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Quantification of rapid temperature change during DO event 12 and phasing with methane inferred from air isotopic measurements

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Abstract

The description of rapid climatic changes during the last glacial period at high northern latitudes has been largely documented through Greenland ice cores that are unique climatic and environmental records. However, Greenland ice isotopic records are biased temperature proxies and it is still a matter of debate whether changes in the high latitudes lead or lag rapid changes elsewhere. We focus here on the study of the mid-glacial Dansgaard Oeschger event 12 (45 ky BP) associated to a large $\delta^{18}O_{ice}$ change in the GRIP (GReenland Ice core Project) ice core. We use combined measurements of CH_4, $\delta^{15}N$ and $\delta^{40}Ar$ in entrapped air associated with a recently developed firn densification and heat diffusion model to infer (i) the phasing between methane and temperature increases and (ii) the amplitude of the temperature change. Our method enables us to overcome the difficulty linked with rapid accumulation change in quantifying the temperature change. We obtain a 12±2.5 °C temperature increase at the beginning of DO event 12 thus confirming that the conventional use of water isotopes in the Greenland ice cores largely underestimates the actual amplitude of rapid temperature change in central Greenland. In agreement with previous studies, methane and temperature increase are in phase at the sampling resolution of that part of our profile (90 years).

Keywords: ice core; Dansgaard-Oeschger; firn; thermal diffusion; temperature quantification; Greenland; Glacial period; rapid climatic change

1. Introduction

Twenty-four rapid climatic changes during the last glacial period have been largely documented in the North Atlantic by ice cores, deep-sea and continental

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records during the last 20 years (e.g. [1–4]). The succession of these rapid events has been related to shifts in the thermohaline circulation modes [5] drastically affecting the North Atlantic region. Some of these shifts appear to be triggered by fresh water inputs through abrupt iceberg discharges probably induced by ice sheet instabilities [6,7]. Through the high resolution record given by Greenland ice cores, each Dansgaard-Oeschger event (hereafter DO event) is reflected as a rapid temperature increase probably caused by a resumption of the thermohaline circulation followed by a slow return to cold conditions induced by fresh water inputs in North Atlantic. However, if the role of both ocean modes and ice rafted events is central for the sequence of those Dansgaard-Oeschger events, some questions remain unresolved. Indeed, if the thermohaline circulation stability is invoked to explain the occurrence of the abrupt warming in the high latitudes [5], it is also suggested that tropical instabilities might have played a role to induce North Atlantic climatic variations [8].

Ice core records from Summit (GReenland Ice core Project, Greenland Ice Sheet Project 2) have provided a wealth of information on DO events. The water isotopes, here $\delta^{18}O_{ice}$ [2,9,10] and chemical records both reveal dramatic and widespread reorganization of atmospheric transport. Ice cores have also revealed strong changes in atmospheric greenhouse gas levels as recorded in air bubbles: both CH_4 [11], mainly produced by tropical and boreal wetlands, and N_2O [12,13], originating from terrestrial soils and the oceans, clearly undergo strong variations associated with DO events (more than half of a glacial–interglacial change) thus indicating large-scale climatic reorganisations. In order to better understand the causality and the sequence of DO events, it is crucial to determine whether high latitudes temperature is modified before or after greenhouse gases concentration. However, because air is enclosed in ice around 70 m below the surface in Greenland (depth of the firn close-off under present-day conditions), the air is younger than the surrounding ice at each depth level. Therefore, the difference, Δage, between the age of the ice and the age of the gas must be precisely evaluated. The use of a densification model [14–16] enables us to estimate the phasing between methane and temperature as deduced from the $\delta^{18}O_{ice}$ record. However, the associated uncertainty is up to 10% of the Δage, that is to say at least 100 years for the onset of a DO event in GRIP mainly because of accumulation rates uncertainties. This is a major limiting factor to accurately determine the phasing between Greenland temperature and gas concentration increases using $\delta^{18}O_{ice}$ as a temperature proxy.

A second problem that we are facing lies in the estimation of rapid DO event temperature change from the isotopic composition of the ice, $\delta^{18}O_{ice}$. Fractionations along the water trajectory between the evaporative regions and the high latitudes where snow precipitates produce a linear relation between $\delta^{18}O_{ice}$ and mean annual temperature that is well obeyed in Greenland and Antarctica:

$$\delta^{18}O_{ice} = \alpha T + \beta$$

Dansgaard [17] found a $\alpha_{spatial}$ value of 0.67 over Greenland. This present-day spatial relationship is also well captured both by simple isotopic model [18] and by general circulation models including water isotopes [19]. Using this relationship as a paleothermometer relies on the assumption that the spatial relationship does not change with time and consequently that the spatial and temporal slopes are similar [20] which is clearly not the case for Central Greenland as shown from comparison with independent estimates of temperature changes.

Such an independent estimate has been achieved by two borehole temperature profile inversions at GISP2 and GRIP [21,22]. This method showed that the interpretation of the $\delta^{18}O_{ice}$ profile using the spatial slope underestimates the Last Glacial Maximum (−21 ky)/Holocene temperature change by about 12 °C (i.e. by 100%). The temporal slope at Summit (GRIP, GISP2) during the last glacial maximum is then half the spatial slope: $\alpha_{temporal}$= 0.32 for the LGM. For the LGM/modern change, atmospheric general circulation model simulations suggest that this discrepancy is probably due to changes in the seasonality of the precipitation between glacial and interglacial periods with a huge decrease of winter snowfall during glacial periods [23–25]. A new method to reconstruct rapid temperature changes, based on air isotopic measurements gave estimates of the temporal relationship between $\delta^{18}O_{ice}$ and temperature for particular abrupt climatic changes at the beginning and at the end of the last glacial period (DO event 19 [26], Bølling-Allerød [16,27,28]). The relationship appears to be intermediate between the current one and the LGM/today warming (note that we do not consider the marine isotopic correction on $\delta^{18}O_{ice}$ because of uncertainties in the marine $\delta^{18}O$ changes during rapid events [29]). Variations of the temporal slope during the last glacial period are easily conceivable because changes in the origin and the seasonality of Greenland precipitation can be modulated for instance by the volume of the Laurentide ice sheet.

In order to bring a new constraint on quantitative temperature estimates during the full glacial period, we use here this recently developed method [26,27,30,31] based on the thermal diffusion of gases in the polar firn to estimate rapid surface temperature changes. This method is the only one currently available to get quantitative estimates of rapid temperature changes during the last glacial period. The method based on borehole temperature inversion is unable to resolve rapid climatic changes because of the smoothing of the temperature signal by heat diffusion in the ice sheet. We applied this method to DO event 12 at GRIP (~−45 ky). This rapid event was chosen to bring a new constraint on paleotemperature reconstructions in full glacial period at the mid-time between Bølling-Allerød and DO event 19 for which similar measurements are available [16,26–28]. Moreover, DO event 12 is associated to a large signal in GRIP $\delta^{18}O_{ice}$ (4.6‰ to be compared to the 7‰ associated with the LGM-modern change) which corresponds to a 6.8 °C change if using the spatial relationship between $\delta^{18}O_{ice}$ and temperature [17]. This large warming reflects a switch from a very cold phase (Heinrich event 5 as recorded in marine sediments through ice rafted debris from iceberg discharge [32]). It is well suited for our method since it is associated with a large transient vertical temperature gradient in the firn that will in turn fractionate the gaseous species through molecular diffusion that is 10 times faster than heat diffusion. The $\delta^{15}N$ and $\delta^{40}Ar$ isotopic anomalies reflecting the rapid temperature changes are then directly measured in the air trapped in the ice. In addition to a quantitative estimate of the temperature change, methane and temperature evolution are measured on the same depth scale, enabling the direct determination of the phasing by the combined gas measurements of $\delta^{15}N$ and methane (we neglect the difference of diffusion coefficient between $^{15}N^{14}N$ and CH_4, which would amount to only a few years of age difference between both signals at close-off). To quantify such rapid surface temperature changes, previous studies have been conducted using $\delta^{15}N$ alone [26,30] or the combination of $\delta^{15}N$ and $\delta^{40}Ar$ [27]. In the present paper we follow the method first introduced by Severinghaus and Brook [27] using both $\delta^{15}N$ and $\delta^{40}Ar$ to isolate the thermal fractionation signal from its gravitational counterpart and we invert the thermal signal to quantify the past surface temperature variation through a recently developed firn densification model including heat diffusion [16]. This methodology is applied on detailed $\delta^{15}N$, $\delta^{40}Ar$ and CH_4 measurements performed on the GRIP ice core (resolution range: 20 cm to 1 m) at the depths corresponding to DO event 12. Sensitivity studies conducted on the speed of the temperature change enable us to estimate the uncertainty of this integrated method.

2. Method

Argon and nitrogen have constant isotopic composition in the atmosphere at the timescale considered here [33,34]. Consequently, changes in $\delta^{15}N$ and $\delta^{40}Ar$ levels in ice cores air can only result from the fractionation process in the firn (superimposed gravitational and thermal effects). The gravitational signal is proportional to the mass difference between the two considered isotopes, other conditions being similar. It is then four times greater for $\delta^{40}Ar$ (ratio $^{40}Ar/^{36}Ar$) than for $\delta^{15}N$ (ratio $^{15}N/^{14}N$). In the following we will therefore scale the $\delta^{40}Ar$ by four to directly compare the gravitational signals. Today, $\delta^{15}N$ or $\delta^{40}Ar/4$ change due to gravitational effect only amounts to ~0.3‰ in GRIP [14].

The thermal fractionation results from an instantaneous vertical temperature gradient in the firn that drives the heaviest isotopes towards the coldest firn end according to:

$$\delta = \Omega \Delta T$$

where Ω is a thermal diffusion coefficient [‰ K^{-1}] that has to be determined for each isotopic pair

[35,36] and ΔT the firn temperature gradient [K]. A 10 K temperature gradient in the firn leads to respectively a ~0.15‰ and ~0.40‰ thermal anomaly for $\delta^{15}N$ and $\delta^{40}Ar$. During the warming part of a DO event (several degrees within a hundred years) such transient temperature gradients arise in the firn and the heavy gas species are driven towards the cold deeper firn where the gas isotopic anomaly is isolated. After the warming phase, the firn becomes homogeneous in temperature and the $\delta^{15}N$ and $\delta^{40}Ar$ signals are supposed to decrease toward the gravitational signal level. In other words, the thermal fractionation results in a $\delta^{15}N/\delta^{40}Ar$ signal that can be viewed as the derivative of the surface temperature with respect to time.

The $\delta^{15}N$ and $\delta^{40}Ar$ anomalies are not the result of a thermal effect alone because the dynamics of firn densification has to be accounted for. Indeed, changes in firn depth are expected to take place in response to rapid warming and associated accumulation changes. From thermodynamic considerations, we know that the accumulation rate must have significantly increased during a DO event (for the warm phase of DO event 12, the accumulation rate is supposed to be twice that of the cold phase [37]). Firn densification models [16,14] therefore forecast a 20-m deepening of the close-off depth corresponding to the warming of the DO events resulting in a larger gravitational signal (20% increase). As a consequence each positive $\delta^{15}N$ and $\delta^{40}Ar$ anomalies corresponding to a DO event are the combinations of both thermal and gravitational effects. The approach developed by Lang et al. [26] and Leuenberger et al. [30], associates the $\delta^{15}N$ measurements with a densification and heat diffusion model [14]. They modify the temperature and accumulation scenarios taking into account a dependence of accumulation rate to temperature deduced from Clausius-Clapeyron laws to reproduce both the full $\delta^{15}N$ signal associated with the DO event and the Δage. However, as pointed out in [26], the high uncertainty associated with the accumulation rate estimate (up to 100% [38]) is a strong limitation to precise temperature reconstructions especially during cold glacial conditions. Indeed, Greenland accumulation rate variations do not only depend on local temperature but reflect large scale reorganisations of the atmospheric circulation [39].

A way to separate the thermal and the gravitational effects and thus to get rid of the uncertain accumulation rate variation is to use the combined isotopic records, $\delta^{15}N$ and $\delta^{40}Ar$ as developed by Severinghaus and Brook [27]. It enables us to define the $\delta^{15}N_{excess}$ only dependent of the firn transient temperature as:

$$\begin{aligned}\delta^{15}N_{excess} &= \delta^{15}N - \delta^{40}\ Ar/4 \\ &= (\Omega_N(T) - \Omega_{Ar}(T)/4)\Delta T\end{aligned}$$

The recent determination of accurate values for the thermal diffusion coefficients for the pairs $^{40}Ar/^{36}Ar$ and $^{15}N/^{14}N$ is a prerequisite to estimate the temperature gradient in the firn and then the surface temperature changes [35,36].

The instantaneous vertical temperature gradient ΔT in the firn is then determined using $\delta^{15}N_{excess}$. However, ΔT has to be converted into temporal changes of surface temperature as it is damped by heat diffusion in the firn. Severinghaus and Brook [27] use a simple heat diffusion model in a firn with constant depth that is forced by a step shape temperature increase. The temperature scenario is then adjusted to fit the measurements with the modeled $\delta^{15}N_{excess}$. One weakness of this approach is to consider an instantaneous increase for the DO event warming while we know from $\delta^{18}O_{ice}$ that the warming can last up to 100 years. This approximation underestimates the surface temperature variations and that is the reason why, Severinghaus et al. [40] modify the temperature forcing shape in relating it linearly to the $\delta^{18}O_{ice}$ evolution with respect to time. The second questionable point of this approach is the choice of a constant depth for the firn during the DO event. Indeed, the deepening of the firn increases the depth on which heat diffusion takes place and, again, this approach can slightly underestimate the surface temperature change. Our approach follows the one by Severinghaus et al. [40] with a more complex firn densification model that dynamically associates heat diffusion and firn densification laws [16]. This model is classically forced by surface temperature and accumulation rate as deduced from the water isotopic profile to respect the dynamics of climate changes and to have a firn dynamical evolution with time according to those surface conditions. Goujon et al. [16] already applied this model to the Bølling Allerød measurements performed by Severinghaus and Brook [27] but the lack of $\delta^{15}N_{excess}$ data made the temperature variation quantification difficult. However, their estimate is significantly different (16 °C) than the value (11 °C) derived by Severinghaus and others [27,28] suggesting a high dependency of the temperature reconstitution on the scenario and firn model. In this study, to estimate the temperature variation associated to the DO event 12, numerous $\delta^{15}N_{excess}$ measurements have been performed and sensitivity studies are conducted using varying surface temperature scenarios as model inputs to explore the dependency of the temperature change quantification on such scenarios.

3. Analytical results

Thirty-eight duplicates measurements of $\delta^{15}N$ and 30 measurements of $\delta^{40}Ar$ (duplicates over the thermal anomaly) were conducted over the depth range from 2270 to 2370 m in the GRIP ice core (Fig. 1). For $\delta^{15}N$, a melt refreeze technique was used to extract the air from the ice samples (10 g), and $\delta^{40}Ar$ was measured from 40 g ice samples after a wet extraction and adsorption of all gases except noble gases through a getter (alloy of zirconium and aluminium heated to 900 and 200 °C [28]). Isotopic measurements were performed on a MAT 252 and corrections were applied to take into account (i) the formation of CO^+ of mass 28–29 that interferes with the $\delta^{15}N$ measurements, and (ii) the influences of the ratios O_2/N_2 and Ar/N_2 on the mass spectrometer source sensitivity, and then on the $\delta^{15}N$ and $\delta^{40}Ar$ measurements. The analytical uncertainty for our $\delta^{15}N$ and $\delta^{40}Ar$ was calculated through the pooled standard deviation from replicates and results respectively in 0.005‰ and 0.018‰ for $\delta^{15}N$ and $\delta^{40}Ar$. Fig. 1 shows clearly the positive $\delta^{15}N$ and $\delta^{40}Ar$ anomalies associated to DO event 12 warming as well as the sharp methane concentration rise on a common depth scale. The 41 methane measurements were performed at LGGE using an automated and recently improved wet extraction method (Chappellaz et al., in preparation).

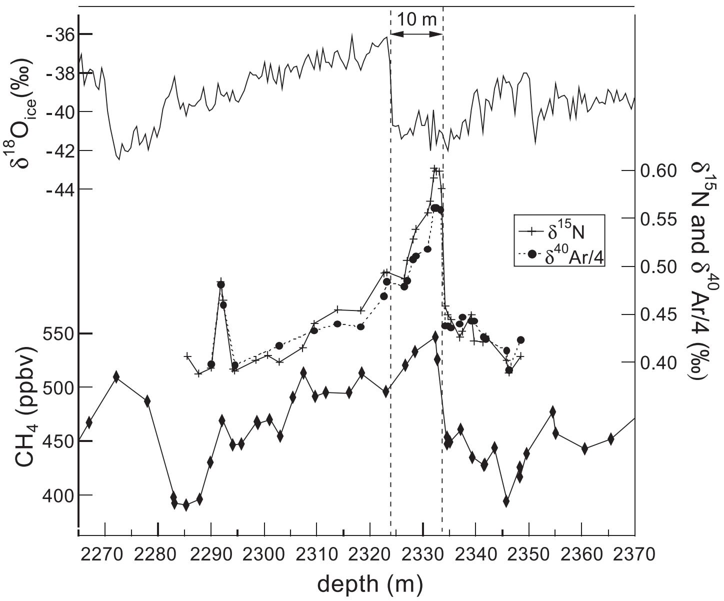

Fig. 1. GRIP DO event 12 records: top panel: $\delta^{18}O_{ice}$ with a 55-cm depth spatial resolution [2], mid panel: $\delta^{15}N$ (solid line) and $\delta^{40}Ar/4$ (dotted line), bottom panel: CH_4 with respect to depth. The Δdepth inferred from the depth difference between the temperature increase recorded in the ice (increase of $\delta^{18}O_{ice}$) and the temperature increase recorded in the gas ($\delta^{15}N$ and $\delta^{40}Ar$ increases) is 10 m.

4. Discussion

4.1. Timing of atmospheric methane change relative to temperature

Fig. 1 shows the methane concentration increase corresponding to DO event 12. The sharp increase of methane from 450 to 550 ppbv confirms the results by Flückiger et al. [13] over DO event 12 on the NorthGRIP ice core. Over the whole event, CH_4 evolution closely follows the one of $\delta^{18}O_{ice}$ suggesting a strong link between temperature and this greenhouse gas. As for DO event 8 and for the last Termination, the CH_4 transition associated with the DO event 12 warming takes place in two steps: a first gradual increase (by 30–50 ppbv over ~1 ky) concomitant with a slow and modest $\delta^{18}O_{ice}$ increase, followed by a rapid jump (by 90–100 ppbv over ~100 years) toward the maximum level of the interstadial. The time resolution of the CH_4 profile from NorthGRIP (~60 years) is slightly better than in our studies [13]. It provides a duration for the CH_4 main transition of about 120 years, i.e. comparable to our findings. The resolution of our methane sampling is about 90 years over the main increase; this puts an upper limit on the phasing estimate between the temperature increase as recorded in the gas by $\delta^{15}N$ and the methane increase. Within this limit, methane and temperature increases are in phase. This is in agreement with the phase relationship revealed by Severinghaus et al. [41] on the Bølling-Allerød and Flückiger et al. [13] on DO event 19. But this contradicts the suggestion of a methane lead by several hundred years over the same DO event 12 observed on the GISP2 ice core [42]. The reason for this discrepancy is unclear: it could result from the sampling step or from outliers within the CH_4 series on GISP2 ice.

5. Quantification of the temperature change

Goujon et al. [16] already applied their model for the conditions of GISP2 at Summit (30 km from GRIP) and the model parameters are very close for the two sites. The basal temperature given in the literature is -8.6 °C for GRIP [22]. We relate the past surface temperature, T_s, to the $\delta^{18}O_{ice}$ profile through a linear relationship with a constant slope $d\delta^{18}O_{ice}/dT_s=\alpha=0.32$ in agreement with the previous estimates on Summit [21,22] for the last glacial maximum. Finally, the accumulation rate was taken from the revised estimate by Johnsen et al. [43]. The validation of those model inputs is first achieved by comparing the present-day temperature profile in the GRIP borehole [44] to the modelled one; the discrepancy is less than 0.6 °C over the entire ice column and less than 0.2 °C in the firn column. The accumulation rate can be tested through our gas measurements by comparing the depth location of the thermal anomaly in the model and in the measurements. The measurements (Fig. 1) indicate a 10 m Δdepth between the temperature increase as recorded in the ice ($\delta^{18}O_{ice}$) and in the air ($\delta^{15}N$, $\delta^{40}Ar$). This Δdepth is the result of the firn close-off depth that isolates the gas thermal anomaly at higher depth than the surface $\delta^{18}O_{ice}$ increase and of the ice thinning rate due to ice sheet flow at the considered depth (~2330 m for DO event 12). Using the previous accumulation rate from Johnsen et al. [37], the $\delta^{15}N$ and $\delta^{40}Ar$ anomalies are predicted 13 m deeper than the $\delta^{18}O_{ice}$ increase indicating the warming in the ice, i.e. a depth shift significantly different from the measured Δdepth. We therefore choose the use of the revised accumulation rate by Johnsen et al. [43] with 15% lower values during the warm phase of each DO event that allows to reconcile the measured and modelled Δdepths (varying the temperature scenarios can not bring them in agreement). Based on that model tuning, sensitivity experiments are conducted by varying locally, over DO event 12, the surface temperature scenario, other things being equal to keep the modeled borehole temperature profile similar to the measured one. The aim is to reproduce the correct transient temperature gradient in the firn with the model and then the measured $\delta^{15}N_{excess}$. For a first approach, the temperature forcing was chosen to follow the $\delta^{18}O_{ice}$ evolution through a linear relationship with a local α value ranging from 0.26 to 0.70 as described in Goujon et al. [16]. Relating $\delta^{18}O_{ice}$ and temperature linearly for the DO event with a constant α value is somehow arbitrary; however we assume for this first approach that $\delta^{18}O_{ice}$ is qualitatively linked to surface temperature and consequently that their variations must have the same shape. Fig. 2 displays the best fit between model and measurements with this simple method, and corresponds to a slope $d\delta^{18}O_{ice}/dT_s=\alpha=0.40$ for DO event 12. Indeed a comparison between the amplitude of δ^{15}N, δ^{40}Ar and $\delta^{15}N_{excess}$ anomalies between the model and the measurements shows a very nice agreement suggesting that the surface temperature scenario described above (α=0.40 over DO event 12, α=0.32 elsewhere resulting in the surface temperature scenario shown in Fig. 2) is close to the true past temperature variation. However, the comparison of the peak shapes is less satisfying especially at the beginning and after the increase corresponding to the warming of DO event 12. At the beginning of the increase, three points marked by crosses between diamonds and triangles cannot be reproduced by the model. They correspond to the increase of δ^{15}N at the beginning of the warming while the δ^{40}Ar signal remains flat. Such δ^{15}N and δ^{40}Ar evolution cannot be reproduced by the model and can not be explained by a different diffusion time for argon and nitrogen since it is not observed for thermal diffusion in firn experiments [45]; however, it is not a measurement artefact since similar measurements performed on other DO events show the same evolution [46]. Moreover, after the peak maximum, the measurements show a slow $\delta^{15}N_{excess}$ decrease while the modelled signals decrease rapidly. This discrepancy can be explained by either an over-estimation of the firn heat conductivity or a bad estimation of the accumulation rate or of the surface temperature forcings but Goujon et al. [16] constrained the firn heat conductivity through measurements in current polar firns and sensitivity experiments (not shown here) lead to the conclusion that $\delta^{15}N_{excess}$ are not influenced by a change in accumulation rate and that such variations result only in different modeled Δdepth. Consequently, we suspect that our assumption in relating the surface temperature to $\delta^{18}O_{ice}$ linearly is questionable. This conclusion is in agreement with deuterium excess measurements indicating a rapid change of hydrological cycle for the water precipitating over GRIP during a Dansgaard-Oeschger event. The change of source temperature modifies the final $\delta^{18}O_{ice}$ for a constant GRIP surface temperature

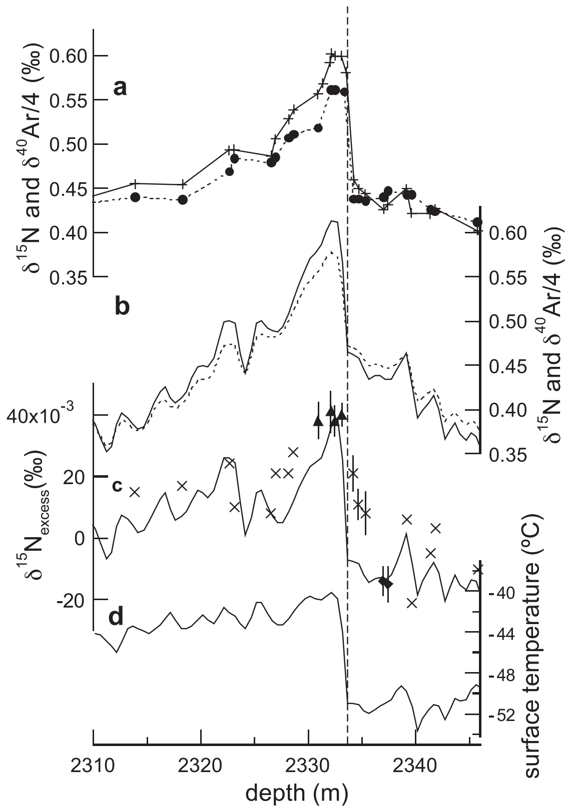

Fig. 2. Comparison between measured and simulated gas isotopic profiles during DO event 12 on a depth scale. (a) δ^{15}N (solid line) and δ^{40}Ar/4 (dotted line) measurements. (b) δ^{15}N (solid line) and δ^{40}Ar/4 (dotted line) simulated with a firn densification and heat diffusion model [16] forced by the accumulation rate calculated by Johnsen et al. [43] and by a "best-guess" surface temperature history derived from the $\delta^{18}O_{ice}$ profile ($\Delta T = \Delta\delta^{18}O_{ice}/0.4$). (c) $\delta^{15}N_{excess}$ deduced from the combined measurements of δ^{15}N and δ^{40}Ar/4 ($\delta^{15}N_{excess} = \delta^{15}N - \delta^{40}Ar/4$, crosses, diamonds and triangles with associated error bars) and $\delta^{15}N_{excess}$ deduced from the simulated δ^{15}N and δ^{40}Ar (solid lines). The $\delta^{15}N_{excess}$ variation between the two diamonds and the four triangles is the result of the rapid temperature increase. Note that the plateau made by the association of the four triangles marking the warm phase confirm that we clearly capture the maximum of the transient temperature gradient even if we do not have any points in the rapid δ^{15}N and δ^{40}Ar increase. (d) Surface temperature scenario deduced from the $\delta^{18}O_{ice}$ profile ($d\delta^{18}O_{ice}/dT = 0.40$ over the DO event 12). The output resolution of the model is 50 cm to respect the sampling frequency for δ^{15}N and δ^{40}Ar measurements. Note that the modeled amplitudes of δ^{15}N and δ^{40}Ar are slightly shifted with respect to the measurements before the onset of the warming. Such differences are probably due to changes in accumulation rate or in the relationship between $\delta^{18}O_{ice}$ and temperature. A change in the convective zone could also bring in better agreement the model and the measurements at that period. The use of the $\delta^{15}N_{excess}$ combined to the firn densification model enables us to get rid of such uncertainties; indeed, sensitivity experiments performed with different accumulation rate and convective zones (not shown here) lead to the conclusion that those parameters do not influence the $\delta^{15}N_{excess}$ values.

because of the change of the distillation history. Indeed the 2‰ decrease in deuterium excess associated with the warming of DO event 12 is estimated to account for a 1–2°C overestimation of the temperature increase for DO event 12 depending on the $\delta^{18}O_{ice}$–temperature relationships [47]. That is the reason why, in the following, we prefer to constrain the surface temperature history through the inversion of $\delta^{15}N_{excess}$ without any relationship with $\delta^{18}O_{ice}$.

$\delta^{15}N_{excess}$ as deduced from the measurements shows a negative value around −0.015‰ before DO 12 (2 points marked as diamonds in Fig. 2). The model also predicts this decrease because, according to the $\delta^{18}O_{ice}$ profile, there is a slight cooling before the main warming making the $\delta^{40}Ar$ signal higher than the $\delta^{15}N$ one. We consequently choose this negative $\delta^{15}N_{excess}$ value as the reference level before the warming (note that such a choice is of main importance for the temperature change estimate; another choice for the $\delta^{15}N_{excess}$ level before the warming would lower it). For the warming, the measured $\delta^{15}N_{excess}$ shows a plateau with 4 points around 0.04‰ (4 triangles on Fig. 2). These extreme values are the result of the rapid temperature change corresponding to the warming of DO event 12. We then try to reproduce the amplitude of this $\delta^{15}N_{excess}$ change (between the points marked with diamonds and the points marked with triangles) with the model forced with different surface temperature scenarios. As we assumed that surface temperature has not to be linearly related to $\delta^{18}O_{ice}$, we run the model with different surface temperature increase amplitudes and durations. Fig. 3 shows an overview of the range of surface temperature changes (6.6–17.2 °C) and warm-

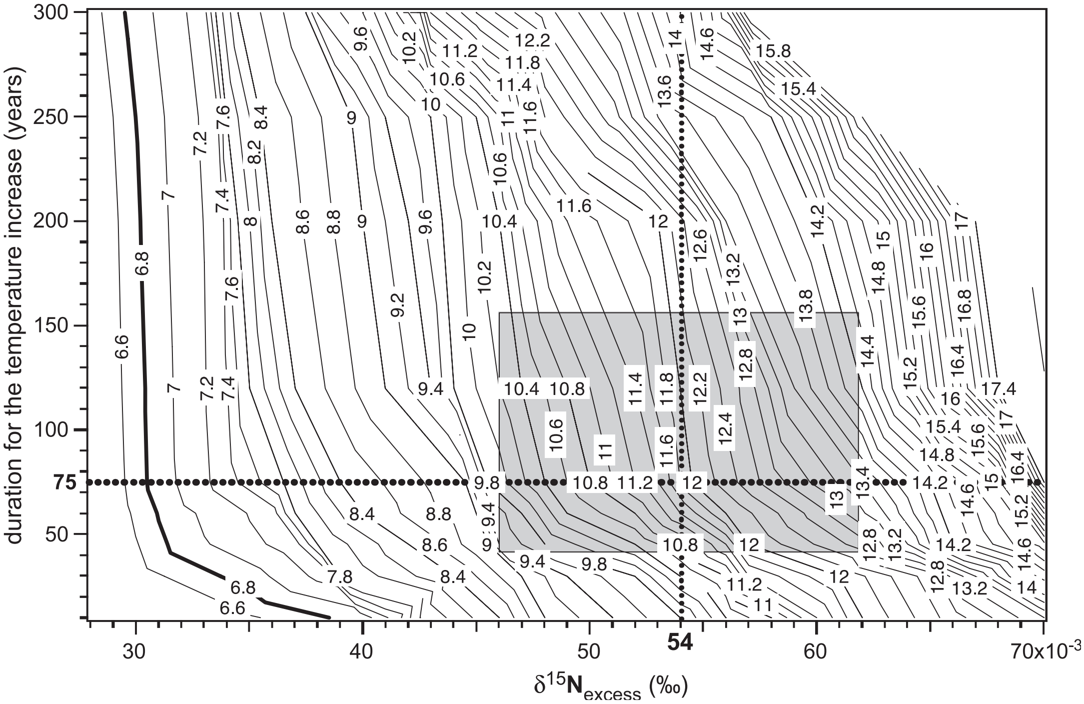

Fig. 3. Sensitivity of modelled $\delta^{15}N_{excess}$ (X axis) to different scenarios of surface temperature increase for DO event 12: different duration for the warming (Y axis) and amplitudes of the warming ("isotherms") were imposed over a large range of values (duration: 10–300 years; temperature: 6.6–17.2 °C). The accumulation rate variation over the transition is from Johnsen et al. [43] and additional sensitivity tests not shown here confirm that it has no influence and consequently that the use of $\delta^{15}N_{excess}$ to infer past temperature changes enables us to get rid of the accumulation rate constrain. The value of the observed $\delta^{15}N_{excess}$ variation (0.054±0.008‰) is reported (solid line and shaded area) and we restrain the possible surface temperature change duration between 30 and 150 years. The best fit is obtained for a 12±2.5 °C temperature change. For reference, the indication of the 6.8 °C temperature change as deduced from the spatial relationship between water isotopes and surface temperature is shown in bold line. The choice of a different accumulation rate [37] or a different convective zone does not modify this figure and therefore the conclusion of the paper.

ing durations (0–300 years while the conventional dating by Johnsen et al. [43] gives a 75-year estimation). The variation of $\delta^{15}N_{excess}$ as inferred from the measurements is 0.054‰. The uncertainty associated to this $\delta^{15}N_{excess}$ variation can be inferred from the analytical uncertainties of measurements. First, we calculate the standard deviation associated to the four points of the plateau (triangles) around 0.0395‰ and the one associated to the two negative values (diamonds) around −0.0145‰ using the quadratic error:

$$\sigma = \sqrt{\sigma^2_{\delta 15N} + \frac{\sigma^2_{\delta 40Ar}}{16}}$$

Then, the standard deviation associated to the $\delta^{15}N_{excess}$ variation is calculated using the variance associated to the maximum value (triangles) and the one of the minimum value (diamonds) as:

$$\sigma^2 = \frac{\sum_{i=1,4}^{\text{triangles}} \sigma_i^2}{4} + \frac{\sum_{i=1,2}^{\text{diamonds}} \sigma_i^2}{2}$$

With the exact analytical uncertainties associated to the specific initial and final $\delta^{15}N$ and $\delta^{40}Ar$ measurements, the final standard deviation value for the $\delta^{15}N_{excess}$ variation is 0.008‰. The $\delta^{15}N_{excess}$ variation with the associated standard deviation was then added on Fig. 3 to show the possible amplitudes of the warming taking into account different speeds for the temperature increase. We restrict the temperature increase durations to a range from 30 to 150 years. Indeed, we assume that the true surface temperature change can not be more than twice as rapid or twice as slow than the one deduced from the Johnsen et al. [43] dating. Over this duration range and according to the $\delta^{15}N_{excess}$ estimation (0.054±0.008‰), we have a direct estimation of the amplitude of the warming at the beginning of DO event 12 of 12.0±2.5 °C (Fig. 3). This temperature change is almost twice the 6.8 °C change estimated by the water isotopes. It should be noticed that taking a surface temperature duration too different from the one inferred by the $\delta^{18}O_{ice}$ profile could lead to a significant different temperature change estimation. As an example, using a step function for the temperature increase as used by Severinghaus and Brook [27] would conclude to a 10 °C temperature change. Part of the discrepancy between the temperature change estimation for the Bøllling-Allerød by Grachev and Severinghaus [27,28] (11 °C) and by Goujon et al. [16] (16 °C) is indeed explained by the different surface temperature scenarios used; however, a large part is due to the relative scarcity of $\delta^{15}N_{excess}$ data that led the authors to choose different "best fits" between data and model outputs. Beyond the sensitivity experiments conducted in the frame of this study, we have also performed tests with different accumulation rate variations over DO event 12 and, as expected from the use of $\delta^{15}N_{excess}$, it does not show any influence on the amplitude of the temperature change inferred while it significantly modifies the Δdepth as pointed out above. Finally, we restrain our $\delta^{15}N_{excess}$ inversion to the quantification of the rapid temperature change because (i) we have a low frequency sampling elsewhere over DO event 12 and since (ii) we did not perform duplicate $\delta^{40}Ar$ measurements except over the increasing part of the signal thus reducing our analytical precision elsewhere.

The temperature change of 12 °C for DO event 12 first confirms that the spatial $\delta^{18}O_{ice}$–T_s relationship clearly underestimates surface temperature changes associated to rapid climatic event in the middle of the last glacial period in Greenland. Secondly, it gives a new constraint for the amplitude of DO events warmings in addition to the Bølling-Allerød (~16 ky BP, 11 °C [27,28] to 16 °C [16]) and the DO event 19 (~70 ky BP, 16 °C [26]). Our method combining detailed $\delta^{15}N_{excess}$ measurements and firnification and heat diffusion modelling has the advantage to reduce the uncertainty on the amplitude of the temperature change deduced. By comparison with the other DO events, the relationship between water isotopes and surface temperature underestimates the temperature change amplitude by about 76% for DO event 12, comparable to the 60–87% for the Bølling-Allerød and 70% for the DO event 19. For the Last Glacial Maximum, the underestimation is 100% (note that this underestimation falls to 70% if we take into account the global marine isotope change between LGM and Holocene to correct the $\delta^{18}O_{ice}$). We have currently very few precise estimations of the temperature during the last glacial and it is therefore difficult to conclude on the evolution of the $\delta^{18}O_{ice}$-temperature relationship all along this period. The current comparison between the different events and

LGM prevent us to conclude on a clear variability of the spatial relationship bias along the glacial period. However, such effect is expected since atmospheric circulation around Greenland went through different climatic conditions at that time. In particular, the ice sheets in North Atlantic varied between small extensions (i.e. total ice sheet extension equivalent to a −60 m of sea level at −50 ky) to large extension (total ice sheet extension equivalent to a −120 m sea level during the LGM) and probably influenced the atmospheric circulation around Greenland [48].

6. Conclusion

We have shown here a new methodology to estimate temperature histories during rapid events together with a detailed study of DO event 12 to resolve the question of phasing between methane concentration and temperature increases. We combine the precise measurements of δ^{15}N, δ^{40}Ar and methane in the air trapped in the GRIP ice core at depths covering the DO event 12 with the use of a newly developed model associating ice and firn densification with heat diffusion. The methane increase was shown to be in phase with the surface temperature increase at a 90 years time resolution thus consistent with previous works performed on other time periods but in conflict with earlier findings from GISP2 ice on the same DO event. Through the combined measurements of δ^{15}N and δ^{40}Ar and the use of firn modeling, we estimate the surface temperature warming to be 12 ± 2.5 °C for DO event 12. We also show that this estimate is not influenced if the speed of the warming is changed by a factor of two with respect to the conventional dating. Our temperature change estimate is also independent of the accumulation rate variation and enables us to better constrain the relationship between $\delta^{18}O_{ice}$ and temperature during the full glacial period. We suggest that this relationship could be variable between different climatic periods in relation with possible reorganisations of the hydrological cycle. One way to explore further this variability is to study complete sequences of DO events following the methodology applied to the particular DO event 12.

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