JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 104, NO. D18, PAGES 22,163–22,170, SEPTEMBER 27, 1999

Delta^{15}N measurements as a calibration tool for the paleothermometer and gas-ice age differences: A case study for the 8200 B.P. event on GRIP ice

Markus C. Leuenberger, Clemens Lang, and Jakob Schwander
Climate and Environmental Physics, Physics Institute, University of Bern, Bern

Abstract. Isotopic composition measurement on atmospheric nitrogen (δ^{15}N) trapped in ice cores is established as a gravitational enrichment indicator. Recently, it was discovered that thermal diffusion has a significant influence on this parameter during periods of large temperature fluctuations [*Severinghaus et al.*, 1998]. Here we present results for the 8200 B.P. event, the largest temperature excursion during the Holocene, which underpin this view and extend it to medium-range temperature changes. The thermal diffusion component is about one third of the gravitational enrichment for this event. The shortness of this cooling event does not significantly affect the gravitational enrichment as documented by rather constant close-off depths. Therefore the δ^{15}N residuals can be directly used to estimate temperature changes, hence calibrating the paleothermometer. Since our δ^{15}N record can resolve temperature variations as short as a few decades, it complements the calibration technique of borehole temperature measurements, for which the resolution decreases rapidly with increasing age. We obtained a relation $\delta^{18}O_{ice}$ - temperature of 0.30±0.11‰/K, which agrees nicely with the temporal dependence for cold periods (about 0.30‰/K) and is significantly lower than today's Greenland spatial relation (0.67‰/K). This corresponds to a range of the surface temperature shift for the 8200 B.P. event in Central Greenland between 5.4 and 11.7 K, with a best estimate of 7.4 K. By matching the δ^{15}N variations with $\delta^{18}O_{ice}$ variations we estimate the mean gas-ice age difference to be –209±15 years, which is in good agreement with model estimates.

1. Introduction

The last 10,000 years (Holocene) have been a relatively stable warm climatic period. One striking exception is a short cooling event of about 100-150 years during the early Holocene starting at about 8200 years before present (B.P.) (i.e., 1950) [*Alley et al.*, 1997; *Dansgaard*, 1987]. This event, recorded quite clearly in Greenland ice cores, was also found in North Atlantic marine and other Northern Hemispheric records [*Klitgaard-Kristensen et al.*, 1998; *Von Grafenstein et al.*, 1998], even in tropical regions [*Alley et al.*, 1997]. The CH_4 data in ice cores also indicate the widespread nature of this event [*Blunier et al.*, 1995; *Chappellaz et al.*, 1993].

We studied this time period on the air in bubbles of the Greenland Ice Core Project (GRIP) ice core. As the isotope ratio of atmospheric nitrogen, δ^{15}N, is constant [*Mariotti*, 1983], all changes in the isotope ratio reflect changes through diffusional processes in the firn which are mainly dependent on temperature and accumulation rate and, in a less pronounced way, on wind speed and perhaps pressure changes at the surface. The firn can be divided into three regimes of different properties concerning the mixing of the air: (1) the convective zone, (2) the diffusive zone and (3) the non-diffusive zone [*Sowers et al.*, 1993]. In the last zone, gases are locked in. Under present conditions the ice at the top of the lock-in zone is about 220 years old. The diffusion delay is approximately 10 years for nitrogen, yielding a gas-ice age difference of about 210 years during the Holocene [*Schwander et al.*, 1997].

Paper number 1999JD900436.
0148-0227/99/1999JD900436$09.00

During the residence time in the diffusive zone the isotopic composition changes, as the air mixing here mainly happens through molecular diffusion without the influence of convection. At least two effects are known which alter the isotopic or elemental composition of the air.

First, molecular diffusion in the gravitational field of the Earth leads to an enrichment of heavier isotopes at the bottom of the firn column. According to the barometric equation we obtain at steady state the following:

$$\Delta\delta^{15}N_{\mathrm{grav}} = \left[\exp\left(\frac{\Delta mgz}{R_g T}\right) - 1\right] 1000‰ \cong \frac{gz}{R_g T}\Delta m 1000‰, \quad (1)$$

where Δm is the mass difference between ^{15}N and ^{14}N (in kilogram per mol), g is the gravitational acceleration, z is the height of the diffusive column, R_g denotes the ideal gas constant, and T is the mean firn temperature. The enrichment of other isotope or element ratios is proportional to $\Delta\delta^{15}$N and their corresponding mass difference [*Craig et al.*, 1988; *Schwander*, 1989; *Sowers et al.*, 1989]. The gravitational settling is therefore dependent on the height of the diffusive column and the mean firn temperature of the site. Changes in the diffusive column height occur as a result of a varying close-off depth due to changes in accumulation rates and tempera-

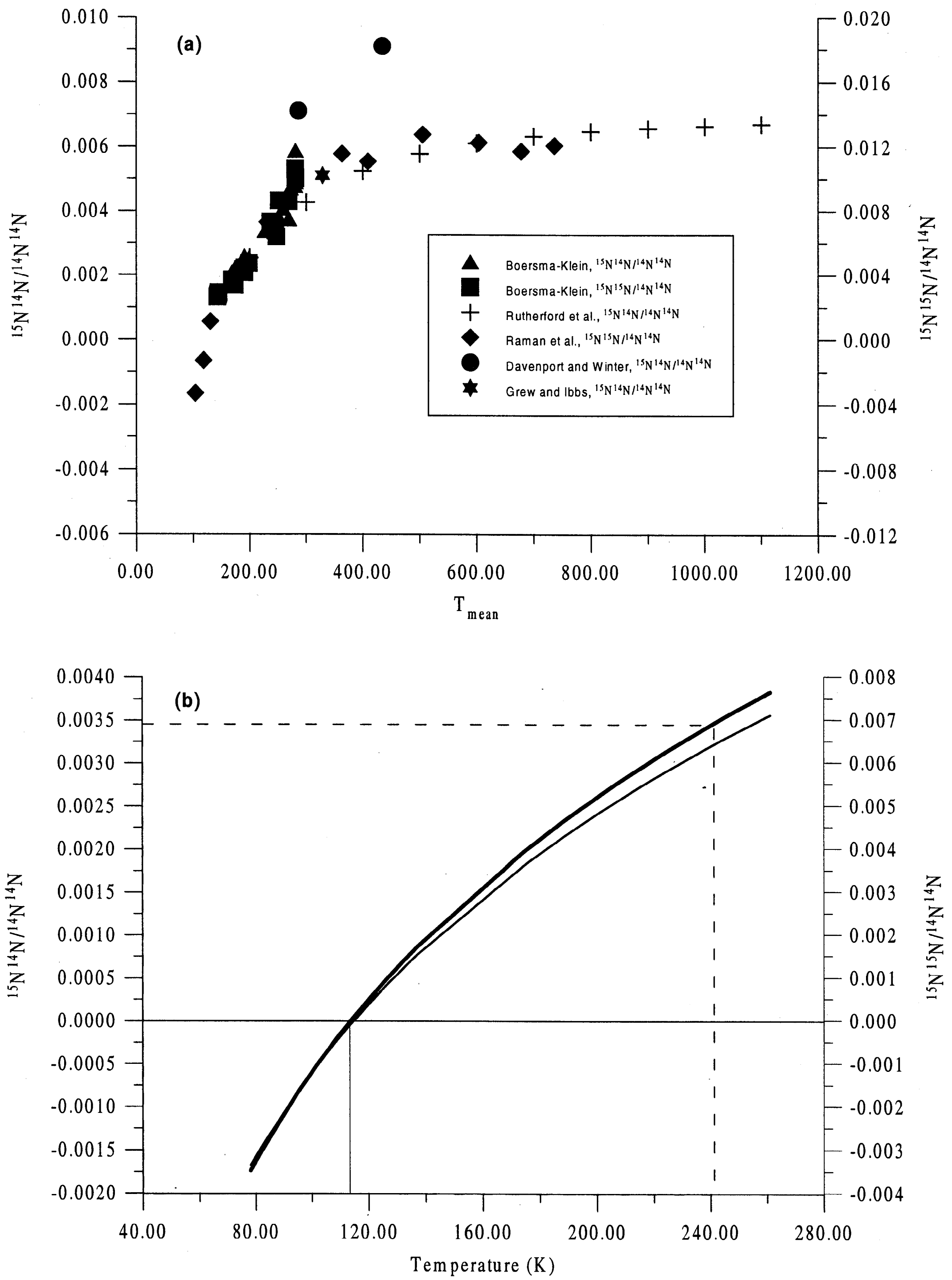

Figure 1. (a) Compilation of measured thermal diffusion fractionation factors versus the mean temperature from five studies for two isotopic compositions of nitrogen, $^{15}N_2$ in $^{14}N_2$ (right scale) and $^{15}N^{14}N$ in $^{14}N_2$ (left scale). T_{mean} is obtained from T_c and T_h according to $T_{mean} = T_cT_h/(T_h-T_c)\ \ln\ (T_h/T_c)$. For definitions, see [*Boersma-Klein and De Vries*, 1966]. Over the whole temperature range there is obviously an nonlinear dependence of this parameter, and it changes sign at a certain temperature (approximately 110 K). For the original *Boersma-Klein and De Vries* [1966] thermal separation results q, a good approximation is the quadratic dependence given by lnq = -0.01844793 $(\ln(T_h/T_c))$^2 + 0.03618010 $\ln(T_h/T_c)$, $r^2 = 0.95$. Grew [1947] showed that for a series of thermal separation factor measurement with constant T_h, the slope of such a dependence at a given temperature corresponds to the thermal diffusion factor at that temperature. We applied this 'slope method' taking into account the constant $T_h = 303$ K and the number of trennschaukels used in that study, which was 8 and obtained $\alpha(T) = 0.00461198\ \ln T - 0.02182912$ for nitrogen isotopes shown as thick solid line in Figure 1b. We expect a thermal diffusion factor at 241 K of (0.003467±0.000003). The basis of the uncertainty is a Monte Carlo simulation for an assumed error of the measured separation factor q of 0.8%. The results for the measured $^{15}N_2/^{14}N_2$ separation is in very good agreement with the theoretically expected ratio close to 2 (thin solid line).

ture or changes in the depth of the convective zone caused by wind velocity variations [*Schwander et al.*, 1997].

The second process, thermal diffusion, is dependent on a temperature gradient in the firn column. This process forces the heavier species to migrate toward the cold end of the firn column. The fractional deviation in equilibrium is given by [*Chapman and Cowling*, 1970]

$$\Delta\delta^{15}\mathrm{N}_{\mathrm{therm}} = \left[\frac{R}{R_0} - 1\right] 1000\,‰ = \left(\left[\frac{T_s}{T_b}\right]^{\alpha_T} - 1\right) 1000\,‰$$

$$\cong \alpha_T \left(\frac{\Delta T}{T_0}\right) 1000\,‰ \qquad (2)$$

where $\Delta T = T_s - T_b$ (Note the approximation $\Delta T/T_b$ to $\Delta T/T_0$), R is the isotope ratio compared to a reference (atmospheric) ratio R_o. T_b and T_s are the temperatures at the bottom and the surface of the diffusive firn column, respectively. T_0 is today's mean site surface temperature; α_T is the thermal diffusion factor of $^{15}N^{14}N/^{14}N^{14}N$ pair in air. A compilation of measurements of this thermal diffusion factor is given in Figure 1a. Its temperature dependence for our required temperature range was measured only by *Boersma-Klein and De Vries* [1966]. From these values, in the range of (142 to 280 K) we calculate a thermal diffusion factor of (0.00347 ± 0.000003) at 241 K (Figure 1b). However, an uncertainty of the absolute value remains since the above measurements were performed on pure nitrogen instead of air. Note that the given value above is significantly lower than the value given by *Grew and Ibbs* [1952] and adopted in the work of *Severinghaus et al.* [1996; 1998], which was based on a combination of data from *Davenport and Winter* [1951] and *Mann* [1948]. A literature search of measured nitrogen thermal diffusion factors documents that the results of *Davenport and Winter* [1951] are offset toward higher values, resulting from an overestimated thermal diffusion of isotopes in their experimental setup. Therefore we renounce these values.

2. Experimental Techniques

Delta ^{15}N was determined on gas from samples of the GRIP ice core from depths between 1300 m and 1400 m (age 7800 to 8780 years B.P. [*Johnsen et al.*, 1995]). We analyzed 51 samples of which three were discarded because of experimental problems. Forty-four samples correspond to 22 different depths (22 duplicate samples). Additionally, four single values from different depths were analyzed. The resolution in the time range from 7600 to 8600 years (gas ages) is better than 50 years (or < 5 m).

Samples of about 18 g were placed in precooled glass vacuum vessels (-35°C) followed by evacuation for 70 min. The ice samples were melted and refrozen again to liberate the enclosed gas in the bubbles and clathrates. The gas was passed through a water trap (-92°C) and frozen at 18 K. We repeated this procedure 3 times until less than 50 ppm of the gas was left. The samples were then analyzed using a MAT-250 mass spectrometer. The $^{15}N/^{14}N$ ratios were measured in simultaneous mode against a working standard gas close to modern air composition with a reproducibility of 0.02‰, which agrees with the mean measured range of duplicates. All $\delta^{15}N$ values are expressed as deviations from modern atmospheric nitrogen isotope ratio. The estimated overall uncertainty is 0.05‰, including uncertainties associated with calibration, extraction shift, and mass spectrometer-specific corrections (i.e., zero enrichment, time-dependent isotope depletion of the working standard during an analysis day, and CO^+ interference from fragmentation of CO_2 (see Table 1)).

Table 1. Applied Corrections for $\delta^{15}N$ Measurements

Correction	$\Delta\delta^{15}N$ (‰)	1σ uncertainty (‰)
Zero enrichment	0	0.020
Drift working standard	<0.15#	0.020
Blank and extraction shift	-0.095	0.034
Calibration against air	+0.058	0.006
CO^+ interference	-0.003	0.002
Overall correction	ca. <0.12	0.045

The stated uncertainty of 0.05‰ is the result of a bunch of uncertainties associated with blank tests, extraction shift, mass spectrometric corrections, CO^+ interference from fragmentation of carbon dioxide), calibration of our working standard, etc. The slightly enriched sample CO_2 concentrations of 405±20 ppmv (melt extraction) give only a small CO^+ correction because our working standard contains 365 ppmv of CO_2. The zero enrichment correction is a combination of two corrections: (1) the zero enrichment shift at the start of the analysis day and (2) its temporal drift. Similarly, the extraction shift is also a combination of two uncertainties: (1) the uncertainty associated with the direct measurement of the reference gas and (2) the uncertainty of the fully processed reference gas.

drifts of working standard (<0.025‰/h, corresponding to <0.15‰ for a daily measurement

3. Results

The $\delta^{15}N$ results are displayed in Figure 2 together with the oxygen isotope record $\delta^{18}O_{ice}$ of the GRIP ice core [*Johnsen et al.*, 1995], which is corrected for changes in seawater $\delta^{18}O$ due to ice volume variations [*Sowers et al.*, 1992]. Since the age of the gas trapped in the ice is younger than the corresponding ice itself, $\delta^{15}N$ and $\delta^{18}O_{ice}$ records differ by the gas-ice age difference. The $\delta^{18}O_{ice}$ data were smoothed with an 11 year running mean to obtain a time resolution that is comparable to the gas data resolution. The $\delta^{15}N$ variations are naturally smoothed due to the firn mixing time of about 10 years at the bottom of firn column.

The two isotope records of $\delta^{15}N$ and $\delta^{18}O_{ice}$ show quite similar variations. The short cooling event around about 8200 years B.P. is documented by a decrease in $\delta^{18}O_{ice}$ and $\delta^{15}N$. Even short changes in $\delta^{18}O_{ice}$ in the range of decades seem to show comparable features in $\delta^{15}N$. However, because of the lower resolution (<50 years) of our $\delta^{15}N$ it is not yet possible to determine to what resolution the correspondence holds, but most of the slopes between two $\delta^{15}N$ data points parallel $\delta^{18}O_{ice}$ changes.

To account for the gas-ice age difference, we shifted the $\delta^{15}N$ data by 209 years for which the correlation with $\delta^{18}O_{ice}$ is at its maximum (see below). Because the accumulation rate changes are quite moderate (see discussion below), a constant gas-ice age difference should be appropriate. To estimate the changes in accumulation rate, we examined the calcium and ammonium records from *Fuhrer et al.* [1993] and found a maximum reduction in accumulation rate of about 25%, which lasted, however, for only a decade. The uncertainty of this estimate is rather large (±5%) due to the shortness of the event. Following the event, there is a rather steady increase in

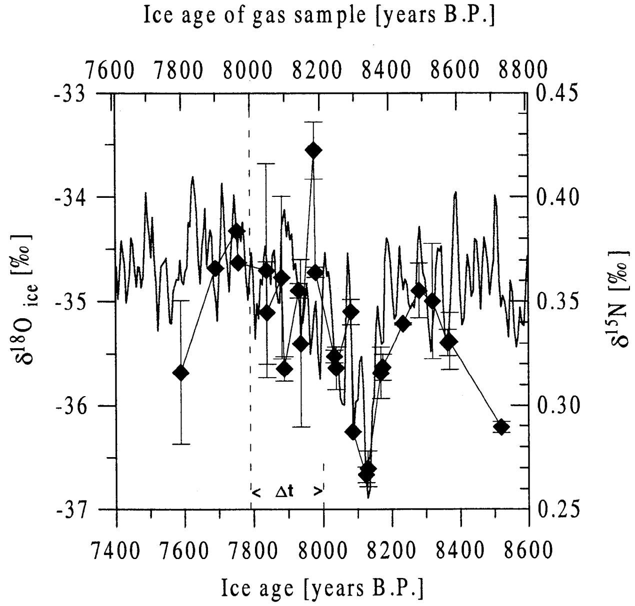

Figure 2. The $\delta^{15}N$ data (diamonds) are mean values and are given as deviations from its ambient air ratio. The range of single values are displayed as error bars. Gas-ice age difference, Δage, is taken as 209 years; see Figure 6, the $\delta^{18}O_{ice}$ record according to SS09 timescale of the GRIP ice core [*Johnsen et al.*, 1995].

the accumulation rate of around 20% which lasts for more than a century, as seen in these records in agreement with results of *Alley* [1997]. The correlation between $\delta^{18}O_{ice}$ and the accumulation rate [*Johnsen et al.*, 1995] yields a similar mean reduction from 0.23 m/yr to 0.21 m/yr (0.17 m/yr at its lowest value but only for a decade) during the event followed by an increase to 0.26 m/yr. On the basis of model results [*Schwander et al.*, 1997] this corresponds to a variation in gas-ice age differences of less than ±15 years. A very small influence on close-off depth and therefore on gravitational fractionation is also documented by the results of model calculations during this period, however they never exceed 0.02 per mil even when the relation between the $\delta^{18}O_{ice}$ and the accumulation rate underestimates short-term fluctuations of accumulation rates. Important could be a deepening of the convective zone due to enhanced wind speed accompanying the cooling [*Colbeck*, 1989; 1997]. However, *Sowers et al.* [1992] found no covariance of $\delta^{15}N$ results from 11 sites with wind speed. From a firn air study at Summit (Greenland), one cannot exclude a convective zone of a few meters [*Schwander et al.*, 1993; *Trudinger et al.*, 1997] at present times. Comparison between measured and modeled $\delta^{15}N$ values for the 8200 year event leads to a rather constant convective zone of 5±1 m under the assumption of a constant relationship between $\delta^{18}O_{ice}$ and temperature (see Figure 4).

4. Discussion

The residual variations in $\delta^{15}N$, remaining after subtracting the rather constant gravitational influence which we obtained from model calculation [*Schwander et al.*, 1997], are interpreted as thermal fractionation in the diffusive firn column (note that no convective zone has been assumed here, because it has no influence on our conclusions, as discussed below, as long as it stays constant). These residuals were compared with estimates of the surface and bottom firn temperatures (T_s, T_b), calculated using the model of *Schwander et al.* [1997], which is based on a dynamic firn densification model with incorporated heat transfer and molecular diffusion. It was extended down to 1000 m to account for the large heat capacity of ice. The model was run for three cases: (1) for the quadratic temperature dependence on $\delta^{18}O_{ice}$ according to *Johnsen et al.* [1995], based on borehole temperature measurements, and two extreme linear dependencies of the temperature with $\delta^{18}O_{ice}$; (2) $\partial\delta^{18}O_{ice}/\partial T$=0.33‰/K; and (3) $\partial\delta^{18}O_{ice}/\partial T$=0.67‰/K. In Figure 3, T_s and T_b are displayed versus ice ages at close-off depths, corresponding to the ice age of the gas sample, from 7,000 to 10,000 years before present for the three different cases. The event occurs at about 8400 years (gas age about 8200 years B.P.) with a maximum temperature change of 4.2°, 6.8°, and 3.3° Celsius based on $\Delta\delta^{18}O_{ice}$ of 2.23‰ for cases 1, 2, and 3, respectively. The minimum temperature is reached at slightly different times due the temperature dependence of the accumulation rate and the temperature diffusion coefficients.

We now compare measured $\delta^{15}N$ values with theoretical estimates of $\delta^{15}N$ from modeled temperatures at the surface and close-off depth of the firn and the variation of the close-off depth itself (Figure 4). The main effect on $\delta^{15}N$ is due to gravitational settling in the firn in the case of the present study. The variation of the modeled close-off depth is negligible, indicated by the very small changes in the gravitational enrichment of $\delta^{15}N$. The measured $\delta^{15}N$ values seem to be slightly lower than the modeled values using the 0.33‰/K T-$\delta^{18}O_{ice}$ dependence. The value of $\delta^{15}N$ = 0.42‰ at 8185 years B.P. is extreme and is treated as an outlier.

Bottom temperatures are still lowered by the influence of the past cold periods (Younger Dryas, glacial). The mean

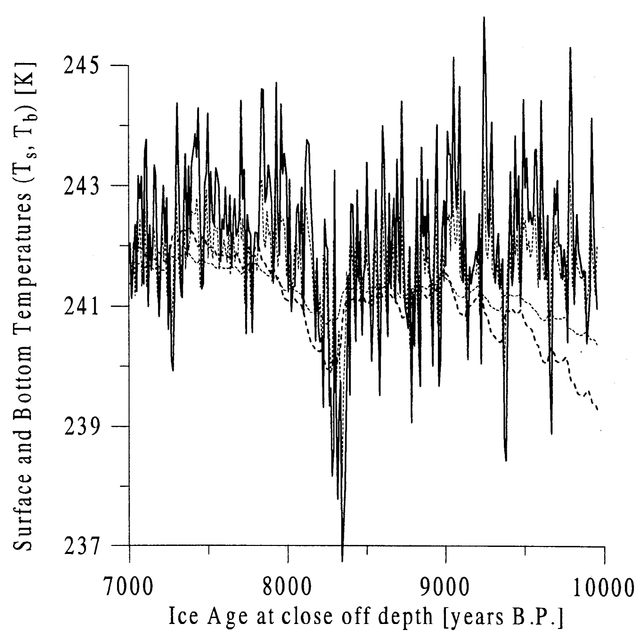

Figure 3. Surface and bottom (close-off) temperature in Kelvin as calculated by the firn densification and heat transfer model of *Schwander et al.* [1997] for ice ages at the close-off depths from 10000 to 7000 years B.P.. The thick lines represent the surface (solid line) and bottom (dotted line) temperatures for the 0.33‰/K scenario, whereas the thin dashed lines represent the 0.67‰/K scenario.

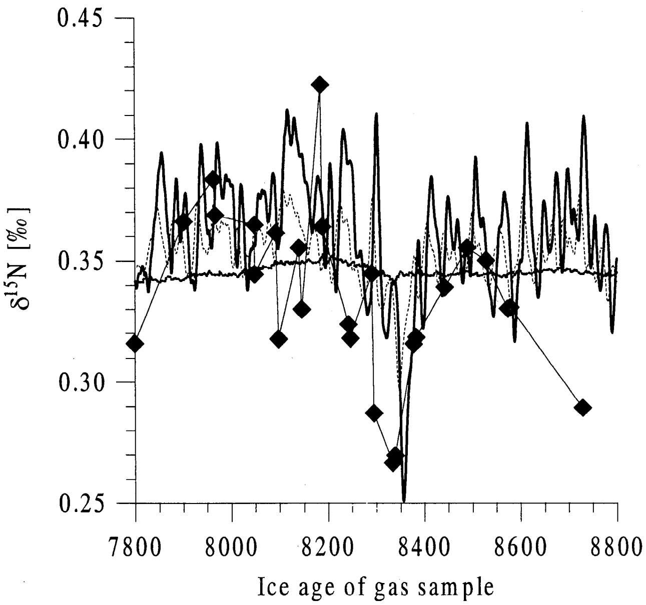

Figure 4. Comparison between modeled (solid line) and measured $\delta^{15}N$ values (rhomboids) during the 8200 year event. Ages are given as ice ages of the gas samples. Here individual gas-ice age differences are calculated on the basis of the firn densification model. The 0.33‰/K and 0.67‰/K scenarios are shown as solid and dotted lines, respectively. The solid dotted line represents variation of the gravitational enrichment and hence the effect on measured $\delta^{15}N$ values due to the variation of the close-off depth, which is mainly driven by accumulation rate changes after the 8200 year event [*Alley et al.*, 1997]. On the basis of the relationship between accumulation rate and $\delta^{18}O_{ice}$ [*Johnsen et al.*, 1995] the effect on the measured $\delta^{15}N$ values is less than 0.02‰ over the whole analyzed period.

value of about 0.33‰ for $\delta^{15}N$ (Figure 4) is the result of a mean diffusion column depth and a slight long-term thermal diffusion effect of 0.01‰ due to a remaining signal of the large Younger Dryas and glacial-interglacial temperature changes. This latter effect is documented by increasing bottom temperatures in Figure 3. Therefore a mean diffusion column depth of 65 to 66 m can be derived from (1). The close-off depths calculated by the model [*Schwander et al.*, 1997], which exclude the nondiffusive zone but not the convective zone, are higher with 70 to 74 m for the 0.33‰/K scenario. This is in agreement with a convective zone of a few meters [*Schwander et al.*, 1993; *Trudinger et al.*, 1997]. Modeling results by *Colbeck* [1989, 1997] could suggest a deeper convective zone during the event, which would account for a part of the measured decrease in $\delta^{15}N$ and hence would lead to a higher estimate of α. However, our model results do not indicate a larger difference between measured and modeled $\delta^{15}N$ values during the 8200 year event, when switching from scenario 0.33‰/K to 0.67‰/K (see Figure 3) and are hence not supporting the hypothesis of a deeper convective zone. In the following, we will discuss the $\delta^{15}N$ values in detail regarding temperature changes and gas-ice age differences.

4.1. Paleotemperature

A large number of studies investigated the strong correlation between $\delta^{18}O_{ice}$ and surface temperature in middle and high latitudes [*Jouzel et al.*, 1997]. Because of the lack of a relation between temporal surface temperature and $\delta^{18}O_{ice}$ a spatial relationship has been applied to reconstruct paleotemperatures. However, recent studies [*Cuffey et al.*, 1994; *Johnsen et al.*, 1995] showed by measuring borehole temperatures that the general assumption of adapting a spatial relationship between $\delta^{18}O_{ice}$ and surface temperature (see equation (3)) is not appropriate to calibrate temperature changes of the past. On the basis of this, there is a need for methods to monitor temporal relationships between $\delta^{18}O_{ice}$ and surface temperature. Borehole temperatures allow us to detect past temperature variations with a resolution that decreases rapidly with age [*Alley and Koci*, 1990]. The $\delta^{15}N$, which is affected by short-term temperature variations, therefore optimally complements the borehole temperature technique.

The surface temperature $\delta^{18}O_{ice}$ relationship is defined as

$$\alpha = \frac{\Delta\delta^{18}O_{ice}}{\Delta T_s}, \tag{3}$$

with $\Delta\delta^{18}O_{ice} = \delta^{18}O_{ice} - \delta_0{}^{18}O_{ice}$ and $\Delta T_s = T_s - T_0$, where $\delta_0{}^{18}O_{ice}$ and T_0 are reference values. We set $\delta_0{}^{18}O_{ice}$ = -34.9‰ and T_0 = 241,45 K [*Gundestrup et al.*, 1994], for example, for the actual mean values from the GRIP location.

According to equation (2) $\delta^{15}N$ variations after substracting the gravitational enrichment reflect directly the temperature difference between the surface and the bottom of the firn, $\Delta T = T_s - T_b$, we can write

$$\alpha' = \frac{\Delta\delta^{18}O_{ice}}{\Delta T}. \tag{4}$$

The surface temperature T_s may be derived, if the temperature at the bottom of the firn, T_b, is known. The temperature change at the bottom of the firn is a convolution of the history of temperature and accumulation rate, taking into account the effect of heat diffusion and advection in the firn and ice layers, and is represented by the function f^* according to equation (5). The influence of heat advection is negligible. Having in mind the small temperature dependencies of ice density ρ, ice heat capacity c, ice heat conductivity k combined with small accumulation changes (< 10% as shown above), the dependence of ΔT_b on the close-off depth is negligible and f^* is approximately a function of the surface temperature change only:

$$\Delta T_b = T_b - T_0 = f^*(\Delta T_s) = f^*\left(\frac{\Delta\delta^{18}O_{ice}}{\alpha}\right). \tag{5}$$

Model calculations show a good proportionality for equation (5) in the momentary value of α^{-1} for the three cases mentioned above for delta-pulse responses. This proportionality remains even for the last glacial-interglacial transition and the whole glacial period. This allows us to simplify equation (5) to

$$\Delta T_b = \frac{f(\Delta\delta^{18}O_{ice})}{\alpha}. \tag{6}$$

The function $f(\Delta\delta^{18}O_{ice})$ is therefore independent of the relation given in (3). Combining equations(3), (4) and (6) we obtain

$$\alpha = \frac{\Delta\delta^{18}O_{ice} - f(\Delta\delta^{18}O_{ice})}{\Delta T}. \quad (7)$$

Applying this relation to our data (see Figure 5), we obtain correlation coefficients (r^2) of 0.52 for the mean values of duplicate samples. The significance level is 0.001, which documents this strong dependence between temperature and $\delta^{18}O_{ice}$. Simple regression analysis yields α = (0.25 ± 0.11)‰/K (95% confidence interval). A more sophisticated linear regression analysis [e.g., *Draper and Smith*, 1998] shows that the estimate of the slope will be biased if the uncertainty for single *x*-values is of similar order as the *x*-value range. An approximation of this shift is given by *Draper and Smith* [1998, formula 3.4.10, p. 90]. Taking this into account, we have underestimated our α value by roughly 20%. Therefore the best estimate of the slope, based on our data, is (0.30±0.11)‰/K for α.

This yields an estimated maximum temperature decrease for the 8200 year event in the range of 5.4 to 11.7 K with a best estimate of 7.4 K for a $\Delta\delta^{18}O_{ice}$ drop of 2.23‰ (see Figure 2). The associated uncertainties are rather high, reflecting the limited resolution of our $\delta^{15}N$, some noise in the $\delta^{18}O_{ice}$ record, and possibly varying α. The calculated value is in very good agreement with the 0.33‰/K scenario for long-term variations derived from borehole temperatures [*Cuffey et al.*, 1995; *Johnsen et al.*, 1995] and significantly lower than the value derived from spatial variation [*Johnsen et al.*, 1989]. However, Holocene values from GRIP borehole examination tend to the higher (spatial) values [*Johnsen et al.*, 1989] in contrast to our estimate for the 8200 year event.

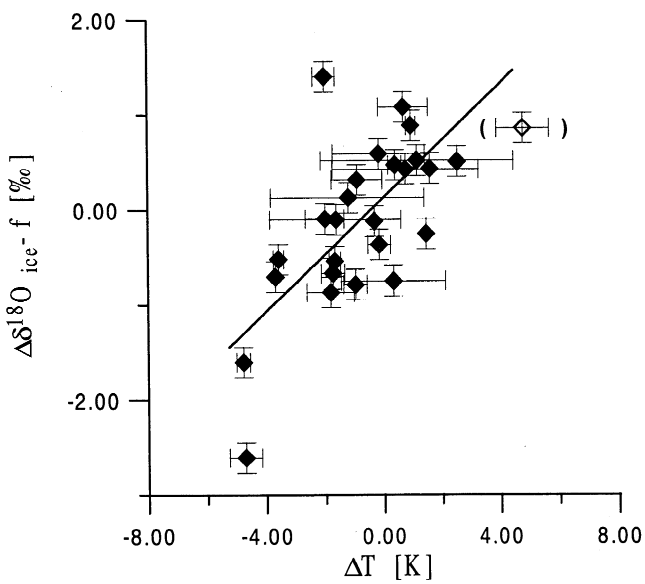

Figure 5. Correlation plot according to equation (7) for calibration of the paleothermometer using $\delta^{15}N$ values. The *y* axis represents short-term $\delta^{18}O_{ice}$ variations, whereas the *x* axis documents temperature changes. The data point in parentheses, $\delta^{15}N_{mean}$ = 0.42‰, is treated as an outlier. Linear regressions of the mean (diamonds, solid line) yield a $\delta^{18}O_{ice}$ - temperature relationships of 0.27±0.11‰/K. The regression is significant to 0.001 according to the t test. (Note that this slope is biased due to similar large values for the *x* range and *x* value error; see text for details). Horizontal error bars document the range of the corresponding two single values, whereas the vertical error bar denotes the uncertainties associated with $\delta^{18}O_{ice}$ determinations.

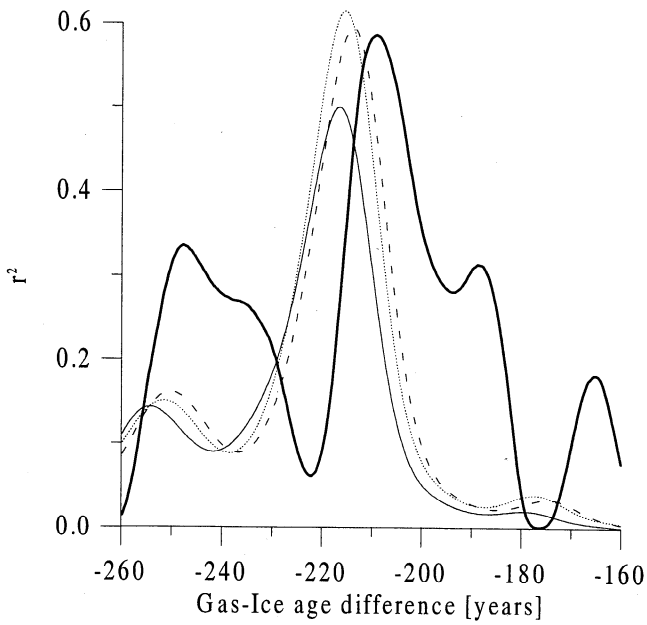

Figure 6. Dependence of the linear correlation coefficient (r^2) of the two temperature proxies $\delta^{18}O_{ice}$ and $\delta^{15}N$ on mean gas-ice age differences for the measured depth range (i.e., 1300-1400 m, 7800-8780 years BP [*Johnsen et al.*, 1995]). This correlation is given for the mean values (thick solid line), excluding $\delta^{15}N$ = 0.42‰. The best correlation is obtained for a gas-ice age difference of -209 years with a half-width value of 15 years. The dashed, thin solid and dotted lines show the linear correlation coefficients dependence which we obtained by correlating $\delta^{18}O_{ice}$ with modeled $\delta^{15}N$ values for variable α according to *Johnsen et al.* [1995], the 0.33‰/K and 0.67‰/K scenarios, respectively. The small offset for the age difference of maximum correlation between the data and the model lies within the estimated uncertainties.

A more detailed record of $\delta^{15}N$ should allow us to further improve this paleothermometer calibration on short-term variations for which the influence of temperature diffusion on the bottom temperature and hence on the derived α value is very small. Model results show that short temperature excursions of 60-70 years should be attenuated in the bottom temperature to 5%, which is negligible.

Furthermore, elemental as well as isotopic composition measurements of noble gases would hopefully permit to separate gravitational enrichment from thermal diffusion influence [*Severinghaus et al.*, 1998]. This separation is particularly important for periods of strong changes in accumulation rate and temperature, where significant variations in close-off depth are expected.

4.2. Gas-Ice Age Difference

To obtain information about the gas-ice age difference (Δage) at 8200 B.P. in the GRIP core and to test the accuracy of the model of *Schwander et al.* [1997], we compared the two independent records containing temperature information, i.e., $\delta^{18}O_{ice}$ and the presented $\delta^{15}N$. While shifting these records with respect to time against each other, we calculated the linear correlation coefficient r^2 for the mean values omitting an outlier ($\delta^{15}N = 0.42$ at $t = 8185$ years B.P.) (solid line) and the single values except the outlying value (dashed line) (Figure 6). The plot shows a distinct correlation maximum at Δage = -209 years with a half-value width of 15 years for the mean values. The maximum of correlation is mainly determined by the strong signal of the 8200 event, hence the gas-ice age difference for this event is obtained. The sharpness of the correlation peak is an upper limit of the Δage variation during the investigated period. The half-value width of 15 years is consistent with our assumption of only small changes in accumulation rates.

For comparison we correlated the modeled $\delta^{15}N$ with $\delta^{18}O_{ice}$ and found a maximum of best correlation for Δage = -215 years and a half-value width of 10 years, largely independent of α. These model results are in good agreement with our measurements (Figure 6).

5. Conclusion

Isotopic measurements of nitrogen, $\delta^{15}N$, for the 8200 year climate event provide a case study of calibrating the paleotemperature and gas-ice age differences. It is an independent tool to fill calibration gaps for short periods which cannot be resolved with the borehole temperature measurements as heat diffusion smooths the short-term variations. The $\delta^{18}O_{ice}$ and $\delta^{15}N$ are parallel for variations as short as a few decades. This paleotemperature calibration could be further constrained by measuring argon isotopes or even better elemental ratios of noble gases, which have different thermal diffusion factors and exhibit larger absolute gravitation effects due to higher mass differences than nitrogen. This would permit to separate the gravitation from thermal diffusion influence. Unfortunately, for this study we were not yet able to perform these measurements but model calculations indicated that this limitation is not crucial for the 8200 year event since the gravitational fractionation is rather constant.

For any synchronization, using global parameters such as CH_4 and $\delta^{18}O_{atm}$, it is necessary to have reliable estimates of gas-ice age differences [*Blunier et al.*, 1997]. By matching $\delta^{15}N$ and $\delta^{18}O_{ice}$ we can determine this age differences for periods with moderate to large temperature changes with a precision that is basically only limited by the uncertainty of the annual layer thickness estimates.

Acknowledgments This work was financially supported by the BEW and the Priority Program Environment of the Swiss National Science Foundation. We appreciate helpful comments from T. Stocker, T. Blunier, and D. Peel. J. P. Severinghaus has provided us with very helpful information of previous experimental work about the thermal diffusion factors, and we are indebted to S. Johnsen for providing us with GRIP $\delta^{18}O_{ice}$ record and the GRIP age scale. We also would like to thank three anonymous reviewers, whose comments improved earlier draft versions of this publication.

References

Alley, R., and B. R. Koci, Recent warming in central Greenland?, *Ann. Glaciol.*, *14*, 6-8, 1990.

Alley, R.B., A. Mayewski, T. Sowers, M. Stuiver, K.C. Taylor, and P.U. Clark, Holocene climatic instability: A prominent, widespread event 8200 yr ago, *Geology*, *25*, 483-486, 1997.

Blunier, T., J. Chappellaz, J. Schwander, B. Stauffer, and D. Raynaud, Variations in atmospheric methane concentration during the Holocene epoch, *Nature*, *374*, 46-49, 1995.

Blunier, T., J. Schwander, B. Stauffer, T. Stocker, A. Dällenbach, J. Indermühle, J. Tschumi, D. Chappellaz, D. Raynaud, and J.-M. Barnola, Timing of the Antarctic Cold Reversal and the atmospheric CO_2 increase with respect to the Younger Dryas event, *Geophys. Res. Lett.*, *24* (21), 2683-2686, 1997.

Boersma-Klein, V., and A.E. De Vries, The influence of the distribution of atomic masses within the molecule on thermal diffusion, *Physica*, *32*, 717-733, 1966.

Chapman, S., and T.G. Cowling, *The Mathematical Theorie of Non-Uniform Gases*, Cambridge Univ. Press, New York, 1970.

Chappellaz, J., T. Blunier, D. Raynaud, J.M. Barnola, J. Schwander, and B. Stauffer, Synchronous changes in atmospheric CH_4 and Greenland climate between 40 and 8 kyr BP, *Nature*, *366*, 443-445, 1993.

Colbeck, S.C., Air movement in snow due to wind pumping, *J. Glaciol.*, *35* (120), 209-213, 1989.

Colbeck, S.C., Model of wind pumping for layered snow, *J. Glaciol.*, *43* (143), 60-65, 1997.

Craig, H., Y. Horibe, and T. Sowers, Gravitational separation of gases and isotopes in polar ice caps, *Science*, *242*, 1675-1678, 1988.

Cuffey, K.M., R.B. Alley, P.M. Grootes, J.M. Bolzan, and S. Anandakrishnan, Calibration of the $\delta^{18}O$ isotopic paleothermometer for central Greenland, using borehole temperatures, *J. Glaciol.*, *40* (135), 341-349, 1994.

Cuffey, K.M., G.D. Clow, R.B. Alley, M. Stuiver, E.D. Waddington, and R.W. Saltus, Large arctic temperature change at the Wisconsin-Holocene glacial transition, *Science*, *270*, 455-458, 1995.

Dansgaard, W., Ice core evidence of abrupt Climatic changes, in *Abrupt Climatic Changes*, edited by W.H. Berger, and L.D. Labeyrie, pp. 223-233, D. Reidel, Norwell, Mass., 1987.

Davenport, A.N., and E.R.S. Winter, Diffusion properties of gases, V, The thermal diffusion of carbon monoxide, nitrogen, and methane, *Trans. Faraday Soc.*, *47*, 1160-1169, 1951.

Draper, N.R., and H. Smith, *Applied Regression Analysis*, 706 pp., John Wiley, New York, 1998.

Fuhrer, K., A. Neftel, M. Anklin, and V. Maggi, Continuous measurements of hydrogen peroxide, formaldehyde, calcium and ammonium concentrations along the new GRIP ice core from Summit, Central Greenland, *Atmos. Environ.*, *27A*, 1873-1880, 1993.

Grew, K.E., Thermal diffusion in mixtures of the inert gases, *Proc. Roy. Soc. A*, *189*, 402-414, 1947.

Grew, K.E., and T.L. Ibbs, *Thermal Diffusion in Gases*, Cambridge Univ. Press, New York, 1952.

Gundestrup, N.S., H.B. Clausen, and B.L. Hansen, The UCPH borehole logger, in *Ice Drilling Technology*, edited by O. Watanabe, pp. 224-233, Natl. Inst. of Polar Res., Tokyo, 1994.

Johnsen, S.J., W. Dansgaard, and J.W.C. White, The origin of Arctic precipitation under present and glacial conditions, *Tellus, Ser. B*, *41*, 452-468, 1989.

Johnsen, S., D. Dahl-Jensen, W. Dansgaard, and N. Gundestrup, Greenland palaeotemperatures derived from GRIP borehole temperature and ice core isotope profiles, *Tellus*, *Ser. B*, *47*, 624-629, 1995.

Jouzel, J., et al., On the validity of the temperature reconstruction from water isotopes in ice cores, *J. Geophys. Res.*, *102*, 26,471-26,487, 1997.

Klitgaard-Kristensen, D., H.P. Sejrup, H. Haflidason, S.J. Johnsen, and M. Spurk, A regional 8200 cal. yr BP cooling event in Northwest Europe, induced by final stages of the Laurentide ice-sheet deglaciation?, *J. Quat. Sci.*, *13* (2), 165-169, 1998.

Mann, A.K., The thermal diffusion constant of nitrogen, *Phys. Rev.*, *73*, 412, 1948.

Mariotti, A., Atmospheric nitrogen is a reliable standard for natural abundance measurements, *Nature*, *303*, 685-687, 1983.

Raman, S., B.P. Mathur, A.J. Howard, J.W. Champlin, and W.W. Watson, Thermal diffusion in polyatomic gases: Isotopic $^{15}N_2$-$^{14}N_2$, *Journal of Chemical Physics*, *49* (11), 4877-4879, 1968.

Rutherford, W.M., W.J. Roos, and K.J. Kaminski, Experimental verification of the thermal diffusion column theory as applied to the separation of isotopically substituted nitrogen and isotopically substituted oxygen, *Journal of Chemical Physics*, *50* (12), 5359-5365, 1969.

Schwander, J., The transformation of snow to ice and the occlusion of gases, in *The Environmental Record in Glaciers and Ice Sheets*, edited by H. Oeschger and C.C. Langway Jr., pp. 53-67, John Wiley, New York, 1989.

Schwander, J., J.-M. Barnola, C. Andrié, M. Leuenberger, A. Ludin,

D. Raynaud, and B. Stauffer, The age of the air in the firn and the ice at Summit, Greenland, *J. Geophys. Res.*, *98*, 2831-2838, 1993.

Schwander, J., T. Sowers, J.-M. Barnola, T. Blunier, B. Malaizé, and A. Fuchs, Age scale of the air in the summit ice: Implication for glacial-interglacial temperature change, *J. Geophys. Res.*, *102* (D16), 19,483-19,494, 1997.

Severinghaus, J.P., M.L. Bender, R.F. Keeling, and W.S. Broecker, Fractionation of soil gases by diffusion of water vapor, gravitational settling and thermal diffusion, *Geochim. and Cosmochim. Acta*, *60*, 1005-1018, 1996.

Severinghaus, J.P., T. Sowers, E.J. Brook, R.B. Alley, and M.L. Bender, Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice, *Nature*, *391*, 141-146, 1998.

Sowers, T.A., M.L. Bender, and D. Raynaud, Elemental and isotopic composition of occluded O_2 and N_2 in polar ice, *J. Geophys. Res.*, *94*, 5137-5150, 1989.

Sowers, T., M. Bender, D. Raynaud, and Y.S. Korotkevich, Delta ^{15}N of N_2 in air trapped in polar ice: A tracer of gas transport in the firn and a possible constraint on ice age-gas age differences, *J. Geophys. Res.*, *97*, 15683-15697, 1992.

Sowers, T., M. Bender, L. Labeyrie, D. Martinson, D. Raynaud, J.J. Pichon, and Y.S. Korotkevich, A 135.000-year Vostok-Specmap common temporal framework, *Paleoceanography*, *8* (6), 737-766, 1993.

Trudinger, C.M., I.G. Enting, D.M. Etheridge, R.J. Francey, V.A. Levchenko, L.P. Steele, D. Raynaud, and L. Arnaud, Modelling air movement and bubble trapping in firn, *J. Geophys. Res.*, *102*, 6747-6763, 1997.

Von Grafenstein, U., H. Erlenkeuser, J. Müller, J. Jouzel, and S. Johnsen, The cold event 8200 years ago documented in oxygen isotope records of precipitation in Europe and Greenland, *Clim. Dyn.*, *14*, 79-81, 1998.

M. Leuenberger (corresponding author), C. Lang, and J. Schwander, Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland. (leuenberger@climate.unibe.ch; lang@climate.unibe.ch; schwander @climate.unibe.ch.)

(Received December 8, 1998; revised April 12, 1999; accepted June 3, 1999.)