Evidence for stratigraphic distortion in the Greenland Ice Core Project (GRIP) ice core during Event 5e1 (120 kyr BP) from gas isotopes

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[1] The disturbed stratigraphy of the ice in the lowest 10% of the Greenland GRIP ice core has been previously demonstrated using gas measurements ($\delta^{18}O$ of O_2 and CH_4) on a few meters depth scale. However, rapid ice isotopic variations (on the scale of 20 cm) are experienced in the bottom of the GRIP ice core with complex chemical signatures that make them difficult to reconcile with a disturbed stratigraphy of the ice. This is the case for event 5e1, first described as a dramatic cooling 120 kyr BP. We analyzed at a 5 cm resolution the isotopic composition of the air from 2 m of the GRIP bottom ice core covering event 5e1. The $\delta^{15}N$ measurements, combined with a basic firn modeling, lead to the solid conclusion that the rapid event 5e1 is not a climatic event. Rapid variations of $\delta^{18}O$ of O_2 ($\delta^{18}O_{atm}$) are in agreement with a disturbed ice stratigraphy. However, the double peak shape of the $\delta^{18}O_{atm}$, recalling chemical data at the same depth, requires processes of diffusion after the mixing or even postcoring, placing limits to the interpretation of some classical paleoclimatic proxies in small scale mixed ice (<1 m). *INDEX TERMS:* 1827 Hydrology: Glaciology (1863); 3344 Meteorology and Atmospheric Dynamics: Paleoclimatology; 3349 Meteorology and Atmospheric Dynamics: Polar meteorology; *KEYWORDS:* ice core, rapid climatic change, air isotopic composition

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1. Introduction

[2] The last interglacial period (130–118 kyr BP, also called Marine Isotope Stage 5e (MIS 5e) from paleo-oceanographic studies [*Martinson et al.*, 1987; *Shackelton et al.*, 2002]) has been subject to numerous paleoenvironmental studies in order to better understand climate mechanisms during warm stages such as ours (see for example *Kukla et al.* [2002] for an overview). The ice core record from Vostok (Antarctica) already gave an overview of the MIS 5e [*Jouzel et al.*, 1987; *Petit et al.*, 1999]. Precious information was expected from the $\delta^{18}O_{ice}$ analysis on the Greenland GRIP ice core. Indeed, the Greenland location is of primary interest when considering climate changes associated to variations in the North Atlantic thermohaline circulation. Among them, rapid climatic events in the Northern hemisphere during the last glacial period (the so-called Dansgaard-Oeschger events) are most clearly visible in the Greenland ice core records [*Dansgaard et al.*, 1993]. As a natural consequence the question of climatic stability in the North Atlantic during the last interglacial arises.

[3] The first $\delta^{18}O_{ice}$ complete record on the European GRIP ice core [*GRIP Project Members*, 1993] revealed astonishing results: the sequence covering the last interglacial had rapid fluctuations in $\delta^{18}O_{ice}$ thus suggesting a climatically unstable interglacial period. The comparison between the GRIP ice core record and the nearby American companion GISP2 showed significant discrepancies below 2750 m depth [*Grootes et al.*, 1993] raising the concern of possible ice stratigraphy perturbations. In addition, long-lived atmospheric gas measurements performed along the bottom 300 m of the GRIP ice core led to the conclusion that stratigraphic disturbances occurred at the bottom of the GRIP and of the GISP2 ice cores by comparison to the well preserved gas records from Antarctica [*Fuchs and Leuenberger*, 1996; *Chappellaz et al.*, 1997; *Landais et al.*, 2003; *Suwa et al.*, 2003]. These analysis proved that the major part of the bottom section of the central Greenland deep ice cores was disturbed. This main conclusion was supported by the observation of microfolds [*Alley et al.*, 1995, 1997] on both ice cores. On the other hand, chemical measurements [*Steffensen et al.*, 1997] performed on detailed parts of the ice core suggested that some $\delta^{18}O_{ice}$ and chemistry fluctuations could still be linked to climatic events since no reasonable

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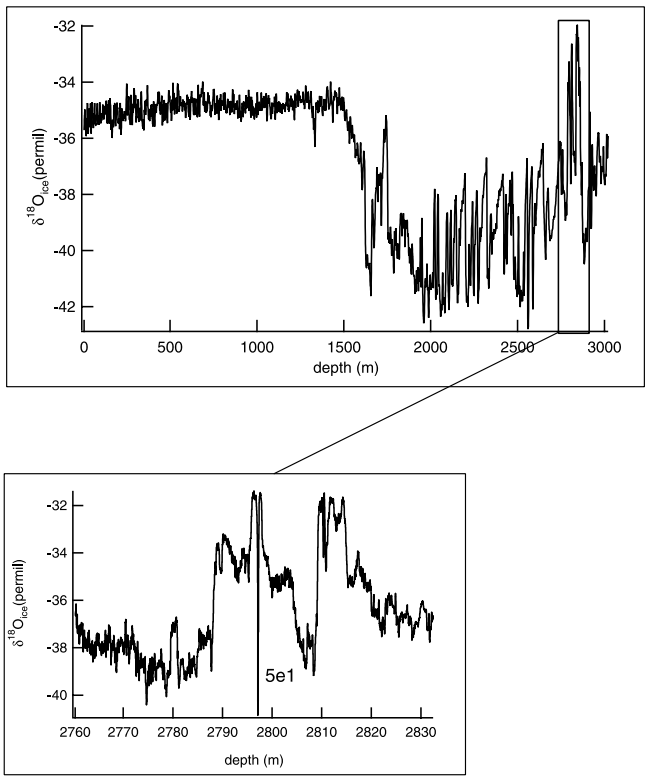

Figure 1. $\delta^{18}O_{ice}$ profile versus depth for the GRIP core. The bottom part of the profile was magnified to focus on the top of the questionable part of the core around event 5e1. Event 5e1 is easily noticeable by a sharp decrease of $\delta^{18}O_{ice}$ around 2797 m.

scenario involving ice mixing followed by diffusion or ion displacements could explain some chemical data (NH_4^+, NO_3^-, MSA).

[4] Among these detailed events, the 5e1 event [*GRIP Project Members*, 1993] initially dated at 120 kyr BP raised numerous questions. According to the $\delta^{18}O_{ice}$ profile (Figure 1), it was first described as a very sharp cooling during 70 years in the mid of the MIS 5e. The amplitude of the cooling can be estimated through the 8‰ $\delta^{18}O_{ice}$ variation. Using the spatial relationship [*Dansgaard*, 1964], the amplitude of the cooling is 10°C but using the temporal relationship, proven to be valid for the temperature variation between the last glacial maximum and today [*Dahl-Jensen et al.*, 1998], the cooling is as high as 20°C. Such an extreme climatic event over Greenland can indeed be envisaged if we recall the temperature drop (estimated to be 7.4°C by *Leuenberger et al.* [1999]) and rise in 200 years at the beginning of the Holocene (8200 yr BP). The largest Dansgaard-Oeschger events have weaker isotopic amplitude for the $\delta^{18}O_{ice}$ variation than event 5e1 8‰ decrease and an associated 16°C surface temperature change [*Lang et al.*, 1999]. As for ice structure, *Alley et al.* [1995] showed that no ice microfolds were encountered above 2847 m that is to say deeper than event 5e1. Very detailed chemistry data were measured (every 2.5 cm) by *Steffensen et al.* [1997] and showed features impossible to reconcile with ice mixing followed by simple diffusion in the ice because in several cases (NH_4^+, NO_3^-, MSA) lateral peaks or troughs can only be created by counter gradient diffusion. These data then supported the original interpretation of *GRIP Project Members* [1993] that some part of the Eemian period in Greenland is indeed unstable. The need to test the reality of event 5e1 is further strengthened by the fact that it has already been used as a matching point for speleothems chronologies [*Lauritzen*, 1995] and Camp Century ice core record [*Johnsen et al.*, 1997]. Confirming or denying its existence is then important information both for relative dating and interglacial climate dynamics.

[5] An approach to clarify the reality of this event is to analyze at a 5 cm scale the isotopic composition of air occluded in the ice on this event. Detailed isotopic gas measurements ($\delta^{15}N$) were conducted on the depth covering event 5e1 using the analytical method first described by *Severinghaus et al.* [1998, 1999] to detect rapid temperature changes, such as the hypothetic 5e1, at the surface of the ice sheet [see also *Caillon et al.*, 2001, 2003; *Lang et al.*, 1999; *Leuenberger et al.*, 1999]. Because the air is trapped at around 70 m depth in the Greenland ice cap firn, the air isotopic anomaly associated to surface (0 m) temperature changes should be found deeper than the $\delta^{18}O_{ice}$ anomaly if no stratigraphic disturbance occurred. Most of chemistry measurements show anomalies at the same depths as for the $\delta^{18}O_{ice}$ anomaly since both are indications of climatic and environmental conditions recorded in the ice. As a result, the $\delta^{15}N$ measurement is an independent mean to check the existence of a climatic event by searching for it at a different depth (calculated through an ice densification model) than the ice anomaly.

[6] In addition to $\delta^{15}N$, $\delta^{18}O_{atm}$ measurements were performed. This parameter is mainly influenced by the ice sheet extent controlling the seawater $\delta^{18}O$ [*Sowers et al.*, 1991] and by the biosphere evolution (Dole effect given by the balance between marine and continental productions, photosynthesis and respiration, [*Bender et al.*, 1994a]). The evolution of $\delta^{18}O_{atm}$ is very slow in response to climatic variations because of the long residence time of O_2 (1200–2000 years) in the atmosphere. $\delta^{18}O_{atm}$ is nil for small ice sheet extent (comparable to the present time) and $\delta^{18}O_{atm}$ peaks at 1–1.3‰ for a large ice sheet extent such as during the Last Glacial Maximum. The biosphere influence was clearly depicted by the decrease of the Dole effect at 175 kyr BP [*Malaizé et al.*, 1999] because of unusual strong monsoon [*Masson et al.*, 2000] and results in a decrease of $\delta^{18}O_{atm}$ from 0.8‰ to 0‰ in some thousands of years. As a conclusion, the evolution of $\delta^{18}O_{atm}$ as depicted by long term climatic records is rather slow with a maximum amplitude of 0.1‰ change in 200 years. In this study, the $\delta^{18}O_{atm}$ profile is difficult to reconcile with such slow variations. At our surprise, it shares numerous features with the ammonium data performed by *Steffensen et al.* [1997], which leads us to re-examine the chemical data. In complement to $\delta^{18}O_{atm}$, O_2/N_2 measurements allow to better constrain diffusion processes that occurred in the ice.

2. Analytical Method

[7] We performed $\delta^{15}N$ and $\delta^{18}O$ measurements on 37 duplicate samples (3–5 cm long; 10g) on the GRIP ice core ranging from 2796.7 to 2799 m depth. The gas extraction was conducted through a melt-refreeze method and the gas was then analyzed with a MAT 252 mass spectrometer.

Corrections were applied according to standard procedure [*Bender et al.*, 1994b; *Severinghaus et al.*, 2001; *Landais et al.*, 2003]. $\delta^{15}N$ was first corrected from the CO_2 influence through the formation of CO^+ in the mass spectrometer source. Second, the ionization efficiency in the mass spectrometer source induces a sensitivity of the measured isotopic ratios of a single element in a gas mixture to variations in the elemental ratios of the mixture. We therefore corrected $\delta^{15}N$ and $\delta^{18}O$ measurements with respect to variations in the O_2/N_2 ratio.

[8] The isotopic composition of the air bubbles is modified by firn physical processes known as gravitational settling [*Craig et al.*, 1988] and thermal diffusion [*Severinghaus et al.*, 1996]. We determined $\delta^{18}O_{atm}$ by correcting the $\delta^{18}O$ total signal for the gravitational effect: $\delta^{18}O_{atm} = \delta^{18}O\text{-}2\,\delta^{15}N$. This subtraction assumes that $\delta^{15}N$ is only of gravitational origin. A possible additional correction concerned the thermal diffusion: assuming a $\delta^{15}N$ thermal fractionation of 0.1‰ (maximum effect), we calculated a maximum deviation of +0.03‰ on the final $\delta^{18}O_{atm}$ value, considering the ratio of thermal sensitivity between the two pairs of isotopes [*Severinghaus et al.*, 2001]. The experimental uncertainties associated with $\delta^{15}N$ and $\delta^{18}O_{atm}$ (calculated using the pooled standard deviation) are respectively 0.007 and 0.03‰ (comparable to the bias induced by thermal effect).

[9] The O_2/N_2 ratios were obtained by mass spectrometry measurements to correct $\delta^{15}N$ and $\delta^{18}O$ for the chemical slope and are expressed as:

$$\delta O_2/N_2 = \left(\frac{(O_2/N_2)_{SAMPLE}}{(O_2/N_2)_{STANDARD}} - 1\right) \times 1000$$

our standard being the modern atmospheric air dried.

[10] The associated 4‰ 1σ reproducibility is rather poor but provides additional information as observed variations can be as high as 50‰ (see last section). In non perturbed ice, the value of $\delta O_2/N_2$ is expected to be slightly negative in the air trapped in the ice (around −10 or −15‰) because of diffusion and/or effusion effects occurring during the pore close-off at the bottom of the polar firn. This effect was observed through numerous studies in the firn air with a $\delta O_2/N_2$, corrected from gravitational effect, up to 5‰ above the pore close-off [*Battle et al.*, 1996; *Bender et al.*, 1994c; *Kamawura*, 2000; *Leuenberger et al.*, 2002; J. Severinghaus, personal communication, 2003] and additional measurements performed outside of this work). *Bender* [2002] showed that variations in $\delta O_2/N_2$ in the Vostok ice core are mostly due to close-off processes and those variations does not exceed ±5‰ around the mean value (−12‰). The depletion of O_2 in trapped gas is probably due to the van der Waals radius of O_2 (2.0 Å) that is smaller than the one of N_2 (2.05 Å). The O_2 molecules could be expelled from closing pores at the firn bottom when nitrogen is already trapped. The driving force that expels molecules at the firn bottom is the pressure difference between the inside of the pore and the surroundings. This exclusion effect should be associated with a fractionation in O_2: preliminary measurements in the firn air close to the pore close-off region revealed that the $\delta^{18}O_{atm}$ are modified by −0.1‰ for a $\delta O_2/N_2$ of +10‰ (J. Severinghaus, unpublished measurements in Antarctica and additional measurements performed outside of this work in Greenland, 2003). This additional fractionation can be explained if we invoke the diffusion or effusion rate dependence with the mass of the molecule. Indeed effusion and diffusion are faster for light molecules than for heavy ones. We expect consequently that ^{16}O is excluded faster than ^{18}O. Consequently, firnification processes are supposed to induce simultaneous changes in $\delta O_2/N_2$ and $\delta^{18}O_{atm}$.

[11] This phenomenon explains neither extremely low values for $\delta O_2/N_2$ (−70‰) nor variations of 50‰ in a few centimeters. Such variations are however observed in the particular zone of clathrates formation [*Ikeda et al.*, 1999, 2000a]. Air hydrates are produced because of the pressure increase between 700 and 1300 m depth in GRIP. Below 1300 m depth in GRIP it is believed that all the air is trapped in hydrates. Observation of clathrates and air bubbles in the transition zone [*Ikeda et al.*, 1999] showed that the $\delta O_2/N_2$ is positive in the clathrates and negative in air bubbles as the result of a preferential diffusion of O_2 from air bubbles to clathrates probably linked to the molecular diameter difference between N_2 and O_2 (an explanation based on inter molecular forces would lead to a higher stability of N_2 in clathrates since N_2 has a higher polarizability than O_2). Additional mass dependent fractionation effects of O_2 isotopes have not yet been clearly demonstrated but were suggested by recent results by M. Leuenberger for the bubbles-clathrates transition zone in the NorthGRIP ice core (M. Leuenberger, personal communication, 2003).

3. Results

3.1. Firn Thermal and Gravitational Modeling

[12] Nitrogen isotopic fluctuations in air trapped in ice core are proxies of rapid climatic changes [*Severinghaus et al.*, 1998; *Severinghaus and Brook*, 1999; *Leuenberger et al.*, 1999; *Lang et al.*, 1999]. As nitrogen has a constant isotopic composition in atmospheric air [*Sowers et al.*, 1989], its isotopic composition in the air trapped in the ice is only affected by physical fractionation processes that occur in the firn, on the top 70–90 m of the ice sheet. This fractionation is the result of molecular diffusion, gravitational fractionation due to the Earth gravitational field, and thermal diffusion driven by vertical temperature gradients in the firn.

[13] The gravity drives the heaviest isotopes (here ^{15}N and ^{18}O) toward the bottom of the firn. The isotopic composition is then dependent on the mass difference between the two considered isotopes, the mean firn temperature and the firn depth according to the following equation:

$$\delta = \frac{\Delta m.g.z}{R.T} \tag{1}$$

where Δm is the mass difference between the two considered isotopes (1 g mol^{-1} for $^{15}N/^{14}N$), g (m s^{-2}) the gravitational acceleration, z (m) the depth of the diffusive zone, R (J mol^{-1} K^{-1}] the gas constant and T (K) the temperature. During interglacial periods, the diffusive zone is ~70 m depth in GRIP and results in a $\delta^{15}N_{grav}$ of the order of 0.33‰; during glacial times, because of the temperature change, the firn deepens (~90 m)

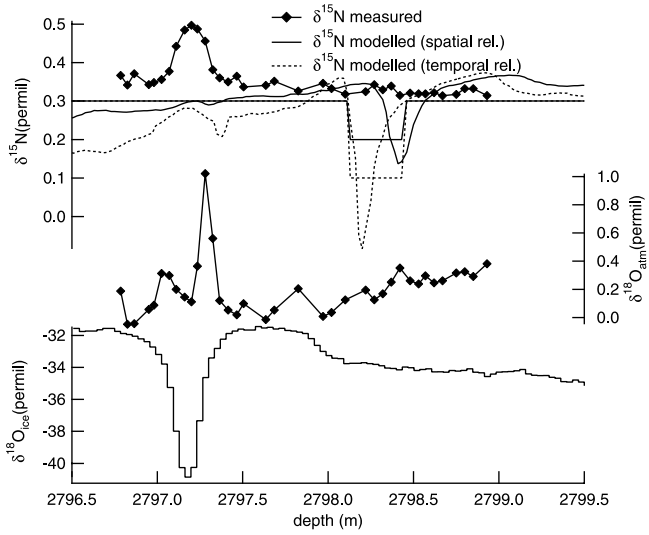

Figure 2. (bottom) Focus on the $\delta^{18}O_{ice}$ profile around event 5e1 figured out by the sharp decrease in $\delta^{18}O_{ice}$. (middle) $\delta^{18}O_{atm}$ evolution versus depth. (top) Solid line with markers stand for the measured $\delta^{15}N$ evolution versus depth, solid/dotted line for the modeled $\delta^{15}N$ evolution versus depth if event 5e1 was a true climatic event with a surface temperature forcing related to the $\delta^{18}O_{ice}$ profile through the spatial ($\Delta\delta^{18}O_{ice}/\Delta T$ = 0.67‰ K^{-1})/temporal ($\Delta\delta^{18}O_{ice}/\Delta T$ = 0.33‰ K^{-1}) relationship. The step shape modeled profiles are obtained with equation (2) and the two other profiles are obtained with the *Goujon et al.* [2003] densification-heat diffusion model.

and results in a $\delta^{15}N_{grav}$ of the order of 0.50‰ [*Schwander et al.*, 1997].

[14] The thermal fractionation is transient and only induced during rapid temperature changes at the surface of the ice sheet. During a rapid climatic cooling, the bottom end remains warmer before complete heat diffusion from the ice surface through the firn. The gas diffusion in the firn is approximately 10 times faster than the heat diffusion [*Paterson*, 1994]. In response to the transient temperature gradient, the thermal diffusion equilibrium drives the lightest isotopes (here ^{14}N) toward the warmest end of the firn. We can model the response of a gas mixture to a temperature gradient by the following equation:

$$\delta = \frac{\alpha_T}{T_{average}} \times \Delta T \qquad (2)$$

where ΔT is the temperature difference between two gas parcels and α_T is a thermal diffusion factor which was experimentally determined by *Grachev and Severinghaus* [2003] for the binary mixture $^{15}N/^{14}N$.

[15] During the pore close-off, the isotopic composition resulting from the gravitational and the thermal effects is recorded in the ice bubbles. In the case of a rapid cooling, the $\delta^{15}N$ trapped at the firn bottom will be depleted relative to a signal resulting from the gravitational effect alone. This thermal anomaly in $\delta^{15}N$ is recorded at the bottom of the firn (70 m depth) while the corresponding $\delta^{18}O_{ice}$ anomaly is recorded in the surface snow. If the isotopic 5e1 event is of climatic origin (cooling of 10°C–20°C in less than 40 years) without flow perturbation, we expect a negative $\delta^{15}N$ anomaly. Because of the occlusion process occurring at the bottom of the firn, a depth difference, Δdepth, will separate the $\delta^{18}O_{ice}$ and the $\delta^{15}N$ anomalies, the $\delta^{15}N$ anomaly standing deeper in the ice core. From the estimation of the thinning function at that depth [*Dansgaard et al.*, 1993] the Δdepth can be estimated to be 1 m if the stratigraphy is not perturbed. Moreover a rapid calculation using equation 2 leads to an expected $\delta^{15}N$ anomaly of 0.1‰–0.2‰. The main uncertainty for the amplitude is related to the choice of the $\delta^{18}O_{ice}$-temperature relationship to estimate ΔT (spatial or temporal relationship) as discussed in the introduction.

[16] This first estimate was made without precisely taking into account the diffusion of heat in the firn that leads to the estimation of ΔT in equation 2. Moreover we attributed a constant depth of 70 m to the firn (typical interglacial value) without taking into account the changes in temperature and accumulation rate derived from the $\delta^{18}O_{ice}$ fluctuations. In order to refine this first estimate we used the densification associated to temperature diffusion model developed by Barnola and Goujon [*Goujon et al.*, 2003]. The model was driven by the $\delta^{18}O_{ice}$ data all along the GRIP core. We performed two runs for the two relationships between $\delta^{18}O_{ice}$ and surface temperature (spatial and temporal). The associated expected $\delta^{15}N$ profile is represented on Figure 2. The simple modeling or the use of the densification-heat diffusion model, with different $\delta^{18}O_{ice}$/temperature slopes, give the same estimation for the depth of the negative $\delta^{15}N$ anomaly (2798.3 m) within 20 cm. The densification-heat diffusion model predicts higher amplitude for the negative $\delta^{15}N$ anomaly (0.15 to 0.4‰) than the calculation with equation 2 (0.1–0.2‰). For comparison, the 100 years cooling at 8200 yr BP was imprinted in the air trapped in the ice as a −0.08‰ anomaly in $\delta^{15}N$ [*Leuenberger et al.*, 1999] interpreted as a 7.4°C temperature decrease. In all cases, the expected $\delta^{15}N$ anomaly amplitude is at least 0.1‰ and thus easily detectable with our 0.007‰ analytical precision.

3.2. Analytical Results

[17] $\delta^{15}N$ analytical results shown on Figure 2 depict a flat profile over the depths where a $\delta^{15}N$ anomaly would be expected if the 5e1 event were a climatic event. On the contrary, $\delta^{15}N$ shows a significant positive anomaly at the same depths as the $\delta^{18}O_{ice}$ anomaly. A climatic event could not result in gas and ice anomalies at the same depth. This result directly demonstrates that event 5e1 is not a climatic event. Moreover, the positive $\delta^{15}N$ anomaly (~0.50‰) is in agreement with gravitational signal in glacial time. Together, our $\delta^{15}N$ data and $\delta^{18}O_{ice}$ data demonstrate the intrusion of 10 cm ice formed in glacial conditions into a section of ice corresponding to interglacial conditions.

[18] More surprising are the $\delta^{18}O_{atm}$ results (Figure 2). The simple result of an inclusion of glacial ice (with characteristic value of 0.5–1‰ for $\delta^{18}O_{atm}$) in interglacial ice (with characteristic value of 0‰ for $\delta^{18}O_{atm}$) would be a $\delta^{18}O_{atm}$ peak of 0.5–1‰ corresponding to the $\delta^{18}O_{ice}$ anomaly. The presence of two $\delta^{18}O_{atm}$ peaks on the flanks of the ice anomaly is at first sight confusing. The rapid variation of $\delta^{18}O_{atm}$ (0.7‰ in less than 5 cm corresponding to less than 20 years in a non disturbed timescale) is

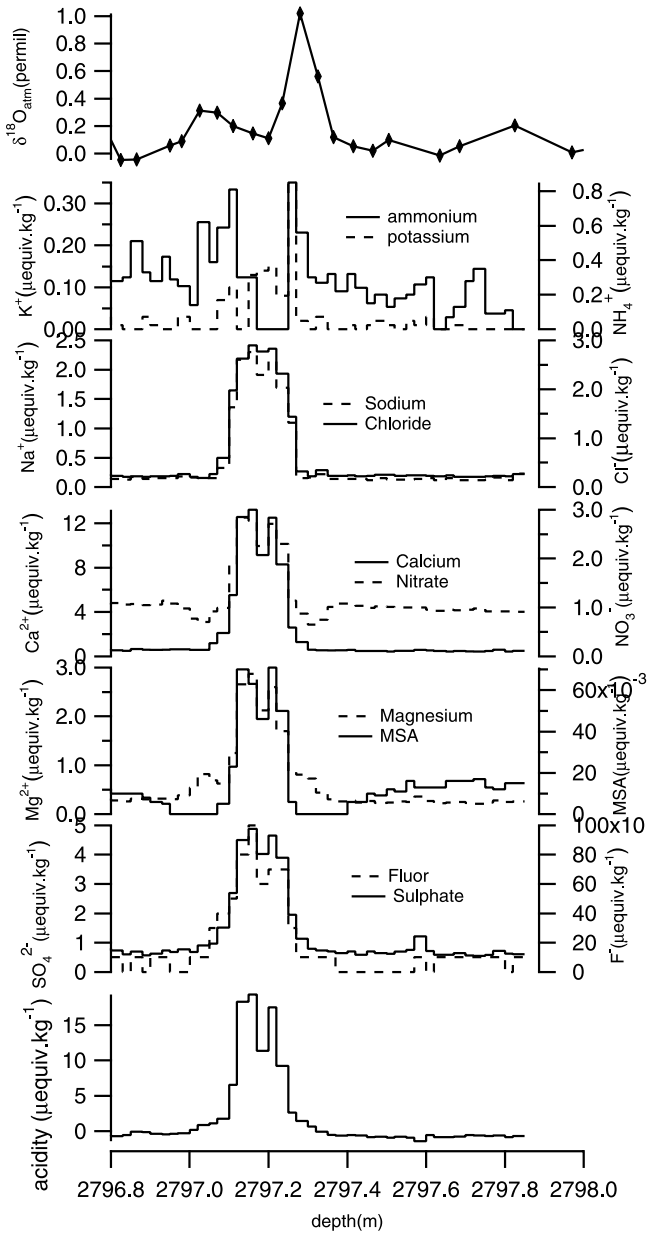

Figure 3. $\delta^{18}O_{atm}$ profile superimposed to chemical results (measured in the ice) extracted from [*Steffensen et al.*, 1997]: potassium (K^+), ammonium (NH_4^+), sodium (Na^+), chloride (Cl^-), calcium (Ca^{2+}), nitrate (NO_3^-), magnesium (Mg^{2+}), methane sulfonate (MSA), fluoride (F^-) and sulphate (SO_4^{2-}). NH_4^+, NO_3^- and MSA show amazing results to be compared to the $\delta^{18}O_{atm}$ profile. Acidity (sum(cations)-sum(anions)) shows a nice bell shape in agreement with $\delta^{18}O_{ice}$ and $\delta^{15}N$ results.

impossible with regards to the oxygen atmospheric residence time. Again the hypothesis of a climatic signal for event 5e1 must be rejected.

3.3. $\delta^{18}O_{atm}$ and Chemistry Measurements

[19] The two-peak shape of $\delta^{18}O_{atm}$ profile and the detailed chemistry data performed by *Steffensen et al.* [1997] on event 5e1 have to be related to ice mixing processes. Calcium (Ca^{2+}), sodium (Na^+), chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}), methane sulfonate (MSA), magnesium (Mg^{2+}), potassium (K^+), ammonium (NH_4^+) and fluoride (F^-) have been measured every 2.5 cm (Figure 3). Na^+, Cl^-, K^+, $Ca2^+$, Mg^{2+}, SO_4^{2-} and F^- have their main sources in sea salt and soil dust. Consequently their concentration in GRIP ice core is highly dependent on the transport strength and the source dryness. It has then been shown [*Legrand and Mayewski*, 1997] that cold and dry periods increase their concentrations in ice core. MSA (over Antarctica) is linked to marine biota as SO_4^{2-}. NO_3^-, MSA (over Greenland) and NH_4^+ are due mainly to soil exhalation and biological production. In addition to this background production, spikes can be induced in sulphate, chloride and fluoride concentrations because of volcanic activity and in ammonium concentration because of biomass burning. In Greenland, over the last 40 kyr, $\delta^{18}O_{ice}$ is anticorrelated to Na^+, Cl^-, Ca^{2+}, K^+, Mg^{2+}, NO_3^-, SO_4^{2-} and F^- [*Legrand and Mayewski*, 1997]. MSA and NH_4^+ are the only species that show temporal behaviors which are not simply related to Greenland temperature fluctuations: MSA concentration decreases after the last glacial maximum until well into the Holocene and then increases again [*Steffensen et al.*, 1997]; ammonium concentration peaks at each summer insolation maximum along the 110 kyr BP record in GRIP [*Meeker et al.*, 1997] as a consequence of increasing biogenic production.

[20] The observed profiles of Na^+, Cl^-, Mg^{2+}, K^+, SO_4^{2-}, Ca^{2+} (Figure 3) show a shape in agreement with intrusion of cold ice in interglacial ice followed by ordinary diffusion in the ice as are depicted by $\delta^{18}O_{ice}$ and $\delta^{15}N$ in the air. NO_3^-, MSA and NH_4^+ profiles behave differently. Nitrate and MSA have lower concentration on the flanks than inside and outside the anomaly. Ammonium has a null concentration inside event 1 but shows peaks on the flanks just as does $\delta^{18}O_{atm}$. This odd behavior of some chemical species cannot be explained by diffusion because in several cases the movement runs counter to diffusion [*Steffensen et al.*, 1997]. However, each chemical component is not independent of the rest and some explanations for postfolding processes have been proposed. The first one invokes the importance of liquid veins [*Barnes et al.*, 2003] to provide a conduit for movements in the ice lattice. *Rempel et al.* [2002] suggest that the impurities have to equalise their concentrations in the liquid veins and that could cause MSA to move into the glacial ice leaving a large depletion on each side.

[21] The acidity profile was calculated as the total ions balance by subtracting the sum of anions to the sum of cations and does not reveal all the strange humps and troughs, present for example in the nitrate profile. We can then postulate that a normal diffusion process took place after folding to ensure the ion balance. The "acidity diffusion" is supposed to be ensured by the ions H_3O^+ and HCO_3^- that try to equalize by diffusion. These ions cannot move by themselves and must then take the weaker counter ions with them. In the acid ice (on the flanks), sulphuric acid is the strongest acid and is therefore totally dissociated into SO_4^{2-} and H_3O^+. On the contrary, weaker acids (nitric acid, MSA and hydrofluoric acid) remain balanced and ions H_3O^+ are easily associated through the equilibrium to the counter ion. Consequently, those acids

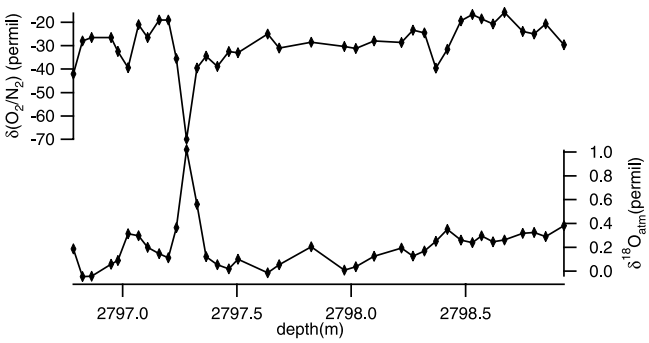

Figure 4. (bottom) $\delta^{18}O_{atm}$ profile versus depth. (top) $\delta O_2/N_2$ profile versus depth. Low values of $\delta O_2/N_2$ correspond to high values of $\delta^{18}O_{atm}$.

tend to be the first forced to leave the acid ice and NO_3^-, MSA and F^- are depleted on the flanks. In the alkaline ice, ammonium is the weakest base then the first to leave. Finally, some chemical reactions could happen during the diffusion process. For example, the MSA^- ion moving into the "peak" can be neutralized because of acidity into a salt of MSA which precipitates. Such chemical reactions may create a lateral gradient of MSA around the peak that in turn enhances the diffusion process (acidity diffusion + counter gradient diffusion).

3.4. Scenarios for $\delta^{18}O_{atm}$ Profile

[22] We discuss here possible explanations which can explain the observed $\delta^{18}O_{atm}$ profile without or with post-folding effects.

[23] 1. No posttrapping or postcoring effects affect $\delta^{18}O_{atm}$ but the mixing is more complicated than the simple intrusion of a 20 cm glacial ice layer: the ice encountered on the flanks is from another origin than the one encountered at the center of event 5e1 and the one outside. It raises the problem of the scale of the mixing. As we are limited to a 5 cm resolution (sample size), we can only propose a new mixing scheme: [interglacial ice outside of event 5e1]-[ice A on the flanks]-[ice B in the center]. Ice A could originate from the very end of the MIS 5e where $\delta^{18}O_{atm}$ is very high (~0.6‰) while $\delta^{15}N$ is still low (~0.33‰) [*Landais et al.*, 2003]. This would be in agreement with $\delta^{18}O_{ice}$ record and the major part of the chemistry data. However, the very low (~0 μequi kg^{-1}) NO_3^- data disagree with this reconstruction: the very late Eemian ice should have values of the order of 2 μequi kg^{-1} (intermediary value between glacial and interglacial). Ice B could be glacial ice from stage 6 as indicated by $\delta^{15}N$ and $\delta^{18}O_{ice}$ data. We do not have chemical value for stage 6 on the GRIP core because of stratigraphic distortion under 2750 m depth but if we assume that the atmospheric circulation state was similar during the last glacial period and the stage 6 then chemical values must be of the same order for both periods. Indeed chemical values at the center of event 5e1 are in agreement with typical glacial values (LGM or end of stage 6). However, $\delta^{18}O_{atm}$ is not compatible with glacial ice: we would expect value of 0.5–1‰ for ice B and we have ~0.15‰. It is still possible to propose stage 6e (minimum of Dole effect due to insolation maximum) for ice B to reconcile $\delta^{18}O_{ice}$ and $\delta^{18}O_{atm}$ on the basis of a comparison with the Antarctic ice core from Vostok covering 420,000 yr BP [*Petit et al.*, 1999; *Malaizé et al.*, 1999]. Some ice with such $\delta^{18}O_{atm}$ and $\delta^{18}O_{ice}$ was indeed identified in the GRIP (2880–2920 m) bottom ice between 2880 and 2920 m, far away from the depth of event 5e1 [*Landais et al.*, 2003]. However, the chemistry data encountered at the center of event 5e1 are not found somewhere else in the GRIP bottom ice [*Steffensen et al.*, 1997] making an explanation based on a simple inclusion of ice from stage 6e very improbable. Other scenarios involving smaller scale mixing can be proposed but we do not have enough resolution to check them.

[24] 2. Post-trapping or postcoring effects occurred and affected $\delta O_2/N_2$ and $\delta^{18}O_{atm}$ values. Comparison of $\delta O_2/N_2$ and $\delta^{18}O_{atm}$ on Figure 4 suggests a mechanism that depletes the air in oxygen relative to nitrogen on the flanks of event 5e1 associated with a fractionation in $^{18}O/^{16}O$. Because we can not resolve the mixing at scale < 5 cm, we begin with the simplest hypothesis for mixing: glacial ice (end of stage 6 or stage 6e) for the 20 cm in the center of event 5e1 and interglacial ice (MIS 5e) in the surroundings. We assume that the folding took place when the ice was close to the bedrock that is to say at depths where clathrates were already formed. *Ikeda et al.* [2000a] and *Uschida et al.* [2000] showed that the dissociation pressure is lower for O_2 hydrates than for N_2 hydrates. Moreover, according to *Lipenkov* [2000], small air bubbles (in ice constituted from small grains) are preferentially transformed to clathrates hydrates. To evoke a postfolding scenario based on clathrates, ice grain size measurements on a small scale around event 5e1 would be necessary. *Thorsteinsson et al.* [1995] did very detailed (1–2 cm) ice grain size measurements between 2797 and 2797.2 m at the beginning of event 5e1. Crystal sizes decrease from 10 mm diameter where $\delta^{18}O_{ice}$ is high to 3–4 mm where $\delta^{18}O_{ice}$ decreases dramatically. Measurements were not further performed on event 5e1 since no ice remains but previous studies combining chemistry data and ice crystal size [*Weiss et al.*, 2002], showed that the size of ice crystal is higher when dust particles are rare and especially when NO_3^- concentration is low. On the depth scale 2797–2797.2 m, the correlation between small/big grain sizes and high/low NO_3^- is confirmed. We can then infer in the absence of existing measurements on the ice grain size on the totality of event 5e1 that the ice corresponding to the middle of event 5e1 is made of small crystals while the flanks are made of large crystals. Post-trapping effects took place. From texture studies [*Thorsteinsson et al.*, 1997; *Dahl-Jensen et al.*, 1997], we know that fine grains sections of the bottom part of the GRIP core are more sensitive to shear stress than coarse grains sections that are more sensitive to compression stress. Pressure should have been more important for clathrates on the flanks of event 5e1. With increasing pressure over clathrates, the cage occupancy rises and even double cage occupancy can take place [*Kuhs et al.*, 2000]. As a consequence the cage occupancy should have been higher on the flanks than inside event 5e1. Diffusion through ice matrix or through liquid veins [*Barnes et al.*, 2003] between one section and the other can result from this occupancy gradient. *Ikeda et al.* [2000b] suggested that 1–3% of the total air content is dissolved in the ice lattice. Since oxygen is more soluble as nitrogen in ice [*Ikeda et al.*, 1999], this

diffusion process would preferentially drive oxygen from the sides to the center of event 5e1. Associated to this diffusion, a mass dependent fractionation would deplete the flanks in ^{16}O. It could be one way to explain why an original signal showing high $\delta^{18}O_{atm}$ in the center (~0.6‰ if we imagine to back-diffuse the ^{16}O from the flanks) can have been transformed to the measured signal. Post-coring effects took place.

[25] As the storage temperature of the ice after drilling was too high (−20°C to −25°C instead of −30°C) according to *Uschida and Hondoh* [2000], some clathrates must have relaxed to air bubbles. After formation of air bubbles in the ice, we expect an extension and possible formation of ice core fractures. Because of its smaller molecular radius, O_2 should escape preferentially from air bubbles out in atmospheric air. Such an explanation was proposed by *Bender et al.* [1995] to explain the sample depletion in O_2 and Ar relative to N_2 in numerous polar ice cores. Moreover, they found a simultaneous enrichment in $\delta^{18}O_{atm}$ for some very poorly preserved samples. Our results show an O_2 depletion that is far from being homogeneous suggesting heterogeneous leaks. The only way to reconcile our results with a loss through micro-cracks is to involve heterogeneity in the grain sizes. *Lipenkov* [2000] showed that clathrates are more stable in small grains size ice. Consequently, less O_2 would have escaped from the center of event 5e1 and both $\delta O_2/N_2$ and $\delta^{18}O_{atm}$ would be more affected on the flanks, in agreement with our results. This explanation is consistent with an initial $\delta^{18}O_{atm}$ of ~0.15‰ for ice inserted at the center of event 5e1 corresponding to stage 6e.

4. Conclusion

[26] The GRIP ice core record has been clearly affected by ice folding as far as 300 m above the bedrock. Evidences had previously been shown on a large depth scale (1 m) by texture, chemistry and gas studies. Using an alternative method based on isotopic measurements in the air trapped in ice core ($\delta^{15}N$ and $\delta^{18}O_{atm}$) and thermal diffusion properties in the firn, we demonstrate that event 5e1 must be ruled out as a true climatic event and that the ice core signal is due to a small scale ice folding (less than 20 cm thick). This result confirms that the GRIP record can not be used to infer climatic instability during the last interglacial period and therefore does not refute the MIS 5e stability shown by high resolution mid latitude records [*Sanchez Goñi et al.*, 1999].

[27] Our results also raise other problems regarding the $\delta^{18}O_{atm}$ profile that shows a parallelism with some chemistry data from *Steffensen et al.* [1997]. Post-trapping effects have probably affected the chemical and possibly the $\delta^{18}O_{atm}$ profile. Post-coring effects have more probably affected the $\delta^{18}O_{atm}$ profile through gas loss. The exploitation of $\delta^{18}O_{atm}$ in the air trapped in the ice and of some chemical data (NH_4^+, MSA, NO_3^-) must then be carried out with care even if such phenomenon is at the time only observed on very small scale folding. The possibility of postcoring diffusion stresses that $\delta^{18}O_{atm}$ should be rather analyzed a short time after coring or in ice preserved at −30°C.

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