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Diffusive equilibration of N_2, O_2 and CO_2 mixing ratios in a 1.5 million years old ice core

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Abstract

In the framework of the International Partnerships in Ice Core Sciences, one of the most important target is to retrieve an Antarctic ice core that extends over the last 1.5 million years, i.e. an ice core that enters the climate era when glacial-interglacial cycles followed the obliquity cycles of the sun. In such an ice core the annual layers of the oldest ice would be thinned by a factor of about 100 and the climatic information of a 10 000 yr interval would be contained in less than 1 m of ice. The gas record in such an Antarctic ice core can potentially reveal the role of greenhouse gas forcing on these 40 000 yr cycles. However, besides the extreme thinning of the annual layers, also the long residence time of the trapped air in the ice and the relatively high ice temperatures near the bedrock favour diffusive exchanges. To investigate the changes in the O_2/N_2 ratio, as well as the trapped CO_2 concentrations, we modelled the diffusive exchange of the trapped gases O_2, N_2 and CO_2 along the vertical axis. Even though the boundary conditions of a potential drilling site are not yet well constrained and the uncertainties in the permeation coefficients of the air constituents in the ice are large, the results suggest that in the oldest ice the precessional variations in the O_2/N_2 ratio will be damped by 50–100 %, whereas CO_2 concentration changes associated with glacial-interglacial variations will experience a damping of only 5 %. This significant attenuation of the precessional O_2/N_2 signal in the ice older than 1 Myr will limit the possibility to use the O_2/N_2 ratio for orbital tuning of the ice core age scale.

1   Introduction

In the framework of the International Partnerships in Ice Core Sciences (IPICS), one target is to retrieve an ice core reaching back in time as far as possible. The main objective of such a core would be to cover Mid-Pleistocene climate transition, the transition interval from the "40 kyr world" prior to about 900 thousand years before present (kyr BP) (Elderfield et al., 2012), where full glacial-interglacial cycles occurred in parallel

to obliquity cycles, to the well-known "100 kyr world" thereafter, where rather short interglacials were observed every about 100 kyr. Accordingly, such an ice core should ideally disclose the last 1.5 million years (Myr) of climate history. The conditions, where such an ice core can be found, are only satisfied in central east Antarctica where it is cold and dry enough (see Fischer et al., 2013). The most important boundary condition for finding such old ice is that no melting occurs at the bottom of the ice sheet. Only in this case the ancient ice may be preserved in the deepest part of the ice sheet. In the case of the EPICA Dome C (EDC) ice core, about 0.6 mm ice per year is melting at the bedrock (Parrenin et al., 2007b) which limits the age of the deepest (undisturbed) ice to about 800 kyr.

A consequence of a frozen bedrock and the preservation of ancient ice in the deep section of an ice core is that the annual layers get extremely thinned in the deep part. Since, in theory, an annual layer could be conserved infinitely long at such a drill site, the annual layers would also be thinned infinitely. Therefore, the question arises by how much the annual layers can be thinned until gas diffusive processes start to deteriorate and eventually remove the signal stored in the trapped atmospheric air. In order to investigate this question we modified the diffusion model of Bereiter et al. (2009) and combined it with an one-dimensional ice flow and ice temperature model. The diffusive exchange of O_2, N_2 and CO_2 is calculated and the behaviour of an initially sinusoidal concentration sequences of these gases with different periods is simulated along the ice core axis, while the ice is compressed and moving down with the vertical ice flow (see results in Sect. 4).

To calculate the diffusive exchange of the air constituents in the ice, permeation coefficients (product of diffusion and solubility) are required for each constituent. These coefficients for O_2, N_2 and CO_2 are very small and a precise measurement is very challenging (Haeberlin, 2012). Therefore, only a few estimates of these parameters, using different approaches, are found in the literature. For O_2 and N_2 we use the "set B" of Bereiter et al. (2009) and call it here "fast set" (FS), but we do not use the "set A" as it provided unrealistic results in that work. In addition, we also use the permeation

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parameters of Salamatin et al. (2001) (referred to as "slow set", SS) and a recent estimate of total air permeability of Uchida et al. (2011). For CO_2 we use the permeation parameter of Ahn et al. (2008) (see Fig. 2 and Sect. 2.3 for more details).

The two parameter sets FS and SS for O_2 and N_2 show differences of up to two orders of magnitudes. A possibility to further constrain these parameters based on ice core measurements of the O_2/N_2 ratio is presented in Sect. 3. Similar to the gas diffusion modelling work shown in Lüthi et al. (2010), which focused on the equilibration between layers of different CO_2 concentrations below the Bubble to Clathrate Transition Zone (BCTZ), the observed equilibration between layers of different O_2/N_2 ratios in the Vostok ice core is compared with a model using the two parameter sets. Such a layering is thought to be induced by a dynamic disequilibrium during clathrate formation (Lüthi et al., 2010). If the Vostok data indeed reflect the equilibration of layered O_2/N_2 ratios on cm-scale, as we think, the experiments allow us to better constrain the effective permeation coefficients for the temperature regime below the BCTZ. However, since this temperature regime is very different from the regime in which a possible equilibration in the Oldest Ice Core takes place, our simulations in Sect. 3 do not allow us to rule out any of the two permeation data sets used in our simulations.

2 Method

2.1 Model setup

The gas diffusion part of the model is based on the model presented in Bereiter et al. (2009) with the difference that the diffusion is calculated vertically (along the ice core axis) and not in radial direction of the ice core. The diffusion equation is adjusted as follows:

$$\frac{\partial C_n}{\partial t} = \frac{\partial}{\partial z}\left(D_n \frac{\partial C_n}{\partial z}\right),$$

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where C_n represents the concentration in the ice of the air constituent n (O_2, N_2 or CO_2), D_n the corresponding diffusion coefficient in ice, and z the vertical direction from $z = 0$ (bottom) to $z = H$ (surface of the ice sheet). The gas exchange of the air enclosures with the surrounding ice is calculated as in Bereiter et al. (2009). The diffusion model is run for discrete intervals of the ice core. D_n and the solubility are a function of the mean temperature of such an interval, that is they are kept independent of z within each interval.

In order to calculate the annual layer thickness of the ice at a certain depth and the corresponding temperature, the following one-dimensional ice flow model is used (Parrenin et al., 2007b):

$$w(z) = -(A - m)u(z) - m, \tag{1}$$

$$u(z) = 1 - \frac{p+2}{p+1}\left(1 - \frac{z}{H}\right) + \frac{1}{p+1}\left(1 - \frac{z}{H}\right)^{p+2}, \tag{2}$$

where $w(z)$ denotes the vertical ice velocity at the height z over the bedrock, A the accumulation rate of ice at the surface, m the melt rate at the bedrock, H the vertical thickness of the ice sheet and p a tuning factor. A, m and H are expressed in ice equivalent of constant density ($921\,\mathrm{kg\,m^{-3}}$). The velocity profile is based on the work of Lliboutry (1979) and is also used for the latest ice core age scales (Parrenin et al., 2007a).

For the temperature $T(z)$, besides H and A, also the surface temperature T_s and the geothermal heat flux Q_g are relevant. Based on the heat diffusion and advection equation

$$\frac{\partial T}{\partial t} = K\frac{\partial^2 T}{\partial z^2} - w\frac{\partial T}{\partial z}, \tag{3}$$

the following equation for the stationary temperature profile $T(z)$ can be derived:

$$T(z) = T_s - C_0 \left(\int e^{f(z')} dz' - \int e^{f(z')} dz' \right),$$
(4)

$$f(z') = \frac{-1}{K}(A - m)\left(z' + p_1\left(1 - \frac{z'}{H}\right)^2 - p_2\left(1 - \frac{z'}{H}\right)^{p+3} \right) - \frac{1}{K}mz',$$
(5)

$$C_0 = \frac{-Q_g}{\lambda}\exp\left(\frac{1}{K}(A - m)(p_1 - p_2)\right),$$
(6)

$$p_1 = \frac{p + 2}{p + 1}\frac{H}{2},$$

$$p_2 = \frac{1}{p + 1}\frac{H}{p + 3},$$

$$\lambda = 2.43\,\mathrm{W\,m^{-1}\,K^{-1}},$$

$$K = 1.42 \cdot 10^{-6}\,\mathrm{m^2\,s^{-1}},$$

where λ is the thermal conductivity, and K the thermal diffusivity of ice calculated for $-30\,°\mathrm{C}$ (Schwander et al., 1997). Q_g is the part of the geothermal heat flux, which is not used for melting of ice at the bottom and is diffusing upwards by heat conduction. In case of no melting at the bottom (Oldest Ice) this is of course equal to the total geothermal heat flux.

Note that in reality λ and K are functions of temperature. Above, we assume λ and K to be constant and calculate the steady state, i.e. we use average boundary conditions (surface temperature, accumulation rate and ice thickness). This allows us to derive the semi-analytical solution for $T(z)$ of Eq. (4). Therefore, the melt rates and geothermal heat fluxes derived in our model may differ quantitatively from the true values at Dome C. However, the temperature in the deeper part of the ice sheet is well represented as illustrated in Fig. 1. The temperature profile of a potential Oldest Ice core site is

expected to be similar with the difference – as mentioned above – that the bedrock temperature must be lower to avoid ice melting.

In a first step, the depth-age distribution (age(z)) is calculated for the given input parameters A, H, m and p by integrating the inverse of the vertical velocity $w(z)$:

$$\text{age}(z) = \int \frac{1}{w(z')}dz',$$

Then, this scale is divided into intervals of equal temporal duration, meaning that an ice particle, which travels down in the ice sheet, would stay within each of these intervals for the same period of time. For each of these intervals an average annual layer thickness and an average ice temperature is calculated using the temperature profile described from solving Eqs. (4) to (6) (see Fig. 1).

The diffusion model is run for each of these intervals starting with the upper most one with a given trapped air composition (see Fig. 4 and 6 for corresponding starting distributions). The simulation time for each interval corresponds to the residence time in the intervals. After the gas composition changes have been calculated for the first interval, the resulting composition is used in the next step for the run in the next lower interval where the length of the trapped gas section is scaled according to the new annual layer thickness, and the permeation coefficients are changed according to the new temperature. This process is repeated downwards through all intervals until the lowest interval is reached.

2.2 Input parameters for the ice core model

In order to start the model, the boundary conditions for the ice flow and temperature model (ice parameters) need to be set as well as the diffusion and solubility coefficients of the gases in the ice (gas parameters). The ice parameters for the different experiments are given in Table 1. In the case of the Vostok and EDC parameters they have been tuned in order to fit the available age-depth relations (age(z)) and borehole temperatures ($T(z)$) as well as possible. However, the parameters were kept as close as

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possible to independent published values. Since the ice flow and temperature model used here assumes steady state conditions, the temporal average of the corresponding parameters are used.

For most of the EDC ice parameters corresponding values can be found in the liter-
ature. The factors A, m, H and T_s are set such that they lie within their uncertainties or agree within 2 % with the values reported in Parrenin et al. (2007a) and Jouzel et al. (2007). The factor p is modified relative to the corresponding value given in Parrenin et al. (2007b) (1.97 ± 0.93) in order to improve the agreement of the modelled age(z) with the ED3 age scale (Parrenin et al., 2007a). The factor Q_g is set such that
$T(0)$ fits the EDC bedrock temperature (see Fig. 1).

In the case of the Vostok ice parameters, not for all parameters corresponding values are found in the literature, and if so, they are mostly less precise compared to the EDC parameters and/or do not cover the full extent of the ice core. However, for the simulations performed under the Vostok conditions (see Sect. 3), it is only necessary that
the modelled age(z) and $T(z)$ roughly represent the corresponding reference records below the BCTZ, between 1250 and 2500 m depth (grey shaded area in Fig. 1), and not down to the bottom of the ice core (3379 m depth). We calibrate our models with the EGT20 age scale of Petit et al. (1999) and the borehole temperature of Salamatin et al. (1994). For the tuning of the Vostok ice parameters, the parameter H was kept
fixed at the value presented in Salamatin et al. (1998) and the other parameters were varied.

The artificial parameters of the Oldest Ice Core are chosen such that the ice 100 m above the bedrock reaches an age of roughly 1.5 million years (aim of IPICS Oldest Ice) and that the bottom ice temperature is 4–5 K below the pressure melting point of
the ice. The reason for the 100 m criterion is that several ice cores show disturbed ice layering due to irregular flow below a certain depth (e.g. EPICA community members, 2006, NEEM community members, 2013). In the EDC ice core this depth lies at about 100 m above the bedrock. The tuning parameter p is estimated using the theoretical calculation of Parrenin et al. (2007b). However, in the case of the EDC and Dome

Fuji ice cores this theoretical value was found to be too high. Parrenin et al. (2007b) suggest that the bedrock topography might cause this discrepancy. Another reason might be that Eq. (2) has been derived for ice sheets far away from ice divides and ice domes (Lliboutry, 1979), which is not fulfilled for the two ice cores. Accordingly, also the p value for an Oldest Ice Core might be closer to the EDC value, which results in less thinning of the deep ice and, hence, a weaker gas diffusion effect. The influence of this different thinning profile is discussed in Sect. 4.

As mentioned in Sect. 1, for finding such old ice it is of fundamental importance that the ice does not melt at the bedrock. Only in this case old ice is preserved in the deep part of the ice sheet. In order to ensure a cold bedrock, the ice thickness is not allowed to be too large. Otherwise, the insulating effect of the ice enables the geothermal heating to heat the bottom ice to the pressure melting point. Observing this constraint we have arbitrarily chosen an ice thickness of 2700 m which permits a cold bedrock under the geothermal conditions we have set.

2.3 Input parameters for the gas diffusion model

The main reason for a limited predictability of the gas exchange effects in the Oldest Ice Core is the uncertainty of the gas parameters (solubility and diffusion coefficients) of N_2, O_2 and CO_2. As mentioned in Sect. 1, these parameters are very difficult to assess since they are very small making measurements under lab conditions very challenging (Haeberlin, 2012). Therefore, the parameters have been estimated in an indirect way. The used experimental approaches do not permit to estimate solubility and diffusivity of the gases separately but only the product of both, the permeability. In fact, it is the permeability that determines the magnitude of the diffusive gas transport in the ice from one air inclusion to another. Thus, an increase of the diffusion coefficient can be compensated by a corresponding decrease of the solubility coefficient and vice versa.

For the CO_2 permeability the estimate of Ahn et al. (2008) is used in all simulations, which is based on analysis of the CO_2 concentration around a layer of refrozen melt water in the Siple Dome ice core. For the permeability of N_2 and O_2 we use two

sets, which are based on different approaches and demonstrate the large spread of such estimates (see Fig. 2). The origin of the "slow set" (SS) is the work of Salamatin et al. (2001) in which the parameters are estimated by reconstructing the O_2/N_2 ratio fractionation between bubbles and clathrates in the BCTZ. The "fast set" (FS) is based on the work of Ikeda-Fukazawa et al. (2004) and Ikeda-Fukazawa et al. (2005) who have calculated the parameters based on a computer model simulating the behaviour of the gas molecules in the ice lattice (molecular simulations). The second set corresponds also to the "set B" parameters used in Bereiter et al. (2009). Since the gas diffusion model requires a solubility and a diffusion coefficient for each gas species, but in most cases only the permeation coefficients are available, we used for all gas species and throughout our calculations diffusion coefficients derived by Ikeda-Fukazawa et al. (2004), which are also based on molecular simulations, and adjusted the solubility coefficients accordingly.

The FS parameters are entirely synthetic based only on molecular simulations. The SS and the CO_2 parameters base on a model that simulates observed air fractionation and diffusive smoothing, respectively, in an ice core. The temperature regimes at which the observations have been performed are indicated by the crosses in Fig. 2. Since they cover only a small temperature range of a few degrees, the temperature sensitivities of the parameters are rather uncertain and the extrapolation of these parameters to temperatures far away from the observed regime may be inaccurate. In contrast to that, the molecular simulations used for the FS parameters have been performed over a wide range of ice temperatures (230–270 °K) allowing to derive a theoretical temperature dependence of the parameters for the full temperature range of our study. These temperature sensitivities are much smaller than the ones of the SS parameters. However, since there is not enough independent proof for or against one of these parameter sets, both sets are used in our simulations.

A recently published estimate of total air permeability in ice (Uchida et al., 2011) is also shown in Fig. 2. This estimate is based on a model that reconstructs observed growth of clathrates in the Dome Fuji ice core due to air permeation in ice. The growth

of the clathrates takes place over a large temperature range from about 240° K to 270° K (indicated by the crosses) for which reason this estimate does not suffer from the extrapolation uncertainty of the other observational based parameters. Provided that the reconstruction model is valid, this estimate suggests even weaker temperature sensitivities of the parameters compared to the other sets and shows the lowest permeabilities for temperatures above −10 °C, which are the most relevant for our Oldest Ice Core experiments (Sect. 4), since the deep ice is exposed to such temperatures for several 100 kyr. However, we can not directly use this estimate for our simulations since separate parameters for the different air constituents are required in order to simulate the effect on the mixing ratios. Nevertheless, we estimate the effect of such a low air permeability on the O_2/N_2 ratio in the Oldest Ice Core simulations by running the model with the FS and SS parameters scaled down with a constant factor to match the total air permeability of Uchida et al. (2011) at about 265° K (see Sect. 4).

3 A constraint for the gas permeability in ice

In this section an experimental constraint for the permeation coefficients is described which is based on a natural phenomenon in deep ice cores. Based on O_2/N_2 ratio data from the Vostok ice core, the constraint is used to test the permeation coefficients of N_2 and O_2 of the two parameter sets used in this work.

Lüthi et al. (2010) showed that in the BCTZ of different Antarctic ice cores the O_2/N_2 ratio and the CO_2 concentration of the trapped air vary between horizontal layers of a few cm vertical extent. This non-climatic signal is explained by a layer-wise transformation of bubbles to clathrates in the BCTZ and the preferential trapping of O_2 and CO_2 in the clathrates relative to N_2, leading to local fluctuations in the CO_2 concentration and O_2/N_2 ratio between these layers. The amplitude of the CO_2 fluctuations declines exponentially below the BCTZ presumably due to gas diffusion through ice. The model presented in Sect. 2 allows us to simulate the decline of these fluctuations, which are compared with the decline in the signal amplitude of such layers found in

ice core records. However, the available O_2/N_2 records do not all resolve the decline. The record must cover the ice core section of approximately 1000 m just beneath the BCTZ (Antarctic ice cores) with an adequate resolution and the vertical extent of the individual ice samples used for the record must not be much larger than the original layering. In the case of the O_2/N_2 ratio records, there exists a record from the Vostok ice core (Bender, 2002) that fulfils these requirements. Note, however, that this record is of discrete samples and no intervals of continuous O_2/N_2 measurements exist for this core.

Figure 3 shows the Vostok O_2/N_2 record in the top part (grey dots) and in the bottom part the absolute value of the residuals of the data points relative to the spline throughout the data less the measurement uncertainty (0.5‰) (grey crosses). The residuals represent the data variations on short time and length scales and, hence, contain also the cm-scale variations due to the layering process in the BCTZ. The bottom of the BCTZ is found at 1250 m depth and an age of 83 kyr BP, respectively, where the residuals are approximately 5‰. From this point on the residuals decline with depth and time supposedly due to diffusive exchange in the ice. Therefore, the exponential fit through the residuals older than 83 kyr BP (black line) is a representation of the average diffusive decline of the layers with time.

In order to simulate this measured decline, the model of Sect. 2 is run with a O_2/N_2 ratio distribution at the start as shown in the example of Fig. 4 (blue line). This distribution in Fig. 4 represents a layered O_2/N_2 ratio with a layer thickness of 3 cm and an amplitude of 4.8‰. The amplitude corresponds to the exponential fit value at the bottom of the BCTZ, where we set the diffusion time to zero in Fig. 5. The layer thickness comes from the work of Lüthi et al. (2010), however, the effective thickness is quite uncertain for which reason simulations with different layer thicknesses have been performed (see below). In the model experiments shown in this section, the simulation starts in the upper most interval of the grey shaded area in Fig. 1.

As seen in Fig. 4, the layers equilibrate with time due to the gas diffusion along the ice core axis. For the comparison of this simulated decline with the one derived

from the data (Fig. 5), the averaged amplitude over one full layer is used. Four different experiments have been performed: (a) with 3 cm layer thickness and the FS parameters (Fig. 5 red line); (b) with a layer thickness of 3 cm and the SS parameters (Fig. 4 and Fig. 5 purple line); (c) with 2.5 cm layer thickness and the SS parameters (Fig. 5 left dashed magenta line); (d) with 5 cm layer thickness and the SS parameters (Fig. 5 right dashed magenta line). The results from the FS parameters (red line) show clearly that this parameter set equilibrates the layered gas composition too fast. The associated lifetime of the variations is more than two orders of magnitudes shorter than what has been observed in the data. The results with the SS parameters also show a shorter lifetime of the variations compared to the data, but the difference is not more than a factor 4.

One large uncertainty in these experiments is the actual thickness of the layers in the Vostok ice core as no continuous intervals of O_2/N_2 measurements exist for this core that could resolve it. In the EDML ice core, where continuous measurements are available, a layer thickness of 2.5 to 3 cm was found (Lüthi et al., 2010). However, the boundary conditions (accumulation rate, number and size of individual precipitation events, mean surface temperature, . . .) of the EDML ice core are not the same as for the Vostok ice core. In this respect, the EDC ice core is much closer to the Vostok core. From the EDC core a short section of layer-resolving O_2/N_2 measurements exist (Lüthi et al., 2010). Unfortunately, the vertical sample length used for this small data set is fairly close to the layer thickness itself and therefore is not clearly resolving the layers. A maximum layer thickness of 5 cm can be found in this set for which reason we also have performed a corresponding simulation.

The results presented in this section suggest that the SS parameters are closer to the effective values compared to the FS parameters and the parameter of Uchida et al. (2011) (close to the FS parameters), at least for the temperature regime below the BCTZ at Vostok (about −40 °C). In principle, an independent set of gas parameters could be derived from our approach, however, they would only be valid for the temperature regime below the BCTZ and not for the much warmer temperatures near

the bedrock. Our approach does not provide a strong constraint on the temperature sensitivities and earlier estimates also show large discrepancies in this regard (see Sect. 2.3). For these reasons, an extrapolation of a set of gas parameters derived from our approach to higher temperatures found near the bedrock would be unreliable. Applying our approach to several O_2/N_2 records from different ice cores might enable to derive also reliable temperature sensitivities of the parameters.

Probably the most delicate point in our approach used here is whether or not the data residuals from the Vostok data set (Fig. 3) reliably reflect the diffusive decline of the O_2/N_2 fluctuations. They might be affected by artefacts due to e.g. bad core quality and gas loss in the section closer to the BCTZ. Therefore, this approach would benefit a lot from a denser set of O_2/N_2 records. This could be obtained from a continuous flow analysis technique as shown in Lüthi et al. (2010), who used the measurement technique of Huber et al. (2003). Such a data set would enable to directly estimate the decline of the layer amplitudes below the BCTZ. Therefore, the approach presented here can provide more precise O_2 and N_2 permeation parameters when such continuous records from below the BCTZ and from different ice cores become available.

4 Gas diffusion in deep ice cores

In this section we present the results of the diffusive gas equilibration of trapped CO_2 and O_2/N_2 signals in deep ice cores during the movement of the gas enclosures near the surface to the bedrock, as obtained by the model described in Sect. 2.1. In all experiments, the simulation starts with a sinusoidal CO_2 concentration and O_2/N_2 ratio variation with an amplitude of 50 ppmv and 5 ‰, respectively, as shown in Fig. 6. The period of the variations are changed between 100, 40, 20, 5 and 1 kyr by adjusting the temporal length of the simulated windows accordingly. In the example of Fig. 6 a window length of 10 kyr has been used which corresponds to a period of 20 kyr. For most possible combination of the two different ice flow and temperature profiles of the EDC and Oldest Ice Core (see Fig. 1), the two gas permeation parameter sets (SS

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and FS, see Fig. 2) and the different signal periods (100, 40, 20, 5 and 1 kyr) one simulation run has been performed resulting in 15 runs in total. The resulting amplitude dampening factors derived from these simulations are summarised in Fig. 7 and 8.

The five periods, which we have chosen for the simulations, roughly represent some typical oscillations of the CO_2 concentration or the O_2/N_2 ratio found in ice cores: (a) 100 kyr represents CO_2 variations associated with the 100 kyr glacial-interglacial cycles (Lüthi et al., 2008), (b) 40 kyr represents CO_2 variations expected during the 40 kyr glacial-interglacial cycles, (c) 20 kyr represents precessional O_2/N_2 variations (Kawamura et al., 2007), (d) 5 kyr represents CO_2 variations associated with Carbon Dioxide Maxima/Antarctic Isotope Maxima (CDM/AIM) events (Bereiter et al., 2012), and (e) 1 kyr represents about the minimum period that does get trapped in low accumulation ice cores without significant dampening by gas diffusion in the firn column (Spahni et al., 2003). The discussion below about the O_2/N_2 ratio focuses on the orbital 20 kyr period since it is the only relevant feature found so far in this proxy. For the CO_2 concentration the 100 kyr, 40 kyr and 5 kyr periods are most important. However, in the figures the results for all periods are plotted for completeness.

The results of the EDC simulations (Fig. 7) show that neither the relevant periods of CO_2 (5 kyr and higher) nor of O_2/N_2 (20 kyr) are strongly affected by the vertical gas exchange in this core, independent of the parameter sets used. For the 5 kyr period in CO_2 the dampening factor after 800 kyr (oldest part of the undisturbed EDC ice core) lies at 5 %, whereas larger periods are not affected at all. The amplitude dampening factor for the 20 kyr period in the O_2/N_2 signal after 800 kyr is 7 % at maximum. Such small dampenings are currently not identifiable since no independent records from another ice core exist for comparison. As the O_2/N_2 model results using the FS parameters show the maximum possible effect that is still in line with the EDC gas records, in which no signal equilibration has been identified so far, the O_2/N_2 results for the Oldest Ice Core simulations using the FS parameters can be interpreted as an upper limit of the equilibration effect that has to be expected. Since no other ice core reaches as far back in time as the EDC ice core and the accumulation rate and, hence, the annual

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layer thickness is relatively small in this ice core, vertical diffusion of gases in the ice does not substantially affect any ice core analysed to date.

The simulations for the Oldest Ice Core (Fig. 8), however, give a different picture and show a clear equilibration effect for the relevant periods of the CO_2 concentration and the O_2/N_2 ratio variations. Due to the strong thinning of the ice by a factor of about 100 after 1.5 Myr and the long residence time of the gas in warm ice near the bedrock. The results imply that the CO_2 signals (Fig. 8) associated with CDM/AIM variations will virtually vanish after 1.5 Myr but that variations associated with glacial-interglacial changes will be dampened by not more than 5 %. This means that the CO_2 changes associated with glacial-interglacial variations are still resolvable in such old ice.

In the case of the trapped O_2/N_2 ratio, the two parameter sets provide clearly different results (Fig. 8). While the SS simulates almost no influence on the 20 kyr period after 0.9 Myr, the FS simulations show already a significant damping of about 30 %. This is substantially more compared to what the model simulates for ice of similar age under EDC conditions using the same parameter set. The reason is the much stronger thinning of the ice older than about 600 kyr in the Oldest Ice Core relative to the EDC ice (see Fig. 1) causing stronger diffusive equilibration in that ice.

After 1.5 Myr both parameter sets show a strong equilibration of the O_2/N_2 signal even for the 40 kyr period. For the 20 kyr period the FS simulation shows a nearly complete equilibration already after 1.3 Myr. In the SS simulations this signal is preserved with an dampening of the original amplitude by 80 % after 1.5 Myr. As mentioned in Sect. 2.2, the tuning factor p of the Oldest Ice Core simulations (Table 1) might be too high and thinning in the deep part might be overestimated. However, an Oldest Ice Core simulation (SS, 20 kyr period) with a lower p value as used for the EDC simulations (see Table 1) but with the same bedrock temperature as before shows only a small difference of 10 % to the standard p value with a dampening of the original amplitude by 70 % after 1.5 Myr. The ice temperature profile of the artificial Oldest Ice Core simulations is set such that no melting occurs at the bedrock with local temperatures of a few degrees below the pressure melting point. One might find a drill site with

much lower bedrock temperatures, for example at a location where the ice sheet is significantly thinner than assumed in our Oldest Ice Core simulations. But a thinner ice sheet also infers thinner annual layers on average, with consequently higher diffusion rates. Alternatively an Oldest Ice Core simulation (SS, 20 kyr period) with unchanged ice sheet thickness but with $Q_g = 50\,\mathrm{mW\,m^{-2}}$ (5° K colder bedrock temperature compared to what is shown in Fig. 1), shows a dampening of the original amplitude by only 55 % after 1.5 Myr, hence, a reduction by 25 %, suggesting that also low bedrock temperatures in the range of 260° K can not prohibit a significant dampening.

As mentioned in Sect. 3, an estimate of total air permeation in ice suggests lower permeability than the SS parameters at temperatures near the bedrock (Uchida et al., 2011). The same estimate suggests also a higher permeability for temperatures below the BCTZ which is not supported by the results in Sect. 3. Nevertheless, we tested the influence of lower permeabilities by running two Oldest Ice Core simulations (20 kyr period) where in one case downscaled FS parameters, and in the other case downscaled SS parameters were used. Both parameter sets were scaled down by a constant factor such that they reached the total air permeability of Uchida et al. (2011) at 265° K (bedrock temperature). This setting results in lower total air permeability compared to Uchida et al. (2011) throughout the ice core with the exception of the very bottom, for which reason these simulations are a minimum scenario. Both runs show a dampening of the original O_2/N_2 amplitude by about 50 % after 1.5 Myr (30 % less as for the standard run) suggesting that also with lower air permeabilities in the range of Uchida et al. (2011) the precessional O_2/N_2 signal is significantly dampened.

In summary, the simulations for the Oldest Ice Core suggest that significant equilibration is likely to occur for O_2/N_2 and CO_2 signals with periods of 40 kyr and 20 kyr, respectively, and periods below that. Slower variations should still be resolvable in 1.5 Myr old ice. Periods shorter than 5 kyr are likely to be smeared out completely. In the case of precessional O_2/N_2 variations with a period of 20 kyr only 50 % or less of the original amplitude is expected to be preserved after 1.5 Myr. In the case of CO_2 CDM/AIM variations (approximately 5 kyr, Bereiter et al., 2012) no preservation is expected in such

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old ice. Due to the uncertainties in the gas parameters in ice, a wide range of amplitude dampening is possible. For example, for precessional O_2/N_2 variations (20 kyr period) the reduction in amplitude varies between 50 % in 1.5 Myr old ice (parameters by Uchida et al., 2011) and complete vanishing (FS) already in 1.3 Myr old ice. However, as suggested by the simulations in Sect. 3, the FS parameters might be too high and, hence, the upper limit estimate is likely to be too pessimistic. Other uncertain parameters such as the ice temperature or the thinning in such an ice core also influence the results presented here but compared to uncertainties in the gas parameters their influence is of secondary importance. Nevertheless, dating the deepest part of the Oldest Ice Core based on orbital tuning of the O_2/N_2 signal (Kawamura et al., 2007) might be challenging or even impossible due to the diffusive equilibration of this signal.

Changes of the ice properties are not included in our model. The size of the ice grains increases with depth (Durand et al., 2009). Larger ice grains might influence the gas permeability of the ice. With increasing depth and temperature water veins may be present along ice grain junctions in the deep part of the ice (Pol et al., 2010), which might increase the gas transport. However, a marginal fraction of clathrates is located along grain boundaries in deep ice (Uchida et al., 2011) and, hence, this effect might be small. Finally, clathrates grow with increasing depth (Uchida et al., 2011), but how this influences the gas exchange between the clathrates is not clear.

Most gases trapped in ice have a lower permeability through the ice lattice than the water molecules of the ice itself since the gas molecules need to go through the step of dissolution in the ice before they can diffuse through the lattice. In addition, in deep ice warmer than $-10\,°C$, such as in the EDC core below 2900 m depth, diffusion along water veins at ice grain junctions is suggested to increase the diffusivity of water molecules causing a doubling of the diffusion length for stable water isotopes to 40 cm near the bedrock (Pol et al., 2010). In our artificial Oldest Ice Cores, a water isotope signal associated with a glacial-interglacial cycle of 40 kyr duration will cover a vertical extent of only a few meters in the 1.5 Myr old part. Considering the roughly three times larger residence time of the ice in conditions above $-10\,°C$ (roughly 700 kyr, see

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example Fig. 1) compared to the EDC core, the diffusion length for water isotopes is expected to increase to 1 m and more. In such a case the 40 kyr isotope signal could be completely lost and trapped gases as well as particulate mineral dust aerosol might then be the only proxy that allows reconstructions of the past glacial-interglacial cycles back to 1.5 Myr. In order to avoid a complete disappearance of the 40 kyr isotope signal, the bedrock ice temperature must be below $-10\,^\circ$C.

5 Conclusions

The simulations of vertical diffusion of trapped gases in an ice sheet and the associated influence on the air composition in ice cores confirm that CO_2 and O_2/N_2 records from ice cores analysed until now do not suffer from a significant signal loss by gas diffusion. In regard to the IPICS target of retrieving a 1.5 million years old ice core, however, this signal loss becomes significant. The results presented here show that the vertical gas exchange will start to considerably influence the CO_2 variations associated with glacial-interglacial changes and precessional O_2/N_2 changes in ice older than 1 Myr. For 1.5 Myr old ice the estimated amplitude damping of a 40 kyr glacial-interglacial CO_2 variation is on the order of 5 % suggesting that CO_2 variations associated with glacial-interglacial changes are likely to be preserved in the 1.5 Myr old ice. The damping of precessional O_2/N_2 changes with a period of 20 kyr lies in the range of 50–80 % after 1.5 Myr. A worst case scenario is that after 1.3 Myr the signal has virtually equilibrated. This suggests that O_2/N_2 variations associated with orbital changes will be significantly dampened or may even have completely disappeared in the deep part of the Oldest Ice Core, making ice core dating by tuning the O_2/N_2 ratio variations to orbital parameters (Kawamura et al., 2007) difficult.

The reason for the large uncertainty range of the simulated gas diffusion effect on the trapped O_2/N_2 ratio is mainly due to the large uncertainties in the gas permeation coefficients in ice. A constraint for gas permeation coefficients presented in this work suggests that the FS parameters, which are used to derive the worst case scenario for

the O_2/N_2 ratio, are much too high for temperatures around $-40\,°C$. However, extrapolating this finding to ice temperatures of about $-10\,°C$, relevant for the effects in the Oldest Ice Core, is critical as the temperature sensitivities of the parameters are weakly constrained. Nevertheless, the method presented here can provide further constraints on the permeation of gas in ice and might also provide better temperature sensitivities in future investigations by applying it to records of different ice cores. The reason for the too high FS values is not clear, however, it is likely that the air permeability of natural ice is also influenced by its crystallographic structure. The FS values have been derived by molecular simulations taking into account a monocrystalline ice structure (Ikeda-Fukazawa et al., 2004) whereas polar ice has a polycrystalline structure possibly leading to a reduction of the permeability.

Water isotopes are generally more mobile in the ice than the trapped gases. Therefore, the signal equilibration due to molecular diffusion is likely to be stronger for water isotope signals. Under conditions expected for the Oldest Ice Core and used for simulations here, it is expected that glacial-interglacial cycles recorded in the water isotopes will be damped substantially in 1.5 Myr old ice. It is possible that this signal will have completely vanished in such an ice core. In this case, trapped gases and mineral dust may be the only paleo-climate indicator in this archive that show glacial-interglacial cycles. Ice temperatures near the bedrock of below $-10\,°C$ are required to preserve the isotope signal (Pol et al., 2010).

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Table 1. Drill site parameters for the different model experiments. The Vostok ice thickness (ice equivalent) is given by Salamatin et al. (1998). The other Vostok parameters are derived from the calibration procedure. For the EDC parameters the accumulation rate (temporal mean), the melt rate and the ice thickness (ice equivalent, temporal mean) of Parrenin et al. (2007a) are used. The EDC surface temperature (temporal mean) is from Jouzel et al. (2007). The EDC tuning parameter and the geothermal heat flux are derived from the calibration procedure. The Oldest Ice Core parameters are artificial and set such that the age and temperature requirements (1.5 Myr 100 m above ground, bottom temperature below pressure melting point) are fulfilled.

	Drill site parameters	Vostok	EDC	Oldest Ice Core
A	Accumulation rate [mm yr^{-1}]	19	18.2	15
m	Melt rate [mm yr^{-1}]	0.8	0.7	0
H	Ice Thickness [m]	3690	3153	2700
p	Tuning parameter	20	3.8	7.3
T_s	Surface temperature [K]	214.5	212.2	213
Q_g	Geothermal heat flux [mW m^{-2}]	45	53.3	55
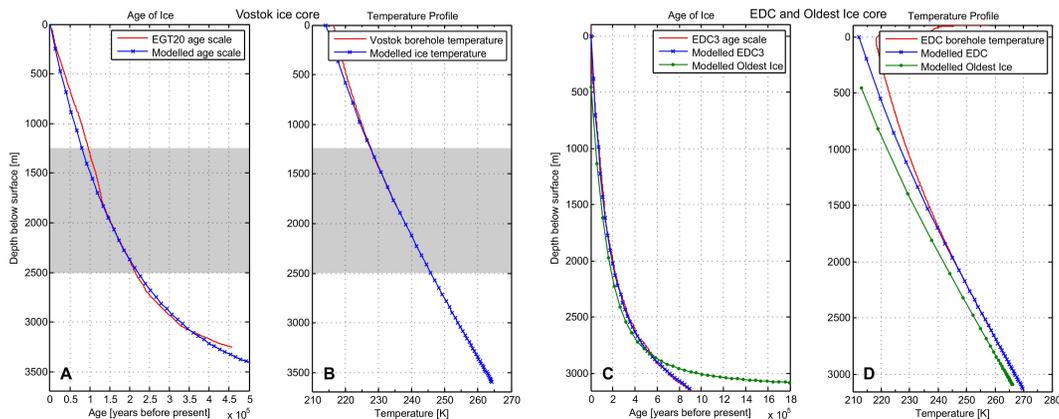
Fig. 1. Age of ice (**A** and **C**) and ice temperature (**B** and **D**) profiles of the Vostok (**A** and **B**) as well as of the EDC and Oldest Ice Core (**C** and **D**). Red lines: reference records for tuning the ice parameters (**A**: EGT20 age scale (Petit et al., 1999); **C**: EDC3 age scale (Parrenin et al., 2007a); **B**: Vostok bore hole temperature (Salamatin et al., 1994); **D**: EDC bore hole temperature measured in December 2004). Blue lines: Modelled ice age and ice temperature profiles using the Vostok (**A** and **B**) and EDC (**C** and **D**) ice parameters (Table 1). Green lines: Modelled ice age and ice temperature profiles using the Oldest Ice Core ice parameters. The grey shaded area marks the depth below the BCTZ for which the simulations of Sect. 3 have been performed. The depth level zero corresponds to the model ice sheet thickness at Vostok (**A** and **B**) and EDC (**C** and **D**) drill site in m ice equivalent.
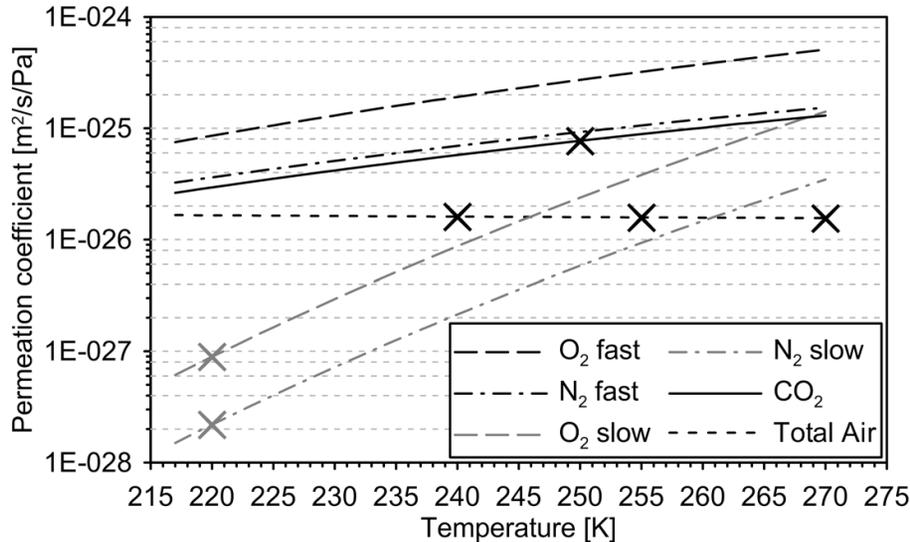
Fig. 2. Comparison of the different estimates of gas permeation coefficients in ice. The black dashed line denoted with "Total Air" represents the total air permeation value of Uchida et al. (2011). The black lines denoted with "fast" represent the "fast set" (FS) (Ikeda-Fukazawa et al., 2005) and the grey lines denoted with "slow" represent the "slow set" (SS) (Salamatin et al., 2001) used for the simulation presented here. The CO_2 permeation coefficient is the same for both sets (Ahn et al., 2008) (solid black line). Most permeation coefficients shown here consist of a solubility and a diffusion parameter. In all these cases the diffusion parameters of Ikeda-Fukazawa et al. (2004) are used whereas the solubility is adjusted accordingly. The crosses indicate for which ice temperature regime the corresponding parameters have an experimental support and, hence, show which parts of the parameters are extrapolated. In the case of the total air parameter the temperature regime covers a larger range as indicated by the crosses.
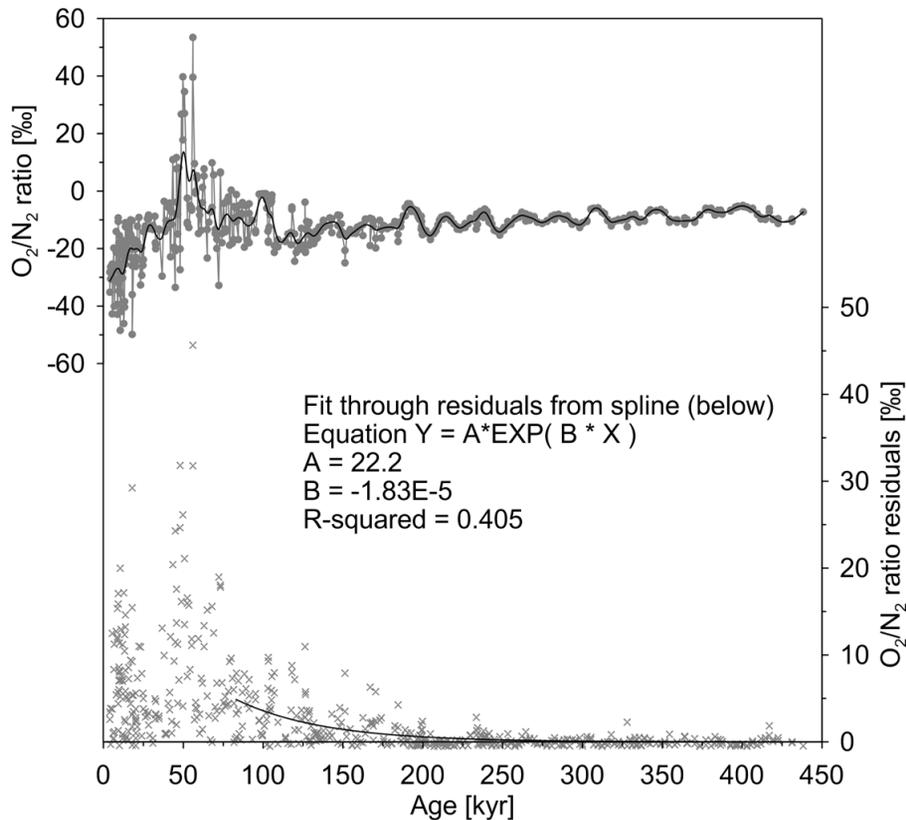
Fig. 3. Top: O_2/N_2 ratio data from the Vostok ice core (Bender, 2002) (grey dots) and the data spline with a cut-off frequency of 11 kyr (Enting, 1987) (black line). Bottom: residuals of the O_2/N_2 ratio values relative the the spline (grey crosses) and the exponential fit through the residuals older than 83 kyr (black line). The text in the middle of the figure shows the fit results.

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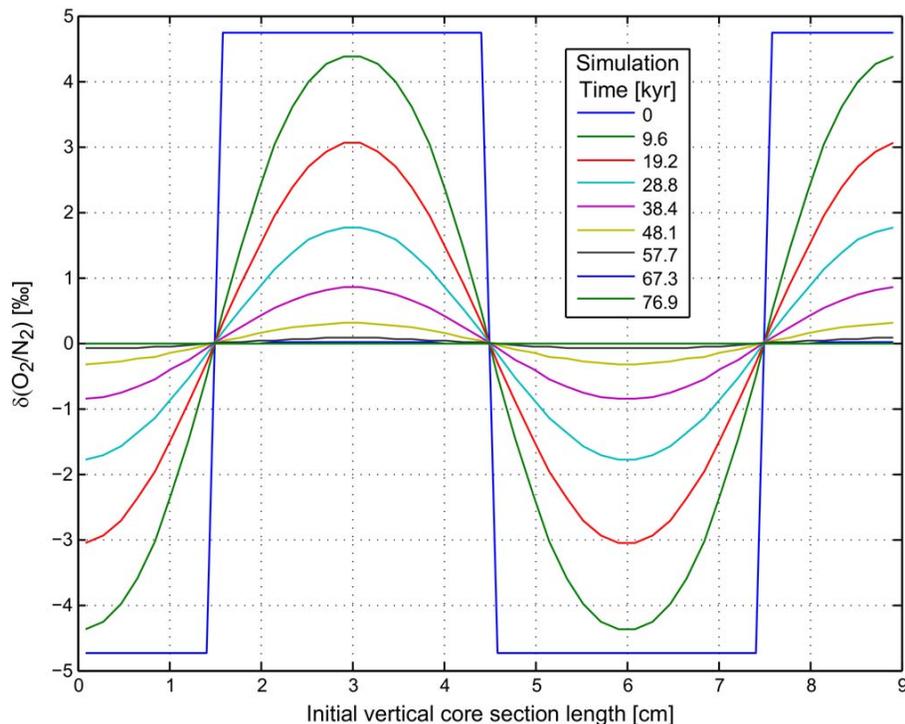
Fig. 4. Example of the model output of the O_2/N_2 layering decline experiments using the SS parameters. The blue line shows the starting O_2/N_2 distribution representing 3 layers (half a layer at each edge) with 3 cm thickness and an amplitude of 4.8‰. The different coloured lines represent simulated distributions after a certain duration in the ice as indicated by the legend (in 1000 yr [kyr]). From these results the corresponding decline in Fig. 5 is calculated (purple line).

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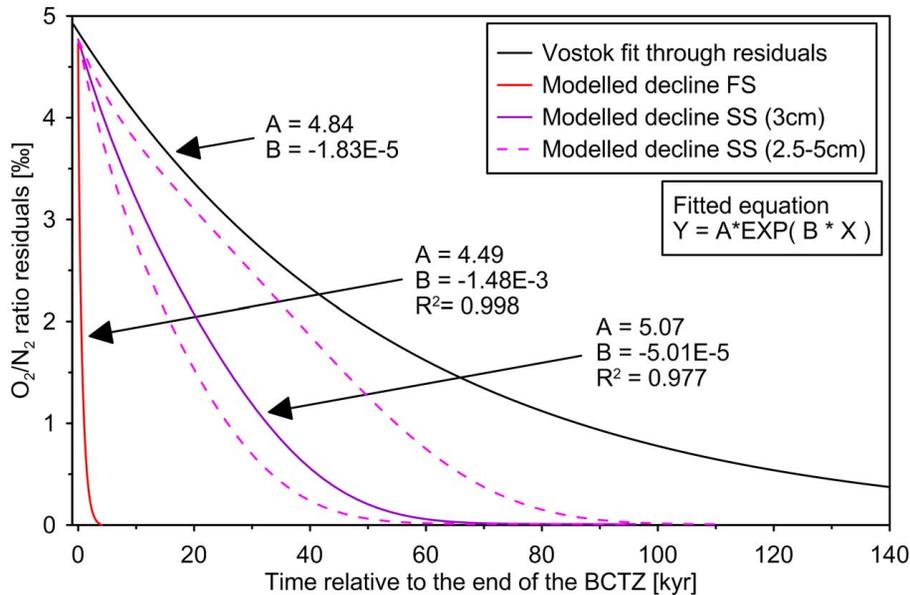
Fig. 5. Comparison of the amplitude decline of the O_2/N_2 fluctuations below the BCTZ derived from the Vostok data (black line, see also Fig. 3) and the modelled decline using different parameter sets (FS or SS) and layer thicknesses. The red line shows the modelled decline using the FS and 3 cm layer thickness, the purple line shows decline using the SS and 3 cm thickness and the magenta lines show the decline using the SS and 2.5 cm (left) and 5 cm (right) thicknesses. The results of the exponential fit through the Vostok data as shown in Fig. 3 as well as through two modelled declines are shown for comparison (arrows indicate the corresponding values).

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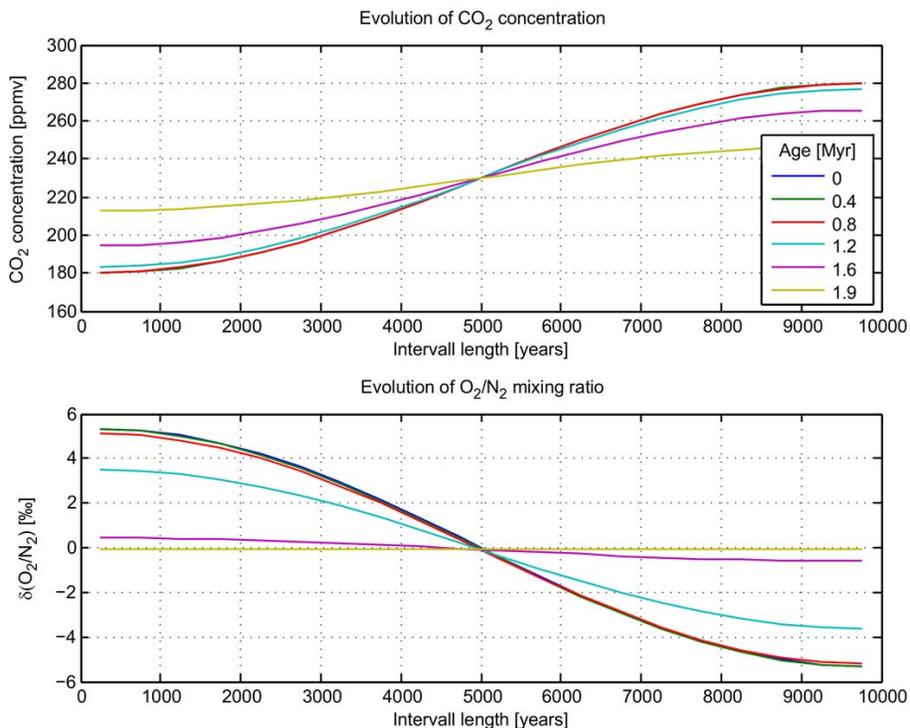
Fig. 6. Example of the model performance showing the simulated changes of the CO_2 concentration (top) and the O_2/N_2 ratio (bottom) for the Oldest Ice Core ice flow and temperature profile (Fig. 1) using the SS parameters. The starting gas distribution (blue line) is half of a sinusoidal oscillation (period 20 kyr) with an amplitude of 50 ppmv (CO_2) and 5 ‰ (O_2/N_2) over the complete simulated time window of 10 kyr. The different coloured lines represent simulated distributions after a certain duration in the ice as indicated by the legend (in million years [Myr]). This simulation is used to calculate the amplitude dampening of the 20 kyr signal (see Fig. 8).
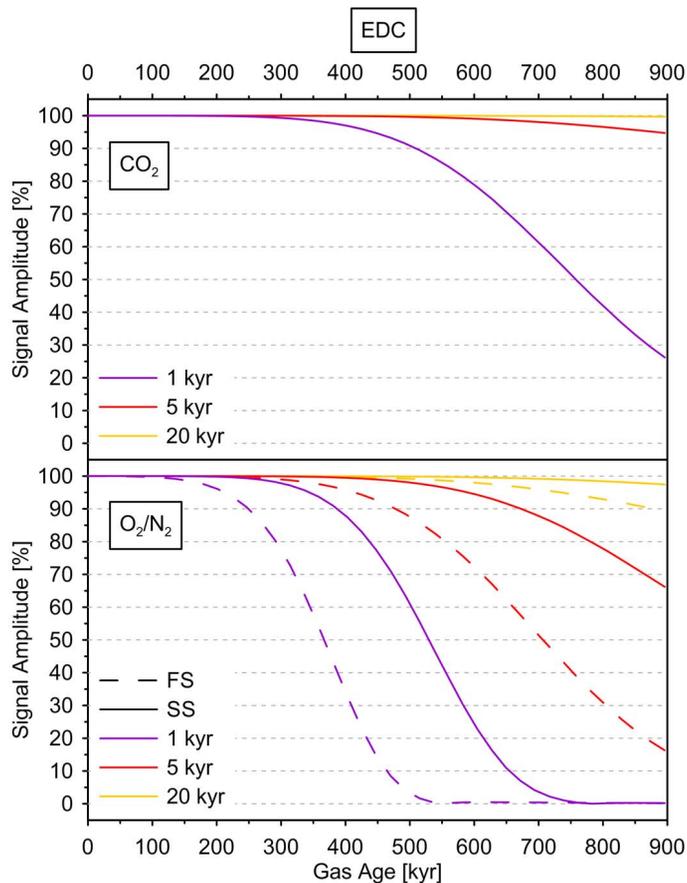
Fig. 7. Simulated amplitude dampening of CO_2 concentration (top) and O_2/N_2 ratio (bottom) signals for the EDC ice flow and temperature profile (Fig. 1). The different coloured lines show the results for different periods of the signal as indicated by the legend.

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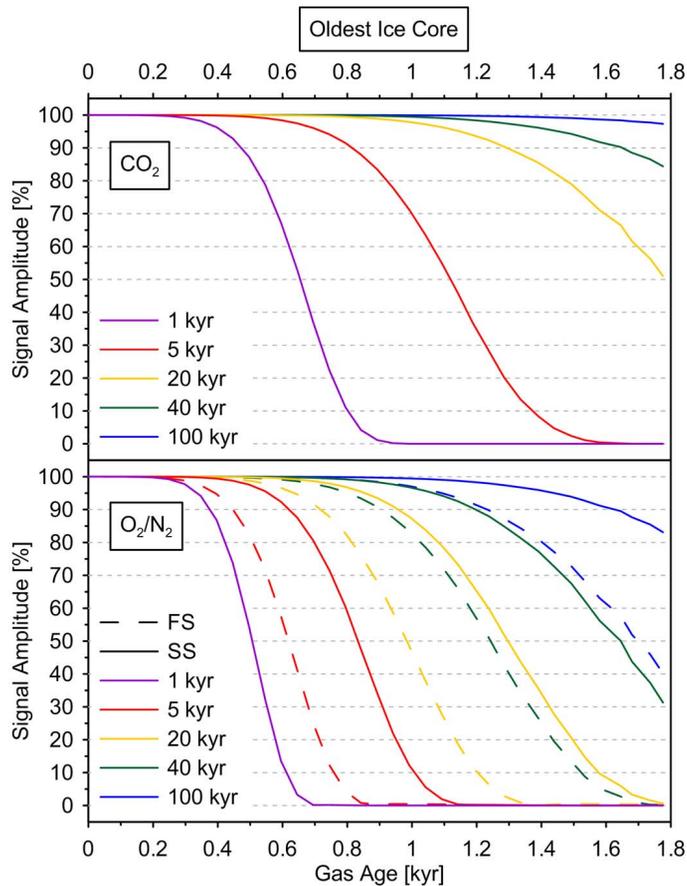
Fig. 8. Simulated amplitude dampening of CO_2 concentration (top) and O_2/N_2 ratio (bottom) signals for the Oldest Ice Core ice flow and temperature profile (Fig. 1). The different coloured lines show the results for different periods of the signal as indicated by the legend.

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