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Age scale of the air in the summit ice: Implication for glacial-interglacial temperature change

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Abstract. The air occluded in ice sheets and glaciers has, in general, a younger age (defined as the time after its isolation from the atmosphere) than the surrounding ice matrix because snow is first transformed into open porous firn, in which the air can exchange with the atmosphere. Only at a certain depth (firn-ice transition) the pores are pinched off and the air is definitely isolated from the atmosphere. The firn-ice transition depth is at around 70 m under present climatic conditions at Summit, central Greenland. The air at this depth is roughly 10 years old due to diffusive mixing, whereas the ice is about 220 years old. This results in an age difference between the air and the ice of 210 years. This difference depends on temperature and accumulation rate and did thus not remain constant during the past. We used a dynamic firn densification model to calculate the firn-ice transition depth and the age of the ice at this depth and an air diffusion model to determine the age of the air at the transition. Past temperatures and accumulation rates have been deduced from the $\delta^{18}O$ record using time independent functions. We present the results of model calculations of two paleotemperature scenarios yielding a record of the age difference between the air and the ice for the Greenland Ice Core Project (GRIP) and the Greenland Ice Sheet Project Two (GISP2) ice cores for the last 100,000 years. During the Holocene, the age difference stayed rather stable around 200 years, while it reached values up to 1400 years during the last glaciation for the colder scenario. The model results are compared with age differences obtained independently by matching corresponding climate events in the methane and $\delta^{18}O$ records assuming a very small phase lag between variations in the Greenland surface temperature and the atmospheric methane. The past firn-ice transition depths are compared with diffusive column heights obtained from $\delta^{15}N$ of N_2 measurements. The results of this study corroborate the large temperature change of 20 to 25 K from the coldest glacial to Holocene climate found by evaluating borehole temperature profiles.

Introduction

Reconstruction of past climates in polar regions is primarily based on time series of climate properties recorded in ice cores. Records of changes in the composition of air can also be deduced from these cores by analyzing the composition of the fossil air which is trapped in the ice sheets. Dating the trapped gases presents a special challenge because the air is younger than the surrounding ice. The age difference reflects the process by which gases are trapped in an ice sheet.

The upper ~50-150 m of an ice sheet is made up of consolidated snow commonly referred to as firn. Air is continuously trapped in the lower 10% of the firn (firn-ice transition) where interstitial pores around the firn grains are progressively closed off until the air is permanently isolated from the overlying atmosphere [*Schwander and Stauffer*, 1984]. Because firn is permeable, air above the firn-ice transition region can exchange with the atmosphere via diffusion. As a consequence, the age of the air in a sample of ice differs from the age of the ice (the age of an individual molecule is defined as the time elapsed since it crossed the atmosphere-snow boundary for the last time).

Owing to the finite diffusivity, the age of the air in firn increases from the surface to the firn-ice transition region. This causes air in the transition region to be ~7-30 years older than the surface air. The net age difference between the mean age of an ice sample and the trapped gases is the mean age of the ice minus the age of the air when they were in the firn-ice transition region. We denote this age difference as Δage and note that in the transition region the magnitude of the age of the ice is typically 10-100 times greater than the age of the air.

Estimates of Δage are important in deducing the temporal relationship between changes in the composition of trapped gases and changes in proxy climate records recorded in the ice matrix. There are two main parameters which impact Δage estimates: the accumulation rate of snow at the surface and the mean annual temperature. Sites with high temperatures and accumulation rates tend to have relatively low Δage values, while colder sites with lower accumulation rates can have present-day Δage values which exceed 2500 years. Estimates of Δage values during the last glacial maximum can be several thousand years larger than today [*Barnola et al.*, 1991; *Sowers et al.*, 1992].

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The present study focuses on estimating Δage values for two deep ice cores recovered near the summit of Greenland by the Greenland Ice Core Project (GRIP) and the Greenland Ice Sheet Project Two (GISP2) (Table 1). In order to calculate Δage values for these two sites over the past 100 ka, we have estimated both the age of the ice and the age of the air in the past close-off region using a dynamic densification model and a model of air mixing in the firn, respectively. In the following sections, we discuss the factors which influence Δage estimates at these two sites under recent climate conditions, apply new paleotemperature estimates at Summit to the construction of a record of Δage variations over the last 100 ka, and finally discuss other records from these cores which bear on our Δage record.

Δage Values at Summit Under Present Climatic Conditions

As mentioned previously, the most important factor to consider when calculating Δage is the age of the ice in the bubble close-off region. The age of the firn in the close-off region is determined by the rate at which firn density increases from surface values of ~350 kg m^{-3} to the density of firn in the close-off region (800-830 kg m^{-3}). The firn densification rate depends mainly on temperature and accumulation rate, while the close-off density (ρ_{co}) is in the first place influenced by the temperature of the site [*Martinerie et al.*, 1994]:

$$1/\rho_{co}\ (\mathrm{kg^{-1}\ m^3}) = 1/\rho_{ice} + 6.95\times10^{-7}\,(t + 273.16) - 4.3\times10^{-5} \quad (1)$$

where

$$\rho_{ice}\ (\mathrm{kg\ m^{-3}}) = 916.5 - 0.14438\,t - 1.5175\times10^{-4}\,t^2 \quad (2)$$

where t is mean annual temperature (in degrees Celsius). Equation (2) is a fit through data reported by *Bader* [1964]. Equation (1) has been derived from total gas measurements. The so defined ρ_{co} is therefore the average density at which bubbles are isolated from the atmosphere. Since bubble close-off occurs over a density or depth range, other definitions of close-off are possible. For example, below we will define close-off as the depth where the diffusivity of the air reaches zero.

Table 1. Geographical and Climatic Data of the GRIP and GISP2 Drilling Sites, in the Summit Area of Greenland.

	GRIP	GISP2
Longitude	37.64° W	38.48° W
Latitude	72.58° N	72.58° N
Elevation	3238 m	3214 m
70-m borehole temperature	-31.7 °C [a]	-31.4 °C [b]
Mean accumulation rate (last 200 years)	0.23 m of ice a^{-1} [c]	0.248 m of ice a^{-1} [d]
Present close-off depth	71 m [e,f]	72 m [f]
Present Δage (for methane)	210 a [e,f]	195 a [f]

GRIP is located at the present position of the ice sheet summit. The distance between GRIP and GISP2 is 28 km.

[a] *Gundestrup et al.* [1994].
[b] *Cuffey et al.* [1995].
[c] *Johnsen et al.* [1992].
[d] *Meese et al.* [1994].
[e] *Schwander et al.* [1993].
[f] this work.

Another factor to consider in estimating the Δage is the fact that the air in the close-off region is older than the air at the surface of the site. The age difference arises from the finite time that it takes for changes in the composition of the atmosphere to be mixed down through the firn to the close-off region. Various physical processes control the mixing of the air in the firn: diffusion, wind pumping, barometric pressure variations, free convection, etc. [*Schwander*, 1996; *Waddington et al.*, 1996]. Gas transport within the interstitial spaces between the firn grains can be categorized into three distinct zones [*Sowers et al.*, 1992]. Near the surface of the firn column, air mixes via convection with the overlying atmosphere. Convection is driven by wind pumping associated with winds traveling over topographic features at the surface of the ice sheet [*Colbeck*, 1989], possibly free convection associated with seasonal temperature variations, and atmospheric pressure fluctuations which tend to flush the upper few meters of firn air as high and low pressure systems pass over a site. This latter effect is, however, of minor importance, since the diffusive equilibration time of the concerned layer is about an order of magnitude shorter than typical synoptic variations. The depth of the convective zone is generally less than 20 m [*Bender et al.*, 1994b; *Schwander et al.*, 1993] and can vary considerably from site to site depending on the surface forcing as well as the horizontal "layering" of the firn (e.g., wind crusts, melt layers, and depth hoar).

Below the convective zone, there is a region of firn where the air mixes predominantly by molecular diffusion. Within this region, gravitational attraction of the different constituents of air cause the heavier species to preferentially migrate toward the base of the diffusive column setting up a gradient in the mixing ratios. This phenomenon is termed gravitational fractionation [*Craig et al.*, 1988; *Schwander*, 1989; *Sowers et al.*, 1989]. Because the isotopic composition of atmospheric N_2 has remained constant throughout the last million years, any variations in the isotopic composition of N_2 in the firn below the convective zone must be related to gravitational fractionation in the diffusive zone [*Sowers et al.*, 1992] (we discuss a special exception to this general rule in the section on comparison of model results with other parameters). The $\delta^{15}N$ of N_2 trapped in ice provides the means of reconstructing the size of the diffusive column in the past with larger $\delta^{15}N$ values being characteristic of larger diffusive zones.

Below the diffusive zone, there may be a region in which air is not able to equilibrate with the overlying diffusive zone because of the tortuous nature of the firn, especially in the nearly impermeable winter layers, just above and within the bubble close-off region. Recent firn air studies [*Battle et al.*, 1996; *Bender et al.*, 1994b; *Etheridge et al.*, 1996; *Schwander et al.*, 1993] show that this zone (termed the nondiffusive zone) is generally less than 10 m at most sites. Because the air in the nondiffusive zone cannot equilibrate with the overlying diffusive column, the gas mixing ratios in a given layer remain practically unchanged, and, for example, $\delta^{15}N$ values remain constant throughout this interval. Therefore the gas mixing ratios at the base of the diffusive column are ultimately recorded in the trapped bubbles below.

If horizontal firn strata are homogeneous and if the extent of the three zones has been determined, then the air mixing can be assessed with a one-dimensional model of gas transport in firn. For those sites which experience periodic summer melting at the surface, resulting in partly impermeable ice layers, the diffusive fluxes must be analyzed in three dimensions.

Analysis of melt events throughout the Holocene section (upper 1565 m) of the GISP2 core showed that a melt feature occurred on average once every 153 years [*Alley and Anandakrishnan*, 1995]. Given that the early Holocene is the warmest period within the last 100 ka, we consider the impact of melt layers on gas transport within the firn to be negligible. The conditions at Summit are therefore ideal for treating vertical gas transport with a one-dimensional model.

Over the last 10 ka, the Δage estimates for the GRIP and GISP2 cores are close to the present values (Table 1) because of the small variations in the temperature and accumulation proxy records from the two cores. As such, we will discuss relevant data used to estimate the present values of Δage as if it applied to either core during the last 10 ka. Before 10 ka before present (B.P.) (the reference date is the year when drilling started, i.e., 1990 A.D.), variations in the proxy records of temperature and accumulation rate are large and the construction of Δage records for this period is discussed in the section on modeling Δage in the past.

Δage at Summit today have been estimated through density and porosity measurements on the firn, analyses of the composition of firn air, and modeling of the gas diffusion in the firn [*Schwander et al.*, 1993]. Porosity measurements of this study have shown that 90% of the bubbles are closed off between 65 and 80 m depth. The age of the firn where ~50% of the air bubbles are closed off (75±2 m) at the GRIP site is 235 ±10 years.

Estimates of the age of the air in the bubble close-off region at GRIP have been made by sampling firn air [*Schwander et al.*, 1993]. The age of the air was deduced using a one-dimensional model of air movement in conjunction with a suite of measured gas species (CO_2, CH_4, and ^{85}Kr) whose atmospheric mixing ratios have been increasing during the past few decades. The diffusion of these gases in firn was modeled using a previously determined record of mixing ratio variations of each species as a surface boundary condition. Diffusion coefficients for each species were estimated from the linear relationship between diffusion coefficients and open porosity determined on firn samples from Siple Station, Antarctica, and the relative diffusivities of each species in air. Because the climatic conditions at Siple and Summit are similar, we expect that the diffusivities in firn of a given density are nearly identical at the two sites.

Modeled profiles of CO_2, CH_4, ^{85}Kr, $\delta^{15}N$ of N_2, and $\delta^{18}O$ of O_2 at GRIP agree closely with measured values and suggest that the diffusivity in the firn approaches zero already when only ~25% of the air bubbles had been closed off (71±1 m), corresponding to an age of the firn of 220 ±5 years. In the following, as well as in Table 1, we refer to this definition of the close-off depth (COD), which is equal to the base of the diffusive zone and is somewhat smaller than the depth corresponding to the close-off density given by (1). The diffusion model yields a mean age for CO_2 molecules at the GRIP firn-ice transition of 12 years with a standard deviation of the age distribution of 7.5 years. For other gases these values are expected to be inversely proportional to their diffusivities. For example, CH_4 diffuses 1.35 times as fast as CO_2, so the mean age of the CH_4 molecules in the Summit firn-ice transition region is $12/1.35 \approx 9$ years.

To estimate the final Δage between the trapped air and the surrounding ice, we need to subtract the age of the air in the bubble close-off region (9 years for CH_4) from the age of the firn in the bubble close-off region (220 years). The resulting Δage estimate is roughly 210 years for GRIP and, assuming the same close-off density, is 195 years for GISP2.

Modeling the Age Difference Between Ice and Air in the Past

The difference between the age of the ice and the age of the air under different climatic conditions can be assessed by the determination of the depth of the firn-ice transition and the age of the ice at this depth using a firn densification model on one hand and the calculation of the age of the air at the transition depth with a diffusion model on the other hand. The essential forcings for these models are the temperature and the accumulation rate.

An empirical, steady state firn densification model, valid for a wide range of temperatures and accumulation rates, has been developed by *Herron and Langway* [1980] (H-L model). For changing climatic conditions, where a dynamic approach is more suitable, the H-L model can easily be transformed into a dynamic version. Another dynamic model based on ice deformation studies carried out by *Pimienta* [1987] has been applied for the Vostok ice core by *Barnola et al.* [1991] (P-B model). A comparison of the dynamic version of the H-L model and the P-B model showed that they differ by much less than the uncertainty arising from the estimated error in past temperatures and accumulation rates for the Summit area. Nevertheless, all results presented in this paper were obtained with the P-B model. In addition, we have incorporated heat transfer to account for the abrupt temperature variations, which are characteristic for a major part of the glacial sections of the Summit cores (see Appendix A).

In order to calculate the age of the ice at the bubble close-off depth, we also need to know the close-off density under past climatic conditions. Equation (1) describes the spatial relation of increasing close-off density with decreasing temperature. This relation was used to estimate the temporal trend in the past. At present the effective air isolation depth at Summit is 71 m, corresponding to a density of about 814 kg m^{-3} or 14 kg m^{-3} lower than the close-off density obtained from total gas measurements (D. Raynaud et al., Air content along the GRIP core: A record of surface climatic parameters and elevation in central Greenland, submitted to *Journal of Geophysical Research*, 1997), on which (1) is based. The difference is due to the presence of the nondiffusive zone. We assume that the size of the nondiffusive zone did not significantly change in the past and have therefore subtracted a constant value of 14 kg m^{-3} from (1) for the Δage calculations.

Since the change in air mixing time in the firn is more than an order of magnitude smaller than the age of the ice at the firn-ice transition, we simply approximated the change in mixing time by assuming that the diffusive equilibration time is proportional to the square of the firn thickness [*Schwander*, 1989] and that $D \propto T^{1.85}$ (T is the absolute temperature) [*Andrussov*, 1969]. We estimate that the change in diffusivity by varying air pressure, arising mainly from changes in ice sheet elevation and shifts in atmospheric circulation, influences the age difference between ice and air over the whole record by less than 1% and we will not consider this effect further. The Δage results given in the following are based on the diffusion coefficient for CH_4. For gases with diffusivities in the range of ±50% of that of CH_4, the difference in Δage is less than 3%.

We have applied the P-B model to a wide range of hypothetical sites with extreme variations in temperature and accumulation rates. We plot the results in Figure 1 as lines of constant Δage. As there is a strong tendency for accumulation to be positively correlated with temperature, most Δage values for realistic sites will hover around a line drawn at 45° in Figure 1.

Temperature and accumulation rate are the most important factors controlling densification and must be prescribed. In the following sections, we discuss recent results from the Summit ice cores which influence the construction of paleotemperature and accumulation rates over the last 100 ka. The timescales we adopt for the cores are those from *Johnsen et al.* [1995] and *Bender et al.* [1994a] for the GRIP and GISP2 cores, respectively.

Estimating Paleotemperatures at Summit

Estimates of past surface temperatures on ice sheets have often been made using the spatial relationship between mean annual surface temperature and the mean $\delta^{18}O$ of the precipitation (hereafter referred to as $\delta^{18}O$) observed over Greenland today. The data were described with the following equation [*Dansgaard*, 1964; *Johnsen et al.*, 1989]:

$$\delta^{18}O\ (‰) = 0.67\ t - 13.7 \qquad (3)$$

where t is mean air temperature in degrees Celsius.

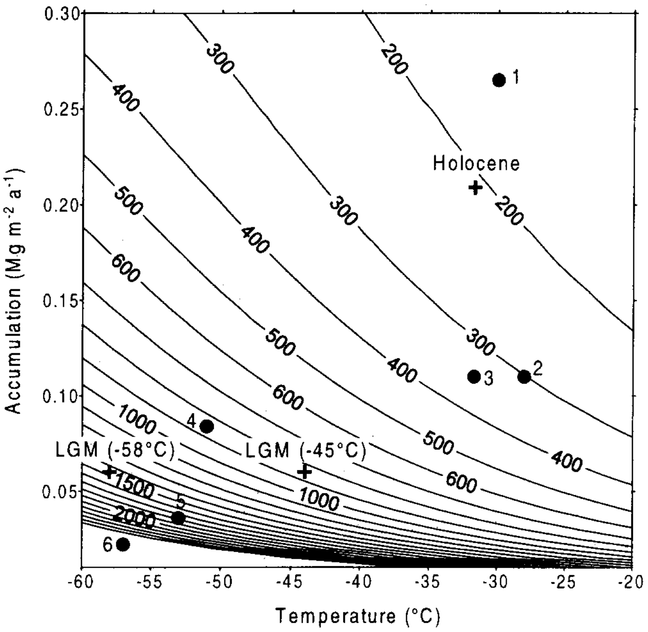

Figure 1. Age difference between the ice and the air of the bubbles as a function of temperature and accumulation rate calculated with the Pimienta-Barnola model for stationary conditions. The plus signs indicate conditions at Summit during Holocene and the two discussed scenarios during Last Glacial Maximum (LGM). A temperature of about -45°C would be expected for the LGM if the present spatial temperature - $\delta^{18}O$ relation is applied as a temporal calibration factor. Around -58°C is expected with the new findings based on temperature measurements in the bore hole. The circles indicate the present temperature and accumulation values of various Greenlandic (G) and Antarctic (A) drilling sites: 1, Crête (G); 2, Byrd (A); 3, North Central (G); 4, south pole (A); 5, Dome C (A); and 6, Vostok (A).

The slope of this function, $d(\delta^{18}O)/dT$ (referred to as $\alpha_{spatial}$) is the product of various equilibrium and kinetic isotope effects associated with evaporation and condensation of water as it travels from its source to the final precipitation site today [*Johnsen et al.*, 1989].

If we want to apply (3) to the $\delta^{18}O$ records from Summit covering the last 100 ka, we need to know whether $d(\delta^{18}O)/dT$ has remained constant through time. Recent studies involving high-precision bore hole temperature measurements [*Cuffey et al.*, 1995; *Johnsen et al.*, 1995] suggest that the long term $d(\delta^{18}O)/dT$ coefficient ($\alpha_{temporal}$) was probably closer to 0.33 (about half the present spatial coefficient). Applying $\alpha_{temporal}$ to the $\delta^{18}O$ records yields a glacial-Holocene temperature shift of 26 K which is roughly twice the temperature shift predicted using $\alpha_{spatial}$. Unfortunately, the borehole inversion techniques cannot resolve the magnitude of the fast temperature variations of the stadial/interstadial events during the last glaciation. It is quite possible that the "true α" has varied with time.

We computed two extreme Δage estimates using $\alpha_{spatial}$ and $\alpha_{temporal}$ for both of the Summit cores over the last 100,000 years. The equations used to reconstruct the temperature records for the two sites are [*Cuffey et al.*, 1995; *Johnsen et al.*, 1989, 1995]:

$$\text{GRIP, GISP2}(\alpha_{spatial}) \quad t\ (°C) = 1/0.67\ (\delta^{18}O + 13.7) \qquad (4)$$

$$\text{GRIP}(\alpha_{temporal}) \quad t\ (°C) = -211.4 - 11.88\ \delta - 0.1925\ \delta^2 \qquad (5)$$

$$\text{GISP2}(\alpha_{temporal}) \quad t\ (°C) = 1/0.33\ (\delta^{18}O + 25) \qquad (6)$$

where δ is $\delta^{18}O$ of ice corrected for sea water composition.

Note that the difference between (5) and (6) does not reflect any physical or climatic differences between the GRIP and GISP2 sites but arises from the way the data were analyzed. Equation (5) produces a varying α between 0.67 and ~0.3 for Holocene and glacial $\delta^{18}O$ values, respectively.

Estimating Paleoaccumulation Rates at Summit

Past accumulation rates λ have been inferred from measured annual layer thicknesses which have been corrected for thinning using ice flow models [*Alley et al.*, 1993; *Johnsen et al.*, 1995]. Layer thicknesses on the GRIP core were not measured continuously, but data coverage is good through the Holocene and the Younger Dryas event. *Alley et al.* [1997] and *Meese et al.* [1997] identified annual layers continuously throughout the upper 1840 m of the GISP2 core and with nearly continuous coverage below 1840 m. Accumulation rates for the GISP2 core were derived by *Cutler et al.* [1995] using the annual layer counts from *Alley et al.* [1993] and an ice flow model which computes the trajectories of each layer of ice and the resulting thinning of the layer as it moves through the ice sheet. The accumulation rate record for the GRIP core was obtained by fitting a curve ($\lambda(\delta^{18}O)$) through the available GRIP data in order to generate a continuous estimate of past accumulation rates [*Johnsen et al.*, 1995].

GRIP

$$\lambda(\text{m of ice a}^{-1}) = 0.23\ \exp(-10.09 - 0.653\ \delta - 0.01042\ \delta^2) \qquad (7)$$

Since variations in the accumulation rate do not necessarily need to be related to temperature and thus $\delta^{18}O$ changes but could be a result of changes in the atmospheric circulation,

(7) could be a too simple approach to estimate past accumulation rates. On the other hand, the annual layer counting techniques are neither unequivocal, and at present we cannot decide which approach is more adequate.

Constructing Δage Profiles for the GRIP and GISP2 Cores

We input the accumulation records and the various temperature estimates from the two cores into the dynamic densification model. The results are depicted in Figure 2. Throughout the Holocene, the climate at Summit was rather stable resulting in little variation in densification. Bubble close-off depths and Δage estimates remained near present values of 70 m and 200 years, respectively.

The highly variable climate during the period before 10 ka B.P. caused considerable fluctuations in Δage. There are two Δage records plotted in Figure 2 for each core. The origin of the two records is the different temperature coefficients which were applied to the $\delta^{18}O$ records in (4)-(6). The maximum Δage values calculated (using $\alpha_{temporal}$) during the glacial period were 1380 and 1020 years for the GRIP and GISP2 cores, respectively. In order to visualize the effect of implementing heat transfer in the P-B model, the dotted lines show the results without heat transfer (GRIP only). Using $\alpha_{spatial}$, maximum Δage values are 880 and 760 years for GRIP and GISP2, respectively. The reason for the difference between GRIP and GISP2 arises mainly from differences in the assumed temperature and accumulation histories.

The model also produces past close-off depths as a function of time (Figure 2). In general, the past close-off depths tend to be deeper during glacial periods in response to the lower temperatures. At both sites, the close-off depths during the glacial period are between 80 and 130 m or about 10-60 m deeper than in the Holocene.

Comparison of Model Results With Other Parameters in the Cores

We can think of two methods to verify the obtained results: (1) If two tracers, one located in the air bubbles and the other bound to the ice matrix, are affected simultaneously by climate changes, we can independently derive age differences by adjusting the timescale of one record for an optimal match of coincident events. (2) If the changes in the past close-off depths are largely manifested as a difference in the diffusive column heights, then we should be able to compare the model results with variations in the $\delta^{15}N$ of trapped N_2 to identify which of the two temperature calibration factors (α) is more appropriate.

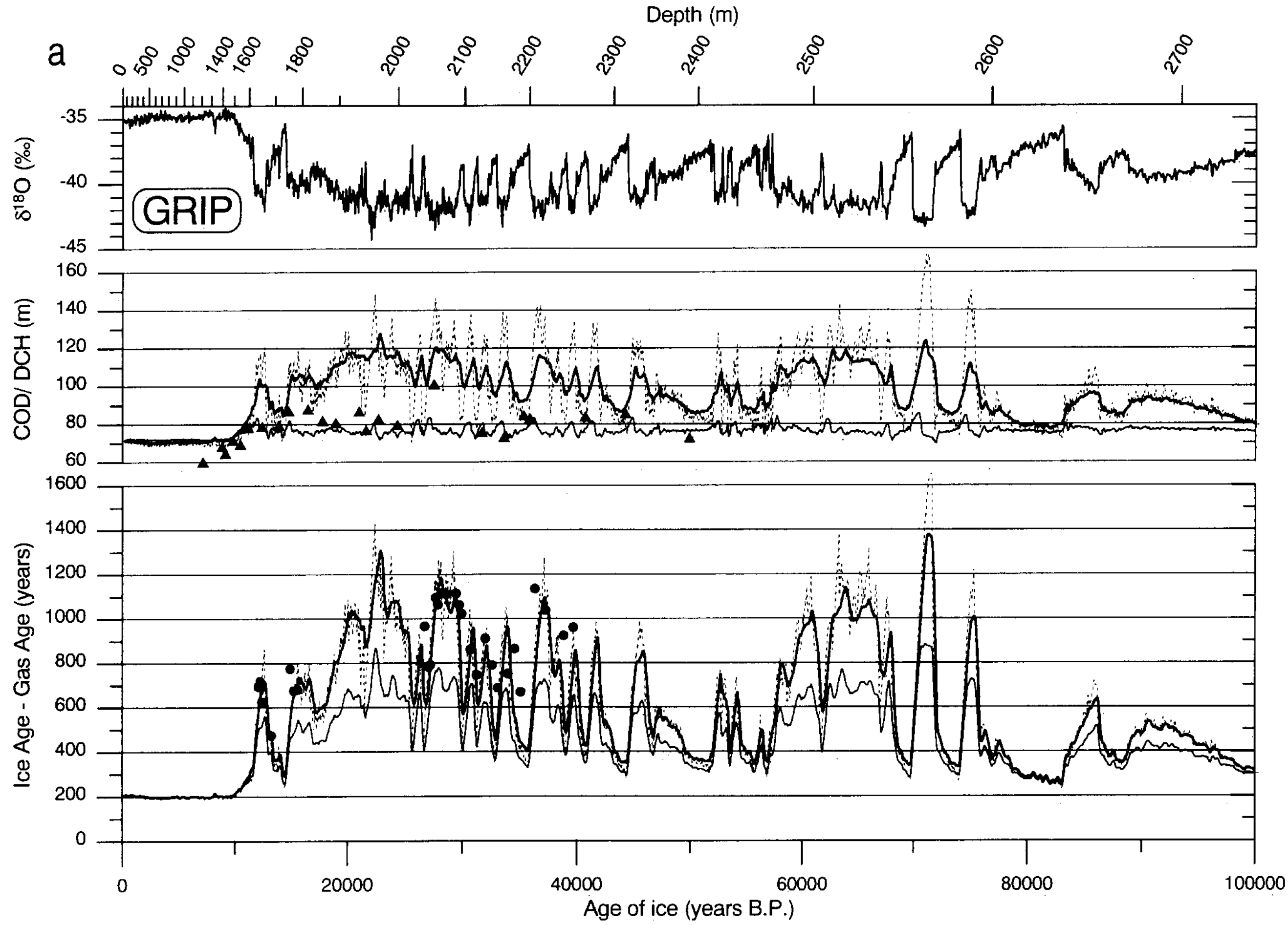

Figure 2. The $\delta^{18}O$ record, model results for close-off depths and Δage, and diffusive column heights from $\delta^{15}N$ for the last 100,000 years (0 years B.P. = 1990 A.D.): (a) GRIP and (b) GISP2. For COD and Δage, heavy line, light line, dotted line (only GRIP) represent the scenarios "$\alpha_{temporal}$," "$\alpha_{spatial}$," and "$\alpha_{temporal}$ without temperature diffusion," respectively. Triangles denote DCH calculated from $\delta^{15}N$ data. Circles are Δages obtained by CH_4 - $\delta^{18}O$ matching.

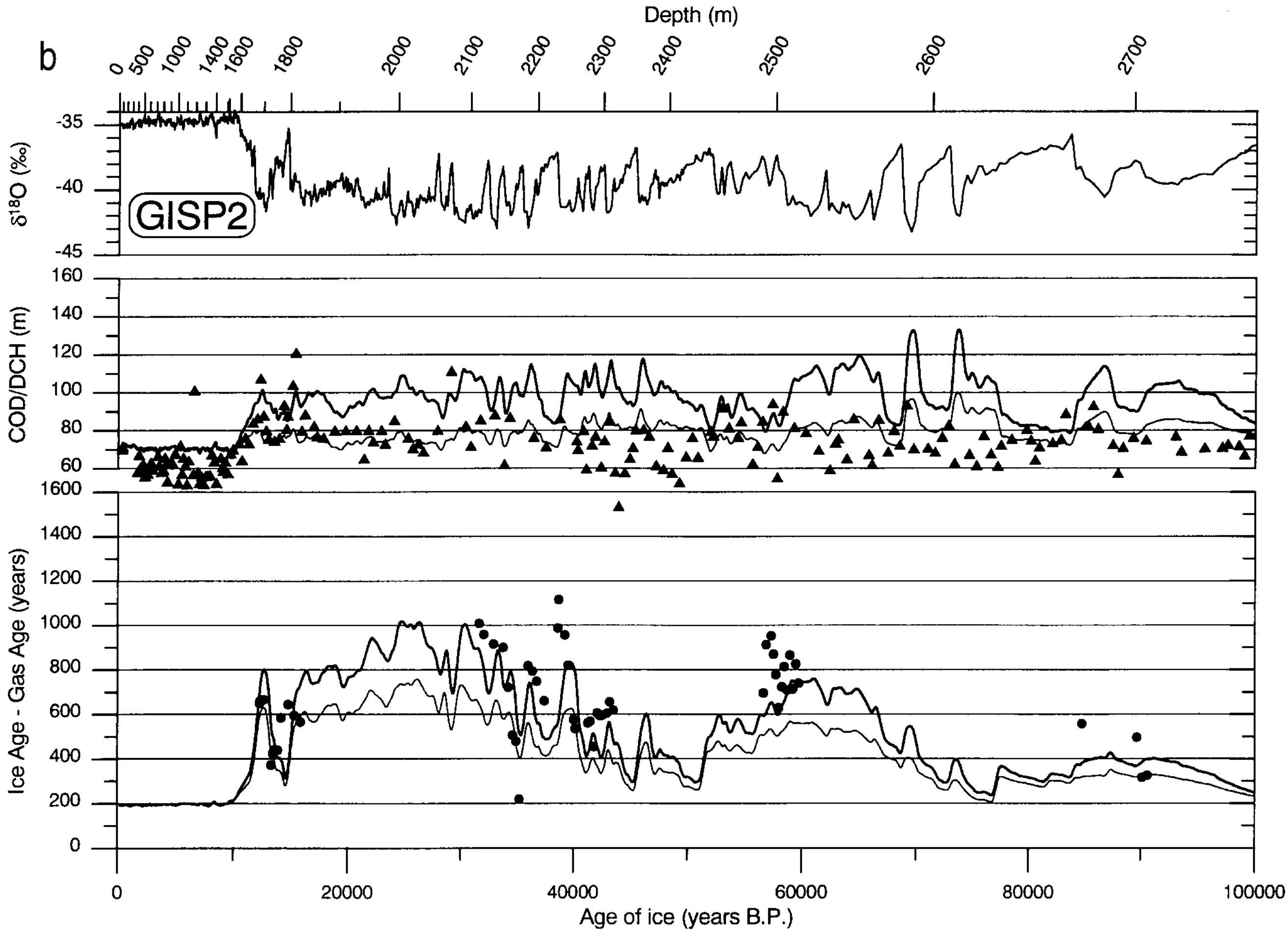

Figure 2. (continued)

Candidates for the first approach are CH_4 and $\delta^{18}O$ showing distinct changes at the onset and termination of interstadial events and the Younger Dryas. Our premise here is that warming in Greenland is synchronous with the rise in atmospheric CH_4 levels. We recognize that CH_4 mixing ratio variations are likely to be coupled with changes in the tropical precipitation [*Blunier et al.*, 1995; *Chappellaz et al.*, 1993a, b] which could change asynchronously with Greenland temperature. However, the rapidity with which both properties change [*Brook et al.*, 1996; *Chappellaz et al.*, 1993a], coupled with the short residence time of atmospheric CH_4, make it likely that the two properties change in concert. A notable exception to this general observation occurs at 102 ka B.P. where atmospheric CH_4 levels started to rise 1-2 ka before the increase in $\delta^{18}O$, at the start of interstadial 23 [*Brook et al.*, 1996]. We realize that by matching variations in CH_4 and $\delta^{18}O$ to determine the gas age scale we risk arguing in a circle. Unless other independent means to reduce the uncertainty in Δage are available, the examination of gas change-temperature phasing is limited to the uncertainty of the phase lag between CH_4 and $\delta^{18}O$.

Given our assumption of a synchronous increase in atmospheric CH_4 levels and Summit temperatures, we can use the CH_4 and $\delta^{18}O$ records to estimate discrete values of Δage. To do this, we compare sections of both cores with high-resolution CH_4 measurements with the $\delta^{18}O$ record. With both CH_4 and $\delta^{18}O$, on the "ice age" timescale, we shift the CH_4 record so it overlays the $\delta^{18}O$ record. The amount of time we need to shift the CH_4 record corresponds to the best estimate of Δage for that section of core. In order to perform the matching as objectively as possible, we have used a Monte Carlo method to shift the CH_4 record forward so it overlays the $\delta^{18}O$ record. The method is described in Appendix B.

The result of such an "event matching" is shown as discrete data in Figure 2. We have used the GRIP methane results published by *Chappellaz et al.* [1993a] and *Blunier et al.* [1995] with some additional, previously unpublished values. The GISP2 CH_4 record was published by *Brook et al.* [1996]. Δages obtained with the "event matching" agree generally better with the ones obtained with the models utilizing $\alpha_{temporal}$ for both GRIP and GISP2.

This supports the temperature history inferred from the in situ temperature profile of the ice sheet. While the borehole temperature method cannot resolve the fast variations during and at the end of the glaciation, the methane-$\delta^{18}O$ event matching provides at least some vague information: Modeled Δage using $\alpha_{temporal}$ and Δage obtained by methane-$\delta^{18}O$ matching are in good agreement as well for negative as for positive temperature shifts (Figure 3), which is in favor with an α of approximately 0.33 also during the fast transitions. We must, however, bear in mind that the limited resolution of the methane record and the fact that there are variations in the two records without counterpart in the other limits the use of the event matching method.

The $\delta^{15}N$ analyses were performed on both the GRIP and GISP2 ice cores using standard techniques [*Fuchs and*

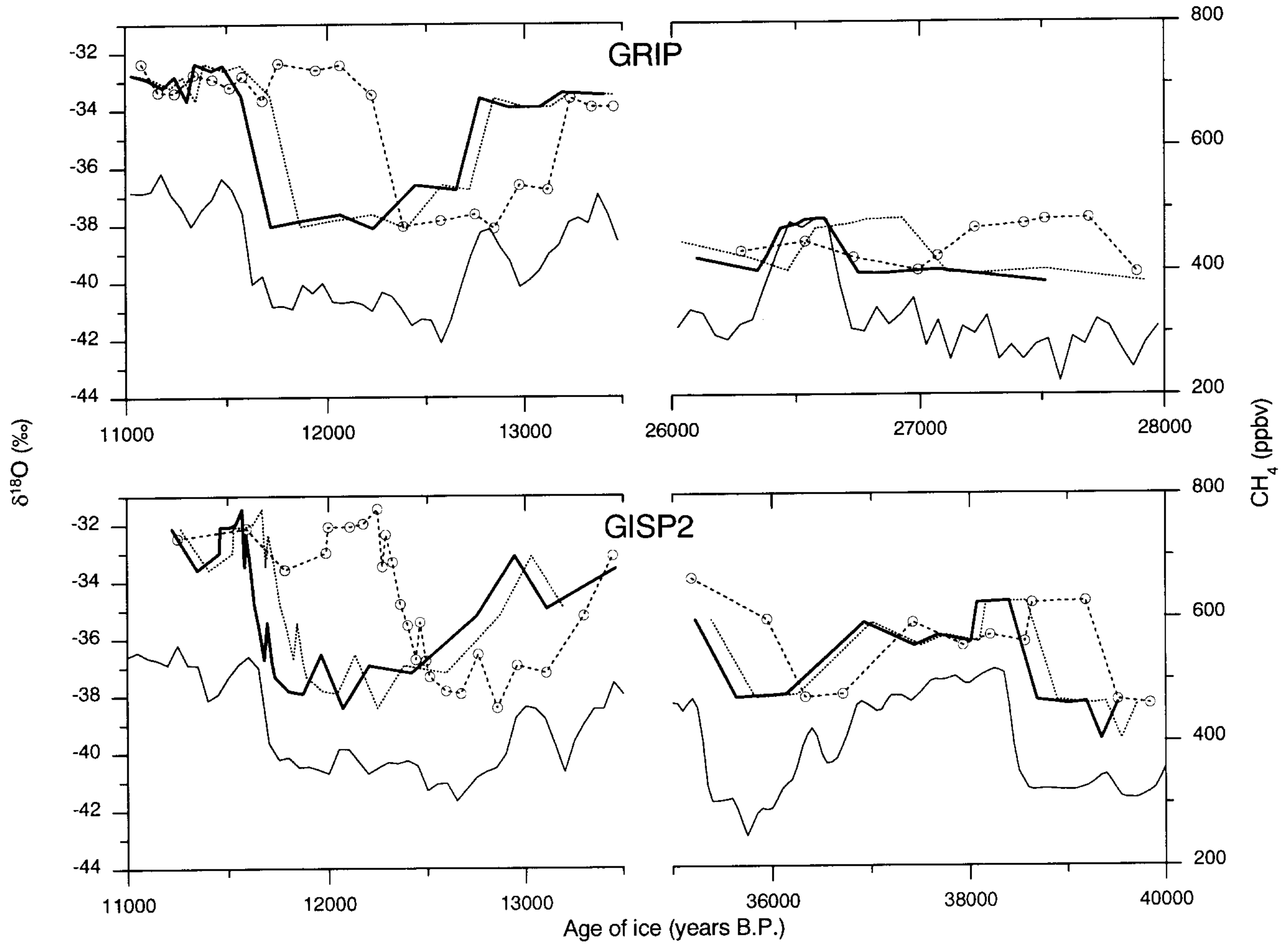

Figure 3. Matching of methane and $\delta^{18}O$ during fast climate variations in selected core section with particularly good resolution of the methane record. Thin solid line, $\delta^{18}O$; dashed line with circles, original methane data on ice age scale; dotted line: shifted methane record by Δages according to the "$\alpha_{spatial}$" scenario; and heavy line, shifted methane record by Δages according to the "$\alpha_{temporal}$" scenario.

Leuenberger, 1996; *Sowers et al.*, 1992; *Sowers et al.*, 1989]. Twenty-nine discrete analyses were made on the GRIP core between 5 and 50 ka B.P. In general, duplicate analyses were made at each of 243 discrete depths in the GISP2 core between 117 and 2804 m. Ten glacial samples with gas ages falling at times of rapid warming were excluded from this study. We believe that these samples, which have $\delta^{15}N$ values >0.47‰, reflect thermal fractionation during periods when surface temperature increased rapidly, producing a temperature gradient in the firn. Under these conditions, the heavier isotope of N_2 (^{15}N) tends to migrate toward the colder region (the bubble close-off region), causing elevated $\delta^{15}N$ values in the trapped gases [*Severinghaus and Sowers*, 1995; *Severinghaus et al.*, 1996]. This phenomenon only occurs during abrupt temperature changes associated with stadial-interstadial transitions. In addition to these 10 samples, 38 samples (analyzed between October 28, 1993 and November 16, 1993) were removed from the GISP2 data set. Neighboring samples run at different times gave $\delta^{15}N$ values which agree well with each other but are offset by about 0.1‰ from samples run during this period.

The average Holocene (0-10 ka B.P.) $\delta^{15}N$ values were 0.30‰ (σ = 0.03‰ and N = 8) and 0.30‰ (σ = 0.04‰ and N = 50) for the GRIP and GISP2 cores, respectively. Results of glacial ice between 20 and 40 ka B.P. averaged 0.44‰ (σ = 0.05‰ and N = 9) and 0.38‰ (σ = 0.05‰ and N = 22) for GRIP and GISP2, respectively. The $\delta^{15}N$ values were used to calculate the height of the diffusive column (DCH) (in meters) using the following equation:

$$\text{DCH (m)} = RT/(g\Delta m)\,(\ln\,(\delta^{15}N/1000 + 1)) \qquad (8)$$

where R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is temperature (K), g is the acceleration due to gravity (9.81 m s^{-2}), and Δm is the mass difference between ^{15}N and ^{14}N (0.001 kg mol^{-1}). The temperature was determined by converting the averaged $\delta^{18}O$ of the firn column above each sample at the moment when it was isolated from the atmosphere, using $\alpha_{temporal}$. Since T varies by only 10% for the entire duration of the record, uncertainties in the temperature introduce a small uncertainty into the computed diffusive column heights.

Diffusive column heights for GISP2 and GRIP are plotted in Figure 2 along with the modeled close-off depths (COD) and the corresponding $\delta^{18}O$ records [*Dansgaard et al.*, 1993; *Grootes et al.*, 1993]. During the Holocene, DCH values averaged 61 m (σ = 7 m and N = 8) and 62 m (σ = 8 m and N = 50) for GRIP and GISP2, respectively. These values are, as expected, less than the calculated COD, which averaged at both sites 71 m (σ = 1 m). (Because the $\delta^{15}N$ data are erratically spaced in time, COD averages indicated here have been calculated with the corresponding COD estimates from the same depth as the $\delta^{15}N$ samples. They may therefore be slightly different from the true temporal average of the whole period considered but are aliased in the same way as the DCH averages.) Mean diffusive column heights at GRIP during the glacial period (20-40 ka B.P.) were 83 m (σ = 8 m and N = 9), while the COD values (based on $\alpha_{temporal}$) amounted to 110 m (σ = 11 m). At GISP2, the mean DCH was 79 m (σ = 10 m and N = 22) with average COD of 99 m (σ = 7 m). The DCH values of GRIP and GISP2 are compatible, considering the relatively low sample number in case of GRIP. The difference between the glacial COD values of GRIP and GISP2 arises from the different underlying accumulation rate and temperature histories.

For the discussion of the results, we will look at the difference COD - DCH, which is equal to the convective zone near the surface. Throughout the Holocene, COD - DCH is roughly 10 m, which is compatible with firn-air measurements [*Bender et al.*, 1997; *Schwander et al.*, 1993]. The size of the convective zone did probably not remain constant through time. A possibly enhanced atmospheric circulation during cold periods, as suggested by the elevated dust concentration [*Mayewski et al.*, 1994], could have two effects on the firn ventilation. On one hand, higher wind speeds tend to increase the convection [*Colbeck*, 1989]. On the other hand, a possible increase in the layering of the firn would reduce ventilation. At this point, we have no way to estimate the net effect. From the late glacial period (40 -20 ka B.P.) to the Holocene, DCH values decreased by about 20 m, suggesting a general decrease in the firn thickness. The $\alpha_{spatial}$ scenario results in COD values for the late glacial period that are generally inferior to the DCHs, which is physically not meaningful. (Note that DCH values in Figure 2 are based on $\alpha_{temporal}$. DCHs based on $\alpha_{spatial}$ would be even slightly larger.) There remains some uncertainty in the estimate of past accumulation rates, which could give rise to wrong COD values. An error in the mean accumulation rate of more than 10% after 40 ka B.P. would, however, result in severe discrepancies to timescales of other paleorecords [*Dansgaard et al.*, 1993]. A 10% change in accumulation rate implies a change in COD of less than 3 m. The $\alpha_{spatial}$ scenario is therefore not compatible with our results between 20 and 40 ka B.P. The $\alpha_{temporal}$ scenario yields COD - DCH values, which were 10 to 20 m larger toward the end of glacial times than during Holocene, while a constant size of the convective zone would be consistent with an intermediate α of about 0.4, and the extreme case of no convective zone would infer an α of about 0.5. At this point, we interpret DCH data as supporting low α values in general, in agreement with the CH_4-$\delta^{18}O$ matching. We cannot, however, rule out the possibility that α varied significantly during stadial/interstadial events.

While toward the end of the glacial age a temperature scenario corresponding to $\alpha < 0.5$ is favored, the situation is less clear for the period from 40-100 ka B.P. COD - DCH differences are highly variable, pointing either to a high variability in the extent of the convective zone and/or to an inadequacy of the paleotemperature and/or paleoaccumulation records.

Summary

For two extreme temperature histories, we have constructed age scales for the gases contained in the bubbles of the GRIP and GISP2 ice cores relative to the age scale for the ice, using a dynamic firn densification/heat transfer model. Independent Δages obtained by matching of corresponding events in the methane and the $\delta^{18}O$ record, as well as diffusive column heights from $\delta^{15}N$, support the temperature-$\delta^{18}O$ relation based on borehole temperature profiles recently published for the GRIP and the GISP2 sites, at least for the last 40 ka.

It is at present difficult to estimate the accuracy of the Δage calculations. Apart from the not definitively known past temperatures, the main uncertainties arise from the accumulation rate estimates and the resulting age scale. These uncertainties are reflected as differences between GRIP and GISP2. The distance between the drilling sites was only 28 km, and the accumulation rate histories are therefore expected to be very similar. Consequently, similar Δages should result. The differences are, indeed, rather small for the last 20 ka, namely, about 20 years in the Holocene and up to 100 years between 10 ka and 20 ka B.P., largely due to the about 10% higher accumulation rate at GISP2. When going farther back, the differences between the GRIP and GISP2 age scales become more significant, and the Δages differ by up to 350 years between 20 ka and 50 ka B.P. and up to 800 years around 70 ka B.P. These differences between GRIP and GISP2 thus give us some indication about the accuracy of the present Δage estimates. Further improvement in the annual layer counting and flow modeling should allow us to significantly reduce the uncertainties in the Δage estimates.

Appendix A: P-B Model With Heat Transfer

In order to calculate past density profiles, we followed basically the approach described by *Barnola et al.* [1991]. For densities $\rho < 550$ kg m^{-3}, we have used the Herron-Langway model [*Herron and Langway*, 1980]:

$$\dot{\rho}(\text{kg m}^{-3}\,\text{s}^{-1}) = \text{k}_0 A(\rho_{\text{ice}} - \rho) \tag{A1}$$

where

$$\text{k}_0 = 0.011\text{e}^{-\left(\frac{10160}{RT}\right)}\ \text{m}^2\,\text{kg}^{-1} \tag{A2}$$

where R is 8.314 J K^{-1} mol^{-1}, T is temperature (in kelvins), A is accumulation rate (kg m^{-2} s^{-1}), ρ_{ice} is pure ice density, and ρ is bulk density.

For 550 kg m^{-3} < ρ < 800 kg m^{-3}, we used the empirical formula by Pimienta [*Barnola et al.*, 1991], based on the sintering model with spherical bubbles of *Wilkinson and Ashby* [1975], which we used for $\rho > 800$ kg m^{-3}:

$$\dot{\rho}\ (\text{kg m}^{-3}\,\text{s}^{-1}) = \text{k}_1 \rho f \Delta p^{\mu} \tag{A3}$$

where

$$\text{k}_1 = 25400\text{e}^{-\left(\frac{60000}{RT}\right)}\ \text{Pa}^{-\mu}\,\text{s}^{-1} \tag{A4}$$

$$f = 10^{(\beta(\rho/\rho_{\text{ice}})^3 + \gamma(\rho/\rho_{\text{ice}})^2 + \delta(\rho/\rho_{\text{ice}}) + \varepsilon)} \tag{A5}$$

where $\rho \leq 800$ kg m^{-3}, β = -29.166, γ = 84.422, δ = -87.425, ε = 30.673.

$$f = (\tfrac{3}{16})(1 - \rho / \rho_{\text{ice}}) / (1 - (1 - \rho / \rho_{\text{ice}})^{1/3})^3 \tag{A6}$$

where $\rho \geq 800$ kg m^{-3}. Δp is effective pressure, that is, overburden pressure of ice minus bubble pressure (in pascal), and $\mu = 3$ (creep exponent).

Equation (A3) is valid for effective pressures between 0.1 MPa and 1 MPa [*Barnes et al.*, 1971], a condition which is fulfilled in the depth range considered here. We have numerically evaluated the equation for heat transfer in the ice sheet [*Paterson*, 1994]:

$$\rho c \frac{\partial T}{\partial t} = k \nabla^2 T - \rho c\left(u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y}\right) + \left(\frac{dk}{dz} - \rho c w\right)\frac{\partial T}{\partial z} + q \quad \text{(A7)}$$

where k is thermal conductivity, c is heat capacity, x and y are horizontal coordinates, z is depth, u and v are horizontal ice velocities, w is vertical ice velocity, and q is internal heat production.

We made the following simplifications in the general equation: (1) No lateral heat transport was considered. This is justified because the horizontal temperature gradients and ice flow velocities are very small in the vicinity of the Summit area. (2) Internal heat production is negligible at the ice divide. (3) The vertical convective heat transport is incorporated in a separate step by adding new annual layers of snow on top of the ice sheet. The effect of all these simplifications is expected to have a small influence on the temperature profile down to 130 m, the lowest computed depth of the firn ice transition. Equation (A7) thus reduces to

$$\rho c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial z^2} + \frac{\partial k}{\partial z}\frac{\partial T}{\partial z} \quad \text{(A8)}$$

Equation (A8) in its finite difference form becomes

$$\rho_i c_i \frac{\Delta T_i}{\Delta t} = \frac{[2k_i + k'(z_i - z_{i-1})](T_{i+1} - T_i)}{(z_{i+1} - z_i)(z_{i+1} - z_{i-1})} - \frac{[2k_i - k'(z_{i+1} - z_i)](T_i - T_{i-1})}{(z_i - z_{i-1})(z_{i+1} - z_{i-1})} \quad \text{(A9)}$$

with

$$k' = \frac{(z_i - z_{i-1})(k_{i+1} - k_i)}{(z_{i+1} - z_i)(z_{i+1} - z_{i-1})} + \frac{(z_{i+1} - z_i)(k_i - k_{i-1})}{(z_i - z_{i-1})(z_{i+1} - z_{i-1})} \quad \text{(A10)}$$

Variables ρ_i, c_i, k_i, z_i, and T_i are the values at the layer midpoints.

For the thermal conductivity of firn we have used

$$k\,(\mathrm{W\,m^{-1}\,K^{-1}}) = k_{\mathrm{ice}}\left(\frac{\rho}{\rho_{\mathrm{ice}}}\right)^{2-0.5\frac{\rho}{\rho_{\mathrm{ice}}}} \quad \text{(A11)}$$

where $k_{\mathrm{ice}} = 9.828\ e^{-0.0057T}$ W m^{-1} K^{-1} [*Paterson*, 1994]. For ρ>200 kg m^{-3}, (A11) is a fit through data collected by *Mellor* [1977] and for $\rho/\rho_i \rightarrow 1$, it converges asymptotically toward the theoretical formula given by *Schwerdtfeger* [1963]. For the specific heat capacity, we used the formula from *Paterson* [1994]:

$$c\ (\mathrm{J\ kg^{-1}\ K^{-1}}) = 152.5 + 7.122\ T \quad \text{(A12)}$$

The heat transfer is calculated with annual layer resolution down to a depth of 300 m. Ten layers of bubble-free ice, each 100 m thick, were added below in order to assess the temperature profile to 1300 m depth. At 1300 m the heat flux was set to zero. Using the method of Crank-Nicolson [*Crank*, 1975] with a time step of 1 year, a numerical accuracy of about 0.1 K in the calculated temperature is obtained during very fast climatic variations (assumed worst case is dT_{surface}/dt = 1 K a^{-1}). Seasonal temperature variations were not considered. The effect of the implementation of heat transfer in the P-B model is depicted in Figure 2a.

Appendix B: Wiggle Matching

Signal correlation methods have been proposed to relate records of the same kind [*Martinson et al.*, 1982; *Pearson*, 1986]. These methods are not very adequate to relate the methane and δ^{18}O records because of their rather different nature and because we want to equate only the fast transitions of the records. Therefore we applied a Monte Carlo method, tuned for an optimal match of transitions.

In the following, we denote the δ^{18}O record with $a(t)$ and the methane record with $b(t)$, where t is the age of the ice. The equation $c(t) = t + \Delta\mathrm{age}(t)$ is a mapping function to relate $a(t)$ and $b(t)$. It is the goal to find $\Delta\mathrm{age}(t)$ for the best match of fast transitions between $a(t)$ and $b(c(t))$. We consider n methane values obtained from ice samples of age t_i ($i \in 1...n$) and search for the best correlations of mapped methane subrecords with δ^{18}O, that is, the best correlation between sequences of k shifted methane values and the isotope record: $\max(\mathrm{corr}(b(c(t_i)), a(t_i)))$; ($i \in j...j+k-1; j \in 1...n-k+1$).

The maximum correlation is searched by varying $\Delta\mathrm{age}(t_i)$ in the k values window randomly within meaningful limits: $\Delta\mathrm{age}_{\mathrm{min}}(t_i)$ = 200 years, $\Delta\mathrm{age}_{\mathrm{max}}(t_i)$ = 1500 years, and $\mathrm{abs}(\Delta\mathrm{age}(t_{i+1}) - \Delta\mathrm{age}(t_i)) \leq t_{i+1} - t_i$; that is, the slope in $\Delta\mathrm{age}(t)$ shall be within ±1. The lower limit (-1) is natural: Δage decreases if more than one annual layer passes the close-off density per year. If m annual layers reach close-off in 1 year, then the age of the ice at the firn-ice transition would decrease by m-1 years while the age of the air would remain roughly constant except from a small change in the diffusive mixing time. Δage would thus decrease by m-1 years over m annual layers corresponding to a slope in $\Delta\mathrm{age}(t)$ of $-(m-1)/m \geq -1$. The upper limit (+1) is somewhat arbitrary and is estimated based on "reasonable" scenarios of variations in temperature and accumulation rate.

The matching procedure is started with the subrecord window placed at one end of the methane record. An initial Δage value is attributed to the first methane point. The other k-1 Δage values are varied q times randomly in discrete 50 year steps. The set of Δage values yielding the best correlation between the mapped methane subrecord and the δ^{18}O record is saved. The window is then shifted by one methane data point, and the random variations are repeated again keeping the first point fixed at the Δage value of the best correlation from the previous window position. The window is shifted until it reaches the other end of the record. It turned out that the method is quite insensitive toward the direction in which the window is moved through the record. The whole procedure is repeated r times for each direction.

For the statistical evaluation of the obtained Δage function, we have considered only Δage values from the best correlations if (1) the correlation coefficient was at least 0.9, (2) the minimum variation in δ^{18}O within the window was 1.5‰ (in order to avoid correlation of very small signals), (3) the slope of the regression of $b(c(t))$ versus $a(t)$ is between 16 and 80 parts per billion by volume/‰ (to avoid matching of signals with very different amplitudes in the two records), and (4) $\mathrm{corr}(b(t_i),t_i) < 0.8$ (to avoid Δage values from a too linear part of the methane record).

For each of the n methane data points we have calculated mean and standard deviation of the Δage values meeting conditions 1 to 4. The mean is considered significant if these conditions were fulfilled at least in 30% of all cases and if the difference between the forward and backward moving window is less than 100 years. The averages of the forward and backward calculations are plotted in Figure 2.

The values of k, q, and r were selected according to the following criteria. The optimal value for k depends on the methane data density. For optimal edge sensitivity, the correlation window should typically span over one climatic interstadial. The number of random variations q is not very critical over a wide range. If q is selected too small, we will fail to find a set of Δages yielding a good correlation coefficient, and the scatter in Δage will be large. If q is chosen too large, the random generator will go through almost all possible variations and find nearly the same result in each run, yielding no information about the bandwidth of similarly good solutions. A good value for q is found if the resulting standard deviation of Δage is insensitive to q. The results were nearly identical for $r > 10$ if q was properly selected. For the results presented in Figure 2, we used $k = 6$, $q = 1500$, and $r = 1000$ for GRIP and $k = 15$, $q = 20000$, and $r = 40$ for GISP2.

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