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Seasonal Variations of Isotope Ratios and CO₂ Concentrations in Firn Air

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Abstract: A first year–round firn air sampling carried out at the British Antarctic station Halley in 2003 shows isotope and CO₂ changes owing to diffusive mixing driven by seasonal variations of surface temperature, and gas composition of the atmosphere.

Seasonal firn temperatures are well reproduced from the atmospheric temperature history. Based on these profiles thermal diffusion is forced with thermal diffusion factors α_T with respect to air. Application of the available literature data for $\alpha_T(^{15}\text{N}^{14}/\text{N}_2)$ leads to a proper prediction of the seasonal thermal amplitude during the entire year. By forcing thermal fractionation with α_T as derived from two different model approaches and taking into account literature data reasonable results can be achieved for CO₂ but not for thermal fractionation of $^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}_2$ in air. The latter is attributed to an inappropriate reproduction of the intermolecular interaction forces by either model.

Neither thermal diffusion nor annual variations in the atmospheric CO₂ concentration seem to have a substantial effect on the CO₂ concentration finally conserved in air bubbles at the close–off level.

Key words: firn air, thermal diffusion, thermal diffusion sensitivity, CO₂, Halley

1 Introduction

Past climatic conditions can be derived from ice cores retrieved from the big ice sheets in Greenland and Antarctica. This paleo–archive is unique as it is the only one providing the history of the atmosphere’s gas composition, which is trapped in air bubbles occluded in the ice. The interpretation of these gas records, however, requires a precise understanding of the air enclosure process.

An ice sheet is formed by accumulation of snow precipitation. The snow flakes initially deposited as a loose

cover on the surface gradually change their shape and merge together. This way the snow layers become densified until finally the snow loses its air permeability, at which point it is considered to be glacier ice. The intermediate stage between snow and ice is called firn. During the diagenesis from snow to ice air is isolated and occluded into the ice. Further densification of the glacier ice results from compression of the occluded air bubbles until the density of ice, ρ_{ice} , is reached.

Snow diagenesis takes place in three different stages, which are settling, sintering and further densification by compaction [14]. Settling is characterized by rounding and rearrangement of the snow grains until grain packing is no longer effective. The corresponding density is referred to as the critical density ρ_{55} [1] empirically determined to be at about 550 kg m^{-3} [14]. Above ρ_{55} sintering [18] is responsible for further densification. Ice grains, which are brought together, stick to one another and form bonds and in doing so, grain centers approach each other. While these bonds are growing, air becomes gradually separated in–between the snow grains [40]. Analysis of the geometric bubble volume by Schwander and Stauffer [33] on an ice core from Siple Station, Antarctica revealed that 80 % of the air is occluded in air bubbles within the density interval $795 \leq \rho \leq 830 \text{ kg m}^{-3}$. From measurements of the total air content on ice samples from various sites Martinerie et al. [25, 26] derived an average air isolation level depending on the annual mean site temperature and ρ_{ice} , which is located in the density interval mentioned above. Following the common language use this isolation level is heretofore referred to as close–off density ρ_{co} as it was established by Sowers et al. [39]. ρ_{co} represents the density at which the air is finally occluded in air bubbles. Thus, considering firn as a porous mixture of air and snow grains covering the uppermost about 50 to 150 m of an ice sheet, this level is also named the firn–ice–transition. Above this density further densification up to ρ_{ice} ($\approx 920 \text{ kg m}^{-3}$, compare Table 2) is possible by external compaction only. A more

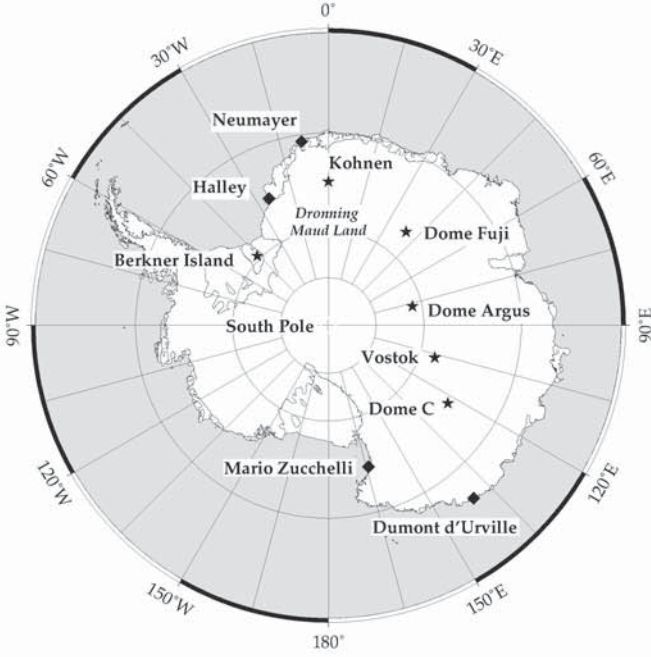


Figure 1: *Geographical map of Antarctica (provided by D. Steinhage, Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany). Research stations are marked by diamonds, while stars represent various deep drilling sites. The British Antarctic overwintering station Halley is located at 75° 35'S, 26° 34'W on the Brunt ice shelf.*

detailed discussion of firn transformation is given in Blunier and Schwander [4].

Air becomes occluded into air bubbles only at the firn–ice–transition. Thus, in the porous firn layer above, firn air can exchange with the overlying atmosphere on a timescale of decades by molecular diffusion. This means that an air bubble contains a mixture of atmospheric air covering a certain time period. This has two implications: The age of the gas is younger compared to the age of the ice at the same depth. Furthermore, the gas age cannot be given as a simple value but has to be expressed by an age distribution function. This age distribution function is convolved with the corresponding atmospheric history of the gas [31]. In addition, a second convolution [31] originates from the gradual air enclosure process [33]. More detailed information about the estimation of the gas age is given in Blunier and Schwander [4].

Air mixing in the porous firn layer is primarily driven by diffusion. In addition, secondary processes such as fractionation effects during bubble close-off [16, 35] or convective mixing [5] overlay diffusive mixing and lead to changes in the composition of the occluded gas. Regarding diffusive mixing the firn column can be divided in three different zones, which are the convective zone, the diffusive zone and the non-diffusive zone [39] (see also Blunier and Schwander [4] for detail).

The convective zone is a well mixed layer located directly below the snow surface, where air mixing is predominantly controlled by surface meteorology.

The diffusive zone reaches from the bottom of the convective zone down to just above the firn–ice–transition. Air mixing in the diffusive zone is strongly driven by diffusion where in addition to ordinary diffusion, gravitational enrichment [6, 30] and thermal separation [21, 38] play an important role.

The non-diffusive zone finally, describes the depth level, in which air no longer exchanges with the atmosphere, but not all air is trapped in bubbles. In this region, fractionation processes occur, which can significantly affect the composition of elemental ratios, such as O_2/N_2 or Ar/N_2 [16, 35].

This study focuses on the fractionation of isotopes and CO_2 in firn air as a result of seasonal variations in the atmospheric parameters gas composition and temperature. Seasonal varying atmospheric concentrations become smoothed in the firn air owing to diffusion. Atmospheric temperature variations lead to thermal gradients in the firn column, which lead to thermal fractionation.

Detailed investigations of temperature induced isotopic fractionation have been carried out by Landais et al. [19] or Kawamura et al. [17] on summer firn air from NorthGRIP or by Severinghaus et al. [36] on summer firn air from Siple Dome. A first study taking into account also the winter season was carried out by Severinghaus et al. [36] on firn air from South Pole. In the present study for the first time firn air profiles covering the entire year are investigated.

In order to simulate the fractionation effects a 1-dimensional diffusion–temperature model based on Schwander et al. [31, 32] is applied (section 2). The model approach requires thermal diffusion factors α_T with respect to air. Apart from $^{15}N^{14}N$ only a few measurements of these quantities are reported in the literature, which only partly cover the polar temperature range. Therefore, two model approaches (according to Leuenberger et al. [21] or van der Valk [43], respectively) are applied in order to calculate the α_T . A detailed description of these models (based on the Lennard–Jones potential) is given in appendix A.

In section 4 simulated firn temperature and firn air profiles are compared with a year-round multi proxy data set sampled at the British Antarctic overwintering station Halley (75° 35'S, 26° 34'W, see Figure 1). Sample collection and analysis are described in section 3, while a small box model developed to correct sample levels for accumulation and firn densification (see appendix B) is applied and evaluated.

2 Simulation of diffusion and heat conduction in the firn

Diffusion in the firn column is simulated with a 1-dimensional diffusion model based on Schwander et al. [31, 32]. The 1-dimensional diffusion equation solved for a time step of about 1.5 days and a vertical resolution

of 2 to 12 cm has the following form:

$$\frac{\partial c_1}{\partial t} = \frac{1}{s_{op}} \frac{\partial}{\partial z} [j_z + j_{grav} + j_{TD}], \quad (1)$$

where s_{op} is the open porosity (see below).

The vertical transfer rate of ordinary diffusion (units $\text{m}^{-2} \text{s}^{-1}$, i.e. particles per area and time) is represented by

$$j_z = -D_e \frac{\partial c_1}{\partial z}. \quad (2)$$

c_1 is the concentration of a gas 1 in m^{-3} (i.e. particles per volume), z the firm depth in m and D_e the effective diffusivity in $\text{m}^2 \text{s}^{-1}$ (see below).

Gravitational separation leads to an accumulation of heavier gas molecules towards the bottom of the firm column. The transfer flux owing to gravitational separation can be expressed as

$$j_{grav} = D_e \frac{m_M g c_1}{kT}, \quad (3)$$

where j_{grav} has the units $\text{m}^{-2} \text{s}^{-1}$. m_M is the molecular weight of a gas species 1 in kg, $g = 9.82 \text{ m s}^{-2}$ the gravitational acceleration, $k = 1.38066 \cdot 10^{-23} \text{ J K}^{-1}$ the Boltzmann constant and T the temperature in K. For stationary conditions the gravitational enrichment can be expressed with the barometric formula

$$\frac{p(z)}{p_0} = \exp\left(-\frac{Mg(-z)}{RT}\right) \quad (4)$$

as stated by Craig and Wiens [6] and Schwander [30]. Equation 4 is the solution of equation 3, when the partial pressure (in Pa) of a gas molecule in depth z , $p(z)$, is related to the corresponding concentration c_1 by $c_1 = \frac{p(z)}{kT}$. $p_0 = c_0 kT$ represents the initial partial pressure in Pa, M the molar mass in kg mol^{-1} of the gas and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ the gas constant. Linking equation 4 with the standard delta notation (equation 13), the gravitational enrichment of an isotope species $^A X$ in depth z results in

$$\Delta \delta^A X_{grav} = \left(\exp \frac{\Delta M g z}{RT} - 1 \right) \cdot 1000 \text{ ‰}. \quad (5)$$

Thus, gravitational fractionation increases with the difference of the molar masses ΔM of two gas species. Furthermore, the gravitational slope increases for a negative temperature gradient in the firm column and vice versa (see Weiler [47] for detail).

The thermal diffusion effect can be described as the tendency of the heavier species to move towards the colder regions [12], i.e. a mass transport driven by a temperature gradient $\frac{\partial T}{\partial z}$. According to the Chapman Enskog theory the thermal diffusion process can be expressed as

$$\frac{\partial n_{10}}{\partial z} = -\frac{\alpha_T n_{10} n_{20}}{T} \frac{\partial T}{\partial z}, \quad (6)$$

providing a binary mixture (i.e. $n_{10} + n_{20} = 1$, where n_{10} is the molar fraction of substance 1 fractionating with respect to substance 2 with molar fraction n_{20}) subject to no external forces, uniform pressure, and provided uniform mean thermal velocities of the gas molecules [12].

Assuming T_1 to be the reference temperature integration of equation 6 in-between the limits T_1 and T_2 leads to

$$\begin{aligned} \Delta \delta^A X_{TD} &= \left[\left(\frac{n_{10}}{n_{20}} \right)_{T_2} - 1 \right] \cdot 1000 \text{ ‰} \\ &= \left[\left(\frac{T_1}{T_2} \right)^{\alpha_T} - 1 \right] \cdot 1000 \text{ ‰}, \end{aligned} \quad (7)$$

where again the standard delta notation (equation 13) was applied (see also Leuenberger et al. [21]). Thus, for stationary conditions and in a binary mixture, thermal fractionation of an isotope species in air $^A X$ can be estimated from the concentration ratio at T_1 and T_2 or from the temperature ratio itself, if α_T is known (see also Weiler [47] for detail).

Combination of Fick's 1st law $j = -D_e \frac{\partial c_1}{\partial z}$ with equation 6 (where $c_1(z) = \frac{n_{10}(z)}{V(z)}$, $V(z)$ is the gas volume) leads to the following form for the transfer flux originating from thermal fractionation j_{TD} (in $\text{m}^{-2} \text{s}^{-1}$):

$$j_{TD} = -D_e \frac{\alpha_T c_1 n_{20}}{T} \frac{\partial T}{\partial z}. \quad (8)$$

α_T denotes the dimensionless thermal diffusion factor depending on the ratio of masses and diameters of the two species of the binary mixture and their corresponding interaction forces ([12], compare appendix A). Temperature driven concentration changes simply following the ideal gas law are neglected in this context as they have a much shorter time constant than diffusion.

Diffusion in the porous firm is ruled by the cross section of the pores but also by their orientation and topography as pore space is tortuous. Pore space in the firm is described by its porosity, while the total porosity s is the sum of open porosity s_{op} and closed porosity s_{cl} [30]. Closed porosity is estimated from measurements of the bubble volume of an ice core from Siple Station, Antarctica [33] as described in Schwander [30] and Blunier and Schwander [4].

Tortuosity in case of gas diffusion through porous media is known as the ratio of the diffusivity in the free space D_0 (in $\text{m}^2 \text{s}^{-1}$) to the diffusivity in the porous medium [8]:

$$q = s_{op} \cdot \frac{D_0}{D_e}, \quad (9)$$

where D_e is the effective diffusivity (units $\text{m}^2 \text{s}^{-1}$). From measurements of the diffusion coefficient on ice samples from Siple Station, Antarctica [34], the following parametrisation of the tortuosity factor is revealed [31]:

$$q_{Par} = 1 + 0.5 \cdot (1 - s_{op}) \cdot (\alpha + (1 - \alpha) \cdot s_{op}^{-\beta}). \quad (10)$$

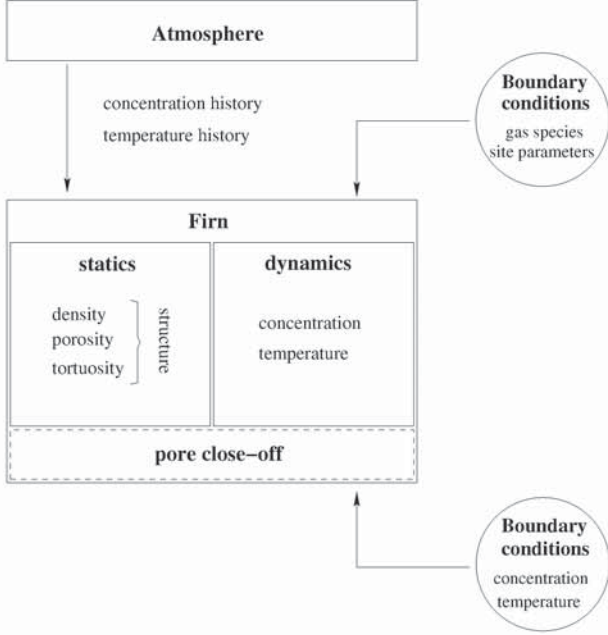


Figure 2: Flow scheme of the diffusion-temperature model based on Schwander et al. [31, 32]. The firn is considered to be static, while concentration as function of temperature and diffusivity is treated dynamically. The firn column is limited by the close-off region at the lower boundary and by the atmosphere on the surface.

As the densification process is dependent on atmospheric temperature variations, snow accumulation and the exposure of the snow surface to the atmosphere, tortuosity has to be determined for each site. This is realized by the pair of the free parameters α and β for which the best agreement between measured and modeled firn air profile of a reference tracer with known atmospheric history (like CO_2 or CH_4) can be achieved ($\alpha = 0.78$ and $\beta = 2.5$ for Siple Station [34]).

Combination of equations 9 and 10 leads to the expression for the effective diffusivity D_e according to

$$D_e = k_{Tp} \cdot s_{op} \cdot \frac{D_0}{q_{Par}}, \quad (11)$$

where the additional factor k_{Tp} expresses the dimensionless correction of the diffusion coefficient to standard temperature (273.15 K) and pressure (1013.25 hPa) according to Andrussov and Schramm [2].

Heat transfer in the firn column is calculated based on heat conduction [32]. The 1-dimensional equation of heat transfer in the firn has the following form [27]:

$$\rho(z)c_{sp} \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(\kappa \frac{\partial T}{\partial z} \right), \quad (12)$$

where κ is the thermal conductivity in $\text{W m}^{-1} \text{K}^{-1}$ depending on temperature and density $\rho(z)$ (in kg m^{-3}) at depth z (according to Schwander et al. [32]). c_{sp} represents the specific heat capacity of ice as function of temperature (according to Paterson [27], units $\text{J kg}^{-1} \text{K}^{-1}$).

gas	M (kg mol^{-1})	c_0 (%)	D_0 ¹⁾ ($10^{-5} \text{ m}^2 \text{ s}^{-1}$)
CO_2	0.044	0.0275	1.188
$^{15}\text{N}^{14}\text{N}$	0.029	0.289	1.569
$^{14}\text{N}_2$	0.028	77.5	1.583
$^{18}\text{O}^{16}\text{O}$	0.034	0.042	1.568
$^{16}\text{O}_2$	0.032	20.9	1.590
^{36}Ar	0.036	0.00281	1.544
^{40}Ar	0.040	0.934	1.509

¹⁾ according to Reid and Sherwood [28]

Table 1: Characteristics of the gas species investigated in this study. M is the molar mass in kg mol^{-1} . c_0 represents the initial ($t = 0$) concentration given in %. D_0 is the free air diffusivity with respect to air ($M = 0.029 \text{ kg mol}^{-1}$) calculated for the site Halley (units $10^{-5} \text{ m}^2 \text{ s}^{-1}$).

The box model is set up such that initially each box contains the same air mass. Thus, owing to decreasing pore volume with depth, for 2000 boxes vertical resolution increases from 2 cm at the surface to 12 cm at the bottom ρ_{co} of the firn column (see Weiler [47] for detail).

Figure 2 gives an overview of the setup of the diffusion model based on Schwander et al. [31, 32]. The firn structure represented by the physical parameters density, porosity and tortuosity is treated statically. In contrast, diffusive mixing, which varies with the temperature distribution in the firn and drives the concentration profile is treated dynamically. The lower boundary of the firn is represented by the pore close-off region, i.e. the close-off density ρ_{co} . Concentration at the lower boundary is arbitrarily held at the initial value c_0 , while temperature is set to the temperature of the overlying box after each time step.

The firn surface on the other hand, is exposed to the atmosphere and thus, atmospheric concentration and temperature histories drive the concentration profiles in the firn. Table 1 summarizes the main information required of each gas for the site Halley. Free air diffusivity D_0 is calculated according to Reid and Sherwood [28] with respect to air ($M = 0.029 \text{ kg mol}^{-1}$). c_0 represents the initial ($t = 0$) atmospheric concentration corresponding to the preindustrial composition of Earth's atmosphere (CO_2 concentration of 1720 AD as reconstructed from Law Dome ice core data [9]). Principal site parameters forcing the diffusion-temperature model are summarized in Table 2 for Halley. Note, that the close-off density ρ_{co} calculated based on Halley site temperature is a theoretical value only necessary to drive the model. This is as Halley is located on the ice shelf, i.e. floating on sea water. Thus, the densification process at larger depth will significantly differ from the conditions of the dry snow zone.

Temporal discretisation of equations 1 and 12 is realized by the implicit Crank-Nicolson scheme [7] in order to simulate dynamic modification of concentration and temperature of the firn air. The Crank-Nicolson scheme

parameter	unit	Halley
θ	$^{\circ}\text{C}$	-19.1 ¹⁾
A^*	$\text{kg m}^{-2} \text{a}^{-1}$	367 ²⁾
p_0	hPa	983 ¹⁾
ρ_0	kg m^{-3}	394.4 ³⁾
ρ_{ice} ⁴⁾	kg m^{-3}	919.3
ρ_{co} ⁵⁾	kg m^{-3}	(818.7)

¹⁾ data provided by BAS, READER project

²⁾ data provided by BAS

³⁾ extrapolated from CRYOSTAT firn core

⁴⁾ according to Bader [3]

⁵⁾ according to Martinerie et al. [25, 26]

Table 2: *Site parameters for Halley. θ is the site temperature in $^{\circ}\text{C}$ based on Halley station temperature (monthly mean values surveyed by British Antarctic Survey (BAS) in the frame of the READER project—REference Antarctic Data for Environmental Research, <http://www.antarctica.ac.uk/met/READER/surface/Halley.All.temperature.txt>), A^* the mean annual accumulation in $\text{kg m}^{-2} \text{s}^{-1}$ as derived from snow stake measurements (data provided by BAS) and p_0 the mean station pressure in hPa (determined from Halley station data provided by BAS, READER project). ρ_0 represents the surface density (based on the density record of the CRYOSTAT firn core, see section 3), ρ_{ice} the ice density calculated according to Bader [3] and ρ_{co} the close-off density (according to Martinerie et al. [25, 26]). All densities are given in kg m^{-3} . Owing to the location of the site Halley on the ice shelf a densification different from densification in the dry snow zone has to be expected. Thus, ρ_{co} is a theoretical value only.*

has the big advantage that it remains stable for any combinations of time step and spatial resolution [7]. A more detailed description of the diffusion–temperature model is given in Weiler [47].

Accuracy of the 1-dimensional diffusion–temperature model is estimated from comparing the model output (numerical solution) to the stationary (analytical) solution of the diffusion equation for gravitation (equation 5) and thermal diffusion (equation 7). The numerical solution is achieved by forcing the model with a constant concentration input and a stationary temperature gradient within the firn column. Combination of the deviations between numerical and analytical solution for gravitation and thermal diffusion (by application of the error propagation rule from Gauss) leads to the following accuracies (for 2000 boxes and a time step of about 1.5 days) [47]: 3.5 per meg for $^{15}\text{N}^{14}\text{N}$ in $^{14}\text{N}_2$, 3.4 per meg for $^{18}\text{O}^{16}\text{O}$ in $^{16}\text{O}_2$, 5.0 per meg for ^{36}Ar in ^{40}Ar and 5.2 pptv for CO_2 .

3 Sample collection and analysis

In order to investigate the effect of seasonal atmospheric variability on the composition of firn air a year-round survey was carried out in the frame of the European project CRYOSTAT (CRYOspheric Studies of At-

mospheric Trends in stratospherically and radiatively important gases) at the new Clean Air Sector Laboratory (CASLAB) located at the British Antarctic overwintering station Halley ($75^{\circ} 35'\text{S}$, $26^{\circ} 34'\text{W}$, see Figure 1) in 2003. To minimise contamination, CASLAB was located 1 km from the main base at Halley, and was normally upwind of the main base and generators. No motorised vehicle access was allowed to CASLAB during operations.

Firn air samples were taken once every two month with a method similar to the “tube method” used by Severinghaus et al. [37, 36] to sample air in sand dunes and firn air at South Pole. An approximately 21 m long firn core (referred to as the CRYOSTAT core) was drilled with a hand auger at a distance of about 80 m upwind of CASLAB. A set of DEKABON–tubes (1/4" OD) with various lengths and a thermistor string were placed in the hole (see Figure 3), which was backfilled with kiln-dried high-purity quartz sand (to 40 cm below the surface) of lower permeability than the surrounding firn in order to seal the hole from surface air. The remaining part of the hole up to the surface was filled with snow to avoid a disturbance of the temperature profile due to heat absorption by the sand. Great care was taken not to trample or otherwise disturb the snow surrounding the firn hole more than necessary either during the preparation work or thereafter. Samples were taken from seven different depth levels (surface, 1 m, 2.5 m, 5 m, 7.5 m, 10 m, 15 m and 20 m, see Figure 3). The DEKABON tubes were fitted with particle traps (quartz wool) at their inlets. Firn temperature was continuously monitored at 0.67 m, 1.67 m, 2.67 m, 3.67 m, 4.67 m, 5.67 m, 8.17 m, 10.67 m, 15.67 m and 20.67 m depth. To monitor actual air temperature additional thermistors were placed on the surface and 1 m above the snow.

Further wider-bore (3/8" OD) DEKABON lines ran back to the CASLAB where a diaphragm vacuum pump and a metal bellows pump were used to evacuate (not the glass flasks), then flush and fill the sample flasks respectively. A non-dispersive infrared gas analyser (LiCOR LI-7000) was used to continuously monitor CO_2 in the air pumped from the firn hole prior to flask filling at each depth layer (maximum 5 minutes of flushing at 5 litre per minute). This was to ensure that all contemporary or stagnant air had been flushed from the lines before sampling.

The data set consists of samples stored in three different types of containers: 0.5 l glass flasks (University of Bern, as from here referred to as GF), 3 l stainless steel containers (RESTEK SilcoCans from University of East Anglia, UK, referred to as SC3) and 6 l stainless steel containers (RESTEK SilcoCans from University of Bern, referred to as SC6). Air was filled in glass flasks for all six sampling dates and depth levels. No samples are available between 0 m and 2.5 m for the December profile as these flasks broke during the filling procedure. In order to have a better coverage of the depth range relevant for seasonality, replicate samples stored in 6 l stainless steel containers were taken (at 0 m, 2.5 m and 7.5 m). Finally, as some of the glass flask samples were of poorer quality, SC3 samples were used to confirm the results.

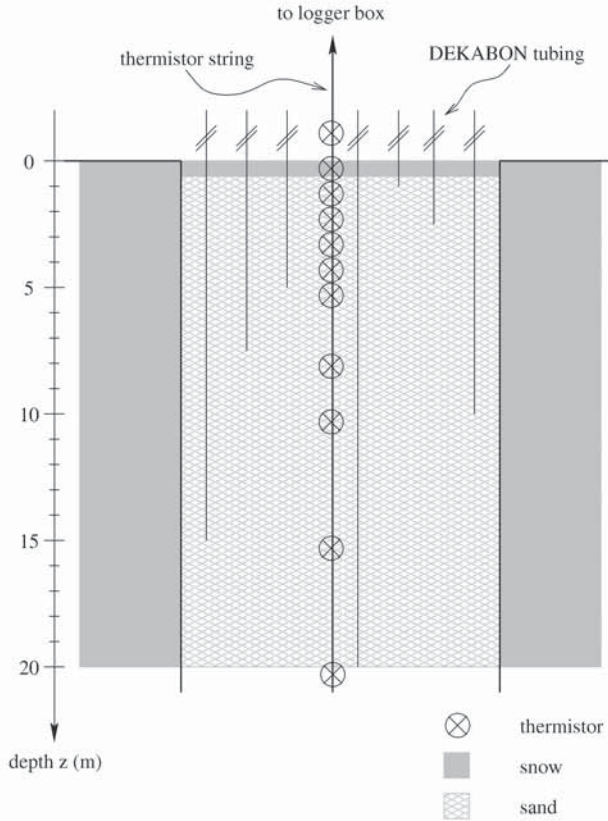


Figure 3: Scheme of the in situ firn air sampling system used at Halley. Each depth level was equipped with a separate DEKABON-tube merging at a multi port valve. To monitor the firn temperature, a thermistor string was installed.

Samples were analysed with an isotope ratio mass spectrometer (IRMS) at the University of Bern. The instrument used is a Finnigan MAT Delta Plus XP IRMS (Thermo Electron, Bremen, Germany) equipped with a special dual inlet allowing measurements in continuous flow (Y-shaped open split [22]). The setup at the University of Bern allows the simultaneous analysis of isotopes ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^{36}\text{Ar}$) and elemental ratios ($\delta\text{CO}_2/\text{N}_2$ relevant for this study). The technique to measure CO_2 concentrations by mass spectrometry is described in Leuenberger et al. [23]. A more detailed description of the experimental set-up is given in Sturm [41].

Results are given in the standard delta notation. This means, that the isotopic (or elemental) ratio of a sample gas $\left[\frac{A}{B}X\right]_{Sa}$ is recorded as the relative deviation from a standard gas $\left[\frac{A}{B}X\right]_{St}$, which has the same composition as the present day atmosphere. Taking BX as the isotope of higher abundance (e.g. $^{14}\text{N}_2$) compared to AX (e.g. $^{15}\text{N}^{14}\text{N}$) the standard delta notation has the following form:

$$\delta^A X = \left(\left[\frac{A}{B}X \right]_{Sa} \left[\frac{A}{B}X \right]_{St}^{-1} - 1 \right) \cdot 1000 \text{‰}. \quad (13)$$

The analytical set-up leads to an instrument precision of (16.9 ± 5.4) per meg (1 per meg = $1 \cdot 10^{-3} \text{‰}$) for $\delta^{15}\text{N}$, (41.3 ± 14.7) per meg for $\delta^{18}\text{O}$, (193.2 ± 64.8) per meg for $\delta^{36}\text{Ar}$ and (60.6 ± 58.6) per meg for $\delta\text{CO}_2/\text{N}_2$ [41].

Owing to experimental problems in the field especially some of the GF-samples are of poorer quality. We use a criterion based on the atmospheric CO_2 history recorded for Halley (flask samples in monthly resolution provided by Thomas J. Conway from NOAA – National Oceanic and Atmospheric Administration, <http://www.esrl.noaa.gov/gmd/> [42]) to identify these outliers. In fact, measured CO_2 surface concentrations are normalised to the NOAA results separately for each container type (GF, SC6, SC3) and analysis run. Based on these offsets CO_2 profiles are shifted. This is to account for variations in the configuration of the mass spectrometer and slight differences in the reference gas (working standard) compared to the NOAA standard (<http://www.esrl.noaa.gov/gmd/ccgg/refgases/stdgases.html>).

Outliers are identified from the normalised data set according to the following criterion: Firm air profiles are affected by atmospheric seasonality down to about 15 m depth as derived from the temperature distribution in the firn (Figure 4) and the firm air profiles (section 4). Within this depth range CO_2 concentrations are expected to vary around the reference value (NOAA data) by ± 0.7 ppmv owing to thermal diffusion (section 4.3), while additional atmospheric seasonality in CO_2 is implicitly considered by the NOAA Halley record. In addition, a concentration reduction with depth of 2 ppmv with respect to the surface value is acceptable, which is the order of magnitude of the recent annual CO_2 increase (compare Tans and Conway [42]) and only weakly smoothed out by air mixing in the firn. Owing to the distinct temporal CO_2 increase no concentrations higher than the corresponding atmospheric value are reasonable below 15 m depth. Only samples with CO_2 concentrations fulfilling these conditions are accepted (compare Weiler [47] for detail). In summary, 19 of the altogether 48 glass flask samples (GF), 5 of the altogether 27 samples stored in 3 litre stainless steel containers (SC3), and 2 of the altogether 18 stored in 6 litre stainless steel containers (SC6) had to be rejected.

In addition, as mentioned above, the data set is subjected to systematic errors originating from experimental problems during the sampling procedure in the field, which occurred mostly in April and June. A measure to identify samples affected by systematic errors is the normalization interval (grey shaded areas in Figure 12 of appendix C) representing the maximum or minimum shift of the profiles in order to equal the NOAA reference on the surface. Only those values covered by the normalization interval are assumed to be realistic. Note, that the February sampling date is not considered for this procedure as diffusive mixing is expected to be overlaid by surface convection in case of this profile (see section 4.2).

Normalisation of the analysed isotopic ratios discussed in this study is carried out on the revised data set. Based on the assumption that isotopic ratios of the working standard represent the current atmosphere isotopes are normalised with respect to a surface value of 0 ‰. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ samples subjected to systematical errors are identified in the same way, as for CO_2 (compare Figures 10 and 11 of appendix C). Due to an unrealistic width of the normalization interval in case of $\delta^{36}\text{Ar}$ no reasonable selection of data points affected by systematic errors was possible. For this reason and owing to the higher experimental uncertainty (see above) the $\delta^{36}\text{Ar}$ profiles are not presented in this study.

4 Firn air mixing driven by atmospheric seasonality

In the following sections the multi-proxy data set (described in section 3) retrieved from Halley firn in 2003 shall be discussed with respect to seasonal variations within the uppermost 25 m of the firn column. The main focus is put on the prediction of seasonally-induced temperature and concentration variations with the 1-dimensional diffusion-temperature model (section 2), while the model is forced with atmospheric temperature and concentration histories. Different predictions of the thermal diffusion factors (Table 3 of appendix A) are applied and results are compared with the firn air data set. In addition, the applicability of a depth correction is investigated on the borehole temperature profiles. The depth correction (described in appendix B) takes into account temporal shifting of the firn air sampling setup and the thermistors owing to accumulation and densification.

4.1 Seasonal variations in firn temperature

Heat transfer in the firn column is calculated according to equation 12, where the thermal conductivity κ is derived from firn density and the thermal conductivity of pure ice [32]. In order to evaluate, whether this model applies to the seasonal temperature variation in the firn column, firn temperatures obtained from borehole measurements (thermistor string, compare section 3) are compared to the modelled temperature profiles.

The temperature model through 2002 is forced with atmospheric Halley station temperature data. From 1957 to 2002 we take monthly mean values surveyed by BAS in the frame of the READER project. For 2003 the atmospheric input is based on high resolution (15 min) temperatures measured 1 m above the surface near Halley Station (data provided by P.S. Anderson, pers. comm.). In order to reach coincidence with the resolution of the previous years the high resolution data set is smoothed with a running mean using a window size of 30 days. Before 1957 Halley temperature input is estimated by the mean station temperature of about 254 K (Table 2).

Figure 4 shows the firn temperature profiles obtained from borehole measurements (black diamonds) together with the temperature model results (black lines) as a func-

tion of firn depth. Borehole temperatures were monitored on firn air sampling dates between February and December of 2003 in three hourly intervals.

A stationary temperature increase of about 2 K between 7.5 m and 20 m depth is observable from the borehole data. This temperature gradient originates from a bottom heat flux induced by sea water as Halley is located on the Brunt ice shelf (compare Figure 1). In order to simulate the effect of this situation on the temperature profile, firn temperature is initialized based on the detected temperature increase between 10 and 20 m depth. According to this trend the lower boundary of the diffusion-temperature model at 90 m depth is held constant, which is sufficient regarding the discussion of seasonality in the firn air profiles. Seasonally induced temperature variations in the uppermost about 10 m (compare Figure 4) do not affect the temperature gradient.

The depth shift owing to densification of the firn and further accumulation is clearly represented by the uppermost sampling level. While a distinct diurnal cycle of about 6 K is initially observable on the surface temperature measured in February 2003 (Figure 4a) variations are attenuated to approximately 1 K at end of April (Figure 4b). At this time, the surface sample is predicted by the box model (appendix B) to be about 0.63 m below the surface. This is in good agreement with a temperature variation of approximately 1 K in February measured by the thermistor in 0.67 m depth. In August the diurnal cycle is not detectable anymore by the uppermost thermistor, which is predicted to be at about 0.9 m depth at this time.

Thus, correction of the sample levels (appendix B) is supported by a good agreement between borehole data (black diamonds in Figure 4) and the output of the temperature model (black lines). An exception is an irregularity detected for August (Figure 4d), where the uppermost borehole temperature values clearly deviate from the prediction of the temperature model. As the shape of the measured temperature profile (slight temperature decrease between the uppermost and the following sample level) is different from the modelled profile (approximately constant temperature within the first meter below the surface) the discrepancy between model and data seems to originate not from the depth correction. Rather smoothing of the atmospheric temperature input (running mean, see above) might be the reason for the lower surface temperature predicted by the temperature model.

Thus, we conclude, that the seasonal cycle in firn temperature induced by atmospheric temperature variations on the surface is well predicted by the temperature model of Schwander et al. [32]. Furthermore, the box model (appendix B) seems to be appropriate in order to simulate the sinking of the sample levels owing to firn densification and further accumulation during the entire year.

Firn air profiles discussed in the following sections are based on these firn temperatures.

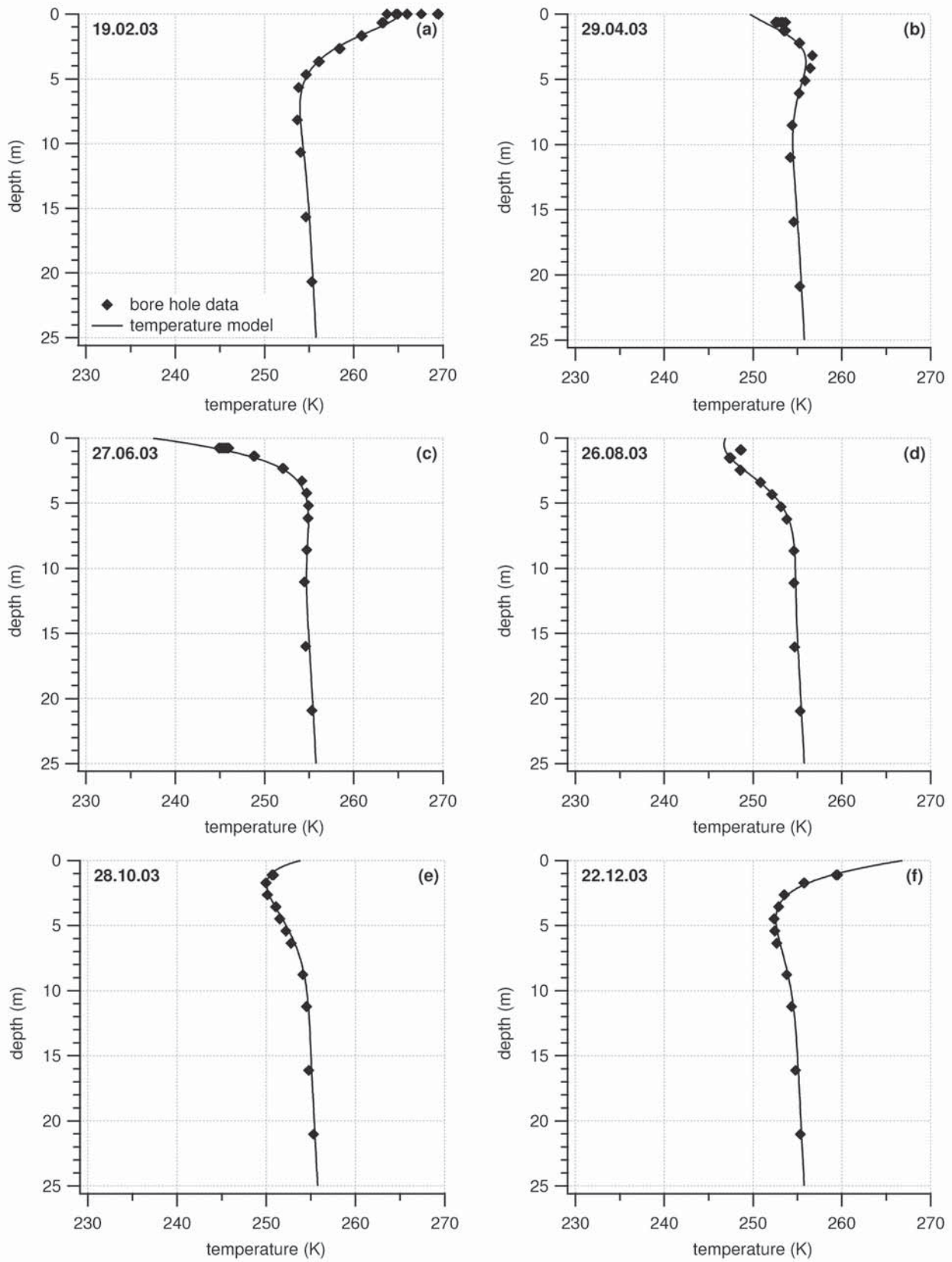


Figure 4: Seasonal temperature variations in Halley fir covering the time range between 19.02.03 (a) and 22.12.03 (f). Firn temperatures as obtained from borehole measurements (thermistor string) are marked by black diamonds, where depth levels are corrected for densification and accumulation applying the box model (described in appendix B). The output of the temperature model is depicted as black line.

4.2 Isotopic fractionation

Isotopic fractionation is investigated for the species $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. Figures 5 and 6 show the profiles revealed for Halley between February (Figures 5a and 6a) and December (Figures 5f and 6f) 2003. As mentioned earlier (section 3) the data set consists of samples stored in various container types (GF, SC3, SC6). In addition, analysis of the sampled firn air was carried out in different runs ranging from 2003 to 2007. Glass flasks (GF) were analysed in 2003 (open triangles), 2004 (filled triangles) and 2005 (reversed filled triangles). Analysis of the 6-liter stainless steel containers (SC6) was carried out in 2003 (circles) and 2004 (filled circles). 3-liter stainless steel containers (SC3) finally, are represented by open squares (2006 run) and filled squares (2007 run).

Under the assumption, that the standard gas (working standard) has the same isotopic composition as the atmosphere in Halley, data are normalized with respect to 0 ‰ on the surface (compare section 3). Thus, compared to the full data set as presented in Figures 10 ($\delta^{15}\text{N}$) and 11 ($\delta^{18}\text{O}$) of appendix C, only data points covered by the normalisation interval (grey shaded areas in Figures 10 and 11) are considered for the following discussion.

Additionally, profiles are corrected for the depth shift owing to firn densification and snow accumulation as described in section B. In contrast to the uppermost thermometer (Figure 3 in section 4.1) surface air represents ambient air and thus, this sample level remains at 0 m depth.

4.2.1 $\delta^{15}\text{N}$

Assuming the atmospheric nitrogen isotopic composition to have remained temporally constant [24] the diffusion–temperature model is forced with a constant concentration input of $c_0 = 0.289\%$ representing the contribution of $^{15}\text{N}^{14}\text{N}$ to Earth’s atmosphere (compare Table 1). Thermal diffusion of $^{15}\text{N}^{14}\text{N}$ with respect to N_2 (representative for air) is simulated with $\alpha_T = 3.7 \cdot 10^{-3}$ (see Table 3 of appendix A) calculated according to the logarithmic fit of Leuenberger et al. [21]. The α_T given by Leuenberger et al. [21] agree well with the measurements of Grachev and Severinghaus [11] (compare Figure 9 of appendix A). Based on this agreement, we use $\pm 3\%$ as the uncertainty for α_T according to Grachev and Severinghaus [11].

Figure 5 shows the normalized Halley $\delta^{15}\text{N}$ firn air profiles. The $\delta^{15}\text{N}$ as the result of diffusive air mixing simulated with the diffusion–temperature model is depicted as black lines. Grey shaded areas represent the uncertainty of α_T . In summer, i.e. when firn temperature is lower within the firn compared to the surface (see Figures 4a and 4f) the heavier $^{15}\text{N}^{14}\text{N}$ (0.029 kg mol^{-1}) is enriched in the firn with respect to $^{14}\text{N}_2$ (0.028 kg mol^{-1}). The opposite behaviour is observable for the winter month (Figures 5c and 5d). Accordingly, the temperature reversal in autumn (Figure 4b) and spring (Figure 4e) is represented by a twofold thermal oscillation in the firn air profiles.

Taking into account the error range of the data (one standard deviation) and the uncertainty of the thermal diffusion factor α_T (grey shaded areas in Figure 5), modelled and measured profiles are in good agreement. Thermal diffusion is represented by the bell-shaped deformation of the profiles. An exception is the February profile, where the seasonal thermal amplitude is overestimated by the diffusion–temperature model by about 0.05 ‰. As α_T of $^{15}\text{N}^{14}\text{N}$ in $^{14}\text{N}_2$ is well determined [21, 11] and the disagreement between model and data is observable independently of the container type or analysis run, it is interpreted as a signal. The attenuation of the thermal oscillation is attributed to surface convection [5] overlaying diffusive mixing, while a convective zone with an extension of not more than 0.5 m is expected [47].

4.2.2 $\delta^{18}\text{O}$

In order to simulate the fractionation of $^{18}\text{O}^{16}\text{O}$ in $^{16}\text{O}_2$, the diffusion–temperature model is forced with a constant input of $c_0 = 0.042\%$ for the simulation of $^{18}\text{O}^{16}\text{O}$ in air and $c_0 = 20.9\%$ for modelling diffusive mixing of $^{16}\text{O}_2$ in air. Both concentrations correspond to the contribution of the isotopes to Earth’s atmosphere (compare Table 1). Concentration input is chosen this way as no notable recent atmospheric variation of $\delta^{18}\text{O}$ could be detected so far [41].

Simulation of thermal fractionation of $\delta^{18}\text{O}$ requires the thermal diffusion factors of $^{18}\text{O}^{16}\text{O}$ in air and $^{16}\text{O}_2$ in air. However, only for the latter quantity measurements are available in literature. Thus, as a first estimate the α_T are calculated following the model approach of Leuenberger and Lang [20] and the model discussed in van der Valk [43] (see appendix A for both). Black lines in Figure 6 represent the forcing according to Leuenberger and Lang [20] (i.e. $\alpha_T = 25.0 \cdot 10^{-3}$ for thermal fractionation of $^{18}\text{O}^{16}\text{O}$ in air and $\alpha_T = 14.6 \cdot 10^{-3}$ for thermal fractionation of $^{16}\text{O}_2$ in air). The model output obtained from $\alpha_T = 23.5 \cdot 10^{-3}$ ($^{18}\text{O}^{16}\text{O}$ in air) and $\alpha_T = 13.9 \cdot 10^{-3}$ ($^{16}\text{O}_2$ in air) according to van der Valk [43] is depicted as black dashed lines. Obviously both approaches lead to similar thermal diffusion factors revealing a maximum deviation of 0.032 ‰ in the predicted thermal oscillation. In addition and even more important both approaches lead to a strong overestimation of the thermal amplitude, when compared to the data set. Thus, thermal diffusion factors α_T estimated according to Leuenberger and Lang [20] and van der Valk [43] seem to be not appropriate to simulate thermal fractionation of $^{18}\text{O}^{16}\text{O}$ or $^{16}\text{O}_2$ in air. The reason is that neither model is able to properly predict the interaction forces involving non-polar but elongated molecules and oxygen belongs to this group (see appendix A for more detail).

In order to get a first idea about thermal fractionation of oxygen isotopes in air, three different approaches are applied:

- (i) α_T of $^{16}\text{O}_2$ in air is derived from measurements of Waldmann [44] carried out at temperatures of

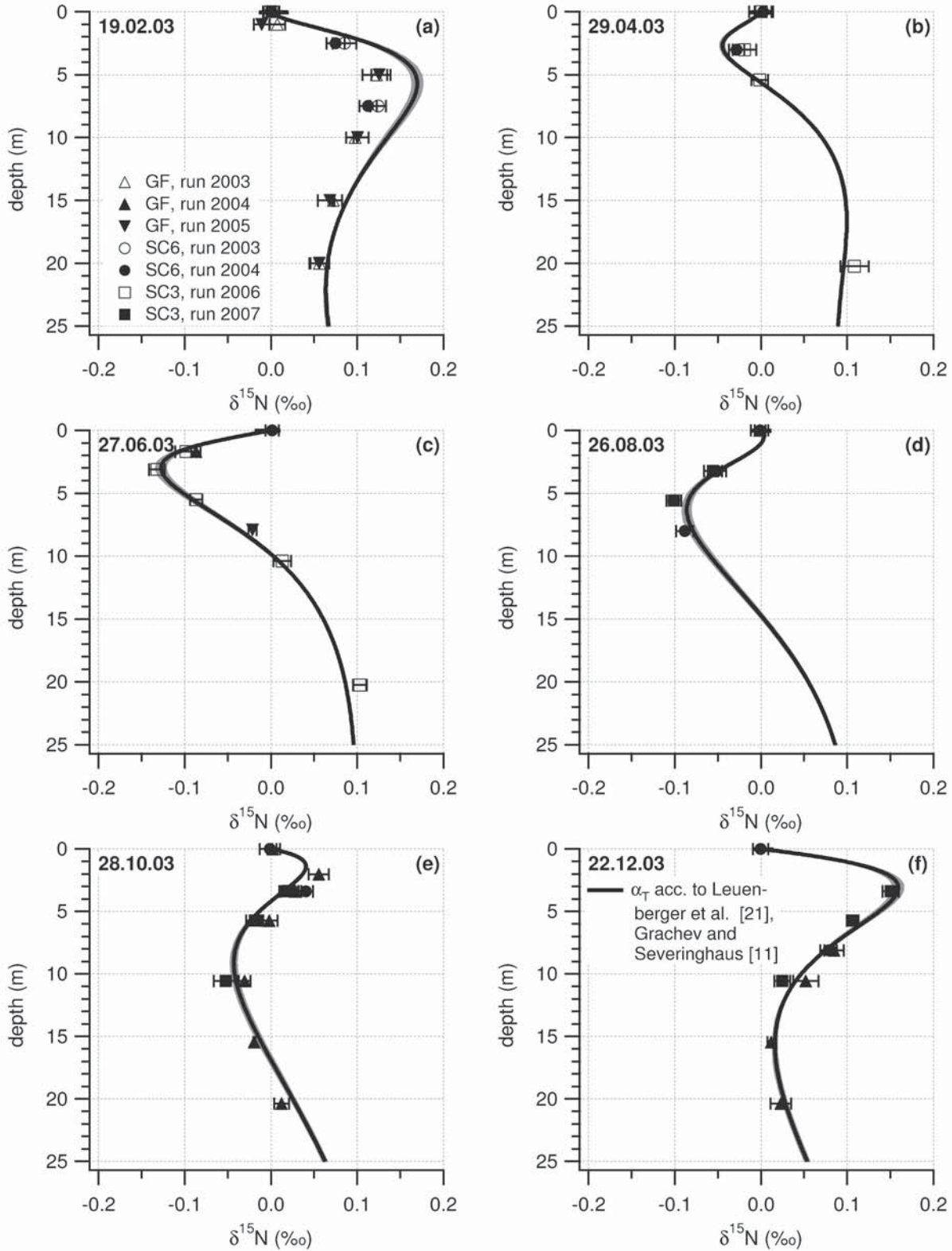


Figure 5: $\delta^{15}\text{N}$ in Halley firn air of 2003. The sampling period reaches from February (a) to December (f) 2003. Open triangles represent the GF samples analysed in 2003, filled triangles the GF samples measured in 2004 and reversed filled triangles the GF samples of the 2005 run. SC6 samples analysed in 2003 are depicted by open circles, those analysed in 2004 are marked by filled circles. Open squares represent the SC3 run of 2006 and filled squares the SC3 samples measured in 2007. Data are revised with respect to systematic errors (appendix C). The output of the diffusion-temperature model based on α_T according to Leuenberger et al. [21] and Grachev and Severinghaus [11] is depicted as black lines. Grey shaded areas represent the 3 % error estimate of α_T as given by Grachev and Severinghaus [11].

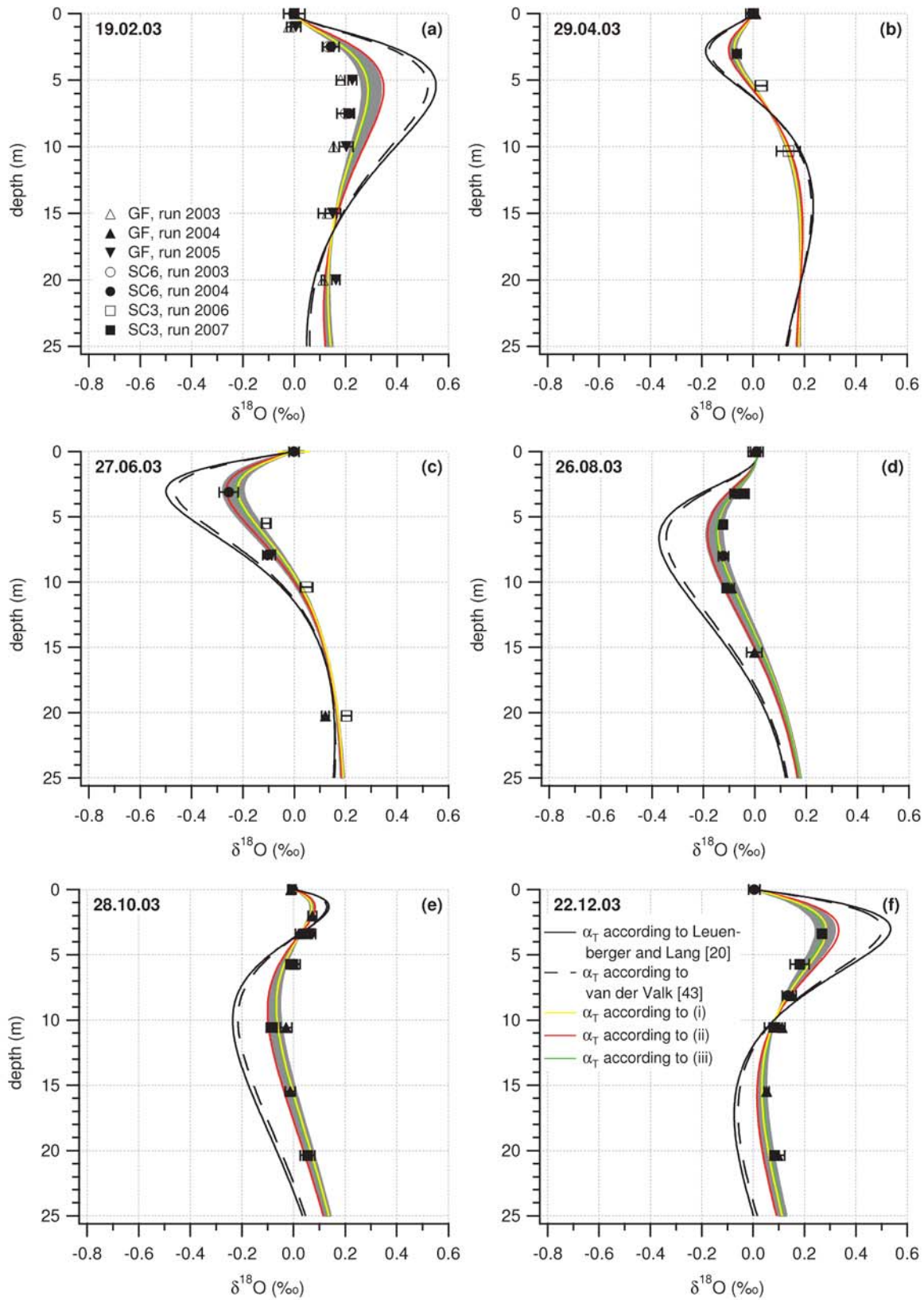


Figure 6: $\delta^{18}\text{O}$ as observed in Halley firn in 2003. Data are labeled in the same way as described in Figure 5. Black lines represent the output of the diffusion–temperature model, when the thermal diffusion factor α_T is calculated according to Leuenberger and Lang [20]. Forcing with α_T according to van der Valk [43] is marked by dashed black lines. The yellow, red, and green scenarios correspond to the cases (i), (ii), and (iii) as described in the text. The uncertainty range as represented by the grey shaded areas is estimated from the variability of the data points (given as one standard deviation) to $\pm 15\%$.

89, 194, and 283 K, as summarized in Grew and Ibbs [12]. Assuming a linear temperature dependence of the α_T as e.g. suggested by Grachev and Severinghaus [10], the corresponding value α_T of $^{16}\text{O}_2$ in air for the Halley mean annual temperature of 254 K is determined to $15.4 \cdot 10^{-3}$ ($\alpha_T(^{16}\text{O}_2 \text{ in air, T}) \cdot 10^3 = -\frac{2003.7}{T} + 23.31$, coefficient of determination is 0.98, no uncertainties are given for the measurements by Waldmann [44]). α_T of $^{18}\text{O}^{16}\text{O}$ in air is derived from matching with the Halley firn air measurements.

- (ii) In this approach the α_T of $^{16}\text{O}_2$ in air and the α_T of $^{18}\text{O}^{16}\text{O}$ in air are calculated from the following set of equations:

$$\alpha_T(^{18}\text{O}^{16}\text{O}/\text{air}) = \alpha_T(^{18}\text{O}^{16}\text{O}/^{16}\text{O}_2) + \alpha_T(^{16}\text{O}_2/\text{air}) \quad (14)$$

$$\alpha_T(^{18}\text{O}^{16}\text{O}/\text{air}) = \frac{M^*(^{18}\text{O}^{16}\text{O}/\text{air})}{M^*(^{16}\text{O}_2/\text{air})} \times \alpha_T(^{16}\text{O}_2/\text{air}), \quad (15)$$

where the M^* are the proportionate mass differences as defined in equation 18 of appendix A (i.e. $M_1 = 0.034$ or $0.032 \text{ kg mol}^{-1}$ and $M_2 = 0.029 \text{ kg mol}^{-1}$). Equation 14 represents the additivity of the thermal diffusion factors (provided each addend is known with respect to a ternary mixture, see van der Valk [43]). Application of the linear mass dependency (equation 15, compare Leuenberger and Lang [20]) implies the interaction forces to be approximated properly by a binary mixture. Knowing thermal fractionation of $^{18}\text{O}^{16}\text{O}$ in $^{16}\text{O}_2$, the α_T of $^{16}\text{O}_2$ in air and α_T of $^{18}\text{O}^{16}\text{O}$ in air can be calculated explicitly. $\alpha_T(^{18}\text{O}^{16}\text{O}/^{16}\text{O}_2)$ is derived from the thermal diffusion sensitivity of oxygen with respect to nitrogen, i.e. the slope $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}}$, times the corresponding α_T of $^{15}\text{N}^{14}\text{N}/^{14}\text{N}_2$ as e.g. suggested by Severinghaus et al. [36]. $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}}$ is 1.55 ± 0.04 in annual average as determined from the Halley firn air profiles, while the temperature dependent thermal fractionation factors of $^{15}\text{N}/^{14}\text{N}_2$ are calculated according to the logarithmic fit of Leuenberger et al. [21]. Mean annual site temperatures, i.e. 254 K in case of Halley, are chosen as a first estimate. In general, $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}}$ increases with rising temperature.

- (iii) Determination of the α_T is carried out in the same way as in case (ii). However, instead of estimating α_T of $^{18}\text{O}^{16}\text{O}$ in $^{16}\text{O}_2$ based on the slope $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}}$, the latter quantity is taken as the variable. This means that $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}}$ is varied until the simulated profiles match the $\delta^{18}\text{O}$ firn air data, which is the case for $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}} = 1.3$.

The best match between the firn air data set and simulated profiles by forcing thermal diffusion of $^{16}\text{O}_2$ in air with $\alpha_T = 15.4 \cdot 10^{-3}$ according to Waldmann [44] (case (i)) is achieved by using $\alpha_T = 18.5 \cdot 10^{-3}$ for the fractionation of $^{18}\text{O}^{16}\text{O}$ in air (compare yellow profiles in Figure 6). The second approach, (ii), leads to a slight overestimation of the firn air data set by the model, as depicted by the red profiles in Figure 6. The corresponding thermal diffusion factors are $\alpha_T = 9.4 \cdot 10^{-3}$ for the fractionation of $^{16}\text{O}_2$ in air and $15.2 \cdot 10^{-3}$ for $^{18}\text{O}^{16}\text{O}$ in air. The best match between data and model using approach (iii) is obtained for the slope $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}} = 1.3$ leading to $\alpha_T(^{16}\text{O}_2/\text{air}) \cdot 10^3 = 7.9$ and $\alpha_T(^{18}\text{O}^{16}\text{O}/\text{air}) \cdot 10^3 = 12.7$ (green profiles in Figure 6).

Assuming the measurements of Waldmann [44] to be representative for thermal fractionation of $^{16}\text{O}_2$ in air, case (i) (yellow profiles in Figure 6) seems to be the most likely. However, application of the additivity (equation 14, van der Valk [43]) leads to a slope $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}} = 0.83$, which is about half of what is expected for the mean annual Halley temperature of 254 K: 1.55 ± 0.04 from Halley data (see above) or 1.66 as derived by Severinghaus et al. [36] from Siple Dome firn air (corresponding to a mean annual temperature of 255 K). On the other hand, taking into account the temperature dependence of $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}}$ (via $\alpha_T(^{15}\text{N}^{14}\text{N}/^{14}\text{N}_2)$, see above) and with it, of $\alpha_T(^{18}\text{O}^{16}\text{O}/^{16}\text{O}_2)$, the $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}} = 1.55 \pm 0.04$ as derived from the Halley profiles (case (ii), simulations depicted in red in figure 6) is more comparable with slopes derived for a much lower mean annual temperature, e.g. $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}} = 1.56 \pm 0.09$ in case of Kohnen-EDML with a mean annual temperature of 228.7 K [47]. The same is valid for case (iii), where a slope of $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}} = 1.3$ only leads to a proper match between firn air data and simulations (green profiles in figure 6).

The effect of disequilibrium with respect to temperature owing to the slightly different diffusion speeds of oxygen and nitrogen in air turns out to be negligible for Halley firn air in this context. Severinghaus et al. [36] obtained the same result from their South Pole and Siple Dome profiles.

Regarding case (i) doubts on the accuracy of the measurements made by Waldmann [44] seem to be allowed. The additivity (equation 14, van der Valk [43]) does only lead to reasonable results, if at least two of the three α_T are available with respect to air (or at least for a ternary system comprised by N_2 , $^{16}\text{O}_2$ and $^{18}\text{O}^{16}\text{O}$ for the case under discussion, in order to properly simulate the interaction forces). Thus, measurements of all three relevant thermal fractionation factors (i.e. of $^{16}\text{O}_2$ and $^{18}\text{O}^{16}\text{O}$ with respect to N_2 in the gas mixture air and of $^{18}\text{O}^{16}\text{O}$ in $^{16}\text{O}_2$ in air) are required for a proper prediction of the α_T .

Having a look at cases (ii) and (iii) the first assumption to be doubted is the applicability of the linear mass dependence (equation 15). As clearly stated by Leuenberger and Lang [20] a linear mass dependence of the α_T

with respect to temperature is valid only for binary mixtures. In order to simulate the relevant interaction forces for thermal fractionation of oxygen isotopes in air properly, a mixture of at least three compounds has to be assumed. Taking the mass dependency $\frac{M^*(^{18}\text{O}^{16}\text{O}/\text{air})}{M^*(^{16}\text{O}_2/\text{air})}$ as a variable and a realistic slope of 1.7 for the mean annual Halley temperature of 254 K a good match between model simulations and Halley firn air can be achieved with $\frac{M^*(^{18}\text{O}^{16}\text{O}/\text{air})}{M^*(^{16}\text{O}_2/\text{air})} \approx 5$. Especially as these assumptions would imply a α_T of $^{16}\text{O}_2$ in air, which is approximately a factor of 10 smaller, than derived from the measurements of Waldmann [44], this neither seems to be a realistic solution.

Assuming the uncertainty of the α_T (grey shaded areas in Figure 6) to be represented by a $\pm 15\%$ interval around the best match between model and data (cases (i) and (iii)) most of the data variability (one standard deviation) is covered by the model for each of the cases (i, ii and iii) for the time range between April (Figure 6b) and December (Figure 6f). As already observed for $\delta^{15}\text{N}$ (Figure 5a) the seasonal thermal amplitude is overestimated by the diffusion–temperature model for February (Figure 6a). This cannot be explained by the unclear prediction of the α_T as the $\delta^{18}\text{O}$ data points are not covered by the uncertainty interval (grey shaded area in Figure 6a). Thus, the assumption of convective mixing overlaying diffusion in Halley is also supported by the behaviour of $\delta^{18}\text{O}$.

In summary, taking into account each of the three approaches (i), (ii) and (iii), no clear prediction can be made for the thermal diffusion factors of $^{18}\text{O}^{16}\text{O}$ in air and $^{16}\text{O}_2$ in air (the α_T pairs leading to a match between model and Halley firn air data together with those derived from the model approaches of Leuenberger and Lang [20] and van der Valk [43] are summarized in Table 3 of appendix A). Thus, in order to confirm the results, measurements of thermal fractionation of oxygen in the gas mixture air are required.

As expected from the mass ratio the heavier $^{18}\text{O}^{16}\text{O}$ ($0.034 \text{ kg mol}^{-1}$) is compared to the surface enriched in the firn with respect to $^{16}\text{O}_2$ ($0.032 \text{ kg mol}^{-1}$, see Table 1) in summer (Figures 6a and 6f). In contrast, a depletion of $^{18}\text{O}^{16}\text{O}$ to $^{16}\text{O}_2$ is observable for winter (Figures 6c and 6d). The intermediate stage, i.e. spring represented by Figure 6e and autumn (Figure 6b) is characterized by a twofold oscillation with a lower amplitude owing to the reversal of firn temperature (see above).

4.3 Thermal fractionation of CO_2

In contrast to the isotopic species discussed in the previous section, CO_2 does not have a constant atmospheric history but shows a strong trend. Recent atmospheric CO_2 concentrations for Halley are available from flask sample data since 1983 in monthly resolution (provided by Thomas J. Conway from NOAA [42]). In order to extend the concentration input to preindustrial times, the atmospheric CO_2 trend as inferred from the Law Dome

ice core [9] is used (back to 1720 AD).

Figure 7 shows the CO_2 profiles revealed for Halley firn between February (Figure 7a) and December (Figure 7f) 2003. Data presented are normalised with respect to the NOAA standard (section 3). Data points obviously subjected to systematic errors are eliminated based on the normalization interval (compare Figure 12 of appendix C). In addition, the data set is corrected for the depth shift of the sample levels owing to densification of the firn and accumulation (appendix B).

Based on firn temperature and concentration input diffusive mixing of CO_2 in Halley firn is modelled with the 1-dimensional diffusion–temperature model (section 2). The strong recent anthropogenic CO_2 rise of more than 2 ppmv a^{-1} (compare NOAA record) is clearly represented by a CO_2 decline of about 4 ppmv between the surface and 20 m depth (Figure 7a to 7f, bold black and bold black dashed lines). Taking into account smoothing of concentration gradients in firn air by ordinary diffusion, this concentration difference is in good agreement with the CO_2 gas age of about 2.6 years before 2003 calculated for 20 m depth.

Thermal diffusion of CO_2 in air is simulated with $\alpha_T = 57.3 \cdot 10^{-3}$ according to Leuenberger and Lang [20] (bold black lines in Figure 7) and $\alpha_T = 67.8 \cdot 10^{-3}$ (Table 3 of appendix A) according to the approach of van der Valk [43] (bold dashed black lines). Owing to the higher standard deviation of some data points (especially of the February profile, compare Figure 7a) and some data points obviously subjected to systematic errors, even if the data set has been revised, no error estimate for α_T can be derived from the data. Experimental estimates for the thermal diffusion factors of CO_2 in N_2 according to Grew and Ibbs [12] are in the range between $36 \cdot 10^{-3}$ ($T = 283 \text{ K}$) and $61 \cdot 10^{-3}$ ($288 \text{ K} \leq T \leq 373 \text{ K}$). The latter estimate is in the same order of magnitude as the findings from the theoretical approaches according to Leuenberger and Lang [20] and van der Valk [43]. However, neither of the empirically revealed values corresponds to polar temperatures ($T = 254 \text{ K}$ for Halley).

In order to separate the effect of thermal diffusion from the imprint of the annual seasonality in the atmospheric CO_2 history, CO_2 firn air profiles are simulated without thermal diffusion, i.e. $j_{TD} = 0$ (fine black lines). The seasonal thermal amplitude is represented by the bell-shaped deformation in the uppermost about 5 m of the CO_2 profiles (compare bold black and bold black dashed lines in Figure 7a to 7f). The magnitude of the seasonal thermal amplitude is not more than 0.7 ppmv (compare fine black and bold black lines at maximum thermal oscillation in Figure 7) corresponding to a temperature difference of about 10 K between the surface and 5 m depth (Figure 7a or 7f) during the entire year. Thus, even for sites with stronger seasonal temperature asymmetry or surface convection (rectifier effect [36, 47]) only minor effect of thermal diffusion of CO_2 on the air conserved in air bubbles of deep ice cores has to be expected.

The observed thermal amplitude is basically confirmed

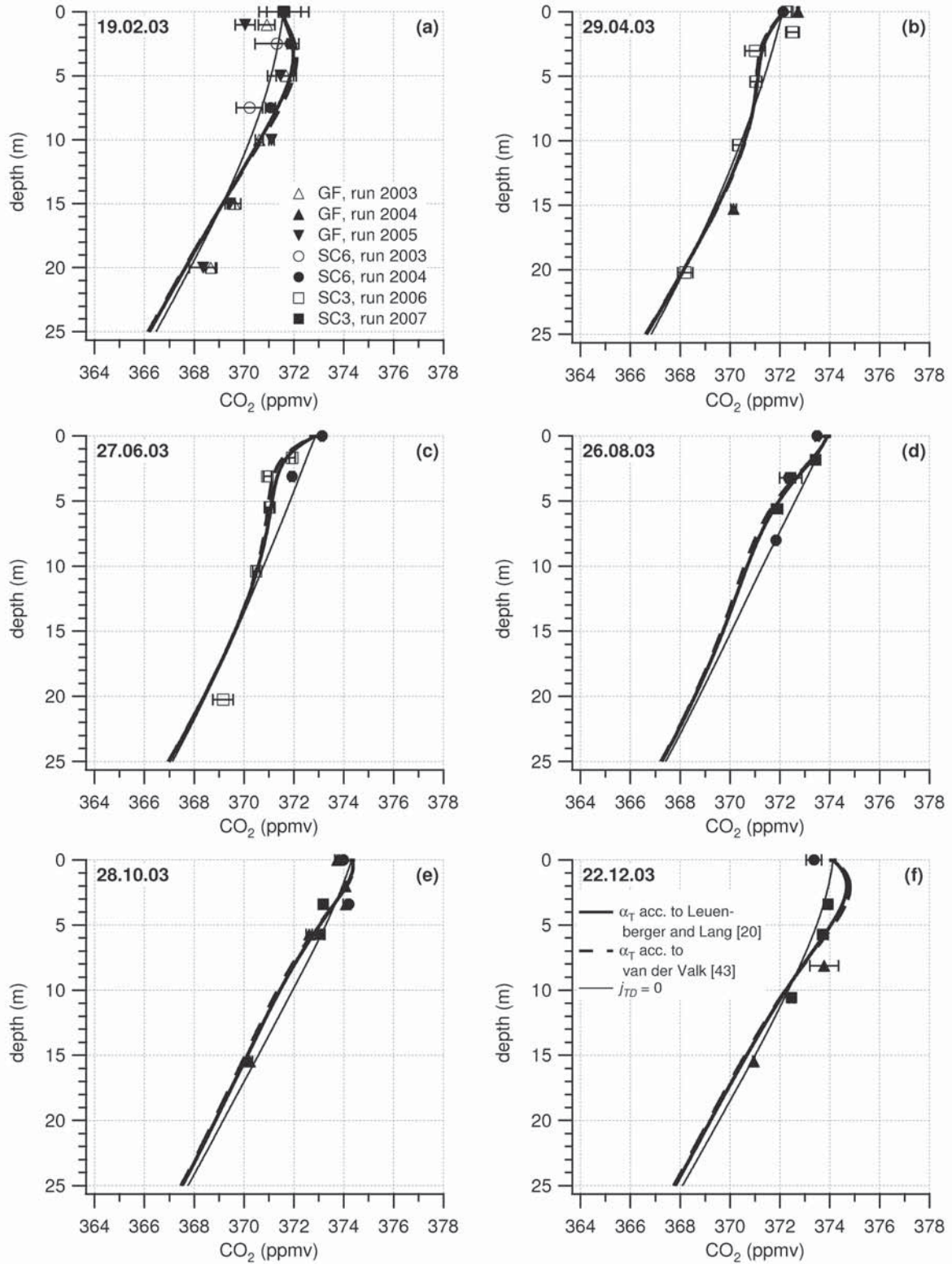


Figure 7: Seasonal CO_2 variations in firn air analysed in Halley between February (a) and December (f) of 2003. Data are normalized and corrected with respect to systematic errors. Data points are marked in the same way than in Figure 5. The output of the diffusion-temperature model based on α_T calculated according to Leuenberger and Lang [20] is marked by bold black lines, while the output achieved via application of α_T according to van der Valk [43] is depicted as bold dashed black lines. Fine black lines represent the prediction of the diffusion-temperature model, when thermal diffusion is switched off (i.e. $j_{TD} = 0$, compare section 2).

by the data points even if they show a strong scatter (owing to experimental problems in the field). In summer, when firn temperature increases towards the surface (compare Figure 4a or 4f) CO_2 in the firn is enriched with respect to air (compare Figure 7a or 7f) owing to its larger molar mass ($0.044 \text{ kg mol}^{-1}$ vs. $0.029 \text{ kg mol}^{-1}$ for air, see Table 1). Accordingly, compared to the surface a depletion of CO_2 is observable in winter (Figure 7c or 7d), which corresponds to the inverted temperature profile (Figure 4c or 4d), i.e. colder temperatures towards the surface. In spring (Figure 7e) and autumn (Figure 7b) the profiles forced by concentration oscillations only (fine black lines) are intersected twice by the model runs accounting for thermal diffusion (bold black or black dashed lines, respectively). This is due to the reversal of the temperature profile from winter towards summer conditions (compare Figure 4c and 4e).

Figure 8 gives a summary of the Halley CO_2 firn air profiles as predicted with the diffusion–temperature model simulated without thermal diffusion ($j_{TD} = 0$) in order to investigate the effect of seasonality in the atmospheric CO_2 history observed in Halley. Different line styles represent the different seasons reaching from mid of February to end of December 2003.

Seasonal atmospheric CO_2 variations have a magnitude of about $\pm 0.5 \text{ ppmv}$ in Halley with a minimum in autumn and a maximum in spring (NOAA data [42]) and are caused by variations of the net primary production of carbon [13]. Net primary production is the remainder of the carbon flux into the terrestrial biosphere (i.e. carbon fixed in photosynthesis by terrestrial plants) and the return of carbon by respiration of terrestrial plants and soil [13]. Carbon consumption by photosynthesis is highest in spring and summer leading to decreasing atmospheric CO_2 concentrations in Halley. Respiration from soils takes also place in winter, which is why atmospheric CO_2 increases in Halley during this season. In addition, for southern latitudes, the ocean–atmosphere gas exchange plays an important role in determining the seasonal cycle of CO_2 [13].

The seasonal variations in the atmospheric CO_2 concentration mentioned above are well reproduced by the diffusion–temperature model. Minimum concentrations appear on the surface in February 2003, i.e. autumn (black line, Figure 8), while the concentration maximum is reached in late October (black short dashed line). A continuous concentration increase can be observed from late April (grey short dashed line) to late August (grey dashed line). The decrease of atmospheric CO_2 in spring and summer is represented by a concentration decline between the October and the late December surface (grey line in Figure 8). The seasonal pattern is visible in the CO_2 firn air profiles down to about 2.5 m depth. At this level, the imprint of the annual anthropogenic CO_2 increase overlays the effect of seasonal variability and the profiles turn back to their original order, i.e. the younger the air, the higher the CO_2 concentration (profiles from 28.10.03 and 22.12.03 intersect at this depth). Thus, a

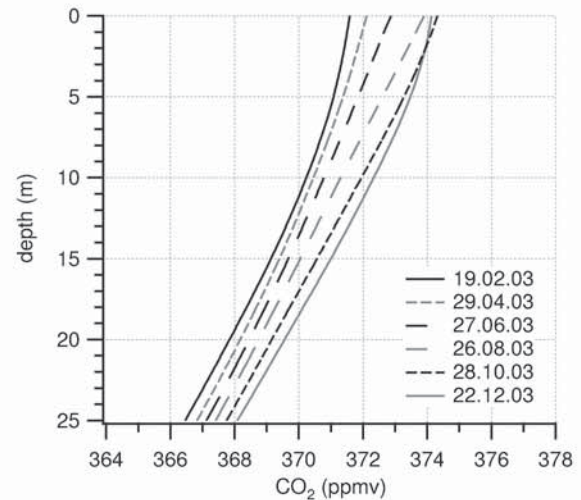


Figure 8: Summary of the Halley CO_2 profiles as function of depth simulated with the diffusion–temperature model, while thermal diffusion is switched off (i.e. $j_{TD} = 0$, compare section 2). Different seasons are represented by various line styles.

seasonality of $\pm 0.5 \text{ ppmv}$ as detected in the atmospheric CO_2 record of Halley only has a minor effect on the CO_2 firn air profiles. In addition, from comparison with the firn air data (Figure 7), seasonal amplitudes in firn air CO_2 are underestimated (fine black lines vs. bold black or bold black dashed lines, respectively in Figure 7), when only the seasonality of the atmospheric CO_2 concentrations detected in Halley is considered. In particular, this is supported by the profiles analysed from February to August 2003 (Figure 7a to 7d). Owing to the very poor sample quality, no clear conclusion can be drawn from the October and December profiles (Figure 7e and 7f).

Taking into account thermal diffusion leads not only to a more realistic seasonal amplitude predicted for the firn air profiles but also to a shift of about 0.2 ppmv (corresponding to a temperature increase of approximately 2 K between 7.5 m and 20 m depth) towards lower CO_2 concentrations (compare Figure 7, fine black vs. bold black or bold black dashed lines, respectively). Therefore, regarding the concentration of the firn air finally occluded in air bubbles at the close-off level, thermal diffusion of CO_2 in firn air plays only a minor role.

5 Conclusions and outlook

The imprint of atmospheric temperature and concentration seasonality on the composition of firn air has been investigated on a multi proxy firn air data set retrieved in Halley in 2003.

Seasonal atmospheric temperature variations leading to temperature oscillations in the firn column are reproduced properly by the temperature–model forced with the surface temperature history from Halley. Thus, the de-

pendency of the thermal conductivity κ on the firm density as calculated according to [32] is sufficient also on a seasonal scale. Furthermore, depth correction owing to firm densification and additional accumulation as predicted with a 1-dimensional box model agrees well with the reduction of the analysed diurnal temperature cycle. Therefore, this box model seems to be appropriate for this purpose.

Thermal fractionation is simulated in the diffusion-temperature model based on [31, 32] with respect to air and for a binary mixture. Within an uncertainty range of $\pm 3\%$ [11] thermal diffusion of $^{15}\text{N}^{14}\text{N}$ in air as forced with the thermal diffusion factor according to the logarithmic fit of Leuenberger et al. [21] (fitting the measurements of Grachev and Severinghaus [11]) leads to a good agreement between firm air data and model prediction. Thermal diffusion of $^{18}\text{O}^{16}\text{O}$ in air, $^{16}\text{O}_2$ in air, and CO_2 in air is forced with two different model approaches (according to Leuenberger and Lang [20], van der Valk [43]) in order to estimate the thermal diffusion factor α_T . As expected from theory, comparison of data and model output reveals that application of neither model leads to a proper prediction of the seasonal thermal amplitude for $\delta^{18}\text{O}$. In contrast, both models predict reasonable α_T in case of CO_2 .

The thermal diffusion factor for CO_2 in air seems to be in the range between $\alpha_T = 57.3 \cdot 10^{-3}$ (according to Leuenberger and Lang [20]) and $\alpha_T = 67.8 \cdot 10^{-3}$ (according to van der Valk [43]). However, the variability of the CO_2 data is on the same order of magnitude as the thermal fractionation (0.7 ppmv in case of Halley, see above). Thus, the α_T derived for CO_2 with respect to air should be confirmed by measurements or extrapolations based on a firm air data set of higher sample quality.

In order to get a first idea about thermal fractionation of $^{16}\text{O}_2$ in air and $^{18}\text{O}^{16}\text{O}$ in air three different scenarios were applied. In summary it can be concluded, that these approaches lead to a realistic estimate for neither α_T . In addition, the measurements of Waldmann [45] seem to be questionable and furthermore, the applicability of the linear mass dependence of the thermal diffusion factors not possible for a gas mixture comprised by more than two species (as already stated by Leuenberger and Lang [20]). Thus, for a clear prediction of the thermal fractionation factors of $^{18}\text{O}^{16}\text{O}$ in air and $^{16}\text{O}_2$ in air detailed experimental investigations are required.

Seasonal oscillations observed in the firm air profiles of CO_2 and the isotopes $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$ act as expected from theory during the entire year. The imprint of both, seasonal atmospheric temperature variations and atmospheric concentration oscillations are well reproduced by the diffusion-temperature model. One exception is the firm air profile sampled in February. The overestimation of the seasonal thermal amplitude observed in case of $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$ is attributed to surface convection overlying diffusive mixing. A convective layer with a vertical extension of not more than 0.5 m is expected for Halley firm [47].

Seasonal concentration oscillations of ± 0.5 ppmv as observed in the atmospheric CO_2 history of Halley influence the firm air profiles only within the uppermost about 2.5 m. Furthermore, forcing the diffusion-temperature model with a constant CO_2 input concentration leads to a thermal amplitude for CO_2 of not more than 0.7 ppmv corresponding to a temperature difference of about 10 K between the surface and 5 m depth. In addition, thermal diffusion leads to a CO_2 shift of about 0.2 ppmv owing to the temperature gradient of about 2 K between 7.5 m and 20 m depth in Halley firm. Thus, neither a concentration seasonality of ± 0.5 ppmv nor thermal diffusion will lead to considerable changes in the composition of the CO_2 , which is finally occluded into air bubbles at the close-off level.

In order to improve the prediction of the thermal diffusion effect by the diffusion-temperature model, more reliable estimations of the thermal diffusion factors of $^{18}\text{O}^{16}\text{O}$ in air, $^{16}\text{O}_2$ in air, and CO_2 in air are desirable. To this end, a firm air data set of higher sample quality would be helpful.

Acknowledgements

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References

- [1] D. L. Anderson and C. S. Benson, "The densification and diagenesis of snow" in W.D. Kingery, editor, *Ice and snow: properties, processes, and applications: proceedings of a conference held at The Massachusetts Institute of Technology*. The M.I.T. Press, 1963.
- [2] L. Andrussov and B. Schramm, "Diffusion in Gasen", in K. Schäfer, editor, *Landolt-Börnstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik*, volume 2: *Eigenschaften der Materie in ihren Aggregatzuständen*, part 5a: *Transportphänomene, Kinetik, homogene Gasgleichgewichte*. Springer, 6th edition, 1969.
- [3] H. Bader, "Density of ice as a function of temperature and stress", in *CRREL Special Report*, vol-

- ume 64. Cold Regions Research and Engineering Laboratory, 1964.
- [4] T. Blunier and J. Schwander, "Gas enclosure in ice: age difference and fractionation", in T. Hondoh, editor, *Physics of Ice core records*. Hokkaido University Press, 2000.
 - [5] S.C. Colbeck, "Air movement in snow due to wind-pumping", *Journal of Glaciology*, 35(120), 1989, pp. 209–213.
 - [6] H. Craig and R.C. Wiens, "Gravitational enrichment of $^{84}\text{Kr}/^{36}\text{Ar}$ ratios in polar ice caps: A measure of firn thickness and accumulation temperature", *Science*, 271, 1996, pp. 1708–1710.
 - [7] J. Crank, *The mathematics of diffusion*, Oxford University Press, 2nd edition, 1975.
 - [8] F.A.L. Dullien, "Single phase flow through porous media and pore structure", *The Chemical Engineering Journal*, 10, 1975, pp. 1–34.
 - [9] R.J. Francey, C.E. Allison, D.M. Etheridge, C.M. Trudinger, I.G. Enting, M. Leuenberger, R.L. Langenfelds, E. Michel, and L.P. Steele, "A 1000-year high precision record of $\delta^{13}\text{C}$ in atmospheric CO_2 ", *Tellus*, 51B, 1999, pp. 170–193.
 - [10] A.M. Grachev and J.P. Severinghaus, "Determining the thermal diffusion factor for $^{40}\text{Ar}/^{36}\text{Ar}$ in air to aid paleoreconstruction of abrupt climate change", *Journal of Physical Chemistry*, 107, 2003, pp. 4636–4642.
 - [11] A.M. Grachev and J.P. Severinghaus, "Laboratory determination of thermal diffusion constants for $^{29}\text{N}_2/^{28}\text{N}_2$ in air at temperatures from -60 to 0°C for reconstruction of magnitudes of abrupt climate changes using the ice core fossil-air paleothermometer", *Geochimica et Cosmochimica Acta*, 67 (3), 2003, pp. 345–360.
 - [12] K.E. Grew and T.L. Ibbs, *Thermal Diffusion in Gases*, Cambridge University Press, 1st edition, 1952.
 - [13] M. Heimann, G. Esser, A. Haxeltine, J. Kaduk, D.W. Kicklighter, W. Knorr, G.W. Sauf, A. Schloss, S. Sitch, U. Wittenberg, and G. Würth, "Evaluation of terrestrial carbon cycle models through simulations of the seasonal cycle of atmospheric CO_2 : First results of a model intercomparison study", *Global Biogeochemical Cycles*, 12, 1998, pp. 1–24.
 - [14] M. M. Herron and C.C. Langway, Jr, "Firn densification: an empirical model", *Journal of Glaciology*, 25, 1980, pp. 373–385.
 - [15] J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird, *Molecular theory of gases and liquids*, John Wiley & Sons, Inc., 2nd edition, 1964.
 - [16] C. Huber, U. Beyerle, M. Leuenberger, J. Schwander, R. Kipfer, R. Spahni, J.P. Severinghaus, and K. Weiler, "Evidence for gas fractionation in air derived from noble gases, oxygen, and nitrogen measurements", *Earth and Planetary Science Letters*, 243, 2006, pp. 61–73.
 - [17] K. Kawamura, J.P. Severinghaus, S. Ishidoya, S. Sugawara, G. Hashida, H. Motoyama, Y. Fujii, S. Aoki, and T. Nakazawa, "Convective mixing of air in firn at four polar sites.", *Earth and Planetary Science Letters*, 244, 2006, pp. 672–682.
 - [18] D. Kuroiwa, "A study of sintering", *Tellus*, 13, 1961, pp. 252–259.
 - [19] A. Landais, N. Caillon, J. Severinghaus, J.-M. Barnola, C. Goujon, J. Jouzel, and V. Masson-Delmotte, "Analyse isotopique de l'air piégé dans la glace pour quantifier les variations de température.", *C. R. Geoscience*, 336, 2004, pp. 963–970.
 - [20] M. Leuenberger and C. Lang, "Thermal diffusion: an important aspect in studies of static air columns such as firn air, sand dunes and soil air", *IEAA, Technical Report*, 2002, pp. 115–127.
 - [21] M. Leuenberger, C. Lang, and J. Schwander, " $\delta^{15}\text{N}$ measurements as a calibration tool for the paleothermometer and gas-ice age differences: A case study for the 8200 b.p. event on GRIP ice", *Journal of Geophysical Research*, 104(D18), 1999, pp. 22163–22170.
 - [22] M. Leuenberger, P. Nyfeler, H.P. Moret, P. Sturm, and Ch. Huber, "A new gas inlet system for an isotope ratio mass spectrometer improves reproducibility", *Rapid communications in mass spectrometry*, 14, 2000, pp. 1543–1551.
 - [23] M. Leuenberger, P. Nyfeler, H.P. Moret, P. Sturm, A. Indermühle, and J. Schwander, " CO_2 concentration measurements on air samples by mass spectrometry", *Rapid communications in mass spectrometry*, 14, 2000, pp. 1552–1557.
 - [24] A. Mariotti, "Atmospheric nitrogen is a reliable standard for natural ^{15}N abundance measurements", *Nature*, 303, 1983, pp. 685–687.
 - [25] P. Martinerie, V.Y. Lipenkov, D. Raynaud, J. Chappellaz, N.I. Barkov, and C. Lorius, "Air content paleo record in the Vostok ice core (Antarctica): A mixed record of climatic and glaciological parameters", *Journal of Geophysical Research*, 99(D5), 1994, pp. 10565–10576.
 - [26] P. Martinerie, D. Raynaud, D.M. Etheridge, J.M. Barnola, and D. Mazaudier, "Physical and climatic parameters which influence the air content in polar ice", *Earth and Planetary Science Letters*, 112, 1992, pp. 1–13.

- [27] W. S. B. Paterson, The Physics of Glaciers, Butterworth–Heinemann, 3rd edition, 2002.
- [28] R.C. Reid and T.K. Sherwood, The Properties of Gases and Liquids, McGraw–Hill, 1977.
- [29] T. Schnabel, J. Vrabec, and H. Hasse, “Unlike Lennard–Jones parameters for vapor–liquid equilibria”, *Journal of Molecular Liquids*, 135, 2007, pp. 170–178.
- [30] J. Schwander. “The transformation of snow to ice and the occlusion of gases”, in H. Oeschger and C.C. Langway, Jr, editors, The Environmental Record in Glaciers and Ice Sheets, John Wiley & Sons, 1989.
- [31] J. Schwander, J.-M. Barnola, C. Andri , M. Leuenberger, A. Ludin, D. Raynaud, and B. Stauffer, “The age of the air in the firn and the ice at Summit, Greenland”, *Journal of Geophysical Research*, 98 (D2), 1993, pp. 2831–2838.
- [32] J. Schwander, T. Sowers, J.-M. Barnola, T. Blunier, A. Fuchs, and B. Malaiz , “Age scale of the air in the Summit ice: Implication for glacial–interglacial temperature change”, *Journal of Geophysical Research*, 102(D16), 1997, pp. 19483–19493.
- [33] J. Schwander and B. Stauffer, “Age difference between polar ice and the air trapped in its bubbles”, *Nature*, 311(5981), 1984, pp. 45–47.
- [34] J. Schwander, B. Stauffer, and A. Sigg, “Air mixing in firn and the age of the air at pore close–off”, *Annals of Glaciology*, 10, 1988, pp. 141–145.
- [35] J.P. Severinghaus and M. Battle, “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 (1–2), 2006, pp. 474–500.
- [36] J.P. Severinghaus, A. Grachev, and M. Battle. “Thermal fractionation of air in polar firn by seasonal temperature gradients”, *Geochemistry Geophysics Geosystems*, 2, 2001.
- [37] J.P. Severinghaus, R.F. Keeling, B.R. Miller, R.F. Weiss, B. Deck, and W.S. Broecker, “Feasibility of using sand dunes as archives of old air”, *Journal of Geophysical Research*, 102(D14), 1997, pp. 16783–16792.
- [38] J.P. Severinghaus, T. Sowers, E.J. Brook, R.B. Alley, and M.L. Bender. “Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice”, *Nature*, 391, 1998, pp. 141–146.
- [39] T. Sowers, M. Bender, D. Raynaud, and Y.S. Korotkevich. “ $\delta^{15}\text{N}$ of N_2 in air trapped in polar ice: a tracer of gas transport in the firn and a possible constraint on ice age–gas age differences”, *Journal of Geophysical Research*, 97(D14), 1992, pp. 15683–15697.
- [40] B. Stauffer, J. Schwander, and H. Oeschger, “Enclosure of air during metamorphosis of dry firn to ice”, *Annals of Glaciology*, 6, 1985, pp. 108–112.
- [41] P. Sturm, Atmospheric oxygen and associated tracers from flask sampling and continuous measurements: tools for studying the global carbon cycle, PhD thesis, University of Bern, Switzerland, 2005.
- [42] P.P. Tans and T.J. Conway, “Monthly atmospheric CO_2 mixing ratios from the NOAA CMDL Carbon Cycle Cooperative Global Air Sampling Network, 1968–2002”, in Trends: A Compendium of Data on Global Change, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A., 2005.
- [43] F. van der Valk, “Thermal diffusion in ternary mixtures, I. Theory”, *Physica*, 29, 1963, pp. 417–426.
- [44] L. Waldmann. “ ber die Druck– und Temperaturabh ngigkeit der W rmeerscheinungen bei der Diffusion.”, *Zeitschrift Naturforschung*, 4, part A, 1949, pp. 105–117.
- [45] L. Waldmann, “Transporterscheinungen in Gasen von mittlerem Druck”, in S. Fl gge, editor, Encyclopedia of Physics, volume XII: Thermodynamics of Gases, Springer, 1958.
- [46] R.C. Weast and M.J. Astle, editors, Handbook of Chemistry and Physics, CRC–Press, 60th edition, 1980.
- [47] K. Weiler. On the Composition of Firn Air and its Dependence on Seasonally Varying Atmospheric Boundary Conditions and the Firn Structure. PhD thesis, University of Bern, Switzerland, 2008.

A Estimation of the thermal diffusion factor

Thermal fractionation can be described as a concentration gradient arising in an initially uniform gas mixture owing to temperature differences within the mixture. Usually the heavier molecules diffuse down the temperature gradient towards the colder end, while the lighter ones tend to the warmer regions. The concentration gradient is counterbalanced by ordinary diffusion, until a quasi steady state is established [12].

The magnitude of thermal diffusion is determined by the thermal diffusion factor α_T , which depends on the concentration of the diffusing species and their molecular interactions. Interactions take place between like (i.e.

molecules of the same type) and unlike (molecules of different types) molecules [29].

For the simulation of the molecular interaction forces different molecular models are available in order to express the potential energy of the system as function of the distance r in-between the molecules. A summary is given on page 339 et seqq. in Waldmann [45]. For the simulation of α_T the Lennard–Jones potential Θ is applied, as it also includes the temperature dependency of α_T . Attraction and repulsion forces are given in the general equation from Lennard–Jones according to

$$F = -\frac{\partial\Theta}{\partial r} = \frac{\kappa}{r^\nu} - \frac{\kappa'}{r^{\nu'}}, \quad (16)$$

where κ and ν refer to the repulsive and κ' and ν' to the attractive force [45]. The theory applies to interactions of non-polar, non-reactive spherical molecules like the noble gases [45].

A.1 Molecular interaction based on the Lennard–Jones (13,7) model

Leuenberger and Lang [20] applied an approach given in Grew and Ibbs [12] to express the interaction forces with the Lennard–Jones (13,7) potential (i.e. $\nu = 13$ and $\nu' = 7$), which has been successful in accounting for the equation of state and other properties of many gases [12]. This approach requires an isotopic mixture, i.e. like and unlike molecules can be assumed to interact with the same law and accordingly, the collision integrals differ only because of the different molecular masses. Furthermore, the mass difference M^* of the molecules is assumed to be small. Provided these conditions the thermal diffusion factor can be expressed as [12, 20]

$$\alpha_T = \frac{15M^*(C-1)(A+1)}{A(11-4B+8A)}. \quad (17)$$

where M^* is the proportionate mass difference

$$M^* = \frac{M_1 - M_2}{M_1 + M_2}. \quad (18)$$

M_1 and M_2 are the molar masses of the gas species (see Table 1). The variables A , B and C represent ratios of the dimensionless integrals Ω_{ij}^{ls} describing the collision cross sections of two interacting molecules i, j . The collision integrals depend on the quantity $\frac{kT}{\epsilon}$. For isotopic mixtures α_T can be expressed directly as a function of the $\frac{kT}{\epsilon}$, where k is the Boltzmann constant, T the temperature and $-\epsilon$ the potential energy of two molecules at the equilibrium separation, i.e. in the minimum of the Lennard–Jones potential ($\frac{\partial\Theta}{\partial r} = 0$ or attractive equal to repulsive force, [12]). $\frac{kT}{\epsilon}$ is approximately equivalent to $\frac{T}{T_c}$, where T_c is the critical temperature [12]. The critical temperature is the temperature above which a substance cannot exist in the liquid state, regardless of the pressure [46]. Thus, given T_c as e.g. tabulated in Weast and Astle [46], the dependency of α_T from $\frac{kT}{\epsilon}$ can be expressed by

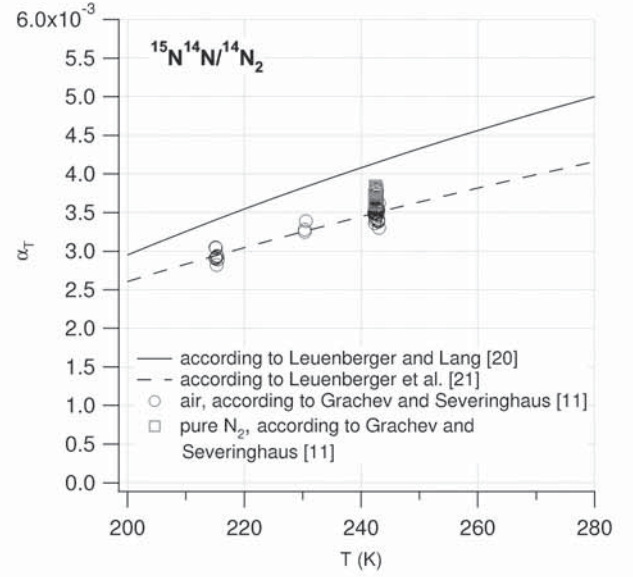


Figure 9: Thermal diffusion factors α_T for $^{15}\text{N}^{14}\text{N}$ to $^{14}\text{N}_2$. Black lines represent the calculation of α_T according to Leuenberger and Lang [20]. Measurements carried out by Grachev and Severinghaus [11] (only “recent” data are considered) for α_T of $^{15}\text{N}^{14}\text{N}$ to $^{14}\text{N}_2$ in pure N_2 are depicted as grey squares. α_T of $^{15}\text{N}^{14}\text{N}$ to $^{14}\text{N}_2$ measured in natural air are marked by black circles. A logarithmic fit through a large amount of data from various authors (compare Leuenberger et al. [21]) for α_T of $^{15}\text{N}^{14}\text{N}$ to $^{14}\text{N}_2$ (dashed black line) matches well with the measurements of Grachev and Severinghaus [11].

A , B and C as tabulated in Grew and Ibbs [12] (Table II A on page 122) for equal proportions of the gas species in a binary mixture, i.e. $c_1 = c_2 = 0.5$.

In Figure 9 thermal fractionation as function of temperature T calculated with the approach of Leuenberger and Lang [20] described above is compared with measurements carried out by Grachev and Severinghaus [11] (for $^{15}\text{N}^{14}\text{N}$ to $^{14}\text{N}_2$). As clearly visible in Figure 9a, Leuenberger and Lang [20] (black line) slightly overestimate thermal fractionation of $^{15}\text{N}^{14}\text{N}$ to $^{14}\text{N}_2$ as measured by Grachev and Severinghaus [11] in pure nitrogen (grey squares) and air (black circles). In contrast, a logarithmic fit ($\alpha_T(T) = 0.00461198 \ln T - 0.02182912$, dashed black line) through a considerable amount of data for α_T of $^{15}\text{N}^{14}\text{N}$ to $^{14}\text{N}_2$ provided by various authors (compare Leuenberger et al. [21]) matches well with the measurements.

As mentioned above, the approach of Leuenberger and Lang [20] is applicable for isotopic mixtures only. In contrast, our diffusion–temperature model (section 2) requires a binary mixture. As a first approach Leuenberger and Lang [20] applied the isotopic model to calculate the thermal fractionation of the species $^{16}\text{O}_2$, $^{18}\text{O}^{16}\text{O}$, and CO_2 in nitrogen. As atmospheric air consists of 78 % nitrogen (Table 1) the approximation of the gas mixture air by nitrogen should be appropriate. In order to derive the ratios of the collision integrals A , B and C (see

above) Leuenberger and Lang [20] combined the critical temperatures of nitrogen and of the corresponding second gas species by weighting with the proportions on the atmospheric air composition (Table 1). Following this approach, the α_T for the annual mean temperature in Halley of about 254 K (Table 2) are summarized in Table 3.

A.2 Molecular interaction as described with the Lennard–Jones (6,12) model

In order to model thermal fractionation of an isotopic mixture in air, a theory to derive thermal diffusion factors in polynary mixtures as given in van der Valk [43] shall be discussed in the following. Fractionation in polynary mixtures can be simulated by pairwise additive interactions [29]. For equilibrium conditions the thermal diffusion process can be expressed as (compare equation 6)

$$\frac{\partial c_k}{\partial z} = -c_k \sum_{j=1}^n c_j \alpha_{kj} \frac{\partial \ln T}{\partial z}, \quad (19)$$

where $c_k \sum_{j=1}^n c_j \alpha_{kj}$ is the polynary thermal diffusion ratio according to Waldmann [45] (with $i, j, k \in \mathbb{N}$). $c_i, c_j, \dots, c_n$ are the concentrations of the n different gas species in the mixture, where the condition $\sum_{k=1}^n c_k = 1$ has to be fulfilled. The α_{ij} are arithmetic variables (i.e. non measurable quantities) with $\alpha_{ij} = -\alpha_{ji}$ and $\alpha_{ii} = 0$. Based on Waldmann [45] the α_{ij} are the result of a 4th order determinant in the numerator and a 3rd order determinant in the denominator [43], namely

$$\alpha_{ij} = - \frac{\det \begin{pmatrix} a_{11} & a_{12} & \dots & a_{1m} & 1 \\ a_{21} & a_{22} & \dots & a_{2m} & 1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nm} & 1 \\ b_{1,ij} & b_{2,ij} & \dots & b_{m,ij} & 0 \end{pmatrix}}{\det \begin{pmatrix} a_{11} & \dots & a_{1m} \\ \vdots & \ddots & \vdots \\ a_{n1} & \dots & a_{nm} \end{pmatrix}}. \quad (20)$$

The matrix elements a_{rs} and $b_{s,ij}$, where $r, s = 1, 2, \dots, n$ are calculated in the following manner:

$$a_{rs} = c_s M_{sr} M_{rs} \frac{F_{rs}^*}{E_{sr}} + \delta_{rs} \sum_{l=1}^n c_l \frac{F_{sl}}{E_{sl}} \quad (21)$$

$$\begin{aligned} b_{i,ij} &= -M_{ji} \frac{6C_{ij}^* - 5}{E_{ij}}, \quad \text{i.e. } s = i \\ b_{j,ij} &= M_{ij} \frac{6C_{ij}^* - 5}{E_{ji}}, \quad \text{i.e. } s = j \\ b_{k,ij} &= 0, \quad \text{i.e. } s = k \neq i, j \end{aligned} \quad (22)$$

In order to solve equation 20 the following symbols and variables have to be defined:

M_{ij} and M_{ji} are the mass relations (compare also

equation 18) calculated according to

$$\begin{aligned} M_{ij} &= \frac{M_i}{M_i + M_j} \\ M_{ji} &= \frac{M_j}{M_j + M_i}, \end{aligned} \quad (23)$$

where M_i and M_j are the molar masses of the gas species i and j (see Table 1).

The variables F_{ij} and F_{ij}^* follow the definitions

$$\begin{aligned} F_{ij} &= 6M_{ij}^2 + (5 - \frac{12}{5} B_{ij}^*) M_{ji}^2 \\ &\quad + \frac{16}{5} M_{ij} M_{ji} A_{ij}^* \\ F_{ij}^* &= -11 + \frac{12}{5} B_{ij}^* + \frac{16}{5} A_{ij}^*, \end{aligned} \quad (24)$$

while the variables E_{ij} are defined by

$$E_{ij} = \frac{2}{5} \sqrt{\frac{2}{M_{ji}} \frac{\Omega_{ii}^{22*}}{\Omega_{ij}^{11*}} \left(\frac{\sigma_{ii}}{\sigma_{ij}} \right)^2}. \quad (25)$$

Similar to the constants A, B, C mentioned above the ratios of the collision integrals have to be defined for the interaction of different molecules. According to Waldmann [45] and Hirschfelder et al. [15] this leads to the following expressions for the A_{ij}^*, B_{ij}^* and C_{ij}^*

$$\begin{aligned} A_{ij}^* &= \frac{\Omega_{12}^{22*}}{\Omega_{12}^{11*}} \\ B_{ij}^* &= \frac{5\Omega_{12}^{12*} - 4\Omega_{12}^{13*}}{\Omega_{12}^{11*}} \\ C_{ij}^* &= \frac{\Omega_{12}^{12*}}{\Omega_{12}^{11*}}, \end{aligned} \quad (26)$$

where the results are all very nearly unity [45, 15]. The star in the superscript implies the collision integrals Ω_{ij}^{ls*} applied to be relative to the collision integrals calculated for the rigid sphere potential (compare Waldmann [45], page 340, paragraph a). A list of the Ω_{ij}^{ls*} needed to calculate the A_{ij}^*, B_{ij}^* and C_{ij}^* is given in Hirschfelder et al. [15] (Table I-M on page 1126 et seq.), while the combination of the two interacting gases i, j is implicitly expressed by the combined reduced temperature T^* . The reduced temperature is defined as $T^* = \frac{kT}{\epsilon}$, where $\frac{\epsilon}{k}$ can be approximated with $\frac{\epsilon}{k} = 0.77T_c$ for spherical non-polar molecules obeying the Lennard–Jones (6,12) potential [15]. Thus, T^* can be expressed as $T^* = \frac{T}{0.77T_c}$ for a certain gas species, where T_c represents the critical temperature. In order to calculate the combined reduced temperature as listed in Hirschfelder et al. [15], combination rules for the energy parameters ϵ forcing the Lennard–Jones (6,12) potential have to be applied. A second force constant necessary to drive the Lennard–Jones (6,12) potential is the combined atomic diameter σ_{ij} .

For like interactions, i.e. $i = j$ these force constants are tabulated in Hirschfelder et al. [15] (Table I-A on page 1110 et seq.). In order to derive the force constants for

gas	$10^3 \cdot \alpha_T$ (with respect to air at 254 K)		
CO ₂	57.3 ²⁾	67.8 ³⁾	
¹⁵ N ¹⁴ N	3.7 ¹⁾		
¹⁴ N ₂		-5.3 ³⁾	
¹⁸ O ¹⁶ O	(25.0) ²⁾	(23.5) ³⁾	
	18.5 ⁴⁾	15.2 ⁵⁾	12.7 ⁶⁾
¹⁶ O ₂	(14.6) ²⁾	(13.9) ³⁾	
	15.4 ⁴⁾	9.4 ⁵⁾	7.9 ⁶⁾

¹⁾ ± 3 %, according to Leuenberger et al. [21].

Grachev and Severinghaus [11]

²⁾ according to Leuenberger and Lang [20]

³⁾ according to van der Valk [43]

Based on Halley $\delta^{18}\text{O}$ profiles of 2003:

⁴⁾ case (i): $\alpha_T(^{16}\text{O}_2/\text{air})$ according to Waldmann [44]

⁵⁾ case (ii): according to equations 14 and 15 with

$$\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}} = 1.55 \pm 0.04 \text{ (derived from Halley)}$$

⁶⁾ case (iii): according to equations 14 and 15 with $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}} = 1.3$

Table 3: Thermal diffusion factors α_T of different gas species investigated in this study calculated with respect to air for 254 K. Thermal fractionation of ¹⁵N¹⁴N in air ¹⁾ is approximated with α_T of ¹⁵N¹⁴N in ¹⁴N₂ from the logarithmic fit of Leuenberger et al. [21] ($\alpha_T(T) = 0.00461198 \ln T - 0.02182912$), which fits the measurements of Grachev and Severinghaus [11]. The values labeled with ²⁾ refer to the approach of Leuenberger and Lang [20], where the gas mixture air is approximated with N₂. Label ³⁾ marks the results of the model of van der Valk [43] for a binary mixture of a gas with air. Superscript ⁴⁾ to ⁶⁾ refer to the α_T of ¹⁸O¹⁶O and ¹⁶O₂ in air as derived from the Halley 2003 $\delta^{18}\text{O}$ profiles (see legend and section 4.2 for detail).

unlike interactions, no rigorous physical framework exists [29]. The most widely used combining rule for the prediction of the unlike force constants is the Lorentz–Berthelot rule [29]. Unlike size parameters are combined by an arithmetic mean according to

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad (27)$$

where σ_{ii} and σ_{jj} are the atomic diameters for like interactions. Based on little physical argument [29] combination of the energy parameters is achieved by the geometric mean

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}, \quad (28)$$

with ϵ_{ii} and ϵ_{jj} representing the energies for like interactions.

This approach can be applied on a ternary mixture c_1 , c_2 in nitrogen. The ternary thermal diffusion factor $\alpha_{ij}^{\text{tern}}$ can be derived from combination of equation 19 applied to the concentrations c_1 and c_2 in a third gas having the concentration c_3 (N₂). Solution of the system of equations leads to the following expression for $\alpha_{ij}^{\text{tern}}$ [43]

$$\alpha_{ij}^{\text{tern}} = [\alpha_{ij} + c_k(\alpha_{ik} - \alpha_{jk} - \alpha_{ij})]. \quad (29)$$

In contrast to the α_{ij} the $\alpha_{ij}^{\text{tern}}$ are measurable quantities.

However, as mentioned above, the model of van der Valk [43] only applies to non-polar, spherical molecules, i.e. noble gases (group 1CLJ, i.e. one-center Lennard–Jones potential in Schnabel et al. [29]). N₂ and O₂ in contrast belong to the group of non-polar but elongated molecules (2CLJ, i.e. symmetric two-center Lennard–Jones potential) [29]. Thus, in order to properly predict the interaction forces of these molecules, models of higher complexity are required.

Despite this limitation the model of van der Valk [43] is used as an additional approach to estimate the thermal diffusion factors for ¹⁴N₂, ¹⁸O¹⁶O, ¹⁶O₂, ⁴⁰Ar, ³⁶Ar and CO₂ in air. In contrast to the model applied by Leuenberger and Lang [20] the approach of van der Valk [43] gives the advantage that the Lennard–Jones (6,12) potential is directly forced with the size and energy parameters of the corresponding gas species.

Table 3 gives an overview of the thermal fractionation factors α_T obtained from the different model approaches discussed above for the gas species investigated in this study. Calculations are carried out with respect to air and for $T = 254$ K. In addition, the results for the α_T of ¹⁶O₂ in air and ¹⁸O¹⁶O in air as derived based on the Halley $\delta^{18}\text{O}$ profiles are given (superscripts ⁴⁾ to ⁶⁾). The basic assumption of case (i)⁴⁾ is $\alpha_T(^{16}\text{O}_2/\text{air}) \cdot 10^3 = 15.4$ according to Waldmann [44]. The α_T derived from cases (ii)⁵⁾ and (iii)⁶⁾ are derived from solving equations 14 (additivity, van der Valk [43]) and 15 (mass dependence, Leuenberger and Lang [20]) based on $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}} = 1.55 \pm 0.04$ (ii) or $\frac{\delta^{18}\text{O}}{\delta^{15}\text{N}} = 1.3$ (iii), respectively (compare section 4.2 for further detail).

B Depth correction

Since the in-situ firm air sampling system in Halley was installed in February 2003 depth levels of both, firm air sampling setup and thermistors, were shifted owing to snow accumulation and settling of the firm. As the annual accumulation of 367 kg m⁻² a⁻¹ (corresponding to about 1 m of snow; Table 2) is quite high in Halley and furthermore, conditions affecting diffusion in the firm column alter considerably in the uppermost meters of the firm, sample levels have to be corrected.

To calculate this depth change, a 1-dimensional forward model has been developed. The firm column is separated into boxes of about 0.5 m height and the depth change due to densification and accumulation is calculated as a function of time. To simulate dynamic densification of the firm, the Herron–Langway model [14] is applied, while seasonal snow accumulation and surface temperature obtained from the meteorological data set (see Tables 2 and 4) are used as forcing parameters.

The empirical Herron–Langway densification model is based on the assumption that during densification of firm the change of porosity is linearly related to the change in

day	net acc. ¹⁾ (m snow)	day	net acc. ¹⁾ (m snow)
29.01.03	-0.081	30.07.03	0.032
19.02.03	0.051	27.08.03	0.139
26.03.03	0.295	25.09.03	0.051
30.04.03	0.094	28.10.03	0.290
15.05.03	0.037	26.11.03	-0.016
25.06.03	0.087	23.12.03	-0.044

¹⁾ snow stake measurements, data provided by British Antarctic Survey (BAS)

Table 4: Monthly mean net accumulation as forcing for the Herron–Langway densification model. The net accumulation refers to the time elapsed since the previous date (beginning of 2003 for January). Negative values of the net accumulation, as observed for January, November and December reflect the amount of fallen snow to be less than ablation by wind or sublimation.

stress due to the weight of the overlying snow [14]:

$$\frac{d\rho}{\rho_{ice} - \rho} = \text{const} \cdot \rho dz, \quad (30)$$

where ρ is the firm density in depth z . This leads to

$$C' = \frac{d \ln \left[\frac{\rho}{\rho_{ice} - \rho} \right]}{dz}, \quad \rho < \rho_{55} \quad (31)$$

$$C'' = \frac{d \ln \left[\frac{\rho}{\rho_{ice} - \rho} \right]}{dz}, \quad \rho_{55} \leq \rho < \rho_{co}, \quad (32)$$

where $C' = \text{const} \cdot \rho_{ice}$ (units m^{-1}) represents densification with depth for densities smaller than the critical density (compare section 1) and accordingly, C'' the densification for $\rho > \rho_{55}$. The densifications C' and C'' are derived from the CRYOSTAT core drilled in Halley to $C' = 0.09 \text{ m}^{-1}$ and $C'' = 0.04 \text{ m}^{-1}$ [47]. In order to derive an expression for the densification rate, the substitution $dz = \frac{A^*}{\rho} dt$ is applied to equations 31 and 32 leading to

$$\frac{d\rho}{dt} = C' \frac{A^*}{\rho_{ice}} (\rho_{ice} - \rho), \quad \rho < \rho_{55} \quad (33)$$

$$\frac{d\rho}{dt} = C'' \frac{A^*}{\rho_{ice}} (\rho_{ice} - \rho), \quad \rho_{55} \leq \rho < \rho_{co}. \quad (34)$$

Hence, dynamic densification of Halley firm is calculated according to equations 33 and 34. The initial mean density profile on the other hand is approximated by application of the Herron–Langway model for stationary conditions [14] based on Halley surface density ρ_0 , mean annual accumulation A^* and temperature T (compare Table 2).

From this initial density profile (at time $t = 0$, i.e. at 19.02.03) the snow mass $m_{s,i}$ of each box can be calculated according to

$$m_{s,i} = \frac{\rho_j^0 + \rho_{j+1}^0}{2} (z_{j+1}^0 - z_j^0) A_{xy}, \quad (35)$$

where $z_{j+1}^0 - z_j^0$ is the 1-dimensional box volume, ρ_j^0 and ρ_{j+1}^0 are the densities at top of box i and box $i + 1$ (i refers to the box midpoints) and $A_{xy} = 1 \text{ m}^2$ is a reference area. To account for mass conservation the mass of each box is held temporally constant.

Exemplarily the time interval between 19.02.03 and 30.04.03 shall be discussed. In this period 0.389 m snow (compare Table 4) are accumulated on top of the original surface from 19.02.03. The surface density ρ_0 is assumed to stay constantly at 394.4 kg m^{-3} (Table 2) during the entire year, thus $\rho_{j-2}^{m+1} = \rho_0^0 = \rho_0$.

Densification as function of time, i.e. from $t = 0$ to $t = t + \Delta t$, is calculated according to equations 33 and 34 for the top of each box i using a simple Euler forward method:

$$\rho_j^{m+1} = C' \frac{A\rho_0}{\rho_{ice}} (\rho_{ice} - \rho_j^0) \Delta t + \rho_j^0, \quad \rho < \rho_{55} \quad (36)$$

$$\rho_j^{m+1} = C'' \frac{A\rho_0}{\rho_{ice}} (\rho_{ice} - \rho_j^0) \Delta t + \rho_j^0, \quad (37)$$

$$\rho_{55} \leq \rho < \rho_{co}.$$

Thus, density ρ_j^{m+1} at time $t = t + \Delta t$ depends on the density at the top of box i of the previous timestep (i.e. ρ_j^0 for the current example), the corresponding net accumulation A^* in $\text{kg m}^{-2} \text{ s}^{-1}$ (i.e. A^* in m snow times ρ_0 in equations 36 and 37), the ice density ρ_{ice} (Table 2) and the densification C' or C'' , respectively as estimated from the initial density profile.

Taking into account mass conservation ($m_{s,i} = \text{const. } \forall t$), the new lower box limits z_j^{m+1} at time $t = t + \Delta t$ are determined according to

$$z_j^{m+1} = z_{j+1}^{m+1} - \frac{m_{s,i}}{\rho_i^{m+1}}, \quad (38)$$

where the lower boundary $z_n^{m+1} = z_n^0$ (at about 60 m depth) is held constant over the time interval Δt . As the densification rate $d\rho/dt$ strongly decreases with depth, this assumption should be appropriate (density increase of less than 0.5 % at 60 m depth during one Δt , i.e. between 19.02.03 and 30.04.03). Thereby, the density ρ_i^{m+1} at the box midpoints is determined from linear interpolation between ρ_j^{m+1} and ρ_{j+1}^{m+1} corresponding to the old box dimensions z_i^0 , z_j^0 and z_{j+1}^0 . New box midpoints finally, are calculated from the average of the corresponding box limits at time $t = t + \Delta t$ according to $z_i^{m+1} = 0.5 \cdot (z_j^{m+1} + z_{j+1}^{m+1})$.

This way, a density increase of nearly 10 % is calculated for the original surface snow of February 2003 (corresponding to about 1.1 m depth shift between February and December of 2003) and still approximately 5 % at 5 m depth (i.e. $\approx 0.7 \text{ m}$ offset in December 2003 compared to February). For the same time period (i.e. 19.02.03 to 22.12.03) a density increase of only 1 % (corresponding to about 0.4 m shift) is calculated for the 20 m depth level. The depth shift of around 1.1 m of the surface level is in good agreement with the total net accumulation at 28.10.03 of about 1 m snow (Table 2).

As the effect of settling (and sintering) and accumulation on the density profile are not separated in the densification model of Herron and Langway [14] (compare equations 33 and 34) ablation events as detected for November and December 2003 (Table 4) cannot be considered (see Weiler [47] for details). Thus, in case of the sampling date 22.12.03 depth levels are shifted by the same offset as calculated for 28.10.03, i.e. the last date with net accumulation (Table 4).

C Data normalization

Taking into account different configurations of the mass spectrometer and variations of the working standard data are normalized. CO₂ profiles are shifted with respect to atmospheric measurements carried out in Halley in 2003 [42]. Isotopes are normalized to 0 ‰ on the surface, where it is assumed that the working standard has the same isotopic composition than the current atmosphere.

Due to experimental problems during sampling in the

field, some of the profiles are of lower sample quality. In order to identify such samples subjected to systematic errors, the maximum or minimum shift required to normalize the data set with respect to the surface is used as a measure (normalization interval). Those samples, which are not covered by the normalization interval are assumed to be subjected to systematic errors and thus, eliminated. Note, that the February profiles are not considered in this respect, as rather surface convection than systematic errors are the reason for the discrepancy between data and model (see section 4.2).

Figures 10, 11 and 12 show the full data sets of the species $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and CO₂ together with the normalization intervals (grey shaded areas). Samples are labeled in the same way than described in Figure 5. Model runs (lines) correspond to those discussed in section 4.2 (Figures 5, 6 and 7). The data set as discussed in section 4.2 is reduced to those samples, which are covered by the normalization interval. Obviously systematic errors have especially occurred during the April and June sampling (Figures 10b and c, 11b and c, 12b and c).

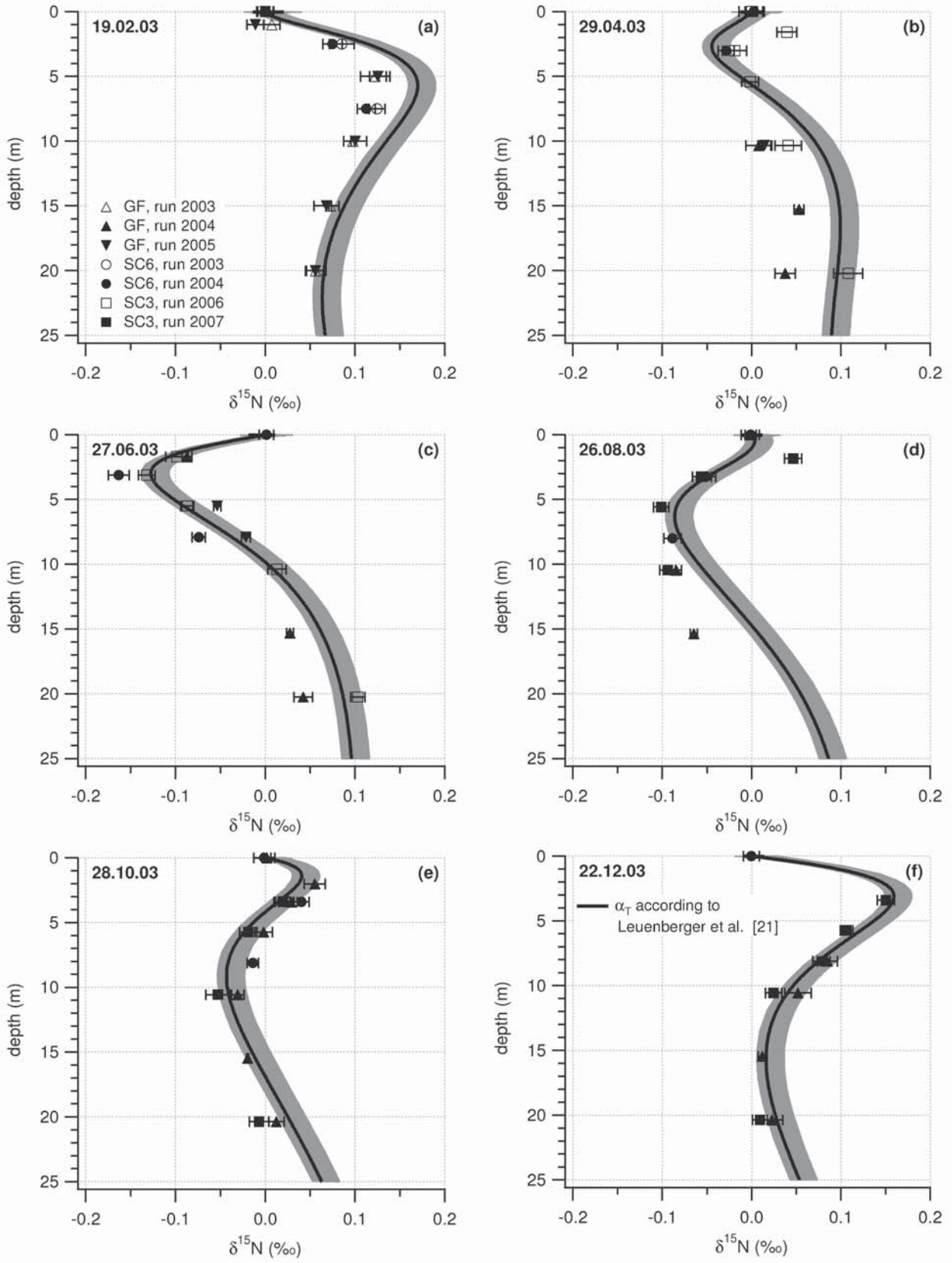


Figure 10: $\delta^{15}\text{N}$ as sampled in Halley between February and December of 2003. Data points are labeled in the same way, than described in Figure 5. Model runs correspond to those discussed in section 4.2 (Figure 5). The normalization interval is represented by the grey shaded areas.

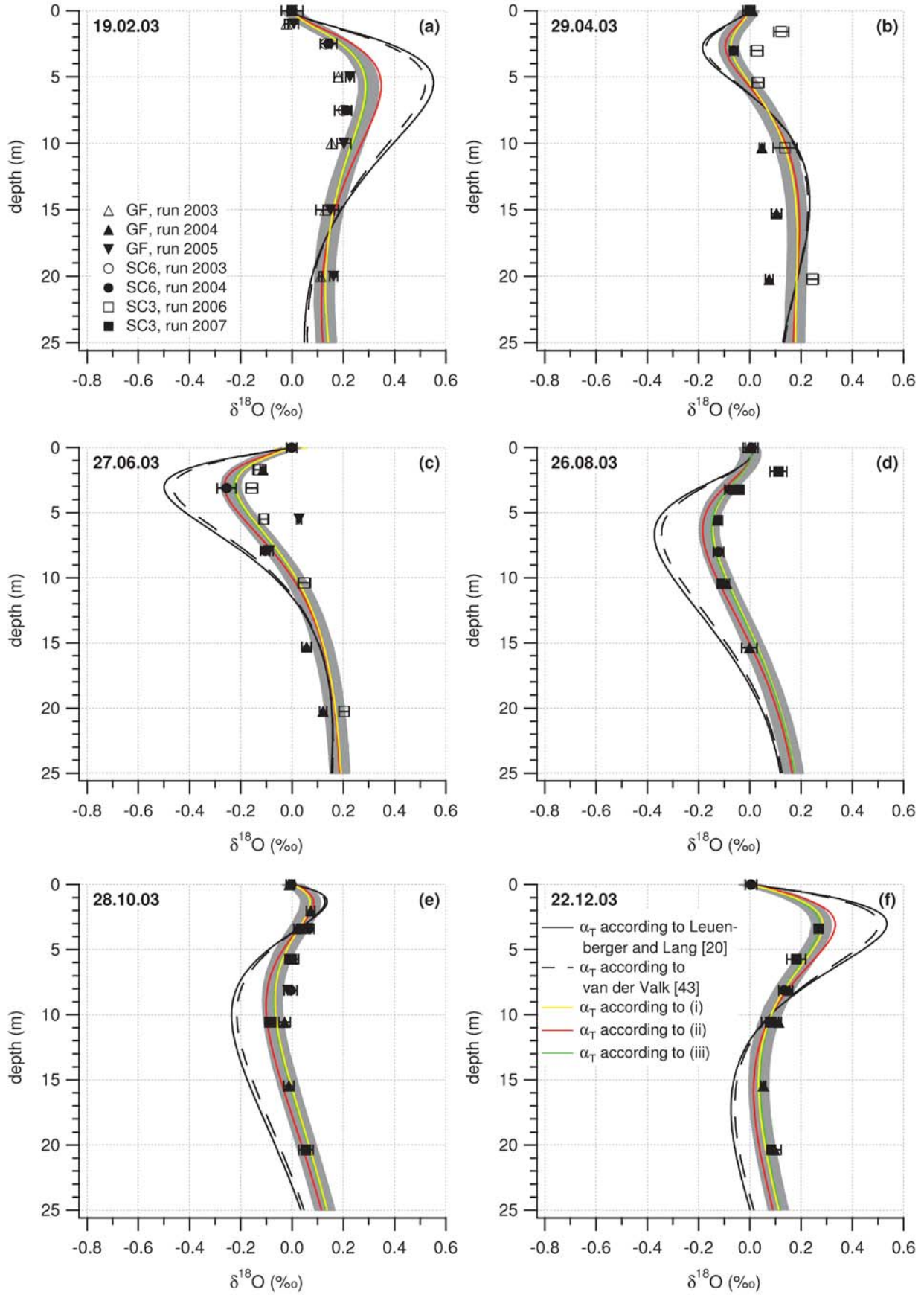


Figure 11: The same figure as Figure 10 but for $\delta^{18}\text{O}$. Model runs correspond to Figure 6 in section 4.2.

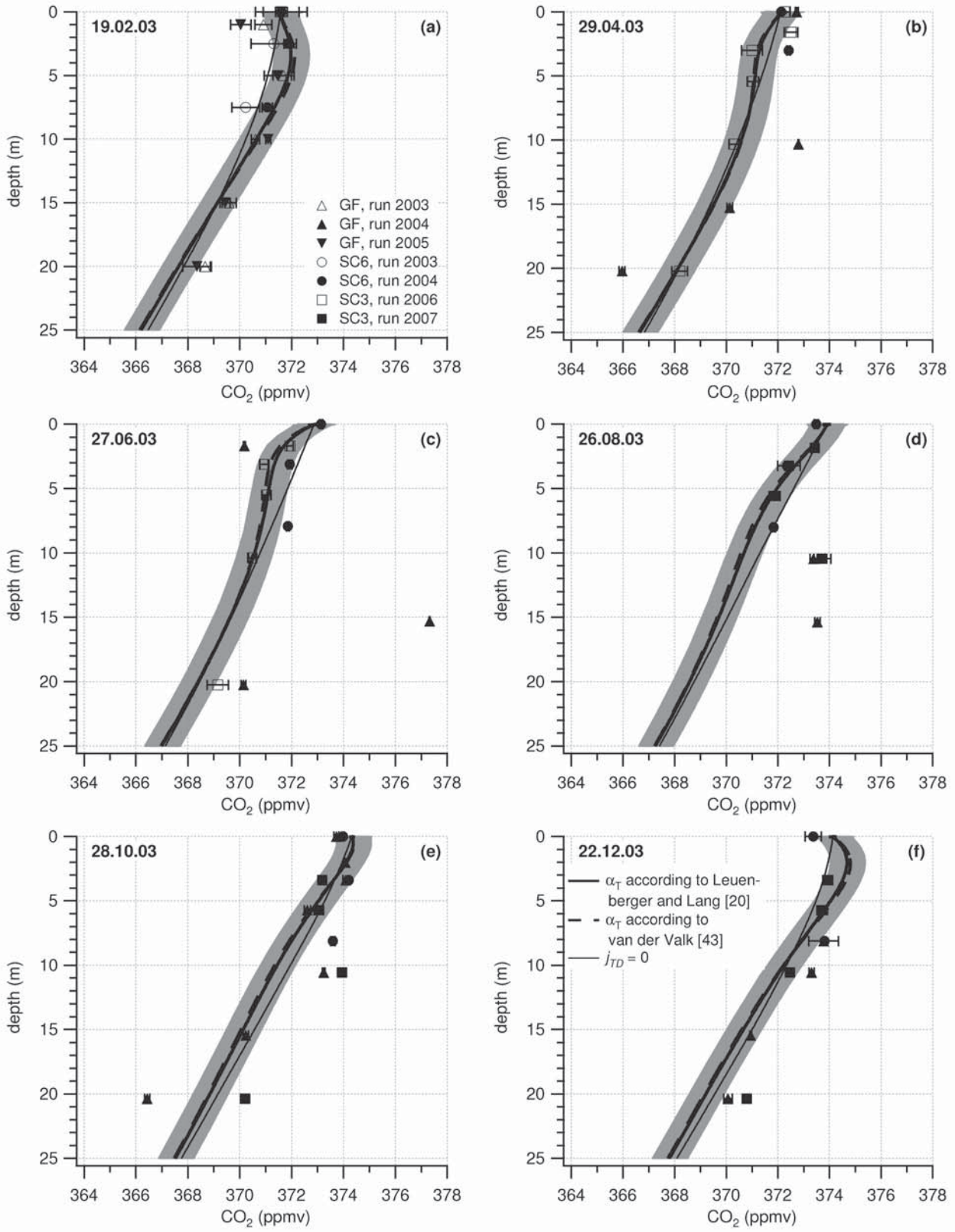


Figure 12: The same figure as Figure 10 but for CO₂. The corresponding Figure in section 4.2 is Figure 7.