.1 m) between the density profile obtained from the density model and the measured density profile. The models of Arnaud, and Herron and Langway deviated less than 2.5% on average for the 9 measured density profiles, being therefore the most accurate density models from this comparison. Both these models yield density profiles very similar to each other. Although, according to Barnola et al. (1991), the model of Herron and Langway over estimates the PCOD by 10 m at South Pole (using an accumulation rate of 8 cm.w.eq.a^{-1}). Nevertheless we have decided to use the Herron and Langway model in our diffusion study, because: a.) it has been validated

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for a wide climatic range from the polar plateau to costal sites which is not the case for the Arnaud model as far as we know. b.) it is easy to implement over the entire continent, whereas the Arnaud model needs some arbitrary site specific tuning for two parameters.

Note that the choice of a density-depth model will probably have a smaller effect on the accuracy of the combined diffusion-climate model to determine the age of CO_2 at PCOD, compared to the other uncertainties involved, particularly, the tortuosity profile and the accuracy of the meteorological input parameters obtained by the RACMO model.

2.2.2 Surface snow density

The surface snow density (ρ_0) is the upper boundary condition in the Herron and Langway density-depth model, which makes ρ_0 an important parameter. We have used 40 individual measurements (Appendix A) to parameterise ρ_0 to annual meteorological variables. The parameterisation is given in Eq. (5).

$$\rho_0 = \alpha_1 + \beta_1 T + \delta_1 A + \varepsilon_1 W. \quad (5)$$

The constants α_1 , β_1 , δ_1 and ε_1 are given in Table 2. T is the annual average surface temperature in K (contributing $\sim 70\%$), A the accumulation rate in m.w.eq.a^{-1} ($\sim 2.5\%$) and W the annual wind speed in m s^{-1} at 10 m above the surface ($\sim 7.5\%$). Figure 3 displays the correlation between the observed surface snow density for the nine sites (Table 1) and the ρ_0 values calculated with Eq. (5). The derived correlation coefficient between measured and parameterised values is $r^2 = 0.80$ (99.9% confidence level).

2.2.3 Pore close-off density

The pore close-off density (ρ_{CO_2}) is used in the diffusion model as a marker for the location of PCOD. We have obtained the pore close-off density from nine sites (Table 1) to parameterise this parameter to annual meteorological variables and we used the

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parameterisation of Martinerie et al. (1994) for comparison (Sects. 3.1 and 3.2.). The parameterisation of Martinerie et al. (1994) is only a function of temperature and is shown in Eq. (6a). According to Martinerie et al. (1994), the pore close-off density has typically a value between 800 and 830 kg m⁻³, being strongly site dependent. The result of the parameterisation of nine sites is given in Eq. (6b).

$$\rho_{CO} = \frac{\rho_{ice}}{\rho_{ice}V_c + 1} \text{ with } V_c = 6.95 \cdot 10^{-4} T - 0.043 \quad (6a)$$

$$\rho_{CO} = \alpha_2 + \beta_2 T + \delta_2 A. \quad (6b)$$

V_c in Eq. (6a) represents the volume of air at pore close-off.

In Eq. (6b), constants α_2 , β_2 and δ_2 are listed in Table 2. Temperature contributes approximately 30% and accumulation 3% to ρ_{CO} in equation 6b. We obtained a negative value for β_2 and a positive value for δ_2 , which means high values for ρ_{CO} at locations with low temperatures and high accumulation rates (high values are found for, for example, the Antarctic Plateau). The correlation coefficient between the observed ρ_{CO} and the ρ_{CO} calculated with Eq. (6) is $r^2 = 0.82$ (99.9% confidence level), as shown in Fig. 3.

2.2.4 Tortuosity

Fabre et al. (2000) studied the tortuosity profile in great detail for 5 sites (4 Antarctic sites). In their study they compared the measured tortuosity profiles with derived model profiles, using an inverse modelling method (similar to this study). They present a linear equation to determine the tortuosity with the open porosity between 0.1 and 0.4. Unfortunately the relation of Fabre et al. (2000), cannot be implemented because the tortuosity profile of the complete firn layer is required in this study (open porosity from 0 to ~0.8). Therefore, we use Eq. (4).

Values between 0.92 and 0.98 were found for the tortuosity constant γ_a , after tuning the diffusion model for each site. This parameter does not show any significant correlation with any meteorological variable. Because γ_a does not strongly vary among the

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sites, we decided to use a constant value of 0.95 ± 0.03 . Values for γ_b were obtained after tuning the nine sites listed in Table 1, again assuming γ_a constant and equal to 0.95. Equation (7) describes the parameterisation for γ_b :

$$\gamma_b = \alpha_3 + \beta_3 T + \delta_3 A + \varphi_3 P \quad (7)$$

The constants α_3 , β_3 , δ_3 and φ_3 are listed in Table 2. Here, γ_b is described as a function of annual surface temperature (contributing ~5%), accumulation rate (~1.5%) and annual surface pressure (~60%). The combination of annual surface temperature and accumulation rate in Eq. (7) and the signs of the parameterisation constants (β and δ) for these two variables suggest a strong dependence on density. The pressure dependence in Eq. (7) can be understood because the tortuosity is the main tuning parameter in the diffusion model, in which atmospheric pressure is an important parameter. The tortuosity is a function of porosity, capillary radius and capillary pressure (Cunningham and Williams, 1980), which also accounts for the pressure dependence in Eq. (7). Figure 3 presents the accuracy of the parameterisation of γ_b . The correlation coefficient for the modelled γ_b and the parameterised γ_b (Eq. 7) is $r^2 = 0.72$ (99.9% confidence level).

To determine the accuracy of the diffusion model with all three parameterisations included, we compared the modelled CO₂ age at PCOD with the firn air age described in site-specific studies (Butler et al., 1999; Sturges et al., 2001; Trudinger et al., 1997, 2002; Kaspers et al., 2004). Figure 4 shows this comparison. We included the obtained uncertainty (2σ) for the modelled age in this graph (described in detail in Sect. 3.3). We did not take the DSS site into account for deriving the correlation coefficient (r^2) because the horizontal resolution in our calculations is too poor to resolve the meteorology in this area (DSS and DEO-8 are located at Law Dome, Fig. 1). The correlation coefficient (r^2) for modelled CO₂ age in firn air at PCOD and the age determined with site-specific parameters is 0.90. This high correlation and slope close to 1, suggests that our derived parameterisations used in the firn air diffusion model yield good results and justify the extrapolation over all of Antarctica.

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3 Results

3.1 Results for density

Figure 5 displays the modelled surface snow density field. High surface snow density is found near the coast in East Antarctica and on the Antarctic Peninsula. The high values are due to the effect of temperature and accumulation and, to a lesser extent, to that of wind speed. On the Antarctic plateau, the surface snow density is on average between 320–360 kg m⁻³, mainly as a result of the low surface temperatures (the structure of Fig. 2a is clearly visible in Fig. 5). The blue ice areas are visible with high surface densities, for example near the Amery ice shelf. The high values on these blue ice areas are a result on the model set-up, when the accumulation rate was zero or even negative the surface density was set to the density of ice.

To model the density profile over the entire Antarctic continent we have used the snow surface density field as input parameter in the density depth model of Herron and Langway (1980). In Fig. 6 we present the PCOD over Antarctica derived from the Herron and Langway model, using the parameterisations for the surface snow density and the pore-close off density (Eq. 6b). The deepest PCOD's are found high on the Antarctic plateau between Dome Fuji and Vostok, mostly due to the low temperatures, whereas low values for PCOD are found on West Antarctica and the coastal sites. Again the blue ice area at Amery ice shelf is clearly visible, with PCOD values of zero.

To understand the relation between temperature, accumulation and PCOD presented in Fig. 6, we derived a contour graph (Fig. 7) from a theoretical study with the Herron and Langway model. Here, the accumulation ranges from 0 to 1 m.w.eq.a⁻¹ and temperature from 210 to 260 K. The figure indicates that the rather uncommon combination of low temperature and high accumulation will generally result in a deeper PCOD, which is consisted with other density depth models (Arnaud et al., 1998; Barnola et al., 1991; Kameda et al., 1994; Craven and Allison, 1998; and Spencer et al., 2001). This also explains the relatively deep PCOD at the South Pole (120 m) compared to Site M and Dome C (around 100 m). The two latter sites have a lower annual mean surface

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temperature, but because South Pole has a higher accumulation rate, the PCOD at South Pole is deeper than the PCOD at Site M and Dome C. However, the deepest pore close-off (150 m) was found for 72° E, 82° S near Dome Argus, where temperature and accumulation are both low.

To determine the influence of the pore close-off density parameterisation, we included the pore close-off density parameterisation of Martinerie et al. (1994) (Eq. 6a) in this study. In Fig. 8, we present the difference in derived PCOD when both pore close-off density parameterisations were used. For the deepest PCOD's found on the Antarctic plateau this results in an increased PCOD of 3 to 4 m when the parameterisation obtained in this study is used compared to the parameterisation of Martinerie et al. (1994). For most parts of Antarctica a decrease of the PCOD is found with our parameterisation, with the exception of places where the accumulation rate is very high (Peninsula and Law Dome). The parameterisation of Martinerie et al. (1994) only depends on the surface temperature, whereas the parameterisation obtained in this study includes the accumulation rate as well. For this reason we have used our obtained parameterisation for the pore close-off density in the diffusion model. Though the difference of both parameterisations is again studied in the next section.

3.2 Age of CO₂ at PCOD

For each grid point, the diffusion model yields the CO₂ concentration at PCOD. From the known history of CO₂, the CO₂ age of the air at PCOD can be readily determined (Schwander et al., 1993). Figure 9 shows the result. The model predicts that the oldest CO₂ in firn air is located in an area between Dome Fuji, Dome Argos and Vostok. This area is characterized by a large PCOD, low temperatures and relatively high atmospheric pressure and accumulation compared to the domes. This can be understood as follows. At the low-temperature locations, the PCOD is deep. The age of CO₂ at PCOD is furthermore depended by the diffusion rate. Here temperature had a direct effect on the diffusion rate; at low temperatures the diffusion rate is low, yielding older air at PCOD. For low surface pressure the effect on the diffusion rate is opposite to that

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of temperature. Here the low surface pressure will increase the diffusion rate, because of fewer chocks between molecules. The result of Fig. 9 is consisted with the conclusions of Fabre et al. (2000), where they studied the tortuosity and diffusion rate for 4 sites on Antarctica. The model predicts the oldest CO₂ in firn air at PCOD to be 148 years (CO₂ age) and that it can be found at 43° E, 78° S.

As an example for trace gas records, we predict an age of 125 years at PCOD for CH₃Cl at 43° E, 78° S. The difference in age between methyl chloride and CO₂ is due to the different molecular mass and gas specific diffusion coefficient (D_{12}) of methyl chloride versus CO₂ (Kaspers et al., 2004). Sampling firn air at 43° E, 78° S, will therefore lengthen the present longest firn air record from South Pole, being 80 years (Butler et al., 1999). Such data could be compared with measurements of methyl chloride concentrations in Siple Dome ice presented by Aydin et al. (2004), showing a sinusoidal (~100 year period) atmospheric concentration over the past 300 years.

From Fig. 9, the youngest firn air at PCOD can be found at the coast and at the coastal side of the mountain ranges (specifically near the Trans Antarctic Mountains). The low age of CO₂ at PCOD near the mountains is mostly due to relatively high temperatures found at these locations. The oldest air outside the East Antarctic plateau at PCOD is found on Berkner Island.

In the previous section the influence of the pore close-off density parameterisation was explained in Fig. 8. Here we present the influence of the pore close-off density parameterisation on the age of CO₂ at PCOD, when the parameterisation of Martinerie et al. (1994) is used. Figure 10 presents the age of CO₂ at PCOD using the parameterisation of Martinerie et al. (1994).

From this figure we can conclude that: 1.) The ages of CO₂ at PCOD are within the same order of magnitude and deviate approximately 2–5 years to the results using Eq. (6b); And 2.) the location of the oldest firn air can be found in the area between Dome Fuji, Dome Argos and Vostok, consistent with Fig. 9. Yet, the determination of the exact position of the site with the oldest firn air calls for a more detailed study of the plateau area.

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3.3 Deriving the model uncertainty

We performed a number of sensitivity tests to estimate the uncertainty in the modelled PCOD and firn air age. We tested the effect of errors in the parameterisations of ρ_{CO} , γ_b and the parameterised density profile. ρ_{CO} and γ_b are important for the location of the PCOD and the open pore structure of the firn layer, while errors in the density profile will introduce an error in diffusion over the total firn air column.

We varied ρ_{CO} by 12 kg m⁻³ (twice the uncertainty of the parameterisation). This typically introduced a change of 5 m in the PCOD at the 'deep' locations (PCOD deeper than 100 m) and 1 to 2 m deviation at the more 'shallow' locations (around 60 m). This change produced a change of approximately 15% in the age of CO₂ at PCOD. Varying the tortuosity profile (γ_b) with twice the uncertainty (15%) yielded a deviation of 30% for the age of CO₂ at PCOD. So the results appear to be more sensitive to the uncertainty in γ_b than in ρ_{CO} .

We systematically varied $\rho_{(z)}$ with 5% along the entire profile, at 0.1 m resolution, which is twice the uncertainty of the Herron and Langway model. This had a significant effect on the PCOD and the local age of CO₂ at PCOD. Figure 11 shows the derived uncertainty (2σ) for the PCOD. The effect is most pronounced for the East Antarctic Plateau. For the deepest pore close-off location (150 m) at 75° E, 86° S, a 15 m uncertainty is found, being 10% (2σ). The deviation of the density profile yielded typically an uncertainty (2σ) of 15–20% over Antarctica (Fig. 11) for determining the PCOD. This yields an uncertainty of approximately 30% in the age of CO₂ at PCOD.

To determine the uncertainty (2σ) in the CO₂ age at pore close-off, all three uncertainties (twice the values given in Table 2 for ρ_{CO} and γ_b , and 5% for the Herron and Langway density model) were imposed. Figure 12 displays the result. The largest absolute deviations are found for the plateau. At 27° E, 81° S, the location of the oldest firn air, the uncertainties are 23 years (1σ) and 38 years (2σ) for 148-year-old air, being, respectively, 16% (1σ) and 26% (2σ). Overall, the age of CO₂ at PCOD has an average uncertainty of 40% (2σ) for locations with younger firn air (around 40 years)

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and of 30% (2σ) for locations containing old firn air (100 years and older).

3.4 Parameterisations of the results

From the obtained results (Sects. 3.1 to 3.3), a second parameterisation step is proposed. Here, parameterised formulas have been formulated to calculate PCOD (h_{PCOD}), the CO_2 age at PCOD ($\text{Age}_{\text{CO}_2, \text{PCOD}}$) and the model error in the calculated age of CO_2 at pore close-off ($\sigma_{\text{Age, PCOD}}$), by using the surface meteorological conditions. The idea of these parameterisations is that they can easily be used in the field to gain knowledge about the expected PCOD and age of CO_2 at PCOD, when the meteorological conditions are known for a specific site, but without tuning a firn diffusion model.

$$h_{\text{PCOD}} = \alpha_1 + \beta_1 T + \delta_1 A \quad (8)$$

$$\text{Age}_{\text{CO}_2, \text{PCOD}} = \alpha_2 + \beta_2 T + \delta_2 A + \varphi_2 P \quad (9)$$

$$\sigma_{\text{Age, PCOD}} = \alpha_3 + \beta_3 T + \varphi_3 P \quad (10)$$

In these formulas, T is the annual mean temperature in K, A the accumulation rate in m.w.eq.a^{-1} and P the atmospheric pressure in hPa. The parameterisation constants are presented in Table 3. The surface atmospheric pressure can be easily parameterised in terms of elevation, as described in Van den Broeke et al. (1999).

4 Summary and conclusions

We successfully combined a modelled meteorological dataset based on output from an atmospheric model for the period 1980–1993 (van Lipzig et al., 2002) and a firn air diffusion model. In order to make this combination, we use a density depth model and had to parameterise the surface density, pore close-off density and the tortuosity of the firn layer. We have used the Herron and Langway density-depth model in the diffusion model after comparing 5 density depth models. We found that the model

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of Arnaud et al. (1998) and Herron and Langway (1980) provide the most accurate results, when compared to nine measured density profiles. To derive the parameterisations for ρ_0 , ρ_{CO} and $\gamma_{(z)}$, we used nine firn air analyses (Butler et al., 1999; Sturges et al., 2001; Trudinger et al., 1997; Kaspers et al., 2004; Table 1). The results of this parameterisation, demonstrate, that the tortuosity and surface density can be related to meteorological parameters, to our knowledge for the first time. The accuracy of the parameterisations for ρ_0 , ρ_{CO} and γ_b was determined by comparing our diffusion model results with earlier published firn air ages at pore close-off (Table 1). A correlation coefficient (r^2) of 0.9 and a slope close to 1, was found for CO_2 ages at pore close-off derived from our study (with only 4 meteorological variables as input) and the CO_2 ages from published firn air analyses. This correlation coefficient gives confidence in the accuracy of our approach. With the diffusion model, the parameterisations yielded a surface snow density field for the entire Antarctic continent. For this surface snow density, the annual surface temperature and accumulation rate are the most important parameters, but wind speed also plays an important role, especially for the coastal sites and near mountain ranges. The lowest values for the surface snow density are found for the East Antarctic plateau, where annual surface temperature and accumulation rate are low. Incorporation of the surface snow density field in the density-depth model of Herron and Langway (1980) yielded the PCOD. After modelling the PCOD for Antarctica, a maximum PCOD of $150 \pm 15 \text{ m}$ (2σ) was found for 72° E , 82° S . The pore close-off density parameterisation is responsible for 3 to 4 m deviation in PCOD, when comparing between the parameterisation for ρ_{CO} in this study (dependent on temperature and accumulation) and the ρ_{CO} parameterisation of Martinierie et al. (1994) (only temperature dependent).

We took the CO_2 data for the past 250 years, as upper boundary condition and modelled the diffusion of CO_2 into the firn layer until PCOD. This enabled us to determine the age of CO_2 at PCOD for the entire Antarctic continent. This study indicates, that the age of the CO_2 at PCOD is older at sites with low annual temperature and relatively high accumulation and surface pressure. This result is consistent with the conclusions

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of Fabre et al. (2000). An important result from the combination between the diffusion model and the RACMO climate model is the prediction of the location where the oldest CO₂ in firn air can be sampled, between Dome Fuji, Dome Argus and Vostok. The oldest air is found at 43° E, 78° S, using our ρ_{CO_2} parameterisation. However, the exact location is debatable, as indicated by the results in case the Martinerie et al. (1994) ρ_{CO_2} parameterisation was used. The age of the CO₂ at PCOD at 43° E, 78° S is expected to be 148±23 (1 σ) and 38 (2 σ) years. No firn gas analyses have been carried out for that location. To give an example (of the practical usefulness of our results), for firn air trace gas analyses, we predict an age of 125 years at PCOD for CH₃Cl at 43° E, 78° S, which would yield a record that is approximately 45 years longer than the trace gas record of Butler et al. (1999).

A number of sensitivity tests were performed to gain insight about model uncertainty. Here, tests were performed where the pore close-off density (ρ_{CO}) and tortuosity (γ_b) parameterisations were varied twice the uncertainty (2 σ) in the diffusion model and the density profile was varied 5% over the total firn column. The sensitivity test revealed that the tortuosity parameterisation and the modelling of density profile caused the largest uncertainty. The derived model uncertainty was 40% (2 σ) for locations containing younger firn air (around 40 years) and 30% (2 σ) for locations containing older firn air (older than 100 years). The model uncertainty can be significantly improved with better parameterisations for the tortuosity, pore close-off density and surface snow density, for which more firn air data need to become available first.

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Appendix

Site	Location	Elevation (m)	T 10m (K)	A (m.w.eq. ⁻¹)	WS m s ⁻¹	ρ_0 kg m ⁻³	Ref.
M	74°59'59"S 15°00'06"E	3453	221.7	0.05	5.7	0.307	Kaspers et al., 2004
S20	70°14'30"S 0.4°48'40"E	48	255.5	0.27	7.4	0.437	Kaspers et al., 2004
DML	77S 10W	2300	235.5	0.08	6.4	0.381	Sturges et al., 2001
Dome C	75S 123E	3240	220.2	0.03	5.0	0.318	Sturges et al., 2001
South Pole	90S	2841	223.8	0.07	6.0	0.427	Butler et al., 1999
Siple	81°40'S 148°49'W	600	247.8	0.14	6.0	0.358	Butler et al., 1999
DSS	66°46'S 112°48'E	1370	254.2	0.15	6.9	0.419	Trudinger et al., 1997
DEO8-2	66°43'S 113°12'E	1250	254.2	1.10	7.0	0.470	Trudinger et al., 1997
Tunu (green)	78°01'N 33°59'E	2400	244.2	0.09	6.3	0.357	Butler et al., 1999
Vostok	78°28'S 106°48'E	3502	216.2	0.02	7.9	0.300	Barkov et al., 1974
Old Byrd	79°59' 120°01'W	1510	245.2	0.16	7.6	0.380	Gow, 1968
Ro.Is.Dome	79°22' 161°41'W		250.5	0.16	6.7	0.370	Herron and Langway, 1980
Little Am V	78°10' 162°13'W	43	249.2	0.22	6.7	0.360	Gow, 1968
J-9	82°22' 168°40'W		245.3	0.09	5.6	0.350	Herron and Langway, 1980
C-7-3	78°20' 179°51'E		247.6	0.11	6.8	0.340	Herron and Langway, 1980
Site A	71°54'S 03°05'E	1520	247.6	0.14	4.7	0.362	Van den Broeke et al., 1999
Site B	72°08'01" 03°10'31"	2044	245.1	0.17	5.4	0.356	Van den Broeke et al., 1999
Site C	72°15'04" 02°53'28"	2400	242.9	0.12	5.4	0.343	Van den Broeke et al., 1999
Site D	72°30' 0'3	2610	238.4	0.11	6.3	0.373	Van den Broeke et al., 1999
Site E	72°40'42" 03°39'46"	2751	236.3	0.06	4.0	0.407	Van den Broeke et al., 1999
Site F	72°51'41" 04°21'05"	2840	234.7	0.02	4.4	0.375	Van den Broeke et al., 1999
Site G	73°02'26" 05°02'39"	2929	233.1	0.03	4.4	0.355	Van den Broeke et al., 1999
Site H	73°23'11" 06°27'38"	3074	230.5	0.04	5.2	0.366	Van den Broeke et al., 1999
Site I	73°43'27" 07°56'26"	3174	228.6	0.05	5.8	0.343	Van den Broeke et al., 1999
Site J	74°02'41" 09°29'30"	3268	226.9	0.06	6.5	0.338	Van den Broeke et al., 1999
Site K	74°21'16" 11°06'13"	3341	225.4	0.05	6.7	0.343	Van den Broeke et al., 1999
Site L	74°38'50" 12°47'27"	3406	223.9	0.05	6.5	0.341	Van den Broeke et al., 1999
Site S15	71°11'30" 04°35'50"	800	252.9	0.24	3.8	0.389	Van den Broeke et al., 1999

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Site	Location		Elevation (m)	T 10m (K)	A (m.w.eq. ⁻¹)	WS m s ⁻¹	ρ_0 kg m ⁻³	Ref.
5	87°48'18"S	59°12'E	2989	219.7	0.06	5.88	0.396	Cameron et al., 1968
5a	idem	idem	3006	219.0	0.055	5.88	0.387	Cameron et al., 1968
6	87°16'48"	58°54'	3034	221.7	0.072	6.367	0.411	Cameron et al., 1968
7	86°45'	58°36'	3106	221.6	0.048	5.84	0.374	Cameron et al., 1968
9	86°44'30"	40°00'	3022	223.6	0.060	6.986	0.393	Cameron et al., 1968
10	86°37'42"	30°36'	2857	225.0	0.074	7.275	0.405	Cameron et al., 1968
13	85°45'48"	08°42'	2695	221.6	0.085	7.826	0.394	Cameron et al., 1968
14	85°26'18"	04°42'	2672	224.3	0.066	8.513	0.394	Cameron et al., 1968
15	85°10'12"	01°48'	2628	223.4	0.093	8.159	0.393	Cameron et al., 1968
16	85°13'18"	07°42'	2679	223.8	0.049	8.384	0.369	Cameron et al., 1968
17	85°10'48"	13°12'	2688	223.4	0.053	8.036	0.365	Cameron et al., 1968
18	84°58'06"	17°54'	2676	224.4	0.078	7.426	0.385	Cameron et al., 1968
19	85°50'48"	21°48'	2683	224.6	0.064	7.847	0.375	Cameron et al., 1968
20	84°41'48"	26°00'	2792	226.5	0.075	6.799	0.397	Cameron et al., 1968
21	84°31'42"	30°06'	2872	227.0	0.060	7.178	0.385	Cameron et al., 1968
22	84°22'12"	33°54'	3046	226.0	0.062	7.09	0.392	Cameron et al., 1968
23	84°10'30"	37°36'	3172	224.4	0.133	7.414	0.397	Cameron et al., 1968
24	83°52'42"	41°18'	3314	221.7	??	7.821	0.392	Cameron et al., 1968
25	83°20'	44°33'	3397	220.5	0.067	8.081	0.375	Cameron et al., 1968
26	83°10'30"	47°28'	3497	219.2	0.057	7.6	0.382	Cameron et al., 1968
27	82°50'12"	50°31'	3577	217.6	0.066	7.3	0.371	Cameron et al., 1968
28	82°27'12"	52°52'	3659	216.5	0.065	6.8	0.363	Cameron et al., 1968
29	82°06'47"	55°02'02"	3718	215.7	0.061	6.8	0.364	Cameron et al., 1968

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Table 1. Locations and elevations of nine firn core sites used for the parameterisations. The meteorological conditions are included; T is the annual surface temperature (T 10 m), A the accumulation rate obtained from the referenced studies, P the annual surface pressure and W the wind speed at 10 m derived from RACMO (except the P and W values for Tunu, these values were obtained from automatic weather stations).

Site	Location	Elevation (m)	T (K) 10 m	A (m.w.eq.a ⁻¹)	P (hpa)	W 10 m (m s ⁻¹)	Ref.
M	75° S, 15° E	3453	221.7	0.05	615	5.7	Broeke et al. (2004)
S20	70° 15' S, 4° 49' E	48	255.5	0.28	993	7.4	Broeke et al. (2004)
DML	77° S, 10° W	2300	238	0.10	730	6.4	Sturges et al. (2001)
Dome C	75° S, 123° E	3240	220.2	0.03	655	5.0	Sturges et al. (2001)
DEO8-2	66° 43' S, 113° 12' E	1250	254	1.1	850	7.0	Trudinger et al. (1997)
DSS	66° 46' S, 112° 48' E	1370	251	0.60	825	6.9	Trudinger et al. (1997)
South Pole	90° S	2841	223.8	0.073	680	6.0	Butler et al. (1999)
SipleDome	81° 40' S, 148° 49' W	600	247.8	0.138	970	6.0	Butler et al. (1999)
Tunu ^a	78° 01' N, 33° 59' E	2400	244.2	0.092	777	6.3	Butler et al. (1999)

^a Located in Greenland.

1839

Table 2. Parameterisation constants from Eqs. (5), (6) and (7) to couple ρ_O , ρ_{CO} and γ_B to meteorological variables.

	α	β	δ	ε	φ	1σ
ρ_O	$7.36 \cdot 10^{-2}$	$1.06 \cdot 10^{-3}$	$6.69 \cdot 10^{-2}$	$4.77 \cdot 10^{-3}$		0.023
ρ_{CO}	1.06	$-1.02 \cdot 10^{-3}$	$2.64 \cdot 10^{-2}$			0.006
γ_B	1.76	$-8.41 \cdot 10^{-5}$	1.16		$2.63 \cdot 10^{-3}$	0.266

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Table 3. Parameterisation constants from Eqs. (7), (8) and (10) relating the final model results directly to meteorological variables.

	α	β	δ	ε	1σ
h_{PCO}	678	-2.60	87.7		8
$\text{Age}_{\text{CO}_2, \text{PCOD}}$	605	-2.74	35.2	0.096	10
$\sigma_{\text{CO}_2, \text{PCOD}}$	168	-0.74		0.026	6

1841

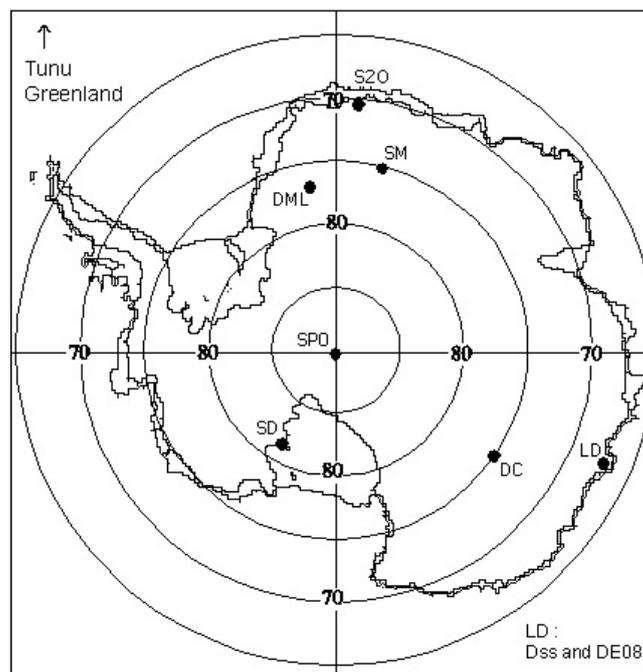


Fig. 1. Locations of the firm air sites used in this study. Elevation and meteorological conditions for these sites are given in Table 1.

1842

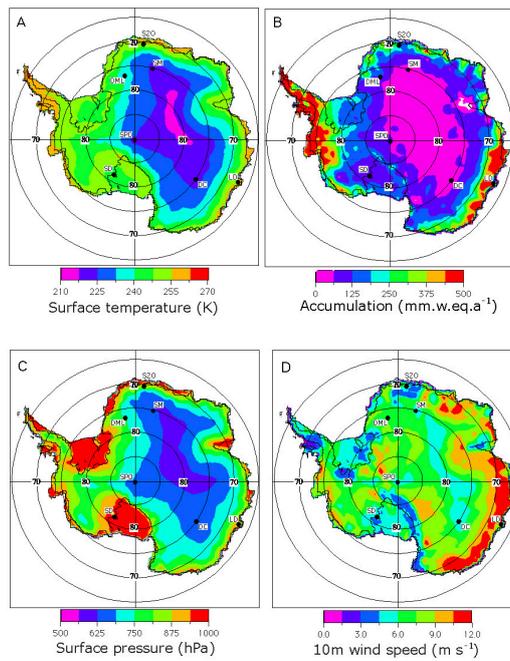


Fig. 2. Input parameters derived from the Regional Atmospheric Climate Model (RACMO/ANT) (van Lipzig et al., 2002) for annual surface temperature in K **(a)**, annual surface pressure in hPa **(b)**, accumulation rate in m.w.eq.a^{-1} (measured by Vaughan et al., 1999) **(c)**, and wind speed at 10 m in m s^{-1} **(d)**.

1843

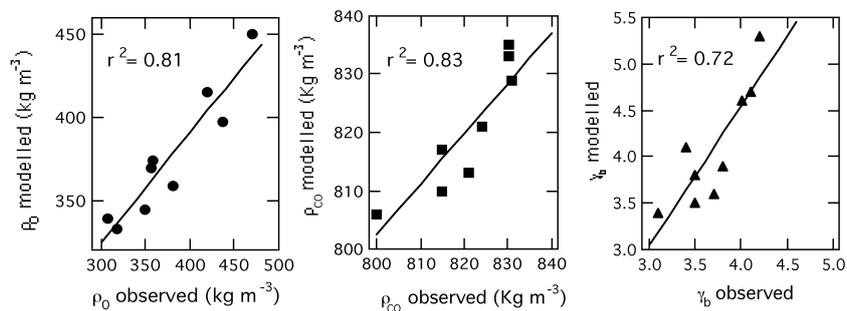


Fig. 3. Parameterisations of ρ_0 , ρ_{CO} and γ_b as a function of the measured and obtained values at the nine specific sites, listed in Table 1.

1844

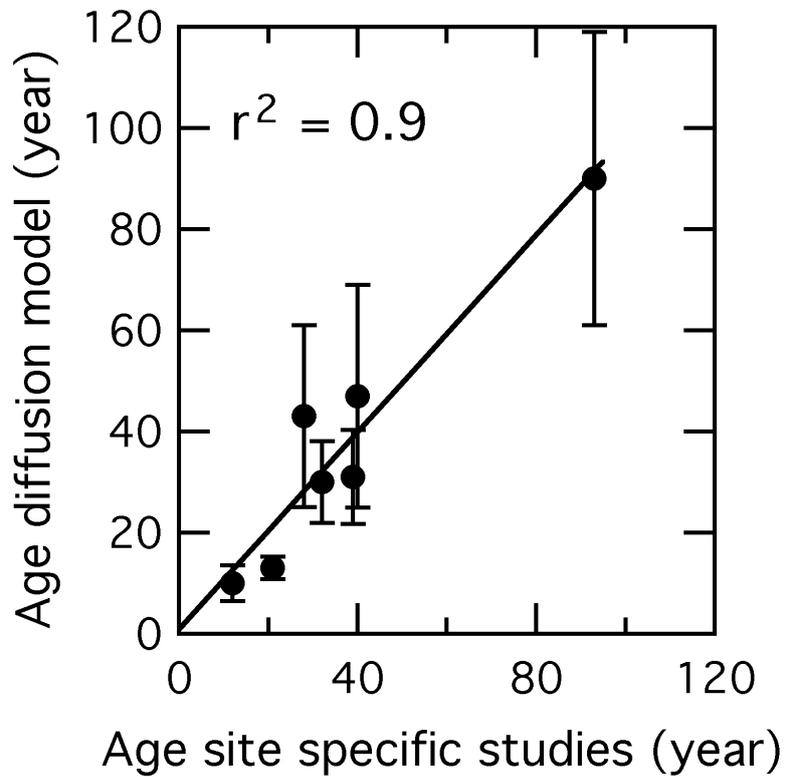


Fig. 4. Comparison between the modelled age of CO₂ at PCOD, using the parameterisations for ρ_0 , ρ_{CO} and γ_b (including the model uncertainty, 2σ), and the obtained age of CO₂ at PCOD derived from site-specific studies (listed in Table 1).

1845

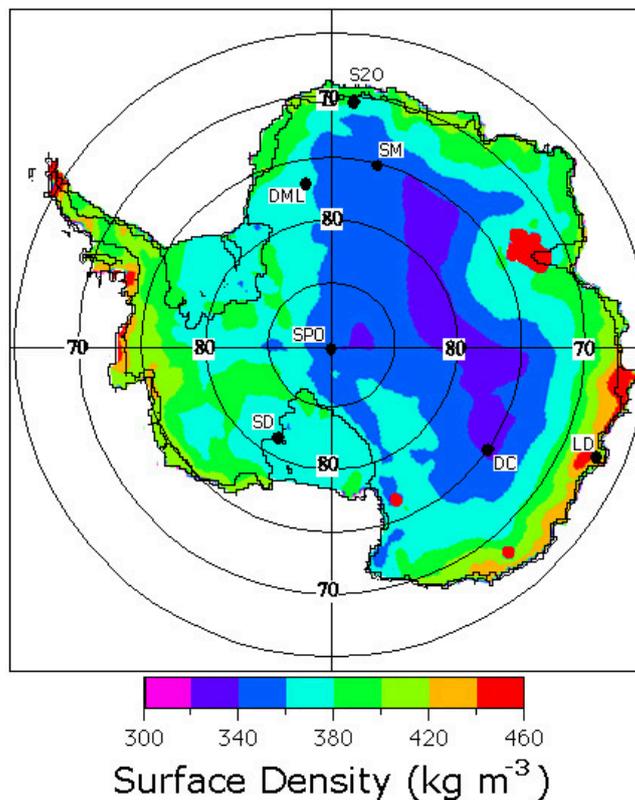


Fig. 5. The surface snow density field in kg m^{-3} , calculated using Eq. (5) in combination with Table 2.

1846

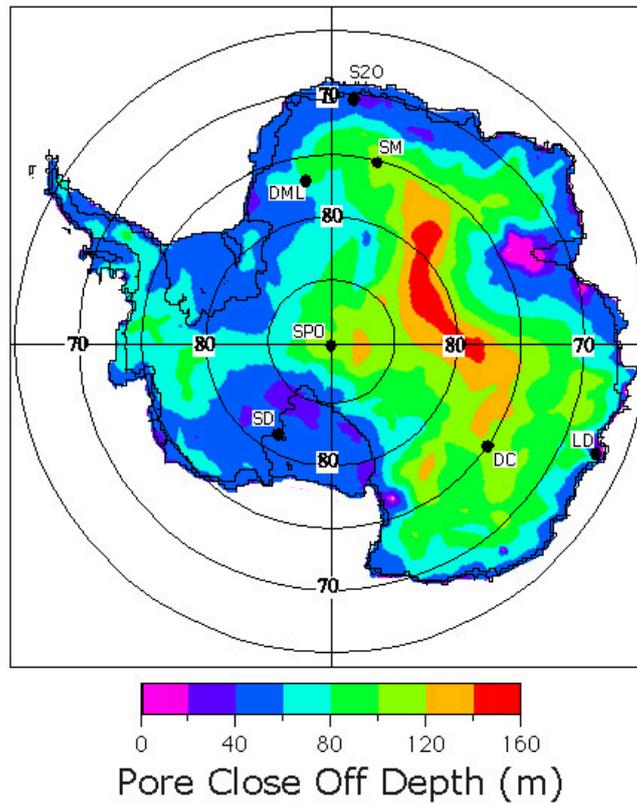


Fig. 6. Depth of the PCOD in m, calculated with the density-depth model of Herron and Langway (1980). The location with the deepest PCOD, being 150 ± 15 m (2σ), is found for 72° E and 82° S.

1847

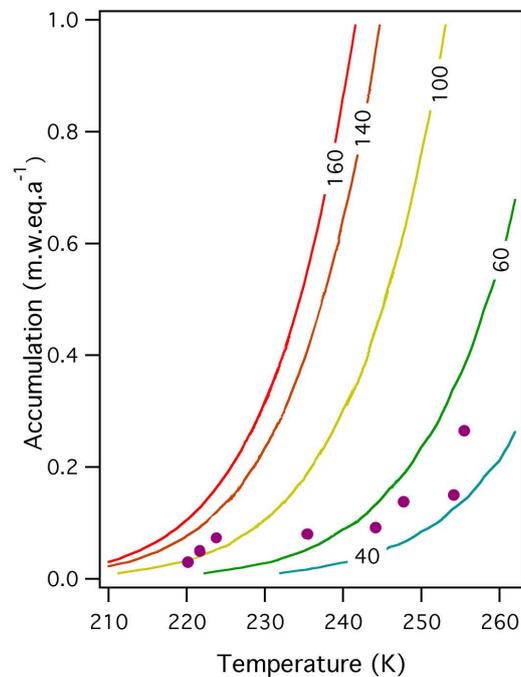


Fig. 7. Theoretically determined PCOD, using the density-depth model Herron and Langway (1980). The contour plot represents different PCOD's in m with varying annual surface temperatures and accumulation rates, varying from, respectively, 210 to 260 K and 0.01 to 1 m.w.eq.a⁻¹. The dots represent the PCOD's of nine sites (Table 1).

1848

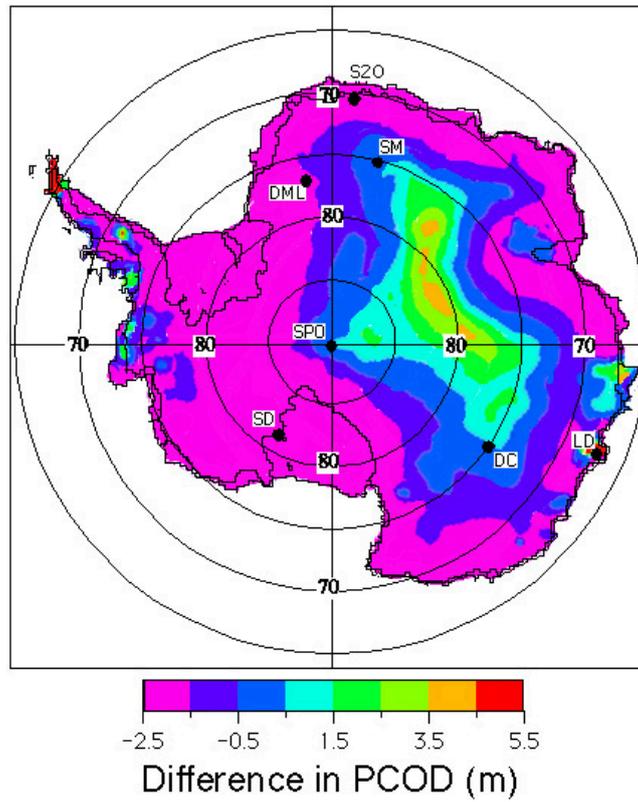


Fig. 8. The difference in PCOD obtained from calculating the PCOD using the pore close-off density parameterisation of Eq. (6b), minus the PCOD calculated using the parameterisation of Martinerie et al. (1994) (Eq. 6a). The difference in PCOD is presented in metres.
1849

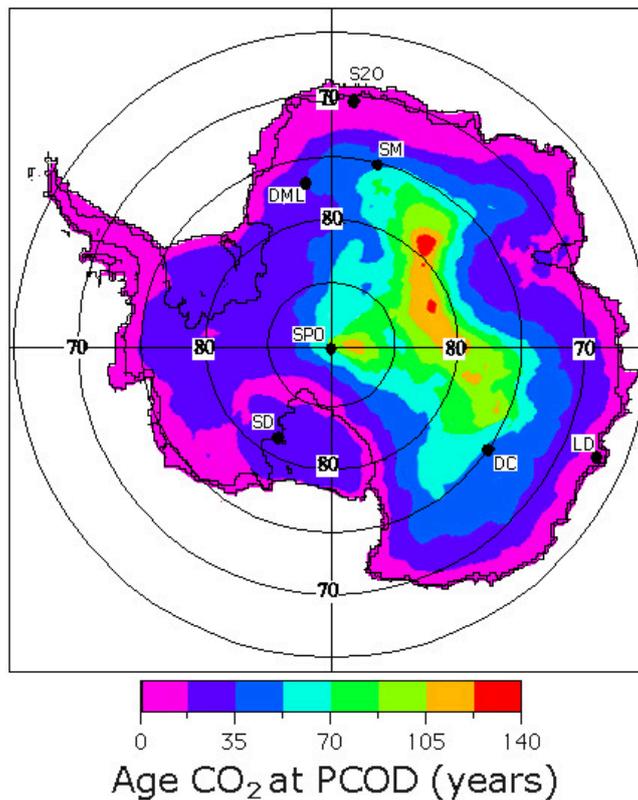


Fig. 9. The mean CO_2 age at PCOD in years for the entire Antarctic continent. The oldest CO_2 at PCOD, being 148 ± 23 years (1σ), is predicted as located at 43° E and 78° S .

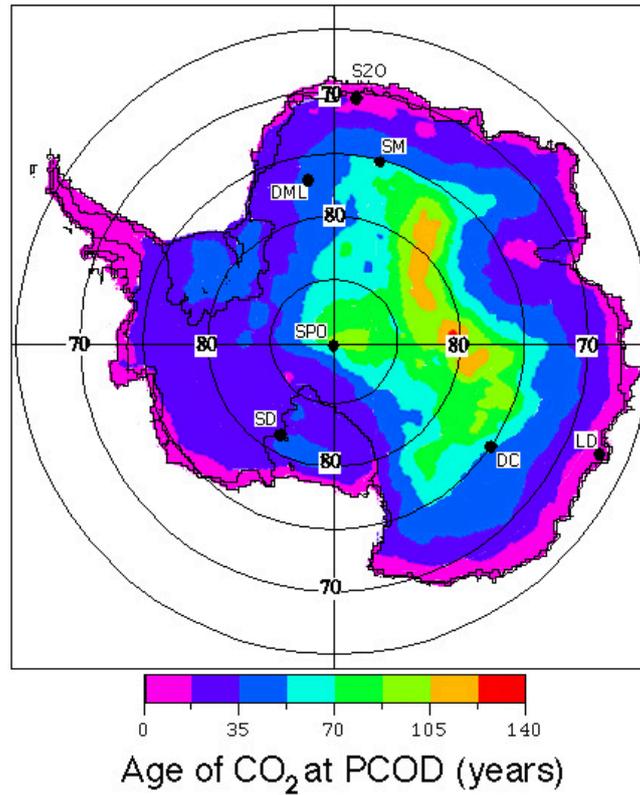


Fig. 10. The mean CO₂ age at PCOD in years, calculated with the pore close-off parameterisation of Martinerie et al. (1994) (Eq. 6a).

1851

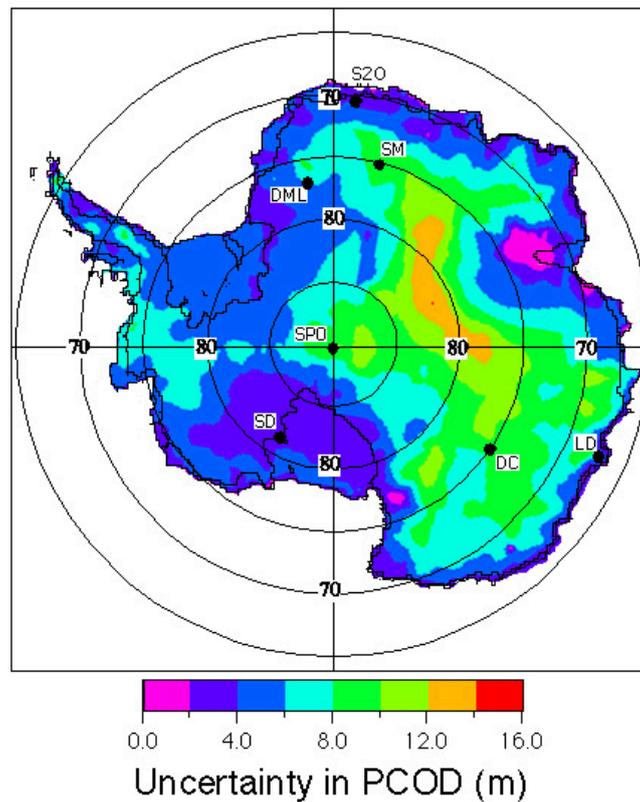


Fig. 11. The uncertainty (2σ) of the PCOD (m), obtained after deviating the density profile 5% every 0.1 m by using the Herron and Langway (1980) model.

1852

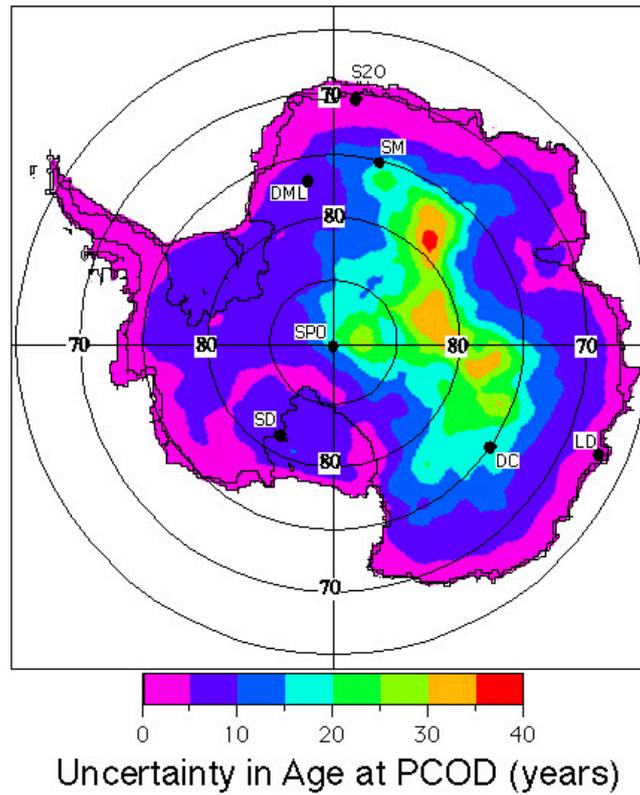


Fig. 12. The model uncertainty in derived CO₂ age at PCOD (2σ , in years). Here, twice the uncertainty (2σ) for the tortuosity (γ_b) and the pore close-off density (ρ_{CO}) and a deviation of 5% in the modelled density profile were taken into account.