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Diffusion of stable isotopes in polar firn and ice: the isotope effect in firn diffusion

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Abstract: Ice core records are often affected by post-depositional processes that need to be better understood to prevent wrong interpretation of the data. Records of stable isotopes are affected by diffusion both in the firn and in the deeper ice. We present a quantitative theory for diffusion in firn that applies the measured tortuosity factors for O₂ and CO₂ in firn to the diffusing water vapor. Because of different fractionation factors, the theory predicts stronger smoothing for $\delta^{18}\text{O}$ than for δD , in excellent agreement with our data. This effect opens up the possibility for using detailed isotope records to estimate paleotemperatures in deeper strata. We show that this differential smoothing can create an artificial annual cycle in deuterium excess, which was not present at the time of deposition. It also increases the slope observed in high resolution data series between δD and $\delta^{18}\text{O}$ variations. For the annual cycles, we observe that this slope can increase from 8 at the surface up to 11 in deeper firn. In the Holocene ice for the GRIP core, we observe much stronger smoothing than predicted from diffusion in solid ice; this suggests an anomalous diffusion process in glacier ice. Possible models for this excess diffusion are discussed i.a., in terms of the thickness of water films on grain boundaries and in veins.

1 Introduction

Deep ice cores provide a wealth of information on past environmental changes [Dansgaard *et al.*, 1993; Grootes *et al.*, 1993; Johnsen *et al.*, 1972; Johnsen *et al.*, 1997; Jouzel *et al.*, 1987; Petit *et al.*, 1997].

Here we discuss only the stable isotope records, δD and $\delta^{18}\text{O}$, which are considered as primary records for obtaining information on paleotemperatures [Cuffey *et al.*, 1995; Johnsen *et al.*, 1995; Jouzel *et al.*, 1997]. In this paper we will primarily address changes of isotope profiles that

occur in firn and ice after snow deposits on the surface.

The isotopic ratios measured in water R_i are defined as the ratio of H_2^{18}O (or HD^{16}O) concentration to the H_2^{16}O concentration. Isotopic ratios are normally expressed as the relative deviation δ_i from a standard having the isotopic ratios S_i . We can thus write $\delta_i = R_i/S_i - 1$ and use this function in differential equations, like equation (1) below, which usually use the actual concentrations. The deuterium excess, $d = \delta\text{D} - 8 \cdot \delta^{18}\text{O}$, [Craig, 1961; Dansgaard, 1964] is another important parameter we use. Its definition reflects the observed slope of 8 between the natural changes of δD and $\delta^{18}\text{O}$ in meteoric water. This parameter is mainly dependent on the physical conditions in the source area [Johnsen *et al.*, 1989; Merlivat and Jouzel, 1979; Vimeux *et al.*, 1999] for mid and high latitude precipitation.

After deposition, the snow is transformed into firn and ice through a densification process that gradually compresses the strata and reduces the thickness of the annual layers. The isotope profiles are not only being affected by this compression, but also by a strong smoothing process that gradually removes the high frequency variations. The annual cycle is thus weakened and can disappear entirely. Below the firn zone the thinning proceeds due to the general strain rates, and diffusion in solid ice continues to smooth the remaining isotope signals. The smoothing of annual δ cycles in the firn was described first by C. C. Langway in his work on the Site-2 core in NW-Greenland [Langway, 1967] and later by W. Dansgaard for several sites in Greenland [Dansgaard *et al.*, 1973]. Models of firn diffusion that assume diffusion in the vapor

phase as the dominant mixing process have been proposed [Cuffey and Steig, 1998; Johnsen, 1977; Johnsen *et al.*, 1999; Whillians and Grootes, 1985]. We present here a model that includes the tortuosity factor [Schwander *et al.*, 1988] for diffusion in porous media; it predicts different smoothing for δD and $\delta^{18}\text{O}$ and is generally in excellent agreement with our data.

The original pre-diffusion δ signal can be estimated using several inversion methods [Bolzan and Pohjola, in press; Cuffey and Steig, 1998; Johnsen, 1977]. This helps increase the accuracy of absolute dating when counting the annual δ cycles [Hammer *et al.*, 1978; Johnsen, 1977; Johnsen *et al.*, 1997] and improves the correlation with meteorological climate series [Bolzan and Pohjola, in press].

Diffusion in the deeper ice depends on glacial flow and the diffusivity of solid ice, as estimated from the in situ temperature history of the layers being considered [Hammer *et al.*, 1978; Johnsen, 1977; Whillians and Grootes, 1985]. We found that ice diffusion in most of the Holocene ice of the GRIP core is much faster than predicted using the Ramseier ice diffusivity data [Johnsen and Andersen, 1997; Johnsen *et al.*, 1999; Ramseier, 1967]. This anomalous diffusion is basely present in the GRIP glacial ice [Johnsen and Andersen, 1997], an observation that suggests impurities significantly affect diffusion in the ice.

2 Diffusion of stable isotopes

2.1 Mathematical formulation

To describe the smoothing of stable isotope profiles from ice cores, we introduce a coordinate system with a

vertical z -axis and an origin that follows a horizontal layer from the surface as it sinks into the firn and ice matrix. The medium in the new coordinate system is assumed to have uniform vertical strain rate $\dot{\epsilon}_z(t)$ and a diffusivity for each isotopic species $\Omega(t)$ that depends on temperature and firn density through the age parameter t . The age t , the time since burial, is known as a function of depth from a deformation model valid for the particular coring site. The model depends mainly on the accumulation rates and densities. With these assumptions, the diffusion equation for the smoothing of an initial stable isotope profile $\delta = \delta(z, 0)$ is

$$\frac{\partial \delta}{\partial t} = \Omega(t) \frac{\partial^2 \delta}{\partial z^2} - \dot{\epsilon}_z(t) z \cdot \frac{\partial \delta}{\partial z}, \quad (1)$$

where $\delta = \delta(z', t)$ is the resulting smoothed and compressed δ profile after time t since deposition and z' accounts for the vertical compression of the original profile during time t according to

$$z' = z \cdot \exp\left(-\int_0^t \dot{\epsilon}_z(t') dt'\right). \quad (2)$$

In solving equation (1) in a homogeneous, uniformly-deforming medium, it is convenient to introduce the diffusion length σ to describe diffusion and its smoothing effects [Johnsen, 1977]. This new parameter is determined by solution of

$$\frac{d\sigma^2}{dt} - 2 \cdot \dot{\epsilon}_z(t) \cdot \sigma^2 = 2 \cdot \Omega(t), \quad (3)$$

where t is age, $\dot{\epsilon}_z(t)$ is the vertical strain rate, and $\Omega(t)$ the diffusivity. After σ is determined it is used as the standard

deviation in the normalized form of the Gaussian clock $\exp(-0.5 \cdot z'^2 / \sigma^2)$. The latter is then folded into the original compressed profile $\delta = \delta(z', 0)$ to calculate the smoothed profile $\delta = \delta(z', t)$. The amplitude A of a harmonic cycle of final wavelength λ is influenced by diffusion through

$$A = A_0 \exp\left(-\frac{1}{2} k^2 \cdot \sigma^2\right), \quad (4)$$

where A_0 is the initial amplitude and $k = 2\pi/\lambda$ is the wave number. λ and σ are known as functions of depth (or age) from the age-deformation model and from the solution of equation (3), respectively. Figure 1 shows the relative amplitude A/A_0 of harmonic cycles of different wavelengths λ exposed to diffusion with a given diffusion length σ .

Similarly, the power spectral densities $P(k)$ of the smoothed data depends on the diffusion length as

$$P(k) = P_0(k) \exp(-k^2 \cdot \sigma^2), \quad (5)$$

where $P_0(k)$ is the spectral density of the compressed profile without diffusion. The diffusion length σ can be estimated from Eqs. (4) and (5) using estimates of the amplitudes of the annual cycle and the spectral densities for the data series, respectively. The latter method seems to work, because the high wave number part of the original spectral density $P_0(k)$ is almost white, (i.e., independent of k). This whiteness is due to the strong depositional noise [Fisher et al., 1985; Johnsen et al., 1997] normally encountered in high resolution ice core δ series.

The above formulation of the diffusion process in moving firn and ice is valid for

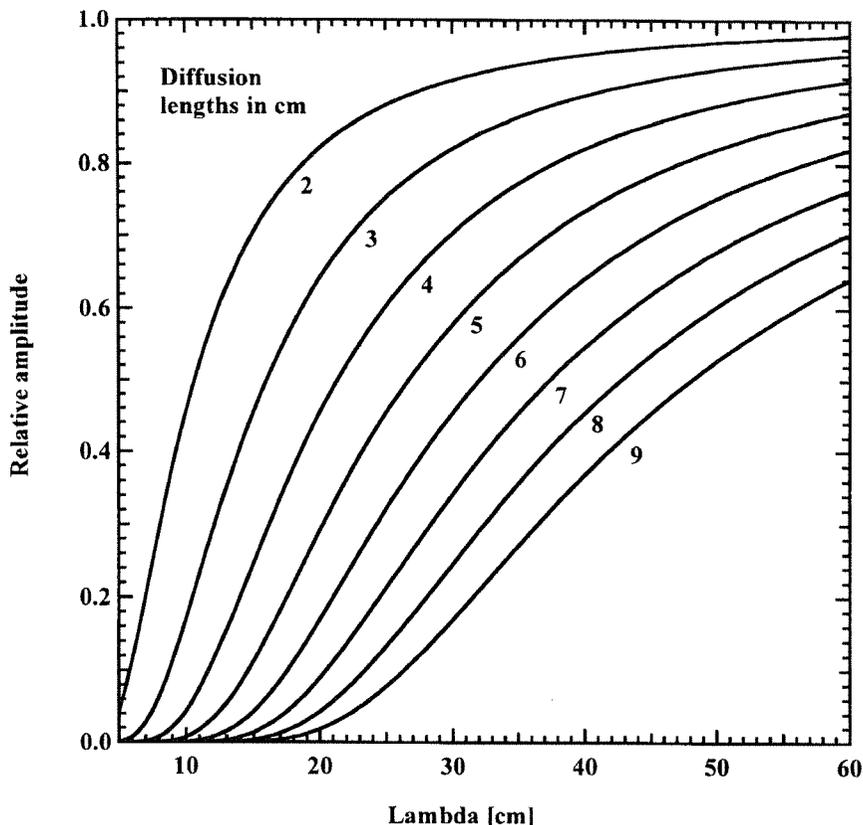


Figure 1: The damping of the amplitude of a harmonic cycle of wavelength λ smoothed by a specified diffusion length.

any other diffusing constituent; one only needs the diffusivity to put in equation (3).

2.2 Firn diffusion

After deposition on the surface, several of the constituents in the ice may undergo changes related mostly to diffusional processes. These changes may not significantly affect the long-term climatic or environmental information contained in the cores, but some of the important annual cycles used for dating can weaken, and eventually vanish, at depth.

2.2.1 The firn diffusivity Ω_f

During densification, when the firn density increases with depth, a substantial intergranular exchange of water molecules

takes place through the vapor phase in the open interconnected pores. The firn diffusivity, Ω_f , used in equations (1) and (3), for diffusion of water molecules in firn was previously modeled without the important tortuosity factor τ and without properly distinguishing between the two heavy isotopic species of the water molecule [Johnsen, 1977; Whillians and Grootes, 1985]. The tortuosity factor accounts for the shape of the open channels in the firn and is defined by $\Omega_e = \Omega_a / \tau$ where Ω_a is the normal diffusivity in air for the diffusing constituent and Ω_e is the effective diffusivity within the pore space. The reduced cross section available for diffusive

fluxes must then be accounted for separately; it is given by the porosity,

$$\phi = 1 - \frac{\rho}{\rho_{ice}}, \quad (6)$$

where ρ and ρ_{ice} are the densities for firm and ice, respectively. Because firm is a porous medium the diffusivity for gases in firm becomes $\Omega_p = \phi \Omega_a / \tau$ [Weissberg, 1963]. The firm diffusivity has been measured in artificial firm blocks [Jean-Baptiste et al., 1998] resulting in direct determination of the tortuosity factors, where also an excellent discussion is given on most aspects of the firm diffusion process.

We will now describe a firm diffusion model [Johnsen, 1977] in which the residence times for water molecules in the vapor phase, Δt_v , and in the solid ice, Δt_s , are used to evaluate the rate of change for σ^2 . When a water molecule is in the pore space, it can absorb on an ice surface and desorb back into the vapor repeatedly until it finally gets buried into the ice. The residence time Δt_v is the mean time a molecule is freely moving around as vapor disregarding the time it is temporarily stuck on ice surfaces. Similarly the residence time Δt_s in the solid ice is the mean time a molecule spends deeper in the ice, not counting the time molecules have on the surface.

In this model, the degree of smoothing depends on the time each molecule is in the pore space. Because annual isotopic cycles can completely vanish in firm cores, we assume that virtually all molecules in the firm (excluding ice layers) repeatedly transfer between the vapor and solid phases.

In the following we will use an index i on all parameters that relate to either of the

heavy molecules $H_2^{18}O$ or $HD^{16}O$ ($i=18, D$). To improve clarity we also use primed parameters for the heavy molecules; for instance, N' and n' are the total number and concentration of the heavy molecules, respectively. Unprimed, they refer to the normal water molecule $H_2^{16}O$.

Our aim is to evaluate the rate of change for the squared diffusion length, σ_i^2 and then use equation (3) with $\dot{\epsilon}_z(t) = 0$ to calculate Ω_{fi} . In this case a constant diffusivity Ω_{fi} gives

$$\frac{d\sigma_i^2}{dt} = 2 \cdot \Omega_{fi} \quad \text{and} \quad \sigma_i^2 = 2 \cdot \Omega_{fi} \cdot t. \quad (7)$$

During one of its periods in vapor phase, Δt_{vi} , a molecule will change its mean square vertical position according to equation (3) as

$$\Delta\sigma_i^2 = 2 \cdot \Omega_{ei} \cdot \Delta t_{vi}. \quad (8)$$

During a time period equal to the residence time Δt_{si} for molecules in the firm grains, most molecules have also spent one period in the pore space and have thus changed their vertical position according to equation (8); therefore,

$$\frac{d\sigma_i^2}{dt} \cong \frac{\Delta\sigma_i^2}{\Delta t_{si}} = 2 \cdot \Omega_{ei} \cdot \frac{\Delta t_{vi}}{\Delta t_{si}} = 2 \cdot \frac{\Omega_{ai}}{\tau} \cdot r_i, \quad (9)$$

where r_i is the ratio between the residence times for the isotope in the pores and ice, respectively. It is shown later that $r_i \ll 1$.

To determine r_i we initially assume like Whillans and Grootes that the firm grains are well mixed and in isotopic equilibrium with the vapor. The transfer rate between vapor and ice for the heavy

isotope is assumed to be proportional to their concentrations n'_{vi} and n'_{si} in vapor and ice, respectively.

To continue, we introduce several similar quantities with indices s and v to refer to the solid and vapor phases, respectively. We denote by n_v and n_s the concentrations of the normal light isotope $H_2^{16}O$. The total number of the light and of the heavy isotopes in 1 kg of firn is denoted by N_v , N_s and N'_{vi} , N'_{si} , respectively. The rate of change of N'_{vi} due to transfer from vapor to ice is thus

$$\frac{dN'_{vi}}{dt} = -k_{vi} \cdot n'_{vi} = -k_{vi} \cdot \frac{N'_{vi}}{V_p} = -\frac{N'_{vi}}{\Delta t_{vi}}, \quad (10)$$

where V_p is the specific pore space volume $1/\rho_f - 1/\rho_{ice}$, k_{vi} is a constant and Δt_{vi} is the residence time of vapor molecules in pore space as defined above. Similarly the rate of change for N'_{si} is

$$\frac{dN'_{si}}{dt} = -k_{si} \cdot n'_{si} = -k_{si} \cdot \frac{N'_{si}}{V_s} = -\frac{N'_{si}}{\Delta t_{si}}, \quad (11)$$

where the ice specific volume $V_s = 1/\rho_{ice}$, k_{si} is a constant and Δt_{si} is the residence time in the ice. Under steady-state conditions the transfer rates from equations (10) and (11) must be equal; giving the important and well known result:

$$r_i = \frac{\Delta t_{vi}}{\Delta t_{si}} = \frac{N'_{vi}}{N'_{si}}, \quad (12)$$

where the parameter r_i is from equation (9).

As we have assumed isotopic equilibrium between vapor and ice we have

$$\frac{N'_{vi}}{N_v} = \frac{1}{\alpha_i} \cdot \frac{N'_{si}}{N_s} \quad \text{or} \quad \frac{N'_{vi}}{N'_{si}} = \frac{1}{\alpha_i} \cdot \frac{N_v}{N_s}, \quad (13)$$

where α_i is the fractionation factor for the isotopic ratios in water vapor over ice.

Combining equation (7), that defines Ω_{fi} , and equations (9), (12) and (13), a useful expression for Ω_{fi} is obtained:

$$\Omega_{fi} = \Omega_{ei} \cdot r_i = \frac{\Omega_{ai}}{\tau} \cdot \frac{1}{\alpha_i} \cdot \frac{N_v}{N_s}. \quad (14)$$

The number of molecules in the solid phase of 1 kg of firn is

$$N_s = \frac{N_A}{m}, \quad (15)$$

where m is the molar weight of water and N_A Avogadro's number.

Using the ideal gas law, the number of molecules in the vapor phase is

$$N_v = \frac{N_A \cdot p \cdot V_p}{R \cdot T}, \quad (16)$$

where p is the saturation pressure over ice at absolute temperature T , and R the gas constant. Combining equations (14), (15) and (16), and also the definition of pore space volume $V_p = 1/\rho_f - 1/\rho_{ice}$, the isotopic diffusivity of firn, Ω_{fi} , is

$$\Omega_{fi} = \frac{m \cdot p \cdot \Omega_{ai}}{R \cdot T \cdot \alpha_i \cdot \tau} \left(\frac{1}{\rho} - \frac{1}{\rho_{ice}} \right). \quad (17)$$

The residence times have dropped out of the analyses.

For the saturation vapor pressure over ice, we use $p = 3.454 \cdot 10^{12} \exp(-6133/T)$ Pa.

The tortuosity factor in firm is assumed to be only a function of the firm density ρ [Jean-Baptiste et al., 1998; Schwander, 1996; Schwander et al., 1988]. A fit to the measured tortuosity factors of Schwander et al. [1988] is conveniently expressed as a function of density by

$$\frac{1}{\tau} = 1 - b \cdot \left(\frac{\rho}{\rho_{ice}} \right)^2 \quad \rho \leq \frac{\rho_{ice}}{\sqrt{b}}, \quad (18)$$

where $b = 1.30$ and $1/\tau = 0$ for $\rho > 804.3 \text{ kg/m}^3$, the effective pore-close-off density for diffusive fluxes. This is also close to the density at which the permeability of firm rapidly drops [Schwander, 1996]. The tortuosity factors measured in Jean-Baptiste et al. [1998] firm block experiment are in good overall agreement with the values given by equation (18). For diffusivity of water vapor in air, we adopt from [Hall and Pruppacher, 1976]

$$\Omega_a = 0.211 \cdot \left(\frac{T}{T_0} \right)^{1.94} \cdot \left(\frac{P_0}{P} \right), \quad (19)$$

in cm^2/s , where T is absolute temperature, P the ambient pressure (atm), $T_0 = 273.15 \text{ K}$ and $P_0 = 1 \text{ atm}$. Equation (19) should be accurate to about 5 to 10 %. For the diffusivity of the heavy isotopic water species in air we have from [Merlivat and Jouzel, 1979] that $\Omega_{a18} = \Omega_a/1.0251$ and $\Omega_{aD} = \Omega_a/1.0285$. Of the two fractionation factors $\alpha_{18} = 0.9722 \exp(11.839/T)$ [Majoube, 1970] and $\alpha_D = 0.9098 \exp(16288/T^2)$ [Merlivat and Nief, 1967], α_D dominates and is highly temperature dependent. This implies that δD profiles have less firm smoothing than $\delta^{18}\text{O}$ profiles.

According to equation (17), at $-32 \text{ }^\circ\text{C}$ and for firm density of 600 kg/m^3 the firm diffusivity for H_2^{18}O is $5 \cdot 10^{-5} \text{ m}^2/\text{yr}$ and for HD^{16}O $4.2 \cdot 10^{-5} \text{ m}^2/\text{yr}$. For ice at the same temperature the diffusivity is $3.5 \cdot 10^{-9} \text{ m}^2/\text{yr}$, which justifies to disregard ice diffusion in the above firm diffusion model. The strain rates used to solve equation (3) were obtained from the Herron-Langway densification model [Herron and Langway, 1980].

We now introduce the tortuosity factor τ and the effective diffusivity Ω_e into the otherwise most rigorous derivation by Whillans and Grootes [1985] for the firm diffusivity Ω_f . Our aim is to show that this more rigorous approach leads to the same results as the approach adopted here that includes diffusion lengths and residence times of water molecules in ice and pore space. Only two changes need to be introduced to the Whillans and Grootes theory. First, their diffusivity parameter used to calculate diffusive fluxes in the firm

$$\Omega = \Omega_a \cdot \left(1 - \frac{\rho}{\rho_c} \right), \quad \rho \leq \rho_c, \quad (20)$$

where ρ_c is the density of impermeable ice, must be replaced by the diffusivity for porous media:

$$\Omega_{pi} = \frac{\Omega_{ai}}{\tau} \cdot \left(1 - \frac{\rho}{\rho_{ice}} \right). \quad (21)$$

Second, the isotope offset $\Delta\delta = \delta_f - \delta_v \cong 1 - \alpha$ should instead be given by $(1 + \delta_f) = \alpha_i \cdot (1 + \delta_v)$. After some algebra, these substitutions give a firm diffusivity Ω_{fi} as implied by a new equation (12) in Whillans

and Grootes [1985] identical to that given by equation (17) above.

The Whillians and Grootes theory has been tested against annual cycles in detailed $\delta^{18}\text{O}$ data from the GISP2B shallow core [Cuffey and Steig, 1998]. Cuffey and Steig found the theory to predict too strong damping of the annual $\delta^{18}\text{O}$ cycles, unless they used a value of 730 kg/m^3 for ρ_c . In fact the model presented by Cuffey and Steig predicts firn diffusion lengths nearly equal to those discussed here for H_2^{18}O . However, this is not entirely consistent because firn at the GISP2 site becomes impermeable at densities close to 822 kg/m^3 [Martinerie et al., 1994]. Including the tortuosity factor as described above can remove this physical inconsistency.

The above analysis assumed that exchange between vapor and ice was facilitated by rapid diffusive mixing of firn grains [Whillians and Grootes, 1985] in agreement with Jean-Baptist et al. [1998] for grains less than 1 mm in diameter. However, this assumption does not hold at the mean temperatures of $-32 \text{ }^\circ\text{C}$ prevailing in Central Greenland for the coarse grained summer layers. A diffusion length of approximately 0.7 mm is needed to mix isotopically a typical firn grain of 2 mm diameter. At temperatures of $-32 \text{ }^\circ\text{C}$ this would take some 50 to 70 years resulting in limited smoothing of these layers contrary to observations of our Greenland cores. Thus there could be another physical process that speeds up the exchange between vapor and ice.

The curvature of the firn ice surface is very nonuniform and will thus create varying equilibrium vapor pressures over the ice surface. The ice matrix would thus be trapping water molecules from the vapor in the open pores at the low pressure sites

and losing molecules at the high pressure sites into pore space. This process corresponds to grain boundary migration and should speed up molecular exchange between vapor and ice. The strong smoothing observed for isotopic profiles in firn implies that virtually none of the molecules in the solid phase can stay there for too long, which justifies the introduction of residence times for the molecules in the solid phase, as was done above. Assuming grain boundary migration as the main process for vapor ice exchange, and using similar analysis as above when we assumed rapid internal grain mixing, results in the same firn diffusivity Ω_f as that in equation (17).

2.2.2 The firn diffusion model

Assuming isothermal firn layers, we solved equation (3), using the densification model developed by Herron and Langway [Herron and Langway, 1980]. To accurately fit Central Greenland density profiles, we used 360 kg/m^3 for the surface density ρ_0 and scaled the parameters k_0 and k_1 in the Herron-Langway densification model by the factors 0.85 and 1.15, respectively. As the firn diffusivity Ω_f (equation 17) is known as a function of the firn density, which in turn is known as a function of time, equation (3) can be transformed using the density ρ as the independent variable instead of the time t . This leads to analytical solutions for the firn diffusion lengths $\sigma(\rho)$ where ρ represents the firn density. The full solution will not be given here but the resulting final diffusion lengths σ_{18} for the H_2^{18}O molecule, expressed as a function of temperature and accumulation rate, are almost identical to the ones shown in Fig. 6 in [Cuffey and Steig, 1998].

An important result of our analytical model is that the ratio between the isotopic diffusion lengths in firm only depends on temperature:

$$\frac{\sigma_{f18}}{\sigma_{fD}} = \sqrt{\frac{\alpha_D}{\alpha_{18}}} \quad (22)$$

Figure 2 shows the modeled firm diffusion lengths for both isotopes as a function of depth for GRIP in Central Greenland and for all Dome C in East-Antarctica [Lorius et al., 1981]. The diffusion length rises rapidly from the

surface and goes through a maximum when the negative strain rates overcome its growth by diffusion. The further lowering of σ_{fi} below the pore closure depth at about 60 m is only due to the vertical strain rates because the ice diffusion is negligible. The two isotopes H_2^{18}O and HD^{16}O have different diffusion lengths. Despite the extremely low 2.7 cm of ice/year accumulation rate used in the calculations, the diffusion lengths for Dome C are much lower due to the very cold temperature of $-55\text{ }^\circ\text{C}$; the accumulation at GRIP is 23 cm of ice/year and the mean annual temperature is $-31.6\text{ }^\circ\text{C}$.

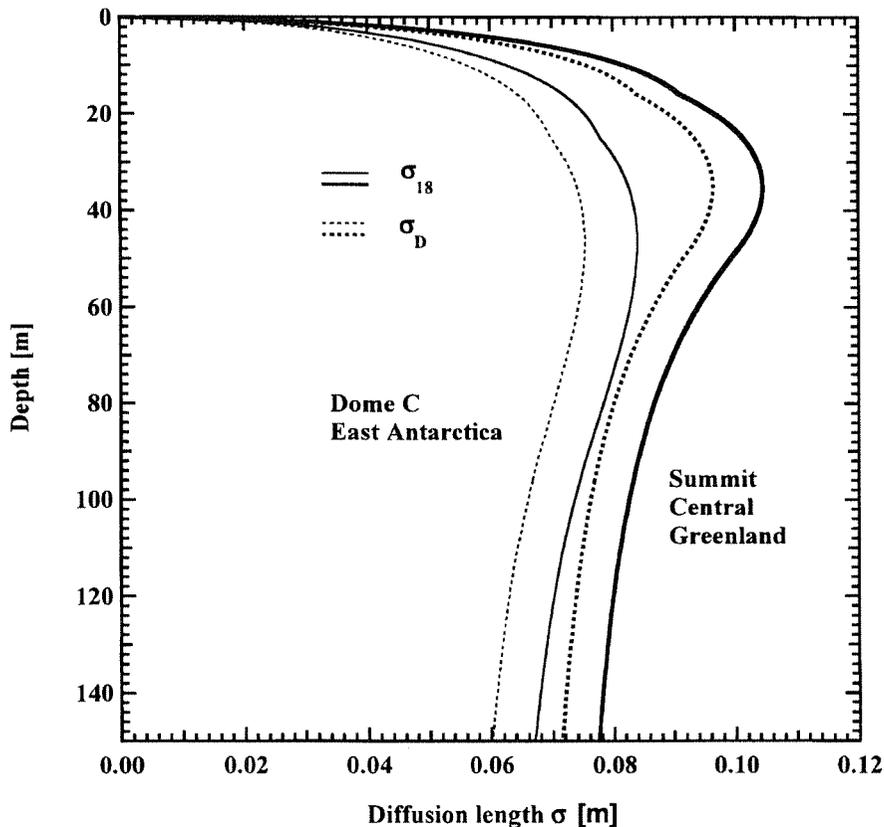


Figure 2: Modeled firm diffusion lengths as a function of depth for both heavy molecule species H_2^{18}O and HD^{16}O at the indicated sites. Below the pore closure depth at some 60 m the diffusion lengths are only shortened by layer compression because the ice diffusion is negligible at these low temperature sites.

Figure 3 shows the amplitudes of the annual $\delta^{18}\text{O}$ cycle (solid stepped curve) as determined in 5 meter long core increments of the NGRIP core using a version of the MEM spectral analysis technique that integrates analytically the peaks in the spectrum [Johnsen and Andersen, 1978]. The initial amplitude is close to 6 ‰ at the surface and rapidly decreases to 0.14 ‰ at a depth of 55 meters where the open pores have nearly closed off. This corresponds to a final diffusion length of 8.5 cm of ice equivalent and implies that each water molecule moved a distance of 8.5 cm vertically from its original, stratigraphic

position on average. The estimated amplitudes agree quite well with the model output shown with the smooth solid curve. The dotted curves show the annual layer thickness determined by the MEM spectral method (stepped curve) which agrees well with the model (smooth curve). The drastic reduction in the annual amplitudes is due to the low ice-accumulation rate of 19.5 cm/year at NGRIP and the relatively high diffusion length of 8.5 cm of ice equivalent. As expected from equation (4) there is a positive correlation between the amplitude and the annual layer thickness (λ) data.

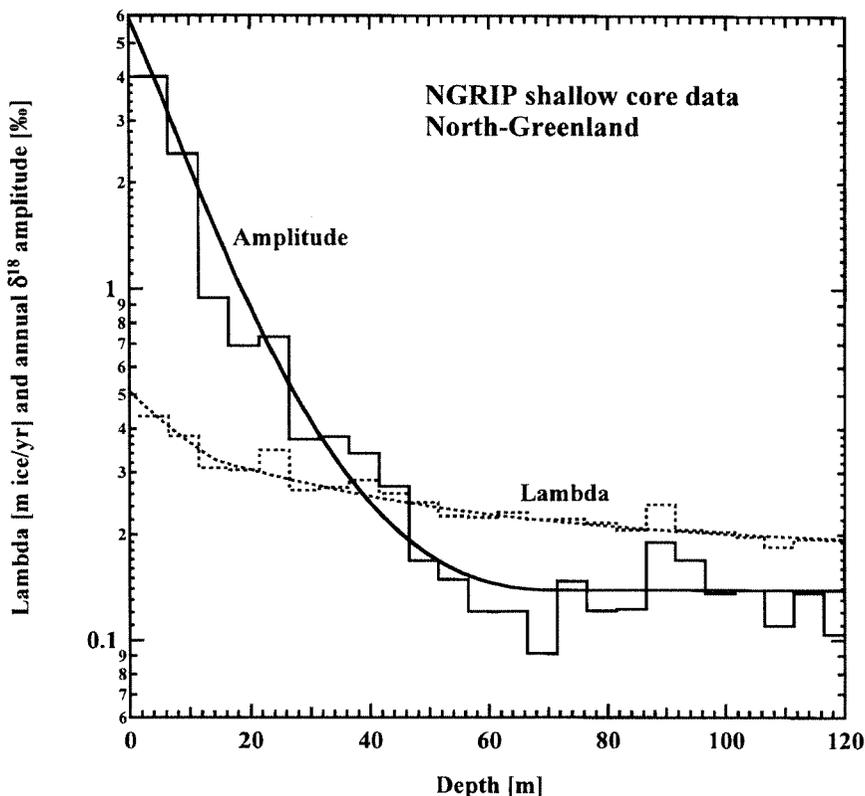


Figure 3: Solid lines: amplitude profiles for the $\delta^{18}\text{O}$ annual cycle at NGRIP [Dahl-Jensen et al., 1997], based on MEM spectral analysis of consecutive 5-m core increments; the smooth curve is the modeled amplitude profile. Dotted lines: the measured and modeled annual layer thickness profiles (λ) using the same method and same 5-m increments; the smooth curve is modeled results.

2.2.3 The isotope effect

Due to a higher vapor ice fractionation constant for HD^{16}O , and thus relatively fewer HD^{16}O diffusing vapor molecules, the firm diffusivity Ω_f is smaller for δD than for $\delta^{18}\text{O}$. This means less smoothing of the δD profiles and that the annual δD amplitude grows during firmification relative to the annual $\delta^{18}\text{O}$ amplitude, which is initially 1/8th of the δD amplitude. This has implications for the deuterium excess signal $d = \delta\text{D} - 8 \cdot \delta^{18}\text{O}$ [Dansgaard, 1964]. Close to the surface the annual excess signal in Greenland lags the annual isotope signals

by some 90° [Johnsen et al., 1989]. This original signal decays due to the general smoothing, while a new type of annual excess signal builds up due to the differential smoothing of δD and $\delta^{18}\text{O}$. The latter, artificial signal is in phase with the annual isotope signal and will dominate if the general smoothing is strong enough. This effect was observed both in our GRIP data and in GISP2 isotope data [J. White personal communication] and supports the firm diffusion model presented here.

Figure 4 shows 2.5 cm resolution isotope data from between 30 and 40-m

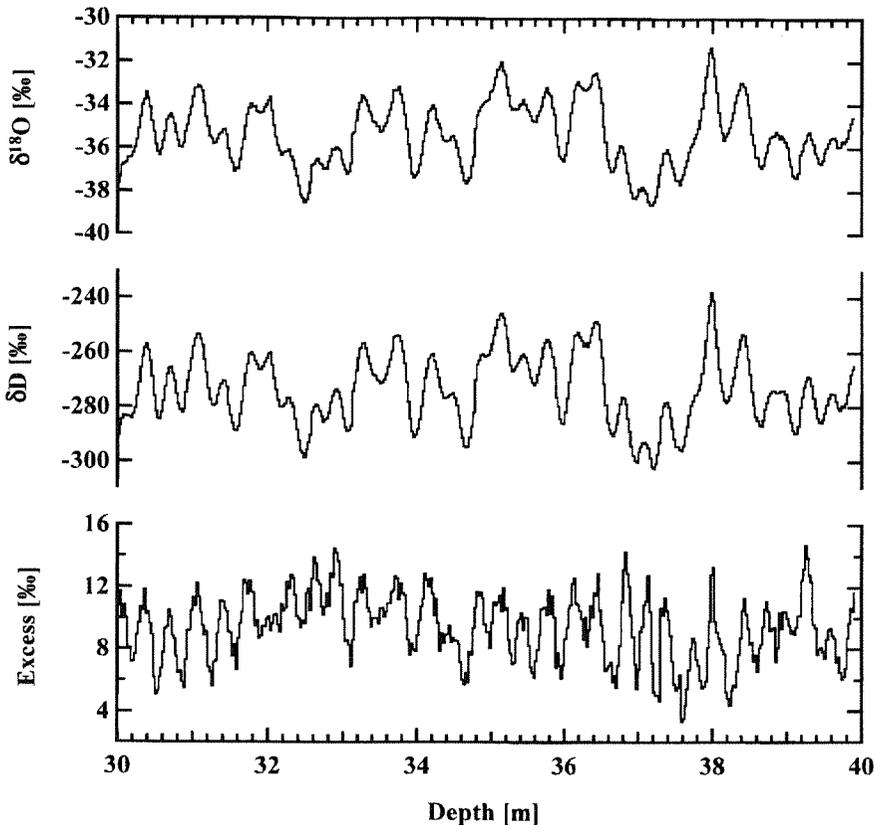


Figure 4: Detailed, 2.5 cm resolution, isotope profiles showing $\delta^{18}\text{O}$, δD and deuterium excess, from the top of the GRIP deep core [Johnsen et al., 1997]. The high summer peak at 38 m depth is due to a summer melt layer from 1889, a layer found in all shallow cores from Greenland. The $\delta^{18}\text{O}$ was measured at the Department of Geophysics, University of Copenhagen and the δD at the LSCE in Saclay.

depth in the GRIP89-3 core [Johnsen *et al.*, 1997], which are strata deposited from 1883 AD to 1914 AD. At this depth all annual isotope amplitudes have decayed to about 10 % of their original signal except the deuterium excess, which apparently retained about 60 % of the original signal. The annual excess signal was generally in phase with the $\delta^{18}\text{O}$ and δD annual signals. At the surface the $\Delta\delta\text{D}/\Delta\delta^{18}\text{O}$ slope was close to 8, but the data in Figure 4 had a larger value due to relative strengthening of the δD annual amplitude. After band pass filtering, this slope was 10.4 while our model gave 11.5. In this case the correlation plot is dominated by the higher accumulation years with less overall damping. This partly explains the observed difference.

Spectral analysis of the data in Figure 4 provides more quantitative results to compare with our model. The MEM power densities are shown in Figure 5 with P_{18} for $\delta^{18}\text{O}$ and P_{D} for δD . The annual peaks at 3.1 cycles/m are significant. At higher wave numbers, the spectral densities drop rapidly down to the white noise level corresponding to measurement errors of 0.6 % for δD and 0.08 % for $\delta^{18}\text{O}$ as expected. This suggests that all firn grains took full part in the cyclic exchange between vapor and ice as assumed in section 2.2.1. To facilitate the comparison with the δD spectral densities, P_{D} , the spectral densities P_{18} for $\delta^{18}\text{O}$ were multiplied by 64. Up to the annual peak, these two curves increasingly deviate. The stronger damping of the $\delta^{18}\text{O}$ signal is due to the larger diffusion length for H_2^{18}O molecules in accordance with equation (5).

The insert in Figure 5 shows $\ln(P_{\text{D}}/P_{18})$ versus k^2 as well as a linear fit to the data from $k^2 = 0$ including the annual peak at

$k^2 = 360 \text{ rad}^2/\text{m}^2$. Using equation (5) this differential damping in the spectral regime is

$$\ln(P_{\text{D}}/P_{18}) = C + \Delta\sigma^2 \cdot k^2, \quad (23)$$

where $C = 2 \cdot \ln(\Delta\delta\text{D}/\Delta\delta^{18}\text{O})$, valid for the long term delta changes and $\Delta\sigma^2 = \sigma_{18}^2 - \sigma_{\text{D}}^2$. Our best fit line gives $C = 4.170$ and $\Delta\sigma^2 = 16.1 \text{ cm}^2$. This corresponds to a long term slope of 8.04 and a $\Delta\sigma = 4.01 \text{ cm}$. The estimated errors are less than 0.1 for the slope and 0.2 cm for $\Delta\sigma$. These results are in good agreement with the expected behavior of the isotopes and with our model results from Figure 2.

Generally, firn diffusion lengths are a function of both temperature and the initial accumulation rate. In a sufficiently cold environment the diffusion length from firnification will be a length scale locked in the deforming ice for a very long time. This raises the possibility of using diffusion lengths as paleoclimate indicators. Absolute values for either σ_{18} or σ_{D} will depend on both temperature and accumulation rate due to the physics of densification and the diffusion rate (Fig. 6 of Cuffey and Steig, 1998). Whether or not variations in diffusion length are caused by climate changes depends on the correlation between accumulation rate and temperature changes. The ratio $\sigma_{18}/\sigma_{\text{D}}$ should be preserved for a long time in cold enough environment and will thus measure paleoclimate more precisely. Equation (22) can constrain the climatic temperature if diffusion lengths for both $\delta^{18}\text{O}$ and δD are determined in an ice core segment, that has not been exposed to measurable diffusion since firnification.

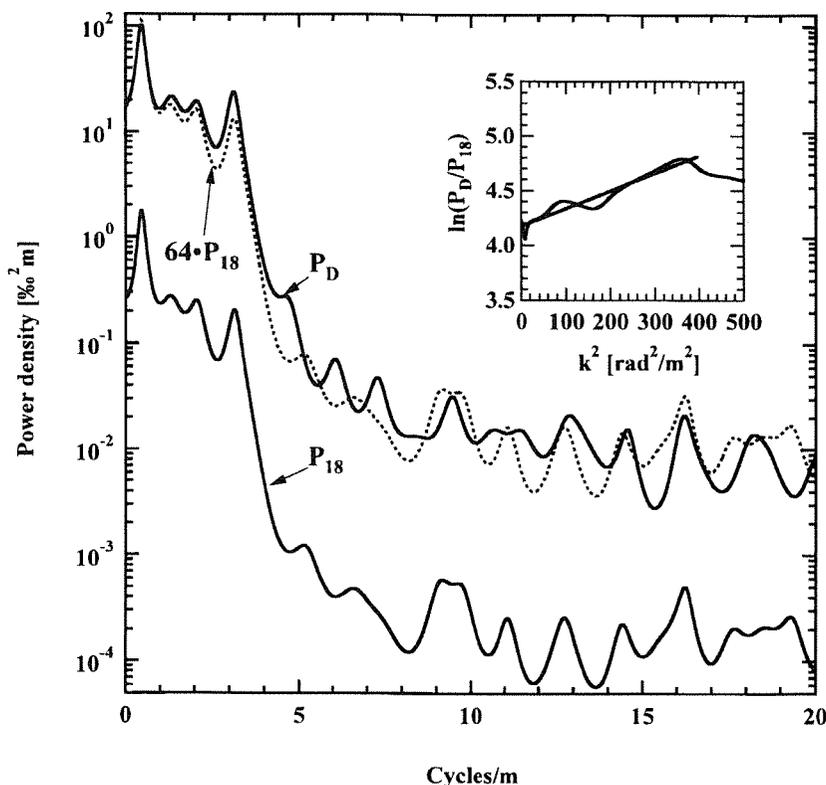


Figure 5: The MEM spectral densities with autoregressive order 40. The $\delta^{18}\text{O}$ and δD data from Figure 4 are marked as P_{18} and P_D , respectively. The annual peaks are the relatively large peaks at 3.1 cycles/m and the flat parts at higher wave numbers reflect the measuring errors. The spectral densities for $\delta^{18}\text{O}$ were multiplied by 64 and are shown as the dotted curve in order to highlight the smaller damping of the δD signal at higher wave numbers. This effect is also seen in the insert plot where k is the wave number. The slope of the best-fit straight line shown in the insert gives the difference for the square of the firm diffusion lengths for HD^{16}O and H_2^{18}O .

2.3 Ice diffusion

Below the firm layers, normal self-diffusion in ice single crystals is expected to dominate further smoothing. To obtain the temperature and strain rate history $\dot{\epsilon}_z(t)$ of layers at greater depths, together with the self diffusion constants Ω_{ice} from the modeled in situ temperature T K, we followed a layer from its transformation to ice and use a coupled temperature ice flow model [Johnsen et al., 1995]. Then equation (3) was solved. We use the measured $\Omega_{ice} = 3.96 \cdot 10^4 \exp(-7273/T)$ m^2/yr [Ramseier, 1967].

The ice diffusion calculations for the GRIP core, using the above ice diffusivity at -32 °C, showed that the diffusion length after firmification is only affected by vertical thinning in the Holocene part of the core. This implies that the amplitudes for the annual $\delta^{18}\text{O}$ cycle should be essentially constant for this period except for the Preboreal part where there was probably less accumulation.

MEM power spectra of detailed $\delta^{18}\text{O}$ profiles from five depth levels in the Holocene ice are shown in Fig. 6. The damping of the $\delta^{18}\text{O}$ signal due to diffusion

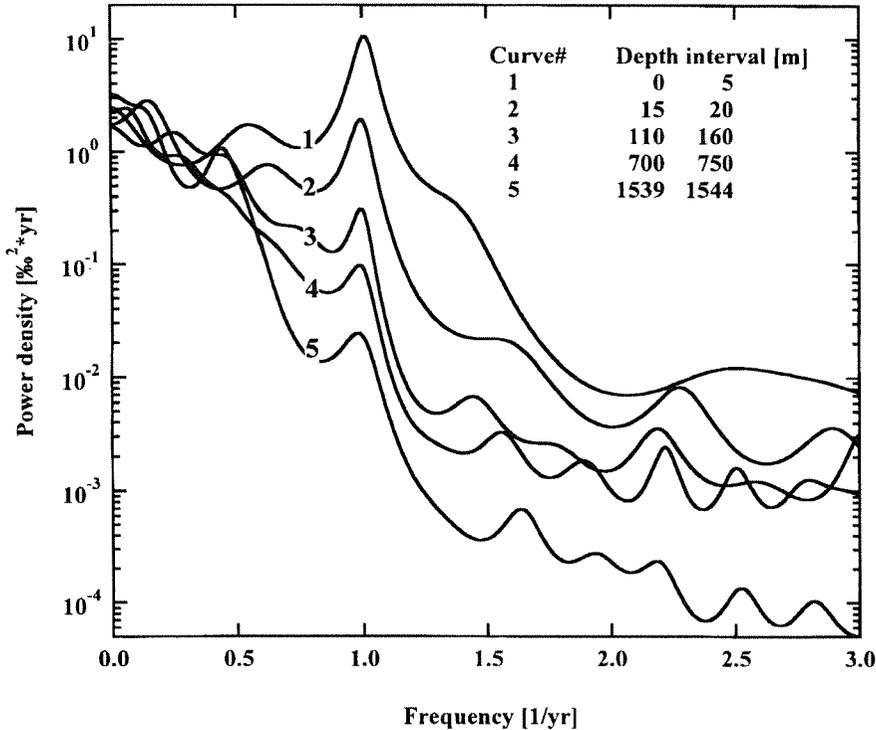


Figure 6: MEM spectral densities ($m=20$) for detailed $\delta^{18}\text{O}$ profiles at different levels in the Holocene part of the GRIP core. The increasing damping of the annual peaks with depth probably indicates an anomalous diffusion process in the Holocene ice instead of significant changes in the accumulation rates.

lowers the spectral densities at higher frequencies down to the nearly-flat white noise level of the measuring errors. The spectral peaks of the annual cycles are clearly discernible on the spectral ramp at 1 cycle/yr. Contrary to model predictions, they are increasingly attenuated by diffusion with depth. Analytical integration of the annual spectral peaks [Johnsen and Andersen, 1978] shows the mean amplitude of the annual $\delta^{18}\text{O}$ cycle is about 5.0 ‰ at the surface, 0.4 ‰ at 130 m, 0.24 ‰ at 725 m and 0.13 ‰ at 1540 m. Furthermore, these results are being supported by the direct determinations of the diffusion length in the GRIP Holocene ice [Johnsen and Andersen, 1997].

These findings are consistent with an ice diffusivity more than an order of magnitude higher than expected from the work of Ramseier on single crystal diffusion at the low ($-32\text{ }^{\circ}\text{C}$) temperature in the GRIP Holocene ice. We thus conclude that processes other than diffusion in single crystals occur in the ice matrix of natural polycrystalline ice. The processes responsible for the observed “excess diffusion”, are believed to be due to diffusion in water films or triple junction veins along the crystal boundaries. Diffusion in the grains and ongoing recrystallization helps to speed up the exchange of molecules between water and ice. The importance of diffusion in veins was pointed out by John Nye, who also

presented a model [Nye, 1998] that explains our observations for the Holocene GRIP ice; the model did not consider the high diffusive resistance in the assumed very narrow (1 μm) veins as discussed below. This type of diffusion processes could also expedite diffusion of ionic impurities and help induce chemical reactions as observed by J. P. Steffensen in the GRIP Eemian ice [Steffensen et al., 1997].

Assuming nearly constant accumulation rate in the Holocene period, the increased damping of the annual $\delta^{18}\text{O}$ cycle with depth (Figure 6) can be explained by assuming an excess diffusivity of $1.0 \cdot 10^{-7} \text{ m}^2/\text{yr}$ for the GRIP Holocene ice. However, the expected value for $-32 \text{ }^\circ\text{C}$ ice is almost 30 times smaller: $3.6 \cdot 10^{-9} \text{ m}^2/\text{yr}$ [Ramseier, 1967].

2.3.1 Models for the excess diffusion

We investigated a set of models for grain boundary diffusion that include ideas developed for the successful firn diffusion model. Instead of diffusion in the vapor phase and rapid exchange with the ice matrix we assumed diffusion in thin water films or veins surrounding the grains. Furthermore, we assume residence times for the molecules in the water phase as well as in the recrystallizing ice grains. We have also mixing inside the grains by diffusion. This is quite effective as typical mixing times, which are of the order of one hundred years, are much smaller than a typical age of Holocene ice. This justifies the use of an equation equivalent to (14) from section 2.2.1. The vapor-phase index v , was replaced by the water-phase index w , and Ω_{ai} was replaced by the self-diffusivity of super cooled water Ω_w . We estimate a tortuosity factor $\tau = 3$ due to the random orientation of the grain surfaces or veins and included a small isotope effect due to

different ice-water fractionation constants α_{swi} : 1.003 for $\delta^{18}\text{O}$ [O'Neil, 1968] and 1.028 for δD [Armason, 1969]. For the excess diffusivity we obtain

$$\Omega_{cbi} = \Omega_w \cdot \frac{N_w}{N_s \cdot \tau \cdot \alpha_{swi}}, \quad (24)$$

where N_w and N_s are the number of molecules in the liquid and solid phase, respectively. The index i refers to one of the heavy isotopes, which we ignore in the following and insert $\alpha_{swi} = 1$.

First we assume diffusion along grain boundaries in a super cooled water film of uniform thickness l_w . Assuming cubic formed crystal grains, the thickness of the water film needed for supporting the observed excess diffusivity is

$$l_w = \varphi \cdot l_c \cdot \frac{\Omega_{cb}}{\Omega_w}. \quad (25)$$

In equation (25), φ is mainly a geometric factor close to unity, l_c the mean crystal size, Ω_{cb} is the observed excess diffusivity and Ω_w the self-diffusivity of super cooled water at the in situ temperature and pressure. Inserting the following values in equation (25): $\varphi = 1.0$, $l_c = 3 \cdot 10^{-3} \text{ m}$ [Thorsteinsson et al., 1997], $\Omega_{cb} = 1.0 \cdot 10^{-7} \text{ m}^2/\text{yr}$ and $\Omega_w = 5.9 \cdot 10^{-3} \text{ m}^2/\text{yr}$ [Gillen et al., 1972] (a value 5 times smaller than for $0 \text{ }^\circ\text{C}$) gives $l_w = 50 \text{ nm}$.

A similar model assuming only diffusion in veins with uniform cross section of $S_w \text{ m}^2$ was also tested. This model might not have an exchange between liquid and solid as efficient as in the previous model, but we still assume it to be sufficiently strong. Assuming cubic shaped crystal grains, the single vein cross section

needed for maintaining the observed diffusivity Ω_{cb} is

$$S_w = \theta \cdot l_c^2 \cdot \frac{\Omega_{cb}}{\Omega_w}, \quad (26)$$

where θ , a geometric factor, is about 1.0. We insert $\theta = 1.0$, use the other constants as in the previous model and obtain $S_w = 1.5 \cdot 10^{-10} \text{ m}^2$ which corresponds to a vein diameter l_v of about 12 μm .

Assuming high purity water between the grains, the values obtained for l_w and l_v are unrealistically large. This questions our findings, the proposed models, or both. However, ionic impurities tend to concentrate in the water phase [Mulvaney *et al.*, 1988; Wolff, 1996], which might partly explain our findings of high interstitial water content [Wetlaufer, 1999]; this works best for acidic impurities as found in the GRIP Holocene ice. In the glacial ice the impurities are mainly non-acidic which could explain the missing glacial ice excess diffusion [E. Wolff, personal communication]. The self diffusivity of super cooled acidic water might be higher than for pure water (due to the much lower viscosity), which according to equations (25) and (26) would reduce the amount of water needed to support the observed excess diffusivity. This possibility together with using more realistic estimates for φ and θ might reduce the values for l_v and l_w to more acceptable levels.

Ongoing laboratory experiments on isotopic diffusion in natural glacier ice at the Institute for Low Temperature Science in Sapporo [H. Narita, personal communication] could determine the usefulness of the above models and help clarify what

processes caused the observed excess diffusivity in the GRIP Holocene ice.

3. Conclusions

We showed that smoothing of stable isotope profiles in firn depends on the isotope. Under favorable conditions, relative difference in smoothing can be quantified and used to estimate paleotemperatures deep in the ice. Using measured tortuosity factors for O_2 and CO_2 , our firn diffusion model gave accurate results which implies their validity for water molecules diffusing, and temporarily adsorbing, in the pore space.

The difference in damping of the $\delta^{18}\text{O}$ and δD annual cycles in firn gives rise to an artificial, and often quite strong, annual deuterium excess cycle that is in phase with the annual cycles for $\delta^{18}\text{O}$ and δD .

We discussed the anomalous smoothing of isotope profiles in the GRIP Holocene ice and its possible cause by diffusion in interstitial water between the crystal grains. The relatively large amount of water needed to explain our data is difficult to explain, but suggests that the water is all acidic. Similarly strong smoothing was not observed in the impure glacial GRIP ice which might be due to the predominant non-acidic impurities found in that ice. More work needs to be done to better understand the processes responsible for the excess isotopic diffusion in glacier ice.

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