How well do different tracers constrain the firn diffusivity profile? Supplementary material

C. M. Trudinger¹, I. G. Enting², P. J. Rayner³, D. M. Etheridge¹, C. Buizert^{4,5}, M. Rubino^{1,4}, P. B. Krummel¹, and T. Blunier⁴

¹Centre for Australian Weather and Climate Research, CSIRO Marine and Atmospheric Research, Aspendale, Victoria, Australia

²MASCOS, University of Melbourne, 3010, Victoria, Australia

³School of Earth Sciences, University of Melbourne, 3010, Victoria, Australia

⁴Centre for Ice and Climate, Niels Bohr Institute, University of Copenhagen, Juliane Maries vej 30, 2100 Copenhagen, Denmark

55

65

70

⁵College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis OR 97331 USA

1 Firn model equations

Here we describe the equations for firn diffusion, convective ⁴⁰ mixing, advection and bubble trapping in a reference frame that moves downwards with the ice as used in the CSIRO

- ⁵ firn model. The equations are related to the equations in a fixed reference frame (relative to the surface) from Romme-laere et al. (1997) and are more rigorously derived than in ⁴⁵ Trudinger et al. (1997), giving more accurate representation of the physics and allowing us to avoid some of the assump-
- tions that were used in the previous version of the CSIRO firn model (most notably the upward flux of air due to compression). We use the following notation:

t. Time (years)

- t'. Time in moving coordinates (years) Although t = t', we distin-15 guish them to clarify partial derivatives
 - z. Real world depth below surface (metres) (positive down)
 - y. Vertical coordinate, fixed to ice (surface equivalent metres).
 - $\tau(z)$. Age of firn/ice at depth z (years)
 - $\rho(z)$. Density (kg/m³)

25

- ²⁰ ρ_{ice} . Density of pure ice at temperature T (kg/m³) (assumes ice is incompressible or compressibility is irrelevant)
 - $\rho_{\rm c}$. Density at close-off (kg/m³)
 - A. Accumulation rate $(kg/m^2/year)$.

s(z). Total porosity (volumetric proportion of void space in firm and ice), $s(z)=1-\rho(z)/\rho_{\rm ice}$

f(z). Open porosity (volumetric proportion of open void space), f(z) = (1 - r(z))s(z)

b(z). Closed porosity (volumetric proportion of trapped void ⁶⁰ space), b(z) = r(z)s(z)

r(z). Fraction of total porosity that is trapped

v(z). Vertical velocity of ice (metre/year) (positive downwards) w(z). Downward velocity of air relative to fixed ice coordinates, positive downwards. (metre/year)

- u(z). Pumping velocity, relative to moving ice, positive down.
- $C_{air}(z)$. Air concentration in the open pore space (mol m⁻³) $C_{air}^{b}(z,t)$. Air concentration in trapped bubbles (mol m⁻³) C(z,t). Trace gas concentration in the open pore space (mol m⁻³)

Correspondence to: C. M. Trudinger (cathy.trudinger@csiro.au)

c(z,t). Trace gas mixing ratio (mole fraction of tracer in dry air) in the open pore space (ppm)

 $C^{b}(z,t)$. Trace gas concentration in the trapped bubbles (mol m⁻³) $c^{b}(z,t)$. Trace gas mixing ratio in the trapped bubbles (ppm)

J(z,t). Trace gas flux in open pores (mol m⁻² s⁻¹)

 $J_{\rm MR}(z,t)$. Trace gas flux in open pores in mole fraction (ppm m s⁻¹)

D(z). Gas diffusion coefficient

- $D_{
 m eddy}(z)$. Eddy diffusion
- M. Molecular weight
- g. Acceleration due to gravity
- *R*. Gas constant
- T. Temperature (K)
- W. Mass per unit area in model layers (kg/m^2)

1.1 Ice conservation and coordinate systems

Unit volume has proportion s of air and 1-s of ice, since mass (per unit volume) is $(1-s) \times \rho_{ice} = \rho$, giving total porosity

$$s(z) = 1 - \rho(z)/\rho_{\text{ice}} \tag{1}$$

The mass of ice (per unit area) above z is

$$\int_0^z \rho(z') dz' \tag{2}$$

and vertical velocity of ice (relative to the surface) is

$$v(z) = A/\rho(z) \tag{3}$$

We wish to use a moving coordinate system, so care is needed in addressing transformations from a fixed coordinate system. This is done in terms of a generic function F(.,.), with the need to consider that as coordinates change, the functional relation will also change, and that the notation should reflect this.

Here we define a number of coordinate systems, along with the transformations and notation for functions. We are interested in the final coordinate system (y,t'), and the others are given to show how (y,t') relates to (z,t). z,t. This is the (depth, time) form and is represented by functions F(z,t).

au,t. This represents the vertical coordinate in terms of age of ice, au(z). It is defined by

75
$$\tau(z) = \frac{1}{A} \int_0^z \rho(z') dz'$$
 (4)

The τ coordinate can be linearly rescaled to give units in terms of distance by multiplying by any fixed velocity. The most obvious choice is surface velocity $v(0) = A/\rho(0)$

 ξ, t' . Where $\xi = \tau - t - a$ with a an arbitrary constant. This coordinate moves with the ice. We use t' = t, with the distinction between t and t' helping clarify the meaning of the various partial derivatives.

y,t'. This is a re-scaled version of ξ , scaled by $v(0) = A/\rho(0)$. Thus

85
$$y = \frac{A}{\rho(0)} [\tau(z) - t - a] = v(0) [\tau(z) - t - a]$$
 (5)

giving

$$\frac{\partial y}{\partial z} = \frac{\rho(z)}{\rho(0)} = \frac{v(0)}{v(z)} \tag{6}$$

and

$$\frac{\partial y}{\partial t} = -\frac{A}{\rho(0)} = -v(0) \tag{7}$$

If we use a 'tilde' notation to indicate functions defined in the (y,t') coordinates then the defining relation is: 130

$$F(z,t) = \tilde{F}(y(z,t),t'(t))$$

giving rise to the relations

$$\frac{\partial F}{\partial z} = \frac{\partial \dot{F}}{\partial y}\frac{\partial y}{\partial z} = \frac{\rho(z)}{\rho(0)}\frac{\partial \dot{F}}{\partial y} = \frac{v(0)}{v(z)}\frac{\partial \dot{F}}{\partial y}$$
(9)

95 and ∂F

$$\frac{\partial F}{\partial t} = \frac{\partial \tilde{F}}{\partial t} = \frac{\partial \tilde{F}}{\partial y} \frac{\partial y}{\partial t} + \frac{\partial \tilde{F}}{\partial t'} = \frac{\partial \tilde{F}}{\partial t'} - \frac{A}{\rho(0)} \frac{\partial \tilde{F}}{\partial y}
= \frac{\partial \tilde{F}}{\partial t'} - v(0) \frac{\partial \tilde{F}}{\partial y} = \frac{\partial \tilde{F}}{\partial t'} - v(z) \frac{\partial F}{\partial z}$$
(10)

For the present analysis, we assume that the ice properties are constant with time (the case of a melt layer moving with

the ice is an exception that will be considered later), so ice properties are functions of z only. For any quantity G that is independent of t, the relations above give:

$$\frac{\partial G}{\partial y} = \frac{v(z)}{v(0)} \frac{\partial G}{\partial z} \tag{11}$$

and

105

$$\frac{\partial \tilde{G}}{\partial t'} = v(0)\frac{\partial \tilde{G}}{\partial y} = v(z)\frac{\partial G}{\partial z}$$
(12)

In the y,t' coordinates, z dependence can be mapped onto either rates of change with respect to t' or y.

1.2 Pore space

The total porosity is partitioned into open porosity f and closed porosity b, as:

$$s(z) = 1 - \frac{\rho(z)}{\rho_{\text{ice}}} = f(z) + b(z)$$
(13)

Moving with the ice, closed porosity changes due to (i) new trapping (which increases *b* with depth) and (ii) bubble compression (which decreases *b* with depth). Open porosity changes due to (i) new trapping (which decreases *f* with depth) and (ii) compression of channels (which decreases *f* with depth). By writing b(z) = r(z)s(z) and f(z) = (1 - r(z))s(z), we can separate the effects of trapping and compression on *f* and *b*:

$$\frac{\partial b}{\partial z} = r \frac{\partial s}{\partial z} + s \frac{\partial r}{\partial z} \tag{14}$$

$$\frac{\partial f}{\partial z} = (1 - r)\frac{\partial s}{\partial z} - s\frac{\partial r}{\partial z}$$
(15)

Like Rommelaere et al. (1997) and Severinghaus and Battle (2006), we assume that the volumetric compression acts equally on open and trapped pore space so that we interpret the term involving $\frac{\partial s}{\partial z}$ as compression and $s \frac{\partial r}{\partial z}$ as trapping.

Figure 1 shows open, closed and total porosity at NEEM, Northern Greenland, with density and open porosity values from the NEEM intercomparison (Buizert et al., 2012). It also shows their derivatives with depth, and these split according to equations 14 and 15, indicating where compression and trapping have most influence on f and b.

In moving coordinates, b and f are functions of time, t': The relations can be found from

$$\frac{\partial}{\partial t}b(z,t) = 0 = \frac{\partial}{\partial t}\tilde{b}(y(z,t),t'(t)) = \frac{\partial\tilde{b}}{\partial y}\frac{\partial y}{\partial t} + \frac{\partial\tilde{b}}{\partial t'}$$
(16)

135 so that

125

(8)

$$\frac{\partial \tilde{b}}{\partial t'} = -\frac{\partial \tilde{b}}{\partial y}\frac{\partial y}{\partial t} = \frac{A}{\rho(0)}\frac{\partial \tilde{b}}{\partial y}$$
(17)

and similarly

$$\frac{\partial \tilde{f}}{\partial t'} = -\frac{\partial \tilde{f}}{\partial y} \frac{\partial y}{\partial t} = \frac{A}{\rho(0)} \frac{\partial \tilde{f}}{\partial y}$$
(18)

1.3 Air conservation in pore space

Like Trudinger et al. (1997) and Rommelaere et al. (1997), we assume that air in open channels, C_{air} , can be described by the barometric equation

$$C_{\rm air}(z) = C_{\rm air}(0) \exp\left(\frac{M_{\rm air}gz}{RT}\right)$$
(19)

In fixed coordinates:

$$\frac{\partial C_{\text{air}}}{\partial t} = 0 \tag{20}$$



Fig. 1. a) Open (f), closed (b) and total (s) porosity at NEEM, b) fraction of total porosity that is closed r, c) $\frac{\partial s}{\partial z}$, $\frac{\partial f}{\partial z}$ and $\frac{\partial b}{\partial z}$, d) $\frac{\partial r}{\partial z}$, e) and f) more terms in the model equations involving derivatives, g) vertical velocities (in m/yr) of ice (v), air (w) and upward flux of air due to compression (-u), h) air pressure in the trapped bubbles (solid) and open firm (dotted).

and

$$\frac{\partial C_{\rm air}}{\partial z} = \frac{M_{\rm air}g}{RT} C_{\rm air} \tag{21}_{190}$$

Moving with the ice, we define $\tilde{C}_{\rm air}(y(z,t),t'(t))$ so that, as above

$$\frac{\partial \hat{C}_{air}}{\partial y} = \frac{\rho(0)}{\rho(z)} \frac{\partial \hat{C}_{air}}{\partial z} = \frac{\rho(0)}{\rho(z)} \frac{M_{air}g}{RT} \tilde{C}_{air} = \frac{\tilde{v}(z)}{v(0)} \frac{M_{air}g}{RT} \tilde{C}_{air}$$
(22)

and

$$\frac{\partial \tilde{C}_{air}}{\partial t'} = -\frac{\partial \tilde{C}_{air}}{\partial y} \frac{\partial y}{\partial t} = v(0) \frac{\partial \tilde{C}_{air}}{\partial y} = v(z) \frac{\partial C_{air}}{\partial z}$$

$$= v(z) \frac{M_{air}g}{RT} C_{air}$$
(23)

Air in open channels in the ice is compressed as the ice
¹⁵⁵ moves down to regions of lower total porosity, and this leads to an upward flux of air (relative to the ice) to maintain the balance described by the barometric equation. We define this ²⁰⁰ flux, denoted by *u*, as positive downwards, so *u* is negative. Air is also trapped into new bubbles, and we assume that a
¹⁶⁰ new bubble formed at depth *z* has the same pressure (when formed) as air in open pores at that depth.

In fixed coordinates, air is carried down with the ice at $_{205}$ velocity v(z) but is also expelled upwards to give net velocity

w(z) = u(z) + v(z). Air conservation in open channels in fixed coordinates can be written as (Rommelaere et al., 1997)

$$\frac{\partial}{\partial t}[fC_{\rm air}] = -\frac{\partial}{\partial z}[wfC_{\rm air}] - C_{\rm air}vs\frac{\partial r}{\partial z}$$
(24)

The left side of the equation is zero, the first term on the right describes flux divergence and the second term describes trapping into new bubbles. Using the product rule on the first term on the right hand side, with Eqn (21) for $\frac{\partial C_{\text{air}}}{\partial z}$ and dividing by C_{air} and f we get

$$\frac{\partial w}{\partial z} + w \left[\frac{M_{\text{air}g}}{RT} + \frac{1}{f} \frac{\partial f}{\partial z} \right] + \frac{vs}{f} \frac{\partial r}{\partial z} = 0$$
(25)

This equation can be solved for w with the boundary condition w = v where f goes to zero. Rommelaere et al., (1997) pointed out that in fixed ice coordinates, the net vertical flux of air downwards, w(z), balances trapping into bubbles. We can calculate u from u = w - v. Figure 1g shows the vertical velocities v, u and w calculated for NEEM.

1.4 Air conservation in bubbles

We need to keep track of the air pressure in the trapped bubbles to determine the change in mole fraction of tracers as new bubbles are formed. After the first bubbles are formed, they move down with the ice and compression causes the closed porosity to decrease and the air pressure to increase. Then as more bubbles are trapped with the same air pressure as in the open pores at that depth, the closed porosity (of bubbles in a layer of ice) increases and the air pressure decreases.

Air conservation in trapped bubbles can be determined from

$$\frac{\partial}{\partial t'} \left[b C_{\rm air}^b \right] = C_{\rm air} v s \frac{\partial r}{\partial z} \tag{26}$$

giving

$$\frac{\partial C_{\text{air}}^b}{\partial z} = -\frac{C_{\text{air}}^b}{b}\frac{\partial b}{\partial z} + C_{\text{air}}\frac{s}{b}\frac{\partial r}{\partial z}$$
(27)

$$= \left(C_{\rm air} - C_{\rm air}^b\right) \frac{1}{r} \frac{\partial r}{\partial z} - C_{\rm air}^b \frac{1}{s} \frac{\partial s}{\partial z}$$
(28)

We can solve this equation using finite difference representation of the derivatives with the boundary condition at the surface

$$C_{\rm air}^b(0) = C_{\rm air}(0) \tag{29}$$

Equation 27 can also be derived by considering the compression and trapping alternately for each time step, as in Rommelaere et al. (1997).

Figure 1h shows the calculated air pressure in bubbles and open firn at NEEM. The calculated air pressure in the bubbles depends on the form of the closed porosity variation with depth. At NEEM we have used the Goujon et al. (2003) parameterisation where closed porosity increases gradually from the surface but is negligible until around 60 m. A spline fit to closed porosity measurements such as that used in Trudinger et al. (1997) gives quite a different variation with depth for the calculated C_{air}^b , but the value when trapping stops is also around $1.4 \times C_{air}(0)$.

1.5 Trace gas conservation in open pore space

The concentration of a generic trace gas, $C_x(z,t)$, (in mol m⁻³) is modelled (in fixed coordinates) in terms of the flux through open firn channels, $J_x(z,t)$, given by

$$J_{x} = -D_{x}\frac{\partial C_{x}}{\partial z} + D_{x}\frac{M_{x}gC_{x}}{RT} - D_{eddy}\left(\frac{\partial C_{x}}{\partial z} - \frac{M_{air}gC_{x}}{RT}\right) + wC_{x}$$
(30)²⁵⁰

The first term describes molecular diffusion, the second term gives the settling due to gravity. The third term describes an 'eddy' diffusion, as introduced by Severinghaus et al. (2001), which is the same for all trace gases and primarily includes²⁵⁵ mixing near the surface due to convection. Note that the eddy diffusion term is parameterised as the deviation from a hydrostatic gradient (J. Severinghaus, pers. comm. 2011). The last term is the total downward flux of air due to advection of ice w = v + u.

The conservation equation (in fixed coordinates) is defined in terms of the full volume where the gas flow per unit area is f(z)J(z,t) and the amount of gas per unit volume is f(z)C(z,t)

$$\frac{\partial}{\partial t}[fC_{x}] = -\frac{\partial}{\partial z}[fJ_{x}] - \lambda fC_{x} - C_{x}vs\frac{\partial r}{\partial z}
= -\frac{\partial}{\partial z}\left[f\left(-D_{x}\frac{\partial C_{x}}{\partial z} + D_{x}\frac{M_{x}gC_{x}}{RT}\right) - D_{eddy}\left(\frac{\partial C_{x}}{\partial z} - \frac{M_{air}gC_{x}}{RT}\right) + wC_{x}\right)\right]
-\lambda fC_{x} - C_{x}vs\frac{\partial r}{\partial z}$$
(31)

The term involving λ is radioactive decay and the last term describes bubble trapping.

We can derive the equivalent equation in moving coordinates using w = u + v and Equation 10

$$\frac{\partial}{\partial t'} \left[\tilde{f}\tilde{C}_{x} \right] - v(0) \frac{\partial}{\partial y} \left[\tilde{f}\tilde{C}_{x} \right] = -\frac{v(0)}{\tilde{v}} \frac{\partial}{\partial y} \left[\tilde{f} \left(-\tilde{D}_{x} \frac{v(0)}{\tilde{v}} \frac{\partial \tilde{C}_{x}}{\partial y} + \tilde{D}_{x} \frac{\partial \tilde{C}_{x}}{\partial x} - \tilde{D}_{eddy} \frac{v(0)}{\tilde{v}} \frac{\partial \tilde{C}_{x}}{\partial y} + \tilde{D}_{eddy} \frac{M_{air} g \tilde{C}_{x}}{RT} + (\tilde{u} + \tilde{v}) \tilde{C}_{x} \right) \right] - \lambda \tilde{f}\tilde{C}_{x} - \tilde{C}_{x} v(0) \tilde{s} \frac{\partial \tilde{r}}{\partial y}$$
(32)

which can be rearranged to give

240

$$\frac{\partial \tilde{C}_{\mathbf{x}}}{\partial t'} = -\frac{v(0)}{v} \frac{\partial}{\partial y} \left[-\tilde{D}_{\mathbf{x}} \frac{v(0)}{\tilde{v}} \frac{\partial \tilde{C}_{\mathbf{x}}}{\partial y} + \tilde{D}_{\mathbf{x}} \frac{M_{\mathbf{x}} g \tilde{C}_{\mathbf{x}}}{RT} \right]$$

$$-\tilde{D}_{eddy}\frac{v(0)}{\tilde{v}}\frac{\partial\tilde{C}_{x}}{\partial y} + \tilde{D}_{eddy}\frac{M_{air}g\tilde{C}_{x}}{RT} + \tilde{u}\tilde{C}_{x}\right]$$

$$-\frac{v(0)}{\tilde{v}}\frac{1}{\tilde{f}}\frac{\partial\tilde{f}}{\partial y}\left[-\tilde{D}_{x}\frac{v(0)}{\tilde{v}}\frac{\partial\tilde{C}_{x}}{\partial y} + \tilde{D}_{x}\frac{M_{x}g\tilde{C}_{x}}{RT} - \tilde{D}_{eddy}\frac{v(0)}{\tilde{v}}\frac{\partial\tilde{C}_{x}}{\partial y} + \tilde{D}_{eddy}\frac{M_{air}g\tilde{C}_{x}}{RT} + \tilde{u}\tilde{C}_{x}\right]$$

$$-\frac{v(0)}{\tilde{v}}\frac{\partial\tilde{v}}{\partial y}\tilde{C}_{x} - \lambda\tilde{C}_{x} - v(0)\frac{\tilde{s}}{\tilde{f}}\frac{\partial\tilde{r}}{\partial y}\tilde{C}_{x} - v(0)\frac{1}{\tilde{f}}\frac{\partial\tilde{f}}{\partial y}\tilde{C}_{x}$$
(33)

where the second term on the left side of Equation 32 has cancelled with a term on the right side. This is the equation for trace gas concentration in moving coordinates. This equation differs from the previous version of the CSIRO firm model (Trudinger et al 1997) in that the flux now includes eddy diffusivity and the upward flux of air due to compression u, and the mass balance equation includes three extra terms.

These equations give results as concentrations, $C_x(z,t)$, in mol m⁻³. However, as mole fraction in dry air is more commonly measured than concentration, we wish to write the diffusion and mass conservation equations in terms of mole fraction, $c_x(z,t)$, where

$$c_{\mathbf{x}}(z,t) = \frac{C_{\mathbf{x}}(z,t)}{C_{\mathrm{air}}(z)}$$
(34)

 $C_{\rm air}(z)$ is described by the barometric equation (eqn 19), giving

$$\frac{\partial C_{\mathbf{x}}}{\partial t} = C_{\mathrm{air}} \frac{\partial c_{\mathbf{x}}}{\partial t}$$
(35)

and

$$\frac{\partial C_{\rm x}}{\partial z} = C_{\rm air} \frac{\partial c_{\rm x}}{\partial z} + c_{\rm x} \frac{M_{\rm air}g}{RT} C_{\rm air} \tag{36}$$

in fixed coordinates.

In moving coordinates, we have

$$\frac{\partial \tilde{C}_{x}}{\partial y} = \frac{v}{v(0)} \frac{\partial C_{x}}{\partial z} = \frac{v}{v(0)} \left(C_{air} \frac{\partial c_{x}}{\partial z} + c_{x} \frac{M_{air}g}{RT} C_{air} \right)$$
$$= \frac{v}{v(0)} C_{air} \frac{v(0)}{v} \frac{\partial \tilde{c}_{x}}{\partial y} + \frac{v}{v(0)} c_{x} \frac{M_{air}g}{RT} C_{air}$$
(37)

giving

$$\frac{\partial \tilde{C}_{\mathbf{x}}}{\partial y} = \frac{\partial (\tilde{c}_{\mathbf{x}} \tilde{C}_{\mathrm{air}})}{\partial y} = \tilde{C}_{\mathrm{air}} \frac{\partial \tilde{c}_{\mathbf{x}}}{\partial y} + \frac{v}{v(0)} \tilde{c}_{\mathbf{x}} \tilde{C}_{\mathrm{air}} \frac{M_{\mathrm{air}g}}{RT}$$
(38)

and from

$$\frac{\partial \tilde{C}_{\mathbf{x}}}{\partial t'} = \frac{\partial C_{\mathbf{x}}}{\partial t} + v \frac{\partial C_{\mathbf{x}}}{\partial z}$$
(39)

we have

$$\frac{\partial \tilde{C}_{\mathbf{x}}}{\partial t'} = \tilde{C}_{\mathrm{air}} \frac{\partial \tilde{c}_{\mathbf{x}}}{\partial t'} + \tilde{v} \tilde{c}_{\mathbf{x}} \tilde{C}_{\mathrm{air}} \frac{M_{\mathrm{air}}g}{RT}$$
(40)

210

We replace C_x by $c_x C_{air}$ in eqn 33, expand and a number of terms will cancel, to leave

Note that a number of terms cancelled using Equation 25. 335

If we define the flux of tracer x in terms of mole fraction in moving coordinates as

$$\tilde{J}_{\rm MRx} = -\tilde{D}_{\rm x} \frac{v(0)}{\tilde{v}} \frac{\partial \tilde{c}_{\rm x}}{\partial y} + \tilde{D}_{\rm x} \frac{(M_{\rm x} - M_{\rm air})g\tilde{c}_{\rm x}}{RT} - \tilde{D}_{\rm eddy} \frac{v(0)}{\tilde{v}} \frac{\partial \tilde{c}_{\rm x}}{\partial y}$$
(42)

then we have

29

300

$$\frac{\partial \tilde{c}_{x}}{\partial t'} = -\frac{v(0)}{\tilde{v}} \frac{\partial}{\partial y} \tilde{J}_{MRx} - \frac{M_{air}g}{RT} \tilde{J}_{MRx} - \frac{v(0)}{\tilde{v}} \frac{1}{\tilde{f}} \frac{\partial \hat{f}}{\partial y} \tilde{J}_{MRx}$$

$$= -\lambda \tilde{c}_{x} - \frac{v(0)}{\tilde{v}} \tilde{u} \frac{\partial \tilde{c}_{x}}{\partial y}$$
(43)₃₄₀

These equations now only differ from those in Trudinger et al. (1997) by the addition of the eddy diffusion term, and the upward compression flux $-u\frac{\partial c_x}{\partial z}$. The other differences that we saw in the concentration equations disappeared when we converted to mole fraction. Notice that the bubble trapping

term has disappeared, as it doesn't directly affect the mole³⁴⁵ fraction in the open firn. Also, the advection term doesn't appear in \tilde{J}_{MRx} , because advection in a gravitational field does not change the mixing ratio, even though the trace gas concentration will change in proportion to the air concentration (Jeff Severinghaus, pers. comm. 2011). ³⁵⁰

The factor $\frac{v(0)}{\tilde{v}}$ in front of the spatial derivatives appears because we are expressing the derivatives in terms of y rather than z. Instead of solving for the derivatives in terms of y, we can solve these equations but evaluate the derivatives in terms of the physical depth z, using

$$\tilde{J}_{\rm MRx} = -\tilde{D}_{\rm x} \frac{\partial \tilde{c}_{\rm x}}{\partial z} + \tilde{D}_{\rm x} \frac{(M_{\rm x} - M_{\rm air})g\tilde{c}_{\rm x}}{RT} - \tilde{D}_{\rm eddy} \frac{\partial \tilde{c}_{\rm x}}{\partial z} \qquad (44)^{35}$$

$$\frac{\partial \tilde{c}_{\mathbf{x}}}{\partial t'} = -\frac{\partial}{\partial z} \tilde{J}_{\mathbf{MRx}} - \frac{M_{\mathrm{air}}g}{RT} \tilde{J}_{\mathbf{MRx}} - \frac{1}{\tilde{f}} \frac{\partial f}{\partial z} \tilde{J}_{\mathbf{MRx}} - \lambda \tilde{c}_{\mathbf{x}} - \tilde{u} \frac{\partial \tilde{c}_{\mathbf{x}}}{\partial z}$$
(45)

1.6 Trace gases in trapped bubbles

We model the trace gas mole fraction for both open and closed pores in all model layers. As soon as closed porosity increases above zero, the model will start to calculate the mole fraction in the trapped bubbles, although if this occurs gradually in the shallow firn (such as in the Goujon et al. (2003) parameterisation), the modelled trapped mole fraction can be associated with a negligible amount of air. Once diffusion has stopped, air is locked into the channels in a particular piece of ice, and the mole fraction of any trace gas in that model layer stays constant (apart from radioactive decay) as the air is progressively trapped into bubbles.

We model the mole fraction in the closed pore space, c_x^b , by considering both the compression of closed pore space and trapping of air into new bubbles. Compression increases the air pressure and trace gas concentration in the bubbles, but not the trace gas mole fraction. As new bubbles are formed we combine the previous trace gas mole fraction in the closed pores with new bubbles.

Conservation of mass gives

$$\frac{\partial}{\partial t'} \left[b C_{\mathbf{x}}^{b} \right] = b \frac{\partial C_{\mathbf{x}}^{b}}{\partial t'} + C_{\mathbf{x}}^{b} \frac{\partial b}{\partial t'} = C_{\mathbf{x}} v s \frac{\partial r}{\partial z} - \lambda b C_{\mathbf{x}}^{b}$$
(46)

leading to

$$\frac{\partial C_{\mathbf{x}}^{b}}{\partial t'} = -C_{\mathbf{x}}^{b} \frac{1}{b} \frac{\partial b}{\partial t'} + C_{\mathbf{x}} \frac{1}{r} \frac{\partial r}{\partial t'} - \lambda C_{\mathbf{x}}^{b}$$
(47)

Using $c_{\rm x}^b = C_{\rm x}^b / C_{\rm air}^b$ we can derive

$$\frac{\partial c_{\mathbf{x}}^{b}}{\partial t'} = \left[c_{\mathbf{x}} - c_{\mathbf{x}}^{b}\right] \frac{C_{\mathrm{air}}}{C_{\mathrm{air}}^{b}} \frac{1}{r} \frac{\partial r}{\partial t'} - \lambda c_{\mathbf{x}}^{b}$$
(48)

This weights the trace gas mole fraction already in old bubbles and that trapped into new bubbles by air content, taking into account compression of the old bubbles that has already occurred. The old CSIRO model weighted by porosity, and didn't take into account compression. The difference between the two methods is actually very small, but taking into account compression is expected to be a more accurate representation of reality. We have assumed that there is no fractionation due to bubble trapping, which may occur for smaller molecules than those considered here (Huber et al., 2006; Battle et al., 2011).

1.7 Implementation

To derive an equation (in moving coordinates) that we can solve with the implicit time stepping, we can expand eqns 44 and 45 and collect terms involving $\frac{\partial^2 c_x}{\partial z^2}$, $\frac{\partial c_x}{\partial z}$ and c_x to get

$$\begin{split} \frac{\partial c_{\mathbf{x}}}{\partial t'} &= \frac{\partial^2 c_{\mathbf{x}}}{\partial z^2} [D_{\mathbf{x}} + D_{\text{eddy}}] \\ &+ \frac{\partial c_{\mathbf{x}}}{\partial z} \left[\frac{\partial D_{\mathbf{x}}}{\partial z} + D_{\mathbf{x}} \left(\frac{(2M_{\text{air}} - M_{\mathbf{x}})g}{RT} + \frac{1}{f} \frac{\partial f}{\partial z} \right) \end{split}$$

315

360

365

$$+\frac{\partial D_{\text{eddy}}}{\partial z} + D_{\text{eddy}} \left(\frac{M_{\text{air}}g}{RT} + \frac{1}{f}\frac{\partial f}{\partial z}\right) - u \right] \\ + c_{\text{x}} \left[\frac{(M_{\text{air}} - M_{\text{x}})g}{RT} \left(\frac{\partial D_{\text{x}}}{\partial z} + D_{\text{x}} \left(\frac{M_{\text{air}}g}{RT} + \frac{1}{f}\frac{\partial f}{\partial z}\right)\right) \\ -\lambda\right]$$
(49)

As already mentioned, the variable y was useful to ensure $_{410}$ that the equations were derived correctly in moving coordinates, but it is more convenient to evaluate the derivatives in terms of z. However, it is very important to account for the fact that layers have different thicknesses in terms of z. When evaluating derivatives in space, we use $_{415}$

$$\frac{\partial c_k}{\partial z} = \frac{c_{k+1} - c_{k-1}}{h_1 + h_2} \tag{50}$$

and

$$\frac{\partial^2 c_k}{\partial z^2} = \frac{c_{k+1}}{h_1 h_2} - c_k \left(\frac{1}{h_2 h_3} + \frac{1}{h_1 h_3}\right) \frac{c_{k-1}}{h_1 h_3} \tag{51}$$

where c_k , c_{k-1} and c_{k+1} are the concentration in the layers k, k-1 and k+1, and $h_1 = z_k - z_{k-1}$, $h_2 = z_{k+1} - z_k$ and $_{420}$ $h_3 = (h_1 + h_2)/2$ are distances between layer centres.

If we want to remove the fractionating effect of gravity, we can set $M_x = M_{air}$. Isotopic ratios are modelled in the firm by modelling each of the isotoperate as appendix tracers

³⁷⁵ firn by modelling each of the isotopomers as separate tracers with their own atmospheric history as a mole fraction, then 425 combining the model output of the tracers at each depth to give the isotopic ratio.

Model layers correspond to equal mass of ice per unit area (in kg m⁻²), denoted W and usually a fraction or multiple of the annual accumulation. Each new layer accumulates in 430 time $\tau = W/A$. The time interval τ is divided into an integer number of timesteps. Initially the surface layer has mass W, and each timestep mass is added to this layer and the

- layers below it are moved downwards, until the surface layer reaches mass 2W. At this point the coordinate system is re-435 labeled, such that the values of quantities in layer k are put into layer k + 1 and the surface layer is reset to mass W. At each model time step we need to recalculate the depth of each layer and the corresponding density, open porosity and
- diffusivity before solving the model equations.

The model is usually run with a time step dt=0.01 yr. In order to speed up the GA calculation, each time a new parameter set is tested the firn model is initially run with dt=0.5 yr until a few years before the end of the calculation when we change to 0.01 yr to the end (to capture the variation causes ⁴⁴⁵ by the seasonal cycle). If Φ for this parameter set is less than 0.4 (for NEEM) above $\Phi_{\rm G}$, the model is rerun with dt=0.01 yr. The difference in Φ between these two cases (at NEEM) varies between about zero and 0.3. The initial fast

- run is about 20 times faster than the rerun. If a wide prior 450 parameter range is used, there can be many parameter sets tested that are a very bad fit to the data, so running first with a large time step offers a significant time saving compared to
- ⁴⁰⁵ running all cases with dt=0.01 yr.

1.8 Convective mixing

We have two options for modelling convective mixing near the surface. The first is a well-mixed layer, similar to that described by Trudinger et al. (2002). In the new version of the model, the model layers start at the depth of the wellmixed layer, where this depth can be tuned by the GA along with diffusivity. The second option for modelling convective mixing involves using an exponentially decreasing eddy diffusion following Severinghaus et al. (2001), where the two parameters describing eddy diffusion (magnitude and length scale) can be tuned by the GA along with diffusivity.

1.9 Melt Layers

440

The ice structure at DE08-2 shows a melt layer at 8.7 m below the surface. Trudinger et al. (1997) found that the agreement between modelled and measured tracers at DE08-2 (SF₆ in particular) was significantly improved by including a melt laver that originated at the surface in the 1989-90 summer and moved with the ice with a reduction of diffusive flux of about 80%. Sofen (2007) also considered a melt layer at Summit. A melt layer moving with the ice is a departure from our assumption that the ice properties at a particular depth are constant with time. For simplicity, we assume that the melt layer affects only molecular diffusion but not any of the other physical properties of the ice (open or closed porosity, bubble trapping, convective mixing/eddy diffusion, air pressure or air flow). When air was collected at DE08-2 in 1993, the melt layer was at 8.7m, so was too shallow to have affected bubble trapping yet. Thus, the assumption that the melt layer has affected only molecular diffusion seems appropriate for DE08-2 but may not be suitable for other sites, particularly for a deeper melt layer. We include the melt layer in the model for DE08-2 by replacing the diffusivity $D_X(z_{ML})$ at the layer boundary corresponding to ice that fell as snow in 1989.77 (i.e. depth z_{ML}) by $\mu D_X(z_{ML})$ where $0 \le \mu \le 1$ and μ is the degree to which the melt layer has reduced molecular diffusion. Although the model equations were derived assuming that the ice properties were constant with time, there were no equations involving time derivatives of diffusivity, so adding time variation to D_X does not pose a problem. Time variation of open or closed porosity would need much more consideration. Although multiplying $D_{\rm X}(z_{\rm ML})$ by μ is equivalent to multiplying the flux $J_{\rm X}(z_{\rm ML})$ by the same value, as was done in Trudinger et al. (1997), there are other differences between the old and new versions of the model (upward flux of air due to compression in the new version and flux smoothing in the old version) that mean that the value of μ here may give a different effect compared to the equivalent parameter in the old model. Here we find that a reduction of diffusion of 89% gives the optimal match to DE08-2 observations.



Fig. 2. Northern hemisphere (black lines) and southern hemisphere (grey lines) atmospheric records used to drive the firn model. HCFC-141b is shown only for the southern hemisphere. The vertical dotted lines indicate the beginning of the Cape Grim Air Archive and/or Cape Grim *in situ* measurements, before which the atmospheric histories of those tracers were based on emissions estimates.

455 2 Atmospheric histories

460

465

We use the atmospheric concentration histories for the high latitude northern hemisphere from Buizert et al. (2012), ⁴⁷⁰ shown in Figure 2. These were compiled from direct atmospheric measurements, firn/ice core measurements from Law Dome in Antarctica, tree-ring data and emissions-based

estimates. Atmospheric records were at monthly resolution starting in the year 1800. 475

The high latitude southern southern hemisphere atmospheric histories for CO_2 and CH_4 are from the Law Dome ice core records (Etheridge et al., 1996, 1998; MacFarling

Meure et al., 2006) and Cape Grim direct atmospheric mea-

surements (Francey et al. (2010) and references therein; Rigby et al. (2008) and references therein). For SF₆, CFCs, HFC-134a and methyl chloroform we use histories based on AGAGE measurements and emission-based model results from Martinerie et al. (2009), consistent with the northern hemisphere records. For ¹⁴CO₂ the southern hemisphere history is based on measurements from tree rings and from Wellington, New Zealand (Manning and Melhuish, 1994), and HCFC-141b is based on measurements at Cape Grim (Cape Grim Air Archive (unpublished data, P. Krummel personal communication) followed by direct atmospheric measurements (O'Doherty et al., 2004)).

Table 1. DE08-2 firn measurements (Etheridge et al., 1996; Trudinger et al., 1997; Etheridge et al., 1998). We use the same uncertainties for all measurements of each tracer, with values given on the last line of the table.

Depth m	CO ₂ ppm	CH ₄ ppb	SF ₆ ppt	$\delta^{15}\mathrm{N}_2$ ‰	14^{14} CO ₂ 10^{-12} ppm
0	-	1673.97	2.7245	-	488.65
10	352.859	1677.44	2.2405	0.0548	-
15	352.377	1674.68	-	0.0629	-
20	351.794	1669.31	2.048	0.0944	-
30	350.056	1658.43	1.772	0.1461	498.48
40	348.464	1642.76	1.544	0.1775	508.54
50	-	-	1.361	-	-
55	346.559	1623.81	-	0.2186	-
60	345.659	1620.87	1.1555	0.2450	516.85
65	345.367	1616.30	-	0.2572	-
70	344.046	1605.80	0.923	0.2788	511.90
75	341.191	1577.16	0.7515	0.2853	-
80	336.843	1511.17	0.434	0.2982	542.22
σ	1.0	10.0	0.05	0.015	10

3 DE08-2 and DSSW20K firn measurements

- ⁴⁸⁰ The firn measurements that we use for DE08-2 (Etheridge et al., 1996; Trudinger et al., 1997; Etheridge et al., 1998) are given in Table 1, and for DSSW20K (Smith et al., 2000; Sturrock et al., 2002; Trudinger et al., 2002) in Table 2. The DSSW20K halocarbon measurements from Sturrock et al. (2002) are now given on the SIO2005 scale. For DSSW20K,
- $_{485}$ (2002) are now given on the SIO2005 scale. For DSSW20K, we chose not to use measurements of SF₆, CFCs and methyl chloroform below 45 m in our model calibration, because their atmospheric histories (for the southern hemisphere) prior to 1978 are based on emissions estimates rather than
- 490 atmospheric measurements. The measurements are given in the table in brackets. The uncertainties used are shown on the last row of the tables. HCFC-141b uses uncertainties of 0.1 ppt for the upper two observations and 0.05 ppt for the rest.

495 **4** Inferring relative diffusion coefficients

500

As described in the main paper, we repeated the Synthetic A and B Subset Ten calculations estimating the relative diffusion coefficients, γ_X , of seven tracers in addition to the diffusivity profile and well-mixed layer depth. Figures 3 and 4 show scatter plots of diffusion coefficients against Φ for all

- solutions tested by the GA that had $\Phi_A < 1.25$ and $\Phi_B < 1.0$. The clustering of points into horizontal lines in Figure 3 is due to the way the GA algorithm works, retaining solutions 510 with low Φ and mutating or breeding them.
- Synthetic A has a steeper rise in Φ for a similar change in relative diffusion coefficient (i.e. a narrower minimum) than



Fig. 3. Scatter plot of relative diffusion coefficients as a function of Φ_A for all solutions tested by the GA that had $\Phi_A < 1.25$ for Synthetic A observations. The vertical axis shows the allowed range of $\pm 10\%$ of the true value. The red horizontal line indicates the true diffusion coefficient used to calculate the synthetic observations.



Fig. 4. Scatter plot of relative diffusion coefficients as a function of $\Phi_{\rm B}$ for all solutions tested by the GA that had $\Phi_{\rm B} < 1.0$ for Synthetic B observations.

Synthetic B. Synthetic A also has more sparse coverage of solutions than Synthetic B in these plots – many more solutions are generated by the GA in Synthetic B in our range of interest than in Synthetic A, despite the same specifications for the GA. This was a feature of scatter plots of all parameters in the synthetic calculations – for Synthetic A they were sparse but Synthetic B they were dense.

Table 2. DSSW20K firn measurements (Smith et al., 2000; Sturrock et al., 2002; Trudinger et al., 2002), not corrected for gravity. The lower measurements of SF_6 , CFC-11, CFC-12, CFC-113 and CH_3CCl_3 in brackets are not used for calibration, because their atmospheric histories are based on emission estimates rather than atmospheric measurements. The same uncertainties are used for all measurements of each tracer, with values given on the last line of the table (the upper two HCFC-141b measurements use an uncertainty of 0.1, and other measurements use 0.05).

Depth	CO_2	CH_4	SF_6	CFC-11	CFC-12	CFC-113	CH_3CCl_3	HFC-134a	HCFC-141b	$\delta^{15} \mathrm{N}_2$	14 CO $_2$
m	ppm	ppb	ppt	ppt	ppt		ppt	ppt	ppt	%0	10^{-12} ppm
15.8	360.01	1706.87	3.37	259.36	524.71	78.96	91.67	2.3547	3.9137	0.0413	494.18
29	357.79	1694.29	2.812	247.26	489.51	71.00	100.53	0.85167	1.358	0.123	481.43
37.8	354.62	1679.86	2.218	-	-	-	-	-	-	0.15513	492.91
41.7	350.75	1660.31	1.643	192.94	385.75	38.41	83.50	0.034667	0.0945	0.16	504.17
44.5	342.27	1584.93	0.896	127.91	267.70	17.15	54.62	0.0	0.04067	0.16263	518.45
47	325.81	1366.51	(0.144)	(27.88)	(69.12)	(1.97)	(11.22)	0.0	0	0.16163	508.72
49.5	317.24	1189.72	(0.026)	(1.98)	(10.16)	(0.2)	(2.13)	0.0	0	0.1627	425.91
52	313.43	1090.54	(0.014)	(0.23)	(1.30)	(0.3)	(1.69)	0.0	0	0.15825	377.84
σ	1.0	10.0	0.1	5.0	10.0	2.0	4.0	0.1	0.1, 0.05	0.015	10.0

5 Dispersion in the lock-in zone

- ⁵¹⁵ The lock-in depth is defined as the depth where impermeable ⁵⁵⁰ winter layers cause vertical mixing to go to zero. Gravitational enrichment essentially stops at the lock-in depth, leading to almost constant values of indicators of gravitational enrichment, such as $\delta^{15}N_2$, below it. The lock-in zone is the
- region below the lock-in depth down to the depth where there are no longer any open pores. Air can be drawn from open summer layers sandwiched between denser winter layers in 555 the lock-in zone, and the gas age through the lock-in zone rises at about the same rate as the age of the surrounding ice.
- ⁵²⁵ Contrary to the assumption of zero diffusion in the lockin zone, Severinghaus et al. (2010) included eddy-diffusive fluxes in the lock-in zone in their model, to improve the fit to ⁵⁶⁰ CO_2 and simulate possible upward mixing of old air due to the increase of pressure in summer layers before bubbles are
- formed. In Buizert et al. (2012) all six firm models required non-zero diffusivity of the order of 0.1 m²y⁻¹ in the lock-in zone, parameterised in different ways using either molecular ⁵⁶⁵ diffusion, eddy diffusion (dispersion) or a mixture of both. Four of the models chose dispersive mixing in the lock-in
- ⁵³⁵ zone to improve the fit to the slow-diffusing gases such as CFC-113 (Severinghaus, 2012), or because it reduced the peak in ¹⁴CO₂ closer to observations while leaving $\delta^{15}N_{2570}$ constant below the lock-in depth. The other two models used molecular diffusion. There was no obvious difference in Φ between models due to the different ways of modelling diffu-
- ⁵⁴⁰ between models due to the different ways of modelling diffusion in the lock-in zone. The different treatment of mixing in the lock-in zone was believed to be the cause of the significant variation in estimates of diffusive fractionation affecting trace gas isotopic ratios, such as δ^{13} CO₂ and δ^{13} CH₄.
- ⁵⁴⁵ More work is needed to understand the processes occurring in the lock-in zone. Because dispersion may be important for diffusive fractionation in particular, we make some 580

preliminary calculations, first testing the sensitivity of our model results to dispersion in the lock-in zone, then adding dispersion to our GA calibration. We are interested primarily in how well we can constrain dispersion in the lock-in zone at the same time as the other diffusion parameters, and how much equifinality increases when we consider dispersion.

5.1 Sensitivity to dispersion

We first tested the sensitivity of our model results to dispersion by adding the dispersive flux in the lock-in zone (the one estimated for NEEM with the CIC model in Buizert et al. (2012), which at its highest value is about 0.1 m² yr⁻¹), to a forward run of the CSIRO firn model with our calibrated molecular diffusivity. Without recalibrating we compared the results with and without the dispersion. For NEEM, there was most difference in ¹⁴CO₂ and methyl chloroform, with dispersion giving a small reduction of the peaks compared to the case without dispersion. There was also a small difference in the concentrations of the CFCs and CH₄ in the lock-in zone.

In Buizert et al. (2012), three of the four models that include dispersion at NEEM had a ratio of eddy to total diffusion of 1.0 by at least 70m, that is, molecular diffusion is zero and there is only dispersive diffusion. In our calculations for NEEM in the main text we have non-zero molecular diffusion to around 77 m (in our best case). The slight increase in $\delta^{15}N_2$ with depth down to about 77 m that this gives (about 0.004 %_o) is about as consistent with the measured $\delta^{15}N_2$ as a constant level. Our molecular diffusion below 70 m is of similar magnitude to the CIC dispersion flux in this depth range.

Using the CIC dispersive flux as a function of open porosity, the difference with and without dispersion in model results at the other sites we consider (DE08, DSSW20K and South Pole) was barely detectable for the reference tracers used in previous sections. At DE08-2, our molecular diffusion is a few times to many times larger than the CIC dispersion over the same open porosity range, so adding the

- ⁵⁸⁵ CIC dispersion of around 0.1 m² yr⁻¹ made hardly any difference. At DSSW20K, we have used the exponentiallydecreasing eddy diffusion for convective mixing near the surface, and this still has a significant contribution in the lock-in zone which already causes a reduction in ¹⁴CO₂ compared
- to cases without it, so adding a small additional dispersion made little difference. At South Pole, we also have molecular diffusion around $0.1 \text{ m}^2 \text{ yr}^{-1}$ below the lock-in depth, and the tracers modelled are not very sensitive to the additional dispersion.

595 5.2 Calibration of dispersion with NEEM synthetic data

Next we tried including dispersion in the model with parameters calibrated by the GA in addition to molecular diffusivity. We specify dispersion as a function of open porosity, f, prescribed as a non-symmetric cosine function (i.e. a cosine function between $-\pi$ and π where the peak could be shifted 630 left or right by scaling each side differently in the horizontal direction). We describe this function with four parameters, as shown in Figure 5: the maximum height of the function D_{max} , the porosity value at the left $(-\pi)$ side of the function

 f_{\min} , the width of the function (in terms of porosity), $f_{wid, 635}$ and the location of the maximum of the function as a fraction of the width, f_{frac} (0.5 would put the peak in the middle, giving a symmetric function). For the open porosity range $f_{\min} < f < f_{\min} + f_{\text{frac}} f_{wid}$, the equation is

610
$$D_{\text{disp}} = \frac{D_{\text{max}}}{2} \left[1 - \cos\left(\pi \frac{f - f_{\text{min}}}{f_{\text{frac}} f_{\text{wid}}}\right) \right]$$
 (52)

and for the range $f_{\rm min} + f_{\rm frac} f_{\rm wid} < f < f_{\rm min} + f_{\rm wid}$

$$D_{\rm disp} = \frac{D_{\rm max}}{2} \left[1 + \cos\left(\pi \frac{f - (f_{\rm min} + f_{\rm frac} f_{\rm wid})}{(1 - f_{\rm frac}) f_{\rm wid}}\right) \right]$$
(53) 645

This form is not as general as our prescription for molecular diffusion, but serves as a starting point to allow some dispersion in the lock-in zone with a few parameters that can be tuned.

We tried two calibration calculations with synthetic NEEM observations, one that used the noisy Synthetic A $_{650}$ observations (i.e. no dispersion in the forward run), and the other that included dispersion in the forward run of the model with the same noise added as Synthetic A. For dispersion in the forward run we used the cosine function with $D_{\text{max}} = 0.1 \text{ m}^2 \text{ yr}^{-1}$, $f_{\text{min}} = 0.002$, $f_{\text{wid}} = 0.17$ and $f_{\text{frac}} = 0.65$. In $_{655}$ both cases we included the 4 parameters describing the dispersion peak in the GA calibration as well as the usual molecular diffusivity and the depth of the well-mixed layer, to see

whether we could resolve dispersion in either case.

There was a difference in the results for the two cases, as 660 shown in Figure 6. The results on the left show the case with



Fig. 5. Function used for dispersion in the lock-in zone, based on a cosine function between $-\pi$ and π with adjustable parameters for the height (D_{max}) , porosity at the left side (f_{min}) , width (f_{wid}) and the peak can be shifted left or right with an additional parameter $(f_{\text{frac}}$ with values between 0 and 1; a value of 0.3 was used in the case shown in the figure).

dispersion in the forward run used to generate the pseudo observations, and on the right without dispersion. The best solution in the case with dispersion is similar to the true dispersion function used, and the difference of the best estimate from the true dispersion is offset by a similar but opposite difference between the true molecular diffusivity and the best estimate. The true molecular diffusion is unfortunately outside the envelope of solutions with Phi < 1.25 for part of the range. In the case without dispersion, there are some accepted solutions with dispersion above 60 m, where molecular diffusion dominates, and there are some narrow dispersion peaks accepted below about 70 m.

These cases had small, Gaussian errors, and had some, although not complete, success in recovering both dispersion and molecular diffusion in the lock-in zone. Realistic errors would make it more difficult. There is certainly an increase in equifinality from including the additional process in calibration.

5.3 Calibration of dispersion for DSSW20K

With 11 tracers for calibration including ${}^{14}\text{CO}_2$, DSSW20K is another site where we might be able to resolve dispersion in the lock-in zone. We are also interested to see whether allowing dispersion in the lock-in zone removes the need for the exponentially-decreasing eddy diffusion to extend down to the lock-in zone. We tuned the model in three ways using DSSW20K observations: (i) the case already shown in the Supplementary Material with parameters for molecular diffusion as well as exponentially-decreasing eddy diffusion for convective mixing near the surface and no additional parameters for dispersion in the lock-in zone, (ii) parameters for molecular diffusion, exponentially-decreasing eddy diffusion for convective mixing near the surface and dispersion in the lock-in zone, (iii) parameters for molecular diffusion, exponentially-decreasing eddy diffusion for convective mixing near the surface and dispersion for convective mixing near the

615



Fig. 6. The left column shows true and estimated a) molecular diffusion and c) dispersion for a case with dispersion in the forward model run used to generate the pseudo-observations for NEEM. Data uncertainties are the same as for Synthetic A. The red dashed line is the true solution, the black solution corresponds to the solution with the lowest Φ , the dotted black lines show the range of solutions with $\Phi < 1.25$, and the blue lines show 19 representative solutions. The right column shows true and estimated b) molecular diffusion and d) dispersion for a case without dispersion in the forward run (observations are Synthetic A).

in the lock-in zone, and (iii) parameters for molecular diffusion, well mixed layer for convective mixing near the surface and dispersion in the lock-in zone. We allowed the magnitude of the dispersion to vary up to $10 \text{ m}^2 \text{ yr}^{-1}$, and the GA 695 preferred a value close to $10 \text{ m}^2 \text{ yr}^{-1}$ for (ii) and around $2 \text{ m}^2 \text{ yr}^{-1}$ for (iii). This is considerably higher than the values used in Buizert et al. (2012) of around 0.1 m² yr⁻¹ and

Severinghaus et al. (2010) of order 0.01 m² yr⁻¹.

- The lowest values of Φ for the 3 DSSW20K cases were 700 0.91, 0.91 and 0.95, respectively, that is, with eddy diffusion for convection, we do equally well with and without dispersion in the lock-in zone, but the well-mixed layer case is not quite as good as the other two cases. We selected representa-
- tive subsets of 20 parameter sets in each case, and calculated ⁷⁰⁵ the isotopic diffusion correction, used to correct observations of $\delta^{13}CO_2$ for fractionation in the firn due to the different rates of diffusion of the isotopes (Trudinger et al., 1997). For this calculation, we used spline fits to CO_2 and $\delta^{13}CO_2$ mea-
- surements from Law Dome and Cape Grim. Figure 7 shows 710 the calculated diffusion correction with depth for our original set of 20 solutions (left plots, with green lines) and for all 60 solutions together (right plots with green, blue and red lines for the three different cases). Each of the ensembles
- ⁶⁸⁵ correspond to confidence levels of 68%, with thresholds of 715 Φ of 1.08, 1.13 and 1.16 for the three cases, respectively. The range in the diffusion correction is shown in Figure 7c for the original 20 cases and all 60 cases. We also show the difference between the best solution and whichever of the
- maximum or minimum is further from the best solution. In-720 cluding dispersion in the calculation has increased the range

considerably.

Our calculations for DSSW20K show that unless it is specifically avoided by selection of parameter prior ranges, it is possible for the exponentially-decreasing eddy diffusion for convection near the surface to extend through the whole firn and have an influence well into the lock-in zone. It is not clear at this point how deep surface pressure fluctuations can penetrate into the firn, and whether a convective influence is expected at depth. The values of the parameters preferred by the GA for DSSW20K were probably chosen to suit both convection near the surface and dispersion in the lock-in zone, rather than just convection near the surface which was the intention. Our specification of molecular diffusion was chosen to avoid being prescriptive about the variation with depth, but the specification for eddy diffusion (both for convection near the surface and dispersion in the lock-in zone) is quite prescriptive. In the SIO model in Buizert et al. (2012), the balance between molecular diffusion and dispersion was specified with a single coefficient varying between 0 and 1, rather than trying to estimate a depth-varying dispersion diffusivity profile that is poorly constrained.

Adding in the possibility of dispersion or eddy diffusion leads to greater equifinality than with molecular diffusion alone, but if evidence for its existence continues to grow it should be accounted for as part of the range of possibilities. There is much less chance of resolving dispersion at sites with fewer tracers for calibration. Tracers with γ_X further from 1.0 or isotopic ratios are more likely to distinguish between molecular diffusion and dispersion than tracers with γ_X near 1.0.



Fig. 7. a) Diffusion correction for δ^{13} CO₂ in the DSSW20K⁷⁶⁵ firn. The black line shows our best case for calibration with exponentially-decreasing eddy diffusion and no dispersion estimated in the lock-in zone. The green lines show results for 19 representative solutions with $\Phi < 1.08$ for this case. b) Same as a, but adding 20 solutions with exponentially-decreasing eddy diffusion⁷⁷⁰ and dispersion in the lock-in zone (blue lines, $\Phi < 1.13$) and 20 solutions with a well-mixed layer for convective mixing and dispersion in the lock-in zone (red lines, $\Phi < 1.16$). c) Range in diffusion correction for the original 20 solutions (green) and all 60 solutions (blue-red line). The black line shows the difference between the⁷⁷⁵ best solution and whichever of the maximum or minimum is further from the best solution.

References

725

730

Battle, M. O., Severinghaus, J. P., Sofen, E. D., D. Plotkin and, A. J. O., Aydin, M., Montzka, S. A., Sowers, T., and Tans, P. P.:

780

- Controls on the movement and composition of firn air at the West 785 Antarctic Ice Sheet Divide, Atmos. Chem. Phys., 11, 11007– 11021, doi:10.5194/acp-11-11007-2011, 2011.
- Buizert, C., Martinerie, P., Petrenko, V. V., Severinghaus, J. P., Trudinger, C. M., Witrant, E., Rosen, J. L., Orsi, A. J., Ru-
- bino, M., Etheridge, D. M., Steele, L. P., Hogan, C., Laube, 790
 J. C., Sturges, W. T., Levchenko, V. A., Smith, A. M., Levin, I., Conway, T. J., Dlugokencky, E. J., Lang, P. M., Kawamura, K., Jenk, T. M., White, J. W. C., Sowers, T., Schwander, J., and Blunier, T.: Gas transport in firm: multiple-tracer characterisation and model intercomparison for NEEM, Northern Green-795
- isation and model intercomparison for NEEM, Northern Green-795
 land, Atmospheric Chemistry and Physics, 12, 4259–4277, doi:

10.5194/acp-12-4259-2012, 2012.

- Etheridge, D. M., Steele, L. P., Langenfelds, R. L., Francey, R. J., Barnola, J. M., and Morgan, V. I.: Natural and anthropogenic changes in atmospheric CO₂ over the last 1000 years from air in Antarctic ice and firn, J. Geophys. Res., 101D, 4115–4128, 1996.
- Etheridge, D. M., Steele, L. P., Francey, R. J., and Langenfelds, R. L.: Atmospheric methane between 1000 AD and present: evidence for anthropogenic emissions and climate variability, J. Geophys. Res., 103D, 15 979–15 993, 1998.
- Francey, R. J., Trudinger, C. M., van der Schoot, M., Krummel, P. B., Steele, L. P., and Langenfelds, R. L.: Differences between trends in atmospheric CO₂ and the reported trends in anthropogenic CO₂ emissions, Tellus B, 62, 316–328, doi: 10.1111/j.1600-0889.2010.00472.x, 2010.
- Goujon, C., Barnola, J. M., and Ritz, C.: Modeling the densification of polar firn including heat diffusion: Application to closeoff characteristics and gas isotopic fractionation for Antarctica and Greenland sites, J. Geophys. Res., 108, 4792, doi:10.1029/ 2002JD003319, 2003.
- Huber, C., Beyerle, U., Leuenberger, M., Schwander, J., Kipfer, R., Spahni, R., Severinghaus, J. P., and Weiler, K.: Evidence for molecular size dependent gas fractionation in firn air derived from noble gases, oxygen, and nitrogen measurements, Earth Planet. Sci. Lett., 243, 61–73, 2006.
- MacFarling Meure, C., Etheridge, D., Trudinger, C., Steele, P., Langenfelds, R., van Ommen, T., Smith, A., and Elkins, J.: Law Dome CO₂, CH₄ and N₂O ice core records extended to 2000 years BP, Geophys. Res. Lett., 33, L14810, doi:10.1029/ 2006GL026152, 2006.
- Manning, M. R. and Melhuish, W. H.: Atmospheric Δ^{14} C record from Wellington, in: Trends '93: A Compendium of Data on Global Change, edited by Boden, T., Kaiser, D., Sepanski, R., and Stoss, F., pp. 193–202, Carbon Dioxide Information Analysis Center, Oak Ridge, U.S.A, 1994.
- Martinerie, P., Nourtier-Mazauric, E., Barnola, J., Sturges, W. T., Worton, D. R., Atlas, E., Gohar, L. K., Shine, K. P., and Brasseur, G. P.: Long-lived halocarbon trends and budgets from atmospheric chemistry modelling constrained with measurements in polar firn, Atmos. Chem. Phys., 9, 3911–3934, 2009.
- O'Doherty, S., Cunnold, D. M., Manning, A., Miller, B. R., Wang, R. H. J., Krummel, P. B., Fraser, P. J., Simmonds, P. G., Mc-Culloch, A., Weiss, R. F., Salameh, P., Porter, L. W., Prinn, R. G., Huang, J., Sturrock, G., Ryall, D., Derwent, R. G., and Montzka, S. A.: Rapid growth of hydrofluorocarbon 134a and hydrochlorofluorocarbons 141b, 142b, and 22 from Advanced Global Atmospheric Gases Experiment (AGAGE) observations at Cape Grim, Tasmania, and Mace Head, Ireland, J. Geophys. Res., 109, D06 310, doi:10.1029/2003JD004277, 2004.
- Rigby, M., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Langenfelds, R. L., Huang, J., Cunnold, D. M., Steele, L. P., Krummel, P. B., Weiss, R. F., O'Doherty, S., Salameh, P. K., Wang, H. J., Harth, C. M., Mühle, J., and Porter, L. W.: Renewed growth of atmospheric methane, Geophys. Res. Lett., 35, L22 805, doi: 10.1029/2008GL036037, 2008.
- Rommelaere, V., Arnaud, L., and Barnola, J.: Reconstructing recent atmospheric trace gas concentrations from polar firm and bubbly ice data by inverse methods, J. Geophys. Res., 102D, 30069– 30083, 1997.
- Severinghaus, J. P.: Interactive comment on "Reconstruction of the

C. M. Trudinger et al.: Constraining firn diffusivity: Supplement

carbon isotopic composition of methane over the last 50 yr based on firn air measurements at 11 polar sites" by C. J. Sapart et al., Atmos. Chem. Phys. Discuss., 12, C1856–C1856, 2012.

- Severinghaus, J. P. and Battle, M. O.: Fractionation of gases in polar ice during bubble close-off: New constraints from firn air Ne, Kr and Xe observations, Earth and Planetary Science Letters, 244, 2006.
- Severinghaus, J. P., Grachev, A., and Battle, M.: Thermal fractionation of air in polar firm by seasonal temperature gradients,
 Geochem. Geophys. Geosyst., 2, 2001.
- Severinghaus, J. P., Albert, M. R., Courville, Z. R., Fahnestock, M. A., Kawamura, K., Montzka, S. A., Mühle, J., Scambos, T. A., Shields, E., Shuman, C. A., Suwa, M., Tans, P., and Weiss, R. F.: Deep air convection in the firm at a zero-accumulation
- site, central Antarctica, Earth and Planetary Science Letters, 293, 359–367, doi:10.1016/j.epsl.2010.03.003, 2010.
- Smith, A. M., Levchencko, V. A., Etheridge, D. M., Lowe, D. C., Hua, Q., Trudinger, C. M., Zoppi, U., and Elcheikh, A.: In search of in-situ radiocarbon in Law Dome ice and firn, Nucl. Instr. and Meth. B, 172, 610–622, 2000.
- Sofen, E. D.: A Study of Gases in Arctic and Antarctic Firn, Honours thesis, Bowdoin College, 2007.
 - Sturrock, G. A., Etheridge, D. M., Trudinger, C. M., Fraser, P. J., and Smith, A. M.: Atmospheric histories of halocarbons from analysis of Antarctic firm air: Major Montreal Protocol species,
- analysis of Antarctic firn air: Major Montreal Protocol specie
 J. Geophys. Res., 107, doi:10.1029/2002JD002548, 2002.
 - Trudinger, C. M., Enting, I. G., Etheridge, D. M., Francey, R. J., Levchenko, V. A., Steele, L. P., Raynaud, D., and Arnaud, L.: Modeling air movement and bubble trapping in firn, J. Geophys.
 Res., 102, 6747–6763, 1997.
- 825 Res., 102, 6
 - Trudinger, C. M., Etheridge, D. M., Rayner, P. J., Enting, I. G., Sturrock, G. A., and Langenfelds, R. L.: Reconstructing atmospheric histories from measurements of air composition in firn, J. Geophys. Res., 107, doi:10.1029/2002JD002545, 2002.